

Carbon Dioxide Capture by Diamine-Grafted SBA-15: A Combined Fourier Transform Infrared and Mass Spectrometry Study

Rajesh A. Khatri,[†] Steven S. C. Chuang,^{*†} Yee Soong,[‡] and McMahan Gray[‡]

Chemical Engineering Department, The University of Akron, Akron, Ohio 44325-3906, and National Energy Technology Laboratory, U.S. Department of Energy, Pittsburgh, Pennsylvania 15236

The adsorption and desorption of CO₂ on diamine-grafted SBA-15 have been studied by infrared spectroscopy coupled with mass spectrometry. Diamine was grafted onto the SBA-15 surface by the reaction of [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane with the surface OH. CO₂ is adsorbed on the diamine-grafted SBA-15 as bidentate carbonate and bidentate and monodentate bicarbonates at 25 °C. Bidentate carbonate and monodentate bicarbonates are the major surface species formed and decomposed during the concentration-swing adsorption/desorption process at 25 °C. Temperature-programmed desorption revealed that the monodentate and bidentate bicarbonates bound stronger to the diamine-grafted SBA-15 surface than the bidentate carbonate. The amount of CO₂ desorbed from the carbonate and bicarbonate between 30 and 120 °C is 2 times more than that of CO₂ adsorbed/desorbed during each cycle of the concentration-swing adsorption/desorption. Desorption at 120 °C removes the majority of the captured CO₂ and regenerates the sorbent for CO₂ capture at low temperature. Regeneration of the sorbent with temperature-swing adsorption gives a significantly higher CO₂ capture capacity than concentration-swing adsorption. The use of a diamine-grafted sorbent, with an adsorption capacity of more than 1000 μmol/g of sorbent and a temperature-swing adsorption process, could be a cost-effective alternative to capture CO₂ from power plant flue gases.

Introduction

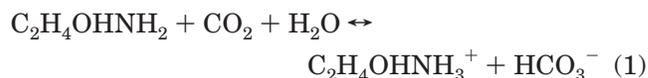
Concerns about the link between increases in the CO₂ concentration in the atmosphere and global climate changes have led to extensive research in limiting the emissions of greenhouse gases. Increased CO₂ emission is a result of fossil fuel usage to meet our growing energy needs. One of the largest sources of CO₂ emission is coal-fired power plants, which contribute to 36% of the anthropogenic CO₂ emission in the United States, and a similar percentage is applicable worldwide.¹ The capture of CO₂ from the coal-fired power plants, stationary sources, is technically feasible as compared with that of CO₂ from mobile sources. The sequestering of CO₂ from the coal-fired power plants could make a substantial reduction in the global CO₂ emission.

Depending on the operating conditions, the concentration of CO₂ in the coal-fired power plant flue gas varies from 10 to 15%.² The first step to sequester CO₂ is the separation of CO₂ from the flue gas.^{3–5} The available approaches for CO₂ capture and separation include the use of solid sorbents for pressure-swing adsorption (PSA), temperature-swing adsorption (TSA), and concentration-swing adsorption (CSA), the employment of liquid amines for absorption, and the utilization of a membrane separation process. These approaches have been used for the removal of CO₂ from closed environments and the natural gas liquefaction process.^{6–9}

The PSA process has been used to capture CO₂ from closed environments, such as space shuttles and submarines, where the concentration of CO₂ is low (i.e., less

than 1% CO₂).⁶ PSA operates at isothermal conditions. The driving force in the PSA process is the difference in the total pressure during adsorption and desorption. TSA has been used for the separation of CO₂ from natural gas in liquefaction processes and SO₂ removal from sulfuric acid plant flue gases.¹⁰ Desorption in the TSA process takes place at a temperature much higher than that of adsorption, while the total pressure is maintained constant. The difference in temperature during the adsorption and desorption cycle is the driving force for the TSA process. External heat is required to break the bonds during desorption and to regenerate the sorbent. A less common adsorption process is the CSA, which has been used to capture gasoline vapors from the carburetor and gas tank in automobiles.¹⁰ In the CSA process, adsorption and desorption take place at the same temperature and total pressure. The driving force in CSA is the partial pressure difference between the inlet gas carrying the adsorbate (i.e., adsorbing gas) and the purge gas, where the adsorbate concentration is mostly zero.

Aqueous alkanolamines have been used in the natural gas processing industry for the sweetening process (removal of acid gases). Primary aqueous alkanolamines react with CO₂ by the following reaction:



Separation of chemically reacted CO₂ and regeneration of the amines require an expensive CO₂-stripping process.¹¹ Adsorption processes with solid sorbents would be preferred over the liquid amine process because of the inherent properties associated with ease in handling of solids and corrosion problems caused by the liquid amines.^{12–14} All of the sorbents for CO₂

* To whom correspondence should be addressed. E-mail: schuang@uakron.edu.

[†] The University of Akron.

