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Evaluation of a Primary Amine-Functionalized Ion-Exchange Resin for CO_2 Capture

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ABSTRACT: A primary amine-functionalized polymeric ion-exchange resin (Lewatit VP OC 1065, Lanxess) was evaluated for use in CO_2 capture applications. The polymeric resin was characterized by SEM, DRIFTS-IR, N_2 adsorption isotherms, and packed bed sorption measurements to determine some of the characteristic properties of the resin. Capture capacities ranging from 1.85 to 1.15 mol CO_2/kg sorbent were obtained in a packed bed reactor exposed to 10 vol % CO_2 in N_2 at adsorption temperatures ranging from 30 to 70 °C. The capture capacity of the resin was stable over 18 adsorption/regeneration cycles. The resin was evaluated through thermogravimetric analysis to have a low moisture adsorption (1.5 mol H_2O/kg sorbent). It is possible to completely regenerate the resin under 1 atm of CO_2 at 200 °C.

■ INTRODUCTION

Carbon dioxide emissions, along with other greenhouse gases, have been implicated as a driving force in climate change.[1] As hydrocarbon based combustion accounts for 83% of these emissions,[2] one solution for reduction in CO_2 emissions is through carbon capture and sequestration (CCS), specifically from postcombustion point sources such as coal and natural gas power facilities. The current state of the art technology for removing CO_2 from the flue gas of a typical pulverized coal power plant is the use of an amine solvent, such as monoethanolamine (MEA) or other advanced solvents, which selectively and reversibly absorb CO_2 in the solution phase.[3−8] In these systems, an amine solvent, at concentrations of 30−40 wt % in water, is contacted with a CO_2 rich flue gas (12−14 vol % CO_2) at temperatures of 40−65 °C.[6,9] The low concentration of the amine in solution is necessary to reduce corrosion and viscosity issues that occur with pure amines. After absorption, the solvents are regenerated in a stripper at temperatures typically near 140 °C producing a pressurized stream of wet CO_2.

The regeneration step carries a considerable parasitic cost on the power facility. The heat of regeneration, especially the energy required to heat the water in the solution, can compose a significant part of the total parasitic energy loss due to the high heat capacity of the amine solvent and water. An alternative to solvent systems that may reduce the parasitic costs of CO_2 capture compared to that of amine solvents is the use of solid sorbents with low heat capacities for CO_2 capture. Solid sorbents generally consist of a high surface area, high pore volume support with a chemical functionality that preferentially interacts with or reacts reversibly with CO_2. The low heat capacity of the solid directly reduces the heat requirement during regeneration. Solids do not have the corrosive properties that liquid amines have, which eliminates the need for dilution with water. Additionally, the gas phase transport of CO_2 to the porous sorbent also provides fast mass transfer of the CO_2 to the functional adsorption sites.

Solid sorbents for CO_2 capture function either by physisorption, as in the case of activated carbon and zeolites, where the sorbent can be regenerated with a pressure swing, or by a chemical reaction with CO_2 usually with amine functional groups.[10−14] The chemical bonds formed by the reactions between CO_2 and the amine group are stronger than those in the physisorption mechanism, requiring elevated temperatures to regenerate the sorbent and release the captured CO_2.

For amine-based sorbents, the amine can be either physically adsorbed through wet impregnation methods, or chemically tethered either during synthesis or as a step in post synthesis. The first class of amines has been investigated in detail in previous works with the impregnation of molecular[15−17] and polymeric amines, such as polyethyleneimine (PEI) in high surface area supports.[18−23] The impregnated polymeric systems in particular have been found to have high capture capacities. However, there are often transport limitations of the CO_2 to the active sites due to diffusion through the impregnated polymer.[22,24] Additionally, leaching of the amine over multiple regeneration cycles continue to pose stability problems for this class of amines.[25−27] These issues limit the performance and long-term viability of impregnated amine systems as CO_2 capture solutions. Finally, as PEI contains a distribution of primary, secondary, and tertiary amines, it is difficult to quantify the capacity in terms of specific molecular mechanisms and to identify clear paths to develop materials with improved performance.

The leaching problem can be solved by covalently attaching amines to solid surfaces, such as the hyperbranched amines covalently attached to silica,[28−31] amine groups functionalized onto a silica or alumina supports,[32−36] or by additives to the PEI to increase stability.[21,37] The surface area and porosity of silica is highly tunable, providing ample opportunities to

balance capacity with diffusion resistance. Furthermore, silica may be an attrition resistant support which could be important for some sorbent-based capture processes. However, it has been reported that the Si−O−C bonds within these systems can be hydrolyzed in steam, one suggested method for regeneration of the sorbent.[23,38,39] Thus, there are issues with these silica supported sorbents due to the hydrothermal stability of the Si−O−C bonds.

Another group of amine sorbents are solid polymeric systems containing amine side groups.[40,41] An advantage of the solid polymeric amine sorbents is that the amines are covalently attached to the polymer backbone in some cases by C−C bonds, which are more hydrothermally stable than Si−O−C bonds. A class of polymeric amines with potential for CO_2 sorbents is ion exchange resins (IER) with amine functionality. These materials are able to scrub CO_2 at low concentrations, like that in confined quarters such as marine and space vehicles, or from air.[42,43] They also may have potential for application in CO_2 capture from fossil energy power plant flue gas. A variety of amine- functionalized IERs exist, ranging from primary to quaternary amine functional groups. In this work we focus on a specific IER, Lewatit VP OC 1065 (Lanxess), which is an almost exclusively primary amine functionalized polystyrene porous bead with cross-linking for structural stability, with a low heat capacity of 1.5 J/(g·K).

