

IV.I.20 Molecular Hydrogen Storage in Novel Binary Clathrate Hydrates at Near-Ambient Temperatures and Pressures

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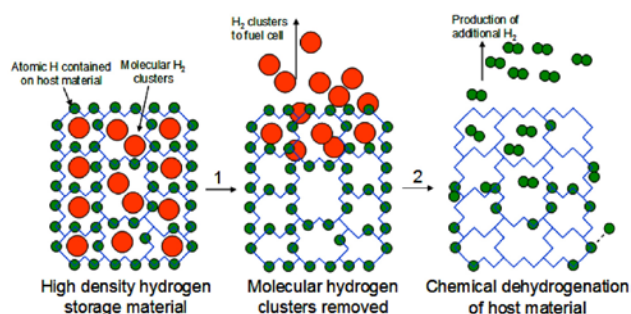


FIGURE 1. A Conceptual Picture of Chemical-Clathrate Hybrid Storage of Hydrogen [6]

Description of Accomplishments:

1. Proof-of-Concept for Novel Chemical-Clathrate Hybrid Storage of Hydrogen

In our previous reports, we showed from X-ray and neutron diffraction, Raman and NMR spectroscopy, and gas analysis that hydrogen can stabilize several clathrate hydrate structures in the presence of different large guests. The structures include sII (tetrahydrofuran + H₂, cyclohexanone + H₂), sH (H₂ with methyl-tert-butyl ether, methylcyclohexane, 2,2,3-trimethylbutane, 1,1-dimethylcyclohexane, or isoamyl alcohol), and a semi-clathrate phase (tetra-*n*-butylammonium bromide + H₂) [1-5]. However, these double hydrogen hydrates fell short in reaching the storage capacity goal, therefore requiring that we devise a new approach to increasing the amount of hydrogen stored in the material.

We have demonstrated for the first time the proof-of-concept of chemical-clathrate hybrid storage of hydrogen using an organic compound hydroquinone [6]. This is the first storage scheme in which both molecular storage of hydrogen within hydrate cavities and chemical storage in the host molecule are utilized. Using Raman spectroscopy, we have confirmed that hydrogen molecules can be enclathrated into hydroquinone. X-ray diffraction analysis shows that in order to provide vacant cavities for the hydrogen molecules, hydroquinone undergoes a structural change from an α -phase to a β -phase under sufficient hydrogen pressure. The host molecule of this clathrate-chemical hybrid system, hydroquinone, has been also used to directly power a fuel cell [5]. At the anode side of the fuel cell, hydroquinone loses its chemically bound hydrogen in the hydroxyl group while producing electricity. This approach in taking advantage of additional chemically stored hydrogen in the host molecule promises an improvement in weight storage capacity of clathrate materials and is the first time that these two systems have been combined in a hybrid technology for hydrogen storage [6].

2. Extending the Chemical-Clathrate Hybrid Concept to a Clathrate Hydrate Hybrid System of Hydrogen

While the presence of large guests such as tetrahydrofuran (THF) and tetra-*n*-butylammonium bromide (TBAB) drastically reduces the formation pressure of hydrogen hydrate at a given temperature, weight storage capacity of hydrogen in the material also decreases because the large guests occupy the large cavities of the hydrate structure. To help overcome this trade-off between stability and weight storage capacity, the chemical-clathrate hybrid concept was applied to clathrate hydrates of hydrogen.

We have recently shown for the first time that tetra-*n*-butylammonium borohydride (TBABh) can store hydrogen both in molecular form in the hydrate cavities and chemically bound to the borohydride anion [7]. Raman spectroscopy was used to confirm the presence of encaged hydrogen in the small cages of the hydrate. X-ray diffraction revealed that the structure of TBABh + H₂ hydrate is analogous to the previously reported structure of TBAB + H₂ hydrate. An acid catalyzed hydrolysis reaction was used to produce additional hydrogen from the borohydride anion, and the reaction showed nearly 100% conversion. Using gas evolution and differential scanning calorimetry measurements, we showed that TBABh + H₂ hydrate is more stable and stores more hydrogen (27%) than the THF + H₂ hydrate system [7].

