Improved Immobilized Carbon Dioxide Capture Sorbents

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Introduction

The rise of greenhouse gases (i.e. CO2, CO, SO2 and NOx) [1] in our atmosphere is promoted by the combustion of fossil fuels for the generation of electricity. Carbon dioxide is considered to be the one of the major greenhouse gases that is directly influencing the global climate changes that are occurring within the earth's ozone layer. It is estimate that 36% of the United State's anthropogenic CO2 [2] is produced from coal-fired power plant. Consequently, the capture of CO_2 from flue-gas streams is an essential step for the carbon management for sequestrating CO_2 from our environment.

The capture and separation of CO_2 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 CO_2 in a dilute stream, such as flue gas, which consist of 15 volume % CO_2 for most coal combustion systems. Amine-based [3-4] wet scrubbing systems have been proposed as capture techniques for CO2 removal from flue gas streams, but are energy intensive due to the large amount of water needed in these systems. Excessive water is required because of the mechanism, corrosiveness and air flow problems created by the use of monoethanolamine (MEA), diethanolamine (DEA), or methyldiethanolamine (MDEA) in these aqueous-based, CO_2-capture systems. The proposed reaction sequences [5] in aqueous system using primary, secondary, and tertiary alkanolamines reacting with dissolve CO_2 are shown below.

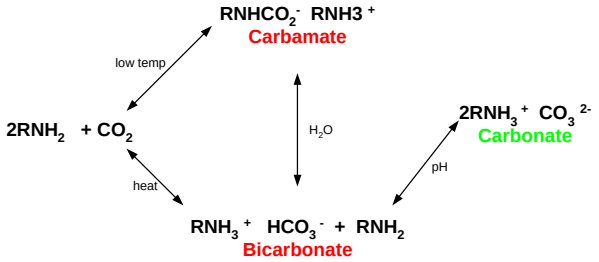

Figure 1. Proposed reaction sequence for the capture of carbon dioxide by liquid amine- based systems.

According to Figure 1, the majority of the CO_2 captured will result in the formation of bicarbonate in these liquid amine capture systems. In aqueous media, there is a requirement of 2 moles of amine/ mole of CO_2 for the formation of stable bicarbonate compounds resulting in the capture of CO_2.

Solid-amine CO_2 sorbents may have similar reactions with gaseous CO_2, water vapor, and the amine site on its surface. As a result, immobilized amine sorbents (IAS) are being used in aircraft, submarine, and spacecraft technologies [6-9]. However, the cost of these sorbents is too expensive for large-scale applications in the utility industry. Thus, SBA-15, a novel amine-based sorbent and a reformulated immobilized amine sorbent (R-IAS), are currently being examined as a cost efficient sorbent for the capture of CO2 from gas streams containing moisture. Consequently, a comparison performance study of the SBA-15, R-IAS and the IAS sorbents will be discussed within this paper.

Experimental

Preparation of the R-IAS. The reformulated immobilized amine sorbent (R-IAS) was prepared by the method described in the literature [8-9]. The exact composition of the secondary amine used in this sorbent will not be discussed due to pending patent applications.

Preparation of SBA-15. SBA-15 was prepared by using TEOS (tetraethylorthosilicate) as a silica precursor, Pluronic P123 ($PEO_{20}PPO_{70}PEO_{20}$, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) as a template, TMB (1,2,3-trimethyl benzene) as an expander, and HCl to control pH. [10-11] The specific steps for preparation of SBA-15 consist of :(1) dissolving 4.0 g of Pluronic P123 in 30 g of water and 120 ml (2.0 M) of HCl solution at room temperature, (2) mixing the resultant solution with 30 g TMB at 35 ^oC for 2 hours, (3) adding 8.5 g TEOS into the resultant homogeneous solution and stirring it at 35 ^oC for 22 hours, (4) aging the solution without stirring at 120 ^oC for 24 hours, and (5) calcining the resultant solid particles from filtering the aging solution in flowing air at –270 ^oC /min to 500 ^oC and holding it 500 ^oC hour for 6 hours. [10-12] The surface area of the SBA-15 was determined by N_2 BET measurement at 77 K.

