

Molecular Hydrogen Storage in Binary THF–H₂ Clathrate Hydrates

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The hydrogen storage capacity of binary THF–H₂ clathrate hydrate has been determined as a function of formation pressure, THF composition, and time. The amount of hydrogen stored in the stoichiometric hydrate increases with pressure and exhibits asymptotic (Langmuir) behavior to approximately 1.0 wt % H₂. This hydrogen concentration corresponds to one hydrogen molecule occupying each of the small 5¹² cavities and one THF molecule in each large 5¹²6⁴ cavity in the hydrate framework. Contrary to previous reports, hydrogen storage was not increased upon decreasing the THF concentration below the stoichiometric 5.6 mol % solution to 0.5 mol %, at constant pressure, even after one week. This provides strong evidence that THF preferentially occupies the large 5¹²6⁴ cavity over hydrogen, for the range of experimental conditions tested. The maximum amount of hydrogen stored in this binary hydrate was about 1.0 wt % at moderate pressure (<60 MPa) and is independent of the initial THF concentration over the range of conditions tested.

1. Introduction

Clathrate hydrates are a class of inclusion compounds (typically formed at high pressure and low temperature), in which host water molecules crystallize into various polyhedral cavities trapping small guest molecules (typically <9 Å).¹ Previous hydrate studies assumed that molecular hydrogen was too small to contribute to the stability of these compounds.² In 2002, Mao et al.³ verified that pure hydrogen hydrate crystallizes as the cubic structure II (sII), with a lattice parameter of ~17 Å. Mao estimated that there were two hydrogen molecules in each of the sixteen small dodecahedral (5¹²) cavities and four hydrogen molecules in each of the eight larger hexakaidecahedral (5¹²6⁴) cavities, yielding a hydrogen storage capacity slightly over 5.0 wt %.

The reversible storage of about 5.0 wt % of molecular hydrogen in hydrate materials, with the sole byproduct being pure water, suggests that pure hydrogen hydrate presents a very attractive hydrogen storage medium. However, the extreme formation conditions required (~200 MPa at 280 K³) significantly reduces the practical feasibility of using this compound as a storage material. In 2004, the addition of tetrahydrofuran (THF) to the lattice of the hydrogen hydrate was demonstrated to reduce the formation pressure by nearly 2 orders of magnitude⁴ (~7 MPa at 280 K). Following the work of Mao et al.,³ conflicting reports have been made in the literature regarding the hydrogen occupancy of the small cavities in both the pure and binary hydrates.

For the pure hydrogen hydrate, numerous theoretical studies, with various levels of complexity, were performed with inconsistent conclusions regarding the hydrogen occupancy in the small cavity.^{5–9} Neutron diffraction studies by Lokshin et al.¹⁰ confirmed quadruple occupancy of hydrogen in the large cavities (double and triple occupancies were also found depending on T and P). However, a maximum of one hydrogen molecule was found to occupy the small cavities. With one hydrogen molecule in the small cages and four in the large, the

hydrogen storage capacity of pure hydrogen hydrates decreases to about 3.8 wt %.

The first report of the binary THF–H₂ hydrate, by Udachin et al.,¹¹ concluded from volumetric measurements that only 91% of the small cages were occupied with hydrogen (with all of the large cages occupied by THF), using a formation pressure of 350 MPa. About a decade later, Florusse et al.⁴ reported approximately one hydrogen molecule was present per small cage of the stoichiometric binary hydrate using gas release measurements. However, NMR spectral broadening indicated that the small cages could potentially contain more than one guest. Recently, Lee et al.¹² reported double occupancy of hydrogen in the small cages of the stoichiometric binary hydrate formed at 12 MPa and 270 K. Furthermore, they suggested that at low concentrations of THF, some of the large cages could become quadruply occupied by hydrogen (forming a non-stoichiometric hydrate), with hydrogen storage slightly greater than 4 wt %. In addition, recent molecular-dynamics simulations¹³ have shown comparable unit cell configurational energies for the binary hydrate with both single and double occupancy of the small cavity, although the single occupancy case had the lowest energy for all cases tested. Recently, high-resolution neutron diffraction studies (formed at 70 MPa) have shown the time-averaged space filling of the small cavity of the stoichiometric binary hydrate to be one hydrogen molecule.¹⁴