To assess the suitability of the IER for CO_2 capture applications, it is necessary to determine the working CO_2 capture capacities, or the δ-loading, for the specific capture-regeneration conditions. The δ-loading is the change in capacity between the adsorption and regeneration stages, and can differ from the total capacity of the resin. One can define the δ-loading, however, as the difference between the total capacity at the adsorption conditions and the total capacity at the regeneration conditions. The difference between total capacity and δ-loading arises as it may not be desirable to fully regenerate in certain CO_2 capture processes, e.g., it may take too long, or require too high a temperature. Thus, the total adsorption capacity generally overestimates the working capacity of a sorbent.

The conditions where high capacities are needed differ for different sorbent process conditions. For example, in a packed bed or countercurrent transport reactor, the sorbent is saturated under flue gas conditions; hence high capacity at ∼10 vol % CO_2 and flue gas temperature is desirable. However, in a fluidized bed that is approximately well mixed, or a cocurrent transport reactor there may only be ∼1 vol % CO_2 present (if 90% of the CO_2 is being captured) where the resin leaves the reactor, and hence a high capacity at ∼1 vol % CO_2 is necessary. Therefore, it is important to characterize a sorbent over a wide range of pressures and temperatures to determine what applications the sorbent might be suitable.

Finally, flue gas contains many components. The largest components are nitrogen and CO_2, followed by water vapor. A good sorbent for CO_2 capture must be selective to CO_2 sorption, and minimize sorption of other species such as water. High surface area activated carbons perform poorly in this respect; in previous work we showed an activated carbon may sorb up to 22 mol H_2O/kg.[15] This parasitic water sorption is detrimental as it may block CO_2 sorption sites or the pores that lead to them, or may introduce a parasitic energy cost associated with drying the resin as well as the concentrated CO_2 stream prior to sequestration. Additional components include other reactive gases such as H_2S, as well as SO_x and

NO_x. These highly reactive gases can also react with sorbents; however, this is out of the scope of the current manuscript.

In this work, we measured the total CO_2 capture capacity of the IER OC 1065 (Lanxess) under a range of pressure and temperature conditions that are relevant for a variety of postcombustion CO_2 capture applications. The manuscript is organized as follows: We first show that the IER has a low moisture sorption capacity, a promising CO_2 capture capacity, and stability under conditions relevant to postcombustion CO_2 capture conditions. We then show that there are two components to the CO_2 capture mechanism, CO_2 solubility in the resin, and a chemical reaction between CO_2 and the resin. We then identify the chemical reaction using vibrational spectroscopy. Finally, we discuss the CO_2 capture capacity under a range of pressure and temperature conditions.

■ EXPERIMENTAL SECTION

Resin Characterization. The resin used in this work is OC 1065, provided by Lanxess. The resin contains a primary benzyl amine repeat unit, shown in Figure 1. The OC 1065 primary
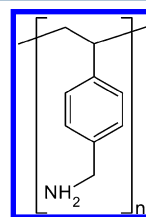

Figure 1. Primary benzyl amine repeat unit in the OC 1065 resin.

amine site is functionalized through phthalamide addition,[44] allowing the nitrogen to be located at any of the unbound benzyl carbons. The manufacturers of this resin report 8−10% of the total polymeric structure to be cross-linked with divinylbenzene to increase the structural stability of the resin.

The resins are spherical beads of polydisperse particles ranging in diameter from 0.3 − 1.2 mm, with a median particle size of 0.7 mm. As received the resins are 50 wt % water, hence a drying step was conducted at 110 °C for 3 h in N_2 to remove a majority of the water before investigation. Surface area and pore properties were obtained from N_2 adsorption isotherms using a Nova 2100 (Quantachrome). The samples were dried in a vacuum oven at 120 °C and 30 mmHg prior to measurement and then degassed in the instrument for 3 h at 120 °C. The BET multipoint surface area was obtained from the linear section for the relative pressure regime of 0.05−0.33, whereas the pore volume and pore size were determined from the BJH method.[45,46] The external morphology of the resins was evaluated through scanning electron microscopy using a Philips XL30 FEG SEM. The molar concentration of N within the resin was determined using energy-dispersive X-ray spectroscopy. The resin was fixed within epoxy and sputtered with two to four nm of Pt to obtain a conductive surface for the SEM analysis.

