# Lewis Base Polymers for Modifying Sorption and Regeneration Abilities of Amine-Based Carbon Dioxide Capture Materials

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ABSTRACT: In this work, we investigate the effects of modifiers on the carbon dioxide (CO_2) capture/release abilities of silica-supported amine-based polymers. The primary amine-based polymers consisted of branched poly(ethylene amine) (PEI) and Jeffamine T-403, having aliphatic and ether-based backbones, respectively. These polymers were dispersed on nanosilica, and their CO_2 capture/release abilities were determined with and without the addition of the Lewis basic polymer modifiers, poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA), and poly(ethylene glycol) (PEG). The

greatest effect for increasing the CO_2 capture capacity was observed for PEG additives while other modifiers lowered the capture capacity. However, PVAc and PMMA were found to significantly influence the kinetics of absorption and desorption. For absorption, modifiers improve mass transfer and offer better coverage of the silica surface so more amine groups are available at the surface of the sorbent for CO_2 binding. Most markedly, while PEG improved desorption, PMMA and PVAc led to even faster desorption rates and higher regeneration abilities at 45 °C without the need for further heating. Thus, a combination of PEG and other Lewis base-containing modifiers have the potential to be used in concert to fine-tune the capacity, mass transfer, regeneration ability, and kinetics for amine-based CO_2 sorbents.

KEYWORDS: Sustainability, Carbon capture, CO_2 capture, Silica nanoparticles, Sorbents, Flue gas
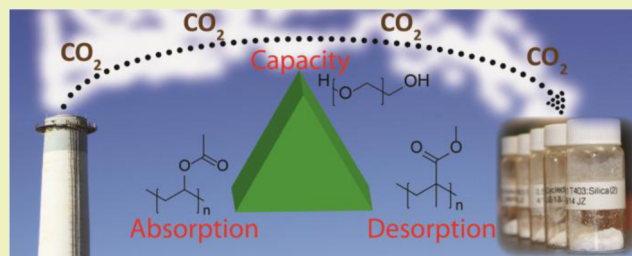
INTRODUCTION

The development of technologies capable of effectively capturing or separating harmful gases of anthropogenic emissions is an area of research with growing urgency. For instance, the development of efficient, reversible, and, very importantly, *economic* capture of greenhouse gases, particularly CO_2, assumes great importance in such endeavors.[1–3] While we may devise a highly efficient method to capture greenhouse gases, if these methods are cost-prohibitive, the implementation will be an arduous struggle. For example, the current commercially available method for post-combustion CO_2 capture, based upon an aqueous solution of monoethanolamine (MEA), despite high reactivity, selectivity, good sorption capacity, and low material cost advantages, has serious inherent drawbacks especially a high energy economic penalty for regeneration leading to an overall steep cost for the system (i.e., capital and operating expense of using a stripper with a reboiler for the regeneration of 30% MEA in aqueous solution accounts for a substantial fraction, roughly two-thirds of the overall CO_2 capture costs for this system[4]). Further, chemical degradation of this system causes serious foaming, corrosion, and solvent loss, contributing up to 21% of the overall expense.[4]

Our research efforts are focused on developing materials capable of specific CO_2 capture with facilitated (low energy cost) release. Currently, such materials remain lacking; while certain porous solid sorbents allow for facile release of CO_2, they do not offer the specificity of amine-based sorbents, which

chemically bind CO_2 but at a high cost for CO_2 release. Our recent study revealed potential paths forward for a CO_2-specific capture with low-energy release technology based on sorbents comprising silica-supported polymers where the polymer units contain terminal primary amine groups and backbone ether functional groups.[5] In this system, the ether backbone proved critical to enhancing the CO_2 facility allowing sorbent regeneration *without* sacrificing the CO_2 binding selectivity provided by the primary amine groups. Further, studies of amine-infused solid sorbents found that incorporation of polyethylene glycol (PEG) polymers substantially improves CO_2 adsorption/desorption rates and overall absorption capacity,[5–15] as well as membrane CO_2 separation abilities.[15,16] The actual mechanism behind such enhancements are not fully understood. One report suggested that the presence of terminal hydroxyl groups in PEG could change, to some extent, the primary amine absorption mechanism of CO_2 so a bicarbonate is formed instead of a carbamate.[17] Others suggested the formation of a carbamate species between the amine, CO_2, and the OH group of PEG (in this case, the OH group replaces another amine in the carbamate complex, allowing for more CO_2 to be captured per amine)[8] and/or lower local viscosities (hence, increased mass transfer).[5,9] While some preliminary
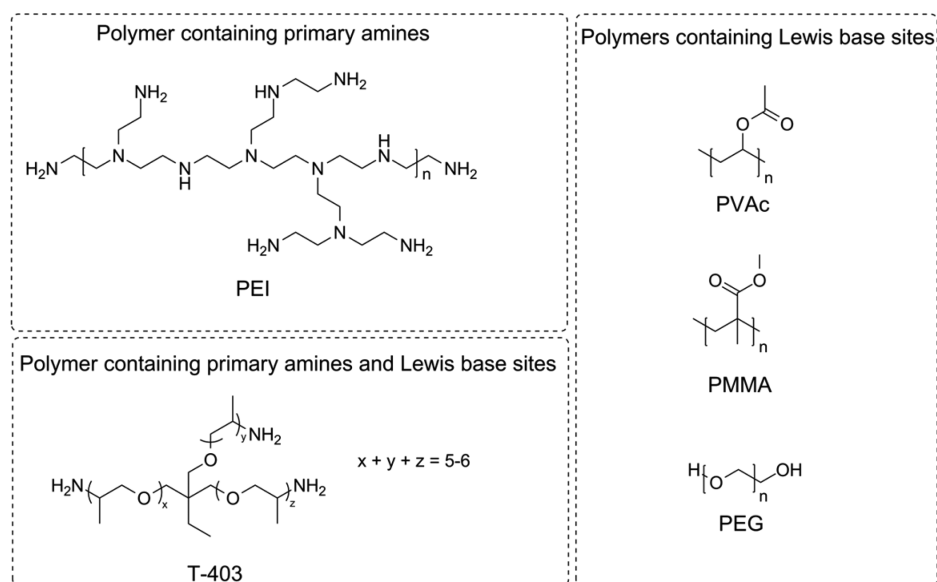
Figure 1. Structure of polymers used in this work.