Reducing the formation pressure is an important initial step toward developing hydrates as a feasible hydrogen storage material. However, with the addition of a second guest, some of the storage capacity will be compromised. In this work, we have quantified the hydrogen storage in the binary THF–H₂ hydrate as a function of both the initial formation pressure and the THF composition using direct gas release and ¹H MAS NMR. The optimal balance between storage capacity and formation conditions will ultimately determine the practical feasibility of this binary hydrate as a hydrogen storage candidate.

2. Experimental

Hydrate Formation. A solution of desired THF (ChromAR 99.8% minimum purity, no preservatives, Mallinckrodt Chemi-

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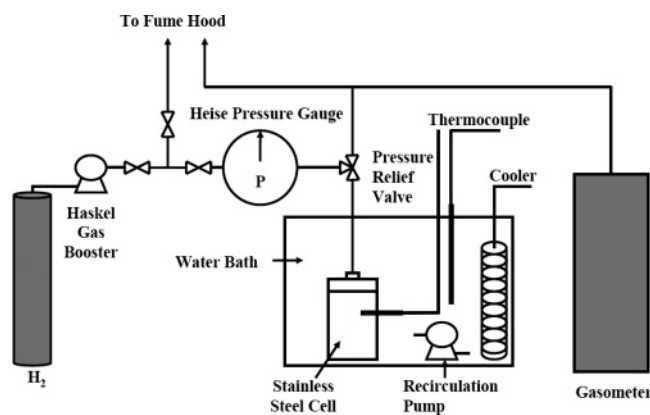


Figure 1. Schematic of experimental apparatus.

icals) composition in deionized water was prepared gravimetrically. Solution compositions ranged from 5.56 mol % THF for stoichiometric (with all the large cages of sII occupied by THF) experiments to 0.5 mol % THF. THF hydrate was formed by placing the solution in a freezer at approximately 250 K for about 3 days. The resulting hydrate, or hydrate and ice for THF compositions below 5.56 mol %, was crushed under liquid nitrogen with a mortar and pestle and sieved to the desired particle size (<45 or <250 μm). Approximately 5 g of sieved THF hydrate (and ice in some cases) was loaded into a chilled 20 cm^3 stainless steel cell and the loaded mass was recorded. For the cases where ice was present, the crushed particles were mixed homogeneously before loading to ensure that the ratio of hydrate to ice remained constant. The cell was sealed and placed into a constant-temperature bath at 270 K. The experimental apparatus is shown in Figure 1.

The cell was slowly purged with hydrogen (UHP 99.999%, General Air) three times, and then pressurized slowly to the desired pressure. The pressure was monitored using a Heise pressure gauge (± 0.0172 MPa for pressures below 34.5 MPa, ± 0.0345 MPa for pressures above 34.5 MPa). For the stoichiometric experiments, the temperature of the bath was cycled between 270 and 278 K every 8–12 h for 7 days. This method is similar to that described by Stern et al.¹⁵ for converting ice particles to methane hydrate. Typically, no further pressure drop was observed after 1 day. For the nonstoichiometric experiments (<5.6 mol % THF), the cell temperature was cycled between 265 and 270 K every 8–12 h for 7 days. This was performed to account for the decreased hydrate stability at lower THF compositions and to avoid increasing the sample temperature above the eutectic transition temperature where ice becomes a more stable phase than hydrate (<1 mol %).^{16,17} The hydrate formation method was based upon the procedure outlined in Lee et al.,¹² as well as personal communications¹⁸ with the authors of this paper.

