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CO_2 sorption in wet ordered mesoporous silica kit-6: effects of water content and mechanism on enhanced sorption capacity

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Abstract The sorption isotherms of CO_2 in wet ordered mesoporous silica KIT-6 with different amounts of pre-adsorbed water were firstly collected experimentally using a volumetric method in the temperature range of 275–281 K. The isotherms show an inflection point indicating CO_2 hydrates form in the pore spaces which is proofed by the enthalpy change calculated at the inflection pressure, and the quantity of water content shows considerable effect on the sorption capacity of CO_2. The highest enhancement of sorption capacity in the presence of water is observed in wet KIT-6 sample with water loadings of 2.48, which is about 12.80 mmol/g and 1.86 times than that on dry sample. However, the saturation capacity is still far less than that what can be stored merely in the form of hydrates due to the low ratio of water utilization because of the large pore and the polar surface of KIT-6.

Keywords Carbon dioxide · KIT-6 · Hydrate · Water · Adsorption

1 Introduction

Carbon dioxide (CO_2), the most prevalent greenhouse gas, has been considered as the major contributor to global warming and climate change. Thus, carbon capture from various emission sources is an important approach to become a carbon neutral and sustainable society.

Up to date, many effective methods proposed for CO_2 capture and separation have been well-developed (Yang et al. 2008), including absorption based on amine solutions, adsorption based on solid porous materials, and membrane technology, etc. Adsorption-based processes are attractive and identified to be the most promising approach for CO_2 capture due to their low energy-penalty and high energy efficiencies. High CO_2 selectivity and capacity are essential when selecting an adsorbent for adsorption process. However, recent studies (Li et al. 2008; Brandani and Ruthven 2004; Zhang et al. 2011; Liu et al. 2007) have shown that many porous solid adsorbents are limited by low selectivity and uptakes for CO_2 in the presence of other gases, especially of water due to the stronger affinities of water with adsorbents than CO_2 resulting in displacing CO_2 and reducing the adsorbents' capacity. As we known, CO_2 molecules could be formed into hydrate through a physical reaction with water when it is sequestered into the ocean deeper than 400 m (Lund et al. 1994). And experiments have also shown that CO_2 hydrate is thermodynamically stable at pressures higher than 4.45 MPa and at temperatures lower than 283.15 K (Lund 1995). Thus, water/steam, which is omnipresent in all existing sources of carbon pollution, is expected to be utilized and reacted with CO_2 molecules to form CO_2 hydrates in the pore spaces of porous media at high pressures and low temperatures. It has been reported that pore-confined effects not only reduce and retard the potential dissolution of CO_2 hydrates into the surrounding water (Simth et al. 2002), but also improve CO_2 hydrates formation kinetics when compared to that in pure water (Kang et al. 2009).

Recently, many porous materials such as activated carbon (Sun et al. 2007), silica gel (Simth et al. 2002), SBA-15

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(Zhou et al. 2005) and various coals (Ozdemir and Schroeder 2009), and porous media solutions (Lee et al. 2002) have been examined for CO_2 storage in the presence of water. However, to the best of our knowledge, there have been no reports about CO_2 hydrate formation in ordered mesoporous silica KIT-6 in the presence of water. Besides, the formation of CO_2 hydrate in the pores of 3-dimentional (3D) structure of KIT-6 may be more rapid and has a shorter induction time than silica gel and activated carbon as 3D pore structure is beneficial for CO_2 diffusion and water cages formation in the pore spaces. Therefore, in this work, equilibrium data of CO_2 in the dry and wet-KIT-6 with different amounts of pre-adsorbed water were measured, and a discussion on the mechanism of the sorption enhancement is presented. These results provide a database for storage simulations of CO_2 in the deep ocean.

