

Solid Amine CO₂ Capture Sorbents

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ABSTRACT

The capture of CO₂ from gas streams has been achieved by the utilization of amine-enriched, solid-sorbent systems. The initial solid sorbents were generated by the chemical treatment of carbon-enriched fly ash concentrates with various amine compounds. It was determined that these amine-enriched fly ash carbon concentrates performed at a 18 % CO₂ capture capacity based on commercially available sorbents. Alternative oxygen rich solids, such as, silica gel, activated carbon, and molecular sieves were examined as potential sorbents for the capture of CO₂ from gas streams. The chemical sorption performance of these solid amine sorbents will be described within this paper.

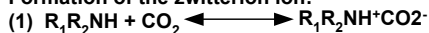
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INTRODUCTION

The concentration of CO₂ in our atmosphere is promoted by the combustion of fossil fuels for the generation of electricity. Capturing CO₂ from flue-gas streams is an essential parameter for the carbon management for sequestering of CO₂ from our environment. Current technologies¹ being considered for CO₂ sequestration include: disposal of CO₂ in deep oceans; depleted oil and gas fields; deep saline formations (aquifers); and recovery of enhanced oil, gas, and coal-bed methane. However, the current cost for the utilization of these types of technologies has proven to be too expensive. Consequently, reducing the cost for the capture of CO₂ will be a critical step in the overall carbon management program.

The physical and chemical adsorption of CO₂ can be achieved by using solvents, cryogenic techniques, membranes, and solid sorbents. The large-scale operation of these technologies is energy intensive when applied to capturing CO₂ in dilute stream, such as flue gas, which consist of 15% CO₂ by volume for most coal combustion systems. Amine-based, solvent-capture systems are the most energy efficient option, but are energy intensive due to the large amount of water needed in these system. Excessive water is required because of the corrosion and air flow problems created by the use of monoethanolamine (MEA), diethanolamine (DEA), or methyldiethanolamine (MDEA) in these aqueous-based, CO₂-capture systems. The proposed reaction sequences for using primary, secondary, and tertiary alkanolamines reacting with dissolve CO₂ are shown below.

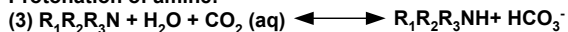
Formation of the zwitterion ion:



Formation of amine carbamate:



Protonation of amine:



Solid-amine CO₂ sorbents should have similar reactions with airborne CO₂, water vapor, and the amine functional group on its surface. Consequently, these types of sorbents are being used in

aircraft, submarine, and spacecraft technologies²⁻⁴. However, the cost of these sorbents is too expensive for large-scale applications in the utility industry. Consequently, the development of economical amine-enriched sorbents based on carbon fly ash and other oxygen rich sorbents will be discussed within this paper.

EXPERIMENTAL PROCEDURES

Samples--A fly ash containing 9.5% of unburned carbon was collected from the bag house of the 500-lbs/hr-combustion unit at the National Energy Technology Laboratory (NETL). The fly-ash sample examined in this study resulted from the combustion of a Pittsburgh-seam coal from the Black Creek mine. A column agglomeration process⁵⁻⁶ developed at NETL was used for the collection of the unburned carbon samples.

The three alternative oxygen rich solid substrates that were examined as CO₂ capture sorbents were a silica gel (grade 3, 8 mesh) from Aldrich Chemical Company, a coal based activated carbon from Calgon Inc. and a 13X molecular sieve from Sud Chemie.

Amine Treatment Process--The actual conditions for incorporating the amine group into the structure of the unburned carbon samples will not be discussed in this paper due to pending patent applications.

CO₂ Capture Capacity--The chemical CO₂ capture capacities were determined by the combination of Diffuse Reflectance Infrared Transform Spectroscopy (DRIFTS) Temperature Programmed Desorption (TPD) and Mass Spectroscopy (MS) analyses. The physical adsorption of CO₂ was not analyzed due to the limitations of the experimental reactor systems. The detailed operating conditions for this procedure were previously described in the literature⁷.

RESULTS AND DISCUSSION

Initially, the original fly-ash concentrates (95) were generated from the feed fly ash (59) by using the column agglomeration process. The amine treated carbon concentrates (95A, 95B, and 95C) were then examined as CO₂ capture sorbents. These samples were placed in a H₂O/CO₂/He stream and DRIFTS, TPD, and MS analyses determined the CO₂ capture capacity. The adsorption/desorption of CO₂ for these samples were determined over the temperature range of 25 –120 °C. Typical DRIFTS and TPD/MS spectra are shown in figures 1 and 2. According to the DRIFTS spectra, the formation of the corresponding carbamate-amine product was indicated by the presence of the two peaks at 1087 and 1148. The other major peaks at approximately 2380 are the physically adsorbed CO₂. The desorption of the CO₂ was observed as the temperature was increased to 120 °C. At this elevated temperature, the TPD/MS spectra indicates the mass numbers (m/e) for the desorption of CO₂ (m/e 44), H₂O (m/e 18), O₂ (m/e 32) and CO or N₂ (m/e 28). The m/e value of 28 may be the decomposition of the surface amine compound or the breakdown of the carbamate amine product. If this is the decomposition of the surface amine compound, it will have a direct effect on the regenerable properties of these sorbents. The overall CO₂ capture capacities are summarized in Table 1.