Hydrate Dissociation and Gas Evolution. After 7 days, the cell was removed from the bath and quenched in liquid nitrogen. Once the internal cell temperature was below 130 K, the cell pressure was released to atmospheric pressure, and the cell was attached to a Ruska gasometer (Cat.# 2331–801 Houston, TX) to measure the volume of hydrogen evolved during hydrate dissociation. The cell was placed into another temperature bath (just above the pure THF hydrate dissociation temperature, i.e. above 4.4 $^{\circ}\text{C}$) to dissociate the contents of the cell in a controlled manner while minimizing THF vaporization. The measurements were calibrated as a function of both available internal cell volume and quench temperature, thus accounting for the contribution from expansion of the cold atmospheric hydrogen,

which could potentially result in deceptively large amounts of hydrogen gas being measured.

Once the cell temperature had equilibrated with the bath temperature, and no further gas was collected, the cell was detached from the gasometer. The cell was dried and the mass was measured again to ensure that this value agreed with the original mass loaded. The amount of hydrogen stored in the hydrate was determined from the gas evolved during hydrate dissociation together with the final liquid mass after hydrate dissociation. Additionally, cross checks were made by performing this calculation from the pressure drop during hydrate formation. Pressure drop–gas dissociation storage values typically agreed within 5% indicating mass balance closure.

For the nonstoichiometric reactions, it was assumed that all available THF was consumed with the stoichiometric amount of water (1THF:17H₂O).¹⁹ The hydrogen storage capacity values were calculated from this hydrate mass and the amount of gas evolved during dissociation. The mass of any excess ice inside the reaction vessel was deducted from the total mass in this calculation. This approach will yield the most liberal amount of hydrogen stored because the potential for excess ice to convert to more hydrate is neglected.

¹H MAS NMR Measurements. For the NMR measurements, only stoichiometric hydrate was considered, and the same hydrate formation procedure as that described above was followed. THF-*d*₈ (99.68% D, Cambridge Isotope Laboratories, Inc.) and D₂O (99.98% D, Cambridge Isotope Laboratories, Inc.) were used to minimize the proton contribution from these components. High purity hydrogen gas (UHP 99.999%) was used. After hydrate formation, the cell was quenched in liquid nitrogen and depressurized, and approximately 0.5 cm^3 of the cell contents were loaded into a zirconium magic-angle spinning (MAS) NMR rotor. ¹H NMR spectra were recorded at a MAS speed of about 6 kHz on a Chemagnetics CMX Infinity 400 NMR spectrometer operating at 400 MHz for ¹H. Single pulse excitation (90° pulse length of 5 μs) and a pulse repetition delay of 5 s were used. The sample temperature was calibrated using liquid methanol,²⁰ and external hexamethyl benzene was assigned a chemical shift of 1.61 ppm. All NMR measurements were performed at atmospheric pressure and 175 K. Measurements below 175 K were not possible on the instrument used. Hydrogen storage capacities were determined from the peak areas of hydrogen and THF in the spectra, correcting for isotopic substitution and the ortho–para hydrogen distribution present at the measurement temperature.²¹

3. Discussion and Results

Stoichiometric Hydrate. The amount of hydrogen stored in the stoichiometric binary THF–H₂ hydrate showed a strong dependence on the initial formation pressure (Figure 2). As the initial formation pressure was increased, the hydrogen storage capacity initially increased, and began to asymptote near 1.0 wt % at higher pressures. Because the results for different particle sizes were within the variance of the measurements, this would suggest that the values reported in Figure 2 are near the two phase (H–V) equilibrium filling values. Integration of ¹H MAS NMR spectra provided hydrogen storage values that were less than those obtained from direct gas release measurements (NMR spectra shown in Figure 3). This discrepancy is probably caused by partial gas release during the NMR measurement.

