

Spectroscopic observation of H₂ migration in structure-I clathrate hydrate

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Abstract—We demonstrate the spectroscopic observation of H₂ migration in the binary structure-I (sI) clathrate hydrate. The H₂ molecules captured into sI small cage (sI-S) at lower temperature migrate to sI large cage (sI-L) through shared pentagonal face of 5¹²6² cage. The hexagonal faces of 5¹²6² cage provide the windows essential for creating continuous diffusion paths for H₂ molecules. It is essential to realize that the vacant channels formed by the linkage of specific cages can play an important role in guest diffusion pathways and occupancy occurring in a complex clathrate hydrate matrix.

Key words: H₂ Migration, Clathrate Hydrate, NMR, Inclusion Compounds, Water Chemistry

INTRODUCTION

Molecular dynamics of guest molecules in clathrate hydrate is indispensable for a complete understanding of unique and complex inclusion phenomena occurring in the cages with highly flexible lattice. Particularly, the (H₂+tetrahydrofuran (THF)) structure-II (sII) hydrate has recently received special attention because of its outstanding stability and storage capacity [1,2]. To date, the real nature of a guest dynamic pattern remains still largely unanswered in spite of its urgency in the field of inclusion chemistry. Focusing on hydrogen guest, Alavi and Ripmeester [3] first addressed the probability of H₂ guest migration between the binary H₂-THF hydrate cages from electronic-structure calculations. According to their calculations, H₂ molecules can migrate through hexagonal faces of the large cages at temperatures above 100 K, but a much higher temperature above 250 K is required for migration through pentagonal faces of the small cages. To our knowledge, the direct experimental observation of H₂ transport between the cages or through channels formed in the host water framework has not yet been reported via either microscopic or macroscopic approaches.

In this study, we demonstrate the spectroscopic observation of H₂ migration in the binary (H₂+CH₄) and (H₂+Xe) structure-I (sI) clathrate hydrates. The synthesis of pure sII hydrogen clathrate hydrate requires the extremely high pressure condition, but with the aid of help gases that promote the lattice formation the binary H₂ sI clathrate hydrate can be readily made [4].

EXPERIMENTAL SECTION

The H₂, CH₄, and Xe gases with a minimum purity of 99.95 mol% used for this study were supplied by Special Gas (Korea). The ¹³CH₄ gas with a minimum purity of 99.0% used for this study was supplied by Cambridge Isotope Laboratories, Inc. as was the deuterium oxide. The frozen deuterium oxide was ground to a fine powder (~200 μm). The powdered deuterium oxide was placed in the

two pressurized cells having 20 cm³ volumes and then exposed to feed gases (feed gas composition of sample 1: H₂ 165 bar+CH₄ 15 bar, sample 2: H₂ 171 bar+Xe 9 bar) at 203 K. When the hydrate formation process was completed, the formed hydrate was finely powdered in the liquid nitrogen vessel.

The powder X-ray diffraction (PXRD) patterns were recorded at 93 K on a Rigaku D/MAX-2500 by using graphite-monochromatized Cu_{Kα1} radiation (λ=1.5406 Å) in the $\theta/2\theta$ scan mode. The XRD experiments were carried out in step mode with a fixed time of 3 s and a step size of 0.03° for 2θ=5°–55° for each hydrate sample. The PXRD pattern could be indexed by using the Check Cell [5] program.

A Bruker (Billerica, MA) AVANCE 400 MHz solid-state NMR spectrometer was used in this study. The powdered samples were placed in a 4 mm o.d. zirconia rotor loaded into a variable temperature probe. All ¹H NMR spectra were recorded with magic angle spinning (MAS) at approximately 7 kHz and the proton resonance peak of tetramethylsilane (TMS), assigned a chemical shift of 0 ppm at 298 K, was used as an external chemical shift reference. The ¹H MAS NMR spectra of the samples were obtained increasing the temperature from 213 to 263 K. The high-power decoupling (HPDEC) ¹³C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with MAS at approximately 7 kHz. A pulse length of 2 μs and a pulse repetition delay of 10 s under proton decoupling were employed with a radio frequency field strength 50 kHz, corresponding to 5-μs 90° pulses. The downfield carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 298 K, was used as an external chemical shift reference. For the mixed hydrate samples, ¹³CH₄ was mixed to obtain higher-intensity CH₄ signals.

To measure the amount of gas guest molecules in the hydrate sample, Young-Lin M600D (Younglin, Seoul, Republic of Korea) Gas Chromatography (GC) was used. The samples were placed in a sealed reactor having the volume of 10 cm³ and remained at the room temperature until the hydrate samples were dissociated completely. Through the 1/16-inch tube, pressure was reduced by a vacuum pump, and 1.0 μl of the gas mixture was fed from the reactor to the GC column. Nitrogen gas was used as the carrier gas, and the GC column was at 55 kPa and 333 K.