[‡] U.S. Department of Energy.

capture and separation were designed for low levels of CO₂; the use of these sorbents for CO₂ separation from the flue gas (10–15% CO₂) will make power generation from coal prohibitively expensive. The cost of CO₂ capture can be drastically reduced if effective low-cost sorbents are designed that have a CO₂ adsorption capacity of more than 1000 μmol/g of sorbent and a long-term regeneration capacity.⁶

Our strategy to develop a high CO₂ adsorption capacity sorbent is to graft amine functional group(s) containing species onto the high surface area supports such as SBA-15 by the silanation approach.^{15–19} A high surface area support will allow us to graft a larger number of active amine sites per gram of support. The nature of the grafted amine functional groups (primary or secondary amine) will determine the amount of CO₂ adsorbed and the energy required for regenerating the sorbent. The interaction between the CO₂ and NH/NH₂ groups is expected to be stronger than van der Waals forces but weaker than a covalent–ionic bond such that the CO₂ bound to the amino groups can be released with the low pressure and temperature steam available in the power plants. CO₂ is a weak acid, while amines are weak bases; this weak acid–base interaction with a binding energy in the range of 50–100 kJ/mol has been used to design solid sorbents for CO₂ capture from various sources.^{6,15,16,20–24}

Our previous results have shown that grafting of monoamine (3-APTS containing one amine group) onto SBA-15 showed CO₂ adsorption capacities up to 408 μmol/g of sorbent with adsorption at 25 °C and regeneration at 120 °C.¹⁵ The adsorption capacity can be further increased if the surface density of amine functional groups per gram of sorbent is increased. One way to improve the surface density of amine functional groups is to graft a diamine containing two amine groups per molecule. However, diamines containing primary amine (R–NH₂) and secondary amine (R–CH₂–NH–CH₂–R') groups may interact with surface OH and other species such as H₂O during grafting, limiting their CO₂ capture capacity.

The objectives of this paper are to investigate the grafting of diamine on the high surface area mesoporous silica material, SBA-15, and determine the CO₂ adsorption capacity of the diamine-grafted SBA-15. The diamine grafting has been studied by transmission infrared (IR) spectroscopy; the adsorption capacity of the sorbent has been studied using a temperature-programmed desorption (TPD) technique monitored by diffuse-reflectance Fourier transform IR (FT-IR) spectroscopy (DRIFTS) coupled with mass spectrometry (MS). Diamine-grafted SBA-15 showed a high adsorption capacity and was further explored for the CSA process with DRIFTS coupled with MS.

Experimental Section

Preparation of SBA-15 and Diamine-Grafted SBA-15 Sorbent. SBA-15 was prepared by using Pluronic 123 as a structure-directing agent, HCl solution for pH control, 1,3,5-trimethylbenzene as a pore expander, and tetraethyl orthosilicate as a silica precursor. The specific steps are described in detail elsewhere.¹⁵ Amine-grafted SBA-15 was prepared by (i) heating 1 g of SBA-15 at 110 °C in a vacuum for 6 h, (ii) impregnating 2.4 mL of [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane (i.e., diamine) in 4 mL of a toluene

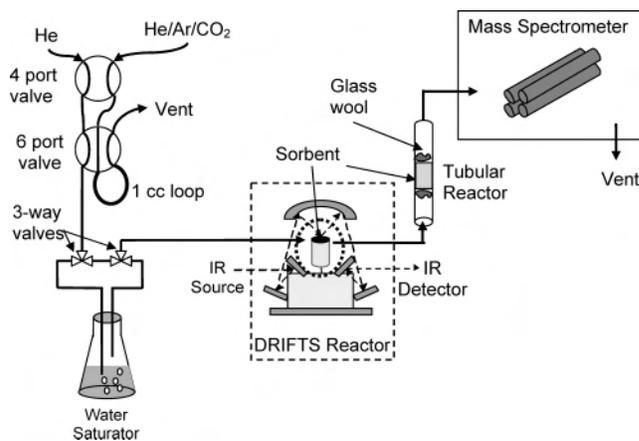


Figure 1. Experimental apparatus for the CO₂ adsorption study.

solution onto the pretreated SBA-15, and (iii) heating the impregnated SBA-15 at 150 °C for 20 h in a vacuum oven.

In Situ IR Study of Grafting of Diamine on SBA-15. A SBA-15 disk weighing 10 mg was placed in a stainless steel IR cell with CaF₂ windows on each end. The schematic and details of the IR cell are presented elsewhere.²⁵ The disk was pretreated in flowing He at 150 °C for 2 h and was exposed to diamine vapor by injecting a diamine–toluene solution (0.6:1 volume ratio) in flowing He at 25 °C. The IR cell was heated to 100 °C for 3 h to drive off the excess solvent. The surface interaction between the diamine and SBA-15 was monitored by in situ transmission IR spectroscopy.

Concentration-Swing Adsorption/Desorption and Partial-Pressure Studies. Figure 1 shows the experimental setup, which includes a four-port valve, a six-port valve, a DRIFTS reactor filled with 30 mg of sorbent followed by a tubular reactor filled with 300 mg of sorbent, and a mass spectrometer. The tubular reactor allowed packing of a sufficient amount of sorbent for adsorbing CO₂, giving the change in the CO₂ effluent concentration for MS measurement. The surface-adsorbed species were monitored by the DRIFTS reactor (Spectra Tech) placed inside a Nicolet 560 FT-IR bench, and the effluent of the reactors was simultaneously analyzed with a Pfeiffer QMS 200 quadrupole mass spectrometer.