Capture Capacity Determination. The CO_2 capture capacity was determined for the IER with a series of adsorption and desorption measurements conducted in a custom built packed bed reactor (Figure 2). A LabVIEW acquisition module (National Instruments SCB-60 and DAQ 6020E) was used to acquire real-time pressure, temperature and volumetric flow within the reactor to characterize the CO_2 adsorbed and desorbed under changes in temperature and partial pressure of
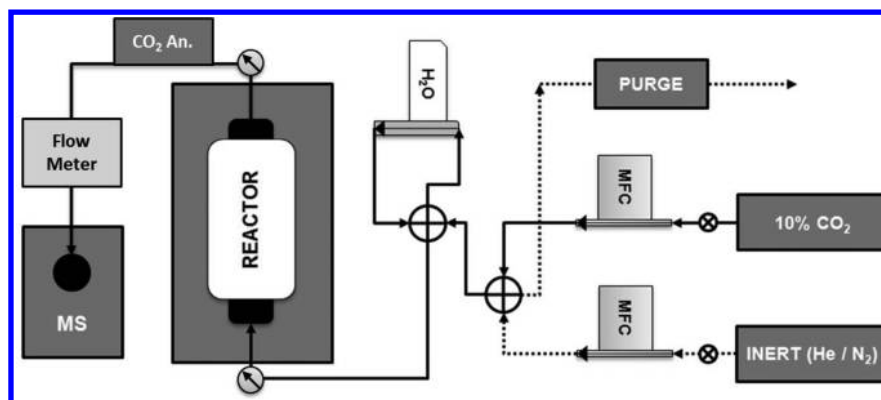
Figure 2. Schematic of packed bed reactor system used for CO_2 capture experiments.

CO_2. The concentration of CO_2 in the reactor was obtained through simultaneous measurements of a (Valtronics 2015SP3) OEM CO_2 analyzer facilitating real-time calibration of a high resolution mass spectrometer (Hiden HPR-20). Quantitative measurement of gas concentrations was determined from a three point calibration procedure conducted prior to every experiment, where the mass spectrometer intensities were calibrated to a pure N_2 stream, a calibrated tank of 10 vol % CO_2 in N_2 and a pure CO_2 stream. Water calibrations were conducted under a dry N_2 stream and a N_2 stream passed through a humidity bottle at a constant temperature. The bottle is capable of saturating the contacting gas to 95% of the saturated vapor pressure at the bottle temperature. The Antoine equation was used to determine the vapor pressure of water at the relevant temperature, which was converted to concentration.

In a typical experiment, a known mass of dried sorbent was suspended within the reactor vessel by glass wool, and placed in contact with the center reactor thermocouple to provide a measurement of sorbent temperature during each cycle. An initial purge step was conducted under an inert N_2 stream where the temperature was elevated to 120 °C to remove CO_2 adsorbed from exposure to air. This step was determined to be necessary, as the resins adsorb around 1 mol CO_2/kg resin on exposure to air at ambient temperature and pressure. After the purge step, CO_2 adsorption was conducted in a N_2 stream containing 10 vol % CO_2 with a flow of 200 mL/min at a constant reactor temperature in the range of 30 to 70 °C. This flow rate resulted in short gas residence time of 2.7 s, or 21 bed volumes of gas per minute. After CO_2 breakthrough was observed, and the CO_2 level exiting the reactor had reached the inlet composition, the resin was then regenerated by switching to a pure N_2 sweep gas and monitoring desorption of CO_2. CO_2 initially desorbs from the resin due to the partial pressure swing (drop in CO_2 partial pressure) caused by the change to inert gas. After 20 min of the pressure swing, the temperature within the reactor was increased at a rate of 3 °C/min up to a maximum temperature of 120 °C. During this ramp cycle, the CO_2 concentration typically returned to 0 vol % by the time the reactor reached 115 °C. The total amount of CO_2 adsorbed and desorbed within the reactor was evaluated by integration of the flow rate and the change in CO_2 concentration as described in our previous work.[15] A void space correction was applied to each measurement, in which the gas trapped within the reactor upon valve changes was corrected. This correction is empirically derived from separate experiments in which an inert support with an equivalent bulk density is placed within

the reactor. Correction of the void space directly from the geometric volume within the closed reactor was determined to be insufficient due to the slow sampling rate of the mass spectrometer (12 s/sample). We obtained good agreement (typically ±0.1 mol CO_2/kg) between the adsorption and desorption capacities indicating complete regeneration of the sorbent.

In conjunction with the packed bed measurements, mass uptake measurements were obtained with a Cahn TG-131 thermogravimetric analyzer (TGA) with control over the gas phase concentrations of CO_2, N_2, and water. These TGA measurements were used to determine water uptake of the resin, in addition to CO_2 capture capacity in 100 vol % CO_2 at 1 atm.

Vibrational Characterization. A series of in situ diffuse reflectance IR (DRIFTS) measurements were conducted on the resin after exposure to CO_2 to identify spectral features associated with captured CO_2 species. The resin was ground with mortar and pestle and diluted to a 10% ratio with KBr to reduce the specular reflection of the IR beam. The resin/KBr mixture was then placed within a packed bed reactor and exposed to a 10 vol % CO_2 stream at 18 °C. The CO_2 loaded amine was then placed in the DRIFTS apparatus for vibrational characterization. All DRIFTS-IR data were collected with a single beam FTIR spectrometer (Thermo Electron Nexus 670 FTIR ESP) equipped with a two chamber environmental cell allowing for in situ background and sample measurements under reaction temperature and pressure conditions. For each measurement, 800 scans were collected with an instrument resolution of 4 cm^{-1} over the infrared range of 4000 to 600 cm^{-1}.

RESULTS AND DISCUSSION

Resin Characterization. N_2 adsorption measurements at 77 K were used to obtain the surface area and pore volume of the OC 1065 resin. The N_2 isotherm measurements were conducted on samples dried for 2 h and for 24 h at 120 °C under vacuum at 30 mmHg. The results of these measurements are shown below in Table 1.

