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Effect of carbon pore structure on the CH_4/N_2 separation

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Abstract The separation between CH_4 and N_2 bears importance in coalbed methane enrichment, and activated carbon is a major adsorbent for industrial PSA (pressure swing adsorption) separation. However, the adsorption of both gases shows supercritical features, and the physicochemical properties are also similar, which results in similar adsorption behavior and renders the separation difficult. To maximize the separation coefficient, the effect of carbon pore structure on the separation was studied and a series of carbons was prepared at different extent of activation. The effect of specific surface area, pore size and pore volume on the separation coefficient was observed and a linear correlation between the separation coefficient and the small pore (0.7–1.3 nm) volume reduced to unit surface area was shown.

Keywords Adsorption · Separation · CH_4/N_2 · Methane enrichment · Activated carbon

1 Introduction

The separation between CH_4 and N_2 bears importance in the enrichment of coalbed methane (CBM). The world's CBM reserve is more than two times higher than that known to natural gas (Jiang 2010). To commercially utilize CBM, methane enrichment is necessary. The methane content in the coalmine's drainage gas is usually 20–45 %. It must be raised to higher than 80 % for the application of chemical raw stock and higher than 90 % for merging into the civil gas system (Engelhard 2005). N_2 is the major component of CBM next to CH_4, and the two gases form the pair of key components of the CBM enrichment. However, the two gases possess similar physicochemical properties, and both are supercritical gases at ambient temperature. The separation between them has been considered as a real challenge (Ruthven 2000). Nonetheless, PSA is a feasible technology for the enrichment especially in middle or small scales due to the relatively lower energy and investment cost (Ruthven 1984; Yang 1987; Ruthven et al. 1994). However, the adsorbent suitable for the PSA separation is still under development (Yang 2003). Adsorption selectivity is of the first importance in selecting adsorbent because less selectivity results in poor separation and higher separation cost. The adsorption selectivity may be shown either in equilibrium adsorption or adsorption kinetics. Although remarkable progress has been made in the latter respect (Jayaraman et al. 2004, 2005; Kouvelos et al. 2007), the industrial PSA separation still relies on the equilibrium difference on activated carbons, though the separation selectivity is not satisfactory (Fatehi et al. 1995; Baksh et al. 1990; Buczek 1996). Here we investigated the effect of structure parameters of porous carbon on the separation coefficient between CH_4 and N_2, and a series of carbon samples were prepared at different extent of activation. Adsorption isotherms were collected on the samples, from which the separation coefficient was evaluated. As result, the effect of structural parameters of carbon pores on the separation may be explicitly shown. The experimental result was further discussed with the analysis based on molecular simulation.

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Table 1 Pore size distribution and total pore volume and surface area of eight samples

Pore size nm	No. 1 cm^3/g	No. 2 cm^3/g	No. 3 cm^3/g	No. 4 cm^3/g	No. 5 cm^3/g	No. 6 cm^3/g	No. 7 cm^3/g	No. 8 cm^3/g
0.7–0.8	0.020	–	–	–	–	–	0.013	0.017
0.8–0.9	0.001	0.129	0.123	–	–	–	–	–
0.9–1.0	0.085	0.041	0.048	0.157	0.155	0.102	0.104	0.071
1.0–1.1	0.027	0.027	0.040	0.034	0.036	0.037	0.027	0.033
1.1–1.3	0.039	0.049	0.074	0.075	0.078	0.048	0.048	0.048
1.3–1.5	0.034	0.000	0.022	0.037	0.013	0.024	0.030	0.076
1.5–1.7	0.031	0.047	0.068	0.086	0.100	0.135	0.148	0.171
1.7–2.0	0.012	0.024	0.040	0.063	0.076	0.071	0.067	0.017
2.0–3.0	0.009	0.018	0.028	0.070	0.117	0.127	0.128	0.041
3.0–4.0	0.001	0.016	0.010	0.014	0.099	0.386	0.458	0.483
4.0–5.0	–	0.003	0.005	–	0.001	0.070	0.109	0.479
>5.0	0.005	0.006	0.015	0.011	0.016	0.032	0.020	0.405
V_{pore} cm^3/g	0.264	0.360	0.473	0.547	0.692	1.033	1.153	1.840
A_{BET} m^2/g	720	876	1143	1368	1700	2312	2578	2803

2 Experimental

2.1 Material

Carbon samples were prepared from carbonized corncobs at different extent of activation in a physical activation process based on steam. Carbon samples were characterized based on the adsorption/desorption isotherms of N_2 at 77 K collected on Micromeritics ASAP 2020. The surface area was calculated with the BET theory (Brunauer et al. 1938) and the pore size distribution was determined with the DFT model (Lastoskie et al. 1993). The surface area, pore volume and pore size distribution are presented in Table 1. All gases used in experiments were provided by Liufang Gas Co. Tianjin. The purity of He and CH_4 is higher than 99.99 % and that of N_2 is higher than 99.9 %. The composition of the gas mixture used in experiments was 86.58 % of He, 7.12 % of CH_4, and 6.30 % of N_2.