2 Experimental

2.1 Synthesis and characterization of KIT-6

KIT-6 with 3D ordered channels was synthesized under acidic conditions using a mixture of poly(alkylene oxide)-based triblock copolymer Pluronic P123 (Aldrich, MW = 5,800) and *n*-butanol (Aladdin, AR) as a structure-directing agent and TEOS (Aladdin, AR) as the silica source according to the following procedure reported in the literature (Kleitz et al. 2003): 4.0 g of P123 is dissolved in 144 g of H_2O and 7.9 g of 35 wt% HCl solution with stirring at 308 K. After complete dissolution, 4.0 g of BuOH is poured into the above solution. After 1 h stirring, 8.6 g of TEOS is added dropwise. The mixture is left under vigorous and constant stirring at 308 K for 24 h. Subsequently, the mixture is transferred into a Teflon lined stainless steel autoclave and aged at 373 K for another 24 h under static conditions. Surfactant-free mesoporous material KIT-6 is obtained after hot filtration, brief ethanol/HCl washing and subsequent calcination at 823 k in air for 6 h.

The as-synthesized product was examined with small-angle X-ray diffraction (XRD), transmission electron microscopy (TEM) and N_2 adsorption/desorption at 77 K. XRD was performed on a Rigaku D/MAX IIIB diffractometer with Cu-butt at the conditions of 40 kV and 30 mA. The scan range was from 0.5° to 5° with a step size of 0.002° and step time 1 s. TEM image was taken from thin edges of particles supported on a porous carbon grid, using TECNAI G^2F-20. The adsorption/desorption isotherm of N_2 at 77 K was collected using ASAP 2020. Before the measurement, KIT-6 sample was degassed under vacuum for 24 h at 473 K. The Brunauer–Emmett–Teller (BET) equation was used to evaluate the specific surface area on the basis of adsorption data at p/p° between 0.05 and 0.2. The pore size distribution (PSD) was determined by applying the Barret–Joyner–Halenda (BJH) method to the adsorption branch. The total pore volume was evaluated from the amount of N_2 adsorbed at $p/p^o = 0.99$.

2.2 Collection of CO_2 sorption data in dry/wet KIT-6

Before the sorption measurement, KIT-6 sample was dried at 473 K for 24 h under vacuum, and then mixed with a measured amount of water to prepare wet samples containing different contents of water. The CO_2 sorption isotherms in the dry and wet samples were performed using a typical volumetric setup adapted for high-pressure studies. Working principle and details were previously presented in the literature (Zhou et al. 2003). The relative precision of pressure transmitter (Keller LEX1) was 0.01 % for the range of 20 MPa, and temperature was kept constant within ± 0.01 °C. Such accuracy in reading pressure and temperature was even higher than that achieved previously (Zhou et al. 2005).

Since each isotherm starts at a pressure of zero, it is necessary and important to vacuum the system. Thus, in order to minimize the evaporation loss of water pre-adsorbed in wet sample, the wet sample was cooled down to 253 K for 4 h every time the adsorption cell was put in a vacuum. The water loss during the experiment could be neglected because the total weigh of the wet sample before and after the isotherm measurement was almost unchanged.

3 Results and discussion

3.1 Textural property of KIT-6

XRD pattern of KIT-6 sample shown in Fig. 1 exhibits two main peaks at 2θ = 0.95° and 1.61°, which is in good agreement with the previously reported value (Kim et al.

