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Amine-Grafted MCM-48 and Silica Xerogel as Superior Sorbents for Acidic Gas Removal from Natural Gas

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In an effort to develop selective solid sorbents for acidic gas (CO_2 and H_2S) removal from natural gas mixtures, we synthesized amine-surface-modified silica xerogel and MCM-48 materials. With large amounts of basic amine groups on the surface, the sorbents are able to selectively bind the acidic gases CO_2 and H_2S . High adsorption capacities and adsorption rates were obtained for both gases. The adsorption–desorption isotherms of the gases and thermogravimetric analysis of the sorbents showed that these sorbents can be regenerated completely under mild conditions such as those used in pressure swing or temperature swing adsorption processes. We have also investigated the effect of moisture on the adsorption of CO_2 and H_2S by TPD-MS and infrared spectroscopy. The results indicated that the presence of water vapor doubled the amount of CO_2 adsorbed and barely affected the H_2S adsorption.

Introduction

The “sweetening” of crude natural gas, i.e., the removal of acidic gases such as carbon dioxide and hydrogen sulfide, is an important process in the natural gas industry. Conventionally, this sweetening is accomplished by gas–liquid absorption–stripping processes using aqueous solutions of alkanolamines.^{1–5} The most commonly used amines include monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). Though a mature technology being applied extensively today, this gas absorption process is highly energy-intensive for regeneration of the solvents and is also plagued by corrosion problems.

Membrane separation is a relatively new technology for gas purification. The advantages include higher energy efficiency, ease of process scale-up, great operational flexibility, and environmental safety. However, such processes are also subjected to limitations, such as possibly higher CH_4 losses and high costs.⁵

As the demand for natural gas has increased in recent years, the need has arisen for the development of a highly efficient method for acid gas removal with lower economic costs. The development of regenerable solid sorbents that have high selectivities for acidic gases and high adsorption capacities is a potential alternative for natural gas purification because such materials are more environmentally benign and easier to handle (solid), and most importantly, they can be regenerated under mild conditions and are thus more energy-efficient.

Although considerable research effort has been devoted to the sweetening of sour natural gases, few studies have been reported on the performance of solid materials as sorbents for CO_2 and H_2S .^{6–9} In principle, many solid materials are potential sorbents for carbon dioxide and hydrogen sulfide, but a review of the recent

literature shows that most of the sorbents studied to date for natural gas cleanup have had at least one major problem that prevents their industrial use. For example, activated carbon and zeolites have been the most widely used solid sorption materials.^{10–13} However, the industrial application of these materials as acidic gas adsorbents is limited because of the low selectivity toward acidic gases for activated carbon and a strong water inhibition effect for zeolite materials.

There has been widespread interest in developing high-surface-area solid sorbents and catalysts, in particular because of their exceptionally high surface areas, which allow binding to occur at a large number of highly dispersed active sites within the framework.^{14–23} Silica and ordered mesoporous silica are ideal solid supports for the active functions because of their large surface areas and/or well-defined pore structures. More importantly, the hydroxyl groups on their surfaces are important for many surface phenomena, such as gas adsorption, surface modification, wetting, and so on.^{24–27} Because of the high concentrations of surface silanol groups (SiOH), silica and ordered mesoporous silicas such as MCM-41 and MCM-48 are the most widely used materials for surface modification, i.e., grafting of functional groups onto the pore walls of the silica via silylation reactions between the surface silanol groups and the grafting material.²⁸

The idea of grafting functional groups onto the pore walls of silica and ordered mesoporous silica is a known strategy for the design of promising new adsorbents and catalysts. For instance, Lasperas et al.¹⁷ and Angeletti et al.¹⁸ used amine-function-modified MCM-41 and silica gel as efficient and reusable heterogeneous catalyst for Knoevenagel condensation reactions. Burwell et al.²¹ reported selective chemisorption of sulfur dioxide on amine-modified silica gel. Leal et al.⁹ studied carbon dioxide adsorption on amine-surface-bonded silica gel, but amount of CO_2 adsorbed (0.3 mmol/g of sorbent at 1 atm CO_2) was far below the requirement for industrial application of the sorbents. To our knowledge, no

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literature report about acid gas H₂S adsorption on amine-surface-modified inorganic materials has yet been published.

In this paper, we first report the adsorption of CO₂ and H₂S on amine-surface-modified silica xerogels and MCM-48. The adsorption of the natural gas component CH₄ is also studied in comparison. Because a certain amount of water vapor is also present in natural gas mixtures, the effect of water vapor on the adsorption of the acidic gases is also studied. The results show that these two materials are excellent sorbents for selective removal of CO₂ and H₂S from natural gas. Moreover, water vapor exhibits a promoting role for CO₂ adsorption and does not affect H₂S adsorption, which makes the removal of water vapor from natural gas prior to acid gas treatment unnecessary.

