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ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JULY 2013

Impact Factor: 2.59 · DOI: 10.1021/ie400582a

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Effects of O_2 and SO_2 on the Capture Capacity of a Primary-Amine Based Polymeric CO_2 Sorbent

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Supporting Information

ABSTRACT: Postcombustion CO_2 capture is most commonly carried out using an amine solution that results in a high parasitic energy cost in the stripper unit due to the need to heat the water, which comprises a majority of the amine solution. It is also well-known that amine solvents suffer from stability issues due to amine leaching and poisoning by flue gas impurities. Solid sorbents provide an alternative to solvent systems that would potentially reduce the energy penalty of carbon capture. However, the cost of using a particular sorbent is greatly affected by the usable lifetime of the sorbent. This work investigated the stability of a primary amine-functionalized ion-exchange resin in the presence of O_2 and SO_2, both of which are constituents of flue gas that have been shown to cause degradation of various amines in solvent processes. The CO_2 capture capacity was measured over multiple capture cycles under continuous exposure to two simulated flue gas streams, one containing 12 vol % CO_2, 4% O_2, 84% N_2, and the other containing 12.5 vol % CO_2, 4% O_2, 431 ppm SO_2, balance N_2 using a custom-built packed bed reactor. The resin maintained its CO_2 capture capacity of 1.31 mol/kg over 17 capture cycles in the presence of O_2 without SO_2. However, the CO_2 capture capacity of the resin decreased rapidly under exposure to SO_2 by an amount of 1.3 mol/kg over 9 capture cycles. Elemental analysis revealed the resin adsorbed 1.0 mol/kg of SO_2. Thermal regeneration was determined to not be possible. The poisoned resin was however, partially regenerated with exposure to 1.5 M NaOH for 3 days resulting in a 43% removal of sulfur, determined through elemental analysis, and a 35% recovery of CO_2 capture capacity. Evidence was also found for amine loss upon prolonged (7 days) continuous exposure to high temperatures (120 °C) in air. It is concluded that desulfurization of the flue gas stream prior to CO_2 capture will greatly improve the economic viability of using this solid sorbent in a postcombustion CO_2 capture process.

INTRODUCTION

It is widely agreed upon that anthropogenic CO_2 emissions are a contributing factor to global climate change.[1] The combustion of fossil fuels such as coal, oil, and natural gas for energy is responsible for a significant fraction of CO_2 emissions.[2] Specifically, 39% of the total U.S. CO_2 emissions in 2009 were due to electricity generation.[3] One potential approach to mitigating the impact of these emissions on climate change is postcombustion carbon capture and sequestration, which would allow the current energy infrastructure to remain largely intact while continued research into alternative fuels and energy production is done.

Postcombustion CO_2 capture from coal requires selective separation of CO_2 from a gas stream at 40−60 °C and nominal gas composition of 12 vol % CO_2, 6% H_2O, 4% O_2, 400 ppm SO_2, and balance N_2, as well as other contaminants such as CO and NO_x.[4] The most mature technology for postcombustion CO_2 capture is absorption via a liquid amine, such as monoethanoloamine (MEA) using an absorber and stripper to capture CO_2 cyclically.[5] Amine solvents react reversibly with CO_2 to form an amine−CO_2 complex that is lower in energy than the reactants. This complex is typically either a carbamate or bicarbonate depending on the structure of the amine, with primary and secondary amines forming the carbamate.[6] A driving force is needed to release CO_2 from the solvent, typically by increasing the temperature of the system and/or decreasing the chemical potential of CO_2 in the system. In practice, MEA is used as part of an aqueous solution, typically 30% MEA.[5] As a result, because of the high heat capacity of water, an additional parasitic energy cost is incurred to heat the solution in the gas stripper. Although much of this heat can be recovered through heat-exchangers, there is still a substantial energy cost due to the water. Additionally, MEA solutions tend to gradually lose MEA over time due to its volatility and through oxidation.[7] Furthermore, it has been shown that flue gas contaminants such as SO_2 can also interact with MEA and reduce its capability for CO_2 capture.[8] It has been found that SO_2 and O_2 accelerate the rate of MEA degradation, to an increasing extent as the concentration of SO_2 increases.[8]

