

Molecular Hydrogen Storage in Novel Binary Clathrate Hydrates at Near-Ambient Temperatures and Pressures

L.J. Rovetto, T.A. Strobel, K.C. Hester, S.F. Dec, C.A. Koh, K.T. Miller, E.D. Sloan
Colorado School of Mines, Center for Hydrate Research
Golden, CO (80401) esloan@mines.edu

Program Scope

Clathrate hydrates are inclusion compounds in which guest molecules occupy the cages formed by a hydrogen-bonded water network [1]. Solid gas clathrate hydrates generally form at high pressures and temperatures near or even above the ice point. Pure hydrogen hydrates have been reported to form cubic structure II hydrates under extreme conditions (200 MPa at 280 K) [2].

We have recently demonstrated that hydrogen molecules can be stored in binary H₂/THF (tetrahydrofuran) clathrate hydrates at pressures nearly two orders of magnitude lower than that in pure hydrogen hydrates [3]. This decreased pressure (Figure 1) makes binary clathrate hydrates a more feasible hydrogen storage material, with a unique combination of advantages not found in any other class of materials. Hydrogen storage is completely reversible in this material, since the gas molecules are free within the clathrate hydrate framework.

Determination of a fundamental understanding of the structure, molecular-level dynamics, and H₂ formation/release rates and mechanisms in these novel crystalline compounds is the main objective of our research.

The final goal of this project is to develop binary clathrate hydrates that will efficiently store and release molecular hydrogen at near-ambient temperatures and pressures, achieving targets for energy density, energy uptake, and release kinetics.

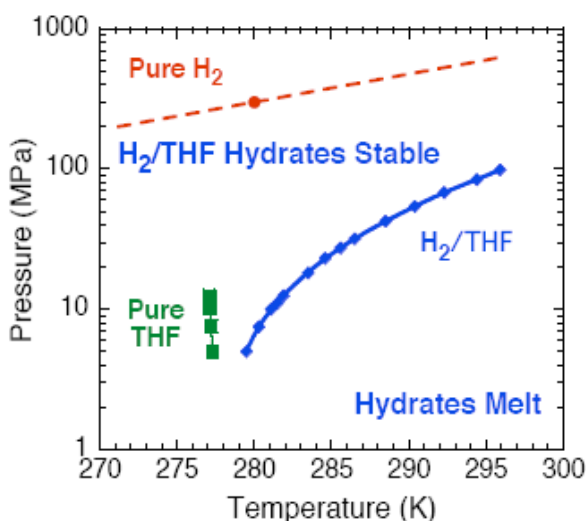


Figure 1. Phase diagram and stability regions of pure H₂ hydrate, pure THF hydrate, and binary H₂/THF hydrate.

Recent Progress

a) Hydrogen Storage Capacity

Several techniques have been employed to determine the hydrogen storage capacity of the stoichiometric THF/H₂ binary hydrate (5.6 mol% THF), which corresponds to all of the large cages of sII hydrate being occupied by THF. The primary technique used was direct gas release measurements from samples prepared from preformed crushed THF hydrate (particle sizes of 45 and 250 μm), and by formation from

the liquid phase. Integration of ^1H MAS NMR spectra, as well as high resolution neutron scattering of the binary THF/ H_2 hydrate was also used to determine the storage capacity.

Our experimental results have shown that stoichiometric tetrahydrofuran (THF) hydrate can store up to about 1.0 wt% hydrogen, which is in agreement with our previous work [3]. The storage capacity of hydrogen increases with increasing pressure. The storage capacity of hydrogen in the binary hydrate shows little dependence on the amount of sub-cooling applied during formation.

Using high resolution neutron diffraction (at Argonne National Laboratory), we have determined the time-space average filling of hydrogen molecules in a binary tetrahydrofuran (THF)- d_8 + D_2 sII clathrate hydrate. The diffusional filling of hydrogen in the lattice of a THF- d_8 clathrate hydrate occurred upon pressurization. The hydrogen molecules were localized in the small dodecahedral cavities at 20 K, with nuclear density from the hydrogen approximately spherically distributed and centered in the small cavity. With a formation pressure of 70 MPa, molecular hydrogen was found to only singly occupy the sII small cavity. The occupancy in the small dodecahedral (5^{12}) cavity is a very important parameter to assess whether these materials will be a viable hydrogen storage medium. Hydrate structures which enable multiple occupancy of hydrogen will likely be required for the increase in stored hydrogen density. An understanding of the occupancy and orientation of hydrogen in the host water lattice will be key in future development and studies of these binary hydrate materials.

