Influence of Moisture on Carbon Dioxide Separation from Simulated Flue Gas by A Novel "Molecular Basket" Adsorbent

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Introduction

Because of its low energy requirements, cost advantages and ease of applicability over a relatively wide range of temperature and pressure, adsorption separation is receiving increasing attention in the separation of CO_2 from various gas mixtures. Preparation of high-capacity, high-selective CO_2 adsorbents is a key factor to realize the energy-efficient adsorption separation. Recently, a new kind of high-capacity, highly-selective CO_2 adsorbents based on a "molecular basket" concept have been developed in our laboratory.[1-3] The adsorption separation of a simulated flue gas mixture, which contains 14.9% CO_2, 4.25% O_2 and 80.85% N_2, showed that a high CO_2 adsorption capacity of 91 ml (STP)/g-PEI and high CO_2/O_2 and CO_2/N_2 separation selectivity of 180 and >1000, respectively. The CO_2 adsorption capacity and CO_2/O_2, CO_2/N_2 separation selectivity with the CO_2 "molecular basket" are much higher than those of the existing adsorbents, such as zeolites and activated carbons, etc. However, several challenges still need to be overcome toward practical application. One of such challenges is the moisture, which is an important component in the gas mixtures of interest, such as flue gas and the gas from reforming for hydrogen production. On the one hand, moisture may react with the active adsorption species of amine groups in the "molecular basket" adsorbent. Therefore, moisture may compete with CO_2 to react with the active adsorption sites. Clarkson et al suggested that CO_2/CH_4 selectivity was greater for dry coals than for moisture-equilibrated coals.[4] On the other hand, the "basket" material of MCM-41 may not be stable under hydrothermal conditions. The preservation of the MCM-41 structure is critically important for the adsorption separation performance of this novel "molecular basket" adsorbent.[2] In this paper, the adsorption separation of CO_2 from simulated moist flue gas mixture containing CO_2, O_2, N_2 and moisture by using the novel "molecular basket" adsorbent is reported. The effects of moisture on the adsorption separation performance and the stability of the CO_2 "molecular adsorbent" are discussed.

Experimental

"Molecular basket" adsorbent was prepared by loading 50 wt% branched polyethylenimine (PEI, Aldrich, Mn=600) into the mesoporous molecular sieve MCM-41 (MCM-41-PEI-50).[2] The adsorption separation was carried out in a flow adsorption system.[3] Simulated dry flue gas mixture contained 14.9% CO_2, 4.25% O_2 and 80.85% N_2. Simulated moist flue gas mixture was prepared by adding moisture to the simulated dry flue gas mixture. The amount of moisture in the gas mixture was controlled by using a liquid syringe pump.

In a typical adsorption/desorption process, 2.0 g adsorbent was placed in the adsorption column. Before the adsorption separation experiment, the adsorbent was heated up to 100 ^oC in helium flow overnight to remove any CO_2 or moisture adsorbed. The temperature was then decreased to 75 ^oC and the simulated dry or moist flue gas mixture was introduced with a flow rate of 10 ml/min. Generally, the adsorption was carried out for 240 minutes. After the adsorption, helium with a flow rate of 50 ml/min was used to perform the desorption at the same temperature. The time for desorption was 300 minutes. The concentration of the gases in the effluent gas mixture was analyzed by on-line GC. Gas flow rate was measured every five minutes. Adsorption capacity in ml (STP) of adsorbate/g adsorbent and desorption capacity in percentage were used to evaluate the adsorbent. The adsorption/desorption capacity was calculated from the mass balance before and after the adsorption. The separation factor, $\alpha_{i/j}$, was calculated from equation 1 as the ratio of the amount of gases adsorbed by the adsorbent, $(n_i/n_j)_{adsorbed}$, over the ratio of the amount of gases fed into the adsorbent bed, $(n_i/n_j)_{feed}$:

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

"Molecular basket" adsorbent before and after adsorption separation was characterized by X-ray diffraction (XRD). The XRD patterns were obtained on a Scintag Pad V using Cu K_α radiation.

