

## Increasing Hydrogen Storage Capacity Using Tetrahydrofuran

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Clathrate hydrates are solid inclusion compounds formed by rearranging the H-bonding between water molecules to form polyhedral cages in which guest molecules can be trapped. Three common structures of clathrate hydrates are structure I (sI), II (sII), and H (sH). Generally, the size of the guest molecule determines which structure is formed. The sII is a cubic structure, composed of small and large cages. The small cage is a dodecahedron comprised of 20 water molecules arranged to form 12 pentagonal faces. The large cage is a hexakaidecahedron comprised of 28 water molecules forming 12 pentagonal and 4 hexagonal faces. The unit cell of sII consists of 16 small and 8 large cages with a lattice constant of  $\sim 1.7$  nm.<sup>1</sup>

Renewable energy has become a primary topic worldwide due to increasing energy costs and concerns about energy availability and the environment. One main area of renewable energy has been hydrogen (H<sub>2</sub>) storage. Therefore, engineering a way to trap H<sub>2</sub> in hydrate cages has gained considerable interest as hydrates potentially offer a reversible and clean storage medium. The sII H<sub>2</sub> hydrate has an ideal H<sub>2</sub> storage amount of 3.81 wt %, assuming the H<sub>2</sub> molecules singly occupy the small cages with clusters of four H<sub>2</sub> in the large cages of the sII hydrate. To form pure sII H<sub>2</sub> hydrate, however, high pressures and low temperatures are required.<sup>2–4</sup> Recently, thermodynamic promoters, such as tetrahydrofuran (THF),<sup>5–9</sup> quaternary ammonium salts,<sup>7,10,11</sup> and amines<sup>12</sup> have been found to alleviate the severe formation conditions of pure H<sub>2</sub> hydrate. One disadvantage of using a promoter molecule, however, is that the promoter molecule itself occupies the large cages instead of a H<sub>2</sub> cluster, and H<sub>2</sub> can only go into the small cages. Thus, by increasing the stability of the hydrate, the overall storage capacity of H<sub>2</sub> is compromised.

Lee et al.<sup>6</sup> suggested the possibility of “forcing” H<sub>2</sub> and THF molecules to compete for the large cages of sII. With decreasing THF concentration, more H<sub>2</sub> molecules were able to occupy the large cages, thus increasing the H<sub>2</sub> storage to 4.0 wt %. However, in spite of efforts by many other researchers, the tuning effect, dependent on [THF], has been unable to be reproduced. Numerous researchers have reported the maximum amount of H<sub>2</sub> stored in THF+H<sub>2</sub> hydrates at  $\sim 1.0$  wt %<sup>8,9,13–17</sup> and confirmed that storage is independent of the [THF].<sup>8,9,13–15</sup>

This study provides new evidence for the presence of H<sub>2</sub> clusters in the large cages of sII by proposing a new method of hydrate preparation. With this method, the H<sub>2</sub> storage capacity increases to 3.4 wt % and depends on the [THF] below the eutectic composition of the THF+water binary system ( $x_{\text{THF}} = 0.0106$ ),<sup>18</sup> similar to the result of Lee et al.<sup>6</sup> The symbol of  $x_{\text{THF}}$  stands for the mole fraction of THF in the THF aqueous solution or the mixture of solid THF + solid ice.

Powdered ice ( $\sim 180$   $\mu\text{m}$ , from deionized water) was mixed with the appropriate amount of solid THF at liquid nitrogen (LN<sub>2</sub>)

temperature. Solid–solid mixtures of  $x_{\text{THF}} = 0.0054$  to 0.0558 were prepared and quenched at LN<sub>2</sub> temperature. A sample ( $\sim 1$  g) was then loaded into a high-pressure cell quenched in LN<sub>2</sub> and then pressurized with H<sub>2</sub> up to 60 MPa. Once pressurized, the sample was placed in a temperature-controlled bath at  $255 \pm 2$  K. As a result of both hydrate formation and temperature change, the pressure of the system was stabilized at  $\sim 70$  MPa after  $\sim 12$ – $24$  h. Under this temperature and pressure condition, H<sub>2</sub> hydrate was not formed without THF (Figure 1, bottom spectrum). This agrees with the phase diagram reported by Lokshin et al.<sup>4</sup> The cell was kept at  $255 \pm 2$  K for 3 days. Once the cell was removed from the bath, it was quenched and kept in LN<sub>2</sub> for  $\sim 15$ – $20$  min. The pressure in the cell was then released and allowed to reach atmospheric pressure for analysis.

