Fundamental Insight into Humid CO₂ Uptake in Direct Air Capture Nanocomposites Using Fluorescence and Portable NMR Relaxometry

Glory A. Russell-Parks,² Noemi Leick,² Maxwell A. T. Marple,¹ Nicholas A. Strange,⁵ Brian G. Trewyn,² Simon H. Pang,⁴ Wade A. Braunecker⁴,⁴*

¹ Department of Chemistry, Colorado School of Mines, 1012 14th Street, Golden, CO 80401

² National Renewable Energy Laboratory, 15013 Denver West Pkwy, Golden, CO 80401

³ Materials Science Program, Colorado School of Mines, 1012 14th Street, Golden, CO 80401

⁴ Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, California 94550

⁵ Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator, Laboratory, Menlo Park, CA 94025

*Email: Wade.Braunecker@nrel.gov

KEYWORDS. Fluorescence, NMR relaxometry, poly(ethylenimine), polymer mobility, direct air capture, carbon capture
**ABSTRACT.** Direct air capture (DAC) technology is being explored as a pathway for reducing greenhouse gas emissions through the efficient removal of CO₂ from the atmosphere. However, there remains a knowledge gap regarding structure-property-performance factors that impact the behavior of these systems in diverse, real-world environments. In aminopolymer-based DAC systems, gas diffusion is tightly coupled with polymer mobility, which is in turn affected by a large matrix of variables, including interactions with the pore wall of the support, nanoconfinement, the presence of co-adsorbates (moisture), and electrostatic crosslinks that develop as a function of CO₂ chemisorption. Higher throughput, benchtop techniques for studying and understanding mobility in these systems would lead to more rapid advances in the field. Here, we demonstrate the value of a fluorescence technique for monitoring polymer mobility within nanocomposite capture materials as a function of CO₂ and water adsorption in a series of humidified polyethylenimine-Al₂O₃ composite materials. The approach allows us to correlate changes in mobility with CO₂ adsorption kinetics as a function of relative humidity. We further couple this information with NMR relaxometry data attained using a portable single-sided magnetic resonance device, and we employ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to correlate the formation of different relative amounts of carbamates and carbonates with the environmental conditions. These results provide a blueprint for using benchtop techniques to promote fundamental understanding in DAC systems that can in turn enable more efficient operation in real-world conditions.
Introduction

While the global clean energy transition continues to gain momentum,¹ certain industries will be intrinsically difficult to fully decarbonize.² Achieving net zero carbon emissions in those instances will ultimately require the use of robust carbon capture, utilization, and storage technologies.³ The deployment of negative emissions technology is also projected to play an increasingly important role in limiting the effects of anthropogenic climate change.⁴-⁶ Amongst the direct air capture (DAC) technologies currently being investigated for pilot and commercial scale deployment, solid adsorbents based on supported amines are garnering much enthusiasm.⁷ Indeed, a diverse array of recent work studying non-volatile aminopolymers loaded onto mesoporous oxide composites is driving extraordinary advances in the field.⁸-¹⁴ However, certain fundamental knowledge gaps remain that will influence how these and similar materials are employed over long cycle times,¹⁵-¹⁷ in different environments,¹⁸,¹⁹ and within different operational design constraints in real-world DAC systems.²⁰

One such knowledge gap involves structure-property-performance relationships associated with polymer segmental mobility in confinement.²¹ The mobility of these aminopolymer sorbents directly influences gas diffusion through these materials.²² As CO₂ reacts with available amines within the polymer matrix, the formation of electrostatic crosslinks in the form of carbamate species can significantly rigidify the polymer,²³ effectively converting it from a liquid or rubbery sorbent into a glassy encapsulant. The physical state of the polymer adsorbent not only affects optimal cycle times for CO₂ sorption; it also governs subsequent O₂ diffusion in and out of the material. As residual oxygen in the sorbent chamber during the CO₂ desorption step can lead to fast sorbent degradation,²⁴ selective O₂ removal prior to CO₂ desorption plays a key role in
optimizing amine-based sorbent lifetimes. This optimization requires fundamental understanding of gas diffusion in these materials, and hence polymer mobility.

Aminopolymer mobility is governed by a matrix of complex and often counterbalancing factors. These include the architecture and molecular weight of the polymeric sorbent; surface and interface effects in thin films; the presence of moisture and other additives that can serve as plasticizers and even change the mechanism of adsorption; partial degradation of the sorbent that can lead to rigid moieties in the polymer; and relative CO$_2$ uptake that results in various degrees of ionic cross-linking. These combined effects on polymer mobility are further influenced and compounded in nano- and meso-porous confinement. We recently outlined the merits and drawbacks of an array of techniques for studying polymer mobility in confinement, which included differential scanning calorimetry, dielectric spectroscopy, NMR, and neutron scattering, among others. However, given the large matrix of variables that influence polymer mobility in confinement that can change as a function of lifetime and cycling, higher throughput techniques for quantifying mobility could lead to more rapid advances in the understanding and deployment of these materials in DAC systems.

Various fluorescent probes have been employed to study polymer mobility and have proven particularly useful for studying mobility in thin films and in confinement where other techniques encounter limitations. We recently detailed the development of a powerful fluorescent probe designed specifically to study aminopolymer mobility, and we demonstrated its usefulness in studying DAC sorbents. Here, we build on that foundational study by examining poly(ethylenimine) (PEI) mobility as a function of CO$_2$ uptake across a wide range of temperatures and relative humidity (RH) in a mesoporous $\gamma$-Al$_2$O$_3$ composite. We further couple this information with NMR relaxometry data attained using a versatile and portable magnetic
resonance device known as NMR Mobile Universal Surface Explorer (MOUSE). We then employ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to correlate the formation of different relative amounts of carbamates and carbonates with the environmental conditions. This approach provides a blueprint for using benchtop analytical techniques to promote fundamental understanding of structure-property-performance relationships that can in turn enable more efficient operation of DAC materials in a variety of real-world climates and environments.

Results and Discussion.

Moisture and Fluorescence.