A promising alternative to liquid amine systems is CO_2 capture with a solid sorbent. A wide variety of solid sorbents can be used for CO_2 capture including physical sorbents, which adsorb primarily through van der Waals interactions, such as zeolites[9] or activated carbon[10] based sorbents as well as a wide range of chemisorbents, which involve chemical reaction between the surface sites and adsorbates. Amine-functionalized chemisorbents can be divided into three main types.[11] The first

Received: February 22, 2013
Revised: July 8, 2013
Accepted: July 9, 2013

type is that of a porous support impregnated physically with an amine species.[4] The second type is that of a polymeric support with covalently bonded side chains containing amine functionality.[12] Lastly, the third type is that of a porous support which contains amine-containing polymers polymerized in situ.[12] Solid sorbents systems present a number of potential advantages over the traditional MEA process. For instance, they typically have lower heat capacities than aqueous amine solutions and thus have a reduced energy cost due to support heating during the regeneration. The gas phase diffusion of CO_2 through the porous sorbent provides fast mass transfer of CO_2 to adsorption sites. On the other hand, successful implementation of a solid sorbent is dependent on many material properties.

A good solid sorbent for CO_2 capture must have several characteristics. These include a high working adsorption capacity, fast adsorption/desorption kinetics, high selectivity to CO_2, a low temperature for regeneration, mechanical stability, thermal stability, chemical stability, and low cost of manufacturing the material.[13] In this work we specifically address the long-term thermal and chemical stability in a simulated flue gas environment of a solid polymeric amine sorbent, the ion-exchange resin Lewatit VP OC 1065 (Lanxess). It is a divinylbenzene polystyrene copolymer with primary amine functionality and 8−10% cross-linking for stability.

Previous work has shown this material to exhibit several favorable characteristics of a CO_2 capture sorbent.[14] It has shown capture capacities from a 10 vol % CO_2 in N_2 stream in the range of 1.85 to 1.15 mol/kg depending on the adsorption temperature ranging from 30 to 70 °C.[14] OC 1065 captures CO_2 through two mechanisms, one tied to a pressure swing desorption and the other to a temperature swing desorption. In our previous work, we decoupled these contributions to the CO_2 capture capacity and showed that the temperature swing component is tied to a chemical reaction between CO_2 and the amine functional group on the resin to from carbamic acid and/or carbamate ion. We also postulated that the pressure swing component is a result of the solubility of CO_2 in the resin.

Thermogravimetric analysis has shown the resin to have relatively low moisture adsorption compared to other sorbents.[14] Low moisture adsorption is important because the sorbent will be required to selectively remove CO_2 from a flue gas stream that is saturated with moisture.[15] Thermogravimetric analysis of the resin exposed to a wet N_2 stream with 9.1 vol % H_2O for 40 min at 50 °C resulted in a moisture uptake of 2.7 wt % or 1.5 mol H_2O/kg resin, which is significantly lower than other values reported in the literature.[16] For example, silica supported sorbents exposed to a lower H_2O concentration of 0.8 vol % for 1 h at 28 °C is reported to have a moisture uptake of 9.5 wt %.[17] Previous work on supported amidine on activated carbon showed greater than 40 wt % moisture adsorption.[16] The resin also has shown to be completely regenerated under an inert N_2 gas stream at 120 °C and under a 100% CO_2 gas stream at 200 °C.[14] In a packed bed reactor, the resin was exposed to a 10 vol % CO_2 stream as the temperature of the reactor was changed back and forth from 50 and 120 °C for 18 cycles. The working capacity remained stable over this time scale.

The key issues we did not address in our previous work are the chemical and thermal stability of OC 1065. In particular the effect of O_2 and SO_2 on the CO_2 capture capacity is of crucial importance for the successful use of a sorbent for postcombustion CO_2 capture applications. SO_2 is of great concern for amine-based sorbents as much work has shown it to react strongly with amines and inhibit CO_2 adsorption in amine-based sorbents as well as to form heat stable salts with amine solvents.[8,18,19] O_2 is also a major concern because amine oxidation has been shown to have a negative impact on CO_2 capture capacity making it a significant factor in determining the useful lifetime of the amine for CO_2 capture from oxidative environments such as postcombustion flue gas.[7,20,21]

