

Adsorption of CO₂, N₂, and O₂ on Natural Zeolites

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Received June 11, 2002

Pressure swing adsorption (PSA) and temperature swing adsorption are potential techniques for removing CO₂ from high-pressure fuel gas streams. Natural zeolites are suitable candidate sorbents for use in the PSA process. Studies of volumetric gas adsorption of CO₂, N₂, and O₂ on three natural zeolites, with different major cations, were conducted at 25 °C up to a pressure of 300 psi (2×10^6 Pa). Preferential adsorption of CO₂ was observed with all three zeolites. The natural zeolite with the highest sodium content and highest surface area showed the highest CO₂ adsorption capacity. Competitive gas adsorption studies also showed that the zeolite with the highest sodium content gave the best separation of CO₂ from the gas mixtures. Contact time did not affect the extent of adsorption of the zeolites. Temperature-programmed desorption studies indicated that the majority of the physically adsorbed CO₂ was desorbed at room temperature, while some strongly bound CO₂ was desorbed at 115 °C.

Introduction

Fossil fuels supply more than 98% of the world's energy needs. However, the combustion of fossil fuels is one of the major sources of the greenhouse gas CO₂. It is necessary to develop technologies that will allow us to utilize the fossil fuels while reducing the emissions of green house gases. Existing commercial CO₂ capture technology is very expensive and energy intensive. Improved technologies for CO₂ capture are necessary to achieve low energy penalties. Pressure swing adsorption (PSA) is one technique that may be applicable for removal of CO₂ from gas streams.

The PSA process is based on preferential adsorption of the desired gas (e.g., CO₂) on a porous adsorbent at high pressure, and recovery of the gas at low pressure. Thus, the porous sorbent can be reused for subsequent adsorption. PSA technology has gained interest because of the low energy requirements and low capital investment costs.^{1,2} Applications of the PSA process to separate and capture carbon dioxide are also being reported.^{3,4} The low recovery rate of CO₂ is one of the problems reported with the PSA process. Development of regenerable sorbents that have high selectivity, high adsorption capacity, and high adsorption/desorption rates for CO₂ capture is critical for the success of the PSA process. Cost of the sorbent is also a major factor that needs to be considered for the process to be economical.

Zeolites have shown promising results for the separation of CO₂ from gas mixtures and can potentially be used for the PSA process.^{1–5} Natural zeolites are inexpensive and can be viable sorbents if they work for the process application. In this research, three natural zeolites were studied. Volumetric gas adsorption studies of CO₂, N₂, and O₂ on the three sorbents were conducted, at 25 °C and up to a pressure of 300 psi ($\sim 2 \times 10^6$ Pa), to determine the equilibrium adsorption capacity of these materials. Studies on competitive adsorption of CO₂ from gas mixtures were conducted utilizing an atmospheric microreactor. Rates of adsorption were determined by utilizing a thermogravimetric analyzer (TGA). Surface elemental characterizations of these sorbents were conducted utilizing X-ray photoelectron spectroscopy.

Experimental Section

The three natural zeolites, natural henschelite-sodium chabazite (sodium aluminosilicate), clinoptilolite (sodium aluminosilicate), and another form of clinoptilolite (potassium calcium aluminosilicate), were obtained by GSA Resources Inc., American Absorbents Natural Products Inc., and St. Cloud Mining Co., respectively. Adsorption isotherms (at 25 °C) of pure CO₂ (99.5%, Jackson Welding Supply Co.), N₂ (99.5%, Jackson Welding Supply Co.), and O₂ (99.6%, Jackson Welding Supply Co.) on the three sorbents were obtained, up to an equilibrium pressure of about 300 psi ($\sim 2 \times 10^6$ Pa), utilizing a volumetric adsorption apparatus.⁵ Approximately 10 mL of the sorbent materials was placed in the sample chamber and was evacuated to $\sim 5 \times 10^{-5}$ Torr. The amount of CO₂ adsorbed was calculated utilizing the pressure measurements before and after the exposure of the sample chamber to CO₂. Baseline data with CO₂ were obtained utilizing 10 mL of glass beads (2 mm diameter).

