

Sorption equilibria of CO₂ on silica-gels in the presence of water

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Abstract The sorption equilibria of carbon dioxide on three types of silica gel (SG) with different pore size distributions in the presence of water were studied experimentally using a volumetric method at 275 K with pressures from 0 to 3.7 MPa. Both the pore size distribution of the silica gel and the quantity of pre-sorbed water impact the formation of the CO₂ hydrates. For wet silicon gel A(SG-A) with water loading ratio of 0.75, the highest CO₂ sorption was about 2.5 mmol of CO₂ per gram of dry sorbent at 275 K. Similarly, the highest sorption was about 2.7 mmol for wet SG-B with $R_w = 0.81$. However, CO₂ hydrate did not form on the wet surface of SG-C due to its large pore sizes.

Keywords Carbon dioxide · Hydrate · Silica gel · Adsorption · Sequestration

1 Introduction

Large quantities of CO₂, a major greenhouse gas, are produced during the combustion of fossil fuels which contribute to global warming. Research on the capture and sequestration of CO₂ has greatly increased during the last several years. Some of the most promising storage options are geological formations (such as shaly caprocks; Busch et al. 2009), saline aquifers (Singh et al. 2011), novel sorbents

(Olivares-Marin et al. 2010), and oil reservoirs or unmineable coals seams (Li et al. 2010; Battistutta et al. 2010; Charrière et al. 2010; Day et al. 2008; Zhang et al. 2011). Another method that has been studied is to sequester CO₂ in the deep ocean by forming gas hydrates. Gas hydrates are crystalline molecules formed by a physical reaction between water and low molecular weight gases, in which the gas molecules are held as guests in water cages, and the structure of the cage is stabilized by the presence of the guest molecules. Low molecular weight gases, such as methane and carbon dioxide, form body-centered cubic lattice structures in hydrate equilibria (Jacobson et al. 2010; Circone et al. 2003; Adisasmito et al. 1991) and gas hydrates can form under conditions of low temperature and high pressure. It has been experimentally determined that CO₂ hydrate is thermodynamically stable at pressures higher than 4.45 MPa and temperatures lower than 10.2 °C (Lund 1995). Therefore oceans depths of 400 m or more should be suitable places for CO₂ sequestration (Lund et al. 1994).

Although much research on CO₂ hydrates has been carried out, the proposal to sequester CO₂ deep in the ocean has not been commercially accepted due to various technological and economic problems. So research is being conducted to overcome these issues. It has been reported that pore spaces can stabilize hydrates and retard their dissolution in zones where surface water flows extremely slowly (Koide et al. 1997). In addition, previous studies (Zhou et al. 2002, 2005) on methane hydrate have shown improved formation kinetics in porous media compared to those in pure water. Therefore the existence of porous media should help overcome the drawbacks of direct injection of CO₂ into sea water. Recent studies have illustrated that it is feasible to combine CO₂ sequestration with the exploitation of flammable ice (Komai et al. 1997; Sivaraman 2003;

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Sun et al. 2008), which will partially offset the costs of CO₂ sequestration. This should aid in the acceptance of the capture and sequestration of CO₂ in the form of hydrates.

Much effort has also focused on the study of the kinetics of the formation and decomposition of CO₂ hydrates in very recent years (Chun and Lee 1996; Lee et al. 2002). Our group has studied CO₂ sorption on activated carbon in the presence of water (Sun et al. 2007; Wang et al. 2008). The adsorption of water vapor and carbon dioxide in relation to the carboxylic functional groups on the surfaces of different types of coal or other porous media solutions has also been examined (Lee et al. 2002; Nishino 2001; Ozdemir and Schroeder 2009). Silica gel (SG) is also important because many submarine sediments are made of naturally porous materials that are very similar to porous silicates. The formation of carbon dioxide hydrate in silica gel pores is more rapid and has a shorter induction time than in pure water (Kang et al. 2009). In this work, the sorption equilibria of CO₂ on silica gels with different pore size distributions (PSDs) in the presence of water have been studied. These experimental results provide a database for storage simulations of CO₂ in the deep ocean.

2 Experiment

Three different types of silica gels, SG-A, SG-B and SG-C, manufactured by Qingdao Haiyang Chemical & Special Silica Gel CO. Ltd, were used. The silica gels were dried at 393 K for 24 h in a vacuum cell before the experiment, and then mixed with a measured amount of water to prepare wet samples containing different amounts of water. The sorption isotherms of the dry and wet samples were collected using the volumetric setup, which was the same as that used for adsorption in previous studies (Zhou et al. 2002). A diagram of the apparatus is shown in Fig. 1.

