

In-Situ Infrared Study of CO₂ Adsorption on SBA-15 Grafted with γ -(Aminopropyl)triethoxysilane

Alex C. C. Chang,[†] Steven S. C. Chuang,^{*,†} McMahan Gray, and Yee Soong[‡]

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

Received August 12, 2002

CO₂ adsorption/desorption on SBA-15 grafted with γ -(aminopropyl)triethoxysilane (APTS) has been studied by infrared spectroscopy coupled with temperature-programmed desorption. SBA-15, a mesoporous silica material with a uniform pore size of 21 nm and a surface area of 200–230 m²/g, provides an OH functional group for grafting of γ -(aminopropyl)triethoxysilane. The amine-grafted SBA-15 adsorbed CO₂ as carbonates and bicarbonates with a total capacity of 200–400 μ mol/g. The heat of CO₂ desorption was determined to be 3.2–4.5 kJ/mol in the presence of H₂O and 6.6–11.0 kJ/mol in the absence of H₂O during temperature-programmed desorption. Repeated CO₂ adsorption/desorption CO₂ cycles shifted the desorption peak temperature downward and decreased the heat of CO₂ adsorption.

Introduction

Aqueous amine solutions have been widely used to separate CO₂ from gaseous streams in natural gas processing, coal gasification, and hydrogen production.^{1,2} The CO₂ separation process using aqueous amines involves absorption of CO₂ into an amine solution and the use of extensive energy for regeneration of amine solution. Although an amine solution is effective for CO₂ adsorption, it presents a corrosion problem to equipment and degrades through oxidation.² The solid sorbents have been used to remove CO₂ from air in enclosed habitable environments such as submarine and spacecraft.^{3–7} The solid sorbent offers a number of advantages: low energy requirement for sorbent regeneration and elimination of corrosion problems. However, these sorbents were not designed for large scale applications such as the removal of CO₂ from flue gas of coal-fired power plants.^{8,9}

Continuous increases in CO₂ emission and its link to global climate changes call for development of effective approaches to address the large stationary CO₂ emission sources, such as coal-fired power plants, which contribute to 36% of the anthropogenic CO₂ emission in the United States.¹⁰ Concentrating CO₂ from the flue gas stream (containing 10–15% CO₂) is the first step to sequester CO₂ emission from coal-fired power plants. Preliminary analysis has suggested that an economically feasible approach should cost less than \$10 to sequester a ton of CO₂ from stationary sources.¹¹ Development of an economic CO₂ separation process requires a highly efficient CO₂ sorbent. The sorbent must possess high CO₂-capture and long-term regeneration capacity at the level above 2000 μ mol/g with a small difference in adsorption and desorption temperatures in the flue gas environment. One potential approach to preparing such a sorbent is to graft CO₂ adsorption sites on the high surface area support.^{6,8,9}

The objective of this paper is to investigate the CO₂ adsorption/desorption process on mesoporous SBA-15 silica grafted with (aminopropyl)triethoxysilane (APTS). The NH₂-functional group in APTS could provide CO₂ adsorption sites; silane offers the linkage to bind APTS to the SBA-15 surface; and SBA-15 possesses a high surface area for grafting APTS, a large uniform pore size to facilitate CO₂ diffusion inside of the pore, and a wall thickness of 35–65 Å which provides a stable structure under hydrothermal condition. CO₂ adsorption/desorption studies show that SBA-15 containing APTS can adsorb up to 400 μ mol/g of CO₂. CO₂ was found to adsorb on the amine sites in the form of

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

[†] The University of Akron.

[‡] National Energy Technology Laboratory, U.S. Department of Energy.

(1) Blauwhoff, P. M. M.; Versteeg, G. F.; Van Swaaij, W. P. M. *Chem. Eng. Sci.* **1984**, *39*, 207–225.

(2) Tontiwachwuthikul, P.; Meisen, A.; Lim, C. J. *J. Chem. Eng. Data* **1991**, *36*, 130–133.

(3) Veawab, A.; Tontiwachwuthikul, P.; Chakma, A. *Ind. Eng. Chem. Res.* **1999**, *38*, 3917–3924.

(4) Satyapal, S.; Filburn, T.; Trela, J.; Strange, J. *Energy Fuels* **2001**, *15*, 250–255.

