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Influence of Moisture on CO₂ Separation from Gas Mixture by a Nanoporous Adsorbent Based on Polyethylenimine-Modified Molecular Sieve MCM-41

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Adsorption separation of CO₂ from simulated flue gas containing CO₂, O₂, and N₂ with and without moisture was investigated using a novel nanoporous adsorbent based on polyethylenimine (PEI)-modified mesoporous molecular sieve MCM-41 in a flow system. The CO₂ adsorption capacity and CO₂ separation selectivity of MCM-41 were greatly improved by loading PEI into its nanosized pore channels, which made the resulting adsorbent operating like a "molecular basket" for CO₂. CO₂ adsorption capacity of the MCM-41-PEI adsorbent for the simulated moist flue gas was higher than that for the simulated dry flue gas. CO₂ separation selectivity of the MCM-41-PEI adsorbent was also improved in the presence of moisture when compared with those in the dry gas condition. The influence of moisture concentrations in the simulated flue gas on the CO₂ adsorption separation performance was also examined. The results of adsorption/desorption separation cycles showed that the MCM-41-PEI adsorbent was stable over 10 cycles of adsorption/desorption operations. The hydrothermal stability of the "molecular basket" adsorbent was better than that of the MCM-41 support alone.

1. Introduction

The continued use of fossil fuels for clean, affordable energy depends on our ability to reduce their environmental impact. Emissions of particulate matter and the oxides of nitrogen (NO_x) and sulfur (SO_x) have attracted much attention. 1-3 Recently, increased CO₂ concentration in the atmosphere due to the emissions of CO₂ from fossil fuel combustion has caused the concerns for global climate change.^{2–10} To stabilize the CO₂ concentration in the atmosphere, control of the CO₂ emission is necessary. Carbon sequestration is considered one of the options. 9,10 Generally, there are three steps in this CO_2 management: separation, transportation, and sequestration. The separation cost constitutes about threefourths of the total cost.^{9,10} The separation of CO₂ can impose severe penalties on power plants by reducing up to about 25% of the net electricity output. The development of a more economical separation technology is highly desired.

Because of its low energy requirement, cost advantage, and ease of applicability over a relatively wide range of temperatures and pressures, adsorption separation is receiving increasing interest in bulk gas separation, gas purification, and other chemical processes. In the case of CO₂ separation, zeolite and carbon molecular sieve adsorbents may be employed because of their high CO₂ adsorption capacity at low CO₂ concentration, rapid mass transfer in the particle, and other factors. ^{11–20} However, CO₂ adsorption capacity of these adsorbents rapidly decline with a slight increase in temperature. ^{18–20} In addition, since these adsorbents also adsorb moisture and other gases, the CO₂ separation selectivity is low. Therefore, several stages of separations are required to get a pure CO₂ stream,

resulting in a large separation system with high operating cost in practical application.²¹ Preparation of high-capacity, highly selective CO₂ adsorbents is the key factor to a more energy-efficient adsorption separation.

Recently, a new kind of high-capacity, highly selective, nanoporous adsorbent for CO2 based on a "molecular basket" concept has been developed in our laboratory. 22-28 To make the "molecular basket" adsorbent, a sterically branched polymer of polyethylenimine (PEI) with numerous CO2-affinity sites and with low heat of adsorption is loaded into a large-pore-volume material of mesoporous molecular sieve MCM-41. The MCM-41-PEI adsorbent can selectively "pack" CO₂ in a condensed form in the mesoporous molecular sieve, thus functioning like a CO2 "molecular basket" and therefore show a high CO₂ adsorption capacity and a high CO₂ selectivity. The combination of MCM-41 and PEI has a synergetic effect on the adsorption of CO₂ by PEI.^{22–24} CO₂ adsorption capacity as high as 125 mL(STP)/(g of PEI) was obtained at 75 °C and pure CO₂ atmosphere, which was 30 times higher than that of MCM-41 and was more than twice that of the pure PEI.^{22,23} The adsorption separation of a simulated flue gas, which contains 14.9% CO_2 , 4.25% O_2 , and 80.85% N_2 , showed a CO_2 adsorption capacity of 91 mL(STP)/(g of PEI) and CO₂/O₂ and CO₂/ N₂ separation selectivities of 180 and >1000, respectively, at 75 °C and atmospheric pressure.24 The CO2 adsorption capacity and CO₂/O₂, CO₂/N₂ separation selectivity of the "molecular basket" adsorbent are much higher than those of the other adsorbents, such as zeolites and activated carbons.