The resin exhibits a moderate pore volume (0.26 cm^3/g) after 2 h of drying, higher than that of impregnated PEI sorbents reported by Yan et al. as 0.07−0.11 cm^3/g.[47] It was found that extensive drying to remove all water from the resin shrinks the resin pore structure deactivating the resin. However, this deactivation is found to occur only under the combination of high temperature (120 °C) and vacuum for long time periods, where the resin is completely dehydrated, not under

Table 1. Textural Properties OC 1065 IER

	OC 1065 120 °C for 2 h in vacuum (30 mmHg)	OC 1065 120 °C for 24 h in vacuum (30 mmHg)
BET surface area (m^2/g)	26.2	11.9
BJH pore volume (cm^3/g)	0.26	0.08
BJH pore radius (nm)	15.4	15.2
bulk density (cm^3/g)	0.45	0.51

the operating temperatures and pressures expected for postcombustion capture. The morphology and macroporous structure of the IER was investigated through SEM, shown in Figure 3. The IER appeared homogeneous in composition, with a highly porous external structure.
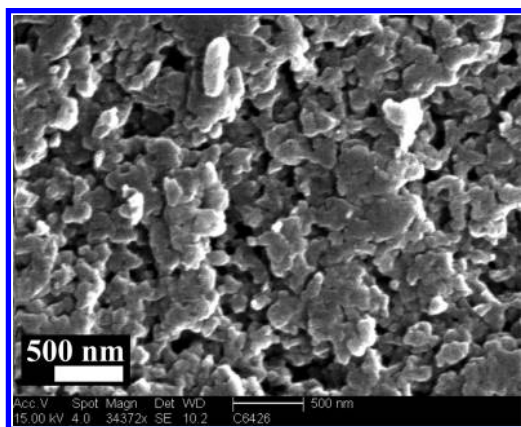

Figure 3. Scanning electron micrograph of OC 1065 IER.

Energy-dispersive X-ray spectroscopy (EDS) provided an estimate of the mass and molar concentration of N within the top 10 μm of the IER. This measurement calculated the IER composition as 11.7 wt % of N with the balance C. The composition of the resin is then 8.3:10.7:81.0 H:N:C on a weight basis, assuming stoichiometric H balance (H cannot be detected in the EDS). The 10.7 wt % N determined from EDS is very close to the 10.5 wt % N to the total mass of the individual monomer shown in Figure 1. When evaluated on a molar basis, the total amine loading is 7.5 mol N/kg resin; however as 8−10 wt % of the resin is cross-linked for increased pore rigidity and structural support, the maximum theoretical amine loading is expected to be on the order of 6.7 mol N/kg resin. This value is roughly twice that of the minimum 3.5 equivalents/kg resin determined by the manufacturer through acid−base titrations. This implies that not all of the N-functionality is available for reaction; some of them may be buried in bulk polymer. Thus, it is necessary to experimentally determine CO_2 capture capacities.

Moisture Tolerance. A sorbent capable of CO_2 capture from postcombustion sources must selectively remove 12−14 vol % CO_2 from a primarily N_2 stream and water concentrations of 12 − 15 vol % H_2O.[19] The water uptake of the dried IER was evaluated through TGA measurements by exposing the resin to a humidified N_2 stream with a water concentration of 9.1 vol % H_2O. The thermogravimetric mass uptake is shown below in Figure 4.
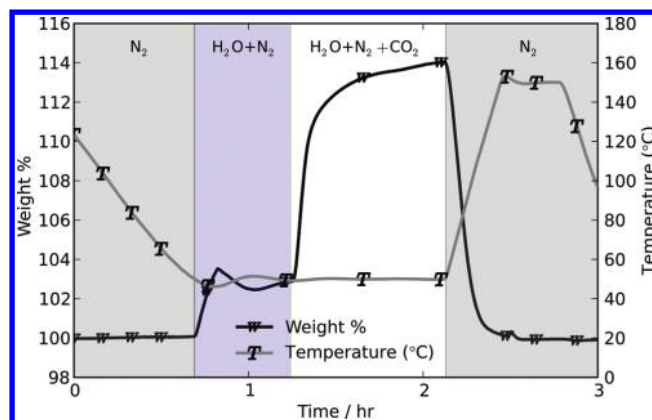
Figure 4. Thermogravimetric mass uptake of water, water with CO_2, with regeneration under N_2 at 150 °C.

The resin was dried under a N_2 stream at 140 °C. The resin was then exposed to a 9.1 vol % H_2O stream at 50 °C until the mass uptake stabilized. Forty minutes of exposure resulted in a mass uptake of only 2.7 wt % water, equivalent to 1.5 mol H_2O/kg. This amount of water sorption is lower than most of those reported in literature. For example, PEI impregnated on PMMA has been reported to have water uptake of 16 wt %,[48] while silica supported sorbents have been reported as 9.5 wt % (in 0.8 vol % H_2O).[49] Other sorbents have much higher water uptake; our previous work characterized CO_2 adsorption on a molecular amine impregnated on activated carbon and found it absorbed more than 40 wt % water.[15]

After the resin was equilibrated in a gas stream containing 9.1 vol % H_2O, CO_2 was introduced at 11.1 vol % into the humidified nitrogen stream, whereupon the mass of the IER rose an additional 10.5 wt %. There is a possibility that part of this amount could be additional water sorption; a possible mechanism for CO_2 capture is the formation of amine-bicarbonate products which requires water. However, Song et al. reports that these amine-based systems tend to sorb more water in the absence of CO_2, because of the high selectivity of the amine sites to CO_2.[50,51] The mass uptake associated with CO_2 capture is then estimated to be 2.3 mol CO_2/kg, a capacity equivalent to approximately 70% of the 3.11 mol/kg obtained with some of the best case hyperbranched amine systems at 25 °C.[30] We find that water does increase the overall capacity of the resin when compared to a dry resin by ∼30%. However, moisture is not required for the CO_2 capture mechanism, as will be shown in the next section.