(5) Birbara, P. J.; Filburn, T. P.; Nalette, T. A. U.S. Patent 5,876,488, 1999.

(6) Birbara, P. J.; Nalette, T. A. U.S. Patent 5,492,683, 1996.

(7) Soong, Y.; Gray, M. L.; Siriwardane, R. V.; Champagne, K. J.; Stevens, R. W., Jr.; Toochinda, P.; Chuang, S. S. C. *Prepr. Symp.—Am. Chem. Soc., Div. Fuel Chem.* **2001**, *46*, 285–286.

(8) Leal, O.; Bolivar, C.; Ovalles, C.; Garcia, J. J.; Espidel, Y. *Inorg. Chim. Acta* **1995**, *240*, 183–189.

(9) Tepper, F.; Udaycak, R. J.; Vancheri, F. J.; Ball, K. E. *Aerosol Med.* **1969**, *40*, 297–300.

(10) Stringer, J. C. Opportunity for Carbon Control in the Electrical Power Industry. In *Carbon Management: Implication for R&D in the Chemical Sciences and Technology*; National Research Council, 2001; p 60.

(11) *Carbon Sequestration Research and Development*; FC/FE/US DOE: Washington, DC, 1999.

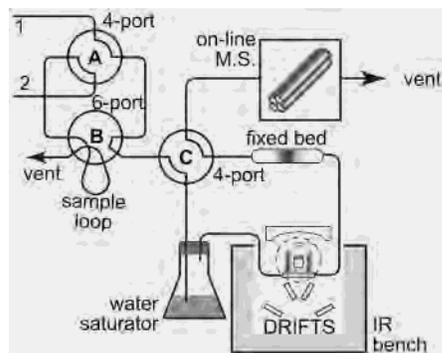


Figure 1. Experimental apparatus.

carbonate and bicarbonate. These species desorb as CO₂, giving peak temperature in the range of 353–393 K during temperature-programmed desorption. Since the SBA-15 used in this study has a surface area of 200–230 m²/g, further increase in the surface area of SBA-15 could bring the CO₂ capture capacity up to a level of economical CO₂ separation.

Experimental Section

Preparation of Mesoporous Material: SBA-15. SBA-15 was prepared by using TEOS (tetraethyl orthosilicate) as a silica precursor, Pluronic P123 (PEO₂₀PPO₇₀PEO₂₀, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol)) as a template, TMB (1,2,3-trimethylbenzene) as an expander, and HCl to control pH.^{12,13} 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 of TMB at 308 K for 2 h, (3) adding 8.5 g of TEOS into the resultant homogeneous solution and stirring it at 308 K for 22 h, (4) aging the solution without stirring at 393 K for 24 h, and (5) calcining the resultant solid particles from filtering the aging solution in flowing air at 3 K/min to 773 K and holding it 773 K for 6 h.^{12–14} The surface area of the untreated SBA-15 and sorbent was determined by N₂ BET measurement at 77 K; the pore size was determined to be 21 nm by SAXS (i.e., small-angle X-ray scattering analysis).

Preparation and Characterization of the Sorbent. SBA-15 grafted with γ -(aminopropyl)triethoxysilane (APTS) was prepared by impregnating an APTS/toluene solution into SBA-15.¹⁵ The impregnated sample was heated at 423 K for 20 h in a vacuum oven to obtain APTS–SBA-15. APTS–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 K α X-rays.

Adsorption and Desorption Studies. The experimental apparatus in Figure 1 includes a flow control manifold, a H₂O saturator, a high temperature/pressure diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) cell with a Fourier transform infrared spectrometer, a fixed bed reactor, and a mass spectrometer (MS). Flow control manifold consists of (1) a 4-port (A) valve for switching the flow from He to He/H₂O, (2) a 6-port (B) valve for the injection of a known amount of CO₂ for calibration, and (3) a 4-port (C) valve for bringing

