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Sorption behavior of binary gas CO₂/CH₄ on ordered mesoporous carbon with the presence of water

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Abstract

Utilizing dynamic adsorptive method, the static equilibrium sorption data of CO₂/CH₄ binary gases with four different concentrations on CMK-3 present with water were collected. Compared with similar system only in bulk water, it was found that the whole adsorptive process was considerable complex which was mixed gas hydrate formation with competitive adsorption. The comprehensive discussions about equilibrium of binary gas on wet CMK-3 have been present here with generating reasonable conclusions. The CO₂/CH₄ selectivity was also calculated as the important support for CO₂/CH₄ separation by using gas hydrate formation in porous materials.

Introduction

Energy and environment are two hot topics in the world. Excessive consumption of oil and coals induces energy crisis and climate change. The alternative choice to facing this challenge is natural gas or other methane-based fuels. However the mixed CO₂ not only lead to a decreasing of the heating value but also increasing the CO₂ emission. CH₄ Purifying especially CO₂ removal is essential when using the nature gas as fuels. Gas hydrate separation method stands out from the common separation methods with advantage of high selectivity. Gas hydrates are non-stoichiometric crystalline compounds held by the Van der Waals force between water and light gas molecules. The clathrate is formed by hydrogen bond of water molecules and stabilized with the occupation of a guest molecule in its center. Previous works usually focused on the phase equilibrium of gas hydrate in bulk solution¹⁻¹⁰. A few researches concerned the gas hydrates in porous media¹¹⁻²⁰. Porous media with hydrophobic surface and proper pore size can promote the kinetics of hydrate formation since of enhancing gas-liquid intersurface by dispersing into meso-pores and the positive effect of potential field in the meso-pore^{21,22}. The present work aims to study the equilibria of hydrates of CH₄+CO₂ on ordered mesoporous carbon CMK-3. Among the three structures of gas hydrates, sI, sII and sH, CH₄, CO₂, and their mixtures form sI hydrates²³. Selectivity of clathrate cages for a guest molecule is mainly determined by the molecular size and the chemical property of the gas²⁴. In the previous work, we had studied the equilibria of hydrates of CH₄+CO₂ on activated carbon with a static volumetric method²⁵. However, the static method is not

favorable for the measurement of mixture because it takes a long time to reach a uniform concentration of mixture of gas in the stainless steel tube with external diameter 3 mm which is used to connect the adsorption cell and reference cell. In this work, we measure the breakthrough curves based on a dynamic method to study the equilibrium of binary hydrates.

Material

The purity of CO₂ and CH₄ were higher than 99.999 % and the mixed gases of CO₂/CH₄, with a CO₂ concentration of 30 %, 50 %, 65 %, 85 % respectively. The gases were supplied by Tianjin LiuFang Co., Ltd., China. The deionized water was used for all of experiment and synthesis program.

CMK-3 was synthesized according to the Reference²⁶. The as-synthesized sample was characterized by the adsorption of nitrogen at 77 K, and the result has been shown in Figure 1a. The isotherms belong to type-IV and a hysteresis loop was observed indicating the existence of mesoporous structure. The specific surface area is 1003 m²/g, which is calculated based on the BET (Brunauer, Emmett and Teller) theory²⁷. The pore volume is 1.01 cm³/g determined based on the amount of N₂ adsorbed at a relative pressure 0.95. The pore size centered at 3.8 nm calculated based on BJH (Barrett-Joyner-Halenda) method as shown in Figure 1 b. The N₂ isotherm collected at 77K on this sample (Fig. S1 supporting information) after whole experiment agree with the isotherm on fresh one indicating that none of structure change happens on CMK-3 during the experiments.

The obtained material was characterized By Transmission

electron microscopy (TEM). TEM image as shown in Fig. 2 present a clearly meso ordered porous structure of CMK-3.