studies have been conducted,[12,18] the true underlying nature of this PEG-induced enhancement effect has not yet been fully explored. Further, PEG is also well known to interact with CO_2 in a Lewis acid−base fashion where the CO_2 carbon acts as a Lewis acid toward the ether oxygens within the PEG backbone.[19−22] Meredith et al. used calculations to demonstrate that when weak chemical interactions between the carbonyl groups of poly(methyl methacrylate) (PMMA) and CO_2 were taken into account, CO_2 solubility within PMMA increased by a factor of 7−16 as compared to excluding these specific interactions.[19] Some of the same authors also demonstrated experimentally that electron-donating functional groups, such as ethers, associated with high pressure CO_2 through Lewis acid−base interactions.[23] In the experimental study, polymer films were impregnated with pressurized CO_2. After decompression and evacuation of any free gaseous CO_2, the IR absorption was measured to determine if Lewis acid−base interactions were present for the CO_2 remaining within the polymer. The splitting of the ν_2 IR mode of CO_2 was observed in polymers possessing electron-donating functional groups and was attributed to their interaction with the carbon of CO_2 in a Lewis acid−base fashion. Given the persistence of this Lewis acid−base interaction after decompression, it is feasible that these types of interactions may also play a role in the underlying mechanism of PEG enhancement of CO_2 sorbtion capacity as observed in amine-based CO_2 sorbents. Thus, similar CO_2 sorption enhancements may be achieved using other Lewis base-functionalized polymers as modifiers.

In order to investigate this possibility, we examine the effects of a Lewis acid−base interaction on CO_2 capture/release properties using different Lewis basic polymers. By elucidating how different polymer functionality affects CO_2 sorption/ desorption, we aim to develop the design rules for low energy cost CO_2 sorbents. Herein, we compare a well-known silica-supported polyethylene imine (PEI) sorbent (where the PEI serves to maintain the chemical specificity for CO_2 binding) and our previously reported silica-supported Jeffamine sorbent with and without incorporation of additional polymers containing Lewis basic sites, seeking to elucidate the effects

of the Lewis acid−base interactions on CO_2 capture and release characteristics.

EXPERIMENTAL METHODS

Materials. Jeffamine T-403 was obtained from Huntsman International, LLC (The Woodlands, TX). Branched poly(ethylene amine) (PEI (M_w ~25,000), poly(vinyl acetate) (PVAc, M_w ~150,000), poly(methyl methacrylate), (PMMA, M_w ~35,000), poly(ethylene glycol) (PEG, M_w ~ 400), fumed silica powder (14 nm), and methanol (≥99.9%) were purchased from Sigma-Aldrich (St. Louis, MO). Carbon dioxide (99.9% grade) and nitrogen (ultrahigh purity) gases were obtained from Air Gas.

Sorbent Preparation. A typical method for the preparation of the polymer/silica hybrid sorbents is illustrated here. Methanolic stock solutions of the polymers were freshly prepared. These polymer stock solutions were added in the required volumes, depending on the desired polymer-to-silica ratio, to a methanol dispersion of a known mass of silica while stirring. These solutions were allowed to continuously stir for at least 1 h followed by heating at 45 °C to drive off the methanol, leaving behind polymer-coated silica as white powder. All ratios of polymer:silica reported in this work are based on mass.

Materials Characterization. All FTIR measurements were performed on a Nicolet 4700 equipped with a Thermo Smart Performer germanium crystal attenuated total reflection (ATR) attachment. The resolution was set to 6 cm⁻¹ with 36 scans accumulated for each sample.

CO_2 Capture/Regeneration Tests. CO_2 capture/regeneration experiments were conducted using a thermogravimetric analyzer (TA Instruments Q50). In a typical experiment, a small sample of the sorbent (~20 mg) was placed within a Pt sample pan, loaded within the TGA instrument, and followed by heating to 80 °C under dry nitrogen (N_2) flow (66 mL/min) in order to prepare the sample by reducing the amount of adsorbed gases and humidity. The temperature was then reduced to 45 °C under N_2 flow. After temperature equilibrium, the gas was switched to CO_2 at the same flow rate of 66 mL/min. The increase in sample mass was recorded over time until CO_2 sorption equilibrium was reached. In order to regenerate the sorbent (CO_2 release), the flowing gas was reverted back to N_2 (66 mL/min), and the mass decline was recorded over time while maintaining the temperature at 45 °C.

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RESULTS AND DISCUSSION

Polymer-coated silica particles were prepared using the polymers shown in Figure 1 and combinations thereof. As controls, we tested sorbents using either PEI, which contains primary amine groups, or T-403, a polyethoxyamine polymer containing both primary amines and Lewis base sites. These two systems were compared in our earlier study[5] where both performed similarly for CO_2 sorption, while the T-403-coated silica gave remarkably enhanced regenerability ability under vacuum at 45 °C over PEI-coated silica. In the study at hand, we modified these control sorbents by making sorbents where half of the polymer mass was now a Lewis -base polymer, (i.e., PMMA, PVAc, or PEG; Figure 1).