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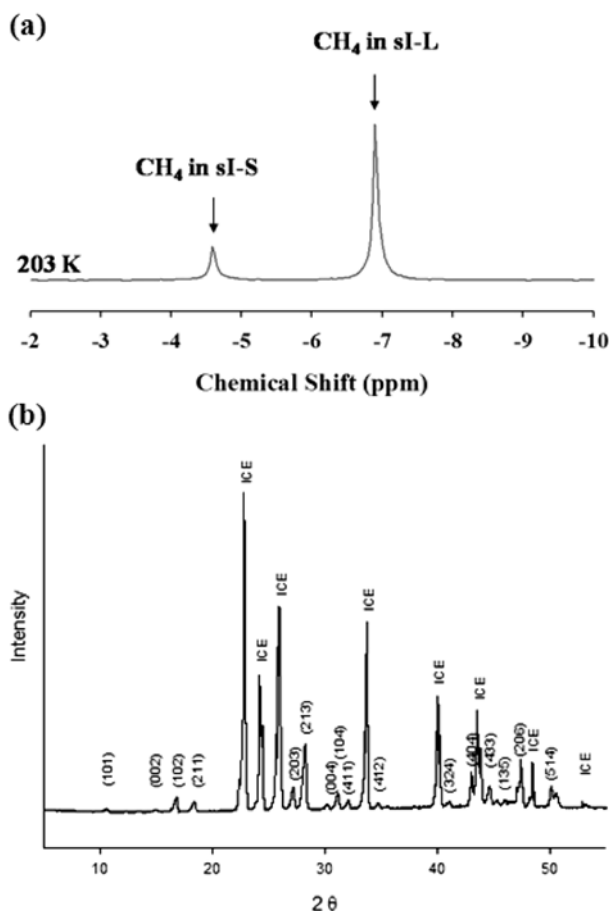


Fig. 1. (a) ^{13}C HPDEC NMR Spectra of binary (H_2+CH_4) sI clathrate hydrates at 203 K and 7 kHz spinning (b) PXRD pattern of mixed (H_2+CH_4) clathrate hydrate. Space group: Pm3n, cell parameter: $a=11.8300 \text{ \AA}$.

RESULTS AND DISCUSSION

The feed gases (H_2 165 bar+ CH_4 15 bar and H_2 171 bar+Xe 9 bar) were directly exposed to D_2O . The samples were stored under liquid nitrogen temperature before being loaded to the NMR equipment. The structure of formed binary (H_2+CH_4) hydrate was confirmed to be sI by HPDEC ^{13}C NMR spectrum and PXRD pattern (Fig. 1). For this binary sI clathrate hydrate, the H_2 guest molecules are considered to preferentially occupy the sI small cages (sI-S) due to its smaller molecular size [6,7]. In the first place, the CH_4 molecules occupy the sI large cages (sI-L) for the stabilization of structural network, then followed by the guest filling in sI-S. The H_2 guest composition of sample checked by gas chromatography measurement was 8.7 mol%. The question arises from the H_2 filling in sI-L and possible diffusion pathway for migration. However, we realize that the in-situ experiment might be the best, but hindered by the inherent NMR limitation.

To see the occupancy pattern of binary guests, the ^1H MAS NMR spectra of the samples were obtained increasing the temperature from 213 to 263 K as shown in Fig. 2. The signals at 4.1 and 6.5 ppm represent the H_2 in sI-S and HDO impurities, respectively [4]. For gaseous H_2 , the peak is known to occur at 4.3–4.5 ppm [8], and thus the peaks below 4 ppm are not linked with the entrapped hy-

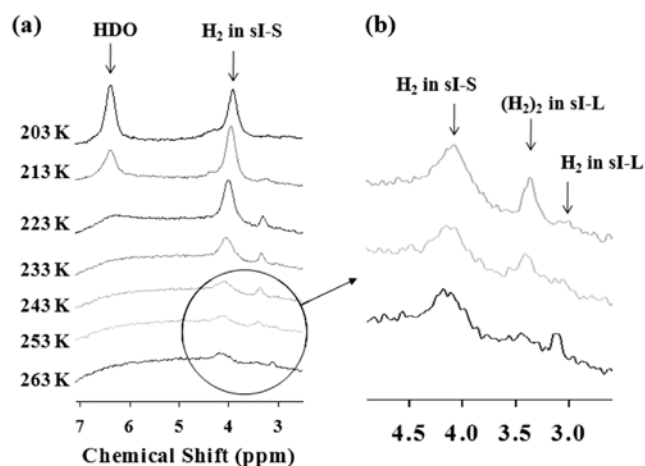


Fig. 2. (a) ^1H MAS Spectra of binary (H_2+CH_4) sI clathrate hydrates obtained increasing the temperature from 213 K to 263 K at 7 kHz spinning (b) magnification of 2.5–5.0 ppm spectra obtained at 243, 253, and 263 K.