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Table 1. Physical Properties of the Three Natural Zeolites

property	zeolite 1 natural herschelite– sodium chabozite (sodium alumino silicate)	zeolite 2 clintopile (sodium alumino silicate– type 4A zeolite)	zeolite 3 clintopile (potassium calcium sodium alumino silicate)
HK pore diameter (Å)	4.3	4.4	4.4
	4.2	4.1	4.5
DFT total pore volume (cm ³ /g)	0.29	0.029	0.024
	0.33	0.029	0.024
DFT surface area (m ² /g)	671	11.2	11.3
	744	18.3	9.6
BET surface area (m ² /g)	485	18.4	13.3
	528	22.8	12.5
Langmuir surface area (m ² /g)	540	23.2	15.9
	590	28.2	15.1

Table 2. Bulk and Surface Elemental Ratios of Three Natural Zeolites

	elemental ratios					
	zeolite 1 natural herschelite– sodium chabozite (sodium alumino silicate)		zeolite 2 clintopile (sodium alumino silicate– type 4A zeolite)		zeolite 3 clintopile (potassium calcium sodium alumino silicate)	
	bulk	surface	bulk	surface	bulk	surface
Al/Si	0.32	0.35	0.19	0.20	0.23	0.38
Na/Si	0.24	0.24	0.10	0.12	0.03	0.01
K/Si	0.02	0.02	0.06	0.02	0.07	0.01
Ca/Si					0.05	0.09

Surface areas and information about micropores were determined utilizing Micromeritics model ASAP 2010 micropore volume analyzer. The samples were first evacuated at 90 °C for 1 h and then at 350 °C for 24 h. Nitrogen adsorption measurements were conducted at liquid nitrogen temperature (77 K). Micropore analyses of the data⁶ were conducted utilizing the Horvath–Kawazoe (HK) method, and slit pore geometry was assumed in the calculations. Density functional theory (DFT) was utilized in total pore volume and surface area calculations.⁶

X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Physical Electronics Model SAM 590 equipped with a model 15-255 GAR analyzer and a 15 kV X-ray source from Physical Electronics.^{7,8} The system was routinely operated within a pressure range of 1.3×10^{-7} to 1.3×10^{-6} Pa (10^{-9} to 10^{-8} Torr). The instrument was calibrated using the photoemission lines $E_B(\text{Cu } 2P_{3/2}) = 932.4$ eV and $E_B(\text{Au } 4f_{7/2}) = 83.8$ eV. The binding energies were referenced to the C(1s) level at 284.6 eV for adventitious carbon. All intensities reported are experimentally determined peak areas divided by the instrumental sensitivity factors. Spectra were obtained with about five different samples and the intensity and binding energy values reported are the averages of values obtained from all sets of data.

Competitive gas adsorption studies were conducted in a lab-scale fixed-bed reactor (Micromeritics Autochem 2910 atmospheric microreactor) at 14.7 psi ($\sim 1.01 \times 10^5$ Pa) using a gas mixture with a composition of 15% CO₂, 82% N₂, and 3% O₂ in the presence of water vapor at ambient temperature. The analysis of the outlet gas stream was conducted utilizing a Pfeiffer Vacuum Thermostat mass spectrometer. The samples were pretreated at 100 °C for 1 h in the microreactor, under helium, prior to the exposure to the gas mixtures containing 15% CO₂, 82% N₂, and 3% O₂ saturated with water vapor.

TGA analysis was conducted utilizing a TA Instruments 951 analyzer. Zeolite samples were heated to 150 °C under nitrogen immediately prior to the adsorption of CO₂. Gas mixtures

containing 2%, 7%, and 15% CO₂, 82%–95% N₂, and 3% O₂ were introduced at 25 °C, and weight gain was recorded as a function of time.

Results and Discussion

Characterization of the Natural Zeolites. Three natural zeolites were used in this study: zeolite 1—natural herschelite-sodium chabozite (sodium alumino silicate); zeolite 2—clinoptilolite (sodium alumino silicate-Type 4A zeolite), and zeolite 3—clinoptilolite (potassium calcium sodium alumino silicate).

The surface areas and pore volumes measured of the three natural zeolites are listed in Table 1. The micropore data were obtained utilizing the HK method and surface area information was obtained from DFT, BET, and Langmuir methods. The surface area and pore volume of zeolite 1 is considerably higher than that of the other two zeolites. The pore diameter (mode) values of the zeolites were very similar for the three zeolites.