Each sorbent was characterized using FTIR to confirm the presence of polymer on the silica nanoparticles. For example, Figure 2 compares the FTIR spectra of bare silica, T-403, and
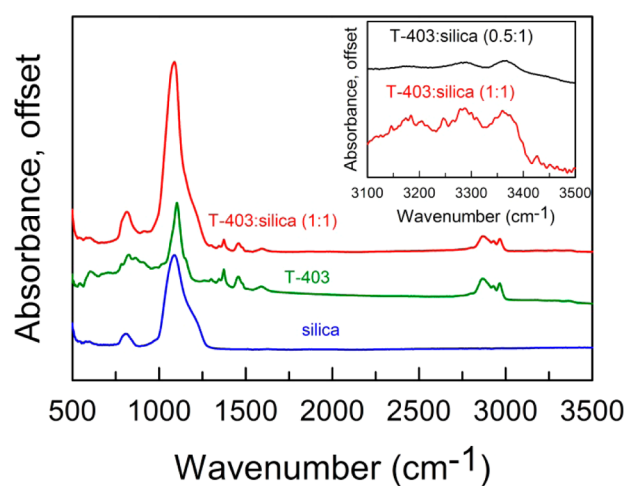
Figure 2. ATR-FTIR profiles for 14 nm silica (blue), neat T-403 (green), and T-403:silica (1:1, w/w) sorbent (red). The primary amine stretches at 3100−3500 cm^{-1} are present for both 1:1 and 0.5:1 T-403:silica sorbents (inset), demonstrating the availability of CO_2-reactive amines in both cases, with a greater relative absorbance (and thus availability) demonstrated for the 1:1 T-403:silica sorbents.

the 1:1 T-403:silica sorbent. The silica framework shows a characteristic strong, broad, IR absorption band at 1110 cm^{-1} with a broad shoulder at 1180 cm^{-1}, while T-403 has characteristic C−O−C stretches in the 1000−1400 cm^{-1} region, C−H antisymmetric and symmetric stretches from 2850−2990 cm^{-1}, and N−H bands at 3100−3400 cm^{-1} (stretching), 1590 cm^{-1} (deformation), and 750−850 cm^{-1} (wagging).[24,25] The deposition of T-403 onto the fumed silica host is clearly evident in the FTIR spectrum of the composite, which contains bands characteristic of both the silica and Jeffamine T-403. In each case, the polymers were shown to be present on the silica surface with primary amine groups from either T-403 or PEI available for CO_2 capture.

Each sorbent was tested for its CO_2 capture/release ability to determine the influence of Lewis base-containing polymers on the sorbent system at 45 °C. The sorbents were introduced into the TGA instrument and dried at 80 °C before equilibrating to 45 °C under N_2 flow. After temperature equilibration, CO_2 was introduced, and the mass increase in each sorbent was recorded over time to track CO_2 sorption. After reaching CO_2 sorption equilibrium, the gas was switched back to N_2, and with the temperature still being constant at 45 °C, the weight loss was

recorded to sorbent regeneration. Data were obtained for several cycles of CO_2 sorption/desorption runs, as shown in Figure 3 for the case of 0.5:0.5:1 PVA:T403:silica.
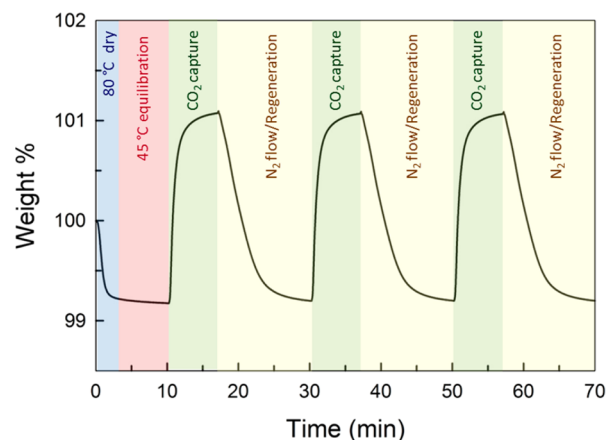
Figure 3. Representative TGA experiment for sequential cycles of CO_2 sorption/desorption. Sorbent material was PVAc:T-403:silica (0.5:0.5:1 mass ratio), gas flow rate was 66 mL/min, and T = 45 °C for both sorption and desorption cycles.

CO_2 Sorption Capacity. The CO_2 sorption capacities (expressed in mg of CO_2/g sorbent) were determined from the equilibrium (maximal) CO_2 sorption amounts for measurements made on at least three independent samples for each sorbent studied. These results are shown in Figure 4 and Table
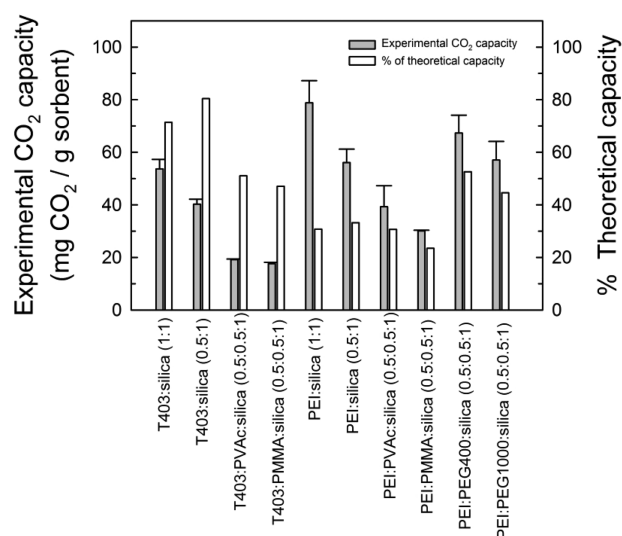
Figure 4. CO_2 sorption capacities of each sorbent studied.