Experimental Section

Preparation of Silica Xerogel and MCM-48. High-porosity silica xerogels were made from tetraethoxysilane (TEOS, 98%, from Aldrich), ethanol, water, HCl, and NH₄OH.²⁹ First, the TEOS stock solution was prepared by mixing TEOS, ethanol, water, and HCl in the molar ratio of 1:3:1:0.0007 under constant reflux for 1.5 h at 333 K. Ten milliliters of TEOS stock solution was gelled by adding 1 mL of 0.05 M NH₄OH. Gelation occurred in approximately 1 h at 310 K. After gelation, the sample was aged for 22 h at 310 K. The sample was then washed with excess ethanol twice at 310 K. Each washing cycle lasted for 24 h. Silica xerogels were obtained by degassing at 200 °C. The BET surface area of the prepared silica xerogel was 816 m²/g.

MCM-48 type silica sample was prepared by a room-temperature synthesis method that was developed by Schumacher and co-workers.³⁰ In a typical preparation, 24 mL of aqueous ammonia (32%, from Aldrich) was added to a mixture of 5.2 g of cetyltrimethyl ammonia bromide (from Aldrich), 240 g of water, and 100 mL of absolute ethanol (99.5%, from Aldrich) during constant stirring. Then, 6.8 g of tetraethoxysilane (TEOS, 98%, from Aldrich) was added, and the whole mixture was stirred at room temperature for 10 h. The white solid was recovered by filtration and washing with distilled water. The MCM-48 material was obtained after 550 °C calcination in air for 10 h. The BET surface area of the sample was 1389 m²/g.

Surface Modifications by Amine Functional Groups. Silica xerogel or MCM-48 were chosen for grafting because of their high surface areas and because they are known to have the highest densities of surface –OH groups.³⁰ Hence, commercial silica gels were not used.

The immobilization of amine functions on the silica surfaces was achieved by refluxing 1.0 g of silica (silica xerogel or MCM-48) with 50 mL of toluene (99.8%, from Aldrich) and 5.0 mL of 3-aminopropyltriethoxy-silane (99%, from Aldrich). The mixture was stirred and refluxed at 343 K for 18 h. The white 3-aminopropyl-functional silica xerogel and MCM-48 were washed repeatedly with toluene and pentane and then dried. Combined DTGA and weight-gain measurements allowed for a quantitative determination of amine groups on the surface. Coverages of about 1.7 and 2.3 mmol of –CH₂CH₂CH₂NH₂ per gram of sorbent were obtained for silica xerogel and MCM-48, respectively.

Sorption Studies. CO₂ and H₂S uptake curves and H₂S adsorption isotherms were measured using a

standard gravimetric method. A Shimadzu TGA-50 automatic recording microbalance was used. Helium (prepurified grade, Metro Welding Supply, 99.995%) was used as the carrier gas. The other gases used in the analysis were CO₂ (5% in helium, Matheson) and H₂S (1% in helium, Cryogenic Gases). Low-concentration H₂S was obtained by blending helium and 1% H₂S gas streams at controlled flow rates. The total flow rate was 250 mL/min. A 5-mg sample was used for each measurement. Calibrations for gas composition changes were made to accurately account for differences in buoyancy and friction losses.

CO₂ and CH₄ adsorption–desorption isotherms were measured using a Micromeritics ASAP 2010 instrument, which is a static volumetric type of apparatus. The isotherms were measured at room temperature. Nitrogen adsorption isotherms at 77 K, also measured with the Micromeritics ASAP 2010 instrument, were used for BET surface area determinations of the sorbents.

Characterizations of the Sorbents. XRD measurement of the MCM-48 sample was carried out with a Rigaku Rotaflex D/Max-C system with Cu Kα ($\lambda = 0.1543$ nm) radiation. The samples were loaded on a sample holder at a depth of 1 mm. XRD patterns were recorded in the range of $2\theta = 1$ –10°.

Temperature-programmed desorption (TPD) experiments were carried out in a fixed-bed quartz reactor with an inner diameter of 10 mm. The temperature was controlled by an Omega programmable temperature controller (CN-2010). First, CO₂ or H₂S adsorption was performed by exposing 0.5 g of sorbent to 5% CO₂ or 1% H₂S (plus 2% water vapor when used for studies on the effect of water) for 6 h. The temperature-programmed desorption (TPD) experiments were then performed by passing helium through the reactor and ramping the temperature from 25 to 120 °C at a rate of 5 °C/min. A magnetic-deflection-type mass spectrometer (AERO VAC, Vacuum Technology, Inc.) was used to monitor the effluent CO₂ or H₂S from the reactor.

Infrared spectroscopy was used to study the characteristic surface species of the silicas and the surface-modified materials. It was also used to study the CO₂ and H₂S adsorption on the amine-modified samples. The infrared spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer with a TGS detector. Self-supporting wafers of 1.3-cm diameter were prepared by pressing 15-mg samples and were loaded into an IR cell with BaF₂ windows. A background spectrum was recorded in flowing He and was subtracted from the sample spectra. In the experiments, the IR spectra were recorded by accumulating 100 scans at a spectral resolution of 2 cm^{–1}.

