

NOVEL AMINE ENRICHED SOLID SORBENTS FOR CARBON DIOXIDE CAPTURE

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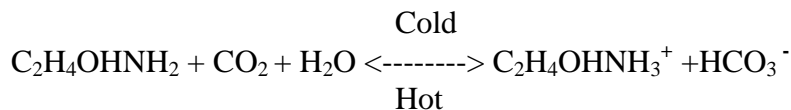
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Introduction

Separation and capture of CO₂ have been identified as a high-priority research topic in several DOE's reports.^{1,2} The costs of separation and capture, including compression to the required pressure for the sequestration step, are generally estimated to comprise about three-fourths of the total cost of ocean or geologic sequestration. An improvement of the separation and capture of CO₂ will reduce the total cost required for sequestration.

The goal of CO₂ separation and capture is to isolate CO₂ from its many sources in a form which is suitable for transport and sequestration. The most likely options for CO₂ separation and capture include chemical absorption, physical and chemical adsorption, low-temperature distillation, gas-separation membranes, mineralization/biomineralization, and vegetation.^{1,2} The CO₂ absorption process using aqueous amine solutions have been extensively used for the removal of CO₂ from gas streams in many industries. This process based on the principles of chemical absorption of CO₂ via monoethanolamine (MEA) or diethanolamine (DEA) is considered to be a potential technique for capturing greenhouse gas emission from flue gas streams. Wet chemical stripping of CO₂ involves one or more reversible chemical reactions between CO₂ and another material such as MEA to produce a liquid species which, upon heating, breaks down to liberate CO₂, and regenerate the original material used to react with CO₂.³ For example, the monoethanol amine process can be illustrated by the following reversible reaction:



The amines (MEA and DEA) are utilized in the aqueous phase, typically containing 25-30 wt% amine. The amine solution enters the top of an absorption tower while the carbon dioxide containing gaseous stream is introduced at the bottom. While intimately contacting the gaseous stream in a

countercurrent fashion, the amine solution chemically absorbs the carbon dioxide from the gaseous stream. Desorption of the adsorbed carbon dioxide then proceeds via a thermal regeneration process. During desorption, carbon dioxide and water evolve from the amine solution and are separated by condensing the water vapor in a heat exchanger. Once regenerated, the amine solution is recycled back to the absorption tower for additional carbon dioxide absorption.

These processes are, in general, energy intensive. The amine solution has a limited lifetime due to degradation through oxidation of the amine. In addition, corrosion problems are usually observed for the aqueous amine process. Recently, several solid sorbents have been utilized to remove carbon dioxide from enclosed environments such as submarine, aircraft, spacecraft or enclosed pressurized chambers.^{4,5} Leal et al., demonstrated the reversible adsorption of CO₂ on amine surface-bonded silica gel.⁶ The porous support provides the amine with structural integrity and a surface for gas/solid contact. The ability to regenerate an adsorbent and the ease of its regeneration are also important considerations. The need for extreme conditions such as high temperatures or very low vacuums makes regeneration more complicated and costly.⁴

Objective

The objective of this research is to develop the novel amine enriched sorbents for the capture of CO₂ from flue gas streams. These novel CO₂ capture sorbents can be prepared by the chemical treatment of the surface oxide material with various amine compounds.⁴⁻⁶

Approach

The material tested in this study was a fly ash with 8% carbon content, namely, sample 59. The sample was first concentrated via the column agglomeration technique to enhance the concentration of carbon to about 52 %, namely, sample 95.⁷ Subsequently, three different amine treatment procedures were applied to sample 95. The treated amine enriched samples were designated as 95A, 95B and 95C.

In order to understand the reaction of CO₂ on these amine-enriched solids and assess their relative CO₂ uptake capabilities, adsorption studies followed by a temperature-programmed-desorption (TPD) technique were conducted under ambient pressure and at temperatures between 30 and 120 °C. Figure 1 illustrates a schematic of the experimental system. All gas flows to the system were regulated with Brooks 5850 mass flow controllers. The 4-port valve allowed for ease of switching between He and 10% CO₂/He flows to the reactor system; moisture was added to either flow stream via a water saturator maintained at ambient temperature (partial pressure of H₂O = 23.36 mmHg). A sample charge of 100 mg was used in each experiment; approximately 15 mg was placed into a Spectra Tech diffuse reflectance infrared Fourier transform infrared spectroscopy (DRIFTS) reactor while the remaining sample was charged to a tubular reactor connected to the effluent of the DRIFTS. Separate temperature control systems existed on each reactor. Each reactor had its own temperature control. The sample in the DRIFTS was examined in situ via a Nicolet Magna 560 infrared spectrometer (IR), allowing observation of CO₂ adsorbate formation/desorption on the sample surface. The gaseous effluent from the DRIFTS-tubular reactor was continuously analyzed by a Balzers QMG 112 mass spectrometer (MS), allowing determination of the CO₂ concentration

in the effluent stream. Capture capacities of the different amine-enriched samples were calculated by MS analysis of the CO₂ (m/e = 44) desorption profile.