We previously detailed the merits of employing fluorescent probes based on tetraphenylethylene (TPE) in a proof-of-concept study for qualitatively comparing aminopolymer mobility across confined mesoporous DAC composites. Here, we develop these probes further to study branched PEI mobility in model DAC systems as a function of real-world operating conditions, beginning with moisture uptake as a function of RH exposure. PEI composites with γ-Al₂O₃ are quite hygroscopic; a composite that is 40 wt.% PEI can uptake as much 1.7 equivalents in weight of water relative to PEI when allowed to equilibrate in a stream of humid N₂ (vide infra). This amount of moisture can significantly alter the mobility of the PEI matrix. However, disentangling the effects of moisture on the fluorescence response of these probes requires a thorough understanding of the quenching mechanisms at play.

TPE-based molecules behave as aggregation induced emission (AIE) probes; they tend to be non-emissive when well solvated in low or non-viscous solvents, where unrestricted intramolecular rotations provide non-radiative pathways for excited state decay. However, in viscous or glassy media, or in an aggregated state, these rotations become restricted to varying
degrees, and a strong wavelength dependent emission is then observed from TPE that is a function of the mobility of its matrix. More details of the mechanism responsible for this behavior have been thoroughly reviewed elsewhere.\textsuperscript{47, 48} In contrast to aggregation caused quenching (ACQ) probes such as perylene,\textsuperscript{49} where water can induce aggregation and $\pi$-stacking interactions that open non-radiative decay pathways, the addition of water to a non-emissive AIE probe solution will often induce aggregation and turn on fluorescence. While high energy vibrations in water molecules can themselves quench fluorescence,\textsuperscript{50} the restriction of intramolecular rotation appears to dominate the fluorescence response of most AIE probes in aqueous solutions.

In this work, we employ tetrakis(4-hydroxyphenyl)ethylene (THPE) as our AIE probe. The hydroxyl groups dramatically enhance its solubility in PEI relative to the parent TPE compound. We recently demonstrated that THPE emits near 460 nm and appears blue in a frozen/glassy/aggregated state, while it appears green and emits closer to 530 nm in a viscous PEI solution.\textsuperscript{35} We further demonstrated that the ratio of emission at these two wavelengths can serve as a measure of the relative mobility of the polymer matrix. The fluorescence of THPE in mixed alcohol/water solutions was also recently investigated.\textsuperscript{51} Between 0 and 82 vol. % water in ethanol, no THPE fluorescence could be detected as the probe was still well solvated. Only when the water fraction was at or above 84 vol. % was blue emission observed, as THPE aggregated/precipitated under these conditions.

Here, we prepared a similar series of THPE solutions in PEI and water to determine the relative volume fractions we could attribute change in the THPE fluorescence response to change in polymer mobility, and at what volume fractions of water we would need to account for probe aggregation. In all cases, the concentration of the probe was 0.1 wt. % relative to the total mass of the solution. Between 0 and 90 vol. % water, we only observed green fluorescence. As can be seen
in Figure 1a, the intensity of the fluorescence systematically decreases as the water content increases and sample viscosity decreases. However, between 90 and 95 vol. % water, THPE began to aggregate and stick to the walls of the cuvette, where its blue emission could be observed. Bright blue emission was pronounced in 100% water, where THPE formed a heterogeneous suspension. The results suggest that changes in the photoluminescence quantum yield (PLQY) of THPE as a function of water concentration in aqueous PEI solutions ≤ 90 vol. % water are not caused by probe aggregation. We acknowledge results in bulk solutions are not perfectly transferable to confined systems. Even though the overall fraction of water present in composites equilibrated at 100% RH (vide infra) is considerably lower than what we measured here in the bulk, it is known that confinement can, in some cases, change the solubility of small molecules relative to bulk solutions. However, the results are an important first step in quantifying AIE response of THPE in humidified PEI.

Figure 1. (a) Series of aqueous-PEI solutions (0 – 100 vol.% water) containing 0.1 wt.% THPE irradiated at 365 nm. The intensity of the green fluorescence systematically decreases as the aqueous-PEI solutions becomes less viscous until above 90 vol. % water, when THPE begins to
aggregate and emit blue light. (b) Fluorescence spectra of 0.4 wt. % THPE in a 40 wt. % PEI:Al₂O₃ composite after equilibrating to a given RH for 72 h. (c) Change in fluorescence of a dry composite of 0.4 wt. % THPE in 40 wt. % PEI:Al₂O₃ as a function of time upon exposure to 100 sccm of a humidified stream of N₂ (100% RH).

Turning to confined systems, we then prepared a series of composite samples equilibrated for 72 h at different values of RH according to a procedure described in the Methods section. The amount of water adsorbed by a 40 wt. % PEI composite (12 mg of PEI in 18 mg of Al₂O₃) at each RH is recorded in Table 1. A systematic increase in moisture uptake between ~2 and 20 mg is observed in this series. The composite also contained ~0.4 wt. % THPE relative to PEI. The emission spectrum of each humidified composite is illustrated in Figure 1b. The emission \( \lambda_{\text{max}} \) are recorded in Table 1.

<table>
<thead>
<tr>
<th>Sat. Salt Solution</th>
<th>RH (%)</th>
<th>H₂O Uptake (mg)</th>
<th>Emission ( \lambda_{\text{max}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>0</td>
<td>---</td>
<td>468</td>
</tr>
<tr>
<td>LiCl</td>
<td>11</td>
<td>1.8</td>
<td>469</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>33</td>
<td>4.0</td>
<td>486</td>
</tr>
<tr>
<td>Mg(NO₃)₂</td>
<td>53</td>
<td>6.2</td>
<td>508</td>
</tr>
<tr>
<td>NaCl</td>
<td>75</td>
<td>10.4</td>
<td>520</td>
</tr>
<tr>
<td>Distilled H₂O</td>
<td>100</td>
<td>20.2</td>
<td>530</td>
</tr>
</tbody>
</table>

*30.0 mg of a 40 wt.% PEI/Al₂O₃ composite (12.0 mg PEI, 18.0 mg Al₂O₃) were equilibrated for 72 h in a sealed chamber with a given saturated salt solution. *0.4 wt% THPE present in the composite was excited at 365 nm.
Several observations are worth noting about the data in Figure 1b. First, if we compare the dry bulk PEI spectrum with that of the dry composite, there is a dramatic blue shift in the emission from $\lambda_{\text{max}}$ of 533 nm to near 468 nm in confinement, consistent with a sharp reduction in mobility of the polymer matrix. These results are also consistent with our previous work in mesoporous silica composites using both tethered and dispersed TPE derivatives.\textsuperscript{35} If we then consider the samples equilibrated to different values of RH, we observe a systematic red shift in $\lambda_{\text{max}}$ as a function of increasing RH. This result is consistent with the literature which has hypothesized that moisture acts as a plasticizer for PEI chains that can weaken the inter- and intramolecular hydrogen bonding and dipole-dipole interactions in PEI,\textsuperscript{23} all which will enhance its mobility. Interestingly, the $\lambda_{\text{max}}$ of the emission spectrum of the composite sample equilibrated to 100% RH is nearly identical to that of the bulk dry sample, suggesting that the effects of confinement and humidity on mobility may counterbalance each other. While care should be exercised in not overinterpreting the fluorescence response, since (as mentioned) the high energy vibrations in water molecules can themselves also contribute to fluorescence quenching, the implications of these fluorescence measurements on PEI mobility are fully consistent with the NMR relaxometry data that will be presented in a subsequent section.