It has been suggested [4] 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%. Non stoichiometric hydrates (below 5.6 mol% to 0.5 mol%), were formed and gas release experiments were performed in order to investigate the possible manipulation of the large cage occupancy. As the THF concentration was decreased from 5.56 mol% 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 [4], THF remains the favorable guest for the large cage, and that multiple hydrogen occupancies 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%.

b) Hydrogen Stabilization Effect

Cyclohexanone is a known sII hydrate former. However, like other large sII formers (e.g. cyclohexane or benzene), a second guest molecule is required to stabilize the structure, and no pure cyclohexanone hydrate is currently known. Through neutron powder diffraction at the Argonne National Laboratory, we have

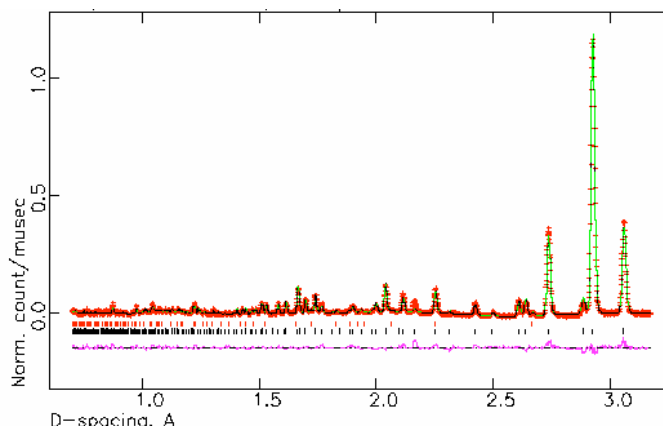
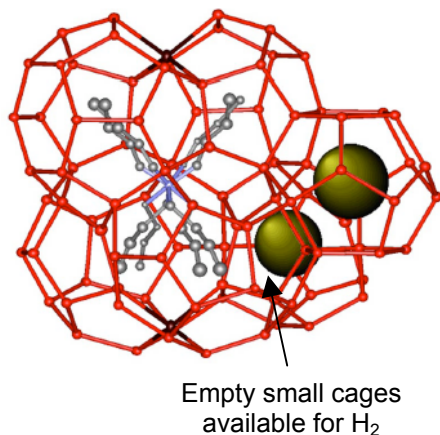


Figure 2. Diffraction pattern for the CHone/ D_2 system. Rietveld profile refinement indicates that D_2 had entered the lattice. The large cavity is fully occupied by CHone molecules whereas occupancy of ~ 0.54 of the small 5^{12} cage was determined for D_2 .

determined that hydrogen acts like a well behaved hydrate former, in the sense that it can stabilize the larger lattice in cooperation with cyclohexanone (CHone) at $-253^{\circ}\text{C}/20\text{ K}$ and 1 atm. (Figure 2).

The ability of hydrogen to stabilize the larger hydrate lattice may have some implication for formation of other hydrate structures with hydrogen, where a second guest molecule is needed for stability, for example sH.

c) First Semi-clathrate formed with H_2



Semi-clathrates, unlike clathrate hydrates, gain their stability from the participation of the guest molecule inside the hydrate cavities. Tetra-n-butylammonium bromide, forms a semi-clathrate with water at atmospheric pressure.

Recently, we have shown for the first time that hydrogen molecules can be encapsulated inside the small cavities of this structure. This gives indication that hydrogen storage inside clathrate compounds is not limited to the classical clathrate hydrate structures, but rather open to a wider variety of water-based host complexes.

Figure 3. TBAB semi-clathrate molecular structure. (Picture from: Shimada et al., Acta Cryst. (2005). C61. 65-66)

d) Hydrotrope effect on Gas Hydrates

It has been reported that the use of hydrotropes molecules promotes gas hydrate thermodynamics [5], by shifting the three phase (H-L_w-V) equilibrium curve to more stabilizing conditions; this would provide reduced pressure requirements for gas hydrate formation, and gas storage/transportation applications.

