ENHANCEMENT OF HYDROGEN STORAGE RATE IN PRE-TREATED SEMI-CLATHRATE HYDRATES

Takaaki Tsuda, Shingo Amano, Yuuya Fujisawa, Shunsuke Hashimoto, Takeshi Sugahara and Kazunari Ohgaki*
Division of Chemical Engineering Science, Graduate School of Engineering Science
Osaka University, Osaka, 560-8531
JAPAN

ABSTRACT
Semi-clathrate hydrates have different lattice structures from ordinary clathrate hydrates, where guest species are incorporated with the hydrogen bonds of water molecules to build up hydrate cages. In the case that tetra-n-butyl ammonium bromide, tetra-n-butyl ammonium fluoride, and trimethylamine are used as an assistant additive, hydrogen storage abilities (both amount and rate) of these hydrates are drastically improved by a specific treatment, which is named as “pre-treatment”. Although we tried to store hydrogen into “fresh” semi-clathrate hydrate by pressurizing with hydrogen, the hydrogen storage abilities are comparatively low. In the present study, the hydrogen storage abilities of the pre-treated hydrates are investigated by means of Raman spectroscopic analysis and p-V-T measurement.

Keywords: semi-clathrate hydrates, hydrogen, storage abilities, absorption

NOMENCLATURE

\[ p \] Pressure [Pa]
\[ T \] Temperature [K]
\[ x \] Composition of additive in aqueous solution [-]
\[ \theta \] Cage occupancy of H\(_2\) [-]

INTRODUCTION
Gas hydrate is one of possible materials for H\(_2\) storage under relatively mild conditions. Since the large part of gas hydrates is composed by water molecule, they consist of easily-available feedstocks and are clean materials. Additionally, reversible H\(_2\) storage and release through the hydrate cages is feasible by pressurizing and depressurizing without the destruction of its structure [1, 2]. For these applications, an assistant additive is desired to reduce the pressure from the high equilibrium pressure (100-360 MPa) of the pure H\(_2\) hydrate [3]. There are two types of gas hydrates distinguished from the viewpoint of lattice structure and guest molecule. One is ordinary clathrate hydrate, which is generally and widely known around the world. A strictly-isolated guest (additive) molecule is trapped in each host cavity. There is not chemical bonds but only interaction of van der Waals force between host and guest molecules. For example, in stoichiometrical structure-II (s-II) H\(_2\)+tetrahydrofuran (THF) hydrate, H\(_2\) molecules occupy the small-cages and THF molecules exist in the larger ones. The other is semi-clathrate hydrate. Curiously, the relatively large guest molecule lies astride some (larger) hydrate cages and it is incorporated with the hydrogen bonds of water molecules, the remaining small-cages are vacant. This type of hydrate has flexible structure and consequently develops the structural transition easily in accordance with the composition and/or pressure change [4, 5]. Recently, we have found that a specific treatment, which we named as “pre-
treatment (in detail, see **Experimental Procedures**), improves the H₂ storage abilities (both amount and rate) of the trimethylamine (TMA) and tetra-n-butyl ammonium bromide (TBAB) semi-clathrate hydrates under their stable conditions [5, 6]. In the present study, TMA, TBAB, and tetra-n-butyl ammonium fluoride (TBAF) have been adopted as additives. It has been investigated how the pre-treatment affects the H₂ storage abilities by means of Raman spectroscopic analysis and p-V-T measurement.

**EXPERIMENTAL**

**Materials**
Research grade H₂ (six-nine purities in mole fraction) was obtained from the Neriki Gas Co., Ltd. The maximum impurity was 0.2 ppm of N₂. Research grade TMA (ca. 28 mass% aqueous solution) was obtained from Tokyo Chemical Industry Co., Ltd. Research grade TBAB (mole fraction purity 0.980) and the distilled water were obtained from the Wako Pure Chemical Industries, Ltd. Research grade TBAF hydrate (mole fraction purity 0.980, not semi-clathrate hydrate) was obtained from Wako Pure Chemical Industries, Ltd. The weight water content of general TBAF hydrates was ~17 mass%, which was analyzed by means of Karl Fischer’s method. In the following chapter, the original water content of reagent is taken into consideration for the data analyses. All of them were used without further purifications.