2.2 Apparatus

Experiments were carried out on a setup schematically shown in Fig. 1. Carbon particles of dimension 0.25–0.38 mm were packed in a tube of length 250 mm and inner diameter 10 mm. Two mass flow controllers Type SY-9312 of precision ±1 % were used to control the flow rate in two passages. One passage was for gas mixture, and another for helium. A backpressure regulator was used to control adsorption pressure and a pressure transducer Type SY-9411 of accuracy ±0.1 % was used to detect the pressure. The zero point of transducers was adjusted automatically to compensate for the fluctuation of room temperature. The pressure at both entrance and exit of the adsorption bed was detected with the same pressure transducer using two T-way valves, and the pressure drop over the adsorption bed was thus obtained. Composition of the effluent stream was analyzed by a Quadruple mass spectrograph manufactured by the Stanford Research Systems, Inc. USA. All parts were connected by stainless steel capillary tubes of inner diameter 2 mm and wall thickness 0.5 mm. Signals of pressure, temperature, flow rate and composition were transferred to a

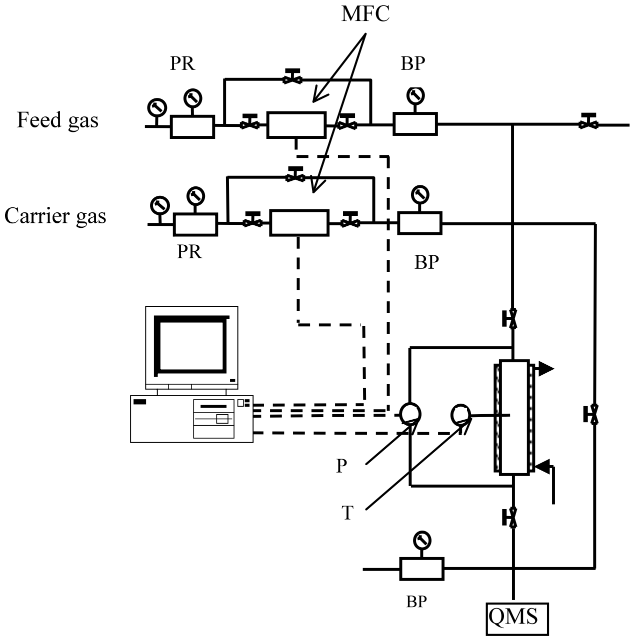

Fig. 1 Schematic flowchart of experimental setup. PR, pressure regulator; MFC, mass flow controller; BP, back-pressure regulator; P, pressure transducer; T, T-type thermocouple; QMS, gas analyzer

computer in using PC-lab cards PCLD-880 and PCL-812PG purchased from the Advantech Co., Ltd. Beijing. The computer recorded the variation of signals with time and issued commands of experiments according to a prescribed program.

3 Theoretical

3.1 Evaluation of separation coefficient based on experiments

The adsorption selectivity of adsorbents was usually reported as the ratio of adsorbed amounts of two gases at a specified temperature and pressure (Buczek 1996) or as the thermodynamically defined separation coefficient (Ruthven et al. 1994):

$$\alpha_{ij} = \frac{(x/y)_i}{(x/y)_j} \tag{1}$$

where x and y is the molar fraction of component i and j in the adsorbed and gas phase at equilibrium. The separation coefficient can be evaluated either based on the adsorption isotherms of pure CH_4 and N_2 or based on breakthrough curves collected experimentally with gas mixtures. In the former case, a prediction model for multi component adsorption is used to determine the composition of equilibrium phases, and the relative prediction error can be less than 10 % (Wu et al. 2007). In the latter case, helium is added to the mixture of CH_4 and N_2 serving as diluting gas because He was supposed not to adsorb on adsorbents. The content of He in mixture is kept larger than 50 % in order for maintaining an isothermal adsorption condition (Yang 1987). Other conditions necessary for the reliability of evaluation include keeping the adsorption bed isothermal, small pressure drop over the sorption bed and plug flow of gas stream. The calculation of separation coefficient based on breakthrough experiments was described in the literature (Yang 1987), and the reliability of evaluation was also previously proven (Wu et al. 2007).