Motivated by this intriguing phenomena and its potential applicability to pure hydrogen hydrates, the effect of p-TSA on the three phase (H-L_w-V) equilibria of three different gas hydrate forming systems (CH₄-water-p-TSA, CH₄+C₂H₆-water-p-TSA and a natural gas mixture-water-p-TSA) has been investigated and quantified in the present work. The equilibrium conditions (H-L_w-V) of these gas hydrate systems were obtained using the isochoric temperature cycle method at different p-TSA concentrations. However, no effect was observed on the hydrate phase equilibria with hydrotrope concentrations in the range of 2000-5000 ppm. Furthermore, at higher concentrations (up to 138 000 ppm), an inhibitor effect on CH₄ hydrate stability was measured. The accuracy of the hydrate equilibrium points, using the temperature cycling procedure, was found to be highly dependent on the heating rate during hydrate dissociation.

Future Plans

Based on our results, with single occupancy of H₂ molecules in the small cavity of sII binary THF/H₂ clathrate, a maximum storage of 1 wt% can be achieved. In order for

clathrate hydrates to be practical hydrogen storage medium, hydrate structures which enable multiple occupancy of hydrogen will likely be required.

Understanding the pressure dependence of the hydrate cavity occupancy is a prerequisite for possible manipulation of the storage capacity in clathrate hydrates. Raman studies of pure H₂ hydrate will be performed in a new high pressure device (up to 60,000 psi). These studies will also provide valuable information on the formation and dissociation mechanism of hydrogen hydrates, necessary for practical applications.

Further search of different sH hydrate formers with the possibility of multiple occupancy of the large cavities, as well as other possible structures are the primary objectives of this project, to achieve the H₂ storage target values.

NMR studies will be carried out in order to investigate the hydrogen diffusion mechanism in ice and different hydrate structures. These studies, in conjunction with determination of dissociation rates of binary H₂ hydrates at different storage conditions, will establish if hydrogen hydrates show self preservation behavior [6], in which case the dissociation rate of the hydrate outside the stability region (i.e. higher temperatures or lower pressures) is extremely low (i.e. weeks or months), offering the possibility of storage of the hydrogen at middle conditions, in a reversible and environmentally friendly storage material.

Publications

- 1) K.C. Hester, T.A. Strobel, A. Huq, A.J. Schultz, E.D. Sloan, C.A. Koh. Molecular Hydrogen Occupancy in Binary THF-H₂ Clathrate Hydrates by High Resolution Neutron Diffraction. *Phys. Rev. Letters*. *Submitted*
- 2) T.A. Strobel, C.J. Taylor, K.C. Hester, S.F. Dec, C.A. Koh, K.T. Miller, E.D. Sloan Jr. Molecular Hydrogen Storage in Binary THF-H₂ Clathrate Hydrates. *J. Phys. Chem. B*. *Submitted*
- 3) L.J. Rovetto, T.A. Strobel, C.A. Koh, E.D. Sloan Jr. Is gas hydrate formation thermodynamically promoted by hydrotrope molecules? *Fluid Phase Equilibria*. *Submitted*
- 4) Neutron diffraction studies of binary hydrates with H₂ and cyclohexanone. *In preparation*

References

- [1] Sloan, E.D., *Clathrate Hydrates of Natural Gas* (Marcel Dekker, New York, 2nd Ed., 1998).
- [2] Mao, W.L., Mao, H-K, Goncharov, A.F., Struzhkin, V.V., Guo, Q., Hu, J., Shu, J., Hemeley, R.J., Somayazulu M., Zhao, Y., *Science*, 297, 2247:2249 (2002)
- [3] Florusse, L.J., Peters, C.J., Schoonman, J., Hester, K.C., Koh, C.A., Dec, S.F., Marsh, K.N., Sloan, E.D. *Science* 306, 469:471 (2004).
- [4] Lee, H.; Lee, J.-W.; Kim, D. Y.; Park, J.; Seo, Y.-T.; Zeng, H.; Moudrakovski; I.L., R.; C.I., R., J.A. *Nature* 434, 743:746 (2005)
- [5] N. Gnanendran, R. Amin, *Fluid Phase Equilib.* 221, 175:187 (2004)
- [6] L.A. Stern, S. Circone, S.H. Kirby, and W.B. Durham, *Can. J. Phys./ Rev. Can. Phys.* 81, 271:283 (2003)