Results and Discussion

Characterizations of the Sorbents. The X-ray diffraction pattern of the MCM-48 sample is displayed in Figure 1. The XRD reflection peaks at $2\theta = 2.78$, 3.20, and 5.20° are well resolved and in good agreement with the reported patterns of MCM-48 materials.³¹

The FTIR spectrum of the MCM-48 sample is compared with that of the amine-modified material. As shown in Figure 2a, the sharp peak at 3743 cm^{–1} on the unmodified MCM-48 is attributed to the free hydroxyl groups on the surface.^{32,33} Silanol groups with hydrogen-bonding interactions were also observed at 3540 cm^{–1} (broad band). Shown in Figure 2b is the FTIR spectrum of the 3-aminopropyl-functionalized MCM-48

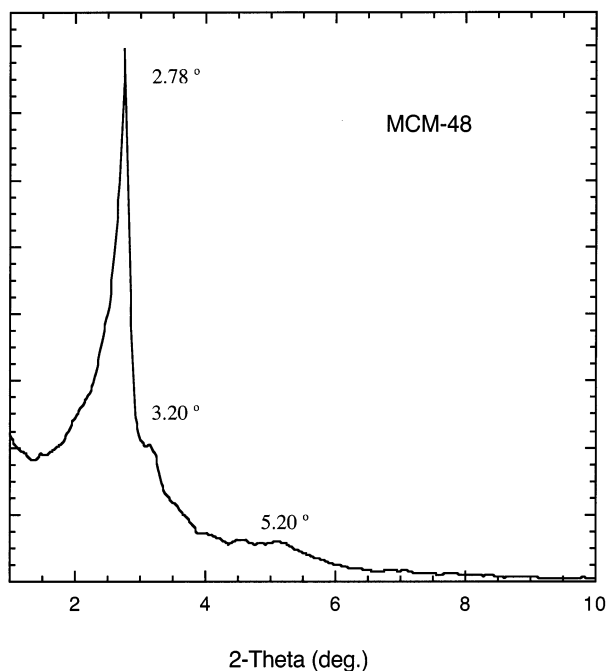


Figure 1. XRD pattern of MCM-48.

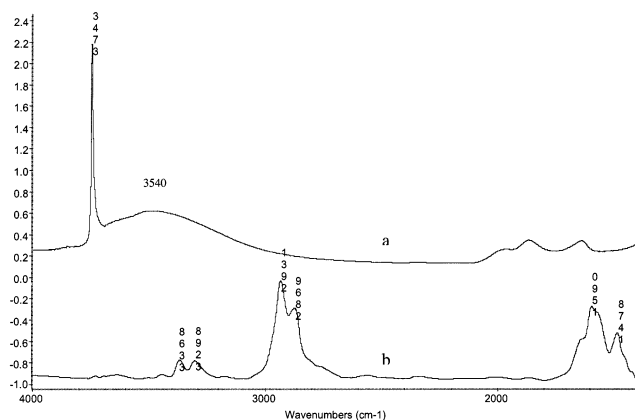


Figure 2. FTIR spectra of (a) MCM-48 and (b) amine-modified MCM-48 at room temperature.

sample. After the surface reactions with 3-aminopropyltriethoxy-silane, the IR bands of the surface hydroxyl groups vanished, indicating that all of the surface hydroxyl groups reacted with the aminopropyltriethoxy-silane. The new IR bands shown in Figure 2b are those attributed to the characteristic vibrations of NH_2 and CH_2 groups. The two IR bands at 3368 and 3298 cm^{-1} are due to the asymmetric and symmetric NH_2 stretchings. The band at 1590 cm^{-1} is attributed to the NH_2 scissoring vibration.^{15,17,34} The bands at 2931 and 2869 cm^{-1} are due to CH stretching in $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ groups. Similar results were observed for silica xerogel and amine-modified silica xerogel (not shown).

The thermal stability of the amine functional groups on MCM-48 was also investigated using infrared spectroscopy. Figure 3 shows the IR bands of the MCM-48 sample exposed to helium at 25–350 °C. The IR intensities of the characteristic amine bands start to decrease at 200 °C, but the amine group bands did not vanish until 350 °C. This indicates that the amine functional groups are strongly bonded to the silica substrate and that the sorbents do not begin to lose the amine component until 200 °C. As will be discussed later, the acid gases can desorb completely at 75 °C or below.