Prior to adsorption, the sorbent was pretreated in flowing He at 30 °C to remove the excess moisture and obtain a clean background spectrum. CO₂ adsorption was carried out by switching the inlet flow from He to 10% CO₂ in He and Ar (tracer) using a four-port valve. The adsorbing gas and He streams were bubbled through a water saturator at room temperature corresponding to a partial pressure of 30 mmHg (equivalent to 4%) in the gas streams. The presence of water enhanced the CO₂ adsorption capacity.^{6,24} The four-port valve allows replacement of one flow stream by another while maintaining the total flow rate across the valve constant. The concentration-swing adsorption/desorption cycle was carried out by switching the inlet flow from an inert gas stream to the adsorbing gas stream containing CO₂. Upon saturation of the sorbent with the adsorbing gas, the inlet stream was switched back to the inert gas stream (He saturated with water). The difference in the partial pressure of CO₂ between the adsorbing and inert streams creates a driving force to desorb weakly adsorbed CO₂. The change in the concentration of CO₂ in the effluent flow was monitored by

MS. The cycle was repeated twice to determine the reproducibility of adsorption and desorption. The effect of the partial pressure on the CO₂ adsorption capacity of the sorbent was studied by varying the partial pressure of CO₂ from 0.05, 0.10, 0.25, to 0.50 atm in the adsorbate stream for each cycle.

TPD Study. Following the adsorption step, the sorbent was regenerated by the TPD technique by heating the sorbent to 120 °C in flowing He at a rate of 10 °C/min. The CO₂ concentration profile during adsorption and desorption was monitored by MS, and the amount of CO₂ was quantified by calibrating the mass spectrometer for CO₂ gas ($m/e = 44$). The calibration factor was obtained by injecting 1 cm³ of a 10% CO₂ pulse in a flowing He stream using the six-port valve and calculating the area corresponding to the amount of CO₂ injected.

IR spectra in this work were collected in three different ways: (i) transmission mode, (ii) DRIFTS mode, and (iii) single-beam DRIFTS mode. DRIFTS is more suitable for an IR study of CO₂ adsorption/desorption on diamine-treated sorbent particles than the transmission IR, in particular for reaction studies at high temperature and high pressure. The DRIFTS reactor gives precise control of the temperature, and the sealed chamber is suitable for gas–solid systems. Despite the above-mentioned advantages of the DRIFTS, it is not applicable for in situ studies involving liquids. Transmission IR spectroscopy was used to study grafting of amines in toluene on the SBA-15 disk.

For the in situ grafting study in a transmission cell, the background spectrum of a dry He-pretreated SBA-15 disk was used as the reference and the data were reported in the form of absorbance. During the DRIFTS study, the spectrum of pretreated diamine-grafted sorbent was used as the reference (i.e., background) spectrum and the data were reported in the form of absorbance. The single-beam spectrum is the reference spectrum, which contains the characteristics of the IR source and bands of the sample placed in the path of the IR beam. The CaF₂ windows used in the transmission reactor cut off the spectrum below 1100 cm⁻¹, while the Zn–Se windows in DRIFTS cut off at 650 cm⁻¹.

Results and Discussion

Figure 2 shows the transmission IR spectra of the SBA-15 disk during heating from 25 to 150 °C in flowing He; a spectrum at 25 °C in a He environment was used as the background spectrum. The IR absorbance intensity of the 3388 cm⁻¹ broad band and the 1630 cm⁻¹ intense band decreased with an increase in the temperature and the time exposed to flowing He at 150 °C due to dehydration of the surface. These bands can be attributed to hydrogen bonding in molecular H₂O and the H–O–H bend, respectively.²⁶ The sharp band at 3750 cm⁻¹ for isolated hydroxyl groups is similar to that observed on the silica materials degassed at high temperatures.²⁶ The isolated hydroxyl groups (silanol groups), which can react with a variety of functional groups, can be used to tailor the surface chemistry of silica and glass materials.

Figure 3 shows the transmission IR spectra during grafting of diamine onto the SBA-15 surface. Exposure of the SBA-15 disk to a diamine–toluene mixture at 100 °C produced IR bands at 1457, 1596, 2844, 2941, 3300, and 3377 cm⁻¹. The band assignments are shown in

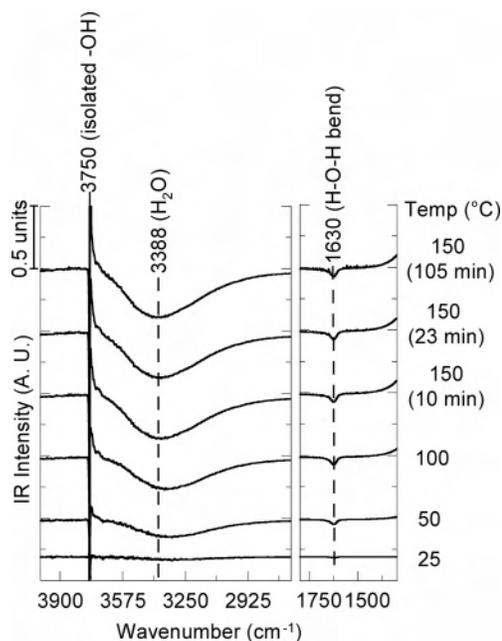


Figure 2. Transmission IR spectra during heating of SBA-15 from 25 to 150 °C.