However, several challenges still need to be overcome toward practical applications. One of such challenges is moisture, which is an important component in boiler flue gas and other industrial gases. On one hand, moisture may interact with the active adsorption species of amine groups in the "molecular basket" adsorbent.

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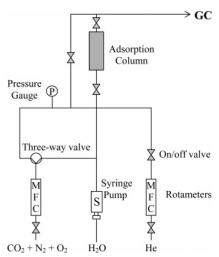


Figure 1. Flow adsorption setup for the CO_2 separation from simulated flue gas.

Therefore, moisture may compete with CO2 for the active adsorption sites. Clarkson and Bustin²⁹ suggested that CO₂/CH₄ selectivity is greater for dry coals than for moisture-equilibrated coals. In addition, the "basket" material of MCM-41 may not be stable under hydrothermal conditions.^{30,31} The preservation of the structure of MCM-41 is critically important for the CO₂ adsorption separation performance of this novel "molecular basket" adsorbent. 22-28 On the other hand, the presence of moisture in the flue gas may promote the CO₂ adsorption by amine group. Theoretically, 2 mol of amine groups could react with 1 mol of CO₂ in the dry condition and 2 mol of CO₂ in the presence of water. However, different results were reported in the literature. Huang et al.³² reported that CO₂ adsorption capacity on an amine-grafted MCM-48 adsorbent doubled in the presence of water vapor. On the contrary, Hiyoshi et al.³³ reported that the presence of water vapor in the gas mixture had no effect on the CO₂ adsorption by an amine-modified SBA-15 adsorbent.

In this paper, the adsorption separation of CO_2 from simulated flue gas containing CO_2 , O_2 , O_2 , O_2 , and water vapor by using the novel "molecular basket" adsorbent of MCM-41-PEI is reported. The effects of moisture on the adsorption separation performance and stability of the CO_2 "molecular basket" adsorbent are discussed.

2. Experimental Section

2.1. Adsorbent and Flow Adsorption System. "Molecular basket" adsorbent (MCM-41-PEI-50) was prepared by loading 50 wt % branched polyethylenimine (PEI, Aldrich, $M_{\rm n}=600$) into the mesoporous molecular sieve MCM-41 and was used as adsorbent for the adsorption separation of CO₂ from simulated flue gases. The details on the preparation and characterization of the MCM-41 and MCM-41-PEI-50 were reported elesewhere. ^{22–27} Simulated dry flue gas contains 14.9% CO₂, 4.25% O₂, and 80.85% N₂. Moisture was added into the simulated dry flue gas to make the simulated moist flue gas. In some experiments, moisture was mixed with helium as the gas mixture.

Figure 1 shows a schematic diagram of the flow adsorption system. There are three gas lines in this online CO_2 monitoring system. Two lines are installed for introducing the simulated dry flue gas and moisture, and the third line is for the helium sweep gas. The simulated moist flue gas was prepared by passing the

simulated dry flue gas through a syringe needle, which was heated at about 120 °C. The gas flow rate was controlled by a rotameter. The amount of moisture in the gas mixture was controlled by a liquid syringe pump. All of the gas line was heated to about 120 °C to avoid any moisture condensation in the gas line. The adsorption temperature was controlled by a temperature-programmable tube furnace. The concentrations of the gases in the gas mixture were measured on-line using a SRI 8610 C gas chromatograph (GC) with molecular sieve 5A and Porapak T columns, and with a TCD detector. The gas flow rate was measured by a soap-film flow meter. The adsorption column was a stainless steel tube with 20 in. in length, 0.5 in. in outer diameter, and 0.35 in. in inner diameter. The adsorbent bed was in the central part of the tube. The remainder of the column was filled with inert glass beads to decrease the dead volume and to minimize the delay for analysis. The dead volume for the adsorption separation system was estimated to be 10 mL.