Figure.1 a: Nitrogen adsorption on CMK-3 at 77 K; b: Pore size distribution of CMK-3

Figure 2. TEM image of CMK-3(a- parallel direction of hole; a0-vertical direction of hole)

Experiment

The sorption equilibrium of pure CO₂ and pure CH₄ in wet CMK-3 were collected using the pressure composition isotherm measurement instrument purchased from Advanced Materials Corporation USA. The binary gas concentrations were analyzed by gas chromatography (2010plus) purchased from shimadzu (Japan) combined with Mol sieve 5A columns purchased from Agilent with He as the carrier gas. During the test, the temperature of injector, column and detector were set at 80 °C, 100°C and 110 °C respectively. The current was set at 80. The flow rate was set at 50 ml/min. Breakthrough curves of mixture gases passing through an adsorption bed are the basis to analyze the equilibria data. The equilibria of mixed gas of CO₂ and CH₄ were measured with a breakthrough curve apparatus shown in Scheme 1. The adsorption bed was designed with the length of 300 mm and the inner diameter of 20 mm. It was fully filled with 2 g CMK-3 preadsorbed 2 g deionized water and immersed in a thermostatic bath. A SY-9312 type mass flow controllers with precision $\pm 1\%$ were used to control the flow rates in the passage of the column. A regulator was used to maintain the back-pressure of adsorption bed and a SY-9411 type pressure transducer with accuracy $\pm 0.1\%$ was used to detect the pressure.

A QMS Series Gas Analyzer purchased from the Stanford Research In. was used to analyze the composition of effluent streams. All parts of the setup were connected by stainless steel capillary tubes of inner diameter 2 mm and wall thickness 0.5 mm. The synthesized CMK-3 was dried at 393 K for 24 h in a vacuum. A definite amount of deionized water was added to dry carbon to prepare the wet sample by following step:

Scheme 1. Breakthrough curve apparatus (PR: pressure regulator; MFC: mass flow controllers; PB: back pressure valve)

Firstly some dry sample was weighted and put in a holder then connect it with another holder containing water. Vacuum this system then put the holder containing sample into cooling water. While the other holder with water keep in room temperature. The vapor of water transfers from one holder to the other and adsorbs on the sample. Weigh the holder of sample until amount of water is equal to the pore volume of CMK-3. The adsorption bed was filled with wet sample, and it was vacuumed before the experiment to drive off the air. To minimize the vaporization loss of water, the bed was cooled to -20 °C for every time of vacuuming. The water loss during the experiment can be ignored. The temperature was raised to 0 °C after the vacuuming for the measurement of breakthrough curves. The mixed gases of CO₂/CH₄ were charged into the vacuum bed with the flow rate of 50 ml/min, and the gas hydrates were formed with the low temperature and desired pressure. Draining of saturated sodium hydrogen carbonate solution method was used to collect the exhaust, the uptake of CO₂ and CH₄ in binary-component were calculated according to gas chromatography.

Calculation

According to the following Equations:

$$N_{CH_4, in} = N_{CH_4, ad} + N_{CH_4, out} - N_{CH_4, bed} \quad \text{Eq 1}$$

$$N_{CO_2, in} = N_{CO_2, ad} + N_{CO_2, out} - N_{CO_2, bed} \quad \text{Eq 2}$$

We can obtained equilibrium uptake of $N_{CH_4, ad}$ and $N_{CO_2, ad}$. The inlet gas mole amount denoted as $N_{CH_4, in}$ and $N_{CO_2, in}$, while the

outlet gas mole amount denoted as $N_{CH_4,out}$, $N_{CO_2,out}$. The gas amount existed in the empty space of the bed defined as $N_{CO_2,bed}$, $N_{CH_4,bed}$, respectively.

Separation factor (α) is calculated as follows:

$$\alpha_{CO_2,CH_4} = \frac{(N_{CO_2,ad} / N_{CH_4,ad})}{(y_{CO_2} / y_{CH_4})} \quad \text{Eq3}$$

y_{CO_2} and y_{CH_4} are the volume concentration of mixed gases, respectively.