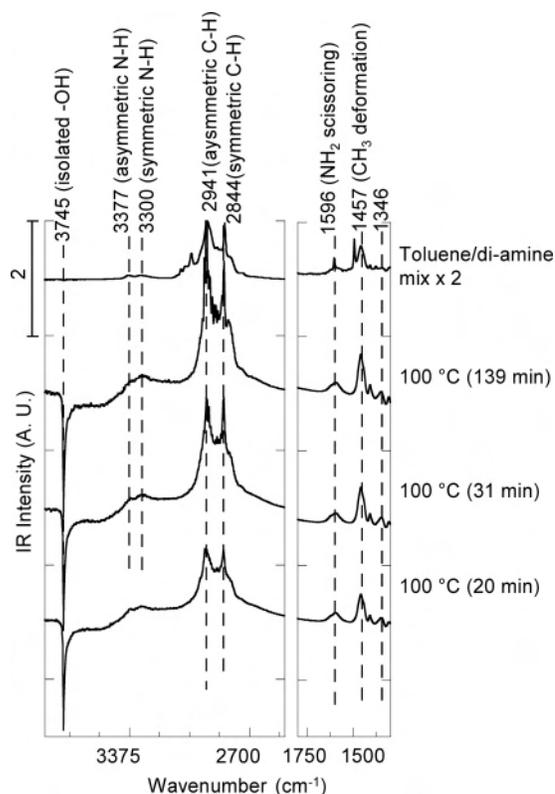


Figure 3. Transmission IR spectra of the SBA-15 disk during grafting of amine with a amine–toluene mixture at 100 °C.

Figure 3.^{15,24,27} The IR spectrum of the diamine–toluene mixture is included in Figure 3 for comparison; toluene gives IR bands at 1492 and 3026 cm⁻¹. The IR bands for CH₃ and NH₂ on the surface of SBA-15 are similar to the bands observed for diamine in toluene (top spectrum in Figure 3), suggesting that NH₂ functional groups of diamine do not react with the hydroxyl groups on the surface. The decrease in isolated surface hydroxyl groups (IR band at 3745 cm⁻¹) suggests the reaction of surface hydroxyl groups (Si–OH) with highly active

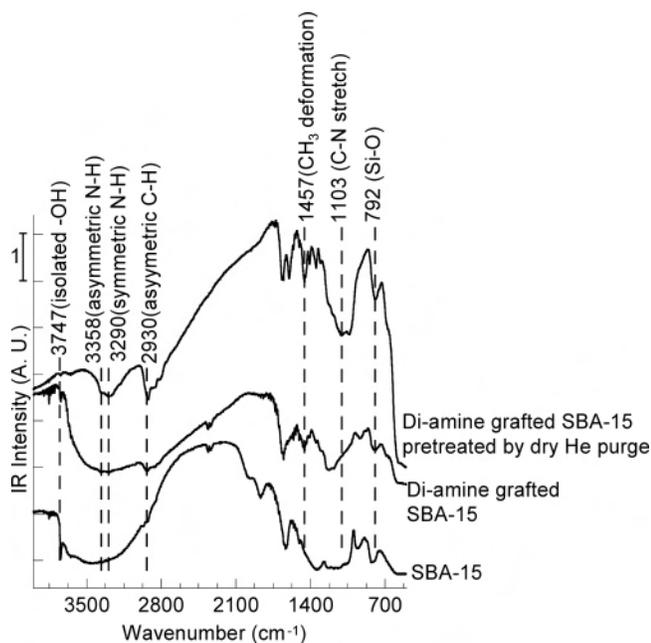
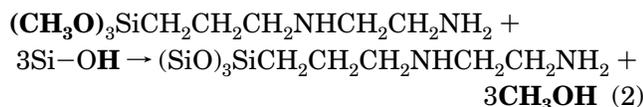


Figure 4. DRIFTS background spectra of (i) SBA-15, (ii) diamine-grafted SBA-15, and (iii) diamine-grafted SBA-15 pretreated in a dry He flow for 1 h at 25 °C.

methoxy groups of a diamine compound by the following reaction:



This is further confirmed by a small amount of CH_3OH formed, which is evidenced by the OH bending vibration of methanol at 1346 cm^{-1} .

Figure 4 compares the DRIFTS spectra of SBA-15, diamine-impregnated SBA-15, and diamine-impregnated SBA-15 treated in flowing He for 1 h at 25 °C. Exposure of the grafted sorbent to dry flowing He for 1 h resulted in the formation of prominent IR bands at 2930 cm^{-1} for asymmetric C-H and 3290 and 3358 cm^{-1} for symmetric and asymmetric N-H stretches, respectively. The broad water band at 3400 cm^{-1} observed in the diamine-grafted SBA-15 disappears during a dry He purge, suggesting desorption of molecular water from the surface of the sorbent. This observation indicates that the molecular water is weakly adsorbed on the silica surface as well as on the diamine-grafted silica surface. The decrease in the IR intensity of the 3747 cm^{-1} band of diamine-grafted SBA-15 compared to SBA-15 further confirms the depletion of isolated OH groups by its reaction with methoxy groups of diamine species.¹⁵

Figure 5 shows MS intensity profiles of CO_2 and Ar (tracer) during CSA cycles. Each adsorption cycle started with a step switch from water-saturated He (30 mL/min) to the water-saturated He/ CO_2 /Ar (25:2:3 mL/min) stream. The step switch produced a sudden change in the concentration of CO_2 /Ar. The sudden change in the concentration created the CO_2 and Ar fronts, which traveled through the DRIFTS, the sorbent bed in the tubular reactor, and then to the MS detector. The Ar profile showed a sharp response in MS, while the response of CO_2 was delayed because of the adsorption of CO_2 on the sorbent. Upon reaching steady state, the