The aim of this work is to investigate the tolerance of the OC 1065 resin to O_2 and SO_2. Both of these constituents are commonly found in flue gas and have been shown to accelerate the rate of degradation of MEA.[8] This work focuses on identifying the effects of these constituents on the working capacity of OC 1065 and seeks to characterize any degradation that is observed. Whether the resin is poisoned by these constituents reversibly or irreversibly as well as the means necessary to restore its activity are important information to determine the feasibility of a sorbent for large-scale CO_2 capture from flue gas. The manuscript is organized as follows: we first present elemental analysis on OC 1065 and comment on the total nitrogen-loading and available amine adsorption sites of the resin. We then show the effect of 4% O_2 in simulated flue gas on the capture capacity of the resin. We then show that the CO_2 capture capacity of the resin decreases as a result of exposure to 431 ppm SO_2 in simulated flue gas. We then investigate the nature of the observed SO_2-poisoning as well as means for regenerating the SO_2 poisoned resin. Finally we comment further on the long-term thermal stability of the resin.

■ METHODS

The CO_2 capture capacity of OC 1065 was measured under a variety of controlled conditions in a custom-built packed bed reactor apparatus.[14] The apparatus is equipped to control and measure key variables such as reactor temperature, flow rate, CO_2 concentration, and pressure drop via a LabVIEW acquisition module. The CO_2 concentration in the reactor effluent is measured simultaneously using both a (Valtronics 2015SP3) OEM CO_2 analyzer and a high-resolution mass spectrometer (Hiden HPR-20). Quantitative measurement of the CO_2 concentration from the mass spectrometer intensity is done through a calibration procedure done prior to every experiment with three gases of known concentrations, typically 0%, 100% CO_2, as well as the test gas, typically either 10 or 12 vol % CO_2.

During a typical packed bed reactor experiment, a sample of resin (3−4 g) is first dried in the oven at 120 °C to constant mass (typically 2−3 h) to eliminate excess water it contains in its shipped state. A sample of the dried resin of known mass is loaded into the tubular reactor (0.375 in i.d.) suspended between two pieces of glass wool making a column approximately 5 in. high. The resin has a bulk density of 630−710 g/L with a column porosity between 0.42 and 0.48 according to the manufacturer's specifications. A purge step is then conducted by passing N_2 at a nominal flow rate of 200 cc/min through the reactor at elevated temperature (up to 120 °C) as the resin captures up to 1 mol CO_2 per kg from exposure to ambient air. The typical pressure drop through the bed is about 0.2 psi. Following the purge step, the reactor is switched offline and the mass spectrometer is calibrated to gases of known CO_2 concentration as described above. Following calibration, adsorption is carried out at a fixed temperature (50 °C in this work). The simulated flue gas is passed through the reactor until breakthrough is observed and the gas composition has returned to the original baseline composition, indicating that adsorption is complete. The reactor is switched offline to prepare for the desorption step. The amount of CO_2 adsorbed is calculated from the average volumetric flow of CO_2 in the effluent stream over the period following breakthrough when the concentration of CO_2 has stabilized to determine a baseline value. The volumetric flow of CO_2 is then subtracted from the baseline value and integrated over the adsorption time to give the volume of CO_2 adsorbed by the resin using eq 1.

$$V_{CO_2} = \int (Qb_{CO_2} - Q(t)C_{CO_2}(t))\,dt \qquad (1)$$

where Qb_{CO_2} (mL/min) is the baseline value of the volumetric CO_2 flow, $Q(t)$ is the measured total volumetric gas flow (mL/min), and $C_{CO_2}(t)$ is the measured CO_2 concentration (vol %) in the effluent stream. This calculated volume of adsorbed CO_2 is converted to a molar quantity using the ideal gas law at the temperature and pressure (25 °C, 1.013 25 bar) of the effluent gas stream and normalized by dividing by the mass of the resin to calculate the adsorption capacity in units of mol/kg. Desorption is carried out via both a pressure swing and temperature swing by passing inert N_2 through the reactor at the constant adsorption temperature for 20 min then increasing the temperature at a rate of 3 °C/min until CO_2 stops desorbing as can be seen in Figure 1.

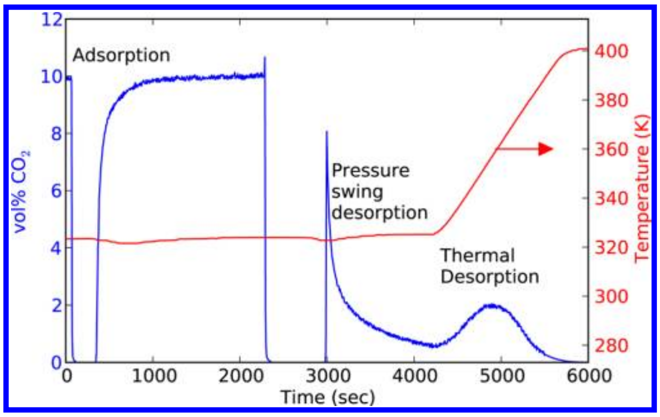

Figure 1. Typical adsorption and desorption data used for capacity calculation.