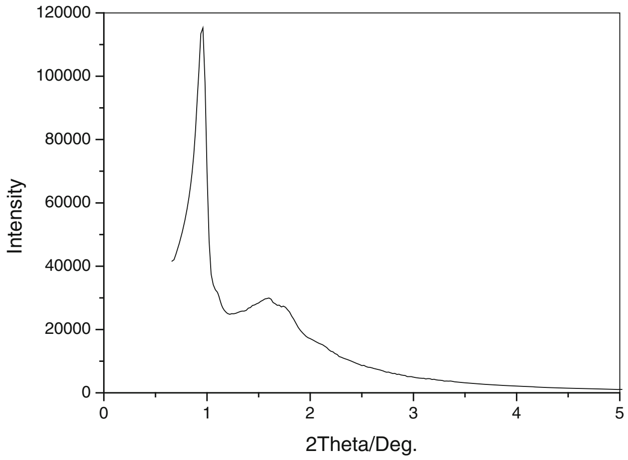

Fig. 1 XRD pattern of KIT-6 sample

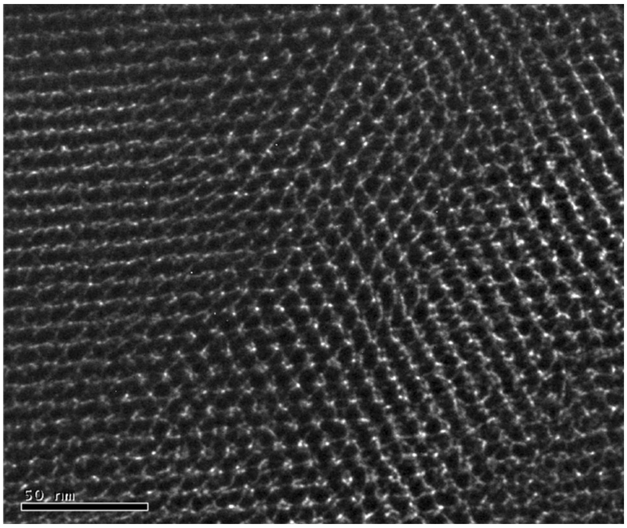

Fig. 2 TEM image of KIT-6 sample

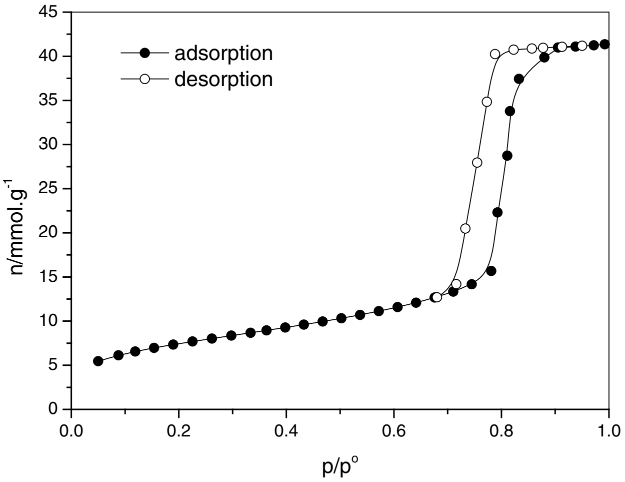

Fig. 3 N_2 adsorption–desorption isotherms of KIT-6 sample at 77 K

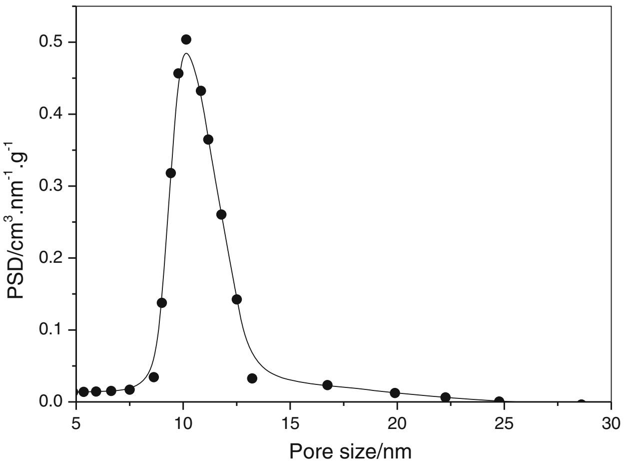

Fig. 4 Pore size distribution of sample KIT-6

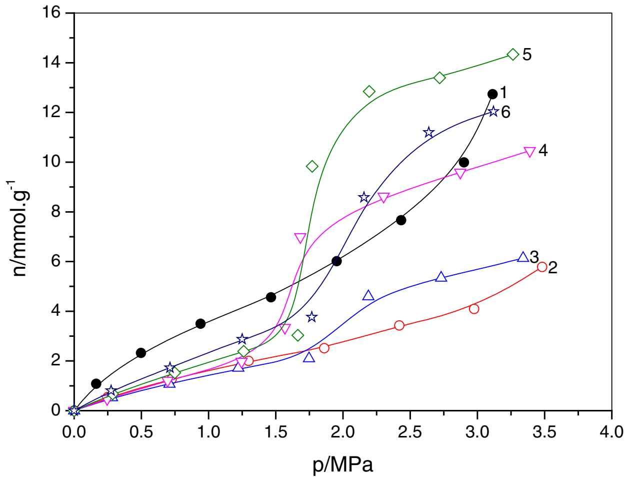

Fig. 5 Sorption isotherms of CO_2 in KIT-6 with different contents of water 1, Rw = 0; 2, Rw = 1.08; 3, Rw = 1.52; 4, Rw = 1.98; 5, Rw = 2.48; 6, Rw = 3.07

2005), indicating excellent structural order with the symmetry being commensurate with the body-centered cubic $Ia\bar{3}d$ space group which is also confirmed by TEM image shown in Fig. 2.

The adsorption/desorption isotherm of nitrogen at 77 K is shown in Fig. 3. It shows the feature of type IV isotherm with a pronounced capillary condensation step, characteristic of high-quality large pore mesoporous material. The presence of an H1 hysteresis indicates channel-like open pores at two ends. The BET specific surface area and the pore volume are 588 m^2/g and 1.43 cm^3/g, respectively. The PSD curve is shown in Fig. 4, which shows a very narrow pore size distribution and the median pore diameter centers at 10.1 nm.

3.2 CO_2 sorption isotherms in dry/wet KIT-6

The sorption isotherms of CO_2 in KIT-6 samples with different amount of water were obtained at 275 K and shown in Fig. 5. The sorption amount of CO_2 is expressed in mmol CO_2 on the basis of per gram of dry KIT-6. The water content in a wet sample is denoted as Rw, the weight ratio of water to dry KIT-6 sample.

