Thermal and Chemical Stability of Regenerable Solid Amine Sorbent for CO$_2$ Capture

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The adsorption and desorption of CO$_2$ and SO$_2$ on an amine-grafted SBA-15 sorbent has been studied by in situ infrared spectroscopy coupled with mass spectrometry. CO$_2$ adsorbed on an amine-grafted sorbent as carbonates and bicarbonates, while SO$_2$ adsorbed as sulfates and sulfites. The CO$_2$ adsorption capacity of the amine-grafted sorbent was almost twice as much as that of a commercial sorbent. The adsorption of CO$_2$ in the presence of H$_2$O and D$_2$O shows an isotopic shift in the IR frequency of adsorbed carbonate and bicarbonate bands, revealing that water plays a role in the CO$_2$ adsorption on amine-grafted sorbents. Although the rate of adsorption of SO$_2$ was slower than that of CO$_2$, the adsorbed S surface species is capable of blocking the active amine sites for CO$_2$ adsorption. A temperature-programmed degradation study of the amine-grafted sorbent showed that the surface amine species are stable up to 250 °C in air.
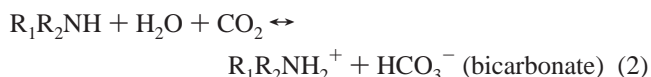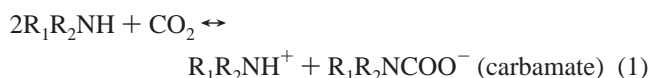
Introduction

The increase in atmospheric CO$_2$ over past centuries is a result of the growing use of fossil fuels. The CO$_2$ concentration in the atmosphere has increased from 280 ppm during the preindustrial time to 377 ppm in 2004.[1] The CO$_2$ concentration is expected to continue to increase before a non-carbon-containing fuel takes over as the dominant energy source.[2] The continuous rise in CO$_2$ concentration and its linkage to global warming demands cost-effective approaches to stabilize the CO$_2$ concentration in the atmosphere.

An examination of various sources of CO$_2$ emission revealed that more than 33% of global CO$_2$ emissions are from coal-fired power plants, which represent the largest stationary source of CO$_2$.[3] The direct capture of CO$_2$ from the highly concentrated and large-volume CO$_2$ stationary source is technically feasible and could be cost-effective for sequestrating CO$_2$. Depending on operating conditions and the type of coal burned, CO$_2$ concentration in the power plant flue gas varies from 10 to 15%, NO from 1500 to 2500 ppm, and SO$_2$ from 500 to 2000 ppm.[4] NO is removed by selective catalytic reduction, while SO$_2$ is captured by the wet lime scrubber, and CO$_2$ is vented to the atmosphere.[5,6]

The available approaches for CO$_2$ capture and separation include the absorption of CO$_2$ in aqueous amines, membrane separation, and adsorption on solid sorbents.[7−18] The absorption of CO$_2$ is carried out in a packed column where the CO$_2$ stream is injected at the bottom of the column while the aqueous amine (R$_1$R$_2$NH) is sprayed from the top of the column at 40 °C. CO$_2$ is absorbed in the aqueous amines to form carbamates and bicarbonates by the following reactions:

$$2R_1R_2NH + CO_2 \leftrightarrow$$
$$R_1R_2NH^+ + R_1R_2NCOO^- \text{ (carbamate)} \quad (1)$$

$$R_1R_2NH + H_2O + CO_2 \leftrightarrow$$
$$R_1R_2NH_2^+ + HCO_3^- \text{ (bicarbonate)} \quad (2)$$

In the absence of water, 1 mole of CO$_2$ reacts with 2 moles of amine to form carbamate by reaction 1; in the presence of water,

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1 mole of CO_2 reacts with 1 mole of amine to form bicarbonate by reaction 2.[7,13,19,20] The CO_2-containing aqueous amine is regenerated by striping at about 110 °C.

The membrane process for CO_2 separation involves the use of either polymer membranes or amine-modified inorganic oxide membranes.[8,21] The membrane process is based on the high permeability of CO_2 through the membrane compared to those of other gases. The membrane process is efficient in separating CO_2 from the gas stream with a small volumetric flow rate and a low CO_2 concentration.[8] As the amount (i.e., flux) of CO_2 required for permeating through the membrane increases, the membrane efficiency for the CO_2 separation decreases and the rate of membrane degradation accelerates because of the presence of contaminants in the feed stream.[8,21,22]

Solid sorbents based on amine-treated polymers have been used for years to capture CO_2 from closed environments, such as space shuttles and submarines, containing less than 1% CO_2.[13,23] A feed stream containing CO_2 is pumped through a packed bed of solid sorbent; CO_2 adsorbs on the sorbent by interaction with the amine functional groups.[24] The sorbent is regenerated by temperature-swing adsorption or pressure-swing adsorption or a combination of both processes.[13]

The current aqueous amine and membrane technologies are cost-effective for the separation of CO_2 from natural gas in the liquefaction process and ammonia synthesis process because of the high value of end products.[25,26] These current technologies, when applied for CO_2 capture from coal-fired power plants, increase the cost of electricity by more than 70%.[3] The cost of CO_2 sequestration can be reduced if an effective CO_2 capture sorbent is developed which has (i) a high CO_2 adsorption capacity ($>1000 \mu$mol/g), (ii) a long-term regeneration capacity in a power plant flue gas environment, and (iii) a low energy requirement for regeneration compared to the large amount of energy required for the aqueous amine process.[27]