Elemental compositions at the surface (measured with XPS) and of the bulk (as reported by the suppliers) are listed in Table 2. The major cation in both zeolite 1 and 2 is sodium, but the sodium content was higher in zeolite 1. The major cations in zeolite 3 are potassium and calcium, while the sodium content of zeolite 3 is very low. The ratio of aluminum to silicon in the bulk was highest in zeolite 1. The surface elemental composition of zeolites 1 and 2 were very similar to that of the bulk. However, in zeolite 3 the surface elemental composition was different from that of the bulk; the amount of calcium and aluminum were higher at the surface, while the amount of sodium and potassium were lower at the surface, than that was observed at the bulk. Since the gas adsorption reactions initially take place at the surfaces, the elements at the surface play an important role in the initial adsorption process.

Adsorption Isotherms. Adsorption isotherms of CO₂, N₂, and O₂ with zeolite 1 and the adsorption

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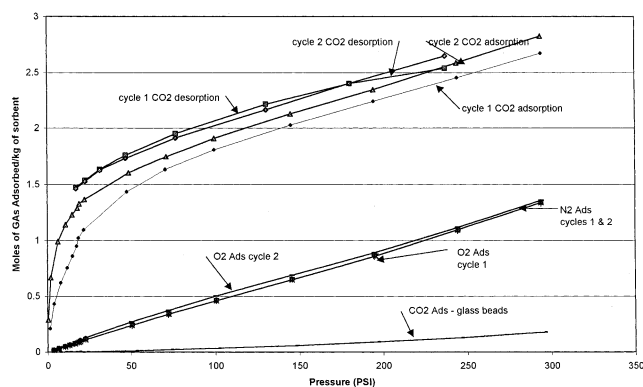


Figure 1. Adsorption and desorption isotherms of zeolite 1.

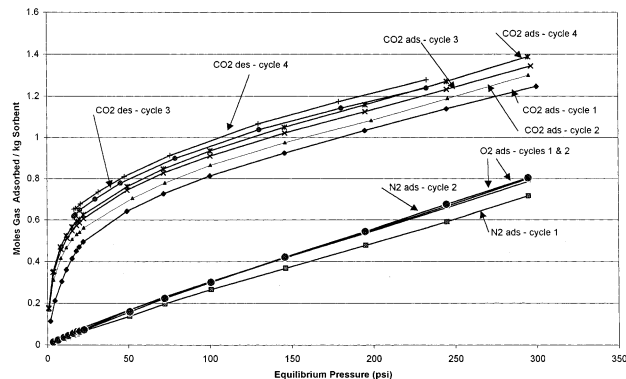


Figure 2. Adsorption and desorption isotherms of zeolite 2.

isotherm of CO₂ for glass beads are shown in Figure 1. The isotherm for CO₂ is higher than that for the other gases, which indicates that there is preferential adsorption of CO₂ on zeolite 1. The amount of CO₂ adsorbed increased rapidly with increasing pressure up to 12 psi, and there was a gradual linear increase in adsorption up to 300 psi. The saturation of CO₂ adsorption was not observed in this pressure range. The adsorption isotherm of the first cycle appeared to be higher than that of the second cycle indicating that some changes in the material may have taken place during the first adsorption cycle. The desorption isotherms of CO₂ were slightly higher than that of the adsorption isotherms indicating that the adsorption is fairly reversible. The amount of CO₂ adsorbed is about 2.5 to 3 mol/kg of the sorbent at 250 to 300 psi. This value is smaller than that was obtained with synthetic zeolite 13X, 4A and activated carbon.⁵

The adsorption isotherms of natural zeolite 2 are shown in Figure 2. Preferential adsorption of CO₂ was also observed with zeolite 2. The adsorption of CO₂ was rapid up to 15 psi, but it was gradual between 15 and 250 psi. The desorption isotherms were slightly higher than the adsorption isotherms, indicating that the adsorption was fairly reversible. A reasonable amount of CO₂ (1.2 to 1.4 mol/kg) was adsorbed at 250 to 300 psi, but it was lower than what was obtained with zeolite 1. The surface area and pore volume of the zeolite 2 are very low but it had a reasonable CO₂ adsorption capacity. The reason for this high CO₂ adsorption capacity with this low surface area zeolite is not clear but it is possible that the defects at the external surface may have participated in adsorption.

