Adsorption and Desorption Properties of Coalbed Methane on SBA-15

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The adsorption and desorption properties of coalbed methane on SBA-15 and activated carbon (AC) with the same process were investigated. For the three adsorbents, the adsorption capacity to coalbed methane is the following sequence, activated carbon > SBA-15. The results showed that coalbed methane desorbed from the surface of SBA-15 is easily compared with the other materials. However activated carbon is easier than both of them. Both of adsorption capacity and adsorption strength of SBA-15 sample to coalbed methane are lower than the other two adsorbents, most likely due to the pore diameter of the SBA-15 sample is larger to the molecular diameter of methane. However SBA-15 sample has a larger pore size and specific surface area relative to conventional materials sample, which result in a large value of adsorption capacity of modified SBA-15 sample to coalbed methane. In addition, although the adsorption capacity of SBA-15 sample to coalbed methane is lower in contrast to activated carbon, modified SBA-15 sample is easy to regenerate and has a short time of desorption. Hence, SBA-15 sample, as an adsorbent, is a good choice for the condition of low concentration of coalbed methane.

Keywords: Coalbed methane, Activated carbon, SBA-15, Adsorption, Desorption.

INTRODUCTION

Coalbed methane is a gas formed as part of the geological process of coal generation and is contained in varying quantities within all coal. Coalbed methane is exceptionally pure compared to conventional natural gas, containing only very small proportions of "wet" compounds (*e.g.*, heavier hydrocarbons such as ethane and butane) and other gases (*e.g.*, hydrogen sulfide and carbon dioxide)[1-4]. Coalbed gas is over 90 percent methane and is suitable for introduction into a commercial pipeline with little or no treatment.

In recent decades, many techniques have been studied and applied to treat coalbed methane, such as adsorption[5], burning[6], membrane separation process[7], biological process[8] and catalytic oxidation[9] *etc*. While adsorption method, which is widely utilized in treating and recycling the low concentration of coalbed methane and had advantages of high removal rate, quite purification and low energy consumption, is a very common process for coalbed methane gas purification in the industry. Among the adsorption technologies, the superior activated carbon as the adsorbent considered being an economical and reasonable process route has been widely used. However, coalbed methane emissions based on industry often contain water vapor, which has great influence on the performances of adsorption and desorption to activated carbon.

Especially, activated carbon is combustible material and its regeneration is difficult[10,11]. Silica gel with the properties of good chemical and thermal stability, high mechanical strength is a common adsorbent, while its pore size distribution is narrow[12]. Zeolites as the adsorbent have numbers of significant features such us good shape selectivity, high adsorption intensity and little effect to adsorbate, thus zeolites as the adsorbent have become the most versatile and valuable adsorbents compared to others[13,14].

In the work reported here, the adsorption and desorption properties for representative coalbed methane, methane, on three inorganic materials (activated carbon and SBA-15) were investigated. It was found that SBA-15 has a greater adsorption property relative to the conventional materials and it is more easily for methane to desorb from the SBA-15 in contrast to activated carbon.

EXPERIMENTAL

Methane was purchased from shanxi Kezhicheng company; SBA-15; activated carbon (AC) were purchased from Nanjing XFNANO Materials Tech Co.,Ltd.

Characterization: The values of specific surface area and pore capacity were obtained from Micromeritics ASAP2020C adsorption apparatus. Prior to the measurement, each sample should be heated at 260 °C for 140 min to remove the physically

adsorbed water and small organic impurities adsorbed in pores. The samples were heated at 10 °C to 550 °C with the rate 5 °C/min to do the temperature-programmed desorption (TPD) experiment, using the Micromertics Autochem 2910 apparatus. Throughout the TPD experiment, the concentration of coalbed methane in the gas stream was monitored by thermal conductivity cell. the thermal conductivity detector of a GC-5890F gas chromatograph (GC).

Methane adsorption: The adsorption experiments of methane, on conventional materials, modified SBA-15 and activated carbon as adsorbent were investigated. The adsorption and desorption experiment was carried out on the traditional experimental set-up[15,16]. The outlet gas samples were analyzed on-line using GC-5890F gas chromatograph (GC).

In this procedure, the zeolites and activated carbon was used with the weight of 60 g, the temperature for adsorption was 50 °C and the area of adsorbent bed was 25 mm × 300 mm.

The equilibrium adsorption capacity of samples is obtained through the following relation[17].

$$q = \frac{F \times c_0 \times 10^{-9}}{W}\left[t_s - \int_0^{t_s} \frac{c_i}{c_0}\, dt\right]$$

where: q is the equilibrium adsorption capacity, (g/g); F is the gas flow rate, (mL/min); C_0 is the concentration of coalbed methane from inlet gas after t min, (mg/m³); C_i is the concentration of coalbed methane from outlet gas after t min, (mg/m³); W is the weight of adsorbent, (g); t_s is the time of equilibrium adsorption, (min).