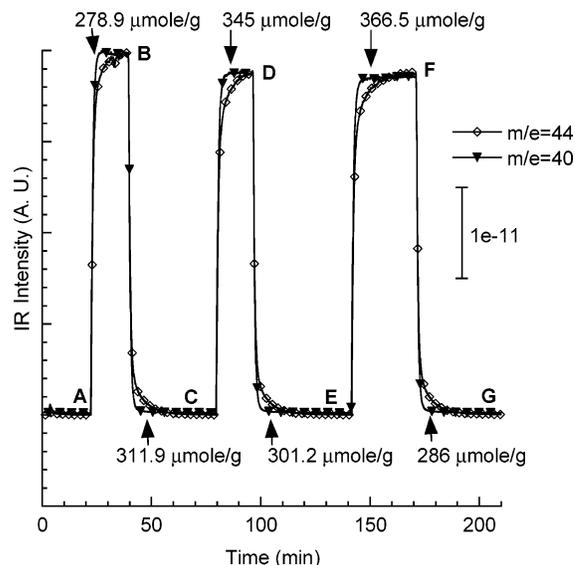


Figure 5. CO_2 MS ($m/e = 44$) intensity during adsorption/desorption cycles on amine-treated SBA-15 with Ar ($m/e = 40$) as a tracer (Ar/He/ $\text{CO}_2 = 25/2/3\text{ cm}^3/\text{min}$).

CO_2 and Ar profiles attained a stable MS baseline. The desorption cycle was initiated by a step switch from He/ CO_2 /Ar to He, the MS intensity of Ar showed a sharp decrease, and the intensity of CO_2 lagged behind because of desorption of weakly adsorbed species from the sorbent. The MS intensity of Ar was normalized to the height of CO_2 ; the amounts of CO_2 adsorbed and desorbed were calculated from the area between the MS profiles of CO_2 and Ar using the calibration factor of CO_2 .

The residual CO_2 on the sorbent in each adsorption/desorption cycle is the difference between the total amount of CO_2 adsorbed and the amount of CO_2 desorbed during each cycle. In the first adsorption cycle, the amount of CO_2 desorbed was more than the amount of CO_2 adsorbed. This was due to the CO_2 adsorbed on the sorbent from the atmosphere prior to the study. In the subsequent cycles, the amount of CO_2 adsorbed was more than that of the amount desorbed, thus increasing the residual CO_2 loading on the sorbent after each cycle. The residual CO_2 on the sorbent is strongly bound to the surface by chemical reaction and has to be desorbed by a stronger force than the partial-pressure driving force in the CSA process. This can be accomplished by TPD.

DRIFTS IR spectra during adsorption are shown in Figure 6. The spectra shown after each adsorption cycle are relative to the starting point A (Figure 5) before adsorption. The interaction of CO_2 with diamine-grafted species produced bidentate bicarbonate species at 1628 cm^{-1} , monodentate bicarbonate at 1470 and 1422 cm^{-1} , monodentate carbonate at 1335 cm^{-1} , and bidentate carbonate at 1541 cm^{-1} .¹⁵ The bands at 929 and 819 cm^{-1} may be attributed to NH_3 rocking vibrations, while the band at 1287 cm^{-1} may be assigned to carbamic acid species.²⁷ The decrease in the IR band at 3303 cm^{-1} for the N-H stretch is due to the depletion of NH_2 bands by the reaction of CO_2 with amine species. The residual CO_2 on the sorbent increased with the number of adsorption/desorption cycles, which is clearly evidenced by the increase in the intensity of IR bands at 1628 , 1541 , and 1422 cm^{-1} corresponding to the species produced by the interaction of CO_2 with diamine.

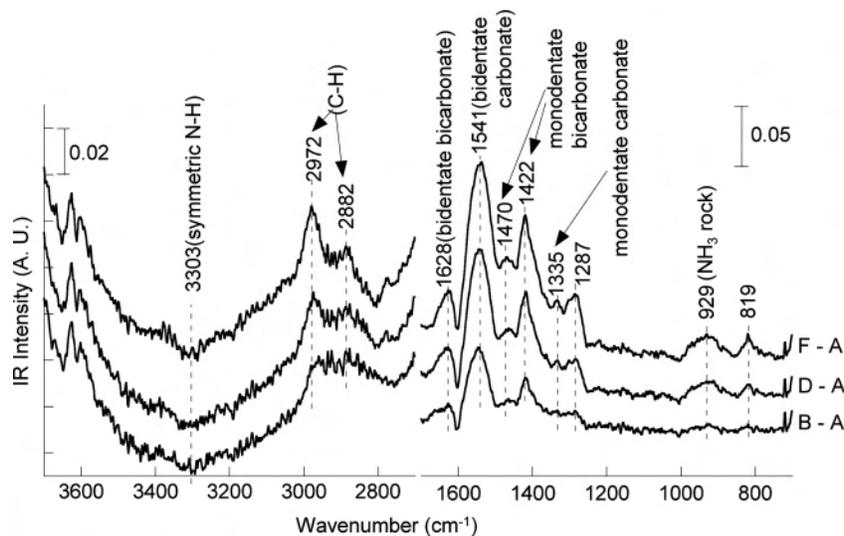


Figure 6. DRIFTS IR spectra during CO₂ CSA cycles on an amine-treated SBA-15 sample.

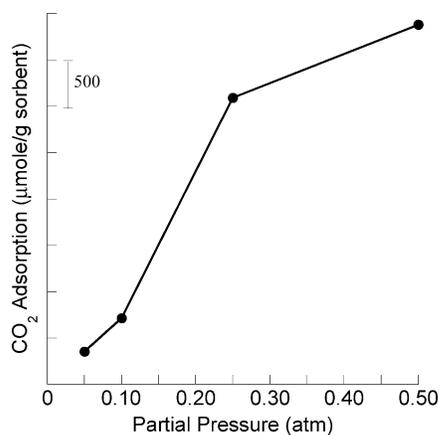


Figure 7. CO₂ adsorption capacity of amine-treated SBA-15 as a function of the partial pressure of CO₂.