Finally, we monitored the fluorescence response of a dry composite by flowing 100 sccm of 100% RH N\textsubscript{2} through the sample over the course of 1 h (Figure 1c). The emission $\lambda_{\text{max}}$ immediately begins red shifting and a new peak grows in near 530 nm, suggesting mobility increases as the sample is becoming humidified. However, the results also indicate the composite has not yet reached equilibrium after just 1 h. Going forward, all samples were allowed to equilibrate at a given RH for 72 h prior to further measurements or manipulation.
CO₂ Adsorption and Aminopolymer Mobility.

Two samples of a 40 wt.% PEI:Al₂O₃ composite (0.4 wt.% THPE) were prepared. The first was kept under a dry, inert (N₂) environment, and the second was pseudo-saturated with CO₂ in a stream of simulated flue gas (45 sccm N₂, 5 sccm CO₂) for 12 h at 30 °C. The fluorescence spectrum of each sample was then recorded at 30, 0, and -30 °C. In previous work,

we demonstrated how quantifying the emission spectra via ratiometric analysis at two wavelengths as a function of temperature can give accurate indication of relative polymer mobilities across different samples. Here, we perform this analysis at these three temperatures as we flow CO₂ over the pristine composite. We then compare how much the mobility of the polymer changes at a given temperature relative to its theoretical ‘limit’ when saturated with CO₂. The normalized data is illustrated in Figure 2.

![Figure 2](image_url)

**Figure 2.** Normalized change in the emission spectra with time of a 40 wt.% PEI:Al₂O₃ composite doped with 0.4 wt% THPE while flowing 45 sccm N₂ and 5 sccm CO₂ at 30 °C (black), 0 °C (red), and -30 °C (blue).
If we first consider the data at 30 °C, we observe that 75% of the total mobility change occurs within the first 1 h of simulated flue gas exposure (black trace, Fig. 2). The remaining changes occur very slowly over the next 11 h. In contrast, after 1 h at 0 °C, mobility only changes by 30% of its pseudo-theoretical limit. Less than 10% change in mobility is seen at -30 °C in this time. The samples at 0 and -30 °C effectively level off after 1 h and do not approach their theoretical limit, even after 12 h of CO₂ exposure. The results can be rationalized by considering that PEI becomes glassier much faster or with less overall CO₂ uptake at colder temperatures, which in turn inhibits further gas diffusion and uptake. The activation barrier for CO₂ adsorption and/or proton transfer may also play a more significant role at these lower temperatures. We contend this technique will be particularly useful for studying an array of materials and additives for understanding and optimizing sub-ambient capture processes,18,53 but we turn now to studying changes in polymer mobility under a variety of simulated DAC conditions, namely 100 sccm of 400 ppm CO₂ in N₂ at different RH.

After equilibrating for 72 h at a given RH, a 40 wt.% PEI:Al₂O₃ composite was loaded into a flow through quartz cuvette, where the exhaust gas was routed through a LiCOR 850 quantitative CO₂/H₂O infrared analyzer. This allowed us to simultaneously monitor CO₂ sorption, RH of the sweep gas, and any changes in the emission spectra of the sample. Six different samples were equilibrated to the same RH values employed in Table 1. Changes in the emission spectra of a representative sample (at 53% RH) as a function of time and CO₂ uptake is illustrated in Figure 3a, with the emission spectra of the other samples shown in Figure S1 in the Supporting Information (SI). Changes in all 6 samples are quantified in Figure 3b, plotted as ratiometric intensities recorded as a function of time.
Figure 3. 40 wt.% PEI:Al₂O₃ composite, 0.4 wt% THPE, pre-equilibrated to a given RH for 72 h, 100 sccm of 400 ppm humid CO₂ in N₂. (a) Change in the emission spectra with time at 53% RH. (b) Summary of ratiometric fluorescence intensity (460 nm/530 nm) of six samples at different RH as a function of time with CO₂ flow.

As can be seen in Fig. 3a for the data at 53% RH, flowing humid CO₂ causes a blue shift in the emission spectra and an overall increase in the PLQY. The data is consistent with a decrease in polymer mobility with CO₂ uptake, and it stands in contrast to the data in Fig. 1c, where flowing CO₂-free moisture over an otherwise dry system causes a redshift in the emission spectra, a decrease in the PLQY, and increased polymer mobility. When comparing the change in the ratiometric intensity of all six composites in Fig. 3b, a few initial observations are worth noting. First, the drier the sample, the more rapid the polymer mobility changes and becomes glassier as it begins uptaking CO₂. Also noteworthy, the data suggests that samples between 0 and 33% RH all reach approximately the same mobility after 90 min under these conditions. Above 33% RH, mobility after 90 min of CO₂ capture trends higher with increased RH.