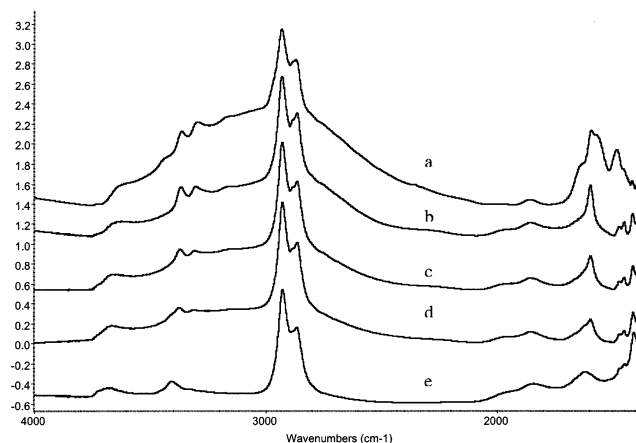


Figure 3. FTIR spectra of amine-modified MCM-48 at different temperatures, (a) 25, (b) 100, (c) 200, (d) 250, and (e) 350 °C.

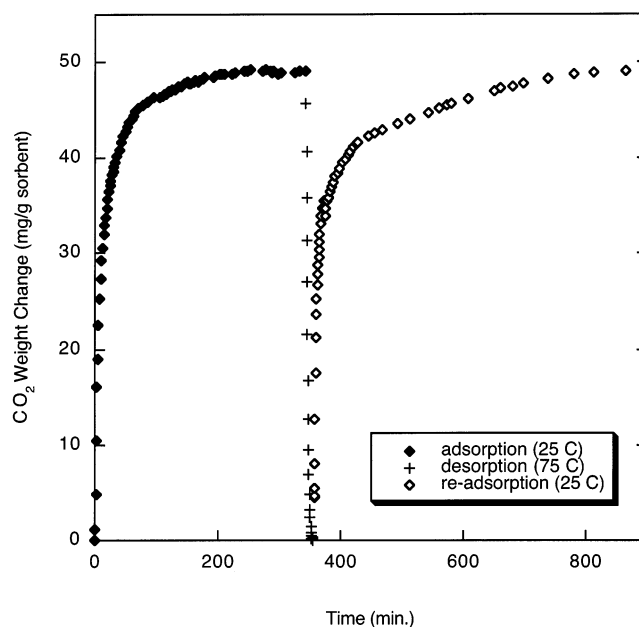


Figure 4. Cyclic CO_2 adsorption-desorption on amine-modified MCM-48.

Thus, it is safe to regenerate the sorbents by temperature swing operations.

Sorption Studies by TGA, Isotherm Measurements. The CO_2 uptake on the 3-aminopropyl-functionalized MCM-48 sample was measured by TGA, and the results are shown in Figure 4. When 5% CO_2 was passed through the sample, a rapid weight gain was observed. The total amount of CO_2 adsorbed at room temperature was 50 mg/g of sorbent, and 80% completion was accomplished in the first 30 min. This result shows the very large capacity and high adsorption rate of CO_2 on the sorbent. CO_2 adsorption was also investigated on the unmodified MCM-48 sample under the same conditions, and a much smaller amount of CO_2 was adsorbed (14 mg/g of sorbent, not shown). The results indicate that the amine-surface-modified MCM-48 has strong affinity to CO_2 because of the weak chemical interactions between the basic amine groups and CO_2 . Also displayed in Figure 4 is the complete adsorption-desorption-adsorption cycle of CO_2 . When the sample was heated in helium at 75 °C, CO_2 desorbed completely in 10 min. After being cooled to room temperature, the sample was used again for CO_2 adsorption under the same conditions. As can be seen from the figure, the CO_2

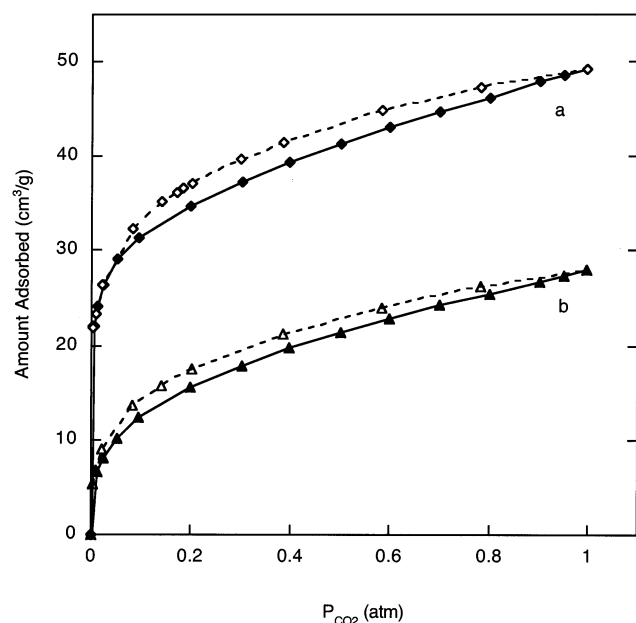


Figure 5. Adsorption-desorption isotherms of CO₂ on (a) amine-modified MCM-48 and (b) amine-modified silica xerogel at room temperature. Open symbols are for desorption; solid symbols are for adsorption.

adsorption performance of the used sample was almost the same as that of the fresh sample. These TGA results show that the sorption-desorption reactions of CO₂ are thermally reversible.