3.2 Evaluation of separation coefficient based on simulation

The Grand Canonical Monte Carlo (GCMC) simulation (Do and Do 2005) was used to evaluate the adsorption at molecular level and to compare with the experimental result. The adsorption software package of Materials Studio of Accelrys Inc. (2006) was applied to obtain adsorption isotherms of gases. The Van der Waals contribution was cut off at five times the collision diameter of fluid. One million cycles were typically needed for the system to reach equilibrium, and additional one million cycles were used to obtain the ensemble average. The width H of a pore was defined as the distance between the atom centers that located at the opposite surfaces. Periodic boundary conditions were imposed on carbon pores only for the x and y directions (Herrera et al. 2008). Simulations were carried out at a fixed pore width and a constant temperature. The H value was set at 0.6, 0.7, 0.75, 0.8, 0.85, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 2.0, 2.5, 3.0, 4.0, and 5.0 nm, which covered a range from micropore to mesopore. Molecular simulation determines the absolute adsorption, i.e., the total number of adsorbed molecules; therefore, the bulk gas density must be subtracted from the total adsorbed molecules in order to obtain the surface excess quantity:

$$n = \frac{N_{\text{tot}} - N_{\text{EOS}}}{N_0 V_{\text{pore}}} \tag{2}$$

where N_{tot} is the total number of molecules in the pore; N_{EOS} is the number of molecules in the pore without adsorption, which was determined by an equation of state; N_0 is the Avogadro constant, and V_{pore} is the pore volume. The separation coefficient on a carbon sample with a special pore size distribution is determined from:

$$\alpha_{ij,\text{av}} = \frac{(x_{i,\text{av}}/x_{j,\text{av}})}{(y_i/y_j)} \tag{3}$$

For the given composition of gas phase, y_i and y_j, the composition of adsorbed phase may vary depending on pore size; therefore, an average composition of the adsorbed phase, $x_{i,\text{av}}$ and $x_{j,\text{av}}$, were used and determined as:

$$x_{i,\text{av}} = \frac{\sum^k n_i}{\sum^k n_i + \sum^k n_j} \tag{4}$$

where k is the pore size index of the PSD function, and n_i and n_j are the molecule numbers adsorbed in the pore indexed with ‘k’. Similarly,

$$x_{j,\text{av}} = \frac{\sum^k n_j}{\sum^k n_i + \sum^k n_j} \tag{5}$$

For a pore indexed with k:

$$n_{k,i} = \rho_{k,i} \times V_{k,i} \tag{6}$$

where $V_{k,i}$ is the volume of the pore with width H_k, which is given by the PSD function, and $\rho_{k,i}$ is the ratio of the adsorbed molecule numbers over the volume of the pore with width H_k.

4 Results and discussion

4.1 Experimental separation coefficient

A typical set of breakthrough curves is shown in Fig. 2. The measurement condition was 298 K and 0.4 MPa of the total pressure. The pressure drop over the adsorption bed was

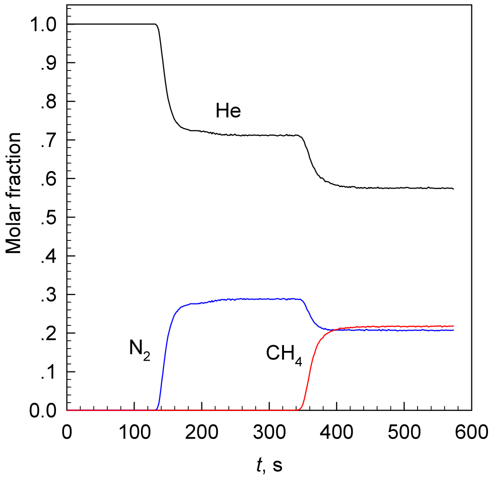

Fig. 2 A typical set of breakthrough curves

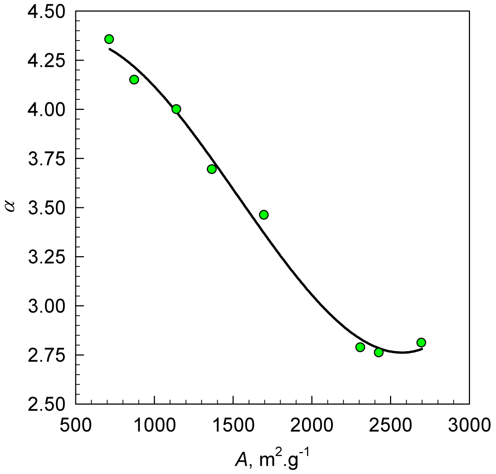

Fig. 3 Variation of separation coefficient with surface area of carbons

less than 0.3 %. The flow rate of gas stream was kept at 200 cm^3/min. The separation coefficients on eight samples changed negatively with the increasing surface area of carbons as shown in Fig. 3.