2.2. Adsorption Separation Procedures. In a typical adsorption/desorption process, about 2.0 g of the adsorbent was used. The length (height) of the adsorbent bed was about 5 in. Before the adsorption experiment, the adsorbent was heated to 100 °C in helium atmosphere at a flow of 50 mL/min and held at that temperature overnight to ensure that there was no carbon dioxide or moisture adsorbed prior to any experiment. Temperature was then decreased to 75 °C, and the dry or moist simulated flue gas was introduced at a flow rate of 10 mL/min. Generally, the adsorption was carried out for 240 min. After adsorption, the gas line was switched to 99.995% pure helium at a flow rate of 50 mL/min to perform the desorption at the same temperature as the adsorption. The time for desorption was 300 min. The concentration of the gases in the effluent gas was analyzed every 5 min when the simulated dry flue gas was used as adsorbate and every 15 min when the simulated moist flue gas was used as adsorbate. The gas flow rate was measured every 5 min during the adsorption/desorption process.

The adsorption capacity in mL(STP) of adsorbate/(g of adsorbent) and the desorption capacity in percentage were used to evaluate the adsorbent. Adsorption/desorption capacity was calculated from the mass balance before and after the adsorption. the separation factor, $\alpha_{i/j}$, was calculated from eq 1 as the ratio of the amount of gases adsorbed by the adsorbent, $(n_i/n_j)_{\text{adsorbed}}$, over the ratio of the amount of gases fed into the adsorbent bed, $(n_i/n_j)_{\text{feed}}$. n_i and n_j are the volumes (mL) of gas i and gas j, respectively.

$$a_{i/j} = \frac{(n_i/n_j)_{\text{adsorbed}}}{(n_i/n_j)_{\text{feed}}}$$
 (1)

The CO_2 adsorbents were characterized before and after adsorption separation by X-ray diffraction (XRD). The XRD patterns were were taken with a Scintag X2 diffractometer using Cu K α radiation ($\lambda = 1.542$ Å) by a Si(Li) Peltier detector. Peak profiling was recorded by Jade 7.1 software by MDI.

3. Results and Discussions

3.1. Adsorption Separation of CO₂ from Simulated Moist Flue Gas. Depending on the types of fuels and the combustion conditions, a flue gas contains about

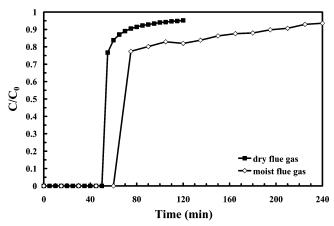


Figure 2. Comparison of CO₂ breakthrough curves for simulated dry/moist flue gas by CO2 "molecular basket" adsorbent. Operation conditions: adsorbent, MCM-41-PEI-50; weight of adsorbent, 2.0 g; temperature, 75 °C; feed flow rate, 10 mL/min. Simulated dry flue gas composition: 14.9% CO₂, 4.25% O₂, and 80.85% N₂. Simulated moist flue gas composition: 13.55% CO₂, 3.86% O₂, 72.72% N₂, and 9.87% H₂O.

8-20% moisture (water vapor). The influence of moisture on the adsorption separation of CO₂ from simulated flue gas was investigated at 75 °C and ambient pressure. Figure 2 compares the CO2 breakthrough curves, where the amount of CO2 was followed as the fraction of the CO₂ concentration in the effluent gas from the adsorption column, C, over that of the CO₂ concentration in the feed, C_0 , for the simulated dry flue gas and simulated moist flue gas with $\sim 10\%$ moisture. In the presence of moisture, the "molecular basket" adsorbent still effectively adsorbed CO₂. At the beginning of the separation, CO₂ was completely adsorbed by the adsorbent and the CO₂ concentration was below the detection limit of the gas chromatography, i.e., <100 ppm. After 60 min of adsorption, CO₂ breakthrough was detected in the effluent gas. Compared with the adsorption separation of CO₂ from simulated dry flue gas under the same conditions, the CO₂ breakthrough time increased when a simulated moist flue gas was used, which indicated that moisture had a promoting effect on the adsorption of CO2 by the "molecular basket" adsorbent. Even after 120 min of adsorption, the "molecular basket" adsorbent still adsorbed ~20% of the CO₂ from the simulated moist flue gas, whereas only 5% of the CO₂ adsorbed from the simulated dry flue gas. After 240 min of adsorption, the adsorbent could only adsorb 6% of the CO₂ from the simulated moist flue gas.