Full interpretation of the data in Fig. 3b requires that CO₂ sorption data for these six samples be considered. We illustrate in Figure S2 of the Supporting Information how we can monitor both adsorption and desorption in a continuous stream of 400 ppm CO₂. Integration of the
area between the curve and the 400 ppm baseline can be used to quantify CO$_2$ uptake in these
experiments, with the adsorption and desorption cycles in full agreement. In Figure 4, we plot the
CO$_2$ adsorption data for all six samples collected concurrently with the fluorescence measurements
above. When individual data traces in this figure approach 400 ppm, it is an indication they have
stopped uptaking significant amounts of CO$_2$ from the 400 ppm stream. Closer inspection of the
data reveals that at 90 min, the driest sample is near saturation, while the sample under 100% RH
has uptaken twice as much CO$_2$ and is still adsorbing it. Indeed, there is a strong correlation of
CO$_2$ uptake with RH. When we consider both fluorescence and CO$_2$ sorption data, we observe that
the dry samples become glassier much faster, despite having uptaken the same or less CO$_2$ than
the wet samples. The results are fully consistent with the literature, where more humid conditions
at low CO$_2$ concentrations have been mainly reported to promote CO$_2$ diffusion and to double the
CO$_2$ capacity compared to anhydrous conditions.$^{54-58}$ We and others hypothesize that the relative
formation of bicarbonates and certain carbamate species in the presence of moisture are
responsible for different degrees of electrostatic crosslinking in these samples that in turn impact
polymer mobility. We probe this hypothesis further in the next two sections by correlating the
polymer mobility data inferred by fluorescence with NMR relaxometry data on these same
samples. We further study the formation of different species in these reactions using DRIFTS to
disentangle specific molecular contributions to polymer mobility.
**Figure 4.** CO$_2$ adsorption kinetics of a 40 wt.% PEI:Al$_2$O$_3$ composite in a stream of 400 ppm CO$_2$ (100 sccm) at various RH.

**NMR Mobile Universal Surface Explorer (MOUSE).**

The NMR MOUSE was originally developed as a compact and mobile tool for non-invasive clinical diagnostics and the investigation of materials properties of arbitrarily large objects.\(^{46}\) The technique has since been used extensively for non-destructive and in field evaluation of rubber and elastomers, cultural heritage items, and food products.\(^{59}\) Unlike traditional NMR, chemical shift information cannot be attained with this technique; however, through the detection of differences in the relaxation times of hydrogen protons, NMR MOUSE data can be used, for example, to differentiate clay-bound water vs. movable water, gas, light oil, and viscous oils present in porous media.\(^{60}\) Here, we use the technique to evaluate the mobility of PEI in Al$_2$O$_3$ as a function of moisture and CO$_2$ uptake, both to corroborate the fluorescence mobility data, and also to demonstrate the value of the technique as a stand-alone diagnostic *in operando* tool for evaluating the health and performance of DAC composites in the field.

We selected twelve samples for this study, namely, the six composites listed in Table 1 that were equilibrated to different values of RH, and a set of six additional composites equilibrated to
those same values of RH but exposed for 90 min to a stream of 400 ppm CO₂. The mobilities of these twelve samples were measured with fluorescence (see the first and last data points of each trace in Fig. 3b). Here, we record and discuss both the transverse, spin-spin relaxation time ($T_2$) as well as the longitudinal, spin-lattice relaxation time ($T_1$) for each sample.

$T_2$ relaxation is a complex phenomenon influenced by a number of mechanisms, a major one being dipolar coupling between spins. $T_2$ values for these twelve samples were determined by collecting an echo train and fitting the amplitude decay curve (Figures S3 and S4 in the SI). Ultimately, this relaxation parameter is a measure of the coherence time of the spins. Strong dipolar coupling in rigid samples induces faster decoherence, while in samples with high molecular mobility, $T_2$ can be longer as the process is less efficient. In polymeric systems, greater entanglements and/or crosslinking density results in a decrease in mobility that manifests as shorter $T_2$ values. In Figure 5, we illustrate the $T_2$ values collected for these twelve samples as a function of RH and CO₂ exposure.

![Figure 5](image.png)

**Figure 5.** Transverse, spin-spin relaxation values ($T_2$) for 40 wt.% PEI:Al₂O₃ composites, equilibrated to 6 different values of RH, before and after exposure to 90 min of 400 ppm CO₂ flow
(T2 and T2 CO2, respectively). In most samples, a biexponential fit of the echo train attenuation data was required, resulting in two components (a and b) with two distinct values of T2. The dashed orange and green lines correspond with the a and b component, respectively, of the bulk anhydrous PEI value of T2.

Performing an inverse Laplace transform on the T2 echo train decay curves produces relaxation spectra (plotted in Fig. S3 and S4) showing most spectra are bimodal with two distinct T2 values per sample, referred to here as the ‘a’ and ‘b’ component of the spectrum. Thus, a biexponential function was used to constrain the fitting of the T2 echo train decay curve to facilitate comparison between samples. This bimodality is observed even in the dry composite that has not seen CO2 and is possibly explained by protons near the branched PEI chain ends relaxing at a significantly different rate than protons in or near the backbone, a phenomenon not uncommon for side-chain bearing polymers. A few general trends are worth noting from the data in Figure 6. First, for both the pristine set of samples and the set exposed to CO2, T2 increases with increasing RH, suggesting moisture increases the polymer mobility. Second, PEI composites that have been exposed to CO2 generally display shorter T2 values than the pristine composites. This trend is particularly evident in the drier samples, indicating CO2 exposure results in a much more rigid matrix in drier conditions. As RH increases, the difference in T2 between pristine and CO2 exposed samples begins to converge until there is no statistical difference at 100% RH. Finally, we note that T2 measured for bulk anhydrous PEI (dashed lines in Figure 5) is quite similar to that of the PEI:Al2O3 composite at 100% RH. Those results are fully consistent with the mobility data implied by fluorescence (compare solid and dashed black traces in Figure 1b).

T1 relaxation is a measure of the rate of energy transfer from the nuclear spin system to neighboring lattice molecules. The frequency of this measurement is dictated by temperature and the magnetic field strength. T1 relaxation is also affected by dipolar spin coupling, as well as
mobility of the lattice molecules, quadrupolar coupling, anisotropy, paramagnetic effects, spin diffusion, etc. Overall, $T_1$ relaxation is a longer process than that of $T_2$. Because processes like polymeric mobility can serve as an energy sink from spins to the lattice, higher mobility in the lattice will lead to shorter $T_1$ relaxation times (in contrast to $T_2$). In Figure S5, we plot $T_1$ values for all twelve samples. Similar trends and conclusions can be inferred here regarding polymer mobility as can be inferred from the $T_2$ and fluorescence experiments, at least for the samples $\leq 75\%$ RH. The 100\% RH samples are clear outliers, being much higher in magnitude than all the other $T_1$ values. We believe this phenomenon is likely due to phase separation of large amounts of water in the 100\% RH samples, which could give rise to an altogether different $T_1$ signal, and was recently invoked to explain other observations in humidified PEI composites. That hypothesis is further supported by the DRIFTS measurements in the next section which illustrate a dramatic increase in the stretching frequency associated with hydroxyl groups near 3650 cm$^{-1}$ for the 100\% RH sample. Regardless, the $T_1$ and $T_2$ data as a whole serve to corroborate the fluorescence mobility data and the interpretation of structure-property-performance relationships.

**Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) study of product formation.**

In dry conditions, CO$_2$ reacts with two amines (primary or secondary) to form ammonium carbamate ion pairs (RNH$_3^+$COO$^-$/R$_2$NH$_2^+$COO$^-$). The stabilization of these ions over two amines not only keeps the capacity low at 0.5 mol bound CO$_2$ per mole of amine,$^{56,66,67}$ but also contributes to crosslinking within the polymer or between polymer chains that significantly impedes subsequent CO$_2$ diffusion.$^{38, 68, 69}$ However, unlike in dry conditions, the exact molecular interactions in humid conditions are still debated. Properties such as adsorbent loading, polymer
molecular weight, amine functionality, the support, its porosity, and acidity, as well as the RH and CO$_2$ concentration all have been reported to affect the interaction of PEI with H$_2$O and CO$_2$.\textsuperscript{54-58} Despite all these variables, humid conditions at low CO$_2$ concentrations have been mainly claimed to promote CO$_2$ diffusion and can even double the CO$_2$ capacity relative to the anhydrous state.\textsuperscript{54-58} While the general proposed mechanism in anhydrous conditions involves ammonium carbamate ion formation and crosslinking, when moisture is present, water-stabilized ammonium bicarbonate or hydronium carbamate ions are thought to bind through one ethylamine (Figure 6).\textsuperscript{66} Note, ammonium carbamates can be present in both dry and humid conditions; they are also the only species illustrated in Figure 6 that result in inter-chain ionic crosslinking.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{molecular_structures.png}
\caption{Possible molecular structures resulting from CO$_2$ capture by PEI in dry (red) and humid (red, blue, and green) conditions.}
\end{figure}

As the fluorescence and NMR experiments clearly suggest that humidity increases polymer mobility, we first verified whether ammonium carbamates were formed in significant concentrations in PEI/Al$_2$O$_3$ when flowing humid CO$_2$. To this end, we performed DRIFTS on pre-humidified PEI/Al$_2$O$_3$, following the same protocol as for the fluorescence measurements, flowing
400 ppm CO$_2$ at 0%, 11%, 33%, 53%, 75% and 100% RH for 90 min. The background for each sample was collected just before exposing the sample to the humidified CO$_2$ stream. From the spectra shown in Figure 7, we can ascertain that the surface reactions between CO$_2$ and PEI/Al$_2$O$_3$ vary with RH. Under dry conditions, the band associated with primary amines in PEI at 3305 – 3602 cm$^{-1}$ is depleted as they are the main binding sites for CO$_2$. In contrast, hydroxyl groups (-OH at 3656 cm$^{-1}$) play an increasing role in the mechanism for 75%-100% RH CO$_2$ streams. Furthermore, as a function of increasing humidity, characteristic bands associated with -CH$_2$ and -CH$_3$ in PEI (at 2792 – 2966 cm$^{-1}$) are less depleted, and the peaks associated with ammonium carbamates (-NH$_3^+$/-NH$_2^+$) spanning from 1800 – 2790 cm$^{-1}$ are less intense. This is especially visible in the time-dependent spectra shown in Figure S6 in the SI, where these features were almost absent after 5 min at 100% RH.

Figure 7. DRIFT spectra of PEI:Al$_2$O$_3$ after 90 min of exposure to 400 ppm CO$_2$ at 0, 11, 33, 53, 75, and 100% RH. The spectra are offset for clarity. A new sample was used for each RH condition. (a) Significant bands and peaks are assigned in the range of 4000 – 1800 cm$^{-1}$. (b) Peaks of interest are assigned between 1800– 1200 cm$^{-1}$, where the peaks increasing as a function of increasing humidity are depicted in dashed blue lines, and the other features are highlighted with solid grey lines. The peak assignment of (a) is recorded in Table S1 and (b) in Table 2. CA refers to carbamic acid, BC to bicarbonate, AC to ammonium carbamate, and HC to hydronium carbamate.
Many species of interest have absorption peaks in the region between 1800 – 1200 cm\(^{-1}\), which makes it challenging to assign peaks properly, sometimes leading to disputes in the community.\(^7\) Furthermore, PEI/Al\(_2\)O\(_3\) is a highly heterogeneous system, with primary, secondary and tertiary amines present in PEI and a large pore size distribution in Al\(_2\)O\(_3\). As such, this composite system is rarely chosen for systematic studies of the role of humidity using DRIFTS. Based on the combined literature from multiple aminopolymers, small molecule amines, and mostly silica-based supports, we propose the tentative peak assignments in Table 2, where the peaks increasing with humidity are listed in bold.

**Table 2. Assignment of IR peaks/bands observed in humidified PEI/Al\(_2\)O\(_3\) composites.**

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
<th>Species</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1293(^{a,b})</td>
<td>N(_{(1)})-CO(_2)</td>
<td>Hydronium carbamate</td>
<td>67</td>
</tr>
<tr>
<td>1324</td>
<td>NCOO skeletal vibration</td>
<td>Ammonium carbamate</td>
<td>55, 68, 71</td>
</tr>
<tr>
<td>1345</td>
<td>C-O sym stretch</td>
<td>Bicarbonate</td>
<td>54, 55</td>
</tr>
<tr>
<td>1380</td>
<td>COO(^{-}) sym stretch</td>
<td>Ammonium carbamate</td>
<td>55, 57, 70</td>
</tr>
<tr>
<td>1412</td>
<td>NH(_3)(^{+}) deformation</td>
<td>NH(_3)(^{+})</td>
<td>72</td>
</tr>
<tr>
<td>1496</td>
<td>NH(_3)(^{+}) sym deformation</td>
<td>NH(_3)(^{+})</td>
<td>55, 72, 73</td>
</tr>
<tr>
<td>1512</td>
<td>CN stretch</td>
<td>Carbamic acid</td>
<td>73</td>
</tr>
<tr>
<td>1545</td>
<td>COO(^{-}) stretch</td>
<td>Ammonium carbamate</td>
<td>68, 73</td>
</tr>
<tr>
<td>1583</td>
<td>COO(^{-}) asym stretch</td>
<td>Hydronium carbamate</td>
<td>67</td>
</tr>
<tr>
<td>1616</td>
<td>C-O asym stretch</td>
<td>Bicarbonate</td>
<td>54</td>
</tr>
<tr>
<td>1633</td>
<td>NH(_3)(^{+}) asym deformation</td>
<td>NH(_3)(^{+})</td>
<td>55, 68, 70, 72, 73</td>
</tr>
<tr>
<td>1699</td>
<td>C=O stretch</td>
<td>Carbamic acid</td>
<td>55, 57, 68, 72, 73</td>
</tr>
</tbody>
</table>