The adsorption isotherms of CO₂ on the amine-surface-modified MCM-48 and silica xerogels at 25 °C are plotted in Figure 5. For both sorbents, the amount of CO₂ adsorbed increased rapidly when the CO₂ partial pressure was increased from 0 to 0.1 atm. Then, the increase in CO₂ adsorption became gradual. At 1 atm, the amount of CO₂ adsorbed reached 50 cm³/g of sorbent on the amine-modified MCM-48 sample. This is equivalent to ca. 2.05 mmol/g of sorbent at STP, which is 7 times more than the amount reported in the literature for CO₂ adsorption on surface-modified silica gels.⁹ The high capacity and steep nature of the CO₂ isotherm on amine-modified MCM-48 make it a potentially suitable adsorbent to be used in industry for natural gas cleanup. At all pressures, the CO₂ adsorption on modified MCM-48 was roughly twice the amount adsorbed on the modified silica xerogel sorbents. This is probably due to the higher surface area of the MCM-48 samples. Also shown in Figure 5 are the desorption isotherms of CO₂ on both sorbents. The adsorption and desorption isotherms are very similar. This indicates that the adsorption of CO₂ on the amine-modified samples is reversible, so the adsorbed CO₂ can also be recovered by lowering the pressure.

H₂S is another type of acidic gas that needs to be removed from natural gas mixtures. We investigated H₂S adsorption on 3-aminopropyl-functionalized MCM-48 and silica xerogel. Figure 6 shows the TGA results of H₂S uptake on the modified MCM-48 sample. When 1000 ppm of H₂S was passed through the sample, 21 mg/g of sorbent was adsorbed in 90 min and 80% completion was obtained in the first 35 min. The high uptake rate and high adsorption capacity at low H₂S concentration indicate that the amine-modified sample is an ideal candidate for scavenging traces of H₂S in natural gas mixtures. The complete adsorption-desorption cycle of H₂S shown in Figure 6 is

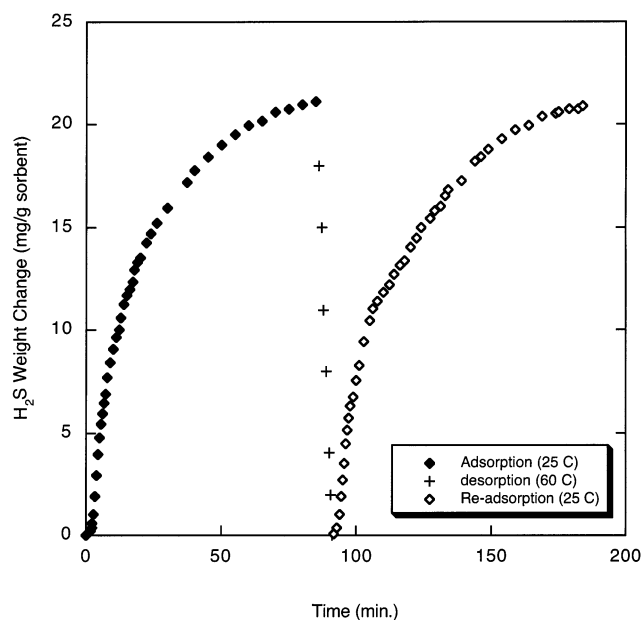


Figure 6. Cyclic H₂S adsorption-desorption on amine-modified MCM-48.

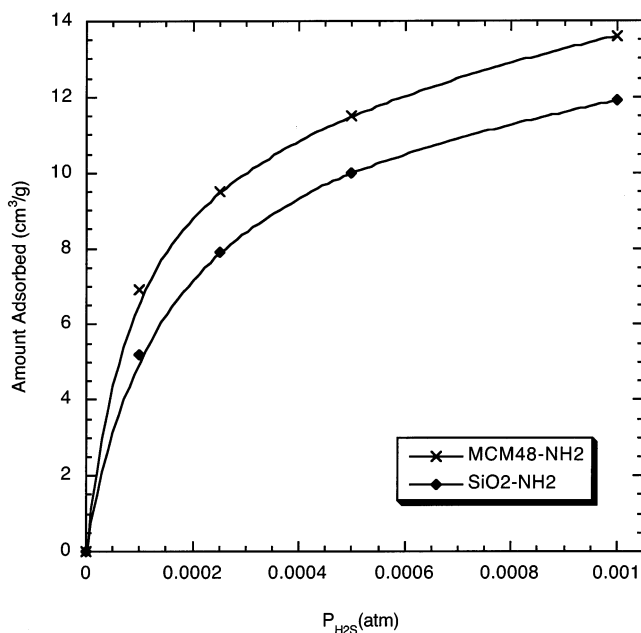


Figure 7. Adsorption isotherms of H₂S on amine-modified silicas at room temperature.

similar to that of CO₂ (Figure 4). H₂S desorbed completely at 60 °C in less than 8 min. The H₂S desorption temperature is lower than that of CO₂ (60 vs 75 °C) because of its weaker chemical interaction with the amine groups. As we know carbonate is a stronger acid than hydrogen sulfide and is therefore more tightly bonded by the basic amine functional groups on the surface. The performance of the regenerated sample also shows an adsorption performance similar to that of the fresh sample.