Results and discussion

The detailed results of adsorptive amount and selectivity depend on different operative pressure and concentrations were summarized in table 1.

Table1 experimental data of different mixed gases

Component	Total P MPa	Partial P MPa		Uptake mmol/g		α
		CH ₄	CO ₂	CH ₄	CO ₂	
30%CO2 70%CH4	4.52	3.16	1.36	1.91	4.53	5.54
	3.75	2.63	1.13	1.47	3.94	6.24
	3.17	2.22	0.95	1.02	3.03	6.97
	2.64	1.85	0.79	0.74	2.03	6.45
	2.13	1.49	0.64	0.45	0.95	4.91
50%CO2 50%CH4	4.48	2.24	2.24	5.60	13.10	2.56
	3.78	1.89	1.89	5.48	9.30	1.32
	3.2	1.6	1.6	4.56	6.80	1.46
	2.68	1.34	1.34	3.19	4.20	1.7
	2.13	1.07	1.07	1.09	2.80	2.34
65%CO2 35%CH4	4.51	1.58	2.93	3.61	18.03	2.69
	3.80	1.33	2.47	2.85	15.42	2.91
	3.28	1.15	2.13	0.94	11.03	6.32
	2.79	0.98	1.81	0.76	9.91	7.02
	2.26	0.79	1.47	0.06	6.57	58.96
85%CO2 15%CH4	4.03	0.60	3.43	2.25	28.43	2.23
	3.75	0.56	3.19	1.94	24.52	2.23
	3.22	0.48	2.74	1.55	21.00	2.39
	2.76	0.41	2.35	0.95	16.76	3.11
	2.24	0.34	1.9	0.12	8.74	12.85

Pure gas hydrate formation

Figure 3. a: pure CO₂ isotherm curve at 273K on wet CMK-3 with $R_w=1$ (R_w : ratio of water mass to dry CMK-3); b: pure CH₄

isotherm curve at 273K on wet CMK-3 with $R_w=1$

As shown in Fig.3 a pure CO₂ adsorptive isotherm curve present 3 inflection points. Before the inflection point A, with increasing of pressure the CO₂ uptake increased slowly due to a small amount CO₂ adsorbed on the carbon walls of CMK-3 and solution in the water. When the pressure reaches the inflection point A (1.24 MPa), the CO₂ uptake present a sharp increase due to the formation of CO₂ hydrate formed by a little water out of the pore. According to thermodynamic data, the formation pressure of CO₂ hydrate in bulk water at 273K is 1.26 MPa, which is consistent with our experimental pressure.²⁸ When the pressure increase to the inflection B (2.41 MPa), the amount sorption of CO₂ sharply increased. Calculating the CO₂ hydrate hydration number (H₂O/CO₂) it was found that the hydrate hydration number (3.6) is lower than the theoretical value 5.75-7.6²⁹ That means under this pressure (2.41 MPa), all the water on CMK-3 has been convert to gas hydrate, besides, there is a considerable quantity of CO₂ absorbed in the empty space formed by the carbon wall of CMK-3 and the gas hydrate crystal. The higher the pressure increase, the more CO₂ hydrate crystal grows in the pore. Until the water in the pores is completely converted into hydrates, and the slit pore formed by CMK-3 and the hydrate crystal is fulfilled with CO₂, the amount sorption of CO₂ gradually become saturated.

The pure CH₄ isotherm curve on wet CMK-3 at 273k was present in Fig.3 b. At the inflection point A, the pressure is about 4MPa which is higher than the methane hydrate formation in bulk water at 273 K. That is because the crystal formed in the pore owes a higher Gibbs surface energy than it formed in bulk water. The final CH₄ uptake reaches 9.8 mmol/g corresponding to a gas hydrate hydration number of 5.66 approaching the theoretic value (5.75)³⁰ revealing a completely conversion of water into gas hydrate. Comparing the maximum uptake of CO₂ (27 mmol/g) to methane (9.8 mmol/g), it was found that the CH₄ uptake is much lower than that of CO₂. The main reason is that the interaction between CH₄ and carbon walls of CMK-3 is weaker than it between CO₂ and carbon walls, CH₄ molecules can't fulfill into the slit pore formed by CMK-3 and the hydrate crystal.

