Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 120 (2007) 257–261
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Tuning clathrate hydrates: Application to hydrogen storage

Do-Youn Kim [1], Youngjune Park, Huen Lee *

Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology,
Daejeon 305-701, Republic of Korea

Abstract

Gas hydrates represent an attractive way of storing large quantities of gases such as methane, although to date there has been little effort to optimize the storage capacity and to understand the trade-offs between storage conditions and storage capacity. In this work, we proposed the peculiar cage occupancy dynamics observed at the mixed hydrates simultaneously containing both one gas and one liquid guest. Liquid guests participating in forming hydrates must be water-soluble and possess the sufficient interaction with surroundings in order to make strong host-guest networks. However, it seems to be almost impossible for small molecules such as hydrogen and methane to replace the relatively large liquid guest molecules and thus an appropriate condition needs to be made for small guests to be enclathrated in large cages. By lowering the concentrations of liquid guests the small gas guests are found to enter the large cages feeling like their home. We also tried to explain this natural phenomenon with solid solution theory for clathrate hydrates. Special types of water-soluble liquid materials, such as THF, 1,4-dioxane, and *t*-BuNH$_2$, form sII double hydrates upon reacting with gas guest molecules. We expect that the storage capacities of gas guests largely depend on both the chemical nature of liquid guests and their relative concentration in host water. This tuning mechanism occurring in the mixed clathrate mixtures appears to be quite general and can be applied to energy and environmental systems including gas storage and transportation fields.

Keywords: Hydrates; Tuning phenomenon; Hydrogen; Gas storage; Methane

1. Introduction

Clathrate hydrates are non-stoichiometric crystalline compounds formed when guest molecules of suitable size and shape are incorporated in well-defined host cages made up of hydrogen-bonded water molecules [1]. Each hydrate lattice is a hydrogen-bonded network of four-connected water molecules and consists of at least two types of polyhedral cages [2]. Three distinct structural families termed, structures I, II, and H, are known, showing distinct structural characteristics such as cage types, distribution of guest molecules, and stability conditions [1,3–6]. The cages can accommodate small gas molecules such as methane, carbon dioxide and hydrogen as well as larger molecules such as THF and neohexane.

Recently, gas hydrates have attracted a great deal of attention because of their great potential as a source of natural gas as there are massive deposits both under the permafrost and in sediment on the continental margins [7]. The ability to store gas in the most efficient manner can be well represented by the unique hydrate property of major significance here, the commonly quoted fact being that 1 volume of sI methane hydrate can store ~160 volumes of gas at STP [8,9]. This consideration has led to the proposition that the hydrate-based technology can be adopted for the storage and transport of natural gas, and extensive efforts have been carried out to develop the efficient storage techniques in both scientific and industrial fields. The stability and cage distribution of clathrate hydrates including H$_2$ clusters have been identified through spectroscopic methods and a statistical mechanical model. Pure H$_2$ clathrate hydrates can be stable at extremely high pressures or low temperatures. Mao et al. [10] reported that H$_2$ clusters stabilized both 5^{12} cages and $5^{12}6^4$ cages of sII clathrate hydrate. More recent studies revealed that the inclusion of H$_2$ molecules can readily occur by introducing water-soluble hydrate promoters such as tetrahydrofuran (THF) within a water lattice at relatively low pressure and moderate temperature conditions [11,12]. In particular, we reported that H$_2$ molecules stored in THF-containing binary clathrates can be

---

* Tel.: +82 42 869 3917; fax: +82 42 869 3910.
E-mail address: h_lee@kaist.ac.kr (H. Lee).

[1] Present address: Research and Development Center, SK Engineering and Construction, 110-300 Seoul, Republic of Korea.

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.09.001

increased by tuning their composition to allow the H_2 guests to enter both the larger and the smaller cages. In addition, Replacement of CH_4 in the hydrate with high pressure CO_2 is alternative option for recovering CH_4 gas from its hydrates under the ocean [13]. This process is a favorable way as long-term storage of CO_2 and enables the ocean floor to remain stabilized even after recovering the CH_4 gas because the CH_4 hydrate has the same structure as the CO_2 hydrate. Several researchers have demonstrated both experimentally and theoretically the occurrence of the replacement in the hydrate using pressurized CO_2 and succeeded in the recovery of CH_4 and the storage of CO_2 in the laboratory scale [14,15].