The adsorption isotherms of H₂S on the amine-modified samples are plotted in Figure 7. Because the amount of H₂S in natural gas mixtures is more than an order of magnitude less than the amount of CO₂, the isotherm measurements for H₂S were performed in much lower pressure range than those for CO₂, i.e., 0–0.001 atm. The adsorption isotherms indicate a high

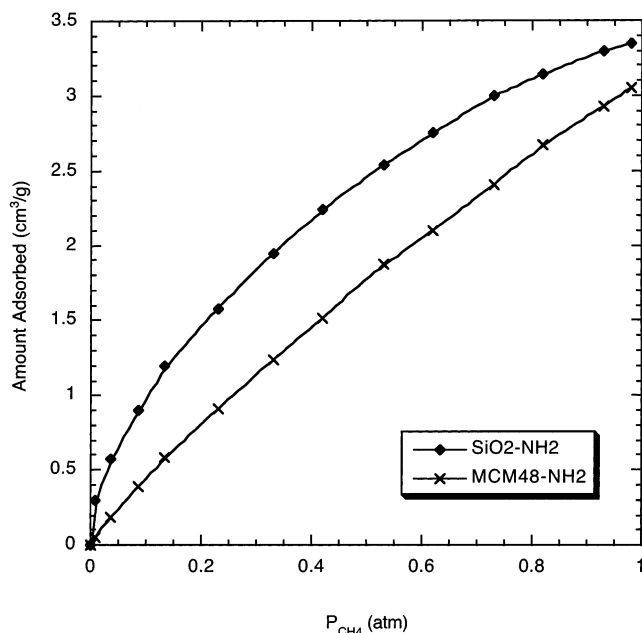


Figure 8. Adsorption isotherms of CH₄ on amine-modified silicas at room temperature.

uptake of H₂S at extremely low pressures. For example, the amount of H₂S adsorbed was 13.5 cm³/g of sorbent on the amine-grafted MCM-48 at 0.001 atm. This is comparable to the amount of CO₂ adsorbed at the same partial pressure, which suggests that amine-modified sorbents can be used to remove CO₂ and H₂S simultaneously because the two gases have similar acidities. Like CO₂, H₂S also desorbs as the pressure is decreased.

The above results suggest that amine-modified MCM-48 and silica xerogel are excellent reversible sorbents for removing the acidic gases CO₂ and H₂S. Because of the high surface areas of the sorbents and high density of amino functional groups on the surface, the sorbents preferentially adsorb large amounts of CO₂ and H₂S. The sorbents can be recovered by temperature or pressure swing under mild conditions.

The adsorption of the major natural gas component CH₄ on the sorbents was also investigated. Equilibrium isotherms for CH₄ on the sorbents are shown in Figure 8. As we can see, the CH₄ uptake is more than an order of magnitude less than the CO₂ uptake at the same partial pressure. The CH₄ uptake increases slowly with increasing pressure. At 1 atm, less than 3.5 cm³/g of sorbent of CH₄ is adsorbed on the sorbents. This is much smaller than the amounts of CO₂ and H₂S adsorbed. The results suggest that amine-grafted MCM-48 and silica xerogel are effective sorbents for the selective removal of CO₂ and H₂S from natural gas.

Water Effect. The water vapor content in natural gas mixtures can vary from less than 1% to more than 10%. It is important to study the effect of water on acidic gas adsorption. On the other hand, water plays the important role of proton transfer agent in the reaction of acidic gas and amine solutions (conventional method of removing acidic gas from natural gas). It is thus important to study the effect of water vapor during this gas–solid adsorption interaction.

We used TPD-MS and infrared spectroscopy to study the effect of water vapor on the adsorption of CO₂ and H₂S on amine-modified MCM-48. TPD can also be used to study the reversibility of the acidic gas adsorption on the sorbents. The TPD profiles for CO₂ are shown in

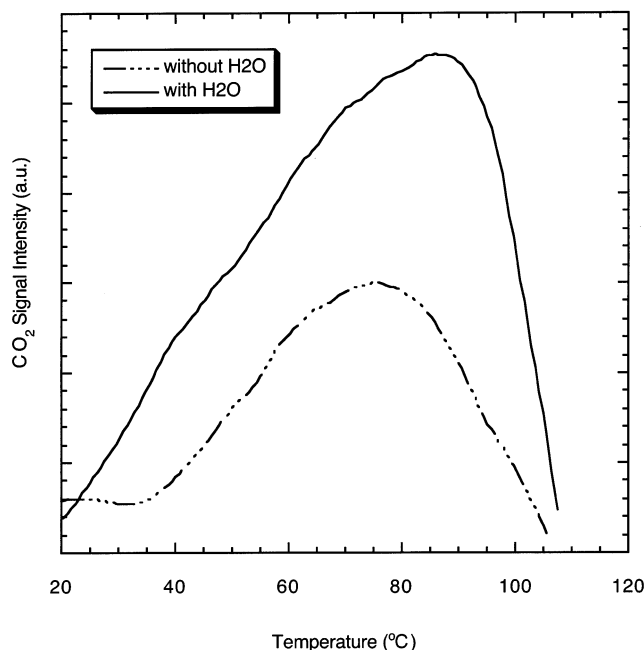


Figure 9. TPD profiles of CO₂ from amine-modified MCM-48.