Two containers of known volume were connected by tubes via a valve C. One container, called the reference

cell, with a volume of V_r , was kept at a constant temperature, T_r , which is usually close to room temperature. The value of V_r includes the volume of the tube between the reference cell and valve C. The other container, the adsorption cell, is where the adsorbent was located and the adsorption equilibrium temperature, T_d , was maintained. The volume of the tube connecting the adsorption cell and valve C was divided into two parts: One part of volume V_t was open to the room, and therefore had the same temperature as the reference cell; the other part, with temperature T_d , was immersed in the atmosphere of the cryostat and, thus, its volume was added to adsorption cell V_d . The amount adsorbed was calculated from the P – V – T readings before and after opening valve C. The precision and reliability of adsorption measurement rely on how accurately P , V , and T were measured and how reliably the compressibility factor was determined. A pressure transmitter model PAA-23/8465.1-200, manufactured by Keller Druckmesstechnik (Switzerland), was used to measure the pressure. The volume of the reference cell was determined by the titration method. Volume V_d was determined by helium at temperature T_r . The amplitude of temperature variation was ± 0.1 °C for both T_r and T_d . Since each isotherm starts at a pressure reading of zero, it is necessary to place the system in a vacuum. To minimize the vaporization loss of water, the wet sample was cooled to -20 °C for every time the adsorption cell was put in a vacuum. The temperature was raised to the specified value after removal from the vacuum. The water loss during the experiment can be ignored, because the total weight of the sample before and after the isotherm measurement was almost unchanged. The adsorption cell containing the sample was kept at 2 ± 0.1 °C. The pressure was measured with a sensitivity of 0.05 % up to 3.7 MPa. The purities of the helium and carbon dioxide used in this experiment were both higher than 99.995 %.

The main characteristics of the samples were determined by adsorption and desorption isotherms of N₂ at 77 K and are shown in Fig. 2. About 0.5 g of sample was dried at 393 K in a vacuum cell for 24 h prior to the adsorption measurements. The adsorption isotherm covered a relative pressure from 10^{-6} to 0.995.

The special surface area of the sample was determined using the BET theory (Bruauer et al. 1938). The total pore volume was calculated from the amount of N₂ adsorbed at a relative pressure of 0.99. The pore size distribution of SG-A was determined by the HK method (Do 1998) and the pore size distributions of SG-B and SG-C were determined by the BJH method (Barrett et al. 1951) applied to the desorption branch of the isotherm. The results are shown in Fig. 3. The main properties of the silica gels are shown in Table 1.

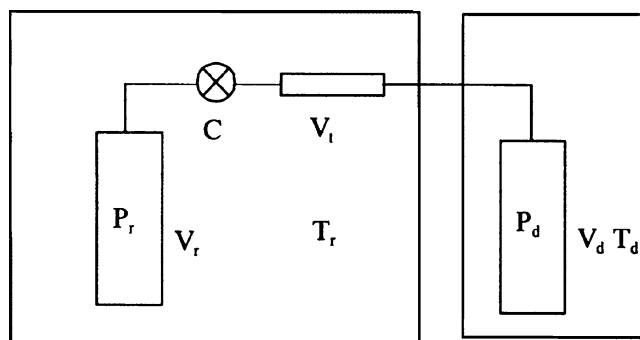


Fig. 1 Experimental apparatus

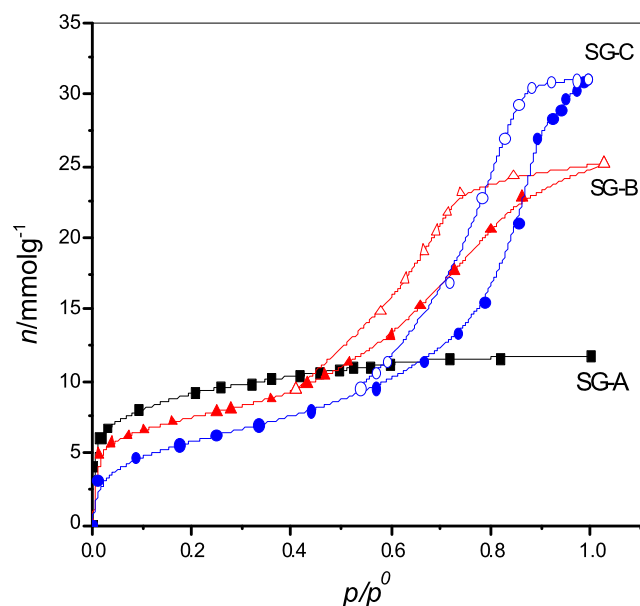


Fig. 2 Nitrogen adsorption and desorption isotherms on silica gels at 77 K (solids: adsorption data, hollows: desorption data)