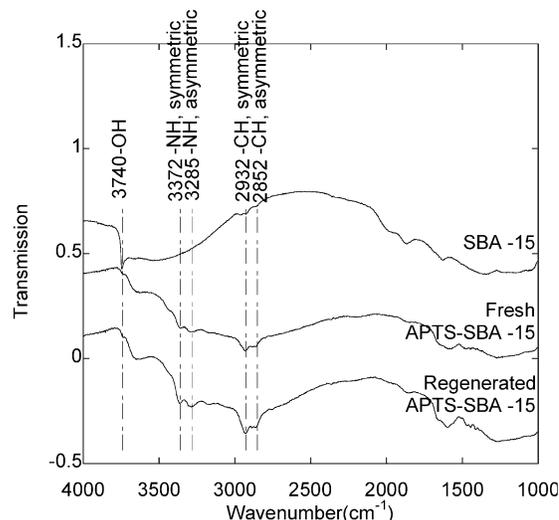


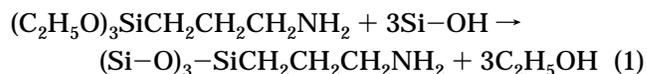
Figure 2. Transmission infrared spectra of SBA-15, fresh APTS–SBA-15, and regenerated APTS–SBA-15.

water vapor into the inlet flow via a saturator. The details of the experimental apparatus have been reported elsewhere.¹⁶

Each adsorption study employed 20 mg of APTS–SBA-15 for the DRIFTS cell and 180 mg for the fixed bed. Sorbent (200 mg) was exposed to a 30 mL/min He flow at 298 K for 1 h to obtain a stable MS baseline for CO₂ and IR background spectra. Valve C was then switched to allow He to flow through the H₂O saturator for adding moisture (23.4 mmHg water vapor) into the inlet He flow. Adsorption of CO₂ on APTS–SBA-15 was initiated by a step switch from the He/H₂O stream to the CO₂/He/H₂O stream with valve A. The flow rate of both streams was kept at 30 mL/min to obtain a step change in CO₂ concentration. The CO₂ stream entering the IR cell contains 4% of CO₂ and 23.4 mmHg of water vapor balanced with helium. Adsorbed CO₂ was removed by temperature-programmed desorption (TPD) in the flow of He or He/H₂O at 30 mL/min at a heating rate of 10 K/min from 298 to 393 K and holding at 393 K for 1 h. He/H₂O flow contains 23.4 mmHg of water vapor. The effluent composition of the DRIFTS/fixed bed reactor was determined by MS; infrared spectra of the adsorbed species during TPD were collected by DRIFTS. Calibration of CO₂ *m/e* = 44 intensity was carried out by injecting 1 mL of 4% CO₂ into 30 mL/min He stream with valve B. The CO₂ MS calibration factor was obtained by dividing the area under the CO₂ MS curve by the number of moles of CO₂ injected.

Results and Discussion

Figure 2 shows the transmission infrared spectra of SBA-15, fresh and regenerated APTS–SBA-15. The regenerated APTS–SBA-15 underwent 3 cycles of CO₂ adsorption/desorption. The decrease in the OH intensity as well as the presence of the N–H bands and the C–H bands suggests that APTS has been grafted on the surface of SBA-15 through the following reaction:



where Si–OH represents the hydroxyl group on the SBA-15 surface. The grafting reaction depleted the majority of the available OH on the SBA-15 surface. Fresh and regenerated APTS–SBA-15 show nearly

(12) Stucky, G. D.; Chmelka, B. F.; Zhao, D.; Melosh, N.; Huo, Q.; Feng, J.; Yang, P.; Pine, D.; Margolese, D.; Lukens, W., Jr.; Fredrickson, G. H.; Schmidt-Winkel, P. *PCT Int. Appl.* 9937705, 1999.

(13) Morey, M. S.; O'Brien, S.; Schwarz, S.; Stucky, G. D. *Chem. Mater.* 2000, 12, 898–911.

(14) Luan, Z.; Maes, E. M.; Heide, P. A. W. v. d.; Zhao, D.; Czernuszewicz, R. S.; Kevan, L. *Chem. Mater.* 1999, 11, 3680–3686.

(15) Vrancken, K. C.; Possemiers, K.; Van Der Voort, P.; Vansant, E. F. *Colloids Surf., A* 1995, 98, 235–241.

(16) Chuang, S. S. C.; Brundage, M. A.; Balakos, M. W.; Srinivas, G. *Appl. Spectrosc.* 1995, 98, 235–241.