Therefore, Rw = 0 represents the dry sample, in which the isotherm (curve 1) shows the typical feature of type-IV form as the adsorption temperature (275 K) is lower than the critical temperature (304 K) of CO_2, indicating CO_2 is condensable in the mesopores of KIT-6 when the relative pressure reaches the value given by Kelvin equation.

However, all isotherms on wet samples except curve 2 show an S-shape with a sharp increase to a much higher level in the sorption amount of CO_2 at an inflection pressure. The similar isotherms were also reported in other materials (Simth et al. 2002; Sun et al. 2007; Zhou et al. 2005). The reason for this sharp increase is due to the formation of CO_2 hydrates in the pore spaces which will be confirmed subsequently through the calculation of enthalpy change of phase transition around the inflection pressure. The inflection pressure where the sorption amount rises sharply is called the hydrate formation pressure and indicates the beginning of hydrate formation. From Fig. 5, we could see that the hydrate formation pressure for curves 4, 5 and 6 is around 1.56 MPa while the hydrate formation pressure for low water content sample (curve 3) increases to about 1.77 MPa, which is explained as that when the water content is low, only the smaller pores are firstly filled with water and used to form hydrate. The hydrate clathrates formed in small pores have very high excess Gibbs free energies on the surface and need a higher formation pressure. Therefore, CO_2 hydrate formation pressure is decided not only by PSD but also by water content, which could be indicated by curve 2 in Fig. 5 where no CO_2 hydrates are obviously observed when water content in wet KIT-6 sample is very low. This maybe because strong interactions between water molecules and silicon hydroxyl groups on the surface of KIT-6 prevent the water close to the surface from being employed to form water cages and further difficult to form CO_2 hydrates.