**Apparatus**
The experimental apparatus for p-V-T measurements contains two high-pressure cells. The inner volume of the larger (cell I) and smaller (cell II) high-pressure cells was ~100 cm³ and ~10 cm³, respectively. 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 details of apparatus are reported in our previous study [1]. The high-pressure optical cell for the Raman spectroscopic analysis had a pair of sapphire (Ti free) windows on both the upper and lower side. This high-pressure optical cell is the same as previous one [7]. The temperature-controlled water was included constantly in the exterior jacket of the high-pressure optical cell. To agitate the contents in the cell, a ruby ball was placed inside it. This enclosed ruby ball was rolled around through the contents by a vibrator applied to the outside of the cell.

The system temperature was measured within an uncertainty of 0.02 K using a thermistor probe (Takara D-632). The system pressure was measured by a pressure gauge (Valcom VPRT) with an estimated maximum uncertainty of 0.1 MPa.

**Procedures**

○ **Sample preparation (fresh hydrates)**
TMA, TBAB, and TBAF aqueous solutions were prepared at each stoichiometrical composition of formation (x_{TMA}=0.083 (hexagonal, [6]), x_{TBAB}=0.037 (tetragonal, [4]), and x_{TBAF}=0.034 (cubic, [5]), the crystal structure of fresh hydrates are shown in parentheses). The additive hydrates were prepared by efficient agitation and cooling to ~260 K in a freezer. To avoid the coexistence of ice, the obtained hydrates are annealed at experimental temperature (more than 273 K) at least 1 day.

○ **Sample preparation (pre-treated hydrates)**
Additive aqueous solutions were prepared at each stoichiometrical composition of formation. The solution was introduced into the high-pressure cell, and pressurized up to a desired pressure (~50 MPa) with H₂. H₂+additive mixed hydrates were prepared from compressed H₂+additive aqueous solution by efficient agitation and cooling to ~260 K in a freezer. To avoid the coexistence of ice, the obtained hydrates are annealed at experimental temperature at least 1 day. H₂ inside the mixed hydrate was completely released by depressurization to atmospheric pressure. These samples were defined as the “pre-treated” hydrates.

○ **p-V-T measurements**
The hydrate samples prepared by above procedures were crushed with a mortar and pestle, and then sieved to the desired particle sizes of ~750 μm. Approximately 3 g of the sieved hydrate was enclosed into the cell II that was cooled down in advance. The cell II was sealed and evacuated at liquefied N₂ temperature. After that, the cell II was immersed in a temperature-controlled water bath (~ 277 K in the TMA hydrate system, ~283 K in the TBAB hydrate system, and ~300 K in the TBAF hydrate system). These temperatures were little bit lower than the equilibrium ones at the ambient pressure, respectively.

H₂ 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 with $H_2$. The initial time was defined as the moment that valve II was opened and $H_2$ contacted with additive hydrates. Then, the system pressure started dropping. After the system pressure reached 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 [8]. In the present study, storage amount of $H_2$ was defined as \( \frac{\text{(mass of } H_2 \text{ absorbed in the additive hydrate)}}{\text{(mass of } H_2 + \text{additive hydrate})} \times 100 \), and $H_2$ occupancy in S-cage, $\theta$ was defined as \( \frac{\text{(experimental } H_2 \text{ amount absorbed in the additive hydrate)}}{\text{(ideal maximum } H_2 \text{ amount included in additive hydrate)}} \).

\[ \text{Raman spectroscopic analysis} \]

Additive aqueous solutions prepared at the each stoichiometric composition were introduced into the evacuated high-pressure optical cell. Then the fresh and pre-treated hydrates were prepared in the same way as above sample preparation. After repressurizing, to consider the $H_2$ diffusivity, isothermal Raman spectra in the hydrate phase was measured at various neighbor positions on the $H_2$ fluid phase, which were $\sim 750 \mu m$ away from the fluid-hydrate interface.