Table 1. XPS and BET Results

sample	C/Si	peak intensity ratio			BET surface area (m ² /gram)
		N/Si	O/Si	Si/Si	
untreated SBA-15		0		1.00	203.6
fresh sample (APTS-SBA-15)	1.50	0.34	1.94	1.00	229.2
He TPD regenerated sample	1.35	0.32	1.97	1.00	196.3
H ₂ O/He TPD regenerated sample	1.32	0.33	2.00	1.00	203.0

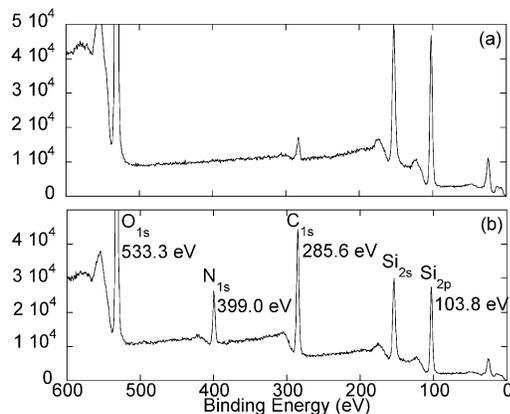


Figure 3. X-ray photoelectron spectra of (a) SBA-15, and (b) fresh APTS-SBA-15.

identical IR intensity for the N-H and C-H bands, indicating that the grafted APTS stays intact during CO₂ adsorption/desorption cycles.

Figure 3, parts a and b, show X-ray photoelectron spectra of the untreated SBA-15 and fresh APTS-SBA-15, respectively. APTS-SBA-15 exhibited a C_{1s} peak and a N_{1s} peak in addition to Si_{2s}, Si_{2p}, and O_{1s} peaks, suggesting the presence of APTS on the SBA-15 surface. Si_{2s} and Si_{2p} peaks on SBA-15 and APTS-SBA-15 gave the same binding energy, indicating that Si from silane is indistinguishable from Si on the SBA-15. The weak carbon peak on SBA-15 in Figure 3a can be attributed to the residual organic on the SBA-15. The XPS intensity ratio listed in Table 1 shows that the N/Si ratio remained at the same level after repeated adsorption/TPD of CO₂ in either He or H₂O/He environment. The XPS results further confirmed that grafted APTS stayed intact on the SBA-15 surface during CO₂ adsorption/desorption cycles.

Figure 4 shows IR spectra of CO₂ adsorption on the fresh APTS-SBA-15. Exposure of APTS-SBA-15 to the He/H₂O stream did not result in any obvious changes in the IR spectra. Flowing the CO₂ over APTS-SBA-15 produced bidentate bicarbonate at 1634 cm⁻¹, bidentate carbonate at 1575 and 1390 cm⁻¹, monodentate bicarbonate at 1493 and 1432 cm⁻¹, and monodentate carbonate at 1337 cm⁻¹.¹⁷⁻²⁰ The structure of these adsorbed species is shown in Table I. Bands in the 1595, 1440, and 1330 cm⁻¹ regions may be associated with carbamic acid. However, the bond energy of carbamic acid's C-N bond is at the level of 300 kJ/mol, which is significantly higher than the heat of CO₂ adsorption on

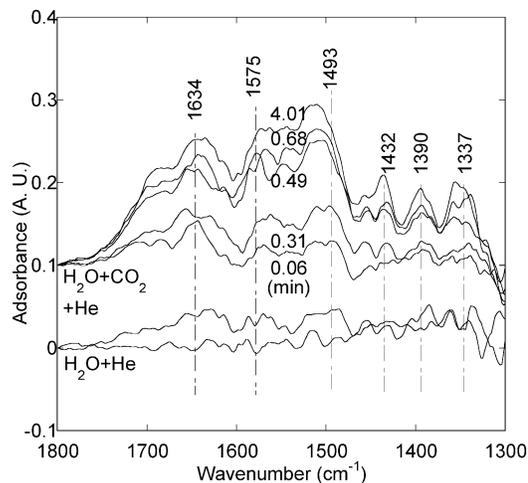
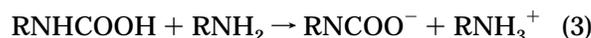


Figure 4. Infrared spectra of CO₂ adsorption on the fresh APTS-SBA-15.

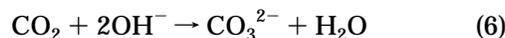
APTS-SBA-15. Carbamic acid (RNHCOOH) has been suggested as a precursor for the formation of R-NH₃⁺ species which involves the following steps:



where R is an alkyl group.