Each sample was first exposed to He at a flow rate of 30 ml/min for 3 hours, prior to any further experiment, to clean the sample surface (confirmed by observing stable background signals of both IR and MS). For the CO₂ absorption study, He flow was then replaced with 10% CO₂ in He at ambient conditions. The moisture content plays an important role in the CO₂ adsorption process; formation of CO₂-amine complexes take place only in its presence. Therefore, after the exposure of 10% CO₂ in He, the flow was redirected through an H₂O saturator; the CO₂/H₂O/He flow over the surface of the sample was maintained for 30 minutes. The CO₂/H₂O/He stream was then replaced by H₂O/He flow to expunge the system of gaseous CO₂.

For the TPD study, the H₂O/He flow was finally replaced with pure He flow to monitor desorption of adsorbed CO₂. Both reactors were heated, simultaneously, from 30 to 120°C at a rate of 10 °C/min and maintained at 120 °C for an additional 20 min. CO₂ desorption amounts were calculated by separate calibration factors that were obtained during each experiment. The calibration factors were obtained by pulsing 1 cc volumes of the 10% CO₂/He (4.089 μmol CO₂) directly to the MS using a 6-port valve. The CO₂ pulse profile (m/e = 44) was integrated and a calibration factor was calculated, equating areas to moles of CO₂. Using this calibration factor, the integrated CO₂ desorption curve could be converted into moles of CO₂ eluded.

Sample regeneration was also assessed via reusing a sample following its adsorption/desorption techniques. Following the TPD, the sample was cooled to ambient temperature and its surface was again cleaned via He flow for 3 h. This was followed by conducting the adsorption and desorption techniques, described above, again.

Results and Discussion

The detail chemical analyses of the amine-enriched sorbents along with the untreated samples are illustrated in Table 1. A significant increase of nitrogen contents from 0.6 to 0.73% was observed on the treated samples. In addition, the oxygen contents also increase to a great extent from 0.77 to as high as 2.81 % on the enriched amine samples. The increase of the nitrogen contents of the treated samples suggested that some nitrogen-contained species were attached and/or bonded to the treated samples. This implies the presence of amine species on the treated samples.

The typical DRIFTS and TPD results obtained from sample 95C are illustrated in Figures 2 and 3, respectively. Exposure of the surface to dry CO₂/He flow did not lead to any observable surface CO₂-amine complex formations; only gaseous CO₂ (centered around 2350 cm⁻¹) was observed. When the CO₂/He flow was switched to the CO₂/H₂O/He, two distinct bands, 1148 cm⁻¹ and 1087 cm⁻¹, were formed shortly thereafter. These bands were assigned tentatively to bidentate carbonate and monodentate carbonate, respectively. It is speculated that the amine chemically absorbs CO₂ and water upon contact with a gaseous stream, thereby forming the amine complexes. The CO₂/H₂O/He stream was then switched to only He flow until the removal of gaseous CO₂ was completed. For the TPD study, the pure He flow was utilized to monitor desorption of adsorbed CO₂. Figure 3 illustrates that the desorption spectrum of the N₂ (or CO), CO₂, O₂ and H₂O as a function of temperature ramping. Two desorption peaks centered 40 and 110 °C from CO₂