1. The sorption capacity for the T-403:silica (1:1) composite was lower than that found in our earlier work[5] (53.7 ± 3.6 vs 69.8 ± 5.3 mg CO_2/g sorbent). However, our current work uses a TGA instrument requiring a much smaller sample size for measuring the CO_2 sorption (~30 mg vs 0.5 g). This clearly indicates that experimental CO_2 sorption capacity is dependent on sample size and the experimental configuration, an important consideration for pilot-scale studies. Similarly, the PEI:silica (1:1) sorbent also showed differences in maximal CO_2 capacity in this work compared to our previous study.[5] However, the smaller sample size in this case gave roughly double the CO_2 sorption capacity (78.8 ± 8.4 vs 36.3 ± 8.4 mg

Table 1. CO$_2$ Sorption Capacities of Sorbents from This Study and Previously Reported Literature Values

sorbent	theoretical maximal CO$_2$ sorption capacity[a] (mg CO$_2$ g^{-1})	experimental CO$_2$ sorption capacity[b] (mg CO$_2$ g^{-1})	% of theor. max. sorbed	% regeneration (10 min of N$_2$)	$t_{50\%}$ regen. (min)
T-403:silica 1:1	75.2	53.7 ± 3.6	71.4	96.3 ± 2.5	4.3
		69.8 ± 5.3 [5,c]	92.8	82.4 ± 12.8 (45 °C, 1 Torr)[5,c]	
T-403:silica 0.5:1	49.6	39.9 ± 1.9	80.4	71.8 ± 13.3	7.0
T-403:PVAc:silica 0.5:0.5:1	37.6	19.2 ± 0.2	51.1	96.5 ± 1.5	2.8
T-403:PMMA:silica 0.5:0.5:1	37.6	17.7 ± 0.5	47.1	97.3 ± 1.9	2.7
PEI:silica 1:1	256	78.8 ± 8.4	30.8	16.2 ± 2.9	>30
		36.3 ± 8.4[5,c]	14.2	3.5 ± 0.9 (45 °C, 12 min, 1 Torr)[5,c]	
		~ 100[9,d]	38.8		
		130 (70 °C)[9,d]	50.7	~ 80% (85 °C, 1 h, vacuum)[9,d]	
PEI:silica 0.5:1	169	56.1 ± 5.1	33.2	20.8 ± 1.8	30.1
PEI:PVAc:silica 0.5:0.5:1	128	39.3 ± 8.0	30.7	34.0 ± 4.2	13.6
PEI:PMMA:silica 0.5:0.5:1	128	30.1 ± 0.2	23.5	44.8 ± 2.3	11.5
PEI:PEG400:silica 0.5:0.5:1	128	67.3 ± 6.8	52.6	35.0 ± 5.9	14.9
PEI:PEG1000:silica 0.5:0.5:1	128	57.1 ± 7.1	44.6	36.8 ± 4.2	14.2
PVAc:silica 0.5:1		0.36 ± 0.18		100 ± 0.1	1.07
PMMA:silica 0.5:1		1.20 ± 0.39		99 ± 0.8	1.42
PEG400:silica 0.5:1		0.88 ± 0.42		100 ± 0.1	0.28
PEG1000:silica 0.5:1		0.70 ± 0.45		100 ± 0.1	1.22

[a]Based on each CO$_2$ reacting with two amino groups to form a carbamate. [b]At 45 °C, unless otherwise noted [c]Our previous study using a larger amount of sorbent than the current study (0.5 g vs ~30 mg) [d]Previous study by Olah and co-workers using precipitated silica in place of fumed silica. However, the group noted no distinct difference in performance when using fumed versus the precipitated silica as the support.

CO$_2$/g sorbent). We note that the higher capacity is in line with the value reported by Olah and co-workers using the same PEI polymer supported on precipitated silica.[9] Given that PEI has 3.4 fold more primary amine sites per gram, it is anticipated that PEI should have a greater CO$_2$ sorption capacity based soley on this criterion. The dependency of CO$_2$ sorption capacity on sorbent scale and experimental configuration is currently under study in our group and will be extended to larger scales.

It is also important to note that, as we previously described,[5] bare fumed silica sorbed less than 10 mg of CO$_2$ per gram of silica. In the current work, we tested PMMA:silica, PVA:silica, PEG400:silica, and PEG1000:silica (0.5:1 polymer:silica) sorbents to determine the ability of the modifier supported on silica to effectively sorb CO$_2$ without a primary amine polymer present. In all cases, the amount of CO$_2$ sorbed was less than 2 mg/mL (Table 1). In the case of PEG400, our data at atmospheric pressure (1.01 bar) is consistent with CO$_2$ mass fraction loadings for PEG400 at CO$_2$ pressures of 53−116 bar[22] with linear regression of mass fraction vs pressure resulting in a r^2 value of 0.998.

Therefore, any significant changes that result from adding modifier silica-supported amine polymers must likely arise from something other than direct interaction of the modifier alone with CO$_2$.