Table 1: TPD CO₂ Desorption Data of Amine Treated Sorbents

Sample #	Treatment	μmol/g CO ₂ Captured
59 Feed Fly Ash	None	24.4
95 Carbon	None	72.9
95 A Carbon	A	81.1
95 B Carbon	B	117.9
95 C Carbon	C	174.6
95C Carbon (regenerated)	C	140.6

As shown in Table 1., the physical absorbed CO₂ in samples 59 and 95 increased with the amine chemical treatment. The best sample was 95C, which had the CO₂ capture capacity of 174.5 μmol/g, and was regenerable for an additional test (140.6 μmol/g). In comparison to commercially available sorbents with surface areas of 1000-1700 m²/g and CO₂ capture capacities of 800-1000 μmol/g, the 95C was only able to achieve 18 % of the CO₂ capture capacity. However, the surface area of the 95C amine- enriched sorbent was only 27 m²/g, which may account for its low CO₂ capture capacity.

Alternative oxygen-rich solid substrates tested as amine-enriched sorbents for the capture of CO₂ are summarized in Table2.

Amine Treated Samples	μmol/g CO ₂ Captured	% CO ₂ Capacity ¹
NETL Fly Ash	24.4	615.5
Treated NETL Fly Ash	174.6	
Silica Gel	4.9	531.2
Treated Silica Gel	31.5	
Calgon Activated Carbon	8.0	258.7
Treated Calgon Activated Carbon	28.7	
Sud Chemie Molecular Sieve 13X	13.6	16.1
Treated Sud Chemie Molecular Sieve 13X	15.8	

¹ the percentage sorbent capacity is the change of the treated support compared to the baseline support.

According to Table 2, this amine treatment can be successfully applied on a variety of oxygen rich solid substrates, such as, silica gels, activated carbons, and molecular sieves. The CO₂ capture capacities were improved for all of the solid substrates tested, however, their performance were lower then the initial NETL fly ash sample examined under these reaction conditions. It is also important to point out that our current CO₂ capture experimental procedures are based only on the chemical absorbed species; physical absorbed CO₂ is purged from the surface prior to the desorption stage. Consequently, additional work is required to refine the experimental procedures (include the physical absorbed CO₂) and to increase capture capacities to the range of 800-1000 μmol/g, which will make them competitive with existing technology. Presently, additional materials with higher surface areas are being treated with this amine process and will be reported in future publications.

CONCLUSION

The amine treatment process was successful in improving the CO₂ capture capacities of these fly-ash carbon concentrates and oxygen rich solid substrates. However, the performance of the regenerable sorbents was only able to reach 18 % of the required CO₂ capture capacity to make them competitive with the existing CO₂ sorbents. Alternative low-cost, high surface oxygen-rich solid substrates and CO₂ capture procedures are being examined and will be reported in future publications.

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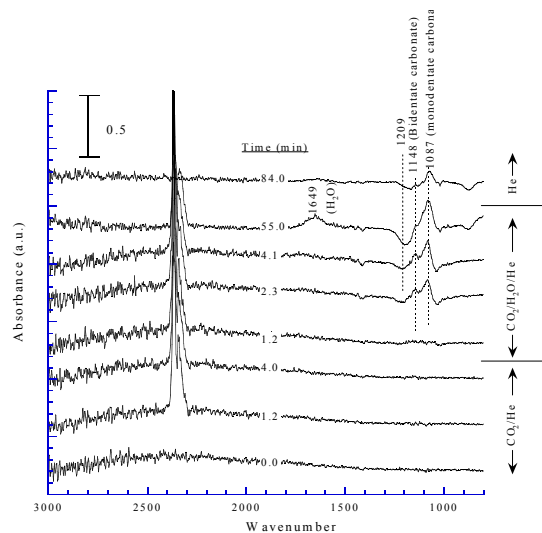


Figure 1: Typical DRIFTS CO₂ absorption spectra for 95C

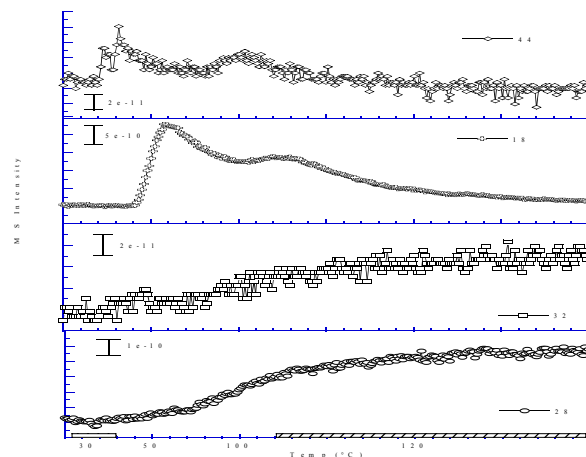


Figure 2: Typical TPD/MS spectra for 95C