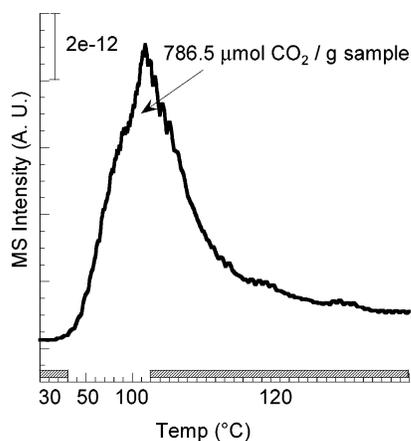


Figure 8. CO₂ MS profile during desorption of CO₂ by a TPD technique.

The effect of the partial pressure of CO₂ in an adsorbate stream on the adsorption capacity of the sorbent is shown in Figure 7. An increase in the partial pressure of CO₂ led to a sharp increase in the total adsorption capacity of the sorbent; at 0.5 atm of CO₂ partial pressure, the adsorption capacity of the sorbent was more than 3500 μmol/g of sorbent. A further increase in the partial pressure would lead to saturation of the sorbent.

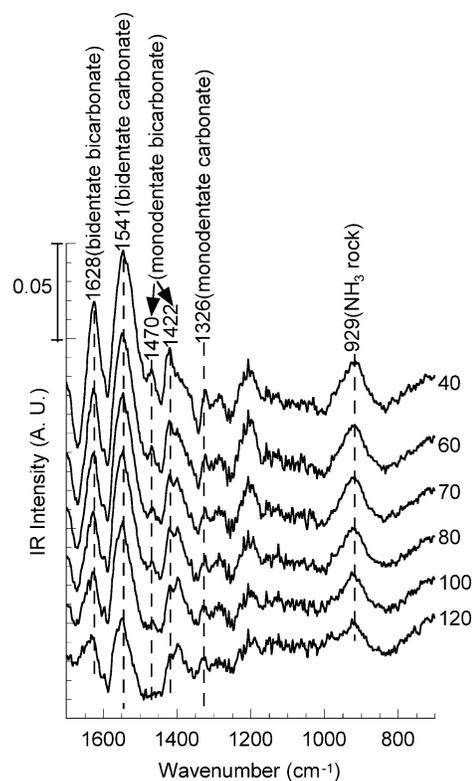
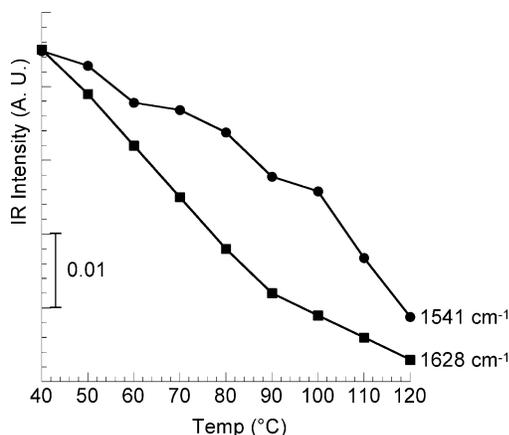


Figure 9. DRIFTS IR spectra during desorption of CO₂ by a TPD technique.

Figures 8 and 9 show the MS intensity and DRIFTS IR spectra during TPD of CO₂ over a diamine-treated sorbent, respectively. The TPD study was carried out after the CSA study using a CO₂ partial pressure of 0.5 atm. The amount of CO₂ desorbed from the sorbent was 786.5 μmol/g, as calculated from the MS intensity profile of CO₂ during TPD. The amount of TPD-desorbed CO₂ is at the levels of the commercial polymer amine sorbent used for CO₂ capture in submarines and space shuttles and other amine-based sorbents reported in the literature, as shown in Table 1. The presence of IR bands corresponding to monodentate and bidentate bicarbonates and bidentate carbonate at 120 °C on the sorbent surface reveals that not all of the adsorbed CO₂ is desorbed at a peak temperature of 120 °C, and a higher temperature is required to desorb the strongly adsorbed

Table 1. CO₂ Capture Capacity of Amine-Based Sorbents

sorbent	CO ₂ capture capacity (μmol/g of sorbent)	adsorption/desorption technique	ref
monoamine-treated mesoporous silica (MCM-48)	1136	TGA and TPD	24
amine-treated mesoporous silica (SBA-15)	400	MS and TPD	15
polymer amine-based sorbent (HSC+)	909	TGA	6
amine-treated silica gel	898	GC	7
diamine-treated mesoporous silica (SBA-15)	768	MS and TPD	this Study

**Figure 10.** IR band peak intensities during TPD.

CO₂. The peak intensity of adsorbed species at 120 °C is almost half that of adsorbed species at 40 °C. Assuming a linear relationship between the amount of adsorbed CO₂ and the IR peak intensity, we can conclude that the amount of CO₂ present on the surface of the sorbent when it first reaches a temperature of 120 °C is half of its total adsorption capacity at 40 °C. Using 120 °C as the CO₂ desorption peak temperature, the binding energy was calculated to be 47.8 kJ/mol, which can be considered the minimum average binding energy of CO₂ on a diamine-treated sorbent.²⁸ This binding energy is about two-thirds of the heat of reaction between CO₂ and aqueous amine (i.e., monoethanolamine),¹¹ indicating that the temperature required for regeneration of the diamine-treated sorbent is lower than those for aqueous alkanolamines.