2. Experimental

To identify clathrate hydrate structure and cage occupancies of guest molecules, a Bruker 400 MHz solid-state NMR spectrometer were used in this study. Spectra were recorded at 243 K by placing the powdered clathrate hydrate samples within a 4 mm o.d. Zr rotor that was loaded into the variable temperature (VT) probe. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with magic angle spinning (MAS) at about 2–4 kHz. The pulse length of 2 μs and pulse repetition delay of 40 s under proton decoupling were employed when the radio frequency field strengths of 50 kHz corresponding to 5 μs 90° pulses were used. Cross-polarization (CP) MAS spectra were also acquired for checking the signals from gas components. The number of acquisitions varied from 400 to 800, depending on the quality of the sample. The clathrate hydrate sample for NMR analysis was prepared from the clathrate hydrate-forming reactor, which was made of a type 316 stainless steel, with an internal volume of about 140 cm^3. The magnetically driven mechanical stirrer was used for uniform mixing during clathrate hydrate formation. The clathrate hydrate-forming reactor was kept in the water–ethanol mixture bath and its temperature was controlled by an externally circulating refrigerator/heater (JEIO TECH, RBC-20). The reactor was maintained at a constant pressure condition by using a microflow syringe pump (ISCO, model 260D) operated by the mode of constant pressure. About 50 cm^3 of the aqueous solution was initially charged into the reactor. When clathrate hydrate formation process was completed, the formed clathrate hydrates were finely powdered in the liquid nitrogen vessel and sampled into the Zr rotor immersed in liquid nitrogen to prevent any clathrate hydrate dissociation. This Zr rotor, having clathrate hydrate samples, was then inserted to the precooled MAS NMR probe. For in situ Raman spectra of the mixed hydrates, a high-pressure Raman cell, which has an internal volume of about 15 cm^3, was newly designed. It was made of 316 stainless steel and equipped with two sapphire windows at the front and back of the cell. The cell content was agitated by a small magnetic spin bar with an

