

## Spectroscopic evidences of the double hydrogen hydrates stabilized with ethane and propane

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**Abstract**—Hydrogen molecules are known to occupy the small cages of structure I (sI) and II (sII) hydrates with the aid of co-guests, leading to the highly stable state of their crystalline framework. For the first time, we synthesized the double hydrogen hydrates incorporated with ethane and propane that play a special role as the hydrate promoters or stabilizers. The resulting hydrate structures cage occupancy was identified by the spectroscopic methods of the PXRD and solid-state NMR. In addition, direct GC analysis confirmed that the encaged hydrogen amounts are 0.127 for sI ethane and 0.370 for sII propane at 120 bar and 270 K. The proper hydrate thermodynamics particularly focusing on the cage occupancy estimated that 0.17 and 0.33 wt% of hydrogen are observed in small cages of sI and sII hydrates. The overall spectroscopic and physicochemical analysis strongly imply that the sII cages act as much more favorable sites than sI cages in storing hydrogen.

Key words: Clathrate Hydrate, Hydrogen, Ethane, Propane, NMR

### INTRODUCTION

The storage of large quantities of hydrogen at mild pressures and temperatures becomes a key factor in establishing a hydrogen-based economy [1]. The conventional storage methods using compressed and liquid hydrogen require extreme conditions that must be overcome for commercial applications. We must also note that the recently reported storage concepts including carbonaceous materials and MOFs possess the inherent limitations on actual storage amount, total weight and efficient operation. With great interest the stability and cage distribution of clathrate hydrates, including H<sub>2</sub> clusters, have recently been explored through powerful spectroscopic methods and statistical mechanical models [2-4]. Mao et al. reported that H<sub>2</sub> clusters are stabilized in both 5<sup>12</sup> and 5<sup>12</sup>6<sup>4</sup> cages of sII clathrate hydrate with a unit cell parameter of 17.047 Å [3]. They conjectured without highly reliable data coming from quantitative measurements that the small and large cages occupy two and four H<sub>2</sub> molecules, respectively. Furthermore, we need to recognize that pure H<sub>2</sub> clathrate hydrates can be only stable at extremely high pressures or low temperatures. More recent studies have revealed that the inclusion of H<sub>2</sub> 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. With the special goal of maximum occupancy, we reported that H<sub>2</sub> molecules stored in THF-containing binary clathrates can be increased by tuning their composition to allow the H<sub>2</sub> guests to enter both the larger and the smaller cages [2]. In addition to sII hydrogen hydrate using the water-soluble liquid guests, Kim and Lee first reported that the mixed sI hydrogen hydrate are formed with carbon dioxide acting as a gaseous guest [4].

A variety of mixed hydrogen hydrates need to be carefully syn-

thesized and examined to meet the specially required purposes. We might take one example from fuel-cell technology. The direct electrochemical oxidation of dry hydrocarbon fuels to generate electrical power has the potential to accelerate substantially the use of fuel cells in transportation and distributed-power applications. Most fuel-cell research has involved the use of hydrogen as the fuel, although the practical generation and storage of hydrogen remains an important technological hurdle [5]. Methane has been successfully oxidized electrochemically, but the susceptibility to carbon formation from other hydrocarbons that may be present or poor power densities have prevented the applications [6]. Park et al. reported the direct electrochemical oxidation of various hydrocarbons (methane, ethane, 1-butane, n-butane and toluene) using a solid-oxide fuel cell at 973 and 1,073 K with a composite anode of copper and ceria (or samaria-doped ceria) [7]. In this regard, it might be interesting to check the possibility of synthesizing the mixed hydrogen hydrates containing both hydrogen and hydrocarbon, used as fuel cell sources. Accordingly, in this work we attempted to provide spectroscopic evidence of the mixed hydrogen hydrates formed with ethane and propane by using the PXRD and solid-state NMR. Additionally, through a GC analysis, we quantitatively evaluated the cage occupancy of hydrogen molecules.