Figure 10 shows the absolute IR peak intensities of adsorbed CO₂ during TPD. The sharp decrease in the peak intensity of the IR band at 1628 cm⁻¹ with an increase in the temperature, compared to the IR band at 1541 cm⁻¹, indicates that the bidentate bicarbonate has a lower binding energy than bidentate carbonate. Similar results were observed during TPD of monoamine-treated SBA-15.¹⁵ The species formed due to interactions of CO₂ with monoamines are similar to those of CO₂ with diamine species.

Comparing the intensity ratios of the peaks at 1541 and 1628 cm⁻¹ in Figures 6 and 9 reveals that bidentate carbonate and monodentate bicarbonate play a key role during CSA while bidentate bicarbonate and bidentate carbonate play a significant role during TSA. This is evidenced by the extent of change in the IR intensity of these species during CSA and TSA. The bidentate carbonate can desorb more than 50% during CSA at 25 °C, suggesting that CO₂ adsorbed as bidentate carbonate species is weakly bound on the surface and can be flushed off by a partial-pressure driving force.

An IR study of CO₂ adsorption on monoamine-treated SBA-15 compared to diamine-treated SBA-15 reveals that the species formed by interaction of CO₂ with different types of amine functional groups (mono- or

diamine) are indistinguishable. This suggests that the interaction of CO₂ with diamines is similar to that with monoamines. Furthermore, the amount of CO₂ adsorbed per gram of sorbent during the TPD at 120 °C for diamine-treated SBA-15 (786.5 μmol/g) is about twice the amount for monoamine-treated SBA-15 (408 μmol/g).¹⁵ These results suggest that the diamine-grafted SBA-15 provides almost twice as many effective amine functional groups as those of monoamine-grafted SBA-15 for CO₂ capture.

The use of a solid sorbent could be a low-cost alternative to capturing CO₂ from power plant flue gases because of its high CO₂ adsorption capacity, low heat capacity, and simplicity of operation. The economic potential of a CO₂ capture process can be determined by the total capital cost and utility cost.²⁹ The capture of CO₂ by the solid sorbent involves the direct adsorption of CO₂ on the amine surface functional groups; the capture of CO₂ by aqueous amines involves the CO₂ mass transfer through the gas-liquid interface and its reaction with aqueous amines. The rate-limiting step for adsorption on the solid sorbent is the diffusion of CO₂ from the flue gas bulk stream to the inside pore of SBA-15; for the aqueous amine process, the rate-limiting step is the CO₂ mass transfer across the gas-liquid interface.³⁰ The rate of the former is normally 3 orders of magnitude higher than that of the latter.³¹ The high adsorption capacity and high rate of mass transfer will lead to a small adsorption bed, resulting in significant savings in construction and equipment costs.

The major utility cost results from the energy consumption in the stripping of CO₂ from a CO₂-rich amine solution for the aqueous amine process and the desorption of CO₂ from the solid sorbents for the solid adsorption process.¹¹ Considering the heat capacity of the sorbent to be 0.8 kJ/kg·K (SiO₂) and that of a 30 wt % monoethanolamine solvent to be 4 kJ/kg·K, the adsorption capacities of 0.044 kg of CO₂/kg of sorbent (equivalent to 1000 μmol/g of sorbent) and 0.036 kg of CO₂/kg of solvent,¹¹ and the regeneration temperature of 120 °C for both processes, the energy required per kilpogram of CO₂ recovered is 1636 kJ for the solid sorbent compared to 10 000 kJ for the liquid amine process. The low energy consumption translates to a low utility cost. Although the operating (i.e., utility) cost for the TSA process with the solid amine-based sorbent is significantly lower than that for the aqueous amine process, the durability and cost of the solid amine sorbent remains to be further improved to reach the DOE target of \$10/ton for CO₂ sequestration.³²

Conclusions

The present study provides insight into the mechanism of diamine grafting on SBA-15 with in situ IR spectroscopy. The isolated surface hydroxyl groups are active moieties on the SBA-15 surface for reaction with methoxy groups of diamine-containing silanes. CO₂ adsorbs on the primary and secondary amine groups,

forming carbonate, bicarbonate, and carbamic acid species. The major species formed by the adsorption of CO₂ on the surface are monodentate bicarbonate, bidentate bicarbonate, and bidentate carbonate. The bidentate bicarbonate species bind stronger to the diamine-grafted SBA-15 than bidentate carbonate. The amount of CO₂ desorbed from the carbonate and bicarbonate between 30 and 120 °C is 2 times more than that of CO₂ adsorbed/desorbed during each cycle of the concentration-swing adsorption/desorption.

The CO₂ capture capacity of diamine-grafted SBA-15 is 2 times that of mono-amine grafted SBA-15 in a TSA (25–120 °C) process. Although TSA is an energy-intensive and costly process, the use of a low-cost solid sorbent with TSA using low-pressure steam from a reboiler could be a cost-effective alternative to capturing CO₂ from power plant flue gases.

Acknowledgment

This work was supported by the Ohio Board Research Challenge Grant. We also thank Thomas Tarkar of Energetics Inc. for the telephonic discussion on the cost analysis of the solid sorbent.

