Effect of Type of Polymers Loaded in Mesoporous Carbon Dioxide "Molecular Basket" Adsorbent on Carbon Dioxide Separation from Gas Mixtures

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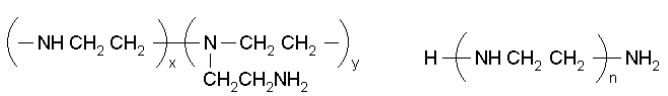
Introduction

Separation of CO_2 from various gaseous streams is becoming increasingly important in the field of energy production and sustainable use of fossil energy.[1] Currently, CO_2 separation is applied in industry during natural gas processing and during hydrogen production processing. On the other hand, significant increase in the global atmospheric CO_2 concentration has caused serious concern for the global climate change and has led to a worldwide effort in research and development on control of CO_2 emission.[2] Moreover, CO_2 also represents an important source of carbon for fuel and chemical feedstock in the future.[3] These have further created a demand for cost-effective CO_2 separation technology.

The known options for carbon dioxide separation include chemical and physical absorption, physical and chemical adsorption, cryogenic separation and membrane separations.[1] The key issue for adsorption separation is to prepare high performance adsorbent. Recently, we developed a new kind of high-capacity, highly selective carbon dioxide adsorbent, which is called carbon dioxide "molecular basket".[4,5] By loading CO_2-philic materials, such as sterically branched polymer polyethylenimine (PEI), into mesoporous molecular sieve MCM-41, carbon dioxide adsorption capacity was significantly increased.[4,5] In this paper, different types of PEI are investigated to further improve the carbon dioxide adsorption separation performance of the novel "molecular basket".

Experimental

The "molecular basket" adsorbents were prepared by modifying the siliceous MCM-41 with PEI through a wet impregnation method.[4,5] Two types PEI, i.e., linear PEI (Aldrich, Mn: ~423) and branch PEI (Aldrich, Mn: ~600) were used. The molecular structures of the linear PEI and the branch PEI are illustrated in Figure 1. From the molecular formula, it can be seen that the branch PEI consists of primary, secondary and tertiary amine groups, while the linear PEI only contains mainly the secondary amine group. The PEI loading for the "molecular basket" adsorbents is 50 wt%. The as-prepared adsorbents are denoted as MCM-PEI-L and MCM-PEI-B, where L represents linear PEI and B represents branch PEI.



(a) (b)

Figure 1. Illustration of the molecular formulas for branch PEI (a) and linear PEI (b).

The adsorption and desorption performance of the adsorbent was measured by using a PE-TGA 7 analyzer.[4,5] Adsorption capacity in mg of adsorbate/g-adsorbent and desorption capacity in percentage were used to evaluate the adsorbent and were calculated from the weight change of the sample in the adsorption/desorption process. Desorption capacity in percentage was defined as the ratio of the amount of the gas desorbed over the amount of gas adsorbed. The adsorption/desorption temperature of 75 ^oC and the adsorption and desorption time of 150 min were selected because our previous investigation showed that the MCM-41-PEI exhibited the best adsorption/desorption performance at 75 ^oC; and that the adsorption nearly reached equilibrium and the desorption was complete after 150 min.[4,5]

The adsorption separation was carried out in a flow adsorption separation system described in reference 6.[6] Simulated flue gas mixture containing 14.9% CO_2, 4.25% O_2 and 80.85% N_2 was used as the adsorbate. The adsorption time was 120 minutes and the desorption time was 600 minutes. The concentration of the gases in the effluent gas and the gas flow rate were measured every 5 minutes. Adsorption capacity in ml (STP) of CO_2/g-adsorbent and desorption capacity in percentage were used to evaluate the performance of the adsorbents. 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, $(n_i/n_j)_{feed}$:

