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Tetra-*n*-butylammonium Borohydride Semiclathrate: A Hybrid Material for Hydrogen Storage

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In this study, we demonstrate that tetra-*n*-butylammonium borohydride [$(n\text{-}C_4H_9)_4NBH_4$] can be used to form a hybrid hydrogen storage material. Powder X-ray diffraction measurements verify the formation of tetra-*n*-butylammonium borohydride semiclathrate, while Raman spectroscopic and direct gas release measurements confirm the storage of molecular hydrogen within the vacant cavities. Subsequent to clathrate decomposition and the release of physically bound H_2, additional hydrogen was produced from the hybrid system via a hydrolysis reaction between the water host molecules and the incorporated BH_4^- anions. The additional hydrogen produced from the hydrolysis reaction resulted in a 170% increase in the gravimetric hydrogen storage capacity, or 27% greater storage than fully occupied THF + H_2 hydrate. The decomposition temperature of tetra-*n*-butylammonium borohydride semiclathrate was measured at 5.7 °C, which is higher than that for pure THF hydrate (4.4 °C). The present results reveal that the BH_4^- anion is capable of stabilizing tetraalkylammonium hydrates.

Many kinds of hydrogen storage materials have been studied as hydrogen is considered a potentially important future energy carrier.[1−3] In particular, clathrate hydrates have been highlighted as a potential storage materials because of the ready availability and nature of the host (water), as well as their ability to concentrate hydrogen in molecular form.[4−9] Although simple (one guest) structure II hydrogen hydrate or $H_2(H_2O)$ filled ice can approach the hydrogen capacity set by the DOE (6 wt % by 2010), severe formation conditions prevent the use of these clathrates for practical hydrogen storage.[4,10] Other hydrogen hydrates which are stable at moderate pressure conditions can store hydrogen with contents near 1 wt %.[11] Therefore, other hydrogen storage materials should be considered to overcome this limitation.[12]

In parallel, certain chemical hydrogen storage schemes utilize the hydrolysis of compounds such as $NaBH_4$ and NH_3BH_3.[13−17] Such schemes have been considered one of the best methods to produce hydrogen as a result of the better reaction kinetics compared to pyrolysis of the same compounds, providing acceptable hydrogen capacity.[13−17] $NaBH_4$, a widely studied material, can generate hydrogen via the following hydrolysis reaction,

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad (1)$$

This process theoretically generates 10.8 wt % of hydrogen capacity; however, because $NaBO_2$ is produced as a byproduct, the actual hydrogen capacity reduces to below 2.9 wt %.[18]

These two different approaches to hydrogen storage, physical storage in clathrate hydrates and chemical hydrogen production via a hydrolysis reaction, have a common ingredient—the presence of water—which is essential to both methods. If the hydrolyzable material can be used to form a clathrate hydrate, one may achieve both stabilization of the hydrate compound and a higher hydrogen capacity by producing additional hydrogen through hydrolysis. However, combining two approaches has rarely been attempted in spite of its potential to hydrogen storage.

Recently, the chemical-clathrate hybrid concept for hydrogen storage was reported in a previous study.[12] The β-phase of hydroquinone was shown to store hydrogen physically within clathrate cavities, as well as chemically through direct oxidation of the host hydroquinone in a hydrogen fuel cell. Although the utilization of hydrogen storage from two independent sources of the same material is a promising concept, novel host materials that have greater physical and chemical storage capacities are needed to improve this hybrid idea. Additionally, novel concepts that exploit different chemical-clathrate hybridization mechanisms should be explored.