### EXPERIMENTAL SECTION

The C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and H<sub>2</sub> gases were supplied by Special Gas Co. and had stated purities of 99.995, 99.9, and 99.999 mol%, respectively. Water was supplied from Sigma-Aldrich Chemical Co. with a purity of 99.1 mol%. The hydrate formation cell had an internal volume of about 50 ml and was charged with approximately 25 ml of liquid water. Two sapphire windows located at the front and back of the cell allowed the visual observation of phase transitions. As the initial step of experiments, pure ice particles, crushed in a mortar and pestle and removed with a 200 µm size sieve, were reacted at

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275 K and pressures of 25 bar for ethane and 5 bar for propane above the anticipated hydrate-forming equilibrium pressures, but below their liquefaction pressures for more than 3 days. After pure hydrocarbon hydrates were formed, the cell was vented in a 253 K refrigerator, pressurized to the pressure of 120 bar with hydrogen gas and placed for 3 days, maintaining 270 K. The crystalline structure of synthesized hydrogen hydrates was determined by powder x-ray diffraction (PXRD, D/MAX-RB, Rigaku) with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) by detecting several diffraction peaks at 1 bar and 123.15 K. The PXRD experiments were performed by step mode with a fixed time of 3 s and a step size of  $0.03^\circ$  in the  $2\theta$  range of  $3\text{--}70^\circ$ . A Bruker 400 MHz solid-state NMR spectrometer was used to determine the pertinent Spectra at 223 K by placing samples within a 4 mm o.d. Zirconia rotor loaded into variable temperature probe. The  $^1\text{H}$  magic angle spinning (MAS) NMR spectra were recorded at a frequency of 400.2 MHz with magic angle spinning (MAS) at about 12 kHz, while the  $^{13}\text{C}$  NMR spectra were recorded at a frequency of 100.6 MHz at about 5 kHz. The downfield hydrogen resonance peak of tetramethylsilane, assigned a chemical shift of 0.0 ppm at 183 K, was used as an external chemical shift reference in  $^1\text{H}$  NMR. The downfield carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference in the  $^{13}\text{C}$  NMR. The pulse length was 4  $\mu\text{s}$  and repetition time delay of 15 s was employed. After hydrogen molecules were captured in the hydrate cages, the vapor phase was vented to 1 atm at 223 K by opening a valve used to isolate the system from the atmosphere. The hydrate compositions were then measured by analyzing gaseous guests engaged in the hydrate structures. For composition measurement of gases dissociated from the hydrate phase, a sampling valve with a loop volume of 1  $\mu\text{L}$  was installed and connected to a gas chromatograph (Hewlett-Packard, 5890A) on-line through a high-pressure metering pump (Milton-Roy, 2396-31). The gas chromatograph (GC) used a thermal conductivity detector (TCD) with a PORAPAK-Q packed column and was preliminarily calibrated for ethane, propane, and hydrogen with nitrogen as the carrier gas.