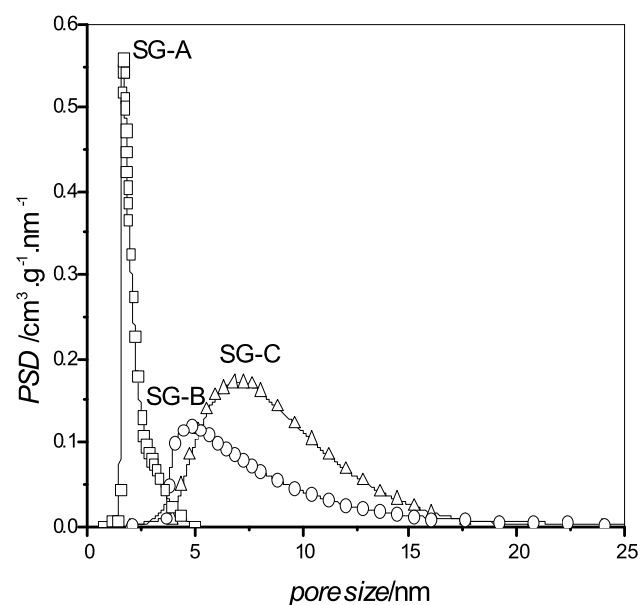


Fig. 3 Pore size distributions of the silica gels

Table 1 Main properties of silica gels

Sample	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Representative pore size/nm
SG-A	650	0.41	1.7
SG-B	575	1.08	5
SG-C	465	1.34	7

3 Results and discussion

3.1 Adsorption isotherms of the dry silica gels

The CO₂ adsorption isotherms on the dry silica gels at 275 K are shown in Fig. 4. The adsorption temperature is lower than the critical temperature of CO₂, thus CO₂ is condensable and the adsorption mechanisms are different for adsorbents with different PSDs. The adsorption isotherm of CO₂ on dry SG-A, a microporous silica gel, has the Type-I form (according to the IUPAC classification, IUPAC 1985), and its adsorption behavior follows a micropore filling mechanism. The adsorption isotherms of CO₂ on dry SG-B and SG-C, two mesoporous silica gels, have the Type-IV form, and capillary condensation takes place when the relative pressure reaches the value given by the Kelvin equation (Gregg and Sing 1982).

3.2 Sorption isotherms of the wet silica gels

The sorption isotherms of CO₂ on the wet silica gels were measured at 275 K. The highest pressure was about 3.7 MPa. The sorption amount is based on the weight of the dry sample and is expressed in mmol CO₂ sorbed per gram of sorbent. The water content in a wet sample is expressed as R_w , the weight ratio of water to silica gel.

The sorption isotherms of CO₂ at 275 K on the wet SG-A are shown in Fig. 4. Curves 2 and 3 show an S-shape with a sharp increase in the amount of sorption at a pressure of 2.3 MPa, which is due to the formation of CO₂ hydrate in the pore spaces. The amount of CO₂ sorbed increases as the

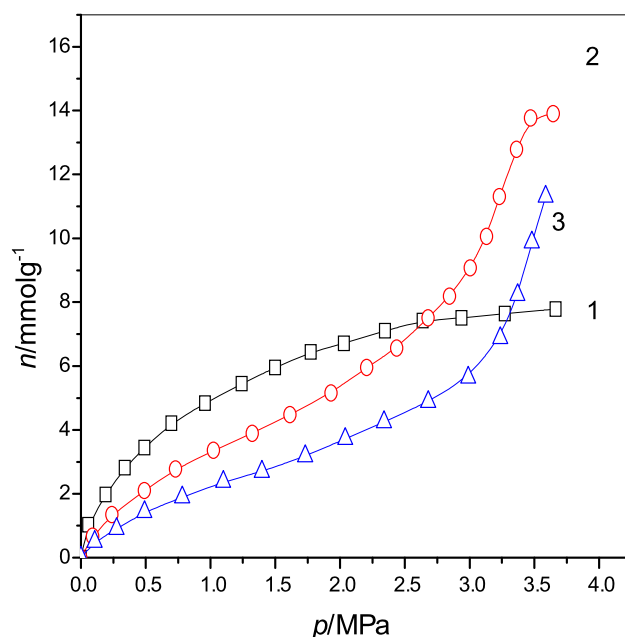


Fig. 4 Adsorption isotherms of CO₂ on dry silica gels at 275 K (1: SG-A, 2: SG-B, 3: SG-C)