The adsorption isotherms of natural zeolite 3 are shown in Figure 3. Preferential adsorption of CO₂ was

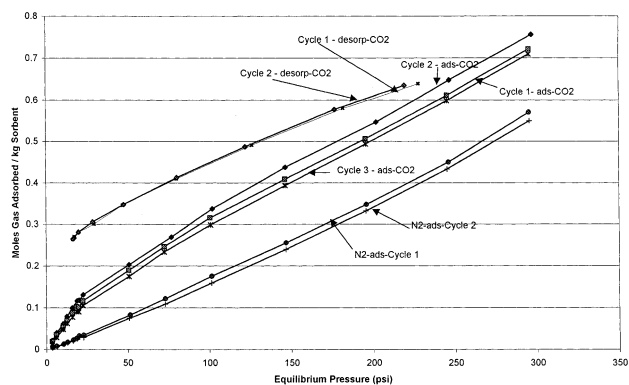


Figure 3. Adsorption and desorption isotherms of zeolite 3.

Table 3. Freundlich Constants for the Three Zeolites

sample	k	$1/n$
zeolite 1	0.0346	0.438
zeolite 1	0.0496	0.308
zeolite 2	0.0159	0.431
zeolite 2	0.0206	0.335
zeolite 3	0.0035	0.752
zeolite 3	0.0032	0.775

also observed with this zeolite. However, the amount of CO₂ adsorption was lower than that of the other two zeolites. The desorption isotherms of CO₂ were slightly higher than the adsorption isotherms, indicating that the adsorption was fairly reversible. The difference in adsorption and desorption isotherms with zeolite 3 was similar to that of the other two zeolites. A reasonable amount of CO₂ (0.7 to 0.8 mol/kg) was adsorbed at 250 to 300 psi.

The adsorption isotherms for the three zeolites can be represented by the Freundlich equation.

$$Q = kP^{1/n} \quad (1)$$

where Q is the amount of CO₂ adsorbed (kg of CO₂/kg of adsorbent), P is the pressure of CO₂ (kPa), and k and n are Freundlich constants. The corresponding Freundlich constants are shown in Table 3. The k values of zeolite 3 are considerably lower than that of the other two zeolites and the value reported for zeolite 13X.⁹ The $1/n$ values for zeolite 3 are higher than that of the other zeolites and the $1/n$ values of all three zeolites are higher than that of the reported value of zeolite 13X.

Since zeolite 1 had the highest adsorption, adsorption isotherms of CO₂ were measured at 30 and 40 °C and heats of adsorption were calculated utilizing the Clausius–Clapeyron equation. The heats of adsorption of zeolite 1 for the coverage of 0.3–0.5 mol of CO₂/kg varied from 37 to 23 kJ/mol.

Competitive Gas Adsorption Studies in the Microreactor. The results of competitive gas adsorption studies conducted with zeolite 1, utilizing a gas mixture containing 15-percent CO₂, 3-percent O₂ and 82-percent N₂, and saturated with water vapor at 25 °C in an atmospheric reactor, are shown in Figure 4. The gas mixture was introduced to 0.86 g of zeolite 1, 1.19 g of zeolite 2 and 1.16 g of zeolite 3, at a flow rate of about 5 cm³/min at 25 °C. After the introduction of the gas mix, the CO₂ concentration decreased to the ppm level

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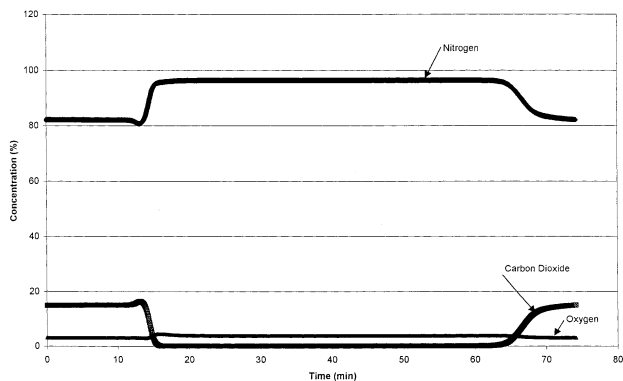


Figure 4. Adsorption of CO₂, N₂, and O₂ on zeolite 1 in atmospheric reactor at 25 °C (15% CO₂, 3% O₂, 82% N₂ and saturated with water vapor).