Raman spectroscopic measurements were performed using a LabRam HR spectrometer with a 532 nm excitation source providing 6 mW at the sample. All measurements were made at atmospheric pressure ( $\sim 0.084$  MPa) and LN<sub>2</sub> temperature. The powder X-ray diffraction (PXRD) pattern was measured on a Siemens D500 diffractometer with Co radiation (wavelength 0.1788965 nm) in the  $\theta/2\theta$  scan mode. The measurements were performed in the step scan mode with a dwell time of 2 s and step size of 0.02°. The PXRD pattern was collected in the range  $2\theta = 5^\circ$ – $65^\circ$ . The measurements were carried out at atmospheric pressure and 90 K with a small amount of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder for calibration. The PXRD pattern indexing and cell refinement were obtained using the Checkcell and PowderX programs.<sup>19</sup>

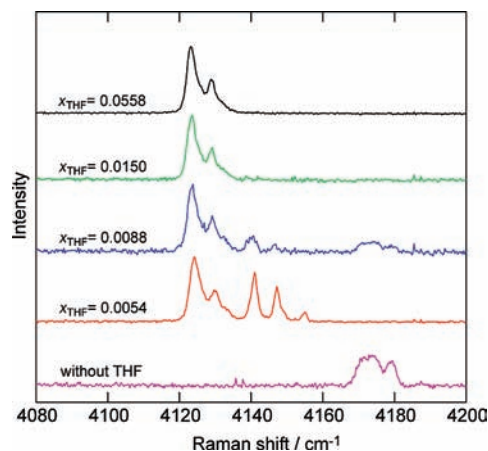
To measure the amount of H<sub>2</sub> stored, the prepared hydrate was placed in a high-pressure cell at LN<sub>2</sub> temperature. After the cell was closed, the sample was then allowed to dissociate at ambient conditions. Then the cell was connected to a Ruska gasometer to measure the volume of gas released. In the measurements, the expansion of the gas volume due to the temperature change from LN<sub>2</sub> temperature was taken into consideration.

Figure 1 shows the Raman spectra of the H<sub>2</sub> vibrons in the THF+H<sub>2</sub> hydrate prepared with varying [THF]; spectra were recorded at LN<sub>2</sub> temperature ( $\sim 76$  K). In the whole composition range, the characteristic Raman peaks derived from the THF molecule trapped in the THF+H<sub>2</sub> hydrate were detected with those from H<sub>2</sub> molecules. The Raman spectra in a compositional range above the eutectic point of the THF+water binary system indicate only small-cage occupancy of H<sub>2</sub> (vibron modes at 4124 and 4130  $\text{cm}^{-1}$  at LN<sub>2</sub> temperature) as reported by Strobel et al.<sup>20</sup> As [THF] is decreased below the eutectic composition, the peaks corresponding to the occupancy of H<sub>2</sub> clusters in the large cages begin to appear from  $\sim 4130$  to 4155  $\text{cm}^{-1}$  (cf. ref 20). The peak intensities of H<sub>2</sub> in large cages increase with further decreases in THF mole fraction. This behavior of H<sub>2</sub> occupancy in large cages is qualitatively similar to that reported as a “tuning effect” by Lee et al.<sup>6</sup> In addition, the drastic change of gas storage amount near the eutectic composition is similar to the result of the methane+THF system

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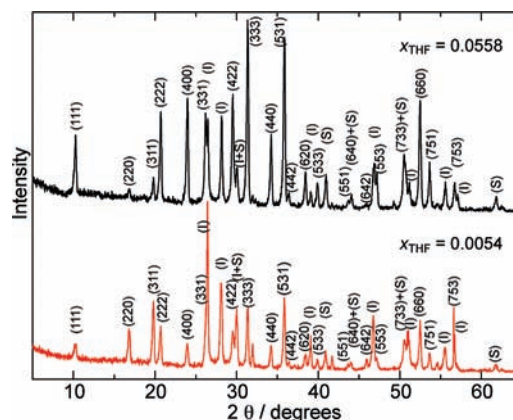
**Figure 1.** Raman spectra corresponding to the H<sub>2</sub> vibrons in the THF+H<sub>2</sub> hydrates with different mole fractions ( $x_{\text{THF}}$ ) of THF recorded at 76 K at ambient pressure.

with a “frozen” THF aqueous solution, which was recently reported by Seo et al.<sup>21</sup> The broad peaks detected from 4168 to 4182 cm<sup>-1</sup> are attributed to H<sub>2</sub> molecules in ice pores.