Our previous study has shown that amine-grafted mesoporous silica has one of the highest CO_2 capture capacities under flowing (i.e, dynamic) conditions at 20−60 °C compared to those of other solid sorbents reported in the literature.[7,9,11,13,27,28] Other low-temperature solid sorbents including activated carbons, carbon nanotubes, and zeolites have shown CO_2 adsorption capacity at room or low temperatures.[29−34] Because of the physisorption nature of CO_2 adsorbed on these solid materials,

a slight increase in temperature can cause a significant decrease in CO_2 sorption capacity. Thus, these materials will not be effective and reliable for CO_2 capture under practical conditions where temperature fluctuation occurs. The key issues that need to be addressed for the development of an effective solid amine sorbent for CO_2 capture include the following:

• The effect of the nature of amine and adsorbed CO_2 species on the CO_2 adsorption capacity of the sorbent

• The effect of SO_2 on the CO_2 adsorption capacity of a solid amine sorbent

• The thermal stability and long-term CO_2 adsorption/regeneration capacity

The objectives of this paper are (i) to investigate the nature of adsorbed CO_2 species on the amine-grafted SBA-15 sorbent and a commercial polymer amine-based sorbent, (ii) to evaluate the SO_2 capture capacity of the amine-grafted SBA-15 sorbent and its effect on CO_2 adsorption capacity, and (iii) to determine the thermal stability of the sorbent. SBA-15 was used as the support because of its high hydrothermal stability as well as its large pores and high surface area for amine grafting. CO_2 and SO_2 adsorption and desorption were studied by a transient technique and temperature-programmed desorption with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) coupled with mass spectrometry (MS). The thermal stability of the sorbents is studied by temperature-programmed degradation with DRIFTS and MS.

Experimental Section

Preparation of SBA-15 and the Amine-Grafted SBA-15 Sorbent. SBA-15 was prepared by using TEOS (tetraethyl orthosilicate) as a silica precursor, Pluronic P123 ($PEO_{20}PPO_{70}PEO_{20}$, triblock copolymer) as a template, 1,3,5-trimethylbenzene as an expander, and HCl for the pH control. The specific steps for the preparation of SBA-15 are described elsewhere.[9,35]

APTS-SBA-15 [i.e., SBA-15 grafted with γ-(aminopropyl)-triethoxysilane] was prepared by impregnating 5.4 mL of an APTS/toluene solution onto 1 g of SBA-15 (the volumetric ratio of APTS to toluene is 1:3.35). The impregnated sample was heated at 150 °C for 20 h in a vacuum oven (150 mm of Hg) to obtain APTS-SBA-15. The commercial sorbent SA9-T, which is an amine immobilized on a polymer support and which has been utilized in CO_2 capture from closed habitats, was used as a reference for comparison.[13,23,36]

Experimental Apparatus. The experimental setup shown in Figure 1 consists of (i) a gas manifold which includes a four-port valve, a six-port valve, and a number of mass flow controllers; (ii) a DRIFTS reactor filled with 30 mg of the sorbent followed by a tubular reactor filled with 300 mg of the sorbent; and (iii) a mass spectrometer for effluent analysis. The tubular reactor was packed with an additional amount of sorbent in line with the DRIFTS reactor to achieve a sufficient change in the concentration of adsorbing gases in the effluent for the analysis by a Pfeiffer QMS 200 quadrupole mass spectrometer (MS). The surface-adsorbed species during adsorption, desorption, and decomposition were monitored by the DRIFTS reactor (Spectra-Tech) placed inside a Nicolet 560 FT-IR bench.

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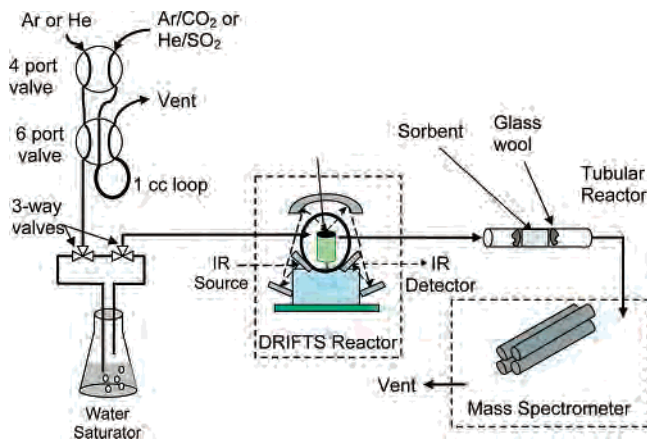
Figure 1. Experimental setup for CO_2 and SO_2 adsorption/desorption study.

Adsorption. The adsorption of CO_2 was carried out by switching the inlet flow from an inert gas stream (Ar) to the adsorbing gas stream (10% CO_2 in Ar) using a four-port valve. The four-port valve allows a smooth switch from one flow stream to another without causing a pressure disturbance to the inlet flow stream. Upon saturation of the sorbent with the adsorbing gas, the inlet stream was switched back to the inert gas stream. The inert gas stream was bubbled through a D_2O saturator at room temperature corresponding to 4% D_2O in the gas streams during adsorption, desorption, and decomposition. D_2O was used to trace the role of water during CO_2 adsorption. The SO_2 adsorption was carried out in a similar way with 2% SO_2/4% H_2O in He.