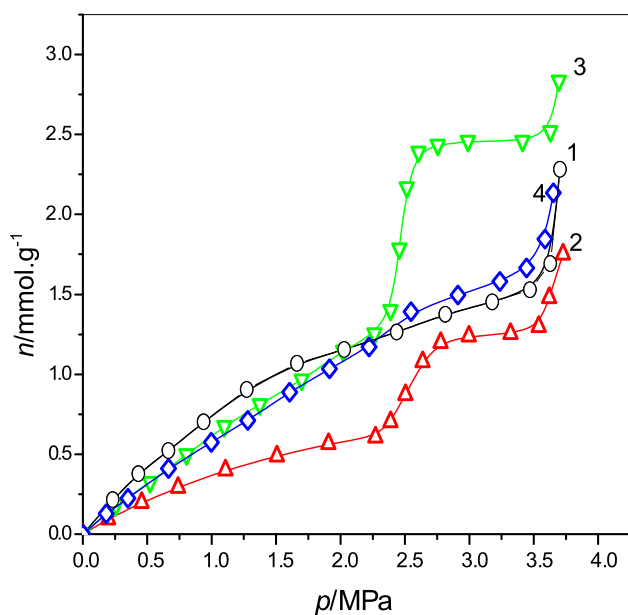


Fig. 5 Sorption isotherms of CO₂ on SG-A with different content of water at 275 K (1: $R_w = 0.33$, 2: $R_w = 0.58$, 3: $R_w = 0.75$, 4: $R_w = 0.82$)

pressure increases until the hydrate formation is complete. As soon as the hydrate formation is completed, the sorption amount does not change although the pressure increases, and then the CO₂ condenses. The inflection pressure where the sorption amount rises sharply is called the hydrate formation pressure and indicates the beginning of hydrate formation. The proofs for this and similar results are reported in our previous studies (Zhou et al. 2005, 2006, 2008). The hydrate formation pressure, around 2.3 MPa, is a little higher than that of CO₂ hydrate formation in pure water (Ma and Zhao 1997). Hydrate clathrate can only form in nanoscale pores which have a very high excess Gibbs free energy on the surface. So hydrate formation in microporous silica requires a greater pressure than in pure water.

The four sorption isotherms in Fig. 5 show the considerable effect that the amount of water has on the isotherm features and on the amount of CO₂ sorption. The amount of CO₂ sorbed on SG-A increases in curves 2 and 3 which have a higher quantity of presorbed water. The highest sorption amount of CO₂ that occurs before the condensation pressure of CO₂ at 275 K is about 2.5 mmol CO₂ per gram of dry sorbent, which is observed in curve 3 with $R_w = 0.75$. An inflection is not observed in curves 1 and 4 before the CO₂ condensation occurs. This indicates that the formation of CO₂ hydrate depends on the amount of water. Strong interactions between the water molecules and the silicon-hydroxyl groups on the surface of the silica gel may prevent the water molecules close to the surface from being used in the formation of the CO₂ hydrates. Therefore hydrate formation dose not occur if R_w is too low, such as in curve 1

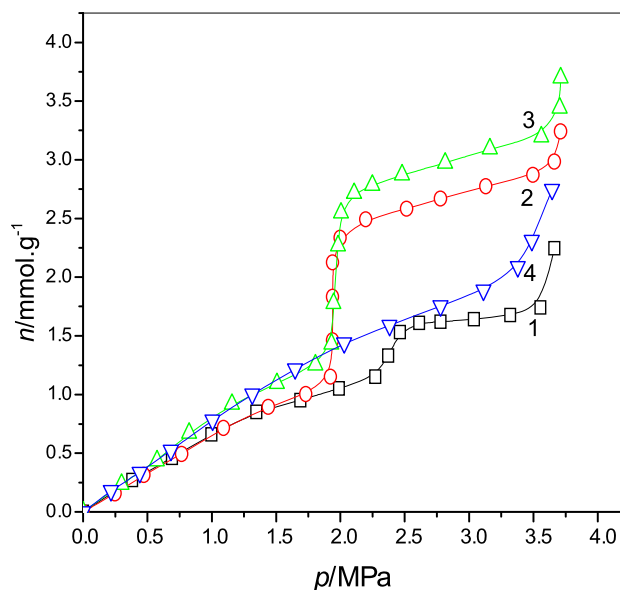


Fig. 6 Sorption isotherms of CO₂ on SG-B with different content of water at 275 K (1: $R_w = 0.61$, 2: $R_w = 0.75$, 3: $R_w = 0.81$, 4: $R_w = 1.05$)

with $R_w = 0.33$. On the other hand, too high of an R_w might block the pore space and prohibit the formation of CO₂ hydrate, such as in curve 4 with $R_w = 0.82$.