The PXRD patterns of THF+H<sub>2</sub> hydrates with  $x_{\text{THF}} = 0.0558$  (close to the stoichiometric concentration of THF hydrate) and 0.0054 recorded at 90 K and atmospheric pressure are shown in Figure 2. Both PXRD patterns clearly indicate that the formed hydrates are sII (*Fd3m*) with  $a = 1.717 \pm 0.001$  nm.

From volumetric gas release measurements, the H<sub>2</sub> storage amount was found to increase to 3.4 wt % with  $x_{\text{THF}} = 0.0050$ , while it was ~1.0 wt % for the mole fraction close to stoichiometry of THF hydrate. The H<sub>2</sub> storage amounts in the present study are ~1.0 wt % smaller than those reported by Lee et al.,<sup>6</sup> who claimed that double H<sub>2</sub> molecules occupy almost all small cages. The results in the present study, accompanied with the Raman spectra of H<sub>2</sub> vibrons, show that the large-cage occupancy of H<sub>2</sub> depends on [THF], while a single H<sub>2</sub> molecule occupies the small cage. Therefore, the storage amount of 3.4 wt % is independent of double H<sub>2</sub> occupancy in the small cage.

One possible reason for successfully repeating the tuning effect here is the formation method using powdered ice and solid THF. In this method, even though the THF is initially solid at 76 K, the solid THF transforms into a liquid (melting point at 164.7 K) while the system temperature is increased up to 255 ± 2 K under H<sub>2</sub>-pressurized conditions. Simultaneously, as solid THF is melted, mobile THF molecules begin to form hydrate with H<sub>2</sub>, with some H<sub>2</sub> molecules entering the large cages as well as the small cages. Hashimoto et al.<sup>13</sup> have reported that, in the case of hydrate preparation from compressed H<sub>2</sub> and THF aqueous solutions, H<sub>2</sub> molecules cannot occupy the large cages, even with a THF mole fraction of 0.010. This difference may result from the formation rate of THF+H<sub>2</sub> hydrate and the experimental pressure and temperature conditions. Lokshin et al.<sup>4</sup> have reported that the formation rate of pure H<sub>2</sub> hydrate from powdered hexagonal ice at 77–273 K is at least 100 times faster compared to the reaction with water. That is, due to the fast formation rate of hydrate, there is a possibility that the THF+H<sub>2</sub> hydrate, which has H<sub>2</sub> molecules in the large cage, may be metastable. To verify the stability of the THF+H<sub>2</sub> hydrate, we compared the Raman spectra of H<sub>2</sub> in the THF+H<sub>2</sub> hydrates (with  $x_{\text{THF}} = 0.003$ ) kept at 255 ± 2 K and ~70 MPa measured after 3 and 7 days. The peak intensity of H<sub>2</sub> showed no decreasing trend in the large-cage occupancy of H<sub>2</sub> during this time period (Figure S1). These results suggest that, even though the THF+H<sub>2</sub> hydrate may be metastable, the large-cage occupancy of H<sub>2</sub> is maintained for at least a week.



**Figure 2.** Powder X-ray diffraction patterns of THF+H<sub>2</sub> hydrates with the THF mole fraction ( $x_{\text{THF}}$ ) of 0.0558 (top) and 0.0054 (bottom) recorded at ambient pressure and 90 K. The symbols of (I) and (S) stand for contributions from ice and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, respectively.

While these results still fall short of the recently revised 2015 DOE target of 5.5 wt %, this study clearly demonstrates the tuning effect of H<sub>2</sub> in hydrates, which may be used and developed for future science and practical applications.

**Acknowledgment.** We acknowledge financial support from the U.S. Department of Energy, Basic Energy Sciences (DOE-BES) under Contract DE-FG02-05ER46242 (for T.S.) and funding from NSF-REMSEC [DMR 0820518]. A.K.S. acknowledges DuPont for a DuPont Young Professor Award.

**Supporting Information Available:** Raman spectra of H<sub>2</sub> vibrons in the THF+H<sub>2</sub> hydrate recorded after 3 and 7 days. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA905819Z