Storage Capacity of Hydrogen in Gas Hydrates

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Abstract. The storage capacity of H$_2$ in the THF, THT, and furan hydrates was studied by $p$-$V$-$T$ measurements. We confirmed that the storage and release processes of H$_2$ in all hydrates could be performed reversibly by pressure swing without destroying of hydrate cages. H$_2$ absorption in both THT and furan hydrates is much faster than THF hydrate in spite of same unit-cell structure. On the other hand, the storage amounts of H$_2$ are coincident in the all additive hydrates and would reach at about 1.0 mass% asymptotically.

1. Introduction
Clathrate hydrate, which is one of ice-like crystalline inclusion compounds, and other clathrate materials [1] have now become a potential tool for H$_2$ storage. In particular, the mixed gas hydrates containing H$_2$ have become the object of an attention as a potential medium that enables us to store H$_2$ under relatively mild conditions [2-10]. An additive component that constructs the clathrate hydrate under moderate conditions plays an important role. To store H$_2$, the clathrate hydrates of additive (additive hydrate) need some empty cages that can entrap H$_2$ molecules. Tetrahydrofuran (THF) is familiar as an additive, which forms the structure-II (s-II) hydrate containing sixteen empty S-cages per unit lattice [11]. Some previous studies [2, 3, 6, 7] have revealed that H$_2$ + THF mixed gas hydrate can generate at much lower pressure than the pure H$_2$ hydrate.

The reversible storage and release of H$_2$ by pressurizing or depressurizing without the destruction of hydrate cages is favorable technique for the application of H$_2$ storage using mixed gas hydrates. This technique is more suitable for H$_2$ storage than H$_2$ absorbing alloys because the heating to release H$_2$ is not necessary. There are a few reports about above storage and release of H$_2$ for the THF hydrate [4, 12]. Their results are coincident with one another on the point of maximum H$_2$ storage amount. Not only storage amount but also storage rate is one of the most important factors for the reversible storage and release of H$_2$.
It is well known that the ratio of small to large cages for the s-H hydrate is greatest among all hydrate unit-cell structures. However, a small help-molecule is essential to prepare the s-H hydrate, and consequently it is impossible to store and release H$_2$ through the additive hydrate without destruction of hydrate cage. It is necessary to seek new additives that fulfill with the following factors: (1) The additive molecule can form the s-II hydrate, which has many empty S-cages per unit-cell. (2) The stability boundary of additive hydrates is laid at similar to or higher-temperature region as possible. (3) The absorption of H$_2$ in the additive hydrates is as fast as possible.

In the present study, THF, tetrahydrothiophene (THT) and furan were adopted as an assistant additive for the H$_2$ storage using gas hydrates. These additives are similar in molecular size and shape to one another and form s-II hydrate [13-15]. The H$_2$ storage amount and rate of THF, THT, and furan hydrates were evaluated by the $p$-$V$-$T$ measurement. The $p$-$V$-$T$ measurements enable in situ analysis in high-pressure cells, and should therefore accurately gauge the storage amount of H$_2$.

2. Experimental Section

2.1. Materials
Research grade H$_2$ of mole fraction purity 99.9999% was obtained from the Neriki Gas Co. Ltd. The maximum impurity was 0.2 ppm of nitrogen. Research grade THF of mole fraction purity 99.7% was obtained from Merck, Ltd., Japan. Research grade THT of mole fraction purity 99% and furan of mole fraction purity 99% were obtained from Tokyo Chemical Industry, Co., Ltd. The distilled water was obtained from the Wako Pure Chemical Industries, Ltd. All of them were used without further purifications.

2.2. Experimental apparatus and procedures
The experimental apparatus for the $p$-$V$-$T$ measurements contains two high-pressure cells. The inner volume of a larger high-pressure cell (cell I) was 100 cm$^3$, and that of the smaller one (cell II) was 10 cm$^3$. The maximum working pressure of these high-pressure cells was 75 MPa. All parts of the cells were immersed in a temperature-controlled water bath.

The system temperature was measured within an uncertainty of 0.02 K using a thermistor probe (Takara D-632). The probe was calibrated with a Pt resistance thermometer defined by ITS-90. The system pressure was measured by a pressure gauge (Valcom VPRT) with an estimated maximum uncertainty of 0.02 MPa (< 10 MPa) and 0.2 MPa (> 10 MPa).