Recently, Lee et al.¹² reported that 2.09 wt % H₂ could be stored in the stoichiometric binary THF–H₂ hydrate with an initial formation pressure of 12.0 MPa. For this hydrate to store

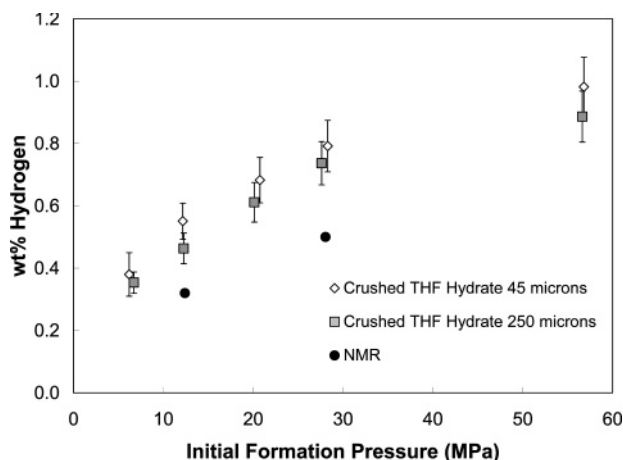


Figure 2. Hydrogen storage capacity in the stoichiometric binary hydrate as a function of initial formation pressure from gas release data and ¹H NMR. Error propagation calculated using the method of Bevington.²⁵

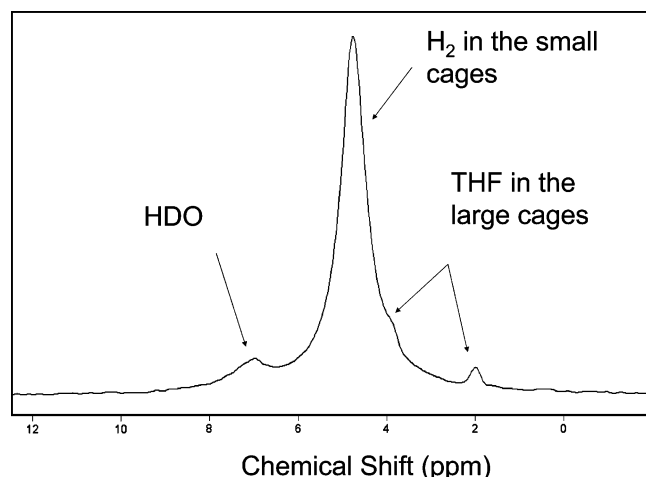


Figure 3. ¹H NMR spectra for the binary hydrate formed at 12.4 MPa. Spectra recorded at atmospheric pressure and 175 K.

2.09 wt % hydrogen, every small cage must be filled with two hydrogen molecules. Contrary to this result, the gas release data presented in Figure 2 suggests that a maximum of one hydrogen molecule occupies the small cavities of the binary hydrate. Although the NMR results show lower storage values than the gas release measurements, they are still consistent with a hydrogen occupancy no greater than one. Observation of the same qualitative trend between independent micro- and macroscopic measurements strongly suggests that only one hydrogen molecule occupies the small cavity in the sII THF–H₂ hydrate. Furthermore, recent high-resolution neutron diffraction data showed that only 1.0 hydrogen molecule is present in each of the small cages of the stoichiometric binary hydrate with a formation pressure of 70 MPa.¹⁴ Additionally, previous gas release studies concluded only 0.91 hydrogen molecules per small cage with a formation pressure of 350 MPa.¹¹ In the work of Lee et al.,¹² the stoichiometric sample was taken to be fully loaded, with two hydrogen molecules per small cage. It is possible that the discrepancy over the small-cage occupancy between the previous study¹² and the current work arises from the reliance on Raman peak areas for quantification of hydrogen content.

If one hydrogen molecule occupies each of the small cavities, and one THF molecule occupies each of the large cavities, the