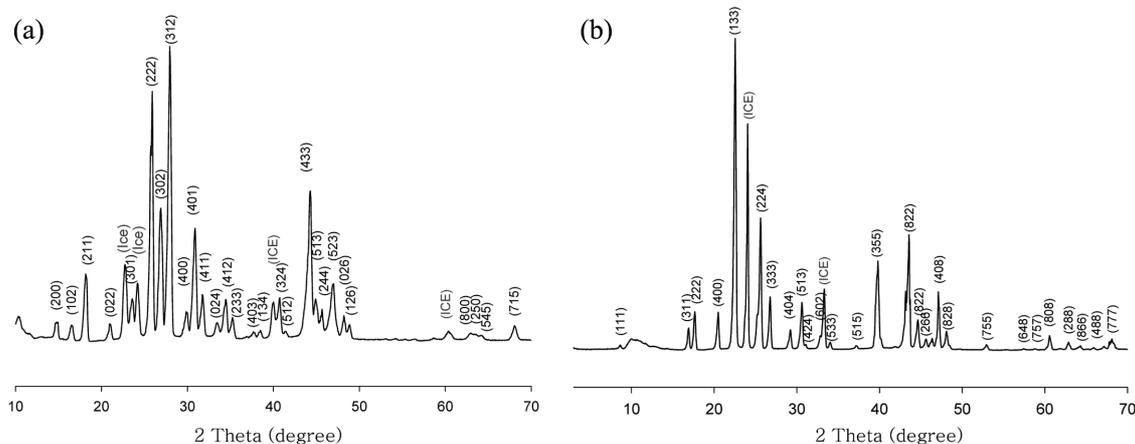
## RESULTS AND DISCUSSION

The accurate amount of hydrogen molecules stored in cages was

**Table 1. The mole fraction and cage occupancy of the mixed ethane+hydrogen and the mixed propane+hydrogen hydrates**

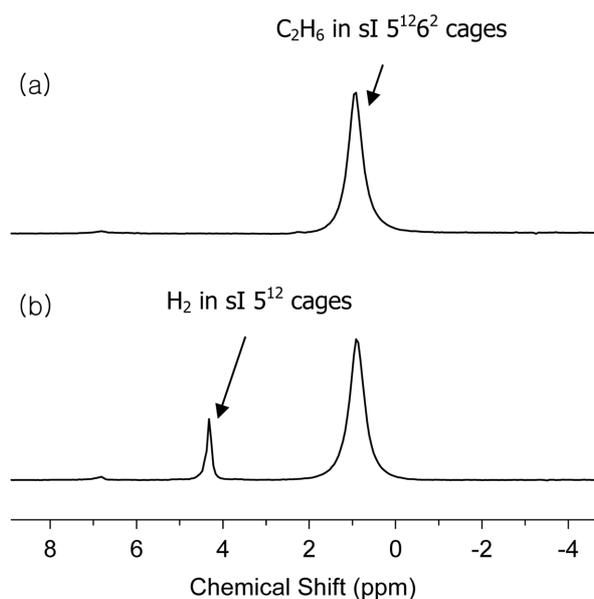
Component	Exp 1.		Exp 2.	
	$\text{H}_2$	$\text{C}_2\text{H}_6$	$\text{H}_2$	$\text{C}_3\text{H}_8$
Mole fraction	0.127	0.873	0.370	0.630
Cage occupancy	0.431	0.988	0.294	0.999

measured by gas chromatography, and the resulting mole ratios of dissociated guest molecules are given in Table 1. The GC results were calibrated for measuring the mole ratios at the same experimental conditions. The guest gas compositions in the hydrate cages are the same as the gas compositions after complete dissociation of hydrates. In Table 1, Exp 1 and 2 confirm that hydrogen molecules can be incorporated into pure ethane or propane hydrates to eventually form the mixed hydrogen and hydrocarbon hydrates. It is well known that pure ethane and propane form sI and sII hydrates, respectively. At this stage, we note that the sI hydrate has 2 small and 6 large cages, while the sII hydrate has 16 small and 8 large cages in the hydrate unit cell. The small to large cage ratio of sII is much higher than that of sI. Thus, we simply expect that the mole fraction of captured hydrogen molecules in sII hydrate is three times higher than that in sI. Accordingly, it seems to be possible to roughly predict the formed hydrate structures from hydrate compositions, but this approach has a great chance to mislead the true structure information. The PXRD was adopted to check any possible structure transition that might appear during hydrogen compression. Fig. 1(a) represents the PXRD pattern of the mixed ethane and hydrogen hydrate. The XRD pattern was indexed by using the Check-Cell program with the space group  $Pm\bar{3}n$  and a unit cell edge of 11.87  $\text{\AA}$ . The calculated unit cell parameter is in good agreement with that of pure methane of structure I determined by Kirchner et al. [8]. Similarly, Fig. 1(b) shows the XRD pattern of the mixed propane and hydrogen hydrate. The calculated unit cell parameter was 17.31  $\text{\AA}$  with sII and space group  $Fd\bar{3}m$ . This result also agreed with the reported value for the unit cell parameter of sII clathrate hydrate [9]. Without any participation of water-soluble co-guests, the pure hydrogen forms sII hydrate under extremely high pressure condition. However, the propane guest plays an equivalent role to THF

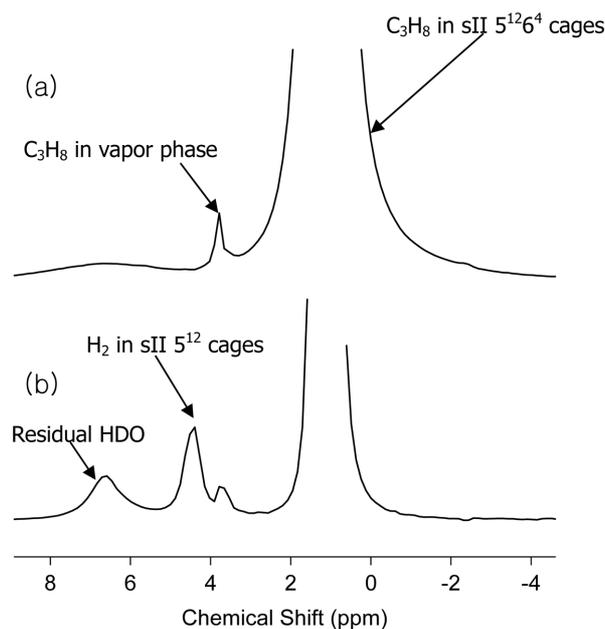


**Fig. 1. Powder X-ray diffraction patterns (a) mixed ethane+hydrogen sI hydrate (b) mixed propane+hydrogen sII hydrate.**