desorption spectra along with the corresponding peaks from H₂O spectra centered around 60 and 120 °C might correlate to the decomposition of CO₂-amine complexes, monodentate carbonate and bidentate carbonate, respectively. The amounts of desorbed CO₂ were calculated by the separate calibration factors obtained for each experiment. The results illustrated in Figure 2 also confirmed that the absorption of CO₂ does not take place in the absence of water and that once flow is switched to He only, the absorbed species can desorb at room temperature. To prevent the desorption of amine-CO₂ complexes during the purging of gaseous CO₂, the CO₂/H₂O/He stream was replaced with H₂O/He instead of only He at the completion of the absorption phase. This proved to be effective method to maintain adsorbates while purging the gaseous CO₂. This finding led to the procedure described above where the TPD is conducted under only He but H₂O/He is used to purge CO₂. It is believed that the presence of moisture is beneficial to the long term stability of the subject material as the carbon dioxide retaining complex is believed to require the presence of a water molecule.⁴ These procedures (using H₂O/He instead of He only during the purging of gaseous CO₂) were applied to all samples. To further investigate the stability of the surface amine species, a repeated experiment was conducted on sample 95C. The amounts of desorbed CO₂ from all samples tested are tabulated in Table 1. Samples 59 and 95 showed some CO₂ capture capability and were probably in the forms of physical/chemical adsorption of CO₂. However, the treated samples 95A, 95B and 95C showed significant enhancement of the CO₂ capture capability. The sample 95C showed more than double the amount of CO₂ released compared to the untreated sample. A repeated experiment was conducted on sample 95C. It was seen that its uptake capability was only slightly degraded after being heated to 120 °C (140.6 μmol/g after regeneration vs. 174.5 μmol/g fresh). More importantly, the repeated run for 95C still showed good CO₂ capture results. This suggested that the sample 95C could be regenerated.

In addition to desorption of CO₂, species with m/e of 28 (CO or N₂) and 32 (O₂) were observed in the reactor effluent (Figure 3). If the m/e = 28 profile represents N₂, this profile would be indicative of surface amine decomposition. It is also reasonable that this profile may be representative of CO, which would result if the complexed CO₂ species decomposed to CO and O on the surface. The fates and origins of m/e of 28 and 32 are still under investigation.

In summary, the amine-enriched samples chemically adsorb CO₂ and water upon contact with a gaseous stream, thereby forming the amine complexes. The temperature gradients drive the reaction between the carbon dioxide, water, and amine in the reverse direction, thereby regenerating the amine and releasing the absorbed carbon dioxide and water.

Conclusions

The untreated materials showed some capability of capture/release of CO₂. The results of the samples being modified by various treatments indicated that the amine-enriched sorbents have the potential of capturing/releasing CO₂ and the amine surface is sufficiently stable to withstand regeneration.

References

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Table 1: TPD CO₂ Desorption Results of Amine-Enriched Sorbents

Sample #	Treatment methods	N, %	O, %	CO ₂ released, μmol/g sample
59 (7% carbon)	none	0.21	0.61	24.4
95 (52% carbon)	none	0.6	0.77	72.9
95A	A	0.73	2.81	81.1
95B	B	0.66	1.78	117.9
95C	C	0.65	2.28	174.5
95C (after regeneration)	C	0.65	2.28	140.6