4.2 Theoretical evaluation and correlation of separation coefficient

The separation coefficient generated in GCMC simulation is shown in Fig. 4. Apparently, the separation coefficient (α) varies basically with pore size. It reaches a peak value in the pore of width 0.75 nm, and pore size will not show significant effect when it becomes larger than 1.3 nm. Therefore, the small pores with width 0.7–1.3 nm contribute the most to the separation. However, the volume of the specified pores does not correlate with the separation coefficient as shown in Fig. 5. It is the pore volume of the specified sizes reduced to unit surface area that correlates linearly with the separation

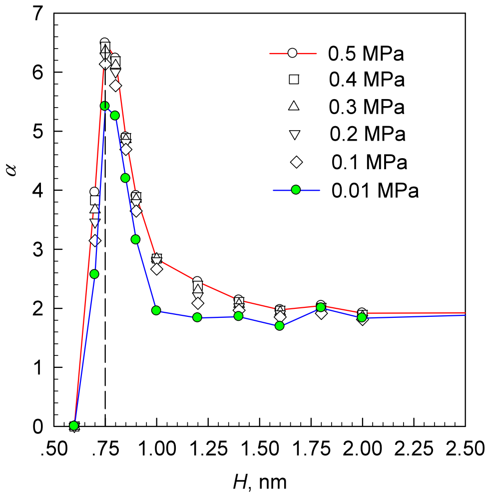

Fig. 4 The separation coefficient based on GCMC simulation

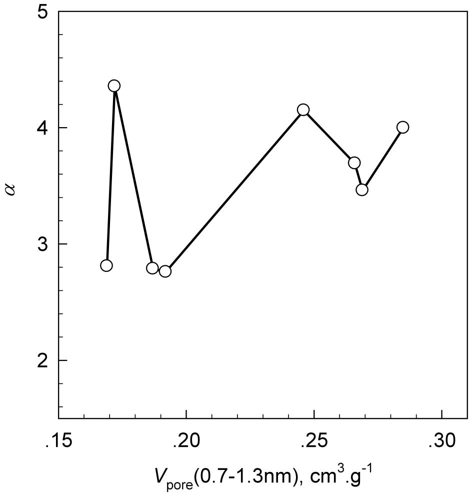

Fig. 5 Correlation of separation coefficient with pore volume for the range 0.7–1.3 nm

coefficient as shown in Fig. 6, and the correlation coefficient was 0.94. Therefore, the direction to improve the separation adsorbent should be: large pore volume for the range of 0.7–1.3 nm per unit specific surface area.

The ratio of pore volume over the specific surface area yields the dimension of the slit pore width; however, there is no linear relationship between α and H as shown in Fig. 4. As is well known that larger specific surface of carbon yields larger adsorption capacity, therefore, a carbon of fully developed surface is preferred in practice. However, the indicated pore structure index must be kept as much as possible during activation in order to maintain a larger separation coefficient. Activated carbon does have a shortcoming being an adsorbent for the separation between nitrogen and methane because methane will not be the column top product in a con-

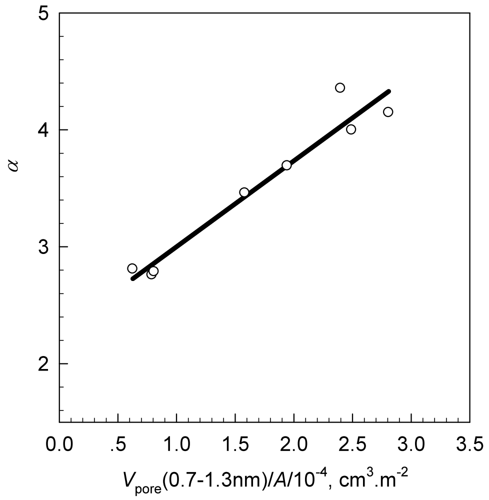

Fig. 6 Correlation of separation coefficient with pore volume for the range 0.7–1.3 nm reduced to unit surface area

ventional PSA process. However, this shortcoming could be mitigated through process modification, for example, with incorporation of a CO_2-displace step as has been shown (Liu et al. 2011).

5 Conclusion

The effect of carbon pore structure on the separation between CH_4 and N_2 was experimentally and theoretically studied. The experimentally measured separation coefficient varies negatively with the increasing surface area of carbons. Theoretical analysis indicated that the adsorption difference of two gases reached peak value in small pores sized for 0.7–1.3 nm. However, the pore volume for the specified range does not directly correlate with the separation coefficient. It is the pore volume in the specified range reduced to unit surface area of carbons that correlates linearly with the separation coefficient.

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