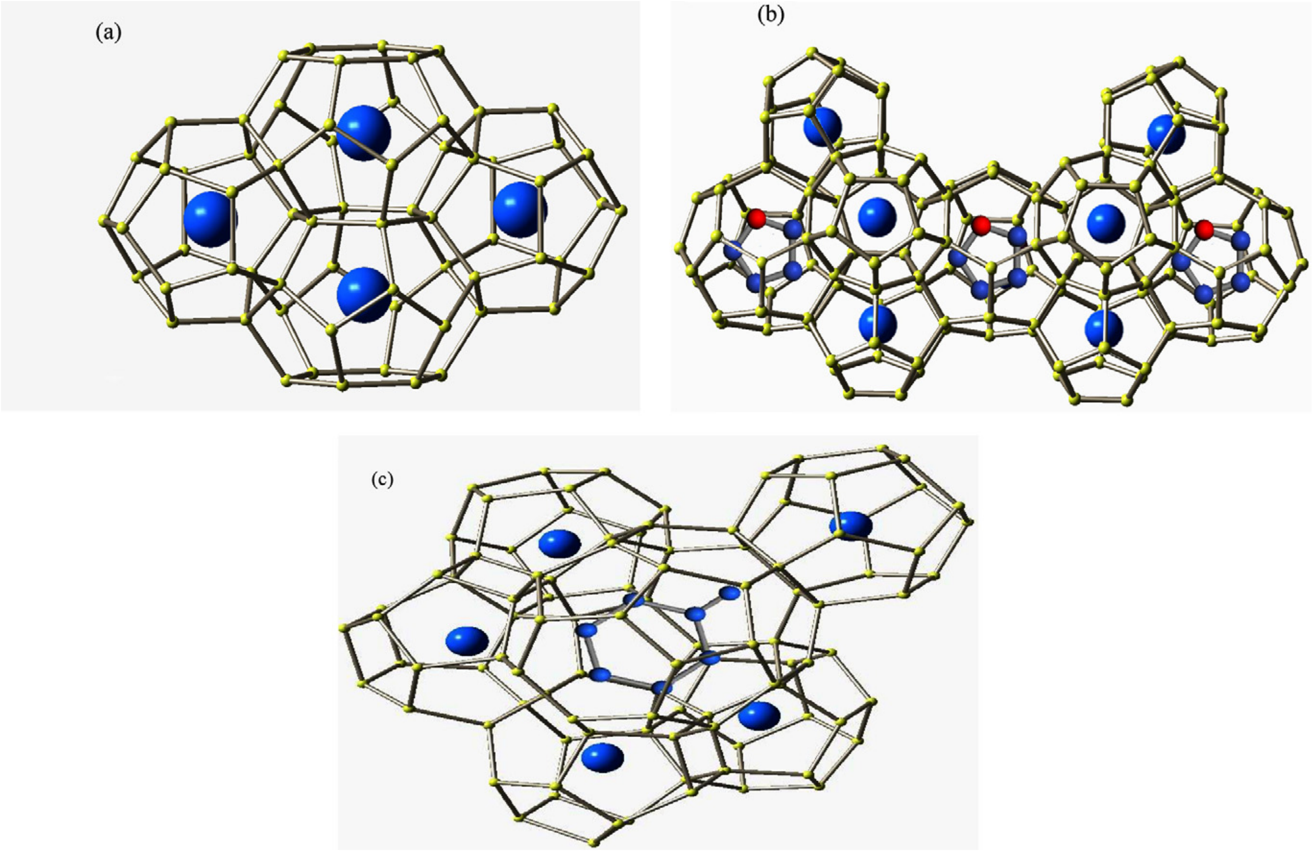

Fig. 1. Crystal structures of gas hydrates. (a) Structure I (unit cell, $2M_S \cdot 6M_L \cdot 46H_2O$), showing CH_4 molecules in M_S and M_L cages. (b) Structure II (unit cell, $16M_S \cdot 8M_L \cdot 136H_2O$), showing CH_4 molecules in M_S cages and THF molecules in M_L cages. (c) Structure H (unit cell, $2M_S \cdot 3M'_S \cdot M_L \cdot 34H_2O$), showing CH_4 molecules in M_S and M'_S cages, and methylcyclohexane in M_L cages.

external magnetic stirrer. The cell temperature was precisely controlled by circulating coolant through two circular grooves around the cell. The Raman spectra were obtained by using the Jobin-Yvon Ramanor U-1000, 1 m double-dispersed monochromator equipped with 1800 grooves/mm holographic grating system and recorded with a photomultiplier tube detector. The excitation source was an Ar/Kr ion laser emitting a 488.0 nm line. An IBM-PC with PRISM software provided control and data acquisition for the system. The scattered radiation was collected at the 180° geometry. The resulting spectra were collected with 0.5 cm^{-1} scanning steps and 2.0 s integration time step. Typically, four scans were averaged to represent each spectrum. The clathrate hydrate nucleation and dissociation steps were repeated at least two times to produce more homogeneous clathrate hydrates.

3. Results and discussion

The gas storage capacity of the different gas hydrate structures can be estimated from the known unit cell sizes and the ideal stoichiometry. Fig. 1 shows the unit cell of hydrate structures and Table 1 lists the gas storage capacities of each hydrate structures in $V_G(\mathrm{STP})/V_H$. We note that the total gas storage capacity for the three hydrate families, taken on an ideal molar basis, is very similar, and indeed the ratios are all close to 170. However, in the case of sII and sH, only the small cages are deemed to be available for methane storage, thus reducing the capacity to below values achievable for sI. However, the pressure at which gas storage is possible in the latter hydrates can be considerably less than for sI hydrate, as has been noted in a number of studies. Consideration of limited experimental data on hydrate stoichiometry, unfortunately, shows that the small cages in sI, sII and sH tend not to be fully occupied. The composition of sI hydrate is known to be $\sim CH_4 \cdot 6.1H_2O$, and from our previous work on CH_4/THF sII hydrate, ^{13}C NMR has shown that methane resides in the small cages at a low fractional occupancy of 0.592 and 0.368 when the THF concentrations are 3.0 and 5.6 mol%, respectively [16]. Similarly, single crystal X-ray diffraction on sH hydrate has shown that methane only occupies the small cages to a level of 80% in a double hydrate with methylcyclohexane. It should be noted that in neither case of sII and H are the large cages of the double hydrate occupied by methane, although the methane size is not restrictive.