In this study, we demonstrate the incorporation of BH_4^-, a common hydrolyzable anion, into a clathrate hydrate to dem-

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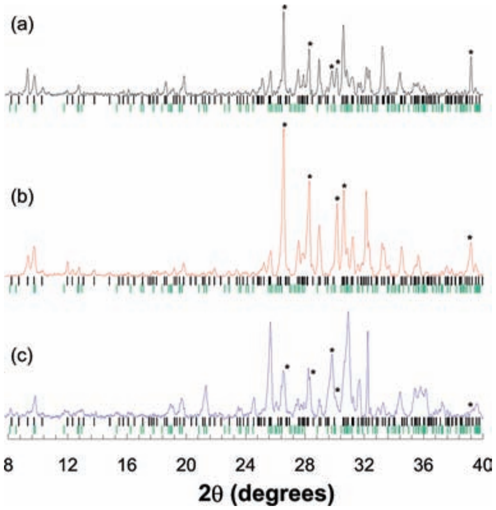

Figure 1. PXRD patterns for (a) TBAB, (b) TBABh, and (c) TBABh + H_2 semiclathrate hydrates obtained at atmospheric pressure and 100 K. For each pattern, the upper tickmarks indicate reflections from the primary tetragonal phase which are coincident for the proposed space groups $P\bar{4}$,[26] $P4/m$[33] and the lower tickmarks indicate reflections from the secondary orthorhombic *Pmma* phase.[19] Asterisks indicate contributions from ice and alumina.

onstrate another chemical-clathrate hybrid concept using water molecules. For this proof-of-concept, tetra-*n*-butylammonium borohydride (TBABh) was used. Tetraalkylammonium salts with suitable anions, such as F^-, Br^-, or OH^-, are known to form clathrate or semiclathrate structures with[19-24] and without[25-30] secondary guests. In particular, tetra-*n*-butylammonium bromide (TBAB) and fluoride (TBAF) semiclathrate hydrates were reported to show better thermodynamic stability than tetrahydrofuran (THF) clathrate hydrate.[20] However, the borohydride anion (BH_4^-) has not been used previously to form a semiclathrate hydrate, perhaps due to its reactive nature with water. In this work, TBABh semiclathrate hydrate with and without molecular hydrogen was synthesized and analyzed by Raman spectroscopy, powder X-ray diffraction (PXRD), and differential scanning calorimeter (DSC). Gas evolution tests indicated that the hydrogen capacity from the semiclathrate increases by producing additional H_2 from the anion−water host framework.

The structure of tetra-*n*-butylammonium (TBA^+) semiclathrate is known to depend on the anion size and water concentration.[31] TBABh was expected to follow similar structural behavior as TBAB,[19] given the proximity of ionic radii (BH_4^-, 2.03 Å; Br^-, 1.96 Å).[32] The phase behavior of the TBAB + H_2O system is quite rich with at least four reported semiclathrate phases below 10 mol % TBAB.[33,34] The exact structure and hydration number of these phases have been a point of controversy;[19,26,33-36] however, most reports are consistent with the formation of a tetragonal *P* lattice near $1TBAB{:}32H_2O$[26,33] and an orthorhombic *P* lattice ranging between $1TBAB{:}36{-}38H_2O$.[19,33] We prepared 2.54 mol % solutions of TBAB and TBABh in H_2O in accordance with the recent single crystal diffraction study of Shimada et al.[19] who formed stoichiometric orthorhombic crystals with a composition of $1TBAB{:}38H_2O$.

The PXRD pattern for TBAB semiclathrate shown in Figure 1a shows mainly tetragonal structure (indexed to $P4/m$ and $P\bar{4}$: $a = 23.515(6)$ and $c = 12.492(44)$ Å) with a small fraction of the orthorhombic phase present. In contrast, the PXRD pattern for TBABh hydrate shown in Figure 1b is identified as almost purely tetragonal structure (indexed to $P4/m$ and $P\bar{4}$: $a = 23.549(21)$ and $c = 12.466(45)$ Å).[37] The persistence of the tetragonal semiclathrate phase is most likely the result of metastability. Recent studies on TBAB semiclathrate indicated metastable three phase coexistence at 2.54 mol % TBAB.[35,36] Gaponenko et al.[33] previously observed the tetragonal TBAB semiclathrate phase to always grow first in this composition range, with the equilibrium orthorhombic phase not appearing for days or even weeks. This scenario is further complicated for the TBABh system in which NaOH was added to prevent premature hydrolysis reaction.[38] Although the amount of added NaOH (molar ratio of $OH^-/BH_4^- = 0.05$) is quite small, a slightly reduced water concentration for TBABh can affect the phase equilibrium between tetragonal and orthorhombic structures.

