



Storage capacity of hydrogen in tetrahydrothiophene and furan clathrate hydrates

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ABSTRACT

The storage capacity of hydrogen in the tetrahydrothiophene and furan hydrates was investigated by means of pressure–volume–temperature measurement. The hydrogen–absorption rate of tetrahydrothiophene and furan hydrates is much larger than that of tetrahydrofuran hydrate in spite of same crystal structure (structure-II). The storage amount of hydrogen at 275.1 K is about 1.2 mol (hydrogen)/mol (tetrahydrothiophene or furan hydrate) (~0.6 mass%) at 41.5 MPa, which is coincident with that of tetrahydrofuran hydrate.

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1. Introduction

Efficient storage and transportation of H_2 under moderate conditions are essential for developing new economy sustained by H_2 energies (Satyapal et al., 2007; von Helmolt and Eberle, 2007). Clathrate hydrate, which is one of crystalline inclusion compounds, has 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 to storage H_2 under relatively mild conditions (Florusse et al., 2004; Lee et al., 2005; Strobel et al., 2006, 2007; Hashimoto et al., 2006, 2007, 2008; Chapoy et al., 2007; Sakamoto et al., 2008). 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 (Hawkins and Davidson, 1966). Some previous studies (Florusse et al., 2004; Lee et al., 2005; Hashimoto et al., 2006, 2007; Strobel et al., 2007) 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 suitable 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 (Strobel et al., 2006; Ogata et al., 2008; Nagai et al., 2008). Their results are coincident with one another on the point of maximum H_2 storage amount. The storage amount of H_2 reaches a plateau of increase {2.0 mol (H_2)/mol (THF hydrate)} in the vicinity of 80 MPa. 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 than that of THF hydrate. (3) The absorption of H_2 in the additive hydrates is faster than that of THF hydrate.

In the present study, tetrahydrothiophene (THT) and furan were adopted as a new assistant additive for the H_2 storage using gas hydrates. These additives have many advantages; harmless to humans, chemically stable, easily obtainable at a low price, etc. These additives are similar in molecule size and shape to THF and form s-II hydrate (Franks, 1973; Ripmeester and Davidson, 1977; Davidson et al., 1986). In addition, THT is often used as a material for the smell attachment to propane or city gas. Therefore, THT is expected to play an important role as the additive for the sensor for the H_2 leakage as well as the H_2 storage.

First of all, thermodynamic stability boundaries of H_2 +THT and furan mixed gas hydrates were determined. In addition, the H_2

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storage amount and rate of THT and furan hydrates were evaluated by the p - V - T measurement. Finally, the results obtained in the present study were discussed by comparison with those of THF hydrate.

2. Experimental section

2.1. Materials

Research grade H_2 (mole fraction purity 0.999999) was obtained from the Neriki Gas Co., Ltd. The maximum impurity was 0.2 ppm of nitrogen. Research grade THT (mole fraction purity 0.99) and furan (mole fraction purity 0.99) were obtained from Tokyo Chemical Industry, Co., Ltd. The distilled water was obtained from the Wako Pure Chemicals Industries, Ltd. All of them were used without further purifications.

2.2. Experimental apparatus

Two types of high-pressure cell were used for phase equilibrium measurements. Both of them are similar to the previous ones (Hashimoto et al., 2006, 2008). The high-pressure cell made of stainless steel had an inner volume of ca. 150 cm^3 (Hashimoto et al., 2006). The maximum working pressure was 10 MPa. The cell had a set of windows for visually observing the phase behavior. The other was pressure-proof glass cell (Hashimoto et al., 2008). The inner volume and maximum working pressure of the high-pressure glass cell were 10 cm^3 and 5 MPa, respectively. All parts of the high-pressure cell were immersed in a temperature-controlled water bath. The contents were agitated using an up-and-down mixing bar driven by an exterior permanent magnetic ring.