We prepared pure THF, THT or furan (additive) hydrate by efficient agitation of the additive + water mixed liquid that was supercooled to ~270 K in a freezer. The mole ratio of THF, THT or furan to water (additive : water) was 1 : 17 (only THF is water-soluble), which was the stoichiometric ratio of formation for s-II additive hydrate. After complete formation of additive hydrate, it was annealed for a day at the experimental temperature (~277.1 K, THF hydrate; ~275.1 K, THT or furan hydrate) that was a little lower than the equilibrium temperature of the additive hydrates at atmospheric pressure, respectively. In the case of THF hydrate, the other experimental temperature (268.2 K) was adopted to investigate the effect of temperature. Then, the hydrates were quenched and taken out from the cell at 263 K. These hydrates were crushed at 263 K with a mortar and pestle, and then sieved to the desired particle sizes of ~750 μm or ~375 μm (THF hydrate). Approximately 3 g of sieved additive hydrate was enclosed into the cell II that was cooled down in advance. The cell II was sealed and evacuated with being cooled in liquefied nitrogen. After that, the cell II was immersed in a temperature-controlled water bath at 277.1 K or 268.2 K (THF hydrate) and 275.1 K (each the THT and furan hydrates).

H$_2$ was introduced into the cell I up to a desired pressure and then the valve II was opened in order to pressurize the additive hydrates by H$_2$. The initial time was defined as the moment that valve II was opened and H$_2$ contacted with additive hydrate. The system pressure started dropping. After the system
pressure reached at a constant value, the storage amount of H₂ was calculated from the amount of pressure change by use of equation of state. The volume ratio of both cells and virial coefficients were determined accurately by Burnett method [16]. In the present study, \( \text{mol (H}_2 \text{)} / \text{mol (add. hyd.)} \) was defined as \( \{\text{substance quantity of H}_2 \text{ absorbed in the additive hydrate} / \text{substance quantity of additive hydrate unit-cell}\} \), and the mass\% was defined as \( \{\text{H}_2 / (\text{H}_2 + \text{additive hydrate}) \times 100\} \).

3. Results & Discussion

Figure 1 shows the time variation of H₂ amount absorbed in the THF (a), THT (b), and furan (c) hydrates. The average particle diameter of each hydrates is ~750 \( \mu \text{m} \). Initial absorption-rate of H₂ becomes large with the increase of initial experimental pressure. H₂ molecules begin to be absorbed in hydrate immediately after contact with the additive-hydrate surface. The fact indicates that H₂ can diffuse almost freely through the hydrate cages [17, 18]. The storage and release of H₂ in additive hydrate can be repeated a few times without the decrease of H₂ storage amount and rate. This result shows that H₂ can be absorbed and released reversibly by pressurizing or depressurizing without

![Figure 1](image_url)

Figure 1 Time variation of H₂ amount absorbed in the THF hydrate (a) at 277.1 K, THT hydrate (b) and furan hydrate (c) at 275.1 K (the particle diameter of each hydrates is ~750 \( \mu \text{m} \)). The solid lines are fitting lines for experimental data.
destroying hydrate cages in THF, THT, and furan hydrates.

Figure 2 shows the comparison of H\textsubscript{2} absorption rate in THF, THT, and furan hydrates for same particle diameter of ~750 \( \mu \text{m} \) under the similar pressure conditions. The pressure stands for the initial pressure shortly after H\textsubscript{2} contacted with the hydrate. The initial experimental pressure is ~32 MPa. In the case of THT and furan hydrates, the absorption of H\textsubscript{2} is completed within three hours, which is much faster than THF hydrate despite almost same temperature and pressure condition. A lot of time (more than 10 hours) is required until THF hydrate completely absorbs the equilibrium storage amount of H\textsubscript{2} at the experimental pressure. The discrepancy of H\textsubscript{2} absorption rate between THT or furan and THF hydrates may be derived from the structural distortion caused by the difference of shape among guest species. The large absorption rate of H\textsubscript{2} for the THT and furan hydrates has advantages in the application of H\textsubscript{2} storage using gas hydrates.

The storage amounts of H\textsubscript{2} in additive hydrates at various experimental pressures are shown in Figure 3. In the present study, the storage amounts of H\textsubscript{2} in all additive hydrates exhibit the similar behavior with one another under similar temperature conditions. The storage amount and rate of THF hydrate at 268.2 K are grater than those of another temperature. There is no difference between the data obtained from different sizes of hydrate particle (~750 \( \mu \text{m} \) vs ~375 \( \mu \text{m} \)). Therefore, it is suggested that difference in particle size on the order of several-hundred micrometers does not affect the storage amount of H\textsubscript{2}. Figure 3 contains previously reported experimental data [4]. Our data are lower than the previous reference data for the THF hydrate [4]. This discrepancy may be derived from the difference of experimental temperature condition. The storage amount of H\textsubscript{2} increases successively as pressure rises and would reach a plateau of 2.0 mol (H\textsubscript{2}) / mol (add. hyd.), which is equivalent to the theoretical value for full occupancy of one H\textsubscript{2} molecule per S-cage in the s-II hydrate.