in forming the sII mixed hydrogen hydrate under mild pressure and temperature surroundings. This promoting behavior of hydrocarbon guest needs to be more carefully explored in order to search potential hydrogen or other gas storage medium. Because of the powerful capturing nature of sII hydrate networks, we considered that the structure transition of pure sI ethane to mixed sII hydrogen hydrates might occur after occupancy competition between hydrogen and ethane. At the present experimental conditions, we only observed the sI hydrate without any small detection of sII lattice. This result almost matches with the sI outcome of mixed carbon dioxide and hydrogen hydrate reported by Kim and Lee [4]. With scientific insight focusing on cage dynamics we might draw the possible conclusion that the short-range interaction between hydrogen and cage framework is much weaker than that between hydrocarbons and cage framework, leading to strong structure dependence on the initially formed pure hydrates. The strong host-guest interaction of pure ethane and propane hydrates makes the original structure to be preserved, eliminating the surrounding effects of external guest such as hydrogen on the lattice transformation. We again remind that ethane or propane molecules only occupy sI or sII large cages, while hydrogen molecules occupy the small cages. However, we must recognize that single or double occupancy of hydrogen molecules in small cages cannot be known from any spectroscopic information at the present level. The cage occupancy can be better understood by using the solid-state NMR. Fig. 2(a) represents the  $^1\text{H}$  MAS NMR spectrum of pure ethane hydrate and indicates that ethane molecules occupy only the large cages as shown by the peak at 0.81 ppm. The  $^1\text{H}$  MAS NMR was taken to determine hydrogen molecules captured in small cages. Fig. 2(b) identifies hydrogen molecules stored in small cages. The peak at 4.2 ppm represents hydrogen molecules in sI small cages. In order to exclude any proton signals from water molecules deuterium oxide ( $\text{D}_2\text{O}$ ) was used to synthesize hydrate samples for NMR experiments. However, a small peak at 6.7 ppm was observed, which comes from



**Fig. 2.**  $^1\text{H}$  MAS NMR spectrum (a) pure ethane hydrate (b) mixed ethane+hydrogen hydrate.



**Fig. 3.**  $^1\text{H}$  MAS NMR spectrum (a) pure propane hydrate (b) mixed propane+hydrogen hydrate.

the residual HDO protons contained in reagent (Sigma-Aldrich  $\text{D}_2\text{O}$ , 99.9 at. %D). For the mixed propane and hydrogen hydrate the peak representing hydrogen molecules in sII small cages was assigned at 4.3 ppm (Fig. 3(a), (b)). Propane peak in sII large cages is observed at 0.4 and 1.9 ppm as shown Fig. 3(a). The small and sharp peak at 3.8 ppm comes from propane gas dissociated in an airtight NMR rotor. The  $^{13}\text{C}$  MAS NMR spectrum of the mixed ethane and hydrogen hydrate is shown in Fig. 4(a), confirming a structure change from sI to sII did not occur. Ethane molecules entrapped in sI large cages were represented by only one peak at 7.7 ppm, which corresponds to the chemical shift of ethane molecules in sI hydrate [10]. In particular, the  $^{13}\text{C}$  MAS NMR spectrum was determined for the mixed propane and hydrogen hydrate in order to identify the synthesized hydrate structure. As shown in Fig. 4(b), two resonance peaks (17.7 and 16.8 ppm) of propane clearly indicate that the sII structure of pure propane hydrate was preserved. It must be, however, noted that since the mixed hydrates are meta-stable at the NMR measurement condition, the resulting quantitative analysis becomes unclear and meaningless. Accordingly, the cage occupancy ratios of each mixed hydrate were calculated from the overall information taken from the GC, PXRD and NMR methods. The cage occupancy of ethane and propane in large cages was obtained from CSMHYD98: Colorado School of Mines Hydrate Prediction Program, while the cage occupancy of hydrogen in small cages was calculated from guest compositions obtained by the GC. As shown in Table 1, the mole fraction of hydrogen contained in the mixed ethane and hydrogen hydrate is found to be 0.127. Further, the cage occupancy of hydrogen and ethane is 0.431 and 0.988, respectively. The stored amount of hydrogen in the mixed sI hydrate was 0.17 wt%, while the hydrogen amount stored in the mixed propane and hydrogen hydrates was 0.33 wt%. The corresponding cage occupancy values of hydrogen and propane are 0.294 and 0.999 in the sII mixed hydrate. The overall results strongly imply that the sII