CO₂ can also react with H₂O and OH⁻ to produce HCO₃⁻ and CO₃²⁻:²¹



The interaction of HCO₃⁻ and CO₃²⁻ with (Si-O)₃-SiCH₂CH₂CH₂NH₃⁺ could lead to the formation of adsorbed carbonate and bicarbonate, listed in Table 2. The CO₂ MS intensity profile, taken simultaneously with the infrared spectra of CO₂ adsorption (Figure 4), is shown in Figure 5. The CO₂ MS intensity profile reflects the relative CO₂ concentration versus time at the effluent of the fixed bed reactor during CO₂ adsorption. The sharp decrease in CO₂ MS intensity profile in Figure 5 and the growth of IR bands for adsorbed CO₂ species in Figure 4 reflect the rapid CO₂ adsorption on the APTS-SBA-15. The CO₂ MS intensity was returned to the initial level upon saturation of the adsorption sites with CO₂. The area of the resulting "well" in the CO₂ MS profile corresponds to the amount of CO₂ adsorbed. The fresh APTS-SBA-15 adsorbed about 30%

(17) Pokrovski, K.; Jung, K. T.; Bell, A. T. *Langmuir* **2001**, *17*, 4297-4303.

(18) Khanna, R. K.; Moore, M. H. *Spectrochim. Acta, Part A* **1999**, *55A*, 961-967.

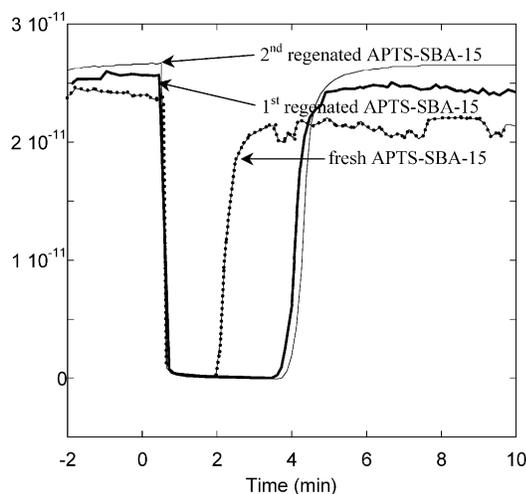
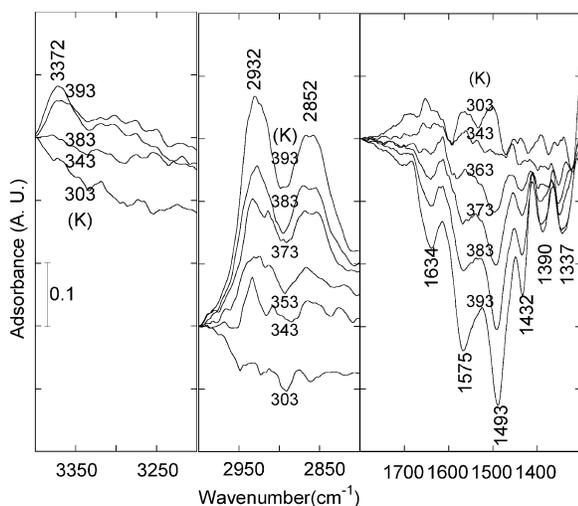
(19) Little, L. H. *Infrared spectra of adsorbed species*; Academic Press: London, New York, 1966.

(20) Davydov, A. A. *Infrared spectroscopy of adsorbed species on the surface of transition metal oxides*; John Wiley & Sons: Chichester; New York, 1990.

(21) Danckwerts, P. V. *Chem. Eng. Sci.* **1979**, *34*, 443-446.