Based on this PXRD confirmation, the implication is that TBABh semiclathrate provides small dodecahedral (5^{12}) cages for hydrogen molecules to occupy, in both the tetragonal and orthorhombic stuructures.[21] To confirm that H_2 could be enclathrated into the 5^{12} cages, the 2.54 mol % TBABh sample was pressurized with H_2 to 70 MPa at 253 K, a condition below the phase boundary of pure hydrogen hydrate,[39] and the PXRD pattern and Raman spectrum were obtained. The PXRD pattern for TBABh + H_2 hydrate (Figure 1c) shows mixed phase of tetragonal (indexed to $P4/m$ and $P\bar{4}$: $a = 23.520(10)$ and $c = 12.449(27)$ Å) and orthorhombic structure (indexed to *Pmma*: $a = 21.053(14)$, $b = 12.642(8)$, and $c = 12.017(17)$ Å).[37] In this case, the influence of external pressure and incorporation of H_2 may also affect the equilibrium structure.

The Raman spectrum of TBABh + H_2 hydrate in the H_2 vibron region (Figure 2a, top) shows two peaks at 4119 and 4124 cm^{-1}, originating from the hydrogen *Q* branch transitions $Q_1(1)$ (ortho) and $Q_1(0)$ (para) [$Q_{\Delta\nu}(J)$, where ν and J are the vibrational and rotational quantum numbers], respectively.[7] Comparing these Raman shifts with THF + H_2 hydrate (Figure 2a, bottom) reveals the presence of the same peak positions, confirming that H_2 is enclathrated into 5^{12} cages. Having confirmed H_2 enclathration in the hydrate cavities from Raman spectroscopy, we clearly conclude that BH_4^- can be used to form a semiclathrate hydrate with H_2.

Further evidence for the TBABh semiclathrate formation was obtained from the B−H stretching region of the Raman spectrum. In TBAB hydrate, one Br^- is substituted for an oxygen−water position on the host lattice, coordinated by four nearest-neighbor water molecules.[19] Similarly, BH_4^- is expected to maintain an equivalent configuration. This BH_4^- incorporation into the host lattice can affect the B−H stretching mode of TBABh. Figure 2b shows the Raman spectra in the B−H stretching region of TBABh powder, aqueous solution, and hydrate. One sharp peak at 2246 cm^{-1} appears in the spectrum of TBABh powder. When TBABh is dissolved into water, this peak broadens and shifts to 2284 cm^{-1}. After the TBABh semiclathrate hydrate is formed as the temperature decreases, the B−H peak broadens further and shifts to 2289 cm^{-1}. The broadening and the blue-shift of the B−H peak strongly imply interaction between BH_4^- and H_2O molecules distinct from the aqueous phase, which is attributed to the BH_4^- incorporation into the water host framework.

From the spectroscopic results, it was confirmed that TBABh hydrate is capable of accommodating molecular hydrogen within the 5^{12} cavities. Therefore, with BH_4^- also incorporated into the clathrate, this material has two independent hydrogen sources: physically trapped and chemically bound. The physically stored and chemically produced hydrogen capacities of TBABh hydrate were measured volumetrically, with and without an acidic catalyst. Without the hydrolysis reaction, 73 ± 3 mL of H_2 (0.82 atm, 293.15 K) was stored in small cavities per