Figure 9. As the temperature was increased from 25 to 120 °C, CO₂ desorption was observed on the sorbents. The desorption was completed at below 110 °C, and the peak temperature was 75 °C. This is consistent with the TGA results shown in Figure 4, which suggested that the sorbents can be regenerated by raising the temperature to 75 °C. Comparing the two TPD curves of CO₂, we can see that water vapor actually enhanced CO₂ adsorption on the amine-modified sample. When the adsorption was performed in the presence of water vapor, the amount of CO₂ desorbed was more than the amount without water. Quantitative analysis of the CO₂ desorption amount according to the peak area indicates that the amount of CO₂ desorbed is twice when the water was present during the adsorption. This result is consistent with the fact that the mechanism for CO₂ removal using amines is dependent on the presence of water. Two moles of amine groups are required to remove every 1 mol of CO₂ molecules (to form carbamate) when water vapor is absent from the reaction, whereas 1 mol of amine groups is effective in removing 1 mol of CO₂ (to form bicarbonate) in the presence of water. This reaction mechanism has been extensively studied in the literature.^{1,4,8,9} It is also interesting to note from the figure that the CO₂ desorption peak temperature was 10 °C higher when water vapor was present during the adsorption, suggesting that the CO₂–amine bonding is enhanced. The effect of water on the adsorption of CO₂ was also evidenced by infrared spectroscopy results (not shown). The IR bands of carbamate, bicarbonate, and NH₃⁺ were stronger with water in the reaction gas than without water in the reaction gas. The above results demonstrate that water vapor enhances CO₂ adsorption on amine-modified MCM-48 adsorbents.

The TPD profiles of H₂S on the amine-modified sample are shown in Figure 10. As the temperature was increased from room temperature to 120 °C, H₂S desorption was complete at 90 °C, and the desorption peak temperature was 60 °C (consistent with the TGA results shown in Figure 6). When we compare the two TPD desorption curves of H₂S, we can see that the amount

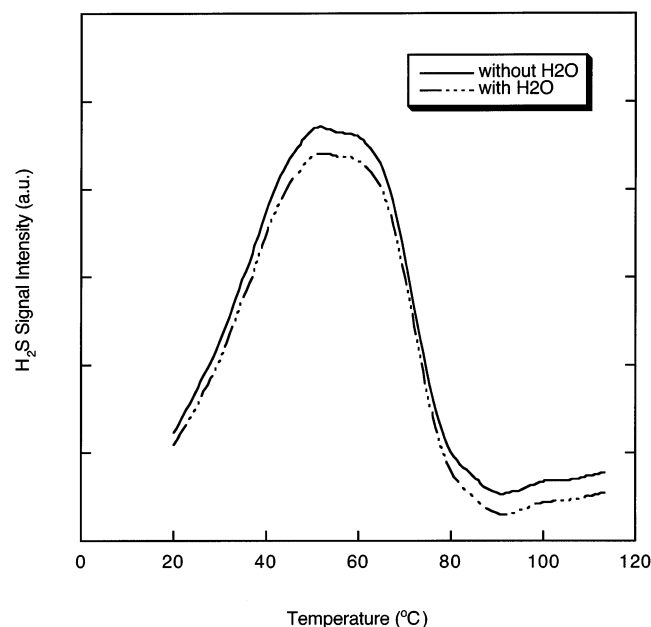


Figure 10. TPD profiles of H_2S from amine-modified MCM-48.

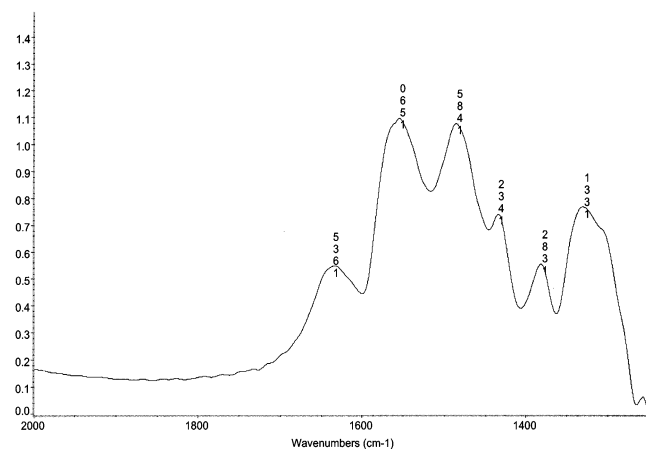


Figure 11. FTIR spectrum at 25 °C after amine-modified MCM-48 was exposed to 5% CO_2 for 30 min.

of H_2S desorbed was only slightly decreased when water vapor was present in the adsorption gas. This is probably due to the much weaker competition at adsorption sites for water than for H_2S . Unlike the effect that water has on CO_2 adsorption on amine groups, water vapor did not improve the H_2S adsorption. In fact, the H_2S adsorption was barely affected by the presence of water.