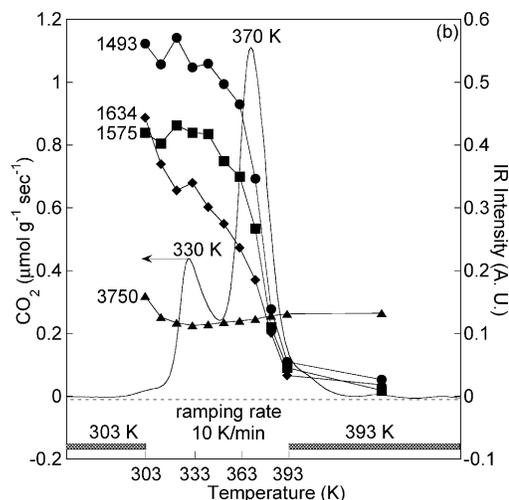
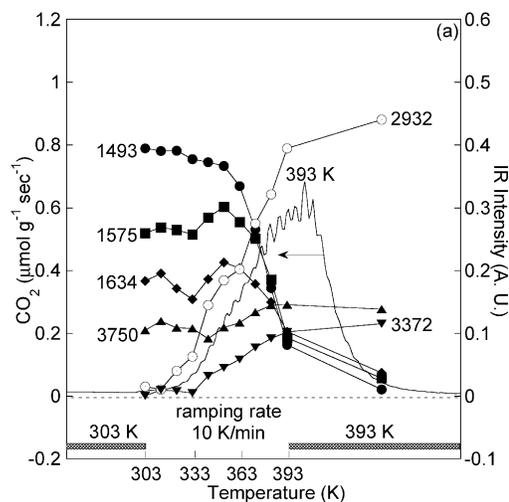
Table 2. Proposed Adsorbed Species on the APTS–SBA-15 Surface

Monodentate Carbonate	Bidentate Carbonate	Monodentate Bicarbonate	Bidentate Bicarbonate	Carbamic Acid
1337 cm ⁻¹	1575, 1390 cm ⁻¹	1493, 1432 cm ⁻¹	1634 cm ⁻¹	1595, 1441, 1330 cm ⁻¹

**Figure 5.** CO₂ MS intensity profiles during CO₂ adsorption.**Figure 6.** Infrared spectra of adsorbed CO₂ during CO₂ TPD in He flow over fresh APTS–SBA-15.

less CO₂ than the regenerated one. This is due to partial saturation of APTS–SBA-15 with ambient CO₂ prior to CO₂ adsorption study.

Figure 6 shows infrared spectra of adsorbed CO₂ species during temperature-programming desorption in the absence of H₂O over the fresh APTS–SBA-15. Increasing temperature led to a decrease in intensity of adsorbed CO₂ species, i.e., bidentate bicarbonate at 1634 cm⁻¹, bidentate carbonate at 1575 and 1390 cm⁻¹,¹⁷ monodentate bicarbonate at 1493 and 1432 cm⁻¹, and monodentate carbonate at 1337 cm⁻¹. The

**Figure 7.** CO₂ desorption rate and IR intensity profiles for adsorbed CO₂ species during TPD in He flow over (a) fresh APTS–SBA-15, and (b) regenerated APTS–SBA-15.

adsorbed species exhibited negative bands as the temperature increased above 353 K. The negative band is due to using the fresh APTS–SBA-15 as the background spectrum which consists of spectra of APTS–SBA-15 and adsorbed CO₂ species from ambient prior to CO₂ adsorption study.

Decreases in IR intensity of adsorbed CO₂ species is accompanied by an increase in the C–H intensity at 2852 and 2932 cm⁻¹ and the N–H intensity at 3372 cm⁻¹ in Figure 6 as well as evolution of CO₂ in Figure 7a. IR intensity profiles in Figure 7a were plotted from the normalized IR intensity of the selected bands in

Table 3. CO₂ Desorption Characteristics

	TPD in He flow			TPD in He/H ₂ O flow		
	amount of CO ₂ des. (μmol/g)	peak temp. (K)	heat of CO ₂ desorption (kJ/mol)	amount of CO ₂ des. (μmol/g)	peak temp. (K)	Heat of CO ₂ desorption (kJ/mol)
Fresh	227	393	6.67	308	375	4.54
1st Reg.	331	393	10.96	357	368	3.90
2nd Reg.	247	370	7.04	406	356	3.22