The sorption isotherms of CO₂ at 275 K on wet SG-B are shown in Fig. 6. The hydrate formation pressure observed for curve 2 and 3 is around 1.9 MPa which is a little lower than that for SG-A. This is due to the larger pore sizes. However, when the water content is low, such as curve 1 with $R_w = 0.61$, the hydrate formation pressure increases to 2.3 MPa. The reason for this higher formation pressure is that when water is adsorbed on the surface of the silica gel, the smaller pores will be filled first, and then the larger pores will be filled. If the water content is low, only the water in the small pores can be used to form hydrates. The hydrate clathrates formed in small pores have very high excess Gibbs free energies on the surface and need a higher generating pressure. Therefore, the hydrate formation pressure is decided not only by the PSD but also by the water content. The hydrate formation is not observed in curve 4 with a high water content for the same reason it was not seen in curve 4 on SG-A.

The sorption isotherms of CO₂ at 275 K on wet SG-C are shown in Fig. 7. There is no obvious pressure inflection in any of the isotherms before the CO₂ condenses. It is likely that the CO₂ hydrate does not form on the wet surface of SG-C due to the large pore sizes. If the pore size is too large, the impetus of the pores for promoting water molecules to form cages disappears, and the formation of hydrates in the pore spaces is similar to that in pure water. It is difficult for hydrates to form in pure water without high-speed stirring.

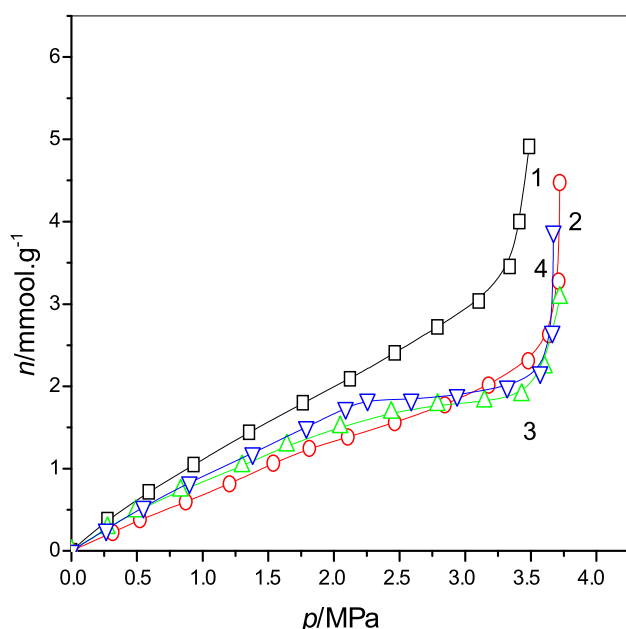


Fig. 7 Sorption isotherms of CO₂ on SG-C with different content of water at 275 K (1: $R_w = 0.5$, 2: $R_w = 1.0$, 3: $R_w = 1.14$, 4: $R_w = 1.24$)

3.3 The sorption mechanism for the wet silica gels

Before the pressure reaches the pressure needed for hydrate formation, the amount of CO₂ fixed on the wet silica gel includes only the quantity of CO₂ adsorbed on the surface and that dissolved in the water. When the pressure reaches the hydrate formation pressure, the amount of CO₂ also includes the hydrate formed in the pore spaces. CO₂ is condensable and its solubility is relatively large which can promote hydrate formation and lead to more CO₂ being fixed. Meanwhile, gaseous CO₂ can also be adsorbed on the surface of the exposed silica gel after the CO₂ hydrates are formed. Therefore, the molar ratio of water to fixed CO₂ may be less than the theoretical value of 5.75 (Charrière et al. 2010) which occurs for activated carbon (Sun et al. 2008). However, this is not the case in this experiment. The effect of R_w on the sorption capacity at 3.5 MPa is shown in Fig. 8, and using these results the molar ratios of H₂O to CO₂ were calculated (Fig. 9). The molar ratios of H₂O to CO₂ are much higher than 5.75 except for $R_w = 0.5$ for SG-C. This indicates that the ratio of water used to form the CO₂ hydrates is relatively low. This is probably due to strong H-bonding between the water and the silicon hydroxyl groups on the surface which prevents the water close to the surface from forming the cages in which the gas molecules can be held as guests to form crystalline inclusion compounds. The first layer of the water pre-adsorbed on the surface is hardly used for forming hydrates, and this effect is likely to extend to subsequent water layers. Only the water far from the surface can be used to form hydrates.