\(^a\)Peaks that increase with RH are listed in bold. \(^b\)Some peak positions shift with humidity. Peak positions are reported for the 100% RH sample.
IR signatures from ammonium carbamate can be observed for all levels of humidity, while other peaks grew or appeared only as humid CO$_2$ was introduced to the system. Such peaks have been assigned to carbamic acid at 1699 cm$^{-1}$ and 1512 cm$^{-1}$, some weak contributions of bicarbonate at 1345 and 1616 cm$^{-1}$ were observed, and the features at 1293 cm$^{-1}$ and 1582 cm$^{-1}$ best fit the absorption of hydronium carbamate, which has been mainly reported for tetraethylenepentamine (TEPA) thin films by Miller and co-workers. The authors also computationally validated the rapid diffusion of CO$_2$ through hydronium carbamate species in TEPA during humid conditions. While the formation of bicarbonates in humid conditions is sometimes put forward as the major mechanism, we measure only subtle contributions from these species, which is in line with the measurement of bicarbonate formation predominantly with tertiary amines or with secondary amines at low PEI loadings. Peaks associated with carbamic acid and hydronium carbamate experience the highest increase in intensity in humid conditions with our materials. As the latter species capture CO$_2$ without promoting inter-chain ionic crosslinking, these results provide support at the molecular level for understanding humidity-promoted polymer mobility observed with both fluorescence and NMR relaxometry measurements.

Finally, we note that Potter and co-workers demonstrated the acidity of Al$_2$O$_3$ supports can impact the reaction mechanism of CO$_2$ with tethered aminopropylsilyl groups in dry conditions. Especially at low amine-loading, CO$_2$ was shown to interact directly with the Al$_2$O$_3$ support, while these interactions were suppressed at higher amine-loadings. We did perform both small and wide-angle X-ray scattering (SAXS, WAXS) measurements to probe the role of Al$_2$O$_3$ in our system (Figure S7). While we observed that the impact of CO$_2$ on the Al$_2$O$_3$ crystal structure is negligible at 100% RH conditions, likely due to the high levels of hydroxylation on the surface of Al$_2$O$_3$, in
dry conditions, the presence of CO$_2$ dramatically degrades the Al$_2$O$_3$ crystal structure (see brief discussion in SI). The result serves to highlight the non-innocent role that the changing support may have on influencing PEI mobility at the polymer-support interface as the composite uptakes CO$_2$. However, a more detailed study of the nature of the degradation of the Al$_2$O$_3$ crystal structure as a function of CO$_2$ capture is outside the scope of this current manuscript and will be reported elsewhere.

**Conclusions.**

This work demonstrated the value of two benchtop techniques for studying polymer mobility within nanocomposite DAC materials as a function of CO$_2$ and water adsorption. First, we assessed the efficacy of employing a fluorescent probe technique for understanding polymer mobility in a series of humidified PEI:Al$_2$O$_3$ composites, correlating measurements of moisture uptake with changes in the emission spectra. We then did the same for CO$_2$ sorption in these materials across a range of temperatures as well as values of RH. We correlated the fluorescence data and implied changes in mobility with data from a second benchtop technique, namely a portable magnetic resonance sensor known as the NMR MOUSE. Changes in spin-spin and spin-lattice relaxation measurements with this technique helped corroborate conclusions drawn from fluorescence regarding polymer mobility. We then coupled all this information with DRIFTS data, which provided molecular level support for understanding the fundamental underpinnings of humidity-promoted polymer mobility in these materials observed with both fluorescence and NMR relaxometry measurements. Given the large matrix of variables that can influence polymer mobility in confinement, which continue to change as a function of sorbent lifetime and cycling, these high throughput techniques for quantifying *in operando* changes in mobility position the
field for rapid advancement in understanding and deployment of these materials in real-world DAC systems.

Methods.

Materials. Tetrakis(4-hydroxyphenyl)ethylene (THPE) was purchased from TCI. Branched polyethyleneimine (PEI, $M_n = 600 \text{ g/mol}$, $M_w = 800 \text{ g/mol}$) was purchased from Sigma; prior to use, PEI was stirred and heated at 100 °C under 25 mtorr vacuum for 72 h to remove any residual volatile organics. Mesoporous $\gamma$-Al$_2$O$_3$ was purchased from Sasol and dried at 100 °C under 25 mtorr vacuum overnight prior to any use. All other reagents and chemicals were purchased from Aldrich and used without purification, unless otherwise noted.

Composite Preparation. Sorbents were prepared by first doping bulk PEI (1 g) with 1 wt.% THPE (10 mg) and stirring under N$_2$ in the dark at 50 °C for 1 h. Mesoporous $\gamma$-Al$_2$O$_3$ (1.5 g) was then impregnated with this mixture, targeting a ~70% pore fill, by first stirring doped PEI and Al$_2$O$_3$ in separate methanol solutions (~10 mg/mL) for 1 h, and then combining and stirring overnight. Methanol was removed from this combined mixture with a rotary evaporator. The composite was then dried at 25 mTorr vacuum overnight at 100 °C in the dark. Thermogravimetric analysis (TGA) was employed to verify the weight fraction of PEI in the composite was ~40 wt.%.

Relative Humidity. Samples were pre-equilibrated to a given RH with the following procedure. 150 mg of 40 wt.% PEI:Al$_2$O$_3$ were evenly dispersed into five quartz cuvettes (30 mg in each). Five different aqueous saturated salt solutions were prepared to create chambers with five different RH values. Nitrogen was bubbled through each saturated solution overnight to remove oxygen. Using an N$_2$ purged glove bag, the cuvettes were transferred under N$_2$ into the chambers, which were then sealed. The samples equilibrated at a given RH for 72 h before the chambers were
opened and the cuvettes were quickly sealed with a Teflon lined cap. The PEI/Al$_2$O$_3$ composites were weighed before and after the 72 h equilibration time to calculate the mass of water adsorbed. For experiments that required both flowing gas and the maintenance of a given RH, a set of mass flow controllers was employed. Dry 400 ppm CO$_2$ passed through one controller, and a second stream of 400 ppm CO$_2$ passed through a separate controller and then a water bubbler. These lines were then combined into one stream for tuning RH, passed through a given sample, and then connected as exhaust gas to a LiCOR 850 quantitative CO$_2$/H$_2$O analyzer.