The experimental apparatus for the p - V - T measurements is the same as the previous one (Ogata et al., 2008). 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 0.01 MPa ($< 10\text{ MPa}$) and 0.1 MPa ($> 10\text{ MPa}$).

2.3. Experimental procedures

2.3.1. Phase equilibrium measurement

The mixture of THT or furan (non-hydrosoluble)+water prepared at stoichiometric mole ratio for the s-II hydrate (feed mole ratio, THT or furan:water = 1:17) was introduced into the high-pressure cell evacuated beforehand in several batches by use of the vacuum pump to remove dissolved air. The content was pressurized carefully up to a desired pressure by supplying H_2 . In order to generate the mixed gas hydrate particle, the cell was cool down to 258 K and the contents were stirred continuously. The formation of gas hydrate can be confirmed through the window of the cell. After the first particle of H_2 +THT or furan mixed gas hydrate was visually observed, the system temperature and agitation were kept constant during at least a day in order to establish the four-phase equilibrium state of gas, aqueous, liquid THT or furan, and hydrate phases. After reaching the four-phase equilibrium state, the equilibrium temperature and pressure were measured. In order to eliminate a hysteresis effect, we repeated the same equilibrium measurements using the fresh mixture of THT or furan+water at the same mole ratios.

Table 1

Four-phase equilibrium (p - T) data for the H_2 +THT and furan mixed gas hydrate systems.

H_2 +THT system		H_2 +furan system	
T (K)	p (MPa)	T (K)	p (MPa)
276.03	0.29	277.29	0.11
276.07	0.60	277.47	0.48
276.14	1.03	277.63	0.97
276.21	1.43	277.81	1.51
276.39	1.96	277.96	1.98
276.63	2.70	278.09	2.44
276.93	3.35	278.37	3.47
277.17	3.88	278.82	4.85
277.91	5.86	279.45	6.85
278.40	7.50	279.74	7.75
278.66	7.99	280.10	8.71
278.94	8.88		

2.3.2. p - V - T measurement

We prepared simple THT or furan hydrate by efficient agitation of the THT or furan+water mixed liquid that was supercooled to $\sim 270\text{ K}$ in a freezer. This temperature was same in the case of THF hydrate (Ogata et al., 2008). The mole ratio of THT or furan to water (additive :water) was 1:17, which was the stoichiometric ratio of formation for s-II THT or furan hydrate. After complete formation of THT or furan hydrate, it was annealed at the experimental temperature ($\sim 275.1\text{ K}$) that was a little lower than the equilibrium temperature of THT and furan hydrates for a day. 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 $\sim 750\text{ }\mu\text{m}$. Approximately 3 g of sieved THT or furan 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 275.1 K (both the THT and furan hydrates), which was lower than the equilibrium temperature of both THT and furan hydrates at atmospheric pressure.

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 THT or furan hydrates by H_2 . The initial time was defined as the moment that valve II was opened and H_2 contacted with THT or furan hydrate. The system pressure started dropping. After the system pressure reached at a constant value, the storage amount of H_2 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 (Katayama and Ohgaki, 1980). In the present study, the mass% was defined as $\{H_2/(H_2+\text{THT or furan hydrates})\}$.

3. Results and discussion

3.1. Thermodynamic stability

Phase equilibrium (pressure-temperature) relations for the H_2 +THT and H_2 +furan mixed gas hydrate systems are summarized in Table 1 and shown in Fig. 1. The phase behavior of the H_2 +THT and H_2 +furan hydrates is similar to that of H_2 +THF hydrate, while the four-phase equilibrium curves of the H_2 +THT and H_2 +furan hydrates shift to the lower temperature of ~ 2 and $\sim 0.5\text{ K}$ than the three-phase equilibrium one of H_2 +THF hydrate (Hashimoto et al., 2006), respectively.

3.2. Storage rate and amount of H_2

The storage rate and amount of H_2 for the THT and furan hydrates at 275.1 K were investigated by p - V - T measurement. Fig. 2 shows

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