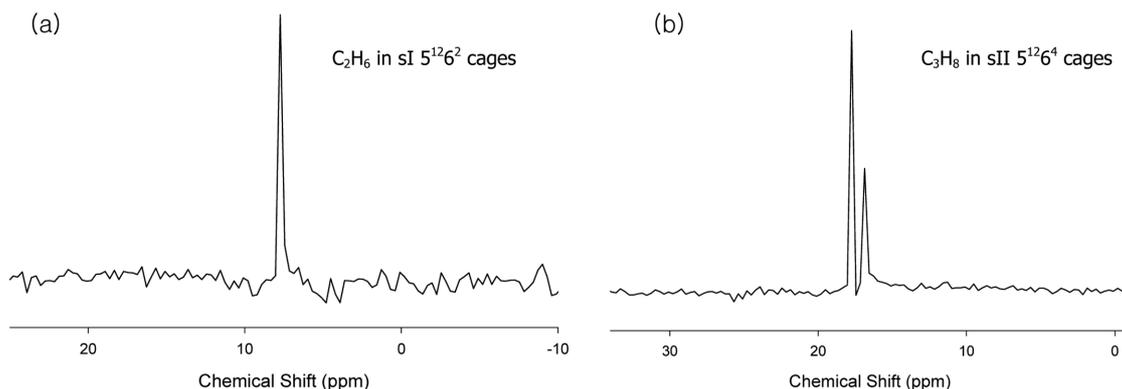


Fig. 4.  $^{13}\text{C}$  MAS NMR spectrum (a) mixed ethane+hydrogen hydrate (b) mixed propane+hydrogen hydrate.

hydrate is more favorable than sI for hydrogen storage.

### CONCLUSION

Low molecular-weight hydrocarbons such as ethane and propane are employed as the coguests for the formation of the mixed hydrogen hydrates. As can be expected, hydrogen molecules are only occupied in the sI and sII small cages, while the hydrocarbons are captured in their large cages. The basic structure information was obtained by using the PXRD, but the detailed cage occupancy ratios between guest components were determined from the NMR spectra. The original crystalline structures of pure ethane and propane hydrates were not transformed to other structures, maintaining the constant lattice parameters. From the present results we strongly suggest that the sII is more favorable than the sI for storing hydrogen in cages. Thus, more sII formers need to be tested for hydrogen storage enhancement. Although the present study is not sufficient for the direct application to both simultaneous hydrogen and hydrocarbon oxidation in fuel cell application (SOFC), we hope that some meaningful conclusions might contribute to developing a new type of fuel cell source such as hydrogen and hydrocarbon mixture.

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### REFERENCES

1. G. D. Berry and S. M. Aceves, *Energy Fuels*, **12**, 49 (1998).
2. H. Lee, J.-W. Lee, D. Y. Kim, J. Park, Y. T. Seo, H. Zeng, I. L. Moudrakovski, C. I. Ratcliffe and J. A. Ripmeester, *Nature*, **434**, 743 (2005).
3. W. L. Mao, H. Mao, A. F. Goncharov, V. V. Struzhkin, Q. Guo, J. Hu, J. Shu, R. J. Hemley, M. Somayazulu and Y. Zhao, *Science*, **297**, 2247 (2002).
4. D. Y. Kim and H. Lee, *J. Am. Chem. Soc.*, **127**, 9996 (2005).
5. R. F. Service, *Science*, **285**, 682 (1999).
6. B. C. H. Steele, *Nature*, **400**, 620 (1999).
7. S. Park, J. M. Vohs and R. J. Gorte, *Nature*, **404**, 265 (2000).
8. M. T. Kirchner, R. Boese, W. E. Billips and L. R. Norman, *J. Am. Chem. Soc.*, **126**, 9407 (2004).
9. T. C. W. Mak and R. K. McMullan, *J. Chem. Phys.*, **42**, 2732 (1965).
10. S. Subramanian, R. A. Kini, S. F. Dec and E. D. Sloan, *Chem. Eng. Sci.*, **55**, 1981 (2000).