**Thermogravimetric analysis (TGA).** PEI content in the Al$_2$O$_3$ composite was estimated using a TA Instrument Q600 TGA apparatus according to a literature procedure.$^{74}$ Weight loss from 120 to 900 °C under a 100 mL/min flow of N$_2$ diluted air was recorded at 10 °C/min and normalized by the residual mass at 900 °C.

**Photoluminescence (PL) spectroscopy.** PL experiments were performed on a custom-built Princeton Instruments spectrometer using a liquid N$_2$-cooled Si CCD (PyLoN) array for collecting visible-NIR spectra (400-900 nm). Intensity calibration was preformed daily using an IntelliCal USB-LSVN (9000-410) calibration lamp. Samples were placed in a 2 mm quartz cuvette and excited with a 365 nm LED (7.5 nm FWHM) in an oxygen-free environment. A 400 nm longpass filter was employed between the sample and collection fiber. Emission spectra were collected from 200 – 800 nm using a 150 g/mm grating with 800 nm blaze and 3 mm slit; 20 spectra were averaged with an overall exposure time of ~5 seconds for each measurement. Temperature control was achieved with an Oxford Instruments OptistatDN sample-in-N$_2$-vapor cryostat. Unless otherwise specified, polymer samples were both cooled and heated at a rate of ~1°C/min. The standard error was calculated by dividing the standard deviation by the square root of the sample size, typically attained from three different independent samples.
**MOUSE T₂ and T₁ Relaxometry Measurements.** T₁ and T₂ NMR relaxometry measurements were carried out with a single-sided PM2 NMR-MOUSE (Mobile Universal Surface Explorer) from Magritek GmbH, operating at a frequency of 28.05 MHz for ¹H with the static magnetic field gradient of 39.9 T/m. Signals are detected by a horizontal slice detection area of 12.5 x 12.5 mm² configured to the max penetration depth of 1.9 mm. For these measurements, a slice thickness of ~50 µm (acquisition time of 12 µs) was used to reduce the echo time and maximize the acquisition volume of signal.

As these samples were contained within a small vial as loose powder, at the start of each measurement a rapid profile incrementing 50 µm steps over the full depth range was first taken to observe the location of maximum signal and the position of the stage was then moved to that location for the T₂ and T₁ measurements. A radio frequency pulse length of 1.8 µs with varying amplitudes was used for the 90° and 180° pulses in the CPMG and T₁ saturation recovery experiments for measuring T₂ and T₁, respectively. For the CPMG experiments an echo time of 32 µs was used with 1000 echoes totaling 32 ms in acquisition time and between 64 to 512 scans were acquired to improve signal to noise. For T₁ saturation recovery experiments the recovery delay was incremented exponentially with 24 steps between 0 to 1200 ms max recovery time, a CPMG detection was used for detecting each T₁ recovery increment using the same echo time of 24 µs, co-additiong the first 10 echoes, and acquiring 64 scans to improve signal to noise. The error bars on T₂ values in Figure 5 represent standard deviation error calculated from the covariance output of the scipy.optimize.curve_fit function in python that uses a non-linear least squares analysis.

**Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).** The surface intermediates formed during the PEI/Al₂O₃ and CO₂ interactions with varying levels of RH were monitored with DRIFTS. A praying mantis cell from Harrick Scientific was employed with ZnSe
windows that remains optically transparent between 4,000 – 800 cm\(^{-1}\). The samples were pre-humidified for 72 h prior to any measurements and were then transferred to the DRIFTS cell. Upon closing the cell, a background was immediately collected over 256 scans and with 4 cm\(^{-1}\) resolution. Subsequently, 100 sccm of anhydrous or humid CO\(_2\) stream was introduced into the chamber, and difference spectra were recorded after 5, 10, 15, 20, 25, 30, 60, and 90 min after the background was acquired. Because of the gas flow, a loss of some of the powder with time from the sample holder attenuated the signal intensity over 90 min from ~5 to 4. After each sample, the humidity of the CO\(_2\) stream was adjusted and equilibrated using a LiCOR-850 in line with the exhaust line, which was also used to monitor the CO\(_2\) and H\(_2\)O concentrations in the gas stream.

ASSOCIATED CONTENT

Supporting Information. Emission spectra, DRIFTS data, NMR relaxometry data, CO\(_2\) cycling experiment, SAXS/WAXS data and discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Wade A. Braunecker - National Renewable Energy Laboratory, 15013 Denver West Pkwy, Golden, CO 80401; Department of Chemistry, Colorado School of Mines, 1500 Illinois St., Golden, CO 80401; https://orcid.org/0000-0003-0773-9580; Email: Wade.Braunecker@nrel.gov
Authors

Glory A. Russell-Parks – Department of Chemistry, Colorado School of Mines, 1500 Illinois St., Golden, CO 80401; National Renewable Energy Laboratory, 15013 Denver West Pkwy, Golden, CO 80401; https://orcid.org/0000-0001-9059-1681

Noemi Leick - National Renewable Energy Laboratory, 15013 Denver West Pkwy, Golden, CO 80401; https://orcid.org/0000-0002-2014-6264

Maxwell A. T. Marple – Materials Science Division, Physical and Life Science Directorate, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, California 94550; https://orcid.org/0000-0001-5251-8301

Nicholas A. Strange - Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator, Laboratory, Menlo Park, CA 94025; https://orcid.org/0000-0001-5699-7274

Brian G. Trewyn - Department of Chemistry, Colorado School of Mines, 1500 Illinois St., Golden, CO 80401; Materials Science Program, Colorado School of Mines, 1500 Illinois St., Golden, CO 80401; National Renewable Energy Laboratory, 15013 Denver West Pkwy, Golden, CO 80401; https://orcid.org/0000-0003-4027-7402

Simon H. Pang – Materials Science Division, Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, California 94550; https://orcid.org/0000-0003-2913-1648