Upon decreasing the amine−polymer percentage to a 0.5:1 polymer:silica mass ratio, the amount of CO$_2$ sorbed decreases as we would expect. However, the lower weight ratio of T-403:silica exhibits an increase in the fraction theoretical capacity for CO$_2$, while this value remains essentially unchanged for the 1:1 and 0.5:1 PEI:silica sorbents. The percent increase in T-403-based sorbent with decreasing T-403 ratio presumable reflects the nanodispersion of T-403 on the silica surface, increasing mass transfer. This dispersion aids in CO$_2$ binding after the sharp increase in polymer viscosity experienced as CO$_2$ binds, as previously described for the 1:1 T403:silica sorbent.[5] Neat T-403 is only capable of absorbing 48.5 mg/g of CO$_2$ before the increasing viscosity prohibits efficient mass transfer.[5] Mass transfer is more efficient at higher CO$_2$ loadings for the lower mass ratio of T-403 as compared to the 1:1 ratio and neat T-403, the percent of theoretical CO$_2$ sorbed decreasing from 80.4% to 71.4%, and 32.2%, respectively. The fraction theoretical capacity obtained for both 1:1 and 0.5:1 PEI:silica samples were comparable, indicating that the PEI dispersion effected both mass loadings equally.
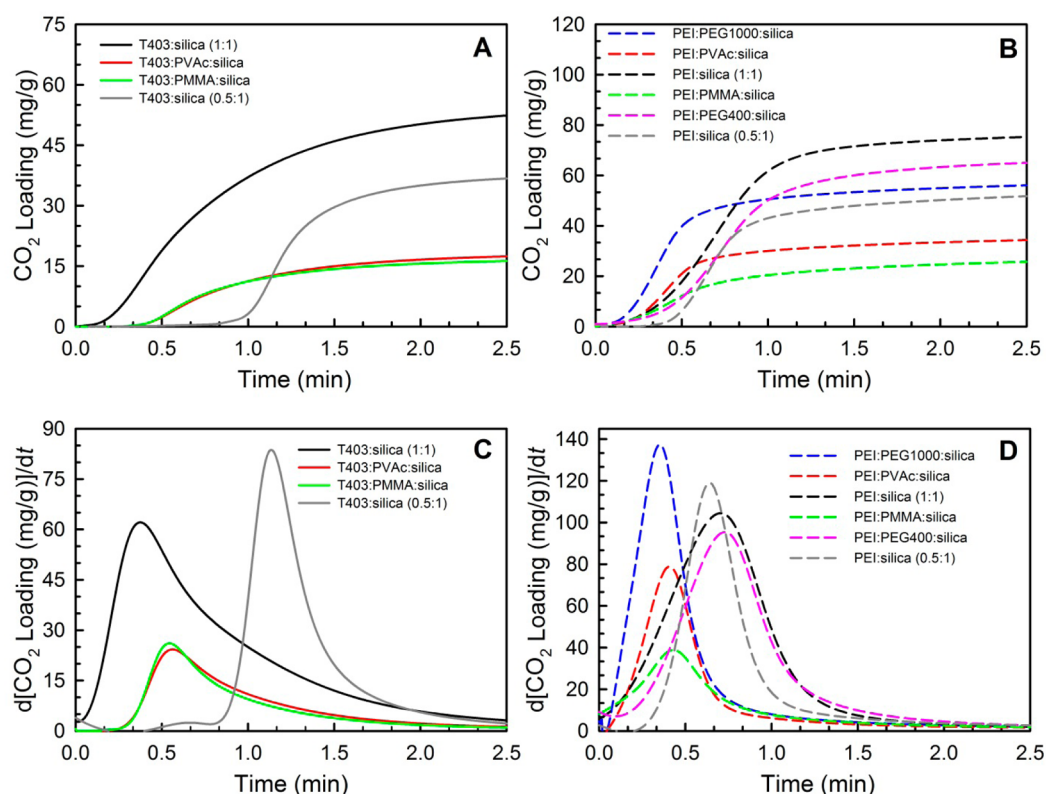
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Figure 5. CO_2 sorption profiles for (A) T-403-based and (B) PEI-based sorbents with and without Lewis base modifiers. Panels C and D represent the first derivative with respect to time of the profiles in panels A and D and therefore represent the instantaneous kinetics of the overall process. All experiments were performed using TGA with a CO_2 flow rate of 66 mL min^{-1}.

The percent theoretical capacity obtained for the T-403:silica samples was higher than the theoretical capacity obtained for the PEI:silica samples. The difference in these two polymers arises due to the PEG-like backbone of the T-403 polymer. Indeed, oxygenated compounds, such as PEG, have been used as solvents for CO_2 removal for many years and have been combined with amine compounds to the same effect of increasing CO_2 sorption.[5,8−14] PEG, when added to amine-containing systems, often increases the CO_2 absorption/desorption rates as well as increasing overall sorption capacity (vide supra). Such benefits are mostly ascribed to the formation of a carbamate species between the amine, CO_2, and the OH group of PEG (in this case, the OH group replaces another amine in the carbamate complex allowing for more CO_2 to be captured per amine[8]) and/or lower local viscosities (hence, increased mass transfer). However, in the case of the T-403, there are only ether groups along the backbone with no OH groups present. Because electron-donating functional groups have been shown to associate with CO_2 through Lewis acid−base interactions by Eckert and co-workers even after decompression and evacuation of free CO_2, it is therefore feasible that such interactions may occur with electron-donating polymers under our experimental conditions especially given the nanodisperse nature of the polymers on silica. As such, the T-403 ether groups and CO_2 may lead to a Lewis acid−base enhancement manifesting in the increased percent of theoretical capacity of CO_2 sorbed for the T-403:silica sorbents vs PEI:silica sorbents. To further test this, we added different Lewis basic polymers (PVAc, PMMA, PEG) to both the T-403- and PEI-based sorbents.