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

Results and Discussions

1. Influence of PEI Type on CO_2 Adsorption/Desorption

Figure 2 shows the single CO_2 adsorption/desorption properties measured by TGA. The CO_2 adsorption capacities are 153.5 mg/g-adsorbent and 117.2 mg/g-adsorbent for MCM-PEI-L and MCM-PEI-B, respectively. The CO_2 adsorption capacity for MCM-PEI-L is 31% higher than that for MCM-PEI-B. The desorption for MCM-PEI-L and MCM-PEI-B are all complete, which indicates that the "molecular adsorbent" may be used in many cyclic operations. Our previous results showed that the MCM-PEI-B was stable in ten cyclic adsorption/desorption operations.[5,6]

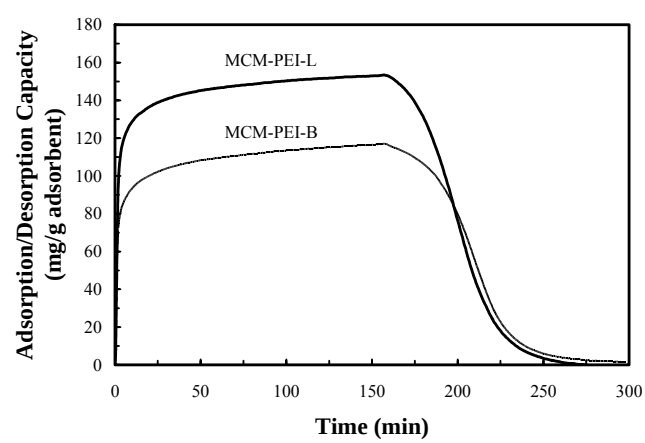


Figure 2. CO_2 adsorption/desorption properties of MCM-PEI-L and MCM-PEI-L measured by TGA.

Types of PEI also greatly affect the CO_2 adsorption/desorption rate of the "molecular basket" adsorbents. From Figure 2, it is clear

that CO_2 desorption rate for MCM-PEI-L is faster than that for MCM-PEI-B. However, the difference in CO_2 adsorption rate for MCM-PEI-L and MCM-PEI-B, especially at the beginning of the adsorption, is not clear from Figure 2. In order to clarify the CO_2 adsorption kinetics, CO_2 adsorption in the first 5 minutes is plotted and shown in Figure 3. Obviously, the rate of CO_2 adsorption for MCM-PEI-L is much faster than that for MCM-PEI-B. Since different types of amines groups have different heats of adsorption, the difference in the CO_2 adsorption/desorption capacity and in the adsorption/desorption rate of the "molecular basket" adsorbents may be explained by the different types of amine groups in the PEI. The fast adsorption and desorption kinetic is important for the adsorption separation.

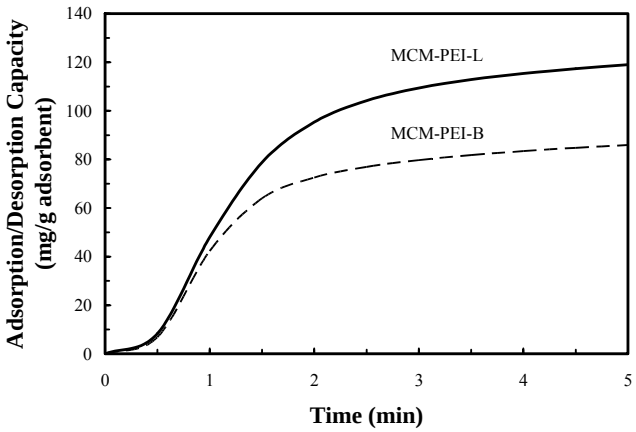


Figure 3. Comparison of the CO_2 adsorption kinetics of MCM-PEI-L and MCM-PEI-B measured by TGA.