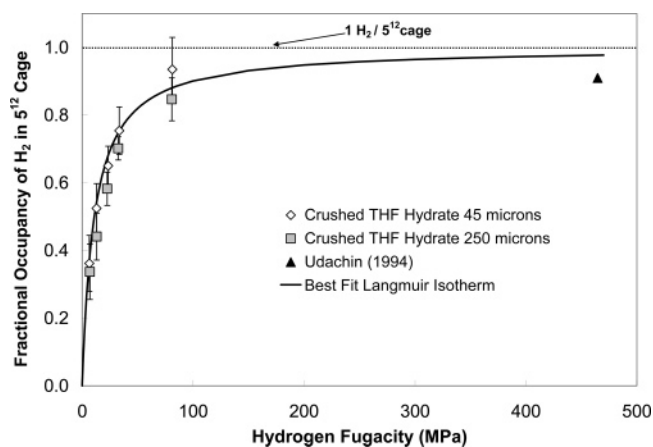


Figure 4. Fractional occupancy of hydrogen in the 5¹² cavity as a function of hydrogen fugacity for stoichiometric THF–H₂ binary hydrate. For the best fit Langmuir isotherm through 45 μm data, C_{H₂} = 0.088 MPa^{−1}.

theoretical storage capacity of the binary hydrate would be 1.05 wt % H₂. Observing that the storage capacity with increasing pressure approaches this theoretical value, it was assumed that a maximum of one hydrogen molecule can occupy each small cavity. With this assumption, the weight percent values reported in Figure 2 were converted into fractional occupancies of the 5¹² cavity. Similar to other gas hydrates with single-cage occupancies, the small-cage occupancy of the THF–H₂ hydrate was found to be modeled well with a single adsorption Langmuir isotherm. To do this, the pressure was thermodynamically corrected to fugacity using the NIST virial equation of state for hydrogen,²¹ and a single adsorption Langmuir isotherm was fit to the data in the form:

$$\theta_{H_{2small}} = \frac{C_{H_{2small}} f_{H_2}}{1 + C_{H_{2small}} f_{H_2}} \quad (1)$$

where f_{H_2} is the hydrogen fugacity and C_{H_2} is adjusted to fit the data for 45 μm particles. The terms for THF are omitted due to the fact that THF is physically too large to fit inside the small cavity of the sII hydrate. When the best-fit Langmuir isotherm was extended to higher pressure, there was reasonable agreement with the result reported by Udachin¹¹ (Figure 4).

Nonstoichiometric Hydrate. Favorable formation conditions are a key parameter in the development of hydrates as suitable candidates for hydrogen storage. However, this aspect must be balanced with an adequate hydrogen storage capacity. With the addition of THF, hydrogen can be stored in the hydrate phase at significantly milder (P,T) conditions than in pure H₂ hydrate. We attribute this increase in stability to the large affinity THF has for the large cages of sII hydrate. Thus, much lower pressures are required to stabilize the binary hydrate than the pure hydrogen hydrate. With the addition of stoichiometric THF, all the large cages of the hydrate are unavailable for storing hydrogen. Therefore, considering that each small cage accommodates at most one hydrogen molecule, the stoichiometric THF binary hydrate can only store a maximum of 1.05 wt % H₂.

Noting the small amount of hydrogen stored in the stoichiometric binary hydrate, there was motivation for increasing the storage capacity above 1.05 wt % by manipulating the large-cage occupancies. If one examines the large-cage occupancy

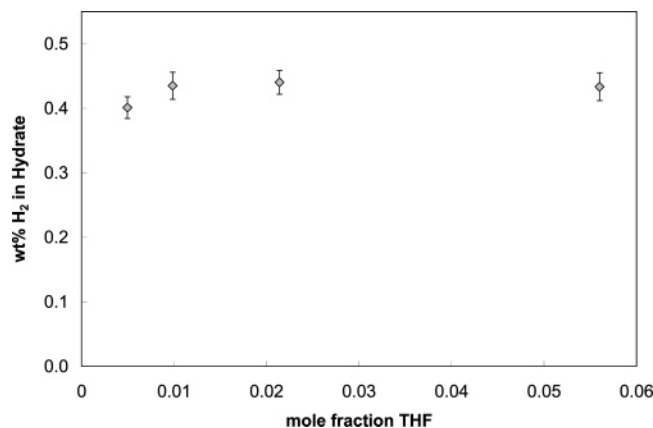


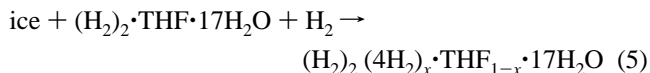
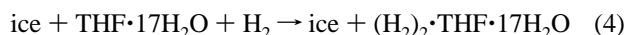
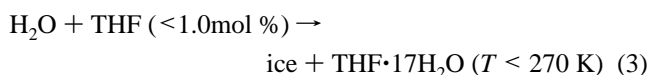
Figure 5. Hydrogen storage capacity as a function of THF composition from gas release data. Samples were formed with a constant initial formation pressure of 13.8 MPa and 250 μm particles.