Temperature-Programmed Desorption. The sorbent-containing adsorbed CO_2 was regenerated via temperature-programmed desorption (TPD) by heating the DRIFTS and tubular reactors simultaneously from room temperature to 120 °C in the Ar stream at a rate of 10 °C/min. The CO_2 concentration profile during TPD was monitored by the MS, and the amount of CO_2 was quantified by calibrating the CO_2 ($m/e = 44$) response on the MS. The calibration factor was obtained by injecting 1 mL of CO_2 gas in a flowing Ar stream using the six-port valve and calculating the area corresponding to the amount of CO_2 injected. SO_2 TPD was carried out in a similar way, and the calibration factor was obtained by injecting 1 mL of SO_2 in a flowing He stream and monitoring the SO_2 ($m/e = 64$) response on the MS.

Thermal Stability (Temperature-Programmed Degradation) Studies. The thermal stability of the sorbent was studied by heating the DRIFTS and tubular reactors from 30 °to 500 °C at a rate of 10 °C/min in the presence of air. The surface of the sorbent during decomposition of the amines was monitored by DRIFTS, and the effluent of the reactors was simultaneously monitored by MS for the possible decomposition products.

IR spectra in this work are reported in two ways: DRIFTS single-beam and DRIFTS absorbance. The single-beam (i.e., background spectra) spectrum of the sorbent contains the characteristics of the source and the sample placed in the path of the IR beam and resembles a transmission spectrum. The DRIFTS absorbance spectra are obtained by using the background spectrum of the sorbent pretreated in a He flow. The absorbance is given by $A = -\log(I/I_0)$, where I and I_0 are spectra and background IR intensities, respectively.

Results and Discussion

Characterization of Sorbent. The DRIFTS single-beam spectra of APTS-SBA-15 and SA9-T are shown in Figure 2. APTS-SBA-15 shows asymmetric and symmetric N−H stretches at 3358 and 3300 cm^{-1} and asymmetric and symmetric C−H stretches at 2946 and 2827 cm^{-1}, respectively.[9,27] The N−H and C−H band region on APTS-SBA-15 is overlapped by a broad water band between 2000 and 3600 due to hydrogen
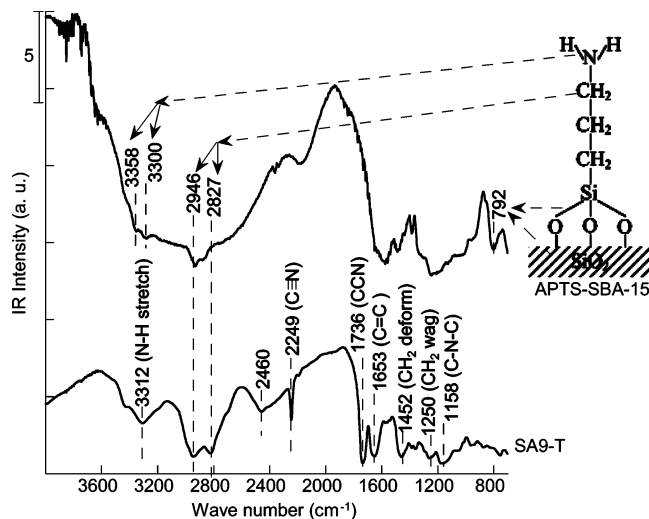
Figure 2. DRIFTS single-beam spectra of amine-grafted APTS-SBA-15 sample and commercial sample SA9-T.
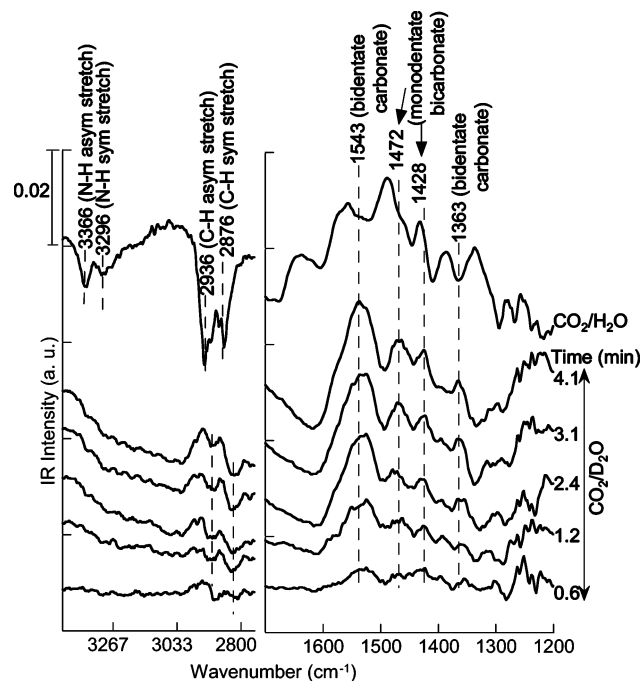
Figure 3. DRIFTS absorbance spectra during CO_2 adsorption on APTS-SBA-15 in the presence of D_2O.

bonding of the molecular water present on the SBA-15 surface.[37] The SA9-T spectrum shows only one mode of N−H stretching vibration at 3312 cm^{-1}, suggesting the presence of a secondary amine. The IR band at 1158 cm^{-1} for C−N−C further confirms the presence of a secondary amine structure on a polymer support.[38] The intense IR bands for C−H, CH_2, and C=C are from the hydrocarbon chain of amines and the polymer support. The absence of the broad band of hydrogen bonding on the SA9-T surface reveals the hydrophobic nature of the supporting polymer.