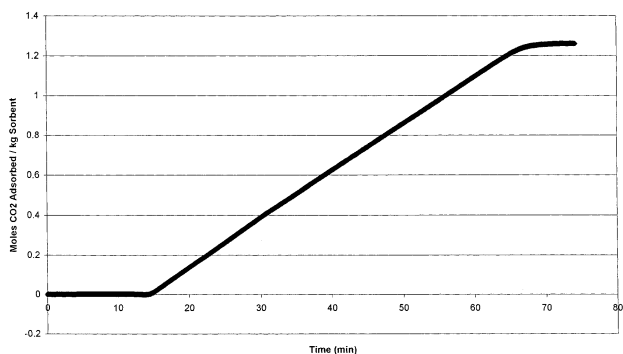


Figure 5. Amount of CO₂ adsorption from 15% CO₂, 82% N₂, 3% O₂ (saturated with water) mixture as a function of time on zeolite 1.

while the nitrogen level increased to 100 percent, until breakthrough. This indicates that there is an excellent separation of CO₂ from the gas mixture. Repeated measurements showed similar separation. The amount of CO₂ adsorbed per kilogram of the sorbent as a function of time, calculated from the breakthrough data, is shown in Figure 5. The total amount of CO₂ adsorbed at breakthrough, or saturation, was about 0.9–1.2 mol/kg of the sorbent during repeated measurements with fresh samples. This value is very similar to that obtained with the equilibrium adsorption isotherms. This indicated that the full capacity of zeolite 1 was utilized by the CO₂ during the competitive gas adsorption. Water vapor and O₂ were also present in the gas mixture and it appeared that both water vapor and O₂ did not affect the adsorption of CO₂.

The results of competitive gas adsorption studies with zeolite 2 are shown in Figure 6. The CO₂ concentration decreased to ppm levels after the gas mixture was introduced to the zeolite 2; it was also possible to get a good separation of CO₂ from the gas mixture. However, the breakthrough time with zeolite 2 was shorter than that with zeolite 1, indicating that the CO₂ adsorption capacity of zeolite 2 is lower than that of zeolite 1. Zeolite 1 has a higher surface area than zeolite 2, and that may have contributed to the higher adsorption capacity of zeolite 1. The amount of CO₂ adsorbed per kilogram of zeolite 2 as a function of time, calculated from the breakthrough data, is shown in Figure 7. The amount of CO₂ adsorbed is about 0.5–0.7 mol/kg of the sorbent during repeated measurements, and it is similar to the value obtained from equilibrium adsorption isotherms. This indicates that the full capacity of the

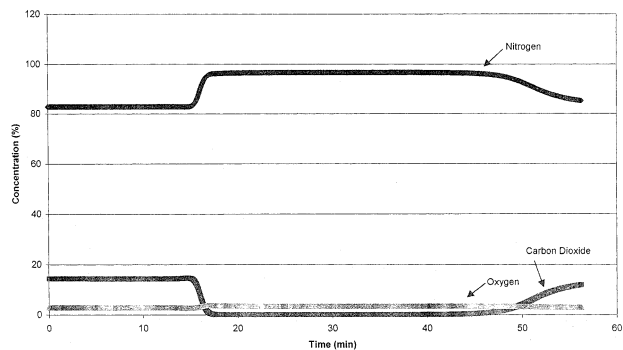


Figure 6. Adsorption of CO₂, N₂, and O₂ on zeolite 2 in atmospheric reactor at 25 °C (15% CO₂, 3% O₂, 82% N₂ and saturated with water vapor).