CO_2 Capture Capacity Evaluation. The experimental results obtained from the packed bed apparatus described above provided CO_2 concentration, flow rate, and temperature measurements within the reactor to give a real time analysis of the conditions within the reactor throughout the adsorption and regeneration phases. Figure 5, below shows four (a) adsorption breakthroughs and (b) regeneration profiles corresponding to dried resin masses of 0.6, 1.6, 2.8, and 5.8 g. Adsorption occurred at 50 °C in a 10 vol % CO_2 stream, followed by regeneration by a switch to N_2 and a temperature ramp. At 200 mL/min, the void space correction for the adsorption phase was measured to be 0.36 mmol, whereas the correction for the desorption stage was only 0.12 mmol for a 3 g sample. As shown by the inset plot, the capacities in mol/kg resin are consistent across these various masses. The regeneration profile in Figure 5b is in terms of molar flow
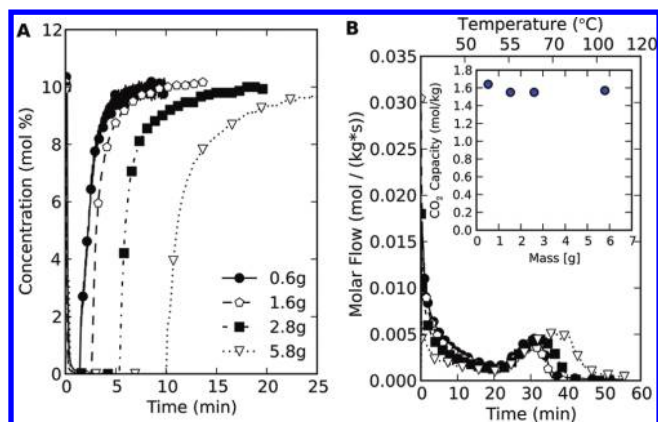
Figure 5. CO_2 adsorption measurements in a packed bed reactor with masses of with 0.6, 1.6, 2.8, and 5.8 g resin. (A) Adsorption breakthrough at 50 °C in 10 vol % CO_2. (B) CO_2 molar flow (mol CO_2/(kg s)) as a function of time with inset of CO_2 working capacity as a function of resin mass.

normalized by the sorbent mass, or mol CO_2/(kg s). This normalizes the results from various masses of resin on a molar basis of CO_2 captured. The temperature measured within the reactor is specified on the upper x axis.

One aforementioned benefit of the OC 1065 resin is the chemically tethered nature of the amine functional group, which should prevent amine leaching. Thermogravimetric and packed bed measurements have confirmed that the resin maintains repeatable capture capacity even after exposure to temperatures in excess of 160 °C, much higher than the 120 °C necessary for complete desorption in inert. Figure 6 shows 18
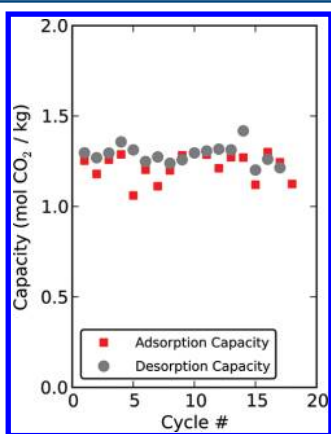

Figure 6. Capture capacity of IER over 18 temperature swing regeneration cycles with 10 vol % CO_2 in N_2 (temperature swing from 50 to 120 °C).

cycles of adsorption/regeneration in which the resin was exposed to a 10 vol % CO_2 in N_2 stream with only temperature cycled between 50 and 120 °C. Over the course of the 18 temperature cycles we obtain good agreement between the adsorption and desorption capacities and no apparent reduction in working capacity.

Effect of Adsorption Temperature on CO_2 Capture Capacity. The operating conditions for capture and regeneration can affect the working capacity of the sorbent. An understanding of the role of both temperature and pressure is therefore necessary to determine the optimal conditions for a particular sorbent to capture CO_2 in a given process, or

alternatively to identify processes suitable for a given sorbent. The previously discussed experiments were all performed at an adsorption temperature of 50 °C. To evaluate the role of adsorption temperature on capture, Figure 7 shows the packed
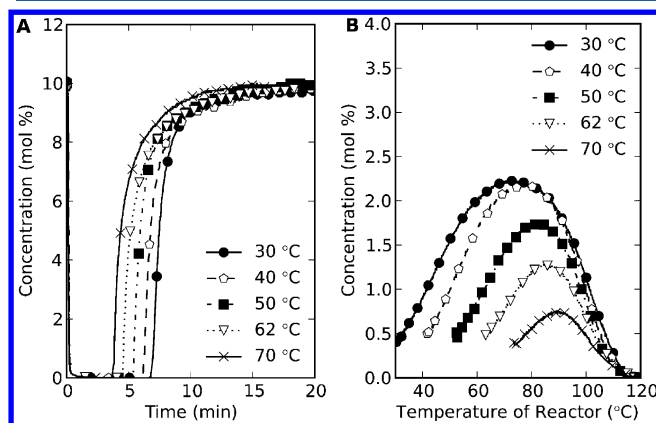
Figure 7. (A) Packed bed adsorption breakthrough curves for CO_2 adsorption onto IER under 10 vol % CO_2 at different adsorption temperatures. (B) Temperature programmed desorption spectra of CO_2 for different adsorption temperatures.