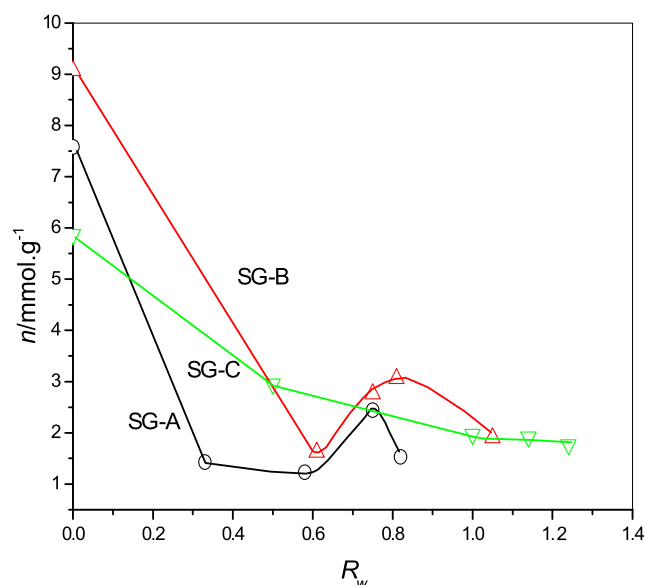


Fig. 8 The effect of R_w on sorption capacity at 3.5 MPa

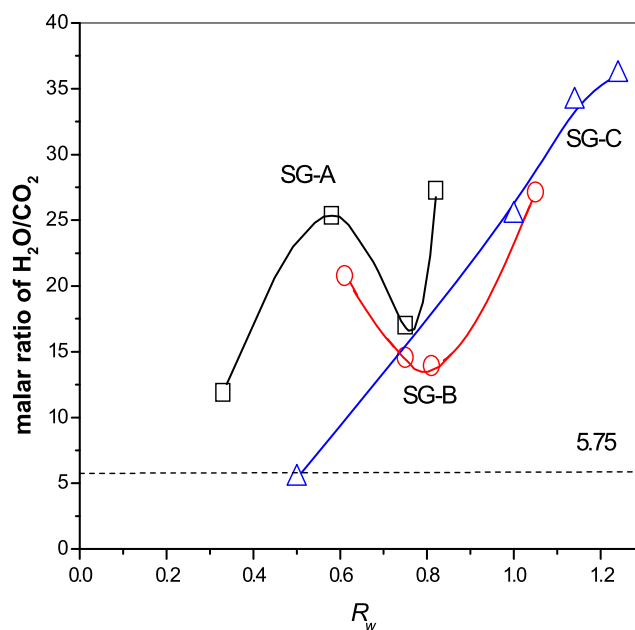


Fig. 9 The molar ratio of H₂O to CO₂

The exception for $R_w = 0.5$ for SG-C is due to the lower R_w , which results in CO₂ being adsorbed on the exposed surface. The adsorbed amount of CO₂ on the dry silica gel is much higher because of its condensability (Fig. 2).

4 Conclusions

The sorption equilibria of CO₂ on wet silica gels show that the amount of CO₂ hydrate formed and its formation pressure are greatly influenced by the quantity of water pre-

sorbed and by the PSD of the silica gel. An ideal PSD can help reduce the formation pressure of the CO₂ hydrate.

1. For the wet SG-A with $R_w = 0.75$ at 275 K, the highest amount of sorbed CO₂ was about 2.5 mmol CO₂ per gram of dry sorbent. The hydrate does not form if the R_w is too low or too high. Similarly, for the wet SG-B with $R_w = 0.81$, the highest sorption amount was about 2.7 mmol.
2. When the pore size is 7 nm or greater, such as in SG-C, the CO₂ hydrate does not form on the wet surface due to the pore sizes being too large. The impetus of pore space for hydrate formation disappears if the pore size is too large.
3. The ratio of water used for forming hydrates is relatively low due to the strong H-bonding between the water and the silicon hydroxyl groups on the surface.

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