To calculate the adsorption capacity and the separation selectivity, the volume of the adsorbed gases was calculated from the mass balance on the basis of the gas flow rates, gas concentrations, and adsorption time. Figures 3-5 compare the adsorbed volume of CO_2 , N_2 , and O_2 by the adsorbent as a function of adsorption time for simulated dry/moist flue gas. CO2 adsorption capacity, which was calculated when the "molecular adsorbent" adsorbed $\sim 5\%$ of CO_2 from the feed, increased from 90.4 mL(STP)/(g of PEI) for simulated dry flue gas to 129.9 mL(STP)/(g of PEI) for simulated moist flue gas. If only the adsorption before CO₂ breakthrough was considered, the CO₂ adsorption capacity at moist condition was also higher than that at dry condition. Meanwhile, the adsorption of O2 was inhibited at the moist condition. The separation selectivity in terms of the CO₂/ O_2 ratio was ~ 180 for simulated dry flue gas and ~ 600 for simulated moist flue gas. Since GC analysis has an

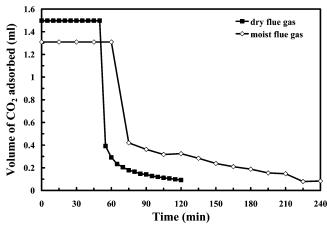


Figure 3. Comparison of the adsorbed volume of CO₂ from simulated dry and moist flue gas by CO2 "molecular basket" adsorbent. Operation conditions: adsorbent, MCM-41-PEI-50; weight of adsorbent, 2.0 g; temperature: 75 °C; feed flow rate, 10 mL/min. Simulated dry flue gas composition: 14.9% CO₂, 4.25% O₂, and 80.85% N₂. Simulated moist flue gas composition: 13.55% CO₂, 3.86% O₂, 72.72% N₂, and 9.87% H₂O.

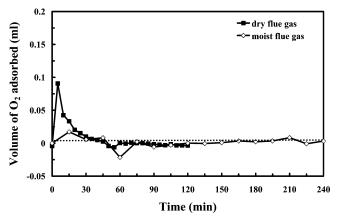


Figure 4. Comparison of the adsorbed volume of O2 from simulated dry and moist flue gas by "molecular basket" adsorbent. Operation conditions: adsorbent, MCM-41-PEI-50; weight of adsorbent, 2.0 g; temperature, 75 °C; feed flow rate, 10 mL/min. Simulated dry flue gas composition: 14.9% CO₂, 4.25% O₂, and 80.85% N₂. Simulated moist flue gas composition: 13.55% CO₂, $3.86\% O_2$, $72.72\% N_2$, and $9.87\% H_2O$.

error up to 5% and the measurement of the gas flow rate has also an error up to 1%, the negative value of the adsorbed N2 may indicate that the adsorption of N2 was below the detection limit of the measurement. However, the molecular adsorbent also adsorbed a significant amount of water.

Figure 6 compares the amounts of water adsorbed with and without CO₂ in the feed. It is clearly shown that the adsorption of water was inhibited in the presence of CO₂. The water adsorption capacity was 117.9 mL(STP)/(g of PEI) with CO₂ in the feed and was 145.0 mL(STP)/(g of PEI) without CO₂ in the feed. Although the water was also adsorbed by the adsorbent, the CO₂ adsorption capacity increased 40% and the separation of water and CO₂ is rather easy in practical applications. The effect of water vapor on the CO2 adsorption by the amine-based MCM-41-PEI adsorbent was different from other amine-based adsorbents described in the literature, where Huang et al.³² reported that CO2 adsorption capacity on an amine-grafted MCM-48 adsorbent doubled in the presence of water vapor, while Hiyoshi et al.³³ reported that CO₂ adsorption capacity on an amine-modified SBA-15 adsorbent

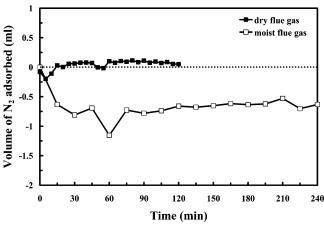


Figure 5. Comparison of the adsorbed volume of N_2 from simulated dry/moist flue gas by "molecular basket" adsorbent. Operation conditions: adsorbent, MCM-41-PEI-50; weight of adsorbent, 2.0 g; temperature, 75 °C; feed flow rate, 10 mL/min. Simulated dry flue gas composition: 14.9% CO_2 , 4.25% O_2 , and 80.85% N_2 . Simulated moist flue gas composition: 13.55% CO_2 , 3.86% O_2 , 72.72% N_2 , and 9.87% H_2O .