3. Raman Spectroscopic Study of Hydrogen Hydrates

Detailed Raman spectroscopic studies have been performed in order to better understand the quantum behavior of hydrogen molecules stored within the

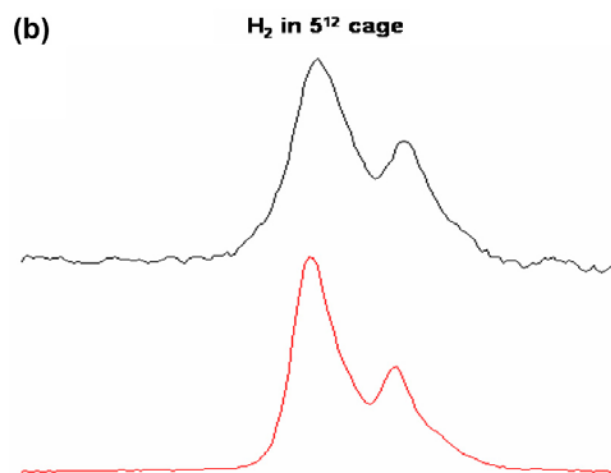
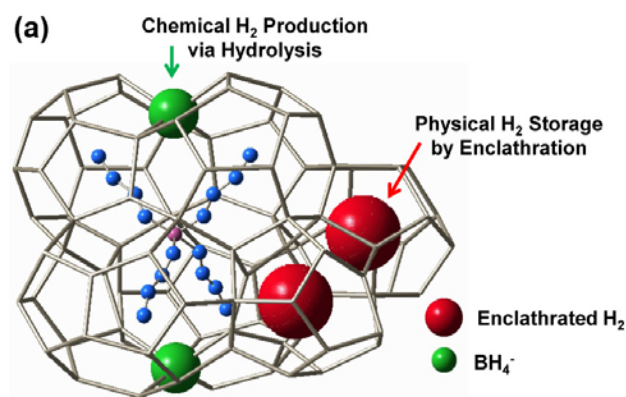


FIGURE 2. (a) Water cavities with enclathrated TBABh and H_2 molecules. TBA^+ is situated within the large cavities, and BH_4^- replaces a water molecule. H_2 is located in the small cavities. (b) Raman spectra of the H_2 vibron region in TBABh + H_2 hydrate at 76 K (top), THF + H_2 hydrate at 76 K (bottom). The similar vibrational modes of H_2 in TBABh hydrate and THF hydrate indicates H_2 is encaged in the small cavities [7].

hydrate cavities. Vibrational bands show that the molecules vibrate at lower frequencies than in the gas phase and a pair of peaks (ortho- and para- H_2) is present for each environment in the hydrogen hydrate. For a simple hydrate of hydrogen, four pairs of peaks are present for single occupancy in the small cavities and double, triple, and quadruple occupancies in the large cavities. Integrating these peaks results in an under-estimation of the large cavity H_2 content, implying that a H_2 molecule in a small cavity is more polarizable than H_2 molecules in a large cavity [8].

Rotational bands show that enclathrated hydrogen molecules have orientationally dependent rotation, suggesting that the small and large cavities are orientationally anisotropic. The Raman spectrum of D_2 hydrate was also analyzed, and this indicated that D_2 was a suitable substitute for H_2 in hydrate formation. From these detailed Raman studies and complementary diffraction and gas evolution analyses, we have

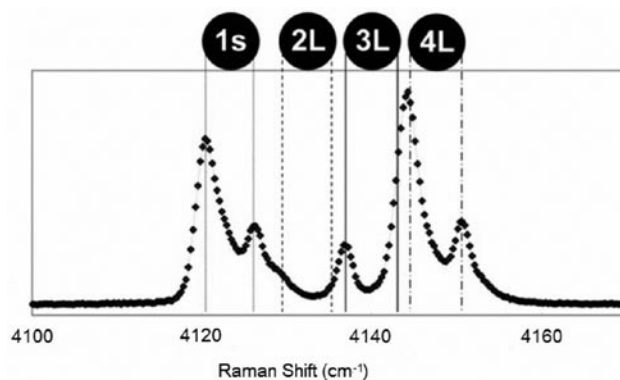


FIGURE 3. The vibron region in the Raman spectrum of simple H_2 hydrate formed at 200 MPa and 250 K measured at atmospheric pressure and 76 K. 1s = 1 H_2 in a small cavity, 2L = 2 H_2 in a large cavity, 3L = 3 H_2 in a large cavity, and 4L = 4 H_2 in a large cavity [8].

demonstrated that Raman spectroscopy is an effective tool in studying the nature of stored hydrogen molecules as well as in determining relative occupancy in different cavities [8].