of a single H_2 molecule in the binary hydrate from the solid solution model of van der Waals and Platteeuw,²²

$$\theta_{\text{H}_{2\text{Large}}} = \frac{C_{\text{H}_{2\text{Large}}} f_{\text{H}_2}}{1 + C_{\text{H}_{2\text{Large}}} f_{\text{H}_2} + C_{\text{THF}_{\text{Large}}} f_{\text{THF}}} \quad (2)$$

one can see that in order for a single H_2 molecule to enter the large cage, the equilibrium adsorption (Langmuir) constant for H_2 multiplied by its fugacity must be comparable to that for THF. Because the Langmuir constant for THF is greater than 6 orders of magnitude larger than H_2 at the same temperature,^{23,24} either the fugacity of H_2 must be dramatically increased or the fugacity of THF must be significantly decreased. One way to decrease the THF fugacity is to decrease its concentration in the liquid phase.

Recently, Lee et al.¹² proposed that by decreasing the THF concentration, it is possible to form a nonstoichiometric THF hydrate with the balance of the large cages quadruply occupied by H_2 . A mechanism for this reaction is given below, modified from Lee et al. to account for the currently observed single hydrogen occupancy of the small cavities.



Storage capacities (for a constant initial formation pressure of 13.8 MPa) versus THF concentrations ranging from 5.56 to 0.5 mol % THF are plotted in Figure 5. After one week of formation, no measurable increase in storage was observed. This indicates that at the conditions tested, THF occupancy in the large cage remains favorable compared to hydrogen and eq 5 of the proposed mechanism is not occurring. Although the phase fractions of hydrate and ice were inferred from the formation of stoichiometric hydrate, if any excess ice did react with the hydrate as proposed in the above mechanism, this would only increase the overall hydrate mass and thus decrease the reported wt % values. However, it appears that the stoichiometric hydrate is the thermodynamically stable phase because the hydrogen concentration remains the same as the stoichiometric case. We attribute the discrepancies between this work and that of Lee et al.¹² to the almost complete reliance of integral Raman band

intensities for quantification of hydrogen storage (in the absence of a calibration curve for direct gas release).

4. Conclusions

The hydrogen storage capacity of the binary THF– H_2 clathrate hydrate has been investigated as a function of both initial formation pressure and THF composition. As the initial formation pressure was increased, the hydrogen storage also increased asymptotically to approximately 1.0 wt %. This storage value corresponds to the storage capacity for the stoichiometric binary hydrate with one hydrogen molecule per small cavity.

The evidence presented in this work shows that the maximum small-cage occupancy of hydrogen in the binary THF– H_2 hydrate is one hydrogen molecule (cf. pure hydrogen hydrate). As the THF concentration was decreased from 5.56 to 0.5 mol %, there was no detectable change in storage capacity with a constant formation pressure of 13.8 MPa. This indicates that, contrary to previous reports, THF remains the favorable guest for the large cage, and that multiple hydrogen occupancies in this system cannot be achieved at moderate pressures. Over the range of experimental conditions tested, the maximum hydrogen storage capacity of the binary sII THF– H_2 hydrate was found to be approximately 1.0 wt %. These results strongly impact the feasibility of using the binary THF– H_2 hydrate as a hydrogen storage material.

Nomenclature

- $\theta_{\text{H}_{2\text{small}}}$ = small-cage hydrogen occupancy
 C_{ij} = Langmuir constant for species i in cage j
 f_i = fugacity of species i

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