bed adsorption breakthroughs and the temperature swing portion of regeneration profile for the OC 1065 resin under adsorption conditions of 10 vol % CO_2 in N_2 and temperatures of 30, 40, 50, 60, and 70 °C. In these experiments, the temperature swing was started after 20 min of passing N_2 across the reactor to simulate a pressure swing desorption, as described previously. The reactor was then heated at 3 °C/min to 120 °C until the concentration of CO_2 reached 0 vol %. Figure 7b, specifically shows the temperature swing stage of desorption, plotting the internal reactor temperature versus the CO_2 concentration out of the reactor.

Figure 8 shows the resultant total capacity measurements separated out into the pressure and temperature swing components. The sum of the pressure and temperature swing contributions (right and left triangles) are equivalent to the measured desorption capacity (squares). The pressure swing contribution is tied to the capacity measured for the first 20 min of desorption on the switch in CO_2 from 10 vol% to pure
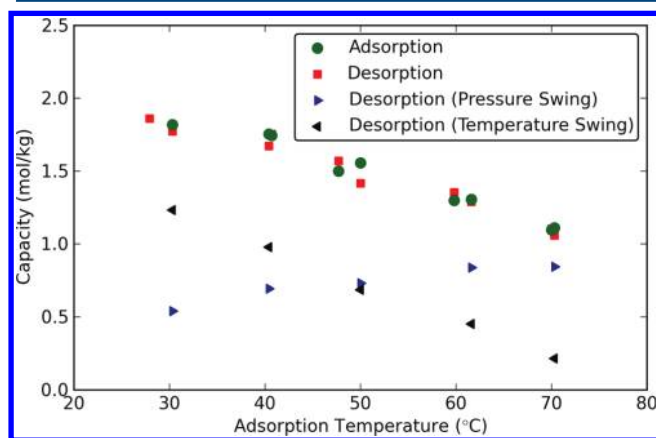

Figure 8. Capture capacity and contributions of pressure and temperature swing to the desorbed capacity of OC 1065: adsorption conditions from 30 to 70 °C in 10 vol % CO_2, regeneration in pure N_2 at 120 °C.

N_2, whereas the temperature swing component is the remaining amount desorbing as the temperature within the reactor increases to 120 °C. For each adsorption temperature we observed consistent adsorption and desorption capacities, demonstrating a closed mass balance on CO_2 in the experiments. The total CO_2 capacity decreases with increasing adsorption temperature. This is expected if the capacity is equilibrium limited, as the sorption is exothermic. There are literature reports of increased capture capacity with increasing temperature, an effect usually attributed to mass transport and diffusional resistance.[18,36,37] In essence, at low temperature, the capacity is limited by the kinetics of CO_2 diffusing into the polymeric amines. As a result, the capacity does not reach its equilibrium value, and may appear lower than thermodynamics would predict. As the temperature is increased, diffusion rates increase, leading to an apparent increase in the capacity up to some temperature where diffusion is no longer rate limiting.

In the case of the IER, increasing adsorption temperatures result in a greater proportion of the capacity tied to the pressure swing rather than the temperature swing of regeneration. The pressure swing part of desorption, which in this case is a result of the reduction in the partial pressure of CO_2 from using an inert sweep gas, removes the CO_2 that is weakly bound and not chemically bound to the resin functional groups. CO_2 is soluble in many polymers, including polystyrene,[52] and this pressure swing desorption is likely tied to the solubility of CO_2 within the resin. The increase in pressure swing capacity at higher temperatures suggests that diffusion might limit adsorption at low temperature, as solubility generally decreases with increased temperature.[53] At 60–70 °C, the pressure swing capacity begins to plateau, suggesting this capacity is close to the equilibrium solubility of the resin exposed to a 10 vol % CO_2 stream. The temperature swing component of the capacity is tied to the chemical reaction between CO_2 and the amine functional groups on the resin as shown in the next section.

CO_2 Capture Mechanism with the Amine Functional Groups. The primary benzyl amine found in the repeat unit of the IER is expected to interact with CO_2 to form either carbamic acid or a carbamate ion.[5] Carbamate ions will form if another amine is close enough to carbamic acid to deprotonate it, or if there are pathways for proton migration to remote amine sites. In-situ DRIFTS IR was used to determine if carbamate formation is the cause of the contribution from the temperature swing desorption. The resin was placed in an environmental chamber where the gas composition and temperature were controlled in situ. The resin was equilibrated to a 10 vol % CO_2 stream in N_2 within the packed bed reactor as in previous sections. After the adsorption step, the resin was removed from the packed bed apparatus and transported to the DRIFTS in situ chamber under a pure N_2 stream. The reactor was heated at step temperature intervals from 20 to 130 °C, where at each point, an IR spectrum was recorded over the range of $4000 - 400$ cm^{-1}. A spectrum showing the change in IR spectrum with increasing temperature is shown in Figure 9.