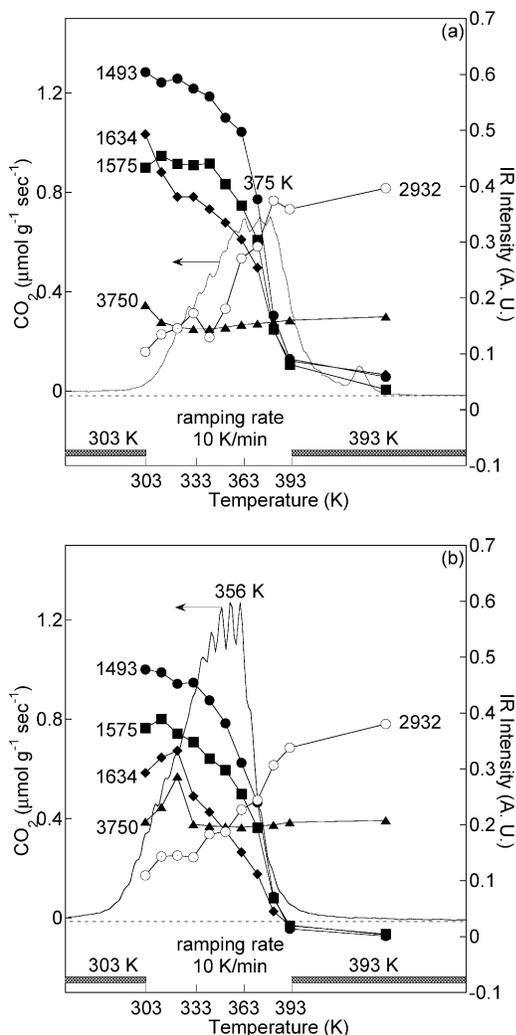
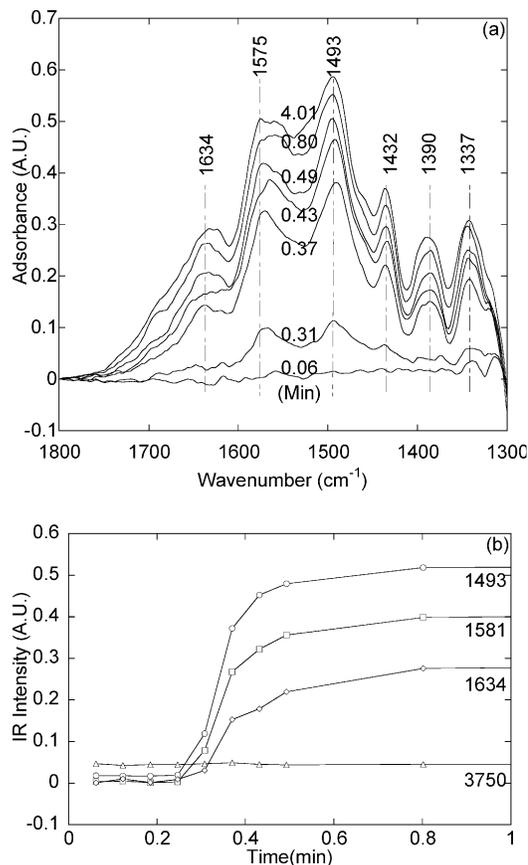
**Figure 8.** CO₂ desorption rate and IR intensity profiles for adsorbed CO₂ species during TPD in He flow over (a) fresh APTS-SBA-15, and (b) regenerated APTS-SBA-15.

Figure 6. The normalization of the IR intensity was achieved by dividing the magnitude of change in band intensity by the maximum intensity change of the band. Comparison of the IR intensity profiles of the adsorbed CO₂ species with the CO₂ evolution rate profile in Figure 7a revealed that the monodentate bicarbonate band at 1493 cm⁻¹ and the bidentate carbonate band at 1575 cm⁻¹ were the major contributors to the CO₂ peak at 393 K. In contrast to the CO₂ desorption behavior on the fresh APTS-SBA-15, the regenerated APTS-SBA-15 in Figure 7b exhibited a rapid decrease in IR intensity of the bidentate bicarbonate band at 1634 cm⁻¹ which resulted in the first CO₂ desorption peak at 330 K. The rest of the CO₂ adsorbed species desorbed, giving a peak at 370 K.