CO_2 Adsorption and TPD Studies on APTS-SBA-15. Figure 3 shows the DRIFTS absorbance spectra during CO_2 adsorption on APTS-SBA-15 in the presence of D_2O. The

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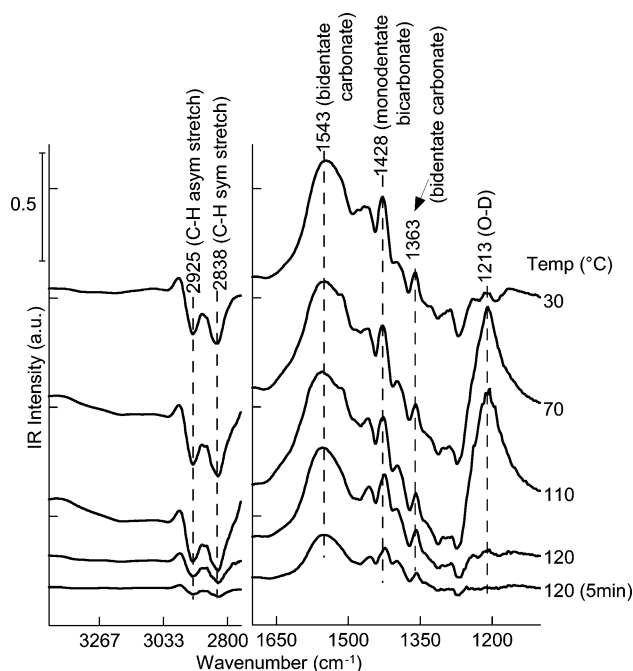**Table 1. Proposed Carbonate and Bicarbonate Structures Formed by CO₂ Adsorbed on APTS-SBA-15**

Bidentate carbonate	Monodentate bicarbonate
1543, 1363 cm⁻¹	1472, 1428 cm⁻¹

exposure of APTS-SBA-15 to CO_2 produced bidentate carbonate species at 1543 and 1363 cm^{-1} and monodentate bicarbonate species at 1472 and 1428 cm^{-1}.[9] The increase in the carbonates and bicarbonates intensities was accompanied by a decrease in the C−H bands at 2936 and 2876 cm^{-1}.

A comparison of the carbonate and bicarbonate species produced on the surface of the sorbent in the presence of H_2O (top spectra) and in the presence of D_2O shows an isotopic shift in their vibrational frequencies. The proposed structures of carbonate and bicarbonate species are shown in Table 1. The D atoms from D_2O, which are associated with the amino group and the bicarbonate group, cause an isotopic shift in the carbonate and bicarbonate vibrational frequency. An isotopic shift caused by an isotope on a neighboring atom or a remote atom is termed as a secondary isotopic shift.[39,40] In the proposed carbonate structure (as shown in Table 1), the D atom is present on the amino group $-CH_2-(NH_2D^+)$ and, hence, shows a secondary isotopic shift in the bidentate carbonate $[-CH_2-(NH_2D^+)]_2CO_3^{2-}$ structure. The shift in the frequencies of carbonates and bicarbonates in the presence of H_2O and D_2O suggest that water does play a role during CO_2 adsorption on amine-based sorbents.

Figures 4 and 5 show the DRIFTS absorbance spectra of adsorbed CO_2 and the MS intensity profile of CO_2 during TPD, respectively. The spectrum at 30 °C shows a significant decrease in C−H band intensity compared to that in Figure 3, which is due to the prolonged exposure of the sorbent to the adsorbing stream. The decrease in the C−H IR band intensity is consistent with our previous studies and is a result of a decrease in the $(\partial\mu/\partial R)^2$ term for the IR absorbance of C−H bonds due to the formation of bulky carbonates and bicarbonates on the surface.[9,41] The intensity of the infrared band is a function of the change in dipole moment (μ) with respect to the internal coordinate (R_i; $i = x, y, z$).

The increase in the temperature led to a decrease in adsorbed carbonate and bicarbonate species at 1543, 1363, and 1428 cm^{-1} and an increase in the C−H vibrational frequency at 2925 and 2838 cm^{-1}. The increase in C−H stretching vibrations is due to the decrease in the surface density of the carbonate and bicarbonate species. Desorption of the carbonate and bicarbonate species led to the formation of gas-phase CO_2 as observed from