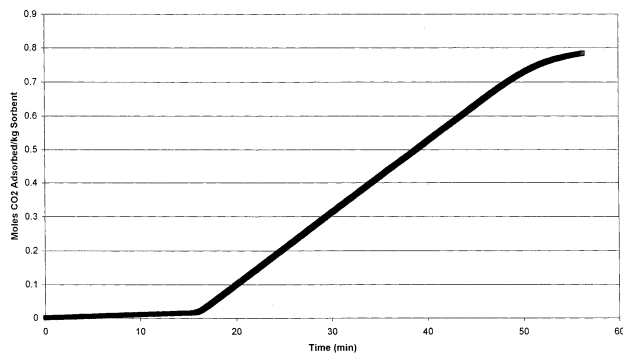


Figure 7. Amount of CO₂ adsorption from 15% CO₂, 82% N₂, 3% O₂ (saturated with water) mixture as a function of time on zeolite 2.

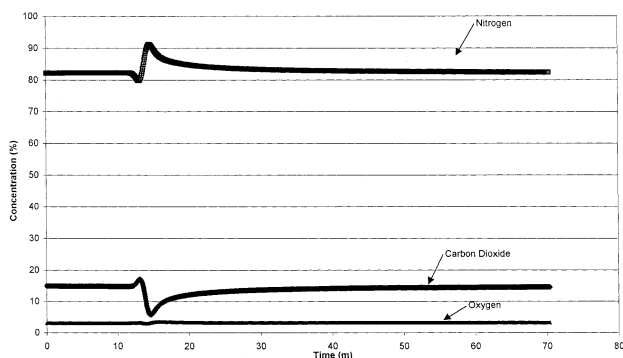


Figure 8. Adsorption of CO₂, N₂, and O₂ on zeolite 3 in atmospheric reactor at 25 °C (15% CO₂, 3% O₂, 82% N₂ and saturated with water vapor).

sorbent was utilized during the competitive gas adsorption in the microreactor.

The results of competitive gas adsorption studies with zeolite 3 are shown in Figure 8. An adequate separation of CO₂ from the gas mixture was not observed with zeolite 3. The kinetic diameter of CO₂ is 3.9 Å, while the pore diameter of the three zeolites was in the range of 4 Å. The pore diameter is sufficient for the CO₂ to enter into the zeolite channels. The differences in adsorption observed with the zeolites should be related to the differences in the chemical nature at the surface, since the average pore diameters are fairly similar for the three zeolites. The major cations of the zeolite 3 are Ca and K, while the major cations of the other two zeolites are Na and K. So the major cation appears to play a main role in separation of CO₂ from gas mixtures. Sodium appears to be the favorable cation for the adsorption of CO₂. Repeated competitive gas adsorption

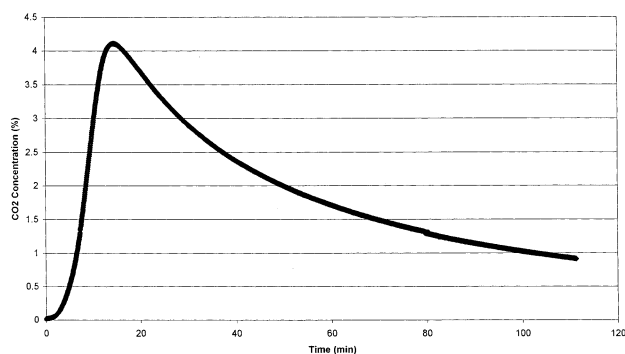


Figure 9. Amount of CO₂ desorbed at 25 °C during the introduction of nitrogen with zeolite 1 after CO₂ adsorption.

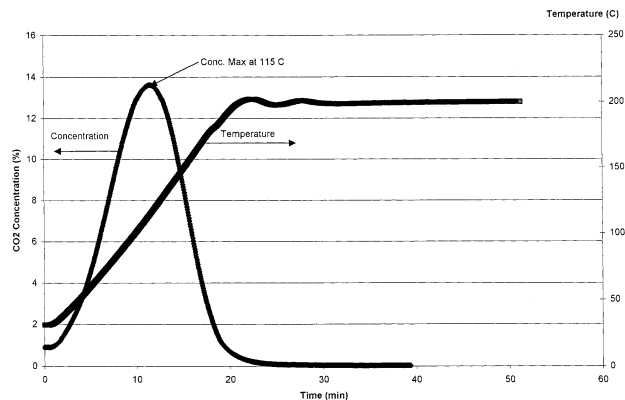


Figure 10. Amount of CO₂ desorbed during temperature-programmed desorption with zeolite 1.

experiments in the microreactor showed similar results with all three zeolites.