The dead volume, or void space due to the volume of gas trapped within the reactor upon valve changes, correction was taken into account in all capacity calculations. This correction was empirically derived from experiments with an inert support with an equivalent bulk density to OC 1065. The void space was found to contribute 0.12 mol of CO_2 to the apparent capacity. All values reported in this manuscript have taken this into account where appropriate.

Equation 2 is used to calculate the volume of CO_2 desorbed.

$$V_{CO_2} = \int Q(t)C_{CO_2}(t)\,dt \qquad (2)$$

The calculated volume of CO_2 is converted to a molar quantity with the ideal gas law and normalized by the mass of the resin to calculate the desorption capacity in units of mol/kg.

The packed bed reactor apparatus can also be used to measure the CO_2 capture capacity over multiple consecutive cycles of adsorption and desorption from a continuous gas stream by simply cycling the reactor temperature without changing the feed stream to the reactor. The capture capacity is then calculated by integrating the flow rate and CO_2 concentration data about the baseline CO_2 flow present in the inlet gas stream.

Elemental analysis was used to identify any changes in chemical composition of the resin as a result of exposure to O_2 and SO_2. The mass-based analysis was carried out by Micro Analysis Inc. and done using combustion for C, H, N, and S and using pyrolysis for O. Surface area and pore size measurements were conducted following packed bed stability tests from N_2 adsorption isotherm experiments using a Nova 2100 (Quantachrome). Samples were degassed at 125 °C for 2.5 h prior to measurement. The surface area was determined through the BET method, and the pore volume and pore size was determined through the BJH method.[22,23]

RESULTS AND DISCUSSION

Estimating Available Amine Sites. In our previous work, the maximum theoretical amine loading was deduced from energy-dispersive X-ray spectroscopy measurements to be 6.7 mol N/kg.[14] However, elemental analysis provides another complementary estimate of the amine loading of the resin. In this work, the value of 7.9% N averaged over four measurements (Table 1) represents an amine loading of 5.9 ± 0.1 mol N/kg. However, since only a fraction of the total amine sites are accessible to reaction with CO_2, the more critical value is the number of accessible amine sites. This value can be estimated from the sulfate loading on the resin following saturation with sulfuric acid, which is based on the average of three measurements (Table 2) was 2.7 mol H_2SO_4/kg. Assuming a 1:1 molar stoichiometry, the amine loading available to reaction is 2.7 mol/kg. This suggests that the measured CO_2 capture capacity of the resin at 50 °C from a pure CO_2 stream, 2.5 mol/kg, is approaching the capacity limit of this sorbent.

Table 1. Mass-Based Elemental Analysis of OC 1065 As Received and Dried (Precision: ±0.30%)

sample	% C	% H	% N	% O	% S
1	81.79	8.25	8.00	3.48	0.00
2	82.09	8.36	7.97	4.13	0.00
3	81.11	8.26	7.94	4.19	0.00
4	81.28	7.85	7.77	3.15	0.00

Table 2. Mass-Based Elemental Analysis of OC 1065 Following Saturation with 1.5 M H_2SO_4 Aqueous Solution (Precision: 0.30%)

sample	% C	% H	% N	% O	% S
1	64.31	7.12	6.03	15.22	6.59
2	63.66	7.08	6.08	16.60	7.00
3	63.15	6.87	6.13	15.16	6.47

Effect of O_2 in Flue Gas on OC 1065. The tolerance of OC 1065 to O_2 was studied by conducting 17 continuous cycles of adsorption and desorption with a test gas of 12 vol % CO_2, 4% O_2, 84% N_2. This gas was passed continuously through the loaded reactor during the entire course of the

dx.doi.org/10.1021/ie400582a | Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

experiment, and adsorption and desorption occurred via a thermal swing between 50 and 127 °C. Each cycle lasted 2 h and 12 min. All capacity calculations are calculated using the baseline concentration of 12% CO_2 for the entire experiment. The resulting calculated capture capacities can be seen in Figure 2. The average capacity was 1.27 mol/kg. Our past work indicated a reproducibility of 0.1 mol/kg, thus we believe that the variations in capacity here are due to precision and not due to any degradation of capacity under these conditions.