Mixed gases hydrate formation

When the concentration of CO₂ is 30%, the pressure is 4.5MPa, both partial pressure of CO₂ (1.36 MPa) and CH₄ (3.16 MPa)

were lower than their gas hydrate formation pressure in the pore of CMK-3. There is no evidently gas hydrate formed deduced from the isotherm curve (Fig. 4 a). In the case of CH₄, the amount of sorption is very low due to the weak interaction with carbon wall of CMK-3. While the amount of CO₂ adsorbed is noticeably improved with the increasing pressure ascribe to a little CO₂ hydrate formed by the water out of pore and part of CO₂ adsorbed on the surface of CMK-3. As shown in Fig. 4 b, for the binary mixture (CO₂ 50%) a significant inflation point appeared in the CO₂ isotherms indicating that the CO₂ hydrates began to form in the pore of CMK-3 and the amount of sorption increased quickly. Whereas another inflation point appeared in CH₄ isotherms is at the pressure of 3.0 MPa, CH₄ uptake level off after it. With increasing of CO₂ concentration, as illustrated in Fig. 4 c and d, the CO₂ uptake can raised over 18 mmol/g and 28 mmol/g respectively revealing gas hydrate formation in the pore of CMK-3, however the CH₄ uptake dropped below 3.61 mmol/g and 2.25 mmol/g respectively.

Figure 4. Respective uptake of CO₂ and CH₄ on wet CMK-3 corresponding to different mixture gas concentration (a: CO₂ 30%, b: CO₂ 50%, c: CO₂ 65%, d: CO₂ 85%)

The comparison of hydrate formation of pure gas and mixed gases

To make it clearly, we compared all five CO₂ isotherm curves and five CH₄ isotherm curves independently collected from different CO₂/CH₄ concentration gases and presented in Fig. 5. For a mixture poor in CO₂ (CO₂ concentration of 30%) the CO₂ uptake is close to it of pure CO₂ under the same partial pressure. That is to say, the mixed CH₄ have not evident effect on the CO₂ adsorption under this condition. As for CH₄, the CH₄ uptake of the mixture (Fig 5 b plot 2) is increasing with a raising

of pressure, and significantly higher than that of pure methane under the same partial pressure. The probable reason is that some empty adsorptive sites can be supplied for CH₄ after CO₂ molecules absorbing on the carbon surface original occupied by pre-adsorbed water molecules.

Figure 5. CO₂ isotherm curves of mixture gas with several CO₂ concentration 1: 100%, 2: 30%, 3: 50%, 4: 65%, 5: 85% (p : partial pressure of CO₂); b CH₄ isotherm curves of mixture gas with several CH₄ concentration 1: 100%, 2: 70%, 3: 50%, 4: 35%, 5: 15% (p : partial pressure of CH₄)

For the 50%/50% CO₂/CH₄ gas mixture, the CO₂ uptake (Fig. 5 a) is obvious higher than pure CO₂ uptake on this system when the partial pressure of CO₂ is over 2 MPa. It proves that CO₂ hydrate has formed and the presence of CH₄ can reduce CO₂ hydrate formation pressure on wet CMK-3. The reasons are presented below: To form CO₂ hydrate, the sufficient pressure should be provided to ensure that CO₂ molecules are close enough to water molecules thus the system energy can reach a minimum value. In mixture gas system, the electron repulsion from CH₄ to CO₂ is stronger than that from CO₂. Therefore CH₄ can shorten the distance between CO₂ molecules and water molecules lead to the whole system reach the lowest energy and CO₂ hydrate form. As to CH₄ in the same system (Fig.5 b), the amount of CH₄ uptake is significantly higher than that of pure CH₄. There are two reasons. One is that the carbon surface of CMK-3 can be exposed to supply the adsorbed space for CH₄ molecules when CO₂ hydrate formation. The other is that after the CO₂ hydrate formation, some CH₄ molecules can also occupied part of gas hydrate cages. The combined two reasons lead to the increase of CH₄ uptake.