Curves 2–6 in Fig. 5 show the considerable effect of water contents on the sorption amount of CO_2. The amount of CO_2 sorbed in the wet KIT-6 increases with the increase of the water content, shown in Fig. 6.The highest storage capacity (12.80 mmol/g) is reached for Rw = 2.48, which is 1.86 times higher than that in dry KIT-6 sample and comparable to those values reported in other literatures shown in Table 1. However, the sorption amount of CO_2 in the wet samples(Rw = 1.08 and 1.52) is less than that of dry KIT-6 sample for low content of water. Although more water loading leads to higher CO_2 sorption amount, too much water loaded may plug up gas passage and leads to fewer hydrates formed as the case with Rw = 3.07. It seems there is a critical content of water, which could be evaluated with the titration method. The critical water content as determined is about 2.5–2.8 cm^3/g for the as-synthesized KIT-6 sample, which is much larger than the pore volume. Therefore, the reason for such condition is that both the interior pore space and the exterior space between the sorbent particles have totally been occupied by extra water, which prevents CO_2 from getting into the pore spaces to form hydrate.

In addition, Fig. 5 shows that remarkable amount of CO_2 is sorbed before the inflection pressure but much lower than that in the dry sample. This is because affinities between water molecules and KIT-6 surface are stronger than that for CO_2, leading to parts of sorption sites are occupied by water molecules. However, the sorption amount of CO_2 before the inflection pressure increases following the increase of water content. It's likely originated from the reaction of CO_2 with water to form HCO_3^-, which leads to more CO_2 fixed.

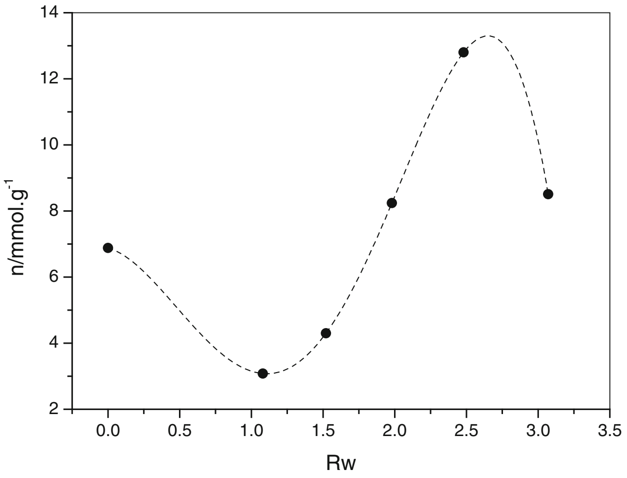

Fig. 6 Effects of Rw on CO_2 sorption amount at 2.2 MPa

Table 1 Storage capacity of CO_2 in other porous materials

Adsorbent	Sorption capacity (mmol/g)	Rw/Pressure	Reference
SG-A	2.5	0.75/3.5 MPa	[Zhenget al. 2012]
SG-B	3.2	0.81/3.5 MPa	
Bamboo carbon	12.1	2.36/2.5 MPa	[Wang et al. 2008]
BY-1	31	1.65/2.2 MPa	[Sun et al. 2007]
KIT-6	12.8	2.48/2.2 MPa	This work

3.3 Discussion on the mechanism of the enhanced sorption

The inflection pressure of isotherms indicates a phase transition and change of sorption mechanism for CO_2, and the enthalpy change of the phase transition could be calculated based on the Clausius–Clapeyron equation. Therefore, additional isotherms at other temperatures (277, 279 and 281 K) are collected at Rw = 2.48 and shown in Fig. 7. The inflection pressures are shifted to higher values with the increase of temperature, but saturation capacities of CO_2 at different temperatures are not affected shown by curves 1, 2 and 3. The inflection pressures are 1.67, 2.50, 3.48, and 4.16 MPa respectively at 275, 277, 279 and