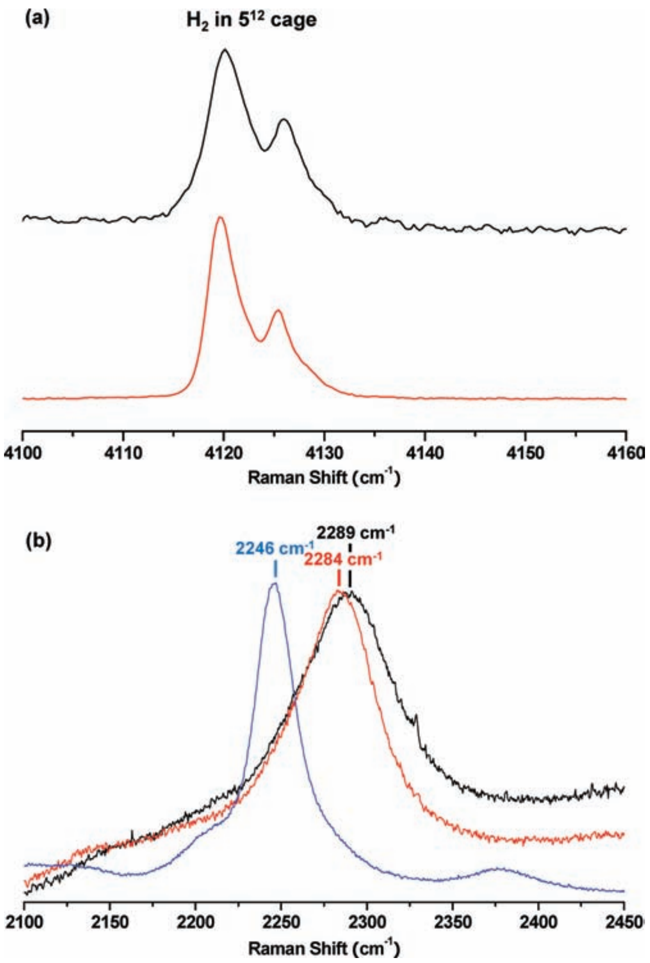

Figure 2. (a) Raman spectra of the H_2 vibron region in TBABh + H_2 hydrate at 76 K (top) and the THF + H_2 hydrate at 76 K (bottom). (b) Raman spectra of the B−H stretching region for the TBABh hydrate (primarily tetragonal phase) at 270 K (peak at 2289 cm^{-1}), the TBABh solution at 284 K (peak at 2284 cm^{-1}), and the TBABh powder at 295 K (peak at 2246 cm^{-1}).

1.0 g of TBABh hydrate (Figure 3a); that is, 0.50 wt % of H_2 was physically stored in the TBABh hydrate.[40] The volumetric measurement was repeated in presence of HCl as a catalyst for the hydrolysis.[41] In this case, the total amount of stored and produced H_2 was 197 ± 4 mL/1.0 g of TBABh hydrate (Figure 3b), implying that 124 mL of H_2/g of TBABh was produced via the hydrolysis reaction between BH_4^- and dissolved host water molecules.[42] The hydrolysis reaction conversion of the BH_4^- host to H_2 was 99.4% for a total of 1.35 wt % of H_2 stored in the TBABh hydrate. Although this amount of hydrogen is lower than 2.9 wt % obtained from the hydrolysis of $NaBH_4$ alone, the hybrid storage material concept may open possibilities for improvement through structural modifications that would allow for a greater number of chemical energy carrier molecular storage sites.

In clathrate hydrates, increased stability usually comes at the expense of hydrogen storage capacity.[4,10−12] For example, the THF + H_2 hydrate, a commonly used binary H_2 hydrate, has moderate formation conditions, but the hydrogen capacity is sacrificed compared with pure hydrogen hydrate.[4,5,11] TBA^+ hydrates, such as TBAB and TBAF, show higher thermodynamic stability than THF hydrate;[20,36,43,44] however, the ideal hydrogen capacity of TBAB is only 0.60 wt %, much less than 1.0 wt % for THF hydrate, when the small cage is fully occupied by H_2 in both hydrates.[11,19]