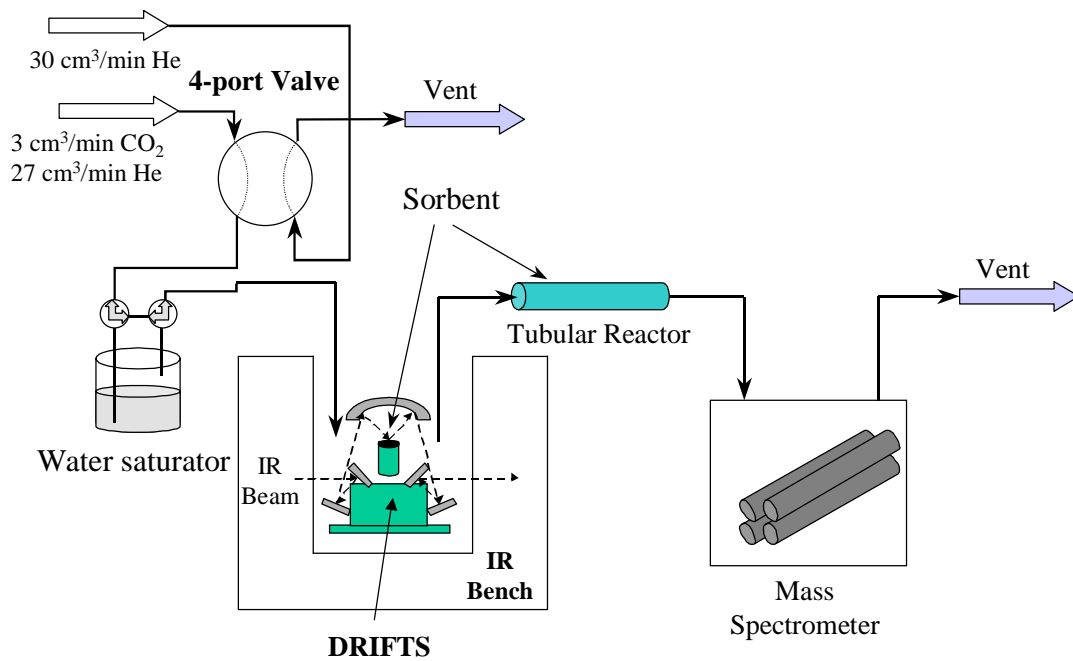


Figure 1. Schematic of experimental system.

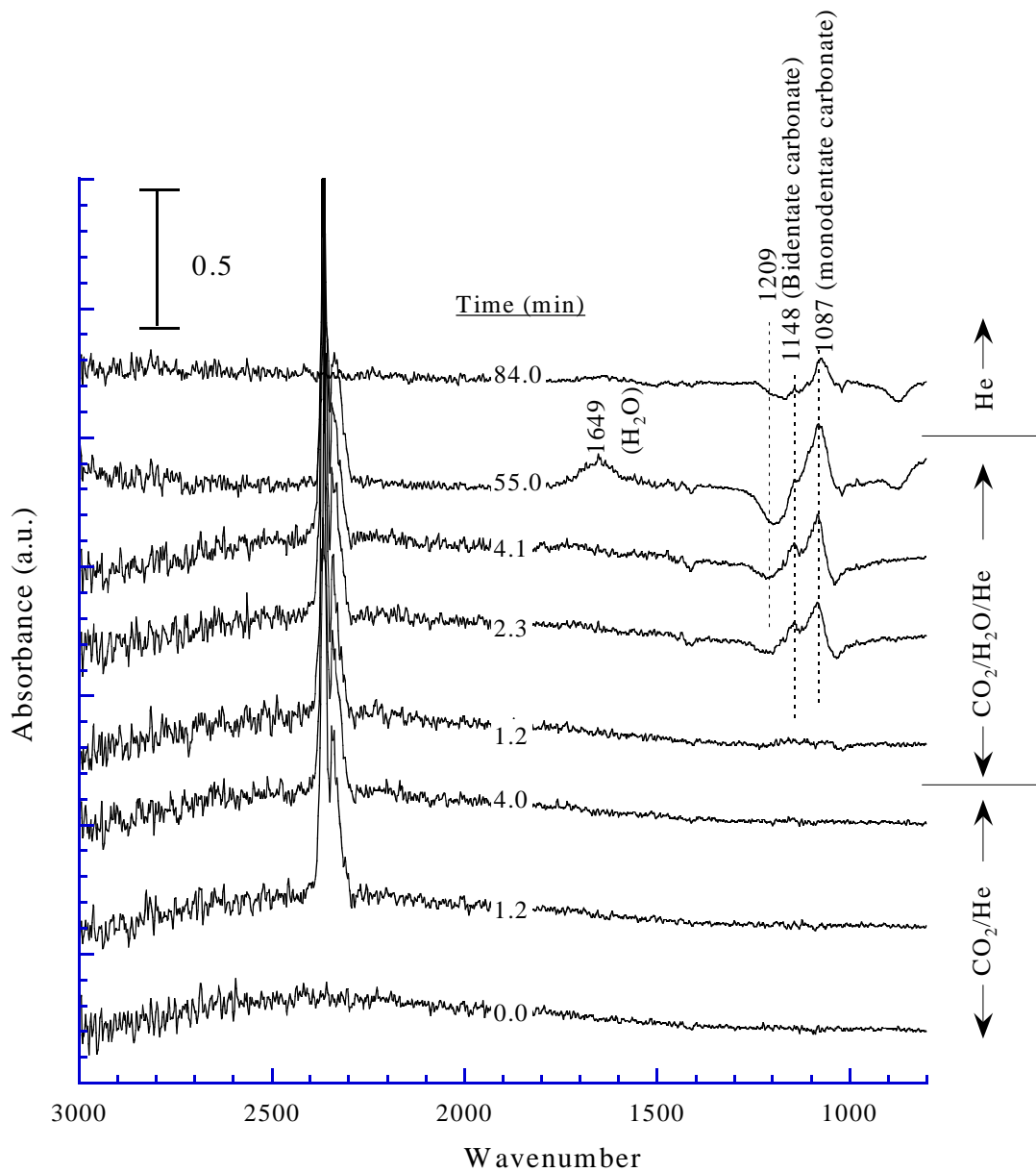


Figure 2. IR analysis of CO₂ adsorption over 95C at ambient temperature. Feed gas composition to the system are shown between brackets at right; times indicated are relative to points of feed composition changes.