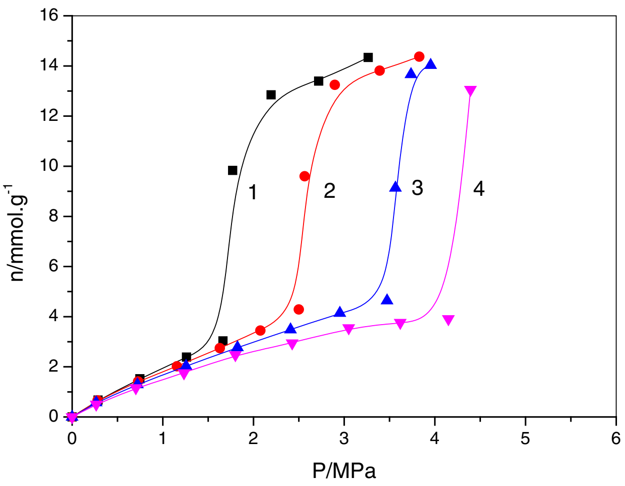

Fig. 7 CO_2 sorption isotherms in the KIT-6 with Rw = 2.48 at different temperatures 1, 275 K; 2, 277 K; 3, 279 K; 4, 281 K

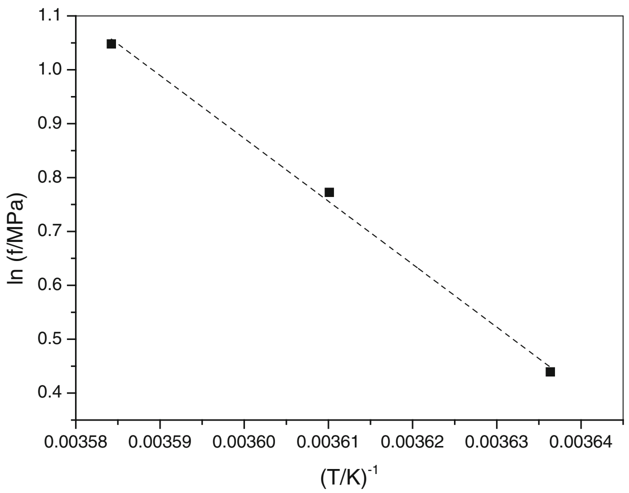

Fig. 8 Plot to evaluate the enthalpy change in KIT-6

Table 2 State data of sorption isotherms jump at different temperatures

Temperature/K	Inflection pressure/Mpa	Saturation pressure/Mpa	ϕ	ln f
275	1.67	3.67	0.93166	0.43922
277	2.50	3.87	0.86752	0.77245
279	3.48	4.07	0.81985	1.04796
281	4.16	4.28	–	–

281 K. However, there is a significant difference in the isotherm forms between curve 4 and others, that is, there is no platform after the inflection pressure, and the inflection pressure (4.16 MPa) is extremely close to the saturated vapor pressure (4.28 MPa) of CO_2 at 281 K. Thus, the sharp increase in sorption amount is considered to be due to the condensation of CO_2 rather than the formation of CO_2 hydrates in the pores. The detailed inflection pressures in KIT-6 and saturation pressures at different temperatures are listed in Table 2.

It's worth noting that at 275 K CO_2 hydrates are difficult to form in the pores larger than 7.0 nm because the impetus of the pores for promoting water molecules to form cages disappears (Zheng et al. 2012). However, CO_2 hydrates could be formed in the pores of KIT-6 sample even at higher temperature, in which the pore size (10.1 nm) is much larger than 7.0 nm. This probably is attributed to the 3D channel structures of KIT-6, which are beneficial for water cages formation and fast diffusions of CO_2 into the pores.