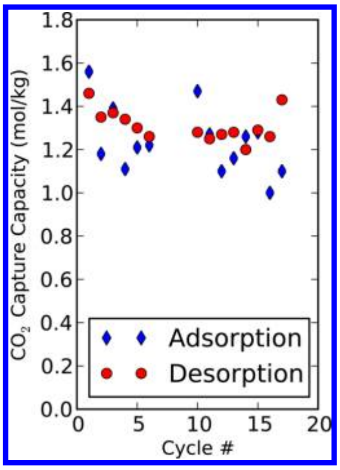

Figure 2. CO_2 capture capacity of resin over 17 temperature swing regeneration cycles in the presence of O_2.

Effect of SO_2 on OC 1065 CO_2 Capture Capacity. A similar experiment was conducted to determine the effect of SO_2, at concentrations typical of coal flue gas, on the CO_2 capture capacity of OC 1065. A test gas of 12.5 vol % CO_2, 4% O_2, 431 ppm SO_2, balance N_2 was passed continuously through the reactor with a thermal swing between 50 and 127 °C conducted as done with the O_2 stability test. This experiment was repeated twice, and the CO_2 capture capacity throughout all three experiment can be seen in Figure 3.

The CO_2 capture capacity of OC 1065 decreased in each cycle of exposure to SO_2 until the capacity was practically gone. The loss of activity occurred rapidly and in a near linear fashion throughout the first seven cycles before stabilizing at a minimal capacity of approximately 0.2 mol/kg. The mass spectrometer intensity of SO_2 and the concentration of CO_2 in the effluent gas stream was tracked with the analyzer and mass spectrometer throughout experiment 1 and can be seen in Figure 4.

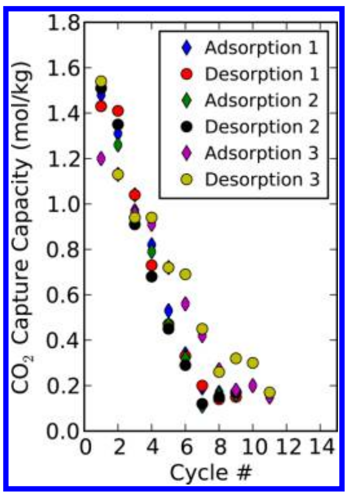

Figure 3. CO_2 capture capacity of resin in presence of SO_2. Experiments 1 and 2 tested a 3 g sample of resin, while experiment 3 tested a 4 g sample of resin.

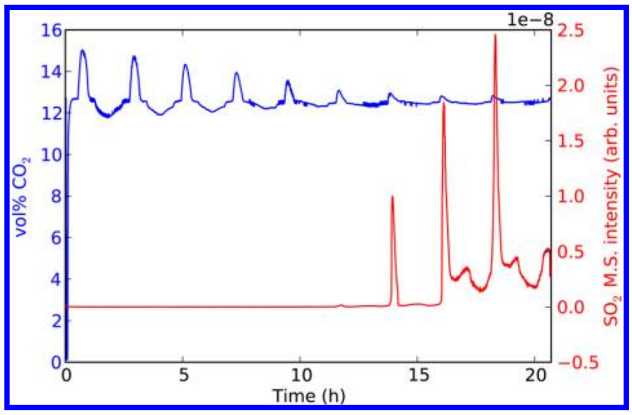

Figure 4. CO_2 and SO_2 variation throughout experiment 1.

It can be seen that during the course of the first six temperature swing regeneration cycles, practically no SO_2 is detected in the mass spectrometer, suggesting that all of the SO_2 is captured by the resin until the resin becomes saturated around the sixth cycle where the first tiny peak is shown for SO_2 in the mass spectrometer signal. After that there are peaks in the SO_2 spectrum that indicate thermally reversible SO_2 species on the resin. During the period prior to the first small peak in the SO_2 intensity, observed at approximately 11.8 h, the amount of SO_2 adsorbed on the resin can be approximated from the SO_2 flow rate into the reactor as 0.82 mol/kg. This value is less than the reduction of CO_2 capture capacity during the same six temperature swing regeneration cycles.