Preparation and Characterization of the Sorbent. SBA-15 grafted with γ -aminopropyltriethoxysilane (APTS) was prepared by impregnating an APTS/toluene solution into SBA-15. [13] The impregnated sample was heated at 423 K for 20 h in a vacuum oven to obtain APTS-SBA-15. ATPTS-SBA-15 denotes the SBA-15 grafted with APTS. X-ray photoelectron spectra (XPS) of SBA-15 and APTS-SBA-15 were determined by a PHI5600ci instrument with monochromatic Al Kα X-rays.

CO_2 Capture Capacity. The chemical CO_2 capture capacities were determined by the combination of Temperature Programmed Desorption (TPD) and Mass Spectroscopy (MS) analyses. The adsorption of CO_2 was achieved in the presence of moisture at 25 ^oC and the total desorption of CO_2 was achieved over the temperature range of 30 – 60 ^oC. The composition of the experimental gas stream used in these test runs was 10% CO_2/H_2O/He. The detailed operating conditions for this procedure were previously described in the literature. [14-15]

XPS Analysis. The amount of nitrogen (N1s Peak) on the surface of the amine-enriched sorbent was determined by XPS analysis. The XPS analysis were conducted at 1 X 10^{-8} torr with the surface analysis depth range from 30 -50 angstroms. Under these conditions the chemically and the strongly adsorbed amines can be determined for each of the CO_2 capture sorbents. The details of this experimental procedure have been reported in the literature. [16]

Results an Discussion

Preliminary results of these types of sorbents have been reported early in the literature. [17] Initially, the performance of the prepared amine-enriched silicon sorbent (SBA-15) and the reformulated immobilized amine sorbent (R-IAS) were compared to an existing industrial solid amine sorbent (IAS). Each sorbent was placed in a 10% CO_2/H_2O/He stream and TPD and MS analyses were conducted to determine the performance of these CO_2 capture sorbents. The adsorption/desorption of CO_2 for these sorbents were determined over the temperature range of 25 – 60 ^oC. According to the TPD/MS analysis, all of the sorbents were successful in the capture of CO_2 from the moist experimental gas streams. The comparison of the CO_2 capture performances and XPS results for these sorbents are summarized in Table 1.

Table 1: TPD CO_2 Desorption and XPS Data of the Amine- Enriched Sorbents

Sorbents	μmol/g CO_2 captured	XPS % Nitrogen (N1s peak)
SBA-15-fresh	2011.4	7.1
SBA-15-1st Regeneration	1908.5	NA
SBA-15-2nd Regeneration	1748.3	NA
IAS-fresh	1603.9	17.7
IAS- 1st Regeneration	1922.6	NA
IAS-2nd Regeneration	1528.1	NA
R-IAS-fresh	4188.1	21.9
R-IAS-1st Regeneration	2690.2	NA
R-IAS-2nd Regeneration	2169.4	NA

As shown in Table 1, the SBA-15 had a lower % nitrogen value of 7.1 verses the IAS % nitrogen value of 17.7. The SBA-15 sorbent was prepared with a primary amine (propyl amine type) while the exact type of the amine used in the IAS was unknown. Despite the differences in the nitrogen values, the sorbents had similar average CO_2 capture capacities. The SBA-15 and the IAS sorbents were regenerated at 60 ^oC over two additional test runs and the average CO_2 capture capacity values were **1889.4 μmol/g** and **1820.8 μmol/g**, respectively. However, there was a significant improvement in the performance of the R-IAS sorbent over the other sorbents when tested under similar conditions. With the increase in the secondary amine loading in the R-IAS which is indicate by the higher % nitrogen value of 21.9, the average CO_2 capacity was increased to **3015.6 μmol/g**. It is assumed that the higher CO_2 capture capacity of the R-IAS can be attributed to the increase loading of the secondary amine. Furthermore, the use of a secondary amine appears to have superior performance over sorbent prepared with primary amine. Currently, additional research for the preparation of SBA-15 and R-IAS sorbents using different secondary amines are now underway and will be reported on in future publications.

Conclusions

Preliminary results indicate that the R-IAS has a higher average CO_2 capture capacity over the SBA-15 sorbent and IAS which is currently being used environmental CO_2 controlled life sorbent. It was determined the higher amine loading and the uses of secondary amines improved the CO_2 capture capacity of these types on immobilized amine sorbents.

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