The enthalpy change at the inflection pressure could be determined using the following equations:

$$\ln f = \frac{\Delta H}{RT} + C$$

$$f = p \times \phi$$

$$\ln \phi = \int_0^p (Z - 1)\frac{dp}{p}$$

where f means fugacity, T is the temperature, R is the universal gas constant, C is a constant, p is the inflection pressure, ϕ is fugacity coefficient, and Z is gas compressibility factor.

The determined values for fugacity and fugacity coefficient are listed in Table 2, and the curve of ln f as a function of 1/T is plotted in Fig. 8, where the linear correlation coefficient is 0.998. Enthalpy change is calculated from the slop to give −97.1 kJ/mol for the formation of CO_2 hydrate in KIT-6, which is much larger than that in coconut shells carbon (−81.9 kJ/mol) (Sun et al. 2007) because the water content and pore size will affect the value of enthalpy change of hydrate formation.

3.4 Molar ratio of H_2O/CO_2

It is reported that CO_2 molecules can form type-I hydrate (Lee et al. 2003), and the theoretical molar ratio of water to fixed carbon dioxide is 5.75 (Charriere et al. 2010). In fact, the sorption amount of CO_2 after the inflection pressure in wet samples includes not only the amount of CO_2 in the form of hydrates but also that dissolved in water as well as that adsorbed on the exposed surface after the hydrates are formed. Therefore, the molar ratio of water to fixed CO_2 may be less than the theoretical value of 5.75, which occurs for activated carbon (Sun et al. 2007) and multiwall carbon nanotube (Sun et al. 2008).

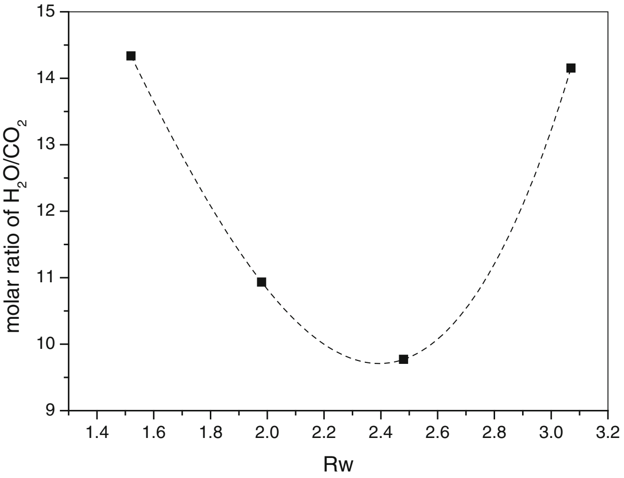

Fig. 9 The molar ratio of H_2O to CO_2 at 3.1 MPa

However, it isn't the case in this work. The molar ratio of H_2O to CO_2 is calculated on the basis of CO_2 sorption amount at 275 K and 3.1 MPa, which is depicted in Fig. 9. The molar ratios are much higher than 5.75, indicating the ratio of water employed to form hydrates is very low. This is probably attributed to the large pores and the strong H-bonding between water and hydroxyl groups on the surface, which prevent the water molecules close to the surface from being used to form water cages, and this effect is likely to extend to subsequent water layers. Thus, only the water far from the surface can be utilized to form hydrates.

4 Conclusions

The sorption isotherms of CO_2 in wet KIT-6 samples show that the quantity of pre-adsorbed water exerts considerable effect on the sorption capacity of CO_2 and as much as 1.86 times' sorption amount than that on dry sample is reached for $Rw = 2.48$. CO_2 hydrate formation in the pore spaces is confirmed to be the major sorption mechanism and responsible for the sharp increase in CO_2 sorption capacity.

In addition, 3D channel structures are beneficial for hydrate formation in pores larger than 10 nm. However, CO_2 storage capacity is much lower than what can be stored merely as hydrates due to the low ratio of water utilization because of the large pores and the polar surface of KIT-6.

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