Figure 2 Comparison of H\textsubscript{2} absorption rate among THF, THF and furan hydrates for same particle diameter of ~750 \( \mu \text{m} \). The lines are fitting lines for experimental data.

Figure 3 The pressure dependance of H\textsubscript{2} storage amount in the THF hydrate at 277.1 K or 268.2 K, THT and furan hydrates at 275.1 K. Strobel et al. [4] have experimented at 270-278 K, ~250 \( \mu \text{m} \).
4. Conclusion
The storage capacity of H\textsubscript{2} in three s-II hydrates (THF, THT, and furan hydrates) was investigated by means of \textit{p-V-T} measurement. We have confirmed that the storage and release processes of H\textsubscript{2} in additive hydrates could be performed reversibly by pressurizing or depressurizing without the destruction of hydrate cages. H\textsubscript{2} absorption in both THT and furan hydrates is much faster than THF hydrate while the storage amount of H\textsubscript{2} in THT and furan hydrates is similar to that of THF hydrate. This result implies that there is the expansion or distortion of hydrate cages or the property of guest species in spite of same unit-cell structure.

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Reference
[1] Strobel, T. A.; Kim, Y.; Andrews, G. S.; Ferrell III, J. R.; Koh, C. A.; Herring, A. M.; Sloan, E. D. 2008 J. Am. Chem. Soc. 130 14975-14977.
[2] Florusse, L. J.; Peters, C. J.; Schoonman, J.; Hester, K. C.; Koh, C. A.; Dec, S. F.; Marsh, K. N.; Sloan, E. D. 2004 Science 306 469-471.
[3] Lee, H.; Lee, J.-W.; Kim, D. Y.; Park, J.; Seo, Y.-T; Zeng, H.; Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. A. 2005 Nature 434 743-746.
[4] Strobel, T. A.; Taylor, C. J.; Hester, K. C.; Dec, S. F.; Koh, C. A.; Miller, K. T.; Sloan, E. D., Jr. 2006 J. Phys. Chem. B 110 17121-17125.
[5] Strobel, T. A.; Koh, C. A.; Miller, K. T.; Sloan, E. D. 2007 Fluid Phase Equilib. 261 382-389.
[6] Hashimoto, S.; Murayama, S.; Sugahara, T.; Sato, H.; Ohgaki, K. 2006 Chem. Eng. Sci. 61 7884-7888.
[7] Hashimoto, S.; Sugahara, T.; Sato, H.; Ohgaki, K. 2007 J. Chem. Eng. Data 52 517-520.
[8] Hashimoto, S.; Sugahara, T.; Moritoki, M.; Sato, H.; Ohgaki, K. 2008 Chem. Eng. Sci. 63 1092-1097.
[9] Chapoy, A.; Anderson, R.; Tohidi, B. 2007 J. Am. Chem. Soc. 129 746-747.
[10] Sakamoto, J.; Hashimoto, S.; Tsuda, T.; Sugahara, T.; Inoue, Y.; Ohgaki, K. 2008 Chem. Eng. Sci. 63 5789-5794.
[11] Hawkins, R. E.; Davidson, D. W. 1966 J. Phys. Chem. 70 1889-1894.
[12] Nagai, Y.; Yoshioka, H.; Ota, M.; Sato, Y.; Inomata, H.; Smith, Jr., R. L.; Peters, C. J. 2008 AIChE J. 54 3007-3016.
[13] Franks, F. 1973 \textit{Water. A Comprehensive Treatise} 2 115-234.
[14] Ripmeester, J. A; Davidson, D. W. 1977 Mol. Cryst. Liq. Cryst. 43 189-195.
[15] Davidson, D. W.; Handa, Y. P.; Ratcliffe, C. I.; Ripmeester, J. A.; Tse, J. S.; Dahn, J. R.; Lee, F.; Calvert, L. D. 1986 Mol. Cryst. Liq. Cryst. 141 141-149.
[16] Katayama, T.; Ohgaki, K. 1980 J. Chem. Eng. Jpn 13 257-262.
[17] Alavi, S.; Ripmeester, J. A. 2007 Angew. Chem., Int. Ed. 46 6102-6105.
[18] Okuchi, T.; Moudrakovski, I. L.; Ripmeester, J. A. 2007 Appl. Phys. Lett. 91 171903-1-3.