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

E. Dendy Sloan (Primary Contact),
Carolyn A. Koh, Steven F. Dec
Colorado School of Mines

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**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, methycyclohexane, 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].

   ![A Conceptual Picture of Chemical-Clathrate Hybrid Storage of Hydrogen](image)

   **FIGURE 1.** A Conceptual Picture of Chemical-Clathrate Hybrid Storage of Hydrogen [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...
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 underestimation 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 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
hydrogen. We are continuing our efforts to develop new materials that can be used for efficient storage of hydrogen.

References:


List of Publications (for the Report Period):


List of People Working on Project:

Graduate Students:
Timothy Strobel (full support), Matt Walsh (full support), Masika Pascall (full support)

Undergraduate Student:
Yongkwan Kim (partial support, 20%)

Visiting Researchers:
Kyuchul Shin (partial support, 20%), Vahid Taghikhani (partial support, 30%)

Post-doctoral Fellow:
Takeshi Sugahara (full support)

Professors:
E. Dendy Sloan (Partial support, 4%), Carolyn A. Koh (Partial support, 6%), Amadeu K. Sum (Partial support, 8%)