When comparing the Lewis base polymer-modified T-403- and PEI-based sorbents, in each case, the PEI-based sorbent with modifiers had higher CO_2 sorption capacities than their T-403 counterparts. This was in-line with the nonmodified T-403- and PEI-based sorbents based on the fact that there is a higher concentration of amines in the PEI-based sorbents. However, based on the percent theoretical capacity obtained, the PVA- and PMMA-modified T403 silica sorbents outperformed their modified PEI counterparts. It is significant to note that the addition of PVA and PMMA modifiers did not significantly enhance the obtained percent of theoretical capacity over either nonmodified sorbent material. In fact, PVA and PMMA modifiers decreased the percent of the theoretical capacity of CO_2 absorbed versus nonmodified T-403 silica, whereas PVA- and PMMA-modified PEI performs similarly to nonmodified PEI. Conversely, when PEG 400 or PEG 1000 was added to PEI, an overall increase in CO_2 capacity was observed giving rise to a 1.3−1.5 fold increase in the percent theoretical capacity obtained. This is in line with previous studies that noted an increase in absorbed CO_2 when PEG was added as a modifier to an amine-containing polymer.[8,9] Further, the lower molecular weight PEG improved the overall sorption capacity even more than the higher molecular weight PEG, an effect also observed in similar systems by Olah and co-workers.[9] This was ascribed to be a result of the lower viscosity of the lower molecular weight PEG and possible bicarbonate formation. Indeed, the CO_2 capacity improvement does not arise from the PEG itself sorbing CO_2, as 0.5:1 PEG:silica sorbents sorb less than 2 mg/mL of CO_2 at equilibrium. However, a close investigation of the ATR-FTIR data for the PEI:PEG400:silica sorbent after CO_2 exposure did not show any significant peak
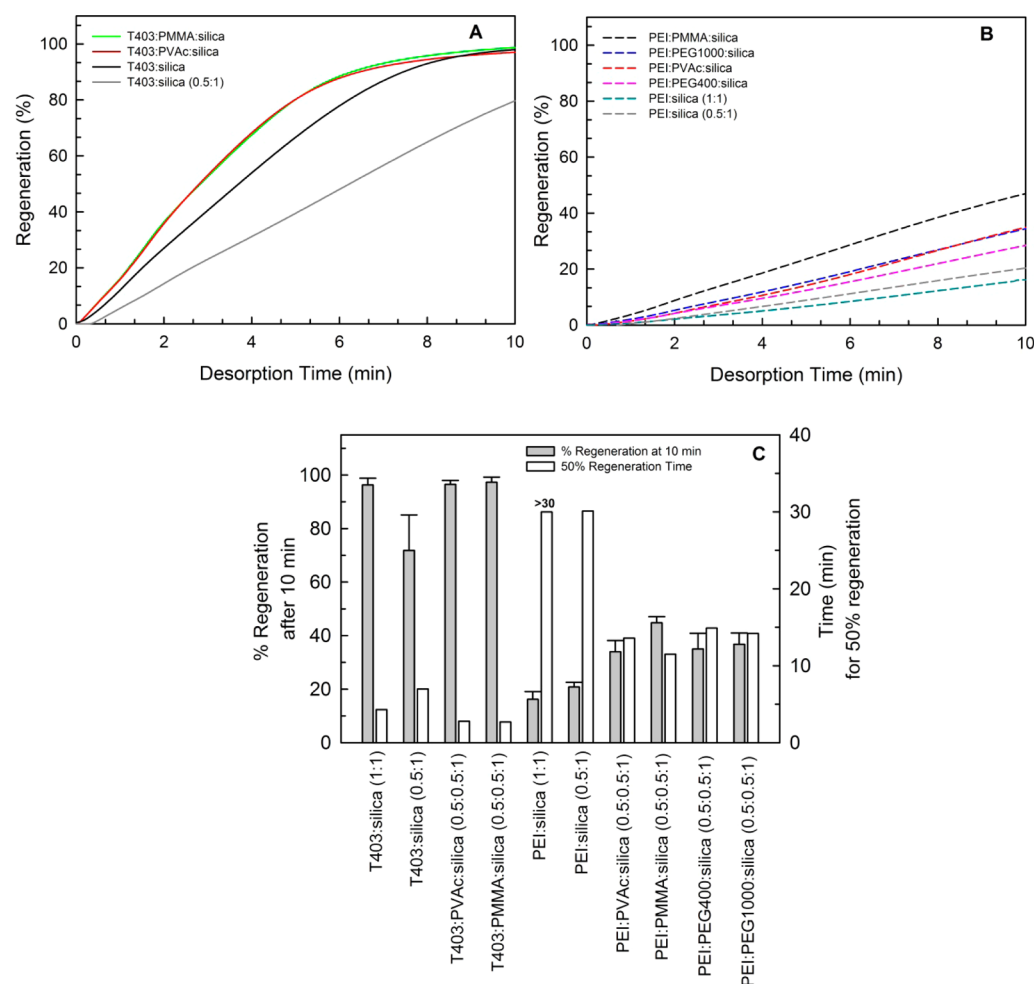
Figure 6. Desorption over time profiles for (A) T-403-based and (B) PEI-based sorbents. Panel C shows the average percent regeneration after 10 min of N_2 flow (66 mL/min) at 45 °C and the time for 50% regeneration to be reached.

difference within the range expected for bicarbonate formation.[26] Yet this does not entirely rule out bicarbonate formation as high loadings of CO_2 were needed for another amine-based system before bicarbonate peaks were apparent within the ATR-FTIR spectra.[27] Therefore, any significant changes that result from adding modifier silica-supported PEI likely arise from an alteration of viscosity with a possible small effect from bicarbonate formation.