FTIR Studies of CO_2 and H_2S Adsorption. The surface interactions of CO_2 and H_2S with the amine-modified samples were further studied using infrared spectroscopy. The spectrum of CO_2 adsorption at ambient temperature is shown in Figure 11. Strong IR bands were observed in the range of 1700–1300 cm^{-1} . The assignment of these bands is complicated. The IR band at 1330 cm^{-1} can be assigned to weakly adsorbed gaseous CO_2 . The vibration band at 1382 cm^{-1} is due to bicarbonate C–O bending.⁹ The HCO_3^- might come from the reaction between CO_2 and residual water. The IR bands at 1432 and 1485 cm^{-1} are due to the asymmetric stretchings of C–O in carbamate.³⁵ The band at 1560 cm^{-1} can be attributed to C–O stretching or symmetric NH_3^+ deformation or the overlap of these two bands. The IR band at 1635 cm^{-1} is probably due to water adsorption or asymmetric NH_3^+ deformation

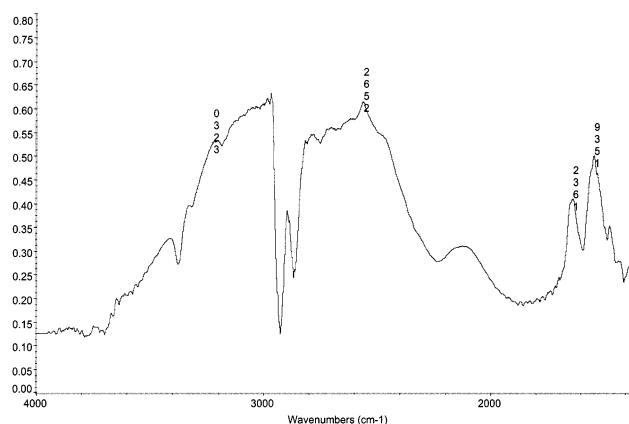


Figure 12. FTIR spectrum at 25 °C after amine-modified MCM-48 was exposed to 1% H_2S for 30 min.

or both.³⁶ When the sample was heated in helium at 50 °C, the peaks for adsorbed species became weaker. All of the surface groups vanished at 75 °C (results not shown). This is consistent with the TPD and TGA results that the sample can be regenerated by heating in inert gas at 75 °C.

Figure 12 shows the IR spectrum of the amine-modified MCM-48 sample after it was exposed to 1% H_2S for 30 min. Evidence of the formation of $\text{NH}_3^+ \text{HS}^-$ group from the weak chemical reaction between H_2S and surface amine groups ($-\text{NH}_2$) was found in this IR spectrum. For example, the two IR band at 1632 and 1539 cm^{-1} were due to asymmetric and symmetric NH_3^+ deformation, respectively. A weak band due to N–H stretching from NH_3^+ groups was observed at 3230 cm^{-1} .³⁶ It is also interesting to observe the characteristic S–H stretching vibration at 2562 cm^{-1} because this band generally exhibits a very weak IR intensity and can sometimes be missed.³⁷ The appearance of inverse IR bands around 3300 and 2900 cm^{-1} is due to the background subtraction. Increasing the sample temperature to 60 °C leads to the disappearance of all of the IR bands due to H_2S adsorption (not shown). This is also consistent with the previous TGA and TPD results.

Conclusions

This study has shown that amine-surface-modified silica xerogel and MCM-48 are able to adsorb selectively CO_2 and H_2S from natural gas streams. This is primarily due to the weak chemical interactions between the basic amine groups and the acidic gases. The sorbents can be restored completely by pressure swing or temperature swing. The success of the sorbents is dependent on the successful grafting of amine groups onto the surface through the reaction of the surface hydroxyl groups of the substrate materials and (3-aminopropyl)silanes. Other nonacidic gases such as water vapor and CH_4 do not affect the performance of the sorbents. Moisture actually doubles the CO_2 adsorption capacity because of the special reaction mechanism between CO_2 and amines. The excellent performances in terms of CO_2 and H_2S adsorption by the amine-modified silicas is attributed to the large amounts of amine groups on the surface resulting from their high surface areas and OH contents.

Acknowledgment

This work was partially funded by Grant NSF CTS-0138190. Helpful discussions with Dr. Laura Boudreau of Chevron are appreciated.

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Received for review June 12, 2002

Revised manuscript received August 21, 2002

Accepted August 23, 2002

IE020440U