This reduction in CO_2 capture capacity could be a result of both physical and chemical effects. To determine whether exposure to SO_2 caused a reduction in either the surface area or pore size of the resin which in turn would decrease the CO_2 capture capacity of the resin, a series of nitrogen adsorption isotherm measurements were carried out on the resin both before and after the SO_2 packed bed experiment. The results of these measurements can be seen in Table 3.

Table 3. Surface Area and Pore Size Analysis of SO_2-Poisoned Resin

	untreated resin	SO_2-poisoned resin
BET surface area (m^2/g)	34	40
BJH pore volume (cc/g)	0.23	0.23
BJH pore radius (nm)	15.4	15.3

A small increase in surface area was observed for the SO_2-poisoned resin, but we do not believe that this is significant (for small surface areas such as these, the surface area is reproducible to approximately 5 m^2/g). The results do not show any significant differences in the surface area, pore volume, or pore radius of the as received and SO_2-poisoned resin. Thus, a reduction in surface area or pore volume is not responsible for the reduction in CO_2 capture capacity and so the reduction in CO_2 capture capacity is predominantly a result of an interaction between SO_2 and the primary amine functional groups in OC 1065.

The adsorption of SO_2 onto the resin was confirmed by the results of mass-based elemental analysis done on the resin following the experiments with O_2 and SO_2, which can be seen in Table 4. The increase in the % S after the SO_2 experiment corresponds to a loading of 0.98 mol/kg. This value is higher than the loading of 0.82 estimated from the flow rate prior to the first tiny peak in SO_2 intensity, indicating that additional SO_2 adsorbed onto the resin during the seventh, eighth, and ninth temperature regeneration cycles. The reduction in CO_2 capture capacity during the same experiment was 1.31 mol/kg. The exact mechanism of degradation aside, it is clear that SO_2 at the concentrations typical of flue gas from coal is a contaminant of great concern if OC 1065 is to be used for postcombustion CO_2 capture applications. It is likely that other sorbents with primary amines will be similarly poisoned by SO_2 as well.

Table 4. Elemental Composition of Resin Following SO_2 Poisoning[a]

sample	% C	% H	% N	% O	% S
following SO_2 experiment no. 1	76.0	6.9	6.8	6.0	2.9

[a]Values are reported as mass percent with a precision of ±0.3%.

Regeneration of SO_2 Poisoned OC 1065. It is of interest to determine whether it is possible to reclaim the activity of the poisoned resin through either thermal or chemical means. This is an advantage for solvents, which can be reclaimed by treatment with activated carbons and ion-exchange resins to remove heat-stable-salts.[6] We first examined the feasibility of poisoned sorbent regeneration via a thermal swing by exposing a sample of poisoned resin to a N_2 environment in the packed bed reactor at temperatures up to 208 °C. We hypothesized that being a stronger acid gas, it could take a higher temperature to desorb SO_2 than CO_2. No significant increase in the mass spectrometer intensity of SO_2 was observed during this experiment (see the Supporting Information). Following this treatment, the sample of resin was tested at an adsorption temperature of 50 °C with a 10 vol % CO_2, N_2 stream and did not exhibit a measurable CO_2 capacity. This shows that the adsorbed SO_2 species is stable up to 208 °C.

We next consider chemical regeneration. Since SO_2 is an acid gas and may interact with the resin through acid−base chemistry, we hypothesized that treatment of the poisoned resin with aqueous NaOH could regenerate the resin in the same way that ion exchange resins are normally regenerated. To simultaneously show that the reaction of an acid with the resin poisons the resin, and to determine whether a reaction of the resin with a strong acid can be reversed using NaOH, a sample of resin was treated with 1.5 M sulfuric acid at room temperature for 1 day, washed in distilled water for 1 day to remove excess acid, and then tested in the packed bed reactor. The result was a complete loss of CO_2 capacity due to protonation of the amines by the acid with sulfate ions providing charge neutrality. The same sample of resin was then treated with 1.5 M NaOH at room temperature for 3 days to deprotonate the amines and remove the sulfate ions, washed in distilled water for 1 day to remove excess base, and tested in the packed bed reactor at 50 °C and 10 vol% CO_2, exhibiting a CO_2 capture capacity of 1.5 mol/kg. This demonstrated that the resin could be completely poisoned by an acid (H_2SO_4) and completely regenerated by a chemical method.