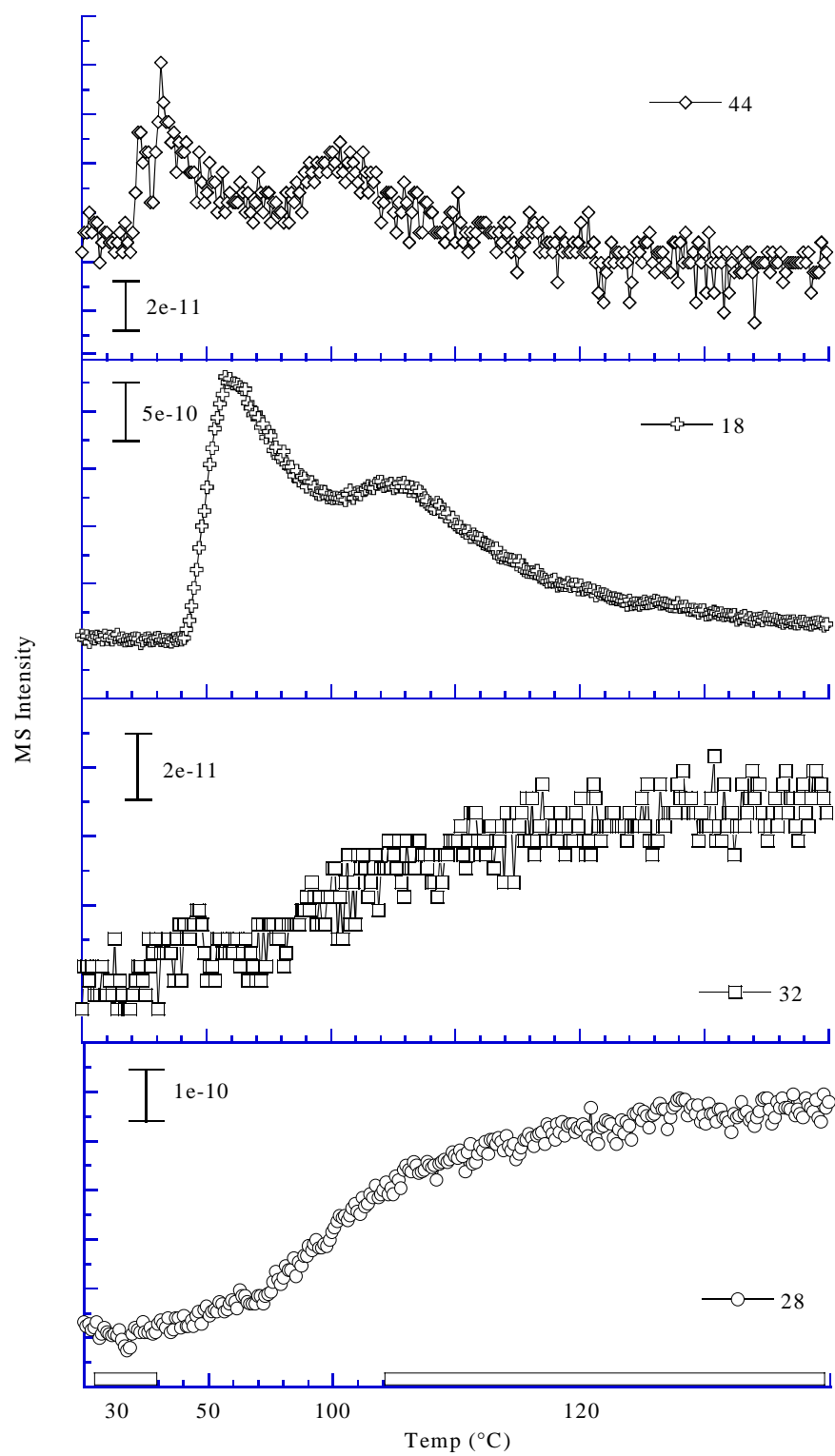


Figure 3. MS analysis of the CO₂ TPD over 95C in He flow.