The effect of contact time on the adsorption was studied by changing the flow rates during the microreactor studies. The amount of CO₂ adsorbed at breakthrough (0.5% CO₂) at flow rates of 5 and 15 cm³/min for zeolite 1 were 1.25 and 1.04 mol/kg, and for zeolite 2 they were 0.75 and 0.73 mol/kg, respectively. This indicates that the contact time does not have a significant effect on the CO₂ adsorption on the two zeolites. Since the average pore sizes of the zeolites are higher than the kinetic diameter¹⁰ of CO₂, there is sufficient time for the interaction of CO₂ with the zeolite surface at both 5 cm³/min and 15 cm³/min.

To identify the different types of CO₂ species adsorbed on the zeolites, temperature-programmed desorption (TPD) studies were conducted in the fixed bed reactor with the zeolites after the CO₂ adsorption from the gas mixture. After the CO₂ adsorption, nitrogen was introduced to the zeolite at 25 °C (10 cm³/min) and CO₂ concentration of the outlet gas was measured with the mass spectrometer. When the CO₂ concentration was below 1%, the temperature was gradually increased to 200 °C at a rate of 8.5 °C/min and the concentration of the CO₂ was measured. The amount of CO₂ desorbed (as a function of time) during the nitrogen purge at 25 °C, and during TPD with zeolite 1, are shown in Figures 9 and 10. As shown in Figure 9, the desorption curve at 25 °C was fairly broad, which indicated that there is continuous distribution of weakly adsorbed CO₂ with different sorption strengths. It is also possible that

the desorption of CO₂ is transport limited at this temperature and this may also have contributed to the broadening of the desorption curve. The ratio of the amount of CO₂ desorbed at 25 °C, under nitrogen, to that desorbed during the TPD (up to 200 °C) is 1.57. This indicates that the majority of the CO₂ was physically (weakly) adsorbed, and desorbed, during the introduction of nitrogen at room temperature. There was also a substantial amount of strongly bound CO₂, and the maximum temperature of desorption of the CO₂ was 115 °C, as shown in Figure 10. Similar results were observed with zeolite 2. The ratio of the amount of CO₂ desorbed during the nitrogen flush to that during the TPD for zeolite 2 is 2.14. This indicates that zeolite 2 had more physically adsorbed CO₂ than zeolite 1. Zeolite 1 contains more sodium than zeolite 2, as shown in Table 2. The presence of more sodium in zeolite 1 may have contributed to the more strongly bound CO₂.

Dewaele and Froment¹¹ have reported the presence of different CO₂ sorption types on Al₂O₃. They observed that the physisorbed CO₂ rapidly desorbed at room temperature while bidentate carbonate desorbed at 100 °C. Parkyns¹² also reported different types of CO₂ adsorption sites on alumina during FTIR studies. The FTIR band resulting from physically adsorbed CO₂ was identified at 2349 cm⁻¹. When surface hydroxyl groups were present on the surface, characteristic bands resulting from bicarbonate groups (3605, 1642, 1480, and 1236 cm⁻¹) were observed. He also observed the formation of some carbonate ions by direct reaction of CO₂ with the Al–O–Al bonds. IR bands after adsorption of CO₂ on silica–alumina¹³ predried at 600 °C indicated the presence of a band at 2345 cm⁻¹ due to weakly held CO₂ and strongly held component at 2377 cm⁻¹. It was possible to evacuate both types of CO₂ at room temperature. A large amount of surface hydroxyl groups was not present in the silica–alumina surface since it was predried at 600 °C. The CO₂ desorbed from the zeolite surface at room temperature is a result of physisorbed CO₂, while the CO₂ desorbed at 115 °C may be a result of either the bicarbonate or bidentate carbonate. The gas mixture utilized during the TPD studies with the zeolite was saturated with water vapor and this may have facilitated the surface formation of hydroxyl groups, which are responsible for the formation of bicarbonates.