Previous work by Tanthana, Khatri, and others have highlighted these key regions associated with CO_2 uptake by amine systems.[21,36,54−56] The region between 1600 and 1200 cm^{-1} contains many of the identifying peaks attributed to carbamate and bicarbonate formation, including many of the carbonyl and carbamate stretching and bending modes. In this region peaks were found assigned to NCOO⁻ skeletal vibrations, 1320, 1431, and 1482 cm^{-1}, and NCOO⁻ stretching
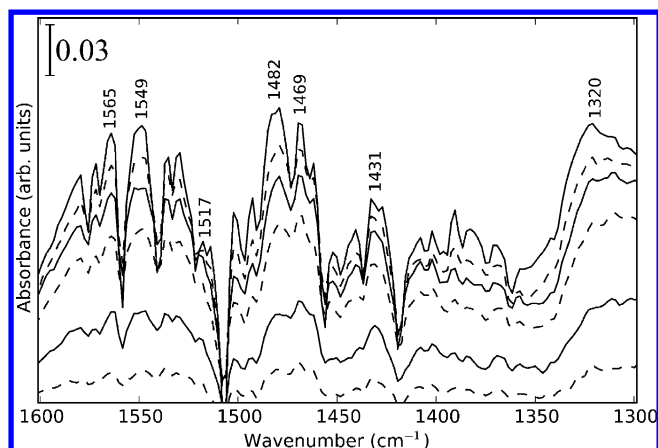
Figure 9. In situ DRIFTS-IR spectrum of CO_2 sorption over OC1065 with equilibrium sorption temperatures of 25 to 115 °C. The temperatures associated with each spectrum from top to bottom were 20, 45, 60, 80, 100, and 115 °C. Each spectrum is the calculated difference between each temperature and the highest temperature measurement of 130 °C.

at 1565 cm^{-1}. These peaks, and others associated with carbamate formation are labeled in Figure 9. This figure shows the difference in IR absorbance at temperatures from top to bottom of 20, 45, 60, 80, 100, and 115 °C subtracted from the spectrum obtained at 130 °C. This temperature is greater than what is necessary for complete CO_2 desorption in the packed bed experiments, allowing a baseline for comparison of the adsorbed species. As the temperature increased within the environmental chamber, the carbamate peaks in addition to several others reduce in amplitude as the amine−CO_2 bonds begin to break. While this was occurring, a large peak appeared in the region of 2350 cm^{-1} due to the formation of gas phase CO_2. Once the temperature reached 120 °C, the broad peak at 1320 cm^{-1} completely disappeared, whereas the other peaks reduced in amplitude, suggesting a complete disappearance of the carbamate species; regeneration of the amine species under these conditions. Upon cooling the chamber, it was observed that the gas-phase CO_2 monitored at 2350 cm^{-1} decreased, whereas the peaks in the above region returned to their initial value, suggesting readsorption of CO_2 trapped within the chamber, and reformation of the carbamate species. In addition to these carbamate peaks, other peaks are labeled that have been attributed in the literature to bicarbonate formation. Specifically, the peaks at 1549 and 1469 cm^{-1} are associated with bicarbonate formation, while the peak at 1517 cm^{-1} is the carbonyl stretch that could be found in both carbamate and bicarbonate formation. Though the OC1065 resin was exposed to CO_2 in a dry atmosphere, the in situ analysis was conducted in an air environment. The presence of humidity in the air, as well as the residual water content of the resin even after drying of 3−5 wt % could explain the additional formation of bicarbonate seen in Figure 9. With this mixed spectrum of peaks attributed to both carbamate and bicarbonate formation, it is not possible to determine if the dominant captured species in the anhydrous packed bed studies is of carbamic acid or carbamate ion form, but there is conclusive evidence that decomposition of one of these species is responsible for the CO_2 that desorbs in the temperature swing.

Effect of CO_2 Partial Pressure on CO_2 Capture Capacity. It is important to understand the effect of the partial pressure of CO_2 on the working capacity of the IER to

evaluate different capture applications as well as different regeneration conditions. Some applications have lower concentrations of CO_2 in the flue gas, e.g., the concentration of CO_2 in the flue gas from a natural gas combined cycle is only about 5 vol %.[57] Additionally, the conditions where high capacity is needed are process dependent, e.g., fluidized bed (~1% vol CO_2) vs counter-current transport reactor (at flue gas concentrations). Recent works have concentrated on the feasibility of steam regeneration with amine based sorbents.[38,58] Two advantages of steam are that it is readily available at the power plant (although using steam directly reduces the power output of the plant), and steam provides an additional driving force for the desorption of CO_2 by reducing the partial pressure of CO_2 above the sorbent. As mentioned previously, steam regeneration poses additional issues from water uptake of the sorbent (and the additional heating costs to dry the sorbent and for dehumidification of the CO_2 after regeneration), as well as the potential for hydrolysis of the bonds that stabilize the amines in the case of functionalized silica sorbents and oxidation of the amines.[59,60] An alternative to steam is regeneration in hot CO_2. One of the possible benefits of regeneration under pure CO_2 is the reduced costs associated with compression, as the desorbing gas coming from the resin will practically be pure CO_2 at elevated pressure. However, regeneration under a pure CO_2 environment will require a higher temperature for regeneration than what is necessary for a combined temperature and pressure swing desorption due to the increased partial pressure of CO_2. There may also be additional reactions that take place such as irreversible urea formation that could deactivate the amines.[26,61]