Notes

The authors declare no competing financial interest.
ACKNOWLEDGMENT

This work was authored in part by Alliance for Sustainable Energy, LLC, the manager and operator of the National Renewable Energy Laboratory for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Work at Lawrence Livermore National Laboratory was performed under the auspices of the U.S. DOE under Contract DE-AC52-07NA27344. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. DOE, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. This work was supported by the U.S. DOE, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division in response to the DOE National Laboratory Announcement Number LAB 20-2303. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

REFERENCES


Supporting Information for:

Fundamental Insight into Humid CO₂ Uptake in Direct Air Capture Nanocomposites Using Fluorescence and Portable NMR Relaxometry

Glory A. Russell-Parks, a,b Noemi Leick, b Maxwell A. T. Marple, d,d Nicholas A. Strange, e Brian G. Trewyn, a,b,c Simon H. Pang, d Wade A. Braunecker a,b,*

a Department of Chemistry, Colorado School of Mines, 1012 14th Street, Golden, CO 80401
b National Renewable Energy Laboratory, 15013 Denver West Pkwy, Golden, CO 80401
c Materials Science Program, Colorado School of Mines, 1012 14th Street, Golden, CO 80401
d Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, California 94550
e Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator, Laboratory, Menlo Park, CA 9402d5

*Email: Wade.Braunecker@nrel.gov

Table of Contents

I. Emission Spectra ........................................................................................................................................S2
II. CO₂ Sorption Cycling Data ..................................................................................................................S3
III. NMR Relaxometry ..................................................................................................................................S4
IV. Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS) ..................................................S7
V. Small Angle and Wide Angle X-Ray Scattering (SAXS, WAXS) .........................................................S9
VI. References ..............................................................................................................................................S10
I. Emission Spectra

Figure S1. 40 wt.% PEI/Al₂O₃ composite, 0.4 wt% THPE, pre-equilibrated to a given RH, 100 sccm of 400 ppm humid CO₂ in N₂. Change in the emission spectra recorded with time for 0, 11, 33, 53, 75, and 100% RH.
II. CO₂ Sorption Cycling Data

**Figure S2.** 30.0 mg of a 40 wt.% PEI:Al₂O₃ composite exposed to continuous flow of 400 ppm CO₂ in dry N₂ (100 sccm), cycled between 48 min at 25°C (adsorption) and 12 min at 100°C (desorption).
Figure S3. 40 wt.% PEI/Al₂O₃ composites, equilibrated to 6 different values of RH for 72 h. (Left) Echo train attenuation data for transverse, spin-spin relaxation ($T_2$). (Right) ILT Relaxation spectra.
Figure S4. 40 wt.% PEI/Al$_2$O$_3$ composites, equilibrated to 6 different values of RH, after exposure to 90 min of 400 ppm CO$_2$ (100 sccm). (Left) Echo train attenuation data for transverse, spin-spin relaxation ($T_2$). (Right) ILT Relaxation spectra.
Figure S5. Longitudinal, spin-lattice relaxation values ($T_1$) for 40 wt.% PEI/Al$_2$O$_3$ composites, equilibrated to 6 different values of RH, before and after 90 min of 400 ppm CO$_2$ flow. The dashed line corresponds with the bulk anhydrous PEI value of $T_1$. 
### IV. Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS)

**Table S1:** Assignment of IR bands observed in Figure 8(a) of the main text.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
<th>Species</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band</td>
<td>Peak(s) center position</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3730 – 3570</td>
<td>3656</td>
<td>O-H stretch</td>
<td>Hydroxyl groups</td>
</tr>
<tr>
<td>3602 - 3305</td>
<td>3466 (p1) 3367 (p2)</td>
<td>N-H, asym stretch (p1), sym stretch (p2)</td>
<td>Primary amines</td>
</tr>
<tr>
<td>3165 - 2966</td>
<td>2995</td>
<td>NH₃⁺ stretch</td>
<td>Ammonium ion from ammonium carbamate</td>
</tr>
<tr>
<td>2966 – 2792</td>
<td>2945 (p1) 2829 (p2)</td>
<td>C-H, asym stretch (p1), sym stretch (p2)</td>
<td>-CH₃ and -CH₂ groups in PEI</td>
</tr>
<tr>
<td>2790 - 1800</td>
<td>2490 (p1) 2129 (p2)</td>
<td>NH₂⁺/NH₃⁺</td>
<td>Ammonium ions from ammonium carbamate</td>
</tr>
</tbody>
</table>

When there is more than one peak associated with the band, p1 and p2 are used to differentiate the peaks.
**Figure S6:** DRIFT spectra taken after 5 (red trace), 10, 15, 20, 25, 30, 60, and 90 min (purple trace) exposure of CO₂ with (a) 0% RH, (b) 11% RH, (c) 33% RH, (d) 53% RH, (e) 75% RH, (f) 100% RH.
V. Small Angle and Wide Angle X-Ray Scattering (SAXS, WAXS)

Figure S7: Ex situ beamline small angle (SAXS) (top) and wide angle X-ray scattering (WAXS) (bottom) of PEI/Al₂O₃ systems used in this study: Al₂O₃ only (red trace), anhydrous PEI/Al₂O₃ (blue trace), PEI/Al₂O₃ after flowing dry CO₂ for 72 h (green trace), hydrated PEI/Al₂O₃ at 100% RH (black trace), hydrated PEI/Al₂O₃ after flowing humid CO₂ at 100% RH (orange trace).
A reaction with CO$_2$ severely degrades the crystal structure of $\gamma$-Al$_2$O$_3$ in the anhydrous material (green trace). This loss in crystallinity indicates that CO$_2$ directly interacts with the reactive surface of $\gamma$-Al$_2$O$_3$ leading to increased disorder that propagates through the $\gamma$-Al$_2$O$_3$ matrix. When the CO$_2$ stream is hydrated (orange trace), the $\gamma$-Al$_2$O$_3$ surface is hydroxylated and appears less reactive to the CO$_2$, causing a lesser degree of disorder. We do not observe the same trend with PEI/SBA-15 samples. SiO$_2$ is less reactive than $\gamma$-Al$_2$O$_3$, and the CO$_2$ capacity of PEI infiltrated in SBA-15 can be up to 2 orders of magnitude less than that infiltrated in $\gamma$-Al$_2$O$_3$.\textsuperscript{7}

VI. References.