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Figure 4. DRIFTS absorbance spectra of adsorbed CO_2 on APTS-SBA-15 during a TPD study with a heating rate of 10 °C/min in flowing Ar/D_2O (4% D_2O).
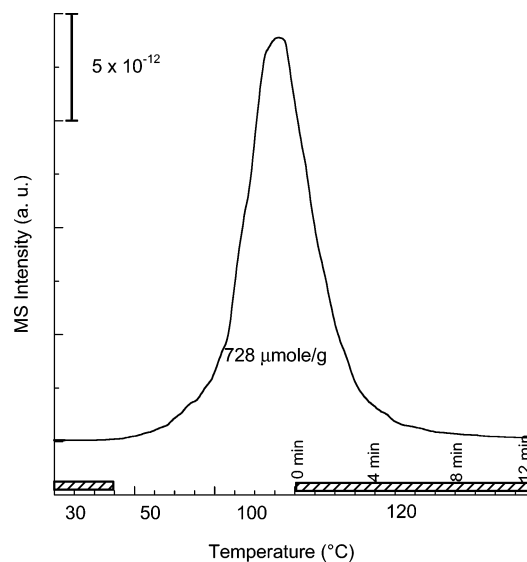
Figure 5. MS intensity profile of CO_2 ($m/e = 44$) during TPD of APTS-SBA-15.
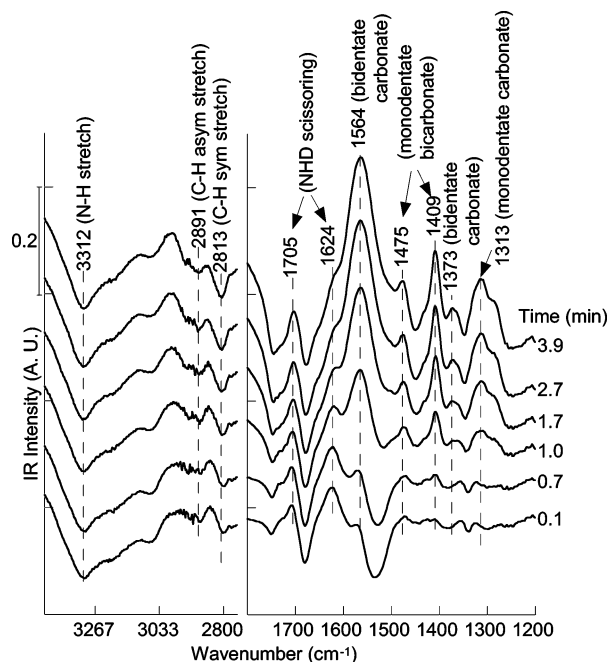
the MS intensity for CO_2, shown in Figure 5. The CO_2 adsorption capacity of APTS-SBA-15 was calculated to be 728 μmol/g of sorbent at a desorption temperature of 120 °C from the MS TPD profile of CO_2. The presence of IR bands for carbonate and bicarbonate species on the spectrum at 120 °C (5 min, see the bottom spectrum of Figure 4) reveals that not all of the CO_2 is desorbed from the surface and a higher desorption temperature is required to remove the residual CO_2. From the degradation study, it was revealed that all of the CO_2 is desorbed at a temperature of 150 °C.

CO_2 Adsorption and TPD Studies on SA9-T. Figure 6 shows DRIFTS absorbance spectra during CO_2 adsorption on SA9-T in the presence of D_2O. Before exposure to CO_2, the sample was exposed to an Ar/D_2O stream. The exposure of SA9-T to D_2O led to the formation of IR bands at 1624 and 1705 cm^{-1}, which could be due to NHD scissoring modes.[38]

**Figure 6.** DRIFTS absorbance spectra during CO_2 adsorption on SA9-T in the presence of D_2O.

The exposure of SA9-T to a CO_2 stream produced prominent IR bands at 1564 and 1373 cm^{-1} for bidentate carbonate, 1475 and 1409 cm^{-1} for monodentate bicarbonate, and 1313 cm^{-1} for monodentate carbonate.[9,27] The IR intensity of the adsorbed carbonate and bicarbonate species increased with the increase in the CO_2 exposure time. The formation of carbonates and bicarbonates led to a decrease in N−H and C−H band intensities similar to that observed for APTS-SBA-15. The shift in the frequency for adsorbed carbonate and bicarbonate species on SA9-T (Figure 6) compared to that of the species on APTS-SBA-15 (Figure 4) is due to the difference in the interaction between CO_2 and the secondary and primary amine species grafted on these sorbents.

Figures 7 and 8 show DRIFTS absorbance spectra and the MS intensity of CO_2 during a TPD study of SA9-T, respectively. The increase in the temperature led to an initial increase in the bands at 1624 and 1564 cm^{-1}, which eventually decreased and completely disappeared shortly after reaching 120 °C. The enhancement of these bands at higher temperatures might be due to the isotopic exchange of D_2O and NH_2 groups. The bands at 1409 and 1313 cm^{-1} for adsorbed carbonates decreased with an increase in temperature and disappeared above a temperature of 70 °C. The MS intensity of CO_2 in Figure 8 shows the desorption peak intensity at 70 °C, a shoulder at 100 °C, and almost all of the CO_2 desorbed when the temperature of the sorbent reached 120 °C. The two desorption peaks (a peak and a shoulder) indicate the presence of two different adsorbed species with different binding energies. The monodentate carbonate and bicarbonates have lower binding energies and desorb at 70 °C, while the bidentate carbonate species desorb at a temperature above 100 °C. These observations are consistent with adsorbed CO_2 species on diamine-grafted SBA-15.[27] The CO_2 adsorption capacity of SA9-T was calculated to be 440 μmol/g of sorbent.