Results and Discussions

1. Adsorption separation of CO_2 from simulated moist flue gas

Figure 1 compares the CO_2 breakthrough curve, where the amount of CO_2 is followed as the fraction of the CO_2 concentration in the effluent gas from the adsorption column, C, over that of the CO_2 concentration in the feed, C_0, during the separation of CO_2 from the simulated flue gas mixtures without moisture and with ~ 10% moisture at 75 ^oC and ambient pressure. In the presence of moisture, the "molecular basket" adsorbent can still effectively adsorb CO_2. At the beginning of the separation, CO_2 was completely adsorbed by the adsorbent and the CO_2 concentration was below the detection limit of the gas chromatography, i.e. < 100 ppm. After 60 minutes of adsorption, CO_2 breakthrough was observed in the effluent gas. Compared with the adsorption separation of CO_2 from simulated dry flue gas mixture under the same conditions, the breakthrough time increased when a moist gas mixture was used, which indicates that moisture has a promoting effect on the adsorption of CO_2 by the "molecular basket" adsorbent. Even after 120 minutes adsorption, the "molecular basket" adsorbent still adsorbed ~ 20% of CO_2 from the simulated moist flue gas mixture, whereas only 5% of CO_2 adsorbed from the simulated dry flue gas mixture. CO_2 adsorption capacity increased from 90.4 ml (STP)/g-PEI for simulated dry flue gas mixture to 129.9 ml (STP)/g-PEI for simulated moist flue gas mixture. The increase in the CO_2 adsorption capacity may be explained by the formation of bicarbonate under the moist condition, rather than carbonate under dry condition.

2. Effect of moisture concentrations in the simulated flue gas mixture on the adsorption separation

Figure 2 shows the relationship between the CO_2 adsorption capacity and the moisture concentrations in the simulated flue gas mixture. Since the simulated moist flue gas mixture was prepared by adding moisture to the simulated dry flue gas mixture, CO_2 concentration in the simulated moist flue gas mixture decreased with the increase of moist concentration. However, although the feed CO_2 concentration decreased, CO_2 adsorption capacity increased with the increase of moist concentration in the simulated flue gas mixture. At low moisture concentration, CO_2 adsorption capacity increased rapidly with the increase of the moisture concentration in the feed. The CO_2 adsorption capacity was 90.4 ml (STP)/g-PEI when dry flue gas mixture was used. When 6% moisture was added to dry flue gas mixture, CO_2 adsorption capacity increased to 109 ml (STP)/g-PEI, which was ~20% higher than that when dry flue gas mixture was

used. When the feed moisture concentration further increased to ~ 10%, CO_2 adsorption capacity increased steadily to 127.4 ml (STP)/g-PEI, which was ~20% higher than that of when the moisture concentration was ~6% and ~40% higher than that of when dry flue gas mixture was used. However, when the moisture concentration increased to 16%, the increase in CO_2 adsorption capacity recessed. CO_2 adsorption capacity was only ~5% higher than that of when the moisture concentration was ~10%. It is interesting to note that, when the feed concentration of moisture is lower than that of the CO_2, CO_2 adsorption capacity increases rapidly with the increase of moisture concentration. When the feed concentration of moisture becomes larger than that of the CO_2, CO_2 adsorption capacity can hardly be further increased by the excess water.

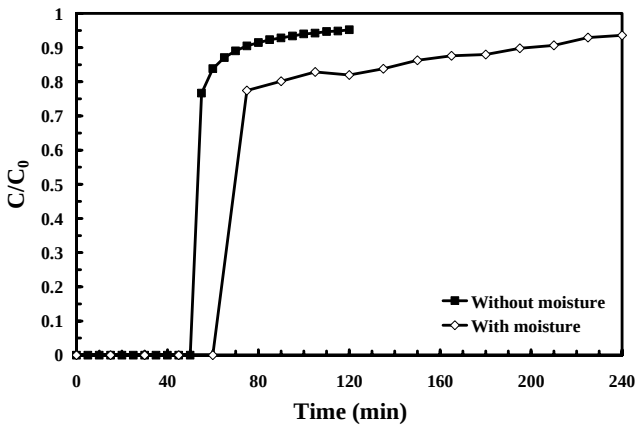

Figure 1. Comparison of CO_2 breakthrough curves with/without moisture in the simulated flue gas. Temperature: 75 ^oC; Feed flow rate: 10 ml/min. Dry feed composition: 14.9% CO_2, 4.25% O_2 and 80.85% N_2; Moist feed composition: 13.55% CO_2, 3.86% O_2, 72.72% N_2 and 9.87% H_2O.