Overall, we found PVAc and PMMA do not act to increase the CO_2 capacity or percent theoretical capacity obtained in a manner similar to PEG. However, PVAc and PMMA were found to significantly influence and in some cases improve the kinetics of absorption and desorption as discussed below.

CO_2 Sorption Kinetics. CO_2 sorption by our sorbents is expected to involve carbamate formation (a relatively fast and thermodynamically controlled process), CO_2 diffusion mass transfer through the polymer layers (a relatively slow process that is viscosity and concentration dependent), and possible Lewis acid–base formation (also a relatively fast and thermodynamically controlled process). Figure 5 shows the time-dependent sorption of CO_2 for T-403 and PEI-based sorbents (panels A and B, respectively) and the instantaneous rate for sorption (panels C and D) calculated by the first-derivative of the plots in panels A and B, respectively. By 2–2.5 min, all the sorbents reach equilibrium CO_2 sorption.

Interestingly, for the two T-403:silica sorbents, a decrease in T-403 from a 1:1 to 0.5:1 weight ratio with silica leads to much slower initial sorption at times less than 1 min. However, near the 1 min mark, the CO_2 sorption rapidly increases for the T-403:silica (0.5:1) sorbent with both T-403:silica sorbents reaching saturation at approximately the same time. Because the relative amount of T-403 is decreased in the (0.5:1) sample, it is expected that mass transfer of CO_2 should also be faster, but the trend in the initial data (<1 min) is inconsistent with this expectation. Therefore, additional processes or configuration differences may be present. We suggest the initial lag in the (0.5:1) T403:silica sorbent may be due to larger amounts of T-403 amines initially interacting with the silica surface because there is greater surface area of silica relative to polymer vs the T-403:silica (1:1) sorbent. This is supported by a decrease in the NH stretching region of the FTIR absorbance observed for the 0.5:1 T-403:silica (Figure 2, inset). Therefore, much less T-403 primary amines are available for CO_2 binding on the outside surface of the sorbent. Thus, CO_2 gas must diffuse a greater distance through the polymer before contact with a primary amine. In the higher T-403 concentration sorbent, there are more free amines at the sorbent surface to interact with CO_2, so binding ensues at shorter times with mass transfer limiting the reaction commencement with internal amines. Near 1 min, CO_2 binding proceeds cooperatively for the T-403:silica (0.5:1) at an apparently faster rate than the T-

403:silica (1:1). This is presumably due to the mass transfer limitations being overcome for the 0.5:1 T-403:silica while mass transfer effects are still present in the 1:1 sorbent. This can also be seen in the derivative peak widths with the wider peak for T-403:silica (1:1), indicating the contribution of mass transfer throughout the first 2.5 min compared to the more narrow peak observed for the T-403:silica (0.5:1). Upon addition of PVAc and PMMA modifiers to T-403:silica (0.5:1), the initial lag time is improved, likely due to the modifier offering more silica coverage and therefore less sites for the T-403 amines to interact with the silica. However, the instantaneous kinetic rates are slower for the modified T-403:silica sorbents than for the neat T-403:silica samples. At the higher CO_2 loadings, mass transfer has an effect on all the sorbents indicated by the tailing of the kinetic peaks.

Similar to the T-403 sorbents, the nonmodified PEI:silica sorbents (Figure 5, C and D) exhibit a lag time effect dependent on the mass ratio of the components with lower PEI loading leading to a slightly longer lag time, although this effect is less dramatic than in the T-403-based sorbents. Also, slighter faster kinetics are obtained for the 0.5:1 PEI:silica sorbent between 0.5 and 1 min. However, the effect of modifiers on CO_2 sorption for PEI:silica sorbents is slightly different than for the T-403:silica sorbents. For example, the lag time effect is nearly eliminated when any Lewis base modifiers are added to the PEI-based sorbents. When the PEG1000 modifier is used, the fastest instantaneous kinetics are obtained for all sorbents studied. However, no kinetic improvement is observed for the PEG400-modified sorbent over neat PEI-based sorbents. Further, the broadened peak, compared to PEG1000-modified sorbents, indicates that mass transfer may have a greater influence in the PEG400-modified sorbent. This is interesting because the enhancement of the overall sorption capacity for lower molecular weight PEG modifiers is thought to be a viscosity (hence, mass transfer) effect. Because overall sorption capacity was improved but not instantaneous kinetics, bicarbonate formation may indeed be playing an additional role in these PEG-modified systems even with bicarbonate formation not yet apparent within the ATR-FTIR spectra. In this case, the OH concentrations will be higher for PEG400 than PEG1000 at the same mass loadings thus leading to overall better capacity as observed. While PVAc and PMMA modifiers do not lead to an improvement in overall sorption capacity of the PEI-based sorbents, they do offer mass transfer enhancement (presumably through modification in the local viscosities) as seen in the narrower peaks in Figure 5D, which reach maximal instantaneous kinetic rates at earlier times. Thus, a combination of PEG- (or OH-)containing and Lewis base-containing modifiers can potentially be used to fine-tune the capacity, mass transfer, and available surface amines of supported CO_2 sorbents.