drogen in cages. A notable observation appears in the spectra measured at temperatures above 223 K. In Fig. 2a, a new peak at $\delta=3.5$ ppm grows with increasing temperature, reaches the maximum and at higher temperatures almost disappears. This proton signal implies that the H_2 diffusion is likely to occur in the hydrate phase to the direction of either sI-S to sI-L or sI-L to sI-S. The more interesting feature appears at higher temperature at which two peaks at 4.1 and 3.5 ppm decrease, but a new small peak arises at $\delta=3.1$ ppm initiating at 243 K. The overall migration process can be clearly described as follows: the partial fraction of H_2 molecules at 4.1 ppm transport to more stable structural position assigned at 3.5 ppm as temperature increases. Further temperature rise drives for the peak at 3.5 ppm to weaken and a peak to newly appear at 3.1 ppm. This observation implies that the migration pathway of H_2 molecules is quite thermally sensitive, altering the H_2 distribution in cages and more significantly in channels. The same experiment was done at 150 bar. We observed that the overall NMR spectrum was same as that at 180 bar, but the peaks at 3.5 and 3.1 ppm appear to be weak, implying that the H_2 occupancy and migration pattern is quite sensitive to external variables. For more evidence of this unique migration pattern occurring in the sI hydrates, we tested the binary (H_2+Xe) clathrate hydrates at 180 bar. The overall spectrum appears to be identical with that of binary (H_2+CH_4) clathrate hydrate, but the peak at 3.5 ppm was too weak to clearly identify (Fig. 3). From two different sI hydrates we realize that particularly the transient peak at 3.5 ppm is quite sensitive to how to synthesize the samples, to the relative H_2 composition in the gaseous guest mixture, namely the partial pressure, and to the thermal variation of the flexible cage lattice.

Thus far, although the vacant channels formed by the linkage of specific cages have not received any attention in the inclusion phenomena of clathrate hydrates, it is essential to realize that these channels can play an important role in guest diffusion and occupancy occurring in a complex clathrate hydrate matrix. We also observe that the sI and sII clathrate hydrates own the intra-crystalline channels composed by like-cage stacking, providing many different patterns of diffusion pathways [9]. Apparently, the presence of guest

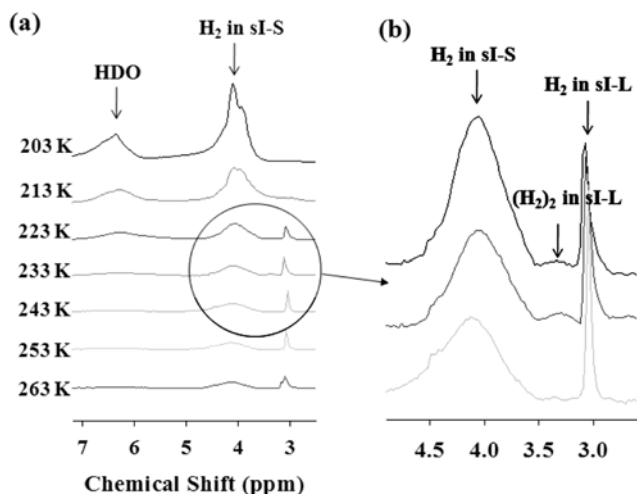


Fig. 3. (a) ¹H MAS Spectra of binary (H₂+Xe) sI clathrate hydrates increasing the temperature from 213 K to 263 K at 7 kHz spinning (b) magnification of 2.5-5.0 ppm spectra obtained at 223, 233, and 243 K.

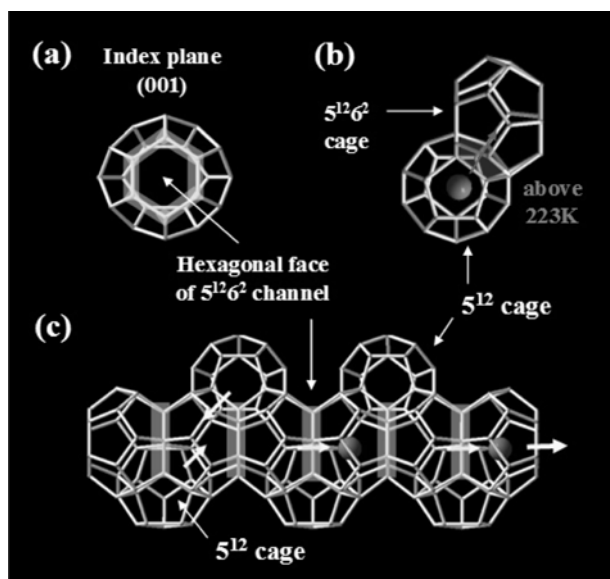


Fig. 4. (a) The entrance of sI-L channel (b) H₂ migration through pentagonal face of sI-S cage (c) H₂ migration in the sI-L channel.