Literature Cited

- Halmann, M. M.; Steinberg, M. *Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology*; Lewis Publishers: Boca Raton, FL, 1998.
- Ertl, G.; Knoezinger, H., Eds. *Handbook of Heterogeneous Catalysis, 5 Volume Set*; Wiley-VCH: Weinheim, Germany, 1997.
- Gupta, H.; Iyer, M. V.; Sakadjian, B. B.; Fan, L.-S. *Int. J. Environ. Technol. Manage.* **2004**, *4*, 3.
- Kim, S.; Ida, J.; Gulians, V. V.; Lin, Y. S. *Int. J. Environ. Technol. Manage.* **2004**, *4*, 21.
- Siriwardane, R. V.; Shen, M.-S.; Fisher, E. P.; Poston, J. A. *Energy Fuels* **2001**, *15*, 279.
- Satyapal, S.; Filburn, T.; Trela, J.; Strange, J. *Energy Fuels* **2001**, *15*, 250.
- Leal, O.; Bolivar, C.; Ovalles, C.; Garcia, J. J.; Espidel, Y. *Inorg. Chim. Acta* **1995**, *240*, 183.
- Birbara, P. J.; Filburn, T. P.; Nalette, T. A. Regenerable solid amine sorbent. U.S. Patent 5,876,488, 1999.
- Birbara, P. J.; Nalette, T. A. Process for forming a regenerable supported amine-polyol sorbent. U.S. Patent 5,620,940, 1997.
- Perry, R. H.; Green, D. W. *Perry's Chemical Engineers' Handbook*, 7th ed.; McGraw-Hill: New York, 1998.
- Chakma, A. *Energy Convers. Manage.* **1997**, *38*, S51.
- Niswander, R. H.; Edwards, D. J.; DuPart, M. S.; Tse, J. *P. Sep. Sci. Technol.* **1993**, *28*, 565.
- Tontiwachwuthikul, P.; Meisen, A.; Lim, C. J. *J. Chem. Eng. Data* **1991**, *36*, 130.
- Veawab, A.; Tontiwachwuthikul, P.; Chakma, A. *Ind. Eng. Chem. Res.* **1999**, *38*, 3917.
- Chang, A. C. C.; Chuang, S. S. C.; Gray, M.; Soong, Y. *Energy Fuels* **2003**, *17*, 468.
- Gray, M. L.; Soong, Y.; Champagne, K. J. Amine-enriched solid sorbents for carbon dioxide capture. U.S. Patent 6,547,854, 2003.
- Gray, M. L.; Soong, Y.; Champagne, K. J.; Baltrus, J.; Stevens, R. W.; Toochinda, P.; Chuang, S. S. C. *Sep. Purif. Technol.* **2004**, *35*, 31.
- Gray, M. L.; Soong, Y.; Champagne, K. J.; Pennline, H.; Baltrus, J.; Stevens, R. W., Jr.; Khatri, R.; Chuang, S. S. C.; Khan, S. *Prepr. Symp.—Am. Chem. Soc., Div. Fuel Chem.* **2003**, *48*, 164.
- Gray, M. L.; Soong, Y.; Champagne, K. J.; Pennline, H. W.; Baltrus, J.; Stevens, R. W., Jr.; Khatri, R.; Chuang, S. S. C. *Int. J. Environ. Technol. Manage.* **2004**, *4*, 82.
- Cheng, Z. H.; Yasukawa, A.; Kandori, K.; Ishikawa, T. *Langmuir* **1998**, *14*, 6681.
- Cinke, M.; Li, J.; Bauschlicher, C. W.; Ricca, A.; Meyyappan, M. *Chem. Phys. Lett.* **2003**, *376*, 761.
- Fifield, L. S.; Fryxell, G. E.; Addleman, R. S.; Aardahl, C. L. *Prepr. Symp.—Am. Chem. Soc., Div. Fuel Chem.* **2004**, *49*, 296.
- Knowles, G. P.; Graham, J. V.; Delaney, S. W.; Chaffee, A. L. *Prepr. Symp.—Am. Chem. Soc., Div. Fuel Chem.* **2004**, *49*, 255.
- Huang, H. Y.; Yang, R. T.; Chinn, D.; Munson, C. L. *Ind. Eng. Chem. Res.* **2003**, *42*, 2427.
- Chuang, S. S. C.; Brundage, M. A.; Balakos, M. W.; Srinivas, G. *Appl. Spectrosc.* **1995**, *49*, 1151.
- Hair, M. L. *Infrared Spectroscopy in Surface Chemistry*; Dekker: New York, 1967.
- Colthup, N.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*, 2nd ed.; Academic Press: New York, 1975.
- Krishnamurthy, R.; Chuang, S. S. C. *Thermochim. Acta* **1995**, *262*, 215.
- Cussler, E. L.; Moggridge, G. D. *Chemical Product Design*; Cambridge University Press: New York, 2001.
- Maccabe, W. J.; Smith, J. C.; Harriott, P. *Unit Operations of Chemical Engineering*, 4th ed.; McGraw-Hill: New York, 1985.
- Fogler, H. S. *Elements of Chemical Reaction Engineering*, 3rd ed.; Prentice Hall: Englewood Cliffs, NJ, 1999.
- Report, D. N. *Carbon Sequestration Technology Roadmap and Program Plan—2004*; Apr 2004. <http://www.netl.doe.gov/coal/Carbon%20Sequestration/pubs/SequestrationRoadmap4-29-04.pdf>.

Received for review October 15, 2004

Revised manuscript received February 14, 2005

Accepted February 18, 2005

IE048997S