2. Effect of PEI Type on CO_2 Separation from Simulated Flue Gas

Figure 4 compares the breakthrough curve of CO_2 in the separation of CO_2 from simulated flue gas, which contains 14.9% CO_2, 4.25% O_2 and 80.85% N_2, for MCM-PEI-L and MCM-PEI-B. At the beginning of the separation, CO_2 is completely adsorbed by the "molecular basket" adsorbents and the CO_2 concentration is below the detection limit of the gas chromatography, i.e. < 100 ppm. After 55 minutes of adsorption, CO_2 began to breakthrough for MCM-PEI-B, while CO_2 is still completely adsorbed for MCM-PEI-L. The breakthrough time for MCM-PEI-L is 90 minutes. The calculated CO_2 breakthrough capacities are 67.1 ml/g-adsorbent and 40.9 ml/g-adsorbent for MCM-PEI-L and MCM-PEI-B, respectively. The CO_2 breakthrough capacity for MCM-PEI-L is 64% higher than that for MCM-PEI-B. Both adsorbents hardly adsorb any N_2 and O_2. The estimated separation factors for CO_2/N_2 and CO_2/O_2 are larger than 1000.

Figure 5 compares the desorption performance of MCM-PEI-L and MCM-PEI-B. For both adsorbents, the adsorbed CO_2 can all be desorbed in 6 hours. However, the rate for CO_2 desorption for the two adsorbent is different. The MCM-PEI-L desorbs CO_2 faster than the MCM-PEI-B, which is in accordance with that observed in the TGA measurements.

Conclusions

Highly effective CO_2 "molecular basket" adsorbent can be prepared by using mesoporous molecular sieve MCM-41 and polyethylene imine with a linear structure. The adsorbent with linear PEI shows not only a higher CO_2 adsorption capacity, but also a faster CO_2 adsorption/desorption rate, than those for the "molecular basket" adsorbent with branched PEI.

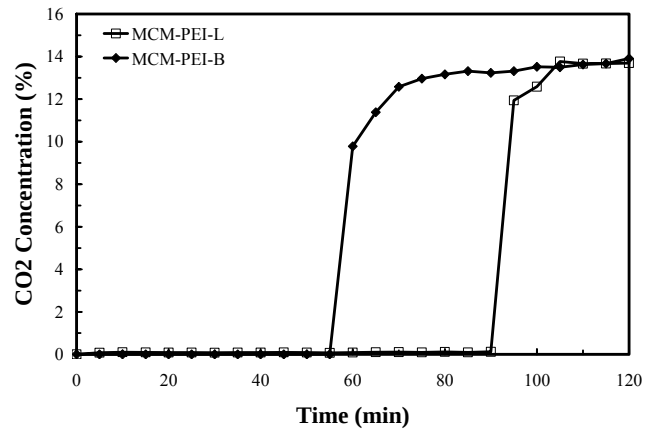


Figure 4. Comparison of CO_2 breakthrough curves in the separation of CO_2 from simulated flue gas for MCM-PEI-L and MCM-PEI-B. Operating condition: Weight of adsorbent: 2.0 g; Feed flow rate: 10 ml/min; Temperature: 75 ^oC.

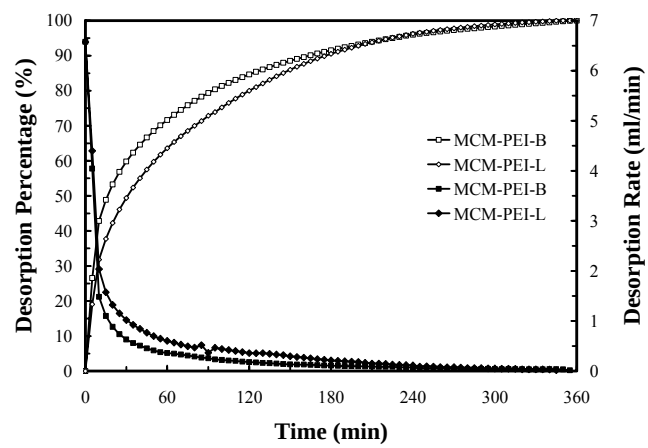


Figure 5. Comparison of CO_2 desorption in the separation of CO_2 from simulated flue gas for MCM-PEI-L and MCM-PEI-B. (◊, □) desorption percentage, (■, ▲) desorption rate.
Operation condition: Weight of adsorbent: 2.0 g; Temperature: 75 ^oC; Sweep gas flow rate: 50 ml/min.

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