molecules in the nearly immobile host frameworks are capable of inducing the crystalline structure to transform to a more stable structure by lowering the chemical potential of the fresh host lattice formation.

Unlike the sII channel pattern composed of small cage (5¹²) stacking, the sI clathrate hydrate has spatial arrangements composed of large cage (5¹²6²) stacking. The 14-hedra (5¹²6²) shares two hexagonal faces and eight of their pentagonal faces with adjacent 14-hedra. The remaining four faces are shared with the 12-hedra (5¹²). It should be noted that there is no direct face-sharing between the 12-hedra (5¹²). The hexagonal faces of 5¹²6² cage provide the windows essential for creating continuous diffusion paths for H₂ molecules (Fig. 4a). The H₂ molecules captured into sI-S at lower temperature migrate

to sI-L through the shared pentagonal face of the 5¹²6² cage (Fig. 4b). Accordingly, a new peak ($\delta=3.5$ ppm) is considered to be the signal from H₂ migrating from neighboring two sI-S cages to one vacant sI-L cage through these window openings, resulting in double occupancy. We note that the sI-L has 4.33 Å of average cage radius, which is the middle value between sI-S (3.95 Å) and sII-L (4.73 Å) [7]. In a specific sI hydrate, the guest molecules, particularly H₂, can be singly or doubly distributed according to the pattern of channels and cages to the direction of lowering the chemical potential and stabilizing the structural composition.

As the temperature increases, the double occupancy of H₂ molecules in sI-L becomes difficult to be kept due to entropy increase of H₂ molecular states. When two H₂ molecules doubly occupied in a sI-L cage meet a neighboring vacant sI-L cage in diffusion channel, one H₂ molecule readily diffuses to the vacant cage through hexagonal openings. Under this circumstance the H₂ molecules undergo only one-dimensional sI-L diffusion because there are no sI-S channels for providing the cross-connecting hexagonal-face openings. As a consequence, the H₂ molecules tend to be evenly distributed in sI-L cages making the single guest occupancy in the most favorable state as the temperature increases. This migration phenomenon reveals that the peak intensity of double H₂ occupancy at 3.5 ppm is gradually reduced, while the singly occupancy peak intensity at 3.1 ppm continuously grows. The H₂ migration temperatures calculated by Alavi and Ripmeester are above 100 K for sII-L and above 250 K for sII-S [3]. They assumed that the cages and H₂ guest molecules in their calculations were considered to be rigid. They also mentioned that the energy barrier to H₂ migration would decrease in the real hydrate system having cage flexibility [3,10,11]. However, for sI clathrate hydrates this study clearly shows that the H₂ molecules in 5¹² cages migrate through pentagonal face at temperatures above 223 K (Fig. 2a). Interestingly, this sI-S migration temperature comes out to be quite comparable to 250 K of the sII-S one from Alavi and Ripmeester [3]. A notable feature for guest distribution and migration is that the peak intensity at 3.5 ppm representing double H₂ occupancy is quite sensitive to externally driven thermal variation and other physical conditions and thus to some extent is in the transitional stage.

CONCLUSION

Thus far, although the vacant channels formed by the linkage of specific cages have not received any attention in the inclusion phenomena of clathrate hydrates, it is essential to realize that these channels can play an important role in guest diffusion pathways and occupancy occurring in a complex clathrate hydrate matrix. In a specific intra-crystalline clathrate hydrate structure, guest molecules of a suitable size and shape may be readily accessible to the resulting patterns of channels and cages, as observed in zeolite inclusion complexes. In principle, the present approach treated for the sI clathrate hydrates might be well applied to the sII clathrate hydrates for the reason that the sII clathrate hydrates stably form the (5¹²) channels compared to the (5¹²6²) channel of sI hydrates. Thus, we realize that the spectroscopic pattern and molecular motions for H₂ migration in the sII hydrates completely differ from those of the present sI outcome. Although several key structural and dynamic characteristics occurring in crystalline clathrate hydrate matrix were addressed,

further extensive work should be done to provide new insights into inclusion chemistry fields.

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