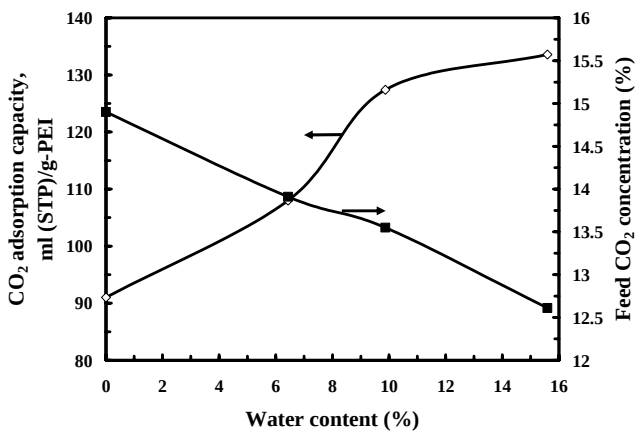

Figure 2. The influence of moisture concentrations in the simulated flue gas mixture on the CO_2 adsorption separation. Operation condition: Weight of adsorbent: 2.0 g; Temperature: 75 ^oC; Feed flow rate: 10 ml/min.

3. Cyclic adsorption/desorption and stability of the adsorbent

For practical application, the adsorbent should not only possess high adsorption capacity and high selectivity, but also show stable performance for hundreds of adsorption/desorption cycles. In our experiment, the cyclical adsorption/desorption was carried out, and the results are shown in Figure 3. During the 10 cycles of separation, CO_2 adsorption capacity hardly changed, which indicated that the desorption was complete and the adsorbent was stable in the cyclic separation process. CO_2 adsorption capacity varied between 138 to 145 ml (STP)/g-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.

The structure of MCM-41 and MCM-41-PEI before and after adsorption separation was characterized by XRD (not shown). The structure of MCM-41 alone collapsed only after 1 cycle operation under 10% moisture, while the structure of MCM-41 for MCM-41-PEI preserved even after 10 cycles of operation. This indicated that loading of PEI into the channels of MCM-41 protect the structure of MCM-41. It is well known that the 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 of 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.[2]

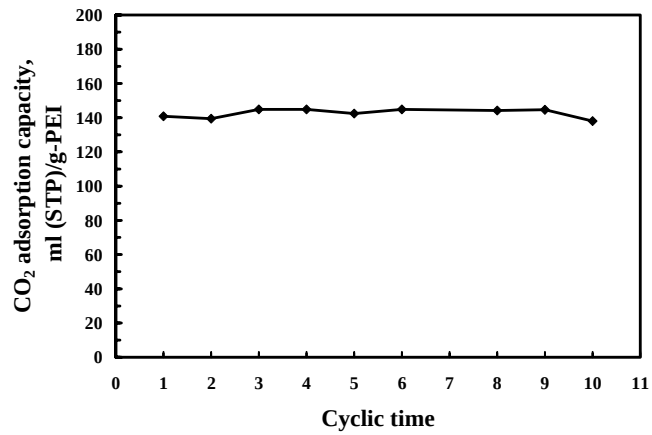

Figure 3. Stability of the "molecular basket" adsorbent in the cyclic CO_2 adsorption/desorption separations. Temperature: 75 ^oC; Feed flow rate: 10 ml/min; Moist flue gas composition: 12.97% CO_2, 3.75% O_2, 70.16% N_2 and 13.12% H_2O

Conclusions

Moisture has a promoting effect on the adsorption separation of CO_2 from simulated flue gas mixture by the novel CO_2 "molecular basket" based on MCM-41-PEI-50. Maximum promoting effect of moisture appears at moisture concentrations approaching that of CO_2 in the flue gas. The cyclic adsorption/desorption separation results show that the novel "molecular basket" adsorbent is stable in the cyclic operations of CO_2 adsorption separation from moist flue gas.

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