In system with CO₂ concentration of 65%, the growth trends of CO₂ uptake is similar to 50%, and higher than the binary gas (CO₂ concentration of 50%) under the same conditions. It is worthy to note that though the CH₄ uptake of is always higher than that of pure CH₄ at the same partial pressure, the highest

CH₄ uptake (4 mmol/g) is lower than the max value in binary gas (CO₂ concentration of 50%). It accounts for that CO₂ molecules is much easier to occupy the hydrate cages and the empty space between gas hydrate and carbon walls than CH₄ molecules under the higher CO₂ partial pressure. For the CO₂ rich mixture (CO₂ concentration of 85%) CH₄ uptake continues reducing and CO₂ uptake is gradually close to the pure component under the same partial pressure which is also consisted with our previous conclusion.

Discussion of CO₂/CH₄ selectivity

For investigating the performance of this system on CO₂/CH₄ separation, CO₂/CH₄ selectivity was calculated and presented in Fig. 6. It was found that the trends of selectivity calculated from different binary gases are obvious different. With high CO₂ concentration (65%, 85%) at low total pressure the selectivity is relatively high. Under a low pressure, the partial pressure of each component cannot reach the gas hydrate formation pressure, so that the uptake of binary components is relatively low. CO₂ can absorb on the carbon walls of CMK-3, while the adsorptive interaction between CH₄ and CMK-3 fulfilled with water is very weak, therefore the significant difference of adsorptive interaction lead to a relative high selectivity. With an increase of pressure, once gas hydrate formed, CH₄ molecules can occupied part of gas hydrate cages and absorbed in the space between CMK-3 and hydrate crystals, thus the CO₂/CH₄ selectivity reduces. When the concentration of CO₂ is lower than 65%, the change of selectivity with pressure is not obvious, because the competition effect of CO₂ on CH₄ adsorption is not very strong upon a relative low CO₂ concentration. Under high pressure the selectivity of binary gas with low CO₂ concentration is evidently higher than that of binary gas with high CO₂ concentration due to the strong competition effect of CO₂.

Figure. 6 CO₂/CH₄ Selectivity depend on four binary gases with different CO₂ concentration. (1:30%, 2:50%, 3: 65%, 4: 85%)

Conclusion

By investigating sorption behavior of binary-component with different concentration of CO₂/CH₄ on wet CMK-3, we have found that CH₄ can reduce CO₂ hydrate formation pressure on wet CMK-3 due to the strong repulsive force from CH₄ to CO₂. On the other hand the adsorption of CO₂ in the system enhanced the adsorption of CH₄. When the pressure is low, adsorbed CO₂ in CMK-3 can supply some adsorbed sites for CH₄, so that the amount of CH₄ sorption in binary-component is higher than that of pure CH₄ in wet CMK-3 under the same pressure. When the pressure is enough high in the system, CO₂ hydrate began to form, and allow some CH₄ molecules enter the hydrate cages, so CH₄ uptake is significantly greater than that of pure component under the same pressure. With the increase of CO₂ partial pressure, CH₄ molecules can be replaced by CO₂ molecules from the hydrate cages and space between gas hydrate and carbon walls. Calculating the CO₂/CH₄ selectivity with different binary ratio, we found that under low pressure and high CO₂ concentration, the selectivity is relatively high. While under high pressure the separation factor change with pressure is not obvious and the value is close to 5. Our results provide important data for CO₂/CH₄ separation by utilizing gas hydrate formation in porous materials.

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Notes

The authors declare no competing financial interest.

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Supporting Information

Sorption behavior of binary gas CO₂ /CH₄ on ordered mesoporous carbon with the presence of water

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Figure S1 N₂ isotherm at 77 K on CMK-3 before and after experiment