RESULTS AND DISCUSSION

Characterization of SBA-15: The values of the pore structural of SBA-15 and activated carbon are summarized in Table-1. Compared with activated carbon, the SBA-15 has a much lower value of the specific surface areas and pore volume. However, SBA-15 sample as promising adsorbent material has a higher specific surface area and pore volume relative to conventional materials, respectively. There is a large difference between the pore volume and micropore volume of SBA-15, indicated that the sample has a large numbers of holes with micropore size and has a more highly external surface areas in contrast to the conventional materials, respectively.

TABLE-1
PORE STRUCTURAL PROPERTIES OF ACTIVATED CARBON, SBA-15

Sample	BET (m² g⁻¹)	Micro-BET (m² g⁻¹)	Micropore size (nm)
Activated carbon	928.75	760.56	0.3-4.0
SBA-15	660.57	257.47	5-6

Adsorption performances of adsorbents: Breakthrough time: The breakthrough times, to reach an outlet gas concentration equal to 50 % of the inlet gas concentration, were performed to evaluate the adsorption properties of the three adsorbents. With a longer breakthrough time as an important index to appraise adsorbent materials, the adsorbents are considered to have good adsorption performance.

Representative results of the breakthrough time from methane adsorbed/desorbed on SBA-15 sample, activated

carbon are shown in Fig. 1, respectively. The breakthrough time of activated carbon is longer than the SBA-15 obviously. The SBA-15 samples with a higher Si/Al ratio were selected in the work reported here. Hence, they have superior hydrophobic performances[16] and would avoid the effect from steam in the gas. In humid environments, however, there is a competitive adsorption between steam and methane, which would seriously limit the adsorption performance of methane in many separation applications.
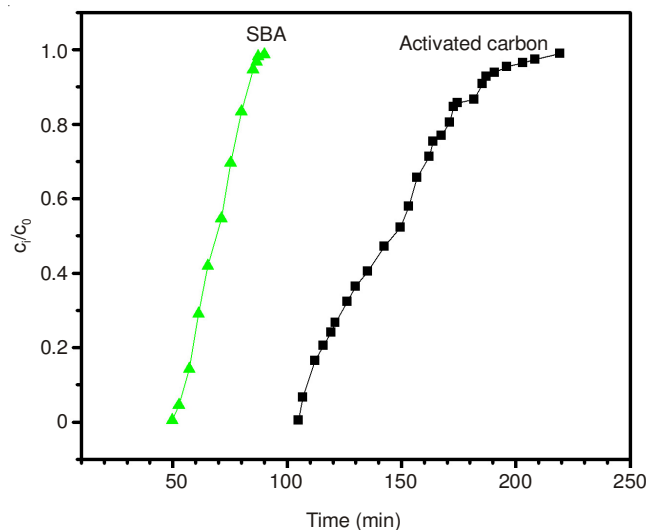

Fig. 1. Adsorption breakthrough curves of methane over activated carbon, SBA-15 (C_0 = 1000 mg/m³, air speed (V) = 10000 mL/(h·g))

Adsorption capacity: The adsorption capacity of the three samples to the methane was studied as listed in Table-2. For the three adsorbents, the adsorption capacity to methane is the following sequence, activated carbon > SBA-15 > conventional materials. Combined with Table-1, the value of adsorption capacity to the methane increases with increasing the value of specific surface area. The result from methane adsorption capacity on SBA-15 sample is far lower than the value of activated carbon, Which may be attributed to that the value of molecular kinetic diameter of methane is 0.188 nm which is lower than the pore size (0.3 and 5 nm) of conventional materials sample. Thus, it is easy for methane to adsorb on the internal pore of the conventional materials.

The value of adsorption capacity per unit area to methane on the three samples is much less than the value of theoretical adsorption per unit area (3.7224×10^{18} molecules per square meter), indicating that methane is not completely adsorbed on the surface of the two sample, if methane obeys the monolayer adsorption as show in Table-2. Methane is easy to adsorb on the internal pore of the samples should be related with the

TABLE-2
EFFECT OF ADSORPTION AGENT ON ADSORPTION CAPACITY AND EQUILIBRIUM TIME
(c_0 = 1000 mg/m³, V (V) = 10000 mL/(h·g))

Sample	Adsorption capacity (g g⁻¹)	Capacity per unit area (M m⁻²)	Equilibrium time (min)
Activated carbon	0.2697	1.8743×10^{18}	216.8
SBA-15	0.0980	1.4864×10^{18}	91.6

limitation of pore size. In addition, although the value of adsorption capacity per unit area and equilibrium adsorption capacity of activated carbon is larger than the SBA-15 samples, the value of the SBA-15 sample is higher compared with the conventional materials sample.