CO_2 Desorption. The ability to regenerate the sorbent (remove CO_2) is imperative for the sorbents ability to be used in a regenerative fashion. Our previous report demonstrated the ability of T-403-modified silica sorbents to be easily regenerated to 82.4% at 45 °C under vacuum while PEI-modified silica could only be merely 3.5% regenerated under the same conditions.[5] To obtain near 80% regeneration for PEI-modified silica, the sorbent must be heated to 85 °C and vacuum applied.[9] While the addition of PEG, or in the case of T-403 a PEG-like backbone, has been shown to increase the regeneration ability for CO_2 sorbents, the mechanism is still unclear. Therefore, we evaluated the regeneration ability of our

sorbents and Lewis base-modified sorbents to better understand this effect. To regenerate our sorbents after CO_2 capture, we flowed N_2 gas at a flow rate of 66 mL/min into the TGA instrument while monitoring the weight loss (CO_2 release) of each sorbent at a temperature of 45 °C as we wanted to investigate the release properties without additional heat.

The desorption profiles for the first 10 min are shown in Figure 6 for T-403- and PEI-based sorbents with the average values with standard deviation presented in Table 1 and Figure 6C. In all cases, the T-403-based sorbents exhibited remarkably faster regeneration and obtained a nearly 3-fold greater regeneration percentage (71.8−97.3%) over the PEI-based sorbents (16−36.8% regeneration) at equilibrium. For the nonmodified T-403-based sorbents, the T403:silica (1:1) sorbent exhibited faster regeneration (obtaining 50% regeneration ($t_{50\%}$ at 4.3 min). Even faster regeneration and greater regeneration ability was observed for the PMMA- and PVAc-modified T-403-based sorbents, which reached 50% regeneration in under 3 min and obtained up to 97.3% regeneration.

Similarly, for the PEI-based sorbents, modifiers increased the regeneration rate with PMMA having the greatest effect (reducing $t_{50\%}$ by more than half). Most strikingly, PMMA and PVAc modifiers both led to regeneration rates faster than observed for PEG modifiers. Likewise, all the modifiers drastically improved the overall regeneration ability for the PEI-based sorbents, but PMMA had the greatest effect, increasing regeneration by up to 1.5-fold. These data show that the ability to improve regeneration is not limited to PEG-based modifiers but can be improved with other Lewis base modifiers, especially PMMA, which outperformed the PEG modifiers in this study for improving regeneration ability and rates for both PEI- and T-403-based sorbents. While the neat modifier:silica sorbents showed $t_{50\%}$ times less than 1.5 min (presumably due to a physical interaction with CO_2 rather than a chemical interaction), the exact mechanism for how the modifiers improve the $t_{50\%}$ for silica-supported amine polymers is still unclear, especially because the neat modifers on silica have such a low CO_2 capacity. Given that PEG-based modifiers can improve CO_2 sorption over other Lewis base modifiers yet other Lewis base modifiers better improved regeneration, the method by which PEG improves CO_2 absorption/desorption for amine-supported sorbents likely occurs by two different processes.

■ CONCLUSION

While T-403-based sorbents are capable of binding and retaining CO_2 at 45 °C as indicated by the mass increase under CO_2 conditions, when pure nitrogen is flowed through the chamber in an open system, bound CO_2 begins to desorb faster and more completely based on equilibrium with the new system environment (pure N_2). Because it is an open system, the driving force for equilibrium is constantly shifting toward more and more CO_2 being removed as fresh N_2 flows through. In this work, we did not explore studies of CO_2/N_2 mixed atmospheres to establish equilibriums for different CO_2/N_2 ratios as we were interested in the understanding, at a fundamental level, how different polymers and additives affect sorption capacity and kinetics of sorption/desorption, so we used pure CO_2 and pure N_2 conditions. Likely, sorbents based on these materials will have a trade-off for sorption/desorption rates and CO_2 capacity in mixed atmospheres. Given the general temperature-dependent nature of CO_2 sorption by primary amines, the T-403-based sorbents may be amenable to

lower temperature applications. Our results do show that one can tune the CO_2 capacity and kinetics (by amine groups and viscosity) and one can tune the regeneration ability by incorporating Lewis base modifiers. Follow-up work by our group aims to address mixed systems such as flue gas conditions (5−10% CO_2, 70−75% N_2, 5−10% H_2O, 3−4% O_2, <800 ppm of NOx, <500 ppm of SOx, and 20 ppm of CO).

The greatest effect for increasing the CO_2 capture capacity was observed using PEG modifiers on PEI-based sorbents, while PMMA and PVAc modifiers only served to lower the overall capture capacity for both PEI and T-403-based sorbents. PVAc, PMMA, and PEG1000 were also found to significantly influence the kinetics of absorption and desorption. However, PEG400 had little effect on sorption kinetics for PEI-based sorbents. For CO_2 sorption, Lewis base modifiers were shown to improve mass transfer and silica surface coverage making more amine groups available at the sorbent surface. Most strikingly, while PEG modifiers improved desorption, PMMA and PVAc led to even faster desorption rates and higher regeneration abilities at 45 °C without the need for further heating. Such improvements in regeneration ability (up to 1.5 fold) and regeneration rates (cutting $t_{50\%}$ times in half) at low temperature are critical to reducing the time and economic costs of regeneration. Thus, a combination of PEG and other Lewis base-containing modifiers have the potential be used in concert to fine-tune the capacity, mass transfer, regeneration ability, and kinetics for amine-based CO_2 sorbents.

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Notes

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