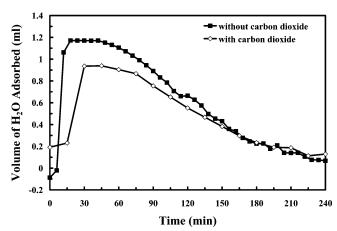


Figure 6. Comparison of the adsorbed volume of H_2O vapor by CO_2 "molecular basket" adsorbent with/without CO_2 in the feed gas mixture. Operation conditions: adsorbent, MCM-41-PEI-50; weight of adsorbent, 2.0 g; temperature, 75 °C; feed flow rate, 10 mL/min. Feed composition without CO_2 : 88.35% He and 11.65% H_2O . Feed composition with CO_2 : 13.55% CO_2 , 3.86% O_2 , 72.72% N_2 , and 9.87% H_2O .

did not change in the presence of moisture. The desorptions of CO_2 and moisture were all complete.

There are two possible reasons that may cause the increase in CO_2 adsorption capacity in the presence of moisture. First, with the adsorption of water, CO_2 may dissolve in water and therefore the CO_2 adsorption capacity increases. Second, the chemical interaction between CO_2 and PEI may be changed in the presence of water. PEI is a polymer with numerous amine groups. In dry conditions, the main reaction between amine and CO_2 is the formation of carbamate, as shown in eqs R1–R3. This limits the adsorption capacity to 1 mol of CO_2 for every 2 mol of amine group.

$$CO_2 + 2RNH_2 \leftrightarrow NH_4^+ + R_2NCOO^-$$
 (R1)

$$CO_2 + 2R_2NH \leftrightarrow R_2NH_2^+ + R_2NCOO^-$$
 (R2)

$$CO_2 + 2R_2N \leftrightarrow R_4N^+ + R_2NCOO^-$$
 (R3)

When moisture is added to the feed, the carbamate ion formed in reactions R1-R3 will further react with

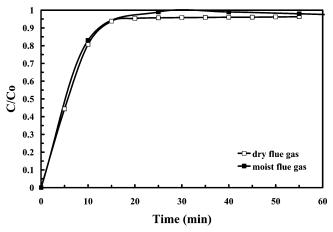


Figure 7. Comparison of the CO_2 breakthrough curve with and without moisture in the simulated flue gas by MCM-41. Operation conditions: adsorbent, MCM-41; weight of adsorbent, 2.0 g; temperature, 75 °C; feed flow rate, 10 mL/min. Simulated dry flue gas composition: 14.9% CO_2 , 4.25% O_2 , and 80.85% N_2 . Simulated moist flue gas composition: 13.62% CO_2 , 3.76% O_2 , 74.29% O_2 , and 8.33% O_2 0, 74.29% O_2 0, and 8.33% O_2 0.

 $\mathrm{CO_2}$ and $\mathrm{H_2O}$ to form bicarbonate in eq R4. The amine group itself can also directly react with $\mathrm{CO_2}$ and $\mathrm{H_2O}$ to form bicarbonate, as shown in reactions R5–R7. Therefore, in the presence of water, 1 mol of amine group can adsorb 1 mol of $\mathrm{CO_2}$.

$$\mathbf{R_2NCOO}^- + 2\mathbf{H_2O} + \mathbf{CO_2} \\ \leftrightarrow \\ \mathbf{R_2NH_2}^+ + 2\mathbf{HCO_3}^- \\ \text{(R4)}$$

$$CO_2 + RNH_2 + H_2O \leftrightarrow RNH_3^+ + HCO_3^-$$
 (R5

$$CO_2 + R_2NH + H_2O \leftrightarrow R_2NH_2^+ + HCO_3^-$$
 (R6)

$$CO_2 + R_3N + H_2O \leftrightarrow R_3NH^+ + HCO_3^-$$
 (R7)

To differentiate these two effects, adsorption separation of CO₂ by MCM-41 support only was carried out with and without moisture in the simulated flue gas. The results are shown in Figure 7. MCM-41 does not have any CO₂ affinity group, and the adsorption separation of CO₂ or H₂O by MCM-41 is mainly physical in nature. Therefore, if significant amounts of CO2 dissolve in the adsorbed H₂O, CO₂ adsorption capacity will be increased. However, adding moisture in the feed hardly influenced the adsorption of CO₂ by MCM-41 alone. CO₂ adsorption capacity was 3.2 mL(STP)/(g of adsorbent) for the simulated dry flue gas and was 3.0 mL(STP)/(g of adsorbent) for the simulated moist flue gas. At the same time, MCM-41 adsorbed significant amounts of water at the moist feed condition. Therefore, the dissolution of CO2 in the adsorbed water was very little and can be negligible. The increase in the CO2 adsorption capacity with the moist gas mixture can be ascribed to the formation of bicarbonate.