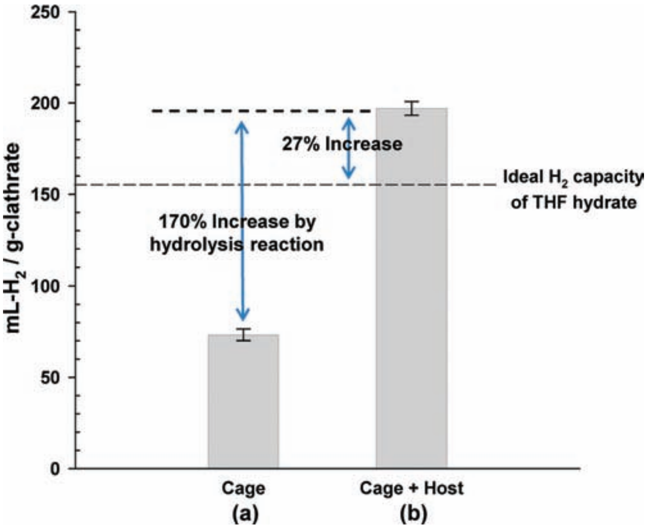

Figure 3. Volumes of H_2 (a) stored in the small cavity of TBABh hydrate and (b) stored in the small cavity and produced via a hydrolysis reaction between water and BH_4^- after hydrate dissociation (0.82 atm, 293.15 K). The gas evolution test was performed three times for each sample.

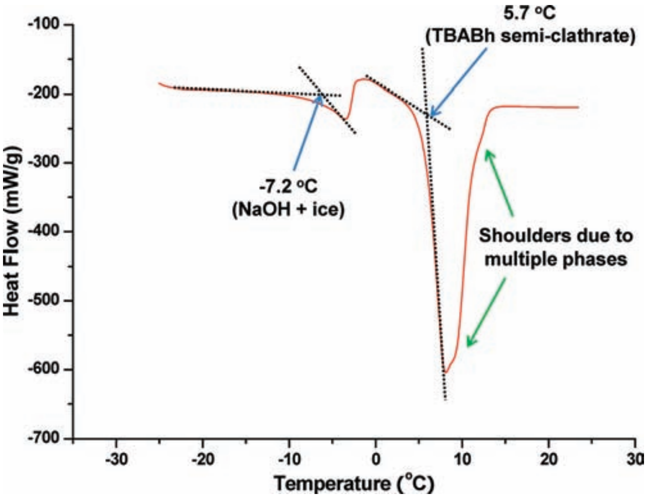

Figure 4. DSC thermogram for the dissociation of 2.54 mol % of TBABh sample.

The stability of TBABh semiclathrate hydrate was verified by DSC. As shown in Figure 4, two peaks appeared during the heating procedure. The first peak (−7.2 °C) is considered to be from the NaOH solution, which was added to prevent premature reaction. From integrating the DSC peaks, it was determined that roughly 12.7 mol % water existed as an ice impurity with NaOH.[45] The second peak (5.7 °C) is attributed to the dissociation endotherm of the TBABh semiclathrate phase. Shoulders on this peak imply that more than one phase exist in this sample. The dissociation point is higher than that of the pure THF hydrate (4.4 °C).[44] Considering the stability of other TBA^+ salt + H_2 semiclathrates, such as TBAB and TBAF,[20,36,43,44] the TBABh + H_2 hydrate would be more stable than THF + H_2 hydrate. With a total hydrogen capacity 27% higher than the fully occupied THF + H_2 hydrate (Figure 3), the thermal stability of TBABh hydrate may help to resolve the incompatibility problem between capacity and stability of hydrogen clathrate materials.

In this study, we suggest a hybrid hydrogen storage material demonstrating the incorporation of hydrolyzable BH_4^- into the clathrate hydrate. There are potentially many other storage schemes in which the chemical energy and physical storage are combined to produce additional hydrogen; thus, further investigations of such hybrid materials should be considered to improve the total hydrogen capacity. The present finding on the TBABh semiclathrate is expected not only to provide a scientific understanding regarding the nature of tetraalkylammonium hydrate but also to present a new approach to hydrogen storage.

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Supporting Information Available: Experimental methods, gas chromatography, and IR spectroscopic data confirming hydrolysis reaction of the BH_4^-. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) The PXRD patterns were indexed using the Check Cell program (a) LMGP-Suite Suite of Programs for the interpretation of X-ray Experiments, by Jean laugier and Bernard Bochu, ENSP/Laboratoire des Matériaux et du Génie Physique, BP 46. 38042 Saint Martin d'Hères, France. www: http://www.inpg.fr/LMGP and http://www.ccp14.ac.uk/tutorial/lmgp/, and by using the Le Bail intensity extraction method within GSAS. . (b) Larson, A. C.; Von Dreele, R. B. *Los Alamos National Laboratory Report LAUR* **1994