This same chemical treatment with NaOH was used on the SO_2-poisoned resin from experiment no. 1. However, we only observed the reclamation of approximately 1/3 (0.49 mol/kg) of the CO_2 capture capacity at the capture conditions of 50 °C and 10 vol % CO_2. Elemental analysis (Table 6) of all these samples showed that the resin poisoned by sulfuric acid indeed took up a lot of sulfur but that the chemical regeneration was able to completely remove all the sulfur. The SO_2-poisoned resin also showed significant uptake of sulfur. The chemical treatment, however, was only able to remove 43% of the sulfur which is in reasonable agreement with the 35% recovery of CO_2 capture capacity. The increase in % O and % S is stoichiometrically consistent with an adsorbed SO_2 species, while the increase in % O and % S from treatment with sulfuric acid solution is stoichiometrically consistent with addition of SO_4-containing species. The CO_2 capture capacity at these conditions of the resin before and after poisoning and regeneration can be seen in Table 5.

Table 5. CO_2 Capture Capacity[a]

	CO_2 capture capacity (mol/kg)
untreated	1.39
sulfuric acid poisoned	0.08
regenerated with NaOH	1.51
SO_2 poisoned	0.1
partially regenerated with NaOH	0.48

[a]At 50 °C, 10 vol % CO_2 of the untreated OC 1065, resin poisoned by 1.5 M H_2SO_4 solution for 1 day, resin regenerated fully by exposure to a 1.5 M NaOH solution for 3 days, resin following the SO_2 packed bed experiment, and SO_2-poisoned resin following 3 day treatment with 1.5 M NaOH solution.

Table 6. Elemental Analysis of Resin Following Treatment with Sulfuric Acid, As Well As Following Regeneration with NaOH

sample	% C	% H	% N	% O	% S
SO_2-poisoned resin partially regenerated with NaOH	76.6	6.8	6.4	4.6	1.7
treated with sulfuric acid	63.2	6.9	6.1	15.2	6.5
fully regenerated with NaOH	80.9	7.8	7.8	3.1	0.0

In all of the work presented here, the gas stream was dry due to limitations of the experimental apparatus employed. SO_2 is known to react with sodium hydroxide solutions to make sodium bisulfite ($NaHSO_3$). We conjecture that the primary amine can react with SO_2 in a similar way that is not very reversible, but we were unable to obtain spectroscopic (Raman or IR) evidence of that reaction. It is possible that the presence of water could promote the formation of the bisulfite ions, which could make SO_2 sorption more reversible. Further investigation of this is outside the current scope of work and would require a different approach to humidifying the gas stream than our apparatus uses.

Thermal Stability of OC 1065 in Air. In the packed bed reactor experiments described above, we have investigated the stability of OC 1065 over time scales much shorter than the estimated 1000 cycles needed for a solid sorbent to be economically viable.[24,25] Long-term thermal stability in an oxidative environment is just as critical to the success of a sorbent as the chemical stability investigated above. In previous work, it was shown that OC 1065 loses its activity from exposure to the combination of high temperature(120 °C) and vacuum for a long time such that the resin becomes completely dehydrated and a significant reduction in surface area and pore size occurs.[14] On the other hand, the packed bed reactor experiments have shown the resin to be quite stable under conditions more typical of postcombustion CO_2 capture where the resin is exposed to high temperature (120 °C) but only during temperature swing desorption where the amine is mostly reacted with CO_2. However, it is known that primary amines can become reactive at high temperatures and can either be oxidized or react with CO_2 to form stable urea groups following in which the sorbent ceases to be effective.[20,26]

To assess the stability of OC 1065 in a hot oxygen-rich environment over longer time scales, a sample of resin was kept at 120 °C in air for 7 days. The CO_2 capture capacity of the sample was then measured in the packed bed reactor at 50 °C from a 10 vol % CO_2, N_2 stream and determined to be 0.28 mol/kg, which is a 79% reduction in capacity from the untreated resin. This reduction is evident in the desorption-profile of the resin before and after this treatment shown in Figure 5. It can be seen that a substantial decrease in both the