To characterize the effectiveness of OC 1065 to be regenerated under pure CO_2 a series of packed bed and thermogravimetric adsorption (TGA) experiments were conducted on the IER in 10 vol % and 100 vol % CO_2 at 1 atm. The results (Figure 10), provided isobaric capacity profiles for the resin to predict the working capacity (δ loading) of the resin over a range of temperatures.
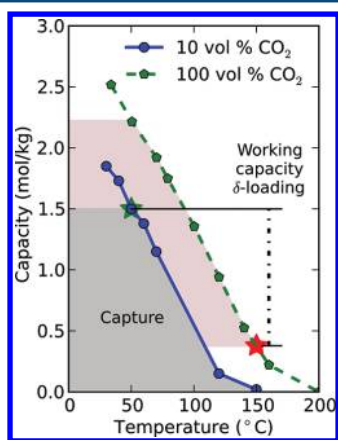

Figure 10. Isobaric CO_2 loadings for 10 vol % and 100 vol % CO_2.

Figure 10 represents the equilibrium CO_2 loading for 10 and 100 vol % CO_2 at temperatures ranging from 30 to 200 °C. The 10 vol % CO_2 measurements were conducted in the packed bed apparatus similar to methods discussed previously, and were corroborated with tests in the TGA to ensure reproducibility between experimental methods. The experiments in 100 vol % CO_2 were performed in a TGA. The resin was first regenerated under inert atmosphere for 20 min at a temperature of 200 °C,

followed by a switch to pure CO_2 at this temperature. At this high temperature, no mass uptake was monitored in pure CO_2. The temperature was then reduced at a controlled rate, with a 30 min hold at each mass measurement to allow the CO_2 to equilibrate with the IER. The weight gain for each step was converted to an equivalent molar capacity for comparison with the 10 vol % CO_2 packed bed measurements. The IER exhibits a very high capture capacity in a pure CO_2 stream (2.5 mol CO_2/kg) at 50 °C. This is the maximum capacity monitored under any experiment in a dry atmosphere, but is still less than the theoretical maximum capacity of 3.37 mol CO_2/kg measured using EDS, as discussed in the first section. This lower capacity, equaling 74% of the maximum theoretical capacity, is likely due to one or more factors associated with CO_2 capture on the IER. First, the porous nature of the resin might contain regions with small pores which are inaccessible to CO_2 under the adsorption operating conditions. The low temperature of adsorption, might also begin to contribute to mass transfer resistances that have been discussed in the more closely packed polymeric amine systems, like PEI.[62] Additionally, as the trend in capacity in pure CO_2 continues to increase with lower temperatures, the resin might not be fully saturated at 42 °C and 1 atm $pCO_2/p°$, requiring higher CO_2 partial pressures or lower temperatures. The results in Figure 10, corroborate with our cycle studies: under constant partial pressure of CO_2, the IER has a large working capacity under only moderate changes in temperature, as a shift from 50 to 150 °C will provide complete desorption in a 10 vol % CO_2 stream. The utility of these isobaric operating lines is that one can estimate the working capacity different regeneration conditions. For example, if capture takes place at 50 °C in 10 vol % CO_2, and regeneration occurs with hot CO_2 at 1 atm, we can estimate the working capacity if we specify the hot CO_2 temperature, say at 150 °C. In Figure 10, the capture conditions are specified by a green star, and the regeneration conditions by a red star for those conditions. To estimate the working capacity of the IER under regeneration in pure CO_2, we simply look at the difference in total capacity of these two points. This process suggests that capture at 50 °C in 10 vol % CO_2 and regeneration under hot 100 vol % CO_2 at 1 atm at 150 °C would provide a working capacity of ~1.2 mol CO_2/kg, as opposed to the 1.5 mol CO_2/kg when regenerated in inert (which could be steam). This is a surprising result, considering we have shifted the partial pressure of CO_2 from 0 to 1 pCO_2/p^0 with a decrease of only 20% in the working capacity. However, the necessary temperature for regeneration has increased from 115 to 150 °C, increasing the heating requirement for regeneration. One must evaluate whether the reduction in compression and drying costs would offset the additional heating requirements, as well as whether there are stability issues to determine the feasibility of the sorbent in this process.

■ CONCLUSIONS

We examined a primary amine-functionalized ion-exchange resin(Lewatit VP OC 1065, Lanxess) for applications in CO_2 capture. The sorbent showed low moisture sorption (1.5 mol/kg) compared to other sorbents. The resin exhibited CO_2 capture capacities in the range of 1 to 2.5 mol/kg depending on the partial pressure of CO_2 and the adsorption temperature, and the CO_2 capture capacity stability was demonstrated over 18 cycles.

The resin captures CO_2 by two mechanisms: CO_2 solubility in the polymer and a chemical reaction between CO_2 and the amines in the polymer to form carbamic acid/carbamate species and possibly bicarbonate species. The CO_2 captured in the form of the carbamate is moderately stable, and must be thermally regenerated. Full regeneration of the sorbent occurs at temperatures below 120 °C with an inert sweep gas, and below 200 °C in 1 atm of pure CO_2. The chemical identify of the carbamic acid/carbamate species was confirmed with infrared spectroscopy.

This resin has potential for a variety of CO_2 capture applications; it is already used for CO_2 capture in confined areas. A notable difference in the properties of this resin compared to other existing sorbents is the apparent ability to regenerate under hot CO_2. This opens new possibilities for process configurations that have not been considered yet.

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Notes

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