4. Thermodynamic Prediction of Hydrates Containing THF and H_2

A thermodynamic model based on the CSMGem framework (an in-house program based on the van der Waals and Platteeuw theory) was developed for hydrate systems containing THF and H_2 . With the newly developed model, thermodynamic predictions of many simple or binary hydrates containing THF or H_2 can be made for the first time. The model predictions are in excellent agreement with experimentally determined p-T phase diagrams. Such a model is very useful since THF is a common additive for reducing the formation pressure of a given hydrate system, and binary hydrates of hydrogen are currently being investigated as a potential storage material. The model also indicates that the degree to which the cavities are filled with hydrogen is largely a function of formation pressure, which has an implication in hydrogen storage, where high occupancy is desired [9].

Summary and Implications

The newly proven concept of chemical-clathrate hybrid storage of hydrogen holds great promise for improving the storage capacity in clathrate materials. Applying this concept to clathrate hydrates resulted in an increased storage capacity while having a large guest present, which greatly reduces the required formation pressure at a given temperature. Using spectroscopic tools, we have obtained new insight into the structure and interactions between the host water molecules and the guest hydrogen molecules in clathrate hydrates of

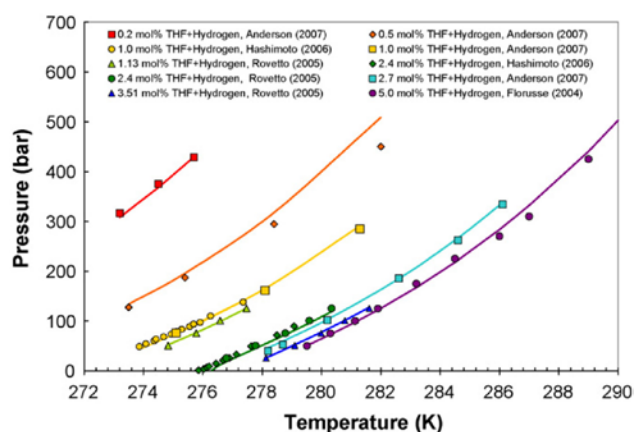


FIGURE 4. Pressure-temperature diagram of THF + H₂ hydrate experimentally determined by various groups (shown as dots) predicted by the newly developed thermodynamic model (shown as solid lines) [9].

hydrogen. We are continuing our efforts to develop new materials that can be used for efficient storage of hydrogen.

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6. *Chemical-Clathrate Hybrid Hydrogen Storage: Storage in Both Guest and Host*, Strobel, T.A.; Kim, Y.; Andrews, G.S.; Ferrell, J.R.; Koh, C.A.; Herring, A.M.; Sloan, E.D., *J. Am. Chem. Soc.*, 130, 14975-14977 (2008).
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8. *Raman Spectroscopic Studies of Hydrogen Clathrate Hydrates*, Strobel, T.A.; Sloan, E.D.; Koh, C.A., *J. Chem. Phys.*, 130, 014506 (2009).
9. *Thermodynamic Predictions of Various Tetrahydrofuran and Hydrogen Clathrate Hydrates*, Strobel, T.A.; Sloan, E.D.; Koh, C.A., *Fluid Phase Equilibria*, (2009), in press.

List of Publications (for the Report Period):

1. *Chemical-Clathrate Hybrid Hydrogen Storage: Storage in Both Guest and Host*, Strobel, T.A.; Kim, Y.; Andrews, G.S.; Ferrell, J.R.; Koh, C.A.; Herring, A.M.; Sloan, E.D., *Journal of the American Chemical Society* (2008), 130, 14975-14977.
2. *Water Cavities of Structure H Clathrate Hydrate Stabilized by Molecular Hydrogen*, Strobel, T.A.; Koh, C.A.; Sloan, E.D., *Journal Physical Chemistry B* (2008), 112, 1885-1888.
3. *Raman Spectroscopic Studies of Hydrogen Clathrate Hydrates*, Strobel, T.A.; Sloan, E.D.; Koh, C.A., *Journal of Chemical Physics* (2009), 130, 014506.
4. *Thermodynamic Predictions of Various Tetrahydrofuran and Hydrogen Clathrate Hydrates*, Strobel, T.A.; Sloan, E.D.; Koh, C.A., *Fluid Phase Equilibria* (2009), in press.
5. *Tetra-*n*-butylammonium Borohydride Semi-clathrate: A Hybrid Clathrate Hydrate for Hydrogen Storage*, Shin, K.; Kim, Y.; Strobel, T.A.; Prasad, P.S.R.; Lee, H.; Sloan, E.D.; Sum, A.K.; Koh, C.A., *Journal of Physical Chemistry B* (2009), submitted.
6. *Microsecond Simulation of Spontaneous Methane Hydrate Nucleation and Growth*, Walsh, M.; Koh, C.A.; Sloan, E.D.; Sum, A.K.; Wu, D., *Science* (2009), submitted.

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