Desorption property: It is well-known that the desorption performances of adsorption materials are very important for its wide application. The desorption properties of methane molecules to the two materials were measured. Fig. 2 shows the temperature programmed desorption cures of methane over different samples. From the temperature programmed desorption spectra, methane is beginning to take off from the porous materials at 50 °C and desorbing completely at 300 °C. The desorption performance of SBA-15 sample for the methane is similar to conventional materials, however it is obviously difficult for methane to desorb from the activated carbon compared with the other two samples.
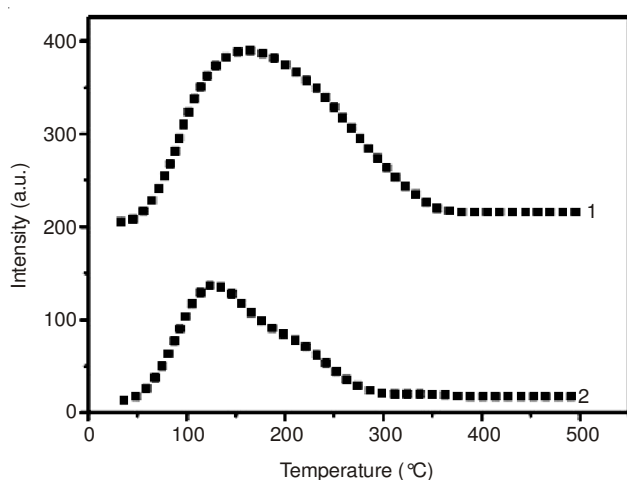

Fig. 2. Temperature-programmed desorption (TPD) of methane over activated carbon (1), SBA-15 (2)

Desorption performance for methane is mainly governed by the molecular diffusion resistance and adsorption strength. Desorption for the gas molecules on the adsorbent surface of activated carbon, with a wide pore size distribution, can be affected by diffusion resistance. While, the molecular kinetic diameter of methane is lower than the pore size of SBA-15, which have regular and uniform channels and a narrower pore-size distribution, thus the properties of desorption for methane on adsorbents mainly depends on the adsorption strength. The external surface properties and adsorption strength of SBA-15 samples are determined by Si/Al ratio. It is generally recognized that the lower Si/Al ratio leads to stronger surface acidity and greater adsorption strength to methane on surface of adsorbents. In this study, SBA-15 exhibit weak adsorption to methane, hence, methane could be easily desorbed from SBA-15.

Adsorption property: Effects of external diffusion resistance of the three adsorbents on the performance of adsorption were investigated by the breakthrough curve of adsorption under the condition of three different air speeds (3500 mL/(h·g), 7000 mL/(h·g). As shown in Fig. 3, the adsorption rate of SBA-15 to methane becomes significantly faster with the increase of air speeds. The phenomenon of breakthrough curve of the two samples steepened sharply and one intersection
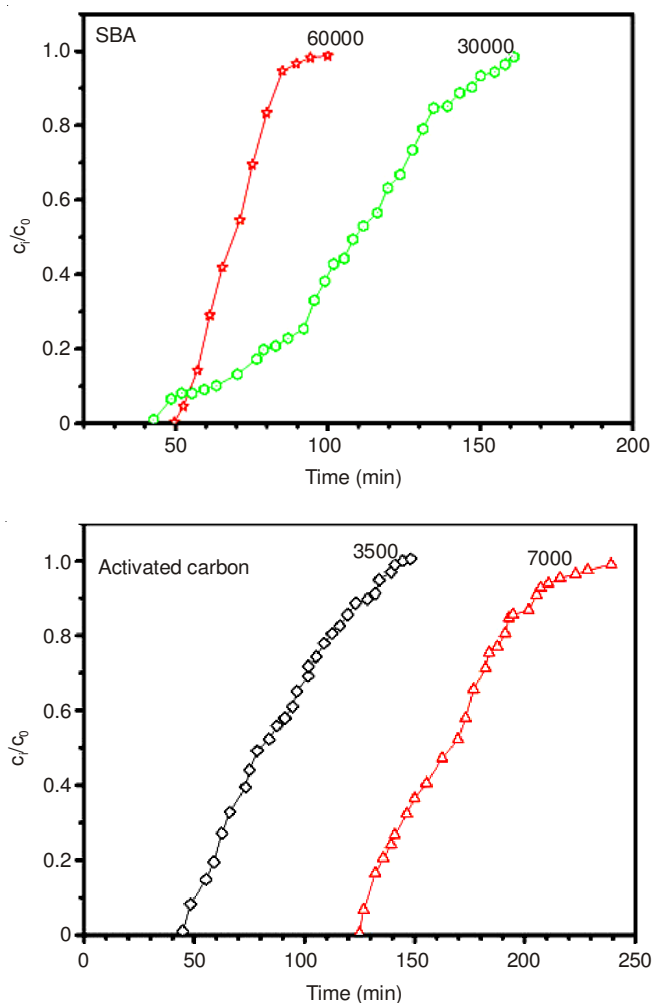