The promoting effect of moisture on the CO₂ adsorption was further clarified by comparing the volume of CO₂ and H₂O adsorbed at different adsorption time in Figure 8. At the beginning of the adsorption, CO₂ was completely adsorbed and little water adsorbed, which indicated that the adsorption of water was inhibited in the presence of CO₂. It also indicated that CO₂ adsorption occurred mainly through reactions R1–R3. Otherwise, the adsorbed amount of water should be equal to that of CO₂ according to reactions R5–R7. The adsorp-

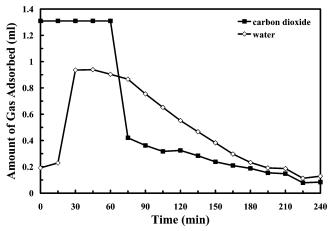


Figure 8. Comparison of the adsorbed volume of CO₂ and H₂O from simulated moist flue gas by CO2 "molecular basket" adsorbent. Operation conditions: adsorbent, MCM-41-PEI-50; weight of adsorbent, 2.0 g; temperature, 75 °C; feed flow rate, 10 mL/ min. Feed composition: 13.55% CO₂, 3.86% O₂, 72.72% N₂, and 9.87% H₂O.

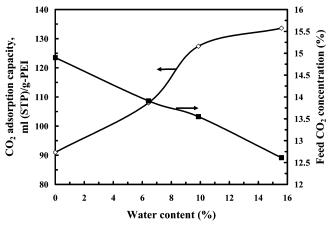


Figure 9. Influence of moisture (vapor) concentrations in the simulated moist flue gas on the CO2 adsorption separation by the "molecular basket" adsorbent. Operation conditions: adsorbent, MCM-41-PEI-50; weight of adsorbent, 2.0 g; temperature, 75 °C; feed flow rate, 10 mL/min.

tion of water sharply increased after 30 min of adsorption, which revealed that the carbamate formed in reactions R1-R3 further reacted with CO2 and water to form bicarbonate through reaction R4. The adsorption of water slightly decreased after 30 min. After 75 min, the amount of water adsorbed was larger than the amount of CO₂ adsorbed.

3.2. Effect of Moisture Concentration in the Simulated Flue Gas. The effect of moisture concentration in the simulated flue gas on the CO2 adsorption separation by the "molecular basket" adsorbent was examined. Figure 9 shows the relationship between the CO₂ adsorption capacity and the moisture concentration in the simulated flue gas. Since the simulated moist flue gas was prepared by adding moisture to the simulated dry flue gas, the CO₂ concentration in the simulated moist flue gas decreased with the increase of moisture concentration. However, although the feed CO₂ concentration decreased, CO2 adsorption capacity increased with the increase of moisture concentration in the simulated flue gas. At low moisture concentration, CO₂ adsorption capacity significantly increased with the increase of the moisture concentration in the feed. The CO₂ adsorption capacity was 90.4 mL(STP)/(g of PEI)

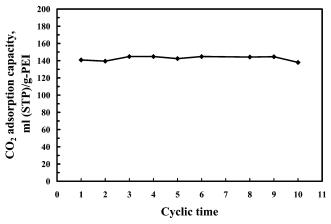


Figure 10. Cyclic CO₂ adsorption separation performance of the "molecular basket" adsorbent. Operation conditions: adsorbent, MCM-41-PEI-50; weight of adsorbent, 2.0 g; temperature, 75 °C; feed flow rate, 10 mL/min. Moist flue gas composition: 12.97% CO₂, 3.75% O₂, 70.16% N₂, and 13.12% H₂O.