Now we can formulate a strategy for improving the actual storage capacity from the values observed experimentally, as double hydrates do represent an opportunity for the tuning of hydrate composition. The ideal solution theory describes the stability of gas hydrate in terms of the minimum cage occupancy [17]:

$$\Delta\mu_w = -kT \sum_i \nu_i \ln(1 - \Theta_i) \tag{1}$$

where $\Delta\mu_w$ is the chemical potential difference between the hypothetical empty lattice and ice or liquid water, ν_i the number of cages of type i divided by the number of water molecules in the unit cell, and Θ_i is the cage occupancy.

If several components of type M are present:

$$\Theta = \sum_M \Theta_{Mi} = \frac{\sum_M C_{Mi} p_i}{1 + \sum_M C_{Mi} p_i} \tag{2}$$

where the C_{Mi} are Langmuir constants and p_i are the partial pressures of components i.

The minimum occupancy requirements for sII hydrate can be calculated using a ‘‘best’’ value of 883.8 J/mol for $\Delta\mu_w$ [18]. This shows that to form a stable sII hydrate, the large cage needs to be occupied to a greater than 99% level no matter what the occupancy is for the small cavity.

For two components (L1: liquid guest) and (G2: gaseous guest), the large cage occupancy becomes:

$$\Theta_L = \Theta_{L1} + \Theta_{G2} \tag{3}$$

$$\Theta_{L1} = \frac{C_{L1} p_1}{1 + C_{L1} p_1 + C_{G2} p_2} \tag{4}$$

$$\Theta_{G2} = \frac{C_{G2} p_2}{1 + C_{L1} p_1 + C_{G2} p_2} \tag{5}$$

Assuming ideal Henry’s law behavior for the liquid guest, $p_1 = kX_1$, where k is Henry’s law constant and X_1 is the mole fraction of component 1 in solution.

When the concentration of the liquid guest 1 is decreased at constant pressure of the gaseous guest 2, Θ_{L1} also decreases, but Θ_{G2} increases. However, this will happen only at the point where $C_{L1}p_1$–$C_{G2}p_2$. If $C_{L1} \gg C_{G2}$, as is the case for a liquid hydrate former 1 such as THF, and a small gaseous guest 2 such as methane, this will require both a high partial pressure of 2 and a low partial pressure (concentration) of 1. Although a more quantitative estimate is possible using the Henry’s law constants for the water-soluble guest former, a good practical measure for lowering the concentration of 1 sufficiently is where the liquid component by itself no longer forms hydrate upon cooling. This occurs at the eutectic composition on the water rich side, which for THF occurs at a concentration ~1 mol%. A sufficiently high partial pressure of component 2 in a solution of concentration less

Table 1
Gas storage capacity of the different hydrate families in terms of the ratio of the volume of gas stored at STP to the volume of the hydrate ($V_g(\mathrm{STP})/V_h$)

Structure unit cell content lattice parameter	CH_4 content $V_g(\mathrm{STP})/V_h$ (all cages)	CH_4 content V_g (STP)/V_h(small cages only)
sI, $2M_S \cdot 6M_L \cdot 46H_2O$, cubic, $a = 1.18$ nm	$174 M_S = M_L = CH_4$	$44 M_S = CH_4$
sII, $16M_S \cdot 8M_L \cdot 136H_2O$, cubic, $a = 1.71$ nm	$171 M_S = M_L = CH_4$	$114 M_S = CH_4$
sH, $2M_S \cdot 3M'_S \cdot M_L \cdot 34H_2O$, hexagonal, $a = 1.22$ nm, $c = 1.00$ nm	$172 M_S = M'_S = M_L = CH_4$	$143 M_S = M'_S = CH_4$