Fig. 3. Breakthrough curve of adsorption under the condition of three different air speeds

appeared from breakthrough curve with the air speed of 7000 mL/(h·g) occurs, because of the external diffusion effects. The rate of adsorption for methane on activated carbon did not change significantly with increasing air speed compared with the SBA-15 samples and the breakthrough curves of different air speed did not intersect, suggesting that the methane is mainly adsorbed on the surface of SBA-15, but did not in the pore. The breakthrough curve of modified SBA-15 sample has a less steepening trend than the curve of conventional materials sample. This is probably because of the SBA-15 sample has a larger specific surface area, thus the breakthrough time for methane on SBA-15 is longer relative to the conventional materials under the condition of the same air speed. These results are in agreement with the conclusion confirmed as shown above.

Conclusion

Adsorption and desorption characteristics of methane on activated carbon and SBA-15 were investigated. The adsorption capacity to methane obtained from SBA-15 material is much larger than that for conventional materials, indicating that SBA-15 material shows a larger specific surface area than conventional materials. Although, the adsorption capacity for SBA-15 sample to methane is lower than activated carbon, it is obviously more easily for methane to desorb from the SBA-

15 sample compared with activated carbon. Hence, SBA-15 has a large adsorption capacity and good desorption properties. The breakthrough time decreases steeply with increasing velocity of adsorbed gas, implying that the adsorption performance of SBA-15 to methane is not satisfactory with high air velocity. In summary, it is worth mentioning that SBA-15 is an excellent adsorbent for methane under lower air speed conditions.

REFERENCES

1. L.H. Nie, S.P. Xu, Y.M. Su and S.Q. Liu, *Chem. Ind. Eng. Prog.*, **27**, 1505 (2008).
2. J. Xn, W.S. Wei and X.J. Bao, *Chin. J. Chem. Eng*., **10**, 56 (2002).
3. J.R. Odum, T.P.W. Jungkamp, R.J. Griffin, H.J.L. Forstner, R.C. Flagan and J.H. Seinfeld, *Environ. Sci. Technol*., **31**, 1890 (1997).
4. R.P. Marathe, S. Farooq and M.P. Srinivasan, *Langmuir*, **21**, 4532 (2005).
5. D. Das, V. Gaur and N. Verma, *Carbon*, **42**, 2949 (2004).
6. W.B. Li and H. Gong, *Acta Phys. Chim. Sin*., **26**, 885 (2010).
7. A. Kumar, J. Dewulf and H. Van Langenhove, *Chem. Eng. J*., **136**, 82 (2008).
8. S. Mudliar, B. Giri, K. Padoley, D. Satpute, R. Dixit, P. Bhatt, R. Pandey, A. Juwarkar and A. Vaidya, *J. Environ. Manage*., **91**, 1039 (2010).
9. K. Demeestere, J. Dewulf and H. Van Langenhove, *Crit. Rev. Environ. Sci. Technol*., **37**, 489 (2007).
10. J.W. Lee, W.G. Shim and H. Moon, *Microporous Mesoporous Mater*., **73**, 109 (2004).
11. W. Makowski and P. Kustrowski, *Microporous Mesoporous Mater*., **102**, 283 (2007).
12. I. Glaznev, I. Ponomarenko, S. Kirik and Y. Aristov, *Int. J. Refrig*., **34**, 1244 (2011).
13. W. Rudzinski, J. Narkiewicz-Michalek, P. Szabelski and A.S.T. Chiang, *Langmuir*, **13**, 1095 (1997).
14. S. Brosillon, M.H. Manero and J.N. Foussard, *Environ. Sci. Technol*., **35**, 3571 (2001).
15. S.J. Bhadra and S. Farooq, *Ind. Eng. Chem. Res*., **50**, 14030 (2011).
16. B. Majumdar, S.J. Bhadra, R.P. Marathe and S. Farooq, *Ind. Eng. Chem. Res*., **50**, 3021 (2011).
17. R. Serna-Guerrero and A. Sayari, *Environ. Sci. Technol*., **41**, 4761 (2007).