The area under the CO₂ TPD profile corresponds to the amount of desorbed CO₂ from the APTS-SBA-15

**Figure 9.** (a) Infrared spectra of CO₂ adsorption on the regenerated APTS-SBA-15 and (b) IR intensity profile for adsorbed CO₂ species.

in Table 3. Regenerated APTS-SBA-15 by TPD in He/H₂O flow exhibited a higher CO₂ adsorption/desorption capacity than those regenerated by TPD in only He. The enhanced CO₂ adsorption capacity on the sorbent regenerated by TPD in He/H₂O can be understood by the fact that H₂O is needed to react with CO₂ to produce carbonate and bicarbonate as shown in reactions 4–6. The CO₂ adsorption capability (μmol-CO₂/g-sorbent) of the APTS-SBA-15 reported in Table 3 is about one-third of that of the commercial solid-polymer amine sorbents.^{5,6} Further increase in the surface area of SBA-15 from 200 to 230 to 800–1000 m²/g will allow increasing the number of grafted APTS to bring the CO₂ sorption capacity above that of commercial solid-amine sorbents.

The CO₂ desorption behavior during the TPD in He/H₂O is shown in Figure 8a and 8b. CO₂ desorption yielded only one peak. Comparison of the CO₂ TPD profile in Figure 8a and b shows that repeated adsorption/desorption of CO₂ shifted the peak temperature from 375 to 356 K and increased the amount of CO₂ adsorbed/desorbed (Table 3). The peak temperature and half width of the peak can be used to obtain the heat of CO₂ desorption.²² The downward shift in peak temperature reflects a decrease in the heat of CO₂ adsorption. The decrease in heat of CO₂ adsorption may be related to the type of adsorbed species. There are more bidentate carbonate species on the twice (2nd)-regenerated

(22) Krishnamurthy, R.; Chuang, S. S. C. *Thermochim. Acta* **1995**, *262*, 215–225.

APTS–SBA-15 than the sample regenerated once. Figure 9 shows the CO₂ adsorption behavior on the singly(1st)-regenerated APTS–SBA-15; the corresponding CO₂ desorption profile is shown in Figure 8b. The adsorbed CO₂ species on the singly regenerated APTS–SBA-15 led to IR bands at the same wavenumber as those on the fresh APTS–SBA-15 in Figure 4. The major difference among these solid amine sorbents is that they adsorbed different amount of bidentate carbonate and bicarbonate.

Regeneration of the C–H stretch bands at 2852 and 2932 cm⁻¹ and N–H at 3372 cm⁻¹ during CO₂ desorption from the fresh APTS–SBA-15 in Figure 6 has also been observed for all of the APTS–SBA-15 sorbent. The rise in the C–H and N–H intensity corresponds to the decrease in carbonate and bicarbonate intensity in Figures 7 and 8, indicating the reversibility of the interaction between grafted RNH₃⁺ and carbonate/bicarbonate. These interactions appear to be weakened in the presence of H₂O, as evidenced by the lower CO₂ desorption peak temperature during TPD in He/H₂O flow. The heat of CO₂ desorption decreased from 6 to 10 kJ/mol during TPD in He flow to 3–4 kJ/mol during TPD in He/H₂O flow. Close examination of the OH bands at 3750 cm⁻¹ and CO₂ desorption profile shows that there is no relationship between intensity of the OH group and heat of CO₂ desorption.

Conclusion

The present study provides a novel approach for the preparation of high efficiency solid CO₂ sorbents. APTS

provides silane to bind amine on the SBA-15 surface. The large uniform pore size of SBA-15 facilitates CO₂ diffusion inside of the pore, allowing rapid CO₂ adsorption on the surface amine sites. SBA-15 containing APTS can adsorb up to 400 μmol/g of CO₂. CO₂ was found to adsorb on the amine sites in the form of carbonate and bicarbonate. These species desorb as CO₂, giving peak temperature between 356 and 393 K. The adsorption capacity can be further enhanced by regeneration of the sorbent in He/H₂O flow. Repeated CO₂ adsorption and sorbent regeneration studies showed that amine grafted on SBA-15 exhibited hydrothermal stability and allowed repeated use without loss of CO₂ capture capacity. Since the SBA-15 used in this study has a surface area of 200–230 m²/g, further increase in the surface area of SBA-15 could bring the CO₂ sorption capacity up to the level for economic separation of CO₂ from the flue gas.

Acknowledgment. Alex C. C. Chang was supported by the University of Akron postdoctoral fellowship. The authors thank Dr. John Baltrus at NETL-US DOE for XPS analysis, Mr. Rajesh Khatri for preparation of SBA-15, and Mr. Pisanu Toochinda and Mr. Robert W. Stevens, Jr., for assistance in revision of the manuscript. This work was partially supported by the University/NETL Student Partnership Program.

EF020176H