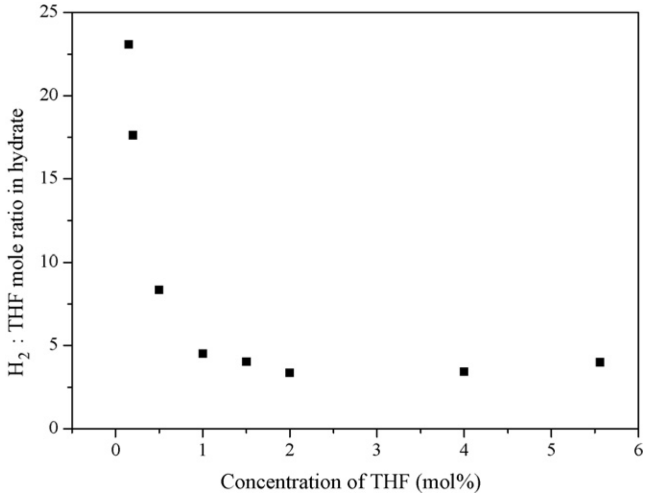

Fig. 2. Mole ratio of H_2 to THF in hydrate phase.

than 1 mol% THF should still result in solid gas hydrate formation, as stability depends only on the total Θ_L.

The above reasoning shows that the ‘‘tuning’’ of a hydrate composition is quite a general phenomenon for sII hydrates that can be accomplished by adjusting the partial pressure and concentration of the gaseous and liquid hydrate formers. It should be possible to have a continuous range of compositions, from having all large cages filled with species 1 to having all cages filled with species 2, by adjusting p_1 and p_2, unless another structure intervenes because of greater thermodynamic stability. The only criterion for producing a stable hydrate is to give a Θ_L value which always needs to be close to 1. Practically this means that either the concentration of 1 in solution must be high enough, or the pressure of 2 must be high enough to give a compound with relative stability with respect to the various components or to other possible hydrate structures. We note that this kind of variable composition is well known for gas mixtures, e.g. methane and propane, but nothing is known about the use of water soluble hydrate formers that are especially favorable for double hydrate formation.

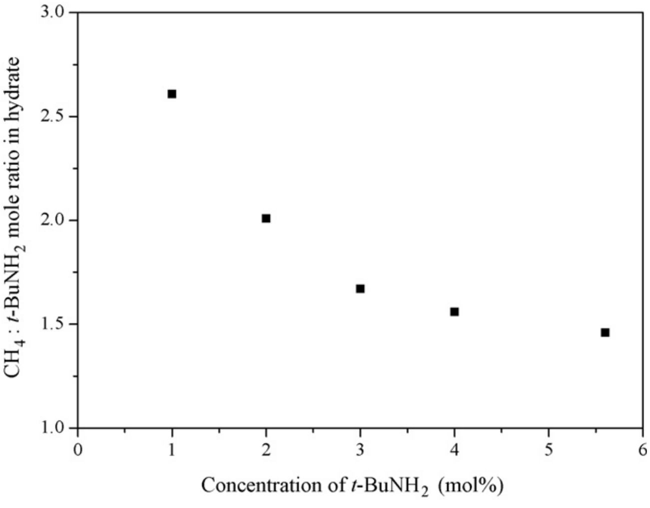

Fig. 3. Mole ratio of CH_4 to t-$BuNH_2$ in hydrate phase.

To experimentally ascertain the tuning phenomenon, we introduced the two kinds of systems, H_2 + THF double hydrate and CH_4 + t-$BuNH_2$ double hydrate. First, by using Raman spectroscopy, we could determine the mole ration of H_2 to THF in hydrate. Fig. 1 shows the variation of H_2 amount stored in hydrate phase according to concentration of THF. As the concentration of THF decreased, the H_2 molecules captured in hydrate phase increased. Especially, below 1.0 mol% of THF, the number of stored H_2 molecules increased rapidly because the H_2 molecules occupied the large cages of double hydrate. For the CH_4 + t-$BuNH_2$ double hydrate, we directly measured the CH_4 content released from the hydrate phase and results were shown in Fig. 2. The captured amount of CH_4 gas also increased as the concentration of t-$BuNH_2$ decreased like as H_2 + THF system. From these experimental results, we expect that the gas storage capacity of sII double hydrate can be enhanced by tuning the concentration of liquid guest molecule (Fig. 3).