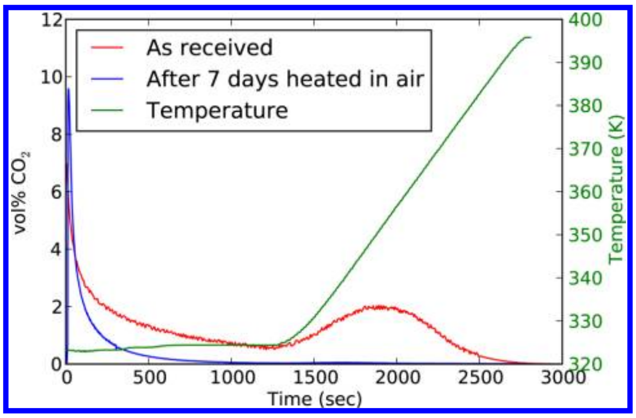

Figure 5. Pressure and temperature swing desorption profiles for resin before and after 7 days at 120 °C.

temperature swing and pressure swing components occurred and that the temperature swing contribution to the desorption capacity was completely eliminated. However, this reduction in CO_2 capture capacity is not a result of a decrease in surface area and pore size as described in our past work. We confirmed this with a series of N_2 adsorption isotherm measurements (Table 7).

Table 7. Surface Area and Pore Size Analysis of Resin Following 7 Days of Exposure to 120 °C in Air

	untreated	after 7 days
BET surface area (m^2/g)	34	42
BJH pore volume (cc/g)	0.23	0.28
BJH pore radius (nm)	15.4	15.3

Elemental analysis revealed a significant reduction in the nitrogen content of the resin (Table 8). The decrease in % N corresponds to a 1.1 mol amine/kg decrease in the amine loading, which is in good agreement with the 1.11 mol CO_2/kg decrease in CO_2 capture capacity. Additionally the % H decreased by an amount corresponding to 7.6 mol H/kg, while the carbon and oxygen-content of the resin remains unchanged

Table 8. Elemental Analysis of Resin after 7 Days Exposure to 120 °C in Air

sample	% C	% H	% N	% O	% S
following 7 day heating treatment	81.8	7.4	6.4	4.0	0.0

within the 0.3% precision of the measurements. Clearly prolonged (days or more) continuous exposure to air at high temperatures (120 °C) leads to irreversible amine loss for OC 1065.

■ CONCLUSIONS

The tolerance of a primary amine-functionalized ion-exchange resin (OC 1065) to O_2 and SO_2 was evaluated in this work. The CO_2 capture capacity remained stable over 17 capture cycles under continuous exposure to a 12% CO_2, 4% O_2, 84% N_2 gas stream indicating that irreversible oxidation did not significantly occur over this time scale. The resin was, however, poisoned quickly by continuous exposure to a 12.5% CO_2, 4% O_2, 431 ppm SO_2, 84% N_2 gas stream resulting in an adsorption of 0.98 mol/kg of SO_2 and a decrease in CO_2 capture capacity of 1.31 mol/kg after only 9 temperature swing regeneration cycles. The poisoned resin was not thermally regenerable. Treating the poisoned resin with NaOH resulted in a 43% SO_2 removal and 35% reclamation of CO_2 capture capacity under 10 vol % CO_2 and 50 °C capture conditions. The difficulty in fully regenerating the poisoned resin is most likely due to an irreversible reaction between SO_2 and the amine due to the stronger acidity of SO_2 in comparison with CO_2. That the poisoned resin is partially regenerable could indicate that SO_2 is adsorbing on the resin through more than one mechanism, one of which is reversible. Additionally, evidence was found for amine oxidation during extended exposure to a hot (120 °C) oxygen-rich environment.

This work highlights, in particular, the negative impact of SO_2 which strongly suggests SO_2 should be removed from the flue gas or converted to SO_4-containing species such as sulfuric acid prior to an amine-based CO_2 capture process. Ultimately, chemical and thermal stability will be an issue with any sorbent, and the process conditions and economics will dictate whether a sorbent is sufficiently chemically and thermally stable.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

All of the data files used in this work, including the representative data of the total volumetric flow rate and the data used in the BET analysis, as well as all of the analysis used in generating the figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge Lanxess for providing us with the samples of OC 1065 used in this work. As part of the National Energy Technology Laboratory's Regional University Alliance (NETL-RUA), a collaborative initiative of the NETL, this technical effort was performed under the RES Contract DE-

FE0004000. This project was funded by the Department of Energy, National Energy Technology Laboratory, an agency of the United States Government through a support contract with URS Energy & Construction Inc. Neither the United States Government nor any agency thereof, nor any of their employees, nor URS Energy & Construction, Inc., nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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