The CO₂ molecule has a large quadrupole moment and is known to react with both Lewis and Bronsted base sites. In the presence of Bronsted and Lewis bases, CO₂ is known to act as a Lewis acid. Electron density is considered to be transferred from the highest occupied molecular orbital of the donor molecule into the lowest unoccupied molecular orbital of the acceptor. Alkali-exchanged zeolites have basic surfaces¹⁴ while the ion exchange by polyvalent cations, such as calcium, has resulted in more acidic surfaces resulting from withdrawal of electron density from Al through the oxygen groups.¹⁵ As shown in Table 2, zeolites 1 and 2 have more sodium than zeolite 3. The major cation in zeolite

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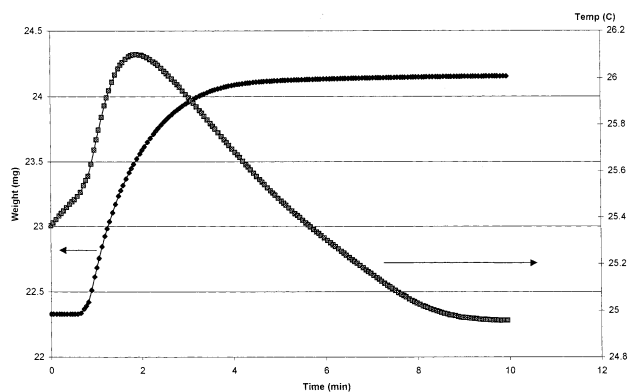


Figure 11. Thermogravimetric analysis of zeolite 1 at 25 °C during the exposure to a gas mix with 15% CO₂, 3% O₂, and 82% N₂.

3 is calcium, and this may contribute to a more acidic surface than with zeolites 1 and 2, which have more alkali. Better separation of CO₂ from gas mixtures and higher CO₂ adsorption capacity observed with zeolites 1 and 2 may be a result of the higher basicity of the surface, resulting from the presence of alkali. The average pore sizes of these three zeolites are similar, and had no contribution to the differences in adsorption observed in this work.

Thermogravimetric Analysis (TGA). The TGA curves of zeolites were obtained utilizing 2%, 7%, and 15% CO₂ mixed with 82% N₂ and 3% O₂. The TGA data for zeolite 1, with 15% CO₂ is shown in Figure 11. A discontinuity in the CO₂ uptake curves was observed during the first 0.3 min after introduction of the CO₂ mixture. It may be a result of the initial displacement of N₂ with the CO₂ mixture, and the sample may not have been exposed to the exact concentration of CO₂ during that time. The slopes of the curves which indicate the rate of CO₂ uptake during the time interval of 0.3 min to 1.3 min are listed in Table 4. The rate of uptake is generally higher for zeolite 1 than for zeolite 2 for all the CO₂ concentrations. The higher rate of CO₂ uptake

Table 4. Rate (mg/min) of the Uptake during 0.3–1.3 min TGA Curves

concentration of CO ₂ (%)	zeolite 1	zeolite 2
2	0.35	0.09
7	1.17	0.59
15	1.05	0.64

of zeolite 1 may be a result of the presence of more sodium and larger surface area. The major cation present in the zeolite appears to play a significant role in both the uptake rate and the adsorption capacity of the sorbent. For both zeolites, the uptake rate appeared to increase when the concentration of the CO₂ increased from 2% to 7%, but appeared to have no significant increase when CO₂ concentration was increased to 15%.

Conclusions

All three natural zeolites utilized in this study showed preferential adsorption of CO₂. The major cations in the zeolites appear to play an important role in the adsorption of CO₂. Zeolites with high sodium content showed the highest CO₂ adsorption capacity during volumetric gas adsorption studies, and highest rates of adsorption during TGA studies. A good separation of CO₂ from a gas mixture of CO₂/N₂/O₂ was also observed with the zeolites with the highest sodium content during the flow reactor studies. Temperature-programmed desorption studies indicate that there are two types of adsorption sites on zeolites. The majority of adsorbed CO₂ was found to be physically adsorbed, and can be desorbed at room temperature. The other type of CO₂ was desorbed at 115 °C and was attributed to either bicarbonate or bidentate carbonate-type species.

Acknowledgment. The authors thank GSA, Environmental Solutions, and St. Cloud Mining Co. for providing zeolites for this research. Assistance with TGA analysis, provided by Donald Floyd and Tom Simonyi of Parsons Infrastructure Inc., is also appreciated. The authors also thank James Poston and Henry Pennline for reviewing the paper.

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