**RESULTS**

The pressure dependence of $H_2$ storage amount for the $H_2$+TBAB semi-clathrate hydrate system is shown in Fig. 1. Before the pre-treatment, the storage amounts of $H_2$ increases with the pressure increasing in a pressure range above $\sim 30$ MPa. In addition, the pre-treated process results in the approximately double storage amount of $H_2$ compared with the case of fresh hydrate. In the case of $H_2$+TBAF semi-clathrate hydrate system, both storage amount of $H_2$ before and after pre-treatment process is comparable with that of the $H_2$+TBAB semi-clathrate hydrate system. These results represent the feasibility of the reversible $H_2$ storage and release, and the storage amount of $H_2$ does not reached a plateau even if the pressure reaches $\sim 200$ MPa. The saturated value extrapolated from the pressure dependence of $H_2$ storage amount would be $\sim 350$ MPa.

The pressure dependence of $H_2$ storage amount for the $H_2$+TMA semi-clathrate hydrate system is shown in Fig. 2. Before the pre-treatment process, the storage amount of $H_2$ increases with the pressure increasing as in the case with above two
ammonium salt systems. In contrast, storage amount of H₂ measured by p-V-T measurement reduces dramatically after pre-treatment process, while, as a result of Raman spectroscopic analysis (Fig. 3), it increases in the pre-treated TMA hydrate. In Fig. 3, it is clear that the Raman peak area of H₂ for the fresh hydrate reaches only about a half of the value obtained from the pre-treated hydrate at the same pressure. Moreover, H₂ storage abilities (both amount and rate) are greatly increased for the pre-treated hydrate.

DISCUSSION
It is inferred that the enhancement of H₂ storage abilities with pre-treatment is derived from the defects of hydrate structure and/or the structural transition. In general, semi-clathrate hydrates have multilayer structures composed of the layers of large cages and those of small cages. That is, the configurations of small cages for the diffusion of H₂ are two-dimensionally connected, not three-dimensionally (e.g. H₂+THF s-II hydrate, cubic diamond-type structure). This geometry would interrupt the effective H₂ diffusion and storage. However, through the pre-treatment containing H₂ desorption, a part of layer of lager cages can be broken down and the H₂ diffusible paths would be developed. In addition, as mentioned previously in the introduction section, semi-clathrate hydrates have flexible structure and are able to transform their structure dependent on the surrounding pressure [4, 5]. The rapid H₂ release makes the position of additive molecule in the cavities shifted a little bit, and consequently the structure transition may occur. In fact, the crystal appearance of TBAB hydrate changes from clear to cloudy at the moment that H₂ was released from the H₂+TBAB mixed hydrate. In the case of TMA hydrate, it would be inferred that the difference of size between TMA and another additive molecules affects the reduction of H₂ storage capacity before and after pre-treatment. Considering only the size of TMA molecule, it can be enclathrated into the large cage of s-II clathrate hydrate. For instance, s-VI tert-butyl amine hydrate is easily transformed to s-II hydrate to be pressurized with H₂ [9]. The structural transition would occur from TMA semi-clathrate hydrate to s-II clathrate hydrate by pre-treatment.

CONCLUSIONS
In this study, H₂ storage abilities of semi-clathrate hydrates and the effect of pre-treatment were investigated by means of Raman spectroscopic analysis and p-V-T measurements. Pre-treatment process means the desorption of H₂ by depressurizing from the H₂+additive semi-clathrate hydrate prepared from additive solution+compressed H₂. In both TBAB and TBAF hydrate systems, H₂ storage abilities were improved drastically by pre-treatment. In TMA hydrate system, on the other hand, they reduce after the pre-treatment. These may be derived from the defects in the hydrate structure and/or structural transition.

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