SO_2 Adsorption and TPD Studies on APTS-SBA-15. The DRIFTS IR spectra during 2% SO_2/He adsorption in the presence of H_2O are shown in Figure 9. The adsorption of SO_2 on APTS-SBA-15 led to an increase in IR bands at 1108, 1200, 1250, 1342, 1533, and 1633 cm^{-1} and a decrease in IR bands
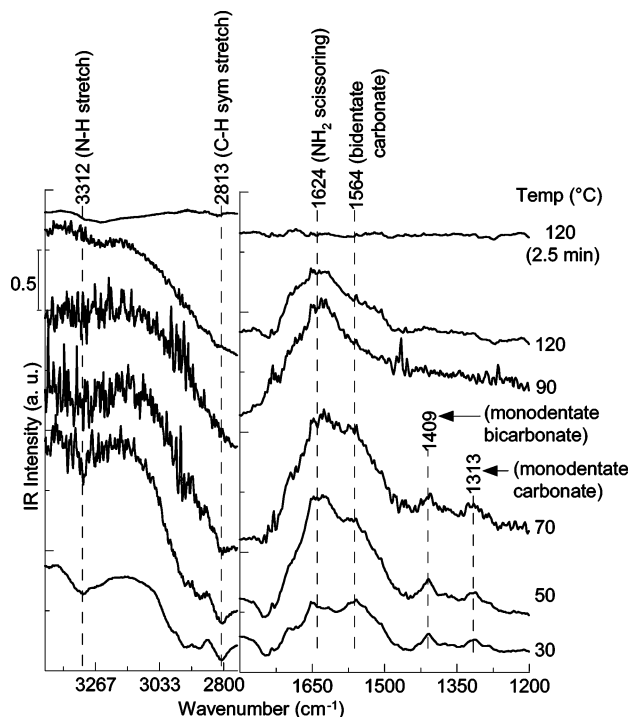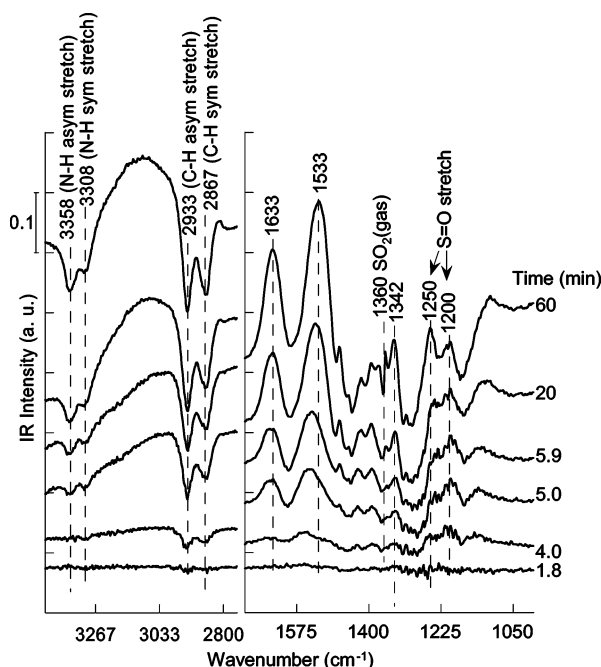

Figure 7. DRIFTS absorbance spectra of adsorbed CO_2 on SA9-T during a TPD study with a heating rate of 10 °C/min in flowing Ar/D_2O (4% D_2O).
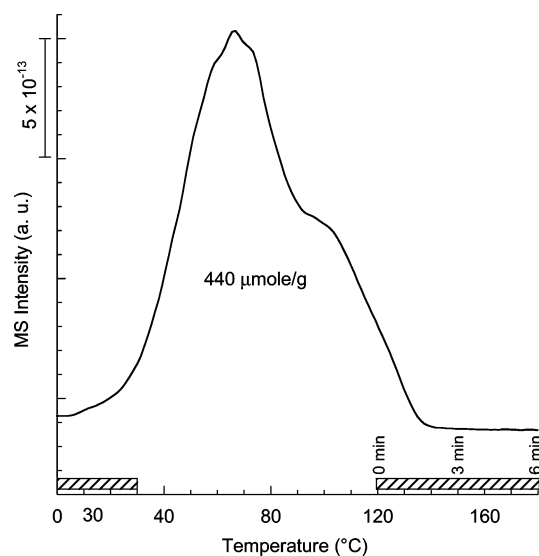

Figure 8. MS intensity profile of CO_2 ($m/e = 44$) during TPD of SA9-T.

at 2867, 2993, 3308, and 3358 cm^{-1}. The bands at 1108, 1200, and 1250 are assigned to the S=O stretching vibrations of sulfates and sulfites formed on the surface of APTS-SBA-15.[41] The sharp decrease in the IR bands at 3308 and 3358 cm^{-1} for N−H symmetric and asymmetric stretches and that in the IR bands at 2867 and 2933 cm^{-1} for C−H symmetric and asymmetric stretches are due to the reaction of surface amine with SO_2 and the formation of sulfates and sulfites on the surface. The bands at 1533 and 1633 cm^{-1} can be attributed to N−O stretching vibrations as there are no IR bands in this region that can be attributed to H−S or S−O vibrations.[38, 41]