4. Conclusions

We have shown that the composition of sII double hydrates can be tuned to optimize gas storage conditions by adjusting the concentration of the water soluble hydrate formers, THF and t-$BuNH_2$ at the specified combinations of temperature and pressure. This tuning mechanism appears to be quite general and can be readily applied for enhancing a gas storage capacity of double hydrate systems including water-soluble hydrate promoters. The solid solution theory describing the stability of gas hydrate indicates that the tuning of a hydrate composition can be detected in most of sII double hydrates. The versatile cage occupancy behavior is also observed at the full concentration range of liquid guest and it must be particularly noted that at the highly dilute liquid guest concentration any types of hydrate structures can’t be formed because at this condition the liquid guest acts as an inhibitor on hydrate formation. The ‘‘tuning mechanism’’ plays an important role in understanding the dynamics of hydrate cages and should be one of the strategies used to enhance the gas-storage capacity of double hydrate systems for application to gas storage and transportation areas.

Acknowledgements

This work was financially supported by the National Research Laboratory (NRL) Program of KOSEF, and also partially performed by the ‘‘Studies on Gas Hydrate Development Technology’’ funded by the Ministry of Commerce, Industry and Energy of Korea.

References

[1] E.D. Sloan, Clathrate Hydrates of Natural Gas, 2nd ed., Marcel Dekker, New York, 1998.
[2] G.A. Jeffrey, Inclusion Compounds, Academic Press, London, 1984.
[3] J.A. Ripmeester, C.I. Ratcliffe, Energy Fuels 12 (1998) 197.
[4] J.A. Ripmeester, C.I. Ratcliffe, I.G. Cameron, J. Phys. Chem. B 108 (2004) 929.
[5] A. Khan, J. Phys. Chem. A 105 (2001) 7429.
[6] A.P. Metha, E.D. Sloan Jr., J. Chem. Eng. Data 38 (1993) 580.

[7] C. Ji, G. Ahmadi, D.H. Smith, Chem. Eng. Sci. 56 (2001) 5801.

[8] A.A. Khokhar, J.S. Gudmundsson, E.D. Sloan Jr., Fluid Phase Equilibr. 150/151 (1998) 383.

[9] J.S. Gudmundsson, M. Mork, O.F. Graff, in: Proceedings of the Fourth International Conference on Gas Hydrates, Yokohama, (2002), p. 997.

[10] W.L. Mao, H. Mao, A.F. Goncharov, V.V. Struzhkin, Q. Guo, J. Hu, J. Shu, R.J. Hemley, M. Somayazulu, Y. Zhao, Science 297 (2002) 2247.

[11] H. Lee, J.-W. Lee, D.Y. Kim, J. Park, Y.T. Seo, H. Zeng, I.L. Moudrakovski, C.I. Ratcliffe, J. Ripmeester, Nature 434 (2005) 743.

[12] L.J. Florusse, C.J. Peters, J. Schoonman, K.C. Hester, C.A. Koh, S.F. Dec, K.N. Marsh, E.D. Sloan, Science 306 (2004) 469.

[13] K. Ohgaki, K. Takano, M. Moritoki, Kagaku Kogaku Ronbunshu 20 (1994) 121.

[14] S. Hirohama, Y. Shimoyama, A. Wakabayashi, S. Tatsuta, N. Nishida, J. Chem. Eng. Jpn. 29 (1996) 1014.

[15] T. Komai, T. Kawamura, S.-P. Kang, K. Nagashima, Y. Yamamoto, J. Phys. Condens. Matter 14 (2002) 11395.

[16] Y.-T. Seo, H. Lee, I.L. Moudrakovski, R.A. Ripmeester, Chem. Phys. Chem. 4 (2003) 379.

[17] J.H. van der Waals, J.C. Platteeuw, Adv. Chem. Phys. 2 (1959) 1.

[18] S. Subramanian, R.A. Kini, S.F. Dec, E.D. Sloan, Chem. Eng. Sci. 55 (2000) (1981).