for simulated dry flue gas. When 6% moisture was added to the simulated dry flue gas, CO2 adsorption capacity increased to 109 mL(STP)/(g of PEI), which was \sim 20% higher than that for simulated dry flue gas. When the feed moisture concentration further increased to \sim 10%, CO₂ adsorption capacity increased steadily to 127.4 mL(STP)/(g of PEI), which was \sim 20% higher than that when the moisture concentration was $\sim 6\%$ and \sim 40% higher than that for simulated dry flue gas. However, when the moisture concentration increased to 16%, the increase in CO₂ adsorption capacity was less pronounced. CO_2 adsorption capacity was only $\sim 5\%$ higher than that when the moisture concentration was $\sim 10\%$. It is interesting to note that, when the feed concentration of moisture is lower than that of CO2, CO2 adsorption capacity increases rapidly with the increase of moisture concentration. When the feed concentration of moisture becomes higher than that of CO₂, CO₂ adsorption capacity can hardly be further increased by the excess water.

3.3. Adsorption/Desorption Cycles. For practical application, the adsorbent should not only possess high adsorption capacity and high selectivity but also show stable performance for thousands of adsorption/desorption cycles. In our experiment, the cyclical adsorption/ desorption was carried out, and the results are shown in Figure 10. During the 10 cycles of separation, CO₂ adsorption capacity hardly changed, indicating that the desorption was complete and the adsorbent was stable in the cyclic separation process. CO₂ adsorption capacity varied between 138 and 145 mL(STP)/(g of PEI). Furthermore, the adsorption selectivity did not change either in the 10 cycles of operation. The stable adsorption and desorption performance suggests that the novel "molecular basket" adsorbent is promising for practical applications.

3.4. Stability of the Adsorbent. The structure of MCM-41 and MCM-41-PEI before and after adsorption separation was characterized by XRD. Figure 11 and Figure 12 show the XRD patterns of MCM-41 and MCM-41-PEI, respectively, before and after the adsorption separation under the moist conditions. The structure of MCM-41 alone collapsed only after 1 cycle of operation under 10% moisture, while the structure of MCM-41 for MCM-41-PEI was preserved even after 10 cycles of operation. This indicated that loading of PEI into the channels of MCM-41 protects the structure of

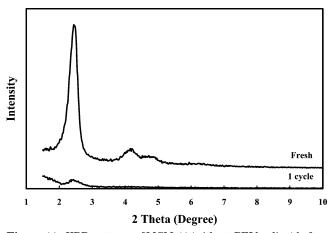


Figure 11. XRD patterns of MCM-41 (without PEI loading) before and after adsorption separation at 75 $^{\circ}\mathrm{C}$ and under simulated moist flue gas condition.

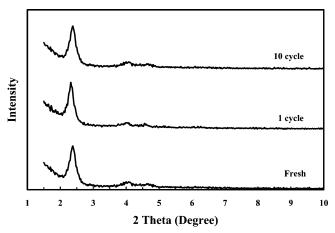


Figure 12. XRD patterns of MCM-41 in the "molecular basket" adsorbent MCM-41-PEI-50 before and after adsorption separation at 75 °C and under simulated moist flue gas condition.

MCM-41. It is well-known that MCM-41 is unstable in the presence of moisture even at medium temperature. Since PEI is more hydrophilic than MCM-41, the adsorption of water by PEI is stronger than that by MCM-41. When PEI is loaded into the channels of MCM-41, water prefers to be adsorbed by PEI. Therefore, the structure of MCM-41 was protected. The preservation of the MCM-41 structure is critically important for the adsorption separation performance of this novel "molecular basket" adsorbent.

4. Conclusion

Novel CO₂ "molecular basket" adsorbent MCM-41-PEI was successfully applied for the separation of CO₂ from simulated flue gas containing CO₂, O₂, N₂, and moisture.

Moisture has a promoting effect on the adsorption separation of CO₂ from simulated flue gas by the novel CO₂ "molecular basket". The loading of PEI into channels of MCM-41 protect the structure of MCM-41.

When the feed concentration of moisture is lower than that of the CO₂, CO₂ adsorption capacity increases rapidly with increasing moisture concentration. When the feed concentration of moisture becomes higher than that of CO₂, CO₂ adsorption capacity can hardly be further increased by the excess water. The maximum promoting effect of moisture appears at moisture concentrations approaching that of CO₂ in the feed gas.

The results of multiple adsorption/desorption separation cycles show that the MCM-41-PEI adsorbent is stable in the cyclic operations of CO2 adsorption separation from moist flue gas.

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