Figure 9 also shows that both high and low concentrations of SO_2, exhibiting the 1360 cm^{-1} band, produced the same type of adsorbed species on APTS-SBA-15, as evidenced by the observation of the adsorbed species giving the same IR bands
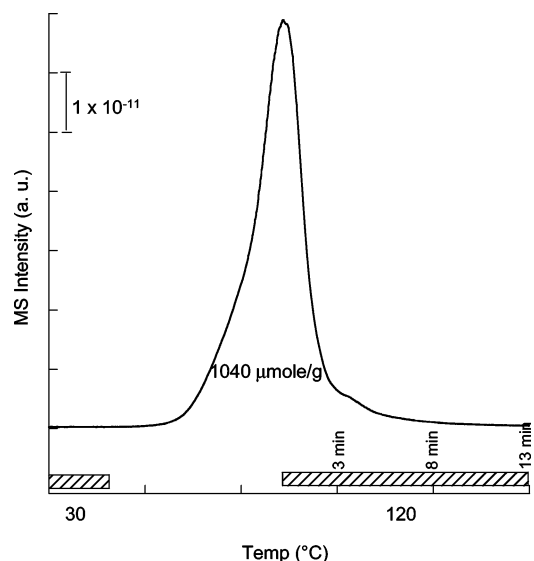
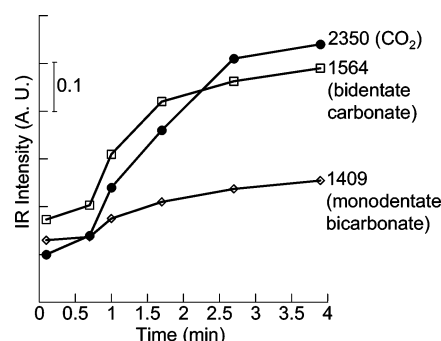**Figure 9.** DRIFTS absorbance spectra during SO₂ adsorption on APTS-SBA-15 in the presence of H₂O.
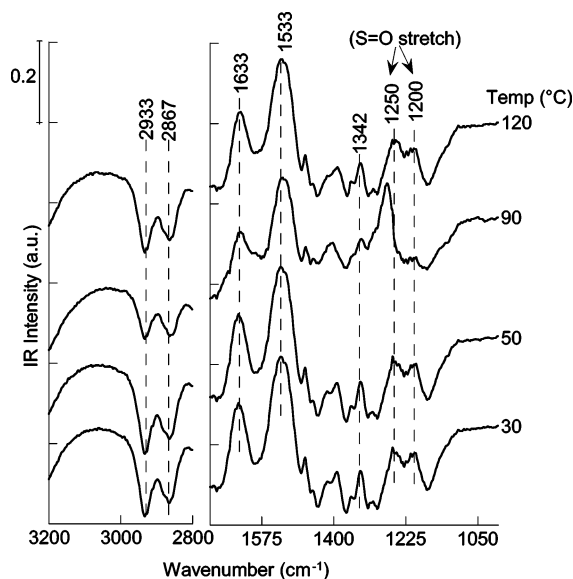
Figure 10. DRIFTS absorbance spectra of adsorbed SO₂ on APTS-SBA-15 during a TPD study with a heating rate of 10 °C/min in flowing He/H₂O (4% H₂O).


Figure 11. MS intensity profile of SO₂ ($m/e = 64$) during TPD of APTS-SBA-15.

Figure 12. IR peak intensity of species during CO₂ adsorption on SA9-T.

in the spectra taken at 5.9 and 60 min. This observation suggests that variation in the SO₂ concentration does not affect the interaction between SO₂ and the grafted amine on SBA-15, allowing extrapolation of the high SO₂ concentration results to the practical flue gas condition of which the SO₂ concentration is 1 order of magnitude lower than that of SO₂ used in this study.

Figures 10 and 11 show DRIFTS IR spectra and the MS intensity during a TPD study of the adsorbed SO₂ on APTS-SBA-15 in the presence of H₂O. The increase in temperature led to a minor decrease in all of the sulfate/sulfite IR bands, while there was no significant change in the N−H and C−H stretching bands, indicating a strong irreversible interaction between SO₂ and the surface amine species. The amount of SO₂ desorbed from the surface was calculated to be more than 1040 μmol/g of sorbent from the MS intensity profile of SO₂ ($m/e =$

64) during the TPD. The SO₂ desorbed from the surface only after the sorbent temperature reached 60 °C, and the peak desorption temperature was at 120 °C. The visual analysis of the sample after the TPD study showed the change in the color of sample from white to yellow, which might be due to the formation of irreversible sulfates/sulfites on the surface. CO₂ adsorption on this sample after regeneration from the SO₂ study showed a negligible CO₂ adsorption capacity, revealing that no free surface amine species were available for bonding with CO₂.

Comparison of APTS-SBA-15 and SA9-T. The growth of IR peak intensities versus time was plotted during CO₂ adsorption on APTS-SBA-15 and SA9-T and during SO₂ adsorption on APTS-SBA-15. A typical plot of the IR peak intensities of carbonate and bicarbonate species on APTS-SBA-15 is shown in Figure 12. The slope of the intensity profile versus the time profile reflects the rate of formation of these adsorbed species and the rate of adsorption of the adsorbing gases. The peak height of adsorbed carbonates/bicarbonates and sulfates/sulfites increased with the increase in exposure time of the sorbent to CO₂ and SO₂, respectively. The rate of formation of carbonate species was higher than that of bicarbonates for APTS-SBA-15 and SA9-T. The relative rate of formation of carbonates/bicarbonates on both the sorbents was about the same. However, the relative rate of SO₂ adsorption as sulfate/sulfite species was much lower than that of CO₂ adsorption as carbonate/bicarbonate, reflecting a higher activation energy for the formation of stable sulfate/sulfite species. These species require the use of a significantly higher temper-
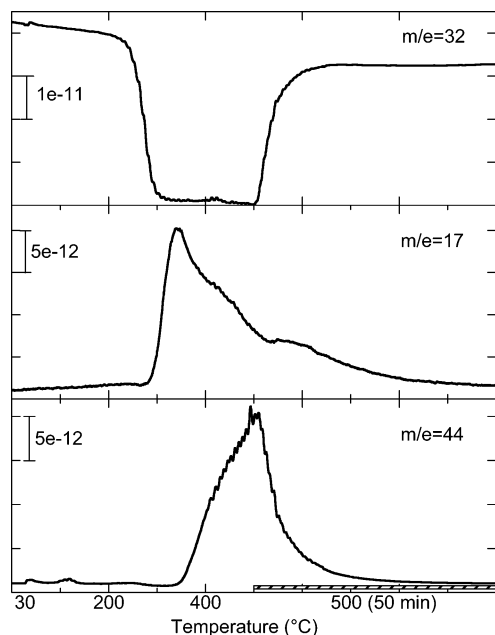
Figure 13. MS intensity profiles during the degradation of APTS-SBA-15 in the presence of air.

ature to decompose than that for the adsorbed carbonates and bicarbonates.

Thermal Stability (Temperature-Programmed Degradation) Study of APTS-SBA-15. Figure 13 shows the temperature-programmed degradation study of fresh APTS-SBA-15 in the presence of air. The ratio of air to He was maintained at 1:2 with a total flow rate of 30 mL/min. The MS profile during degradation shows that the increase in temperature over 270 °C led to the consumption of oxygen from air and the simultaneous decomposition of surface NH_2 groups in the form of NH_3 ($m/e = 17$). The oxidation of surface hydrocarbons to CO_2 began at 325 °C. It is interesting to note that the peak of the MS profile of NH_3 is at a temperature of 325 °C where the oxidation of hydrocarbons begins. This observation suggests that the surface NH groups are decomposed followed by the oxidation of the hydrocarbon backbone of the silane. A similar study with APTS on an MCM-48 support was carried out by Huang et al., and the amine species were stable up to 225 °C.[11] Another study by Zheng et al. with ethylenediamine supported on SBA-15 showed an amine loss at 300 °C.[7] The amine species on the SBA-15 support in this study are stable up to 250 °C, and any further increase in temperature would lead to the decomposition of the amine above 270 °C and the combustion of hydrocarbon species above 325 °C.

The performance of APTS-SBA-15 as a CO_2 capture sorbent will be determined by the interaction of CO_2 and other key contaminants in the flue gas with the amine functional groups. The infrared study showed that CO_2 adsorbed as carbonates and bicarbonates in the presence of D_2O on APTS-SBA-15 and the commercial SA9-T sorbent. The adsorption of CO_2 led to a decrease in the IR intensity of C−H and N−H bands which was reversible during temperature-programmed desorption. The isotopic shift observed in the IR bands of carbonates and bicarbonates on the APTS-SBA-15 sorbent indicates that D_2O

plays a role in the CO_2 adsorption process. The desorption of CO_2 from the secondary amine of the SA9-T sorbent at a lower temperature compared to that of the APTS-SBA-15 sorbent suggests a stronger interaction between the primary amine functional groups on APTS-SBA-15 and CO_2. This is consistent with the heat of reaction data for primary and secondary amines in aqueous solutions with CO_2.[42]

The thermal stability studies define the range for the operation of this sorbent. The APTS-SBA-15 sorbent is stable up to 250 °C; CO_2 may be adsorbed at 40 °C and can be regenerated at 120 °C. Although one of our previous studies has shown that the APTS-SBA-15 sorbent does not lose its CO_2 adsorption capacity with three regeneration cycles, a long-term stability study is required to determine the long-term stability of these sorbents.[9] The adsorption of SO_2 led to the formation of sulfates and sulfites and an irreversible decrease in the C−H and N−H IR band intensities. The regenerated APTS-SBA-15 sorbent after SO_2 adsorption showed a negligible CO_2 adsorption capacity. These results clearly indicate that amine-based CO_2 absorption columns have to be placed downstream of a SO_2 scrubber. SO_2 in the flue gas will react irreversibly with the sorbent, and hence, a provision for a CO_2 adsorber bypass should be made in case of a failure of the SO_2 scrubber.

Conclusions

The APTS-grafted SBA-15 shows a high CO_2 adsorption capacity in the presence of water, and the difference in the vibrational frequencies of adsorbed CO_2 species in the presence of D_2O and H_2O reveals that water plays an important role during CO_2 adsorption. The CO_2 adsorbs on the surface as carbonates and bicarbonates on APTS-SBA-15 and the commercial sample SA9-T. The rate of formation of carbonate species was higher than that of bicarbonate species during CO_2 adsorption on both sorbents. Temperature-programmed desorption studies revealed that the nature of the amine on the surface affects the regeneration temperature of the sorbent. The SA9-T sample with a secondary amine can be regenerated at a lower temperature, while the APTS-SBA-15 requires a temperature above 120 °C for complete regeneration.

SO_2 adsorbs strongly on the APTS-SBA-15 sample, and the exact structure of the adsorbed SO_2 species remains to be determined. The rate of adsorption of SO_2 is slower than that of CO_2 on the APTS-SBA-15 sorbent. The solid amine sorbent shows a high SO_2 adsorption capacity, but it cannot be regenerated for further CO_2/SO_2 adsorption. Temperature-programmed degradation of APTS-SBA-15 revealed that the amine species are thermally stable up to 250 °C in the air and degrade above this temperature, while the combustion of the hydrocarbon chain begins at 325 °C.

(42) Chakma, A. *Energy Convers. Manage.* **1997**, *38* (Suppl., Proceedings of the Third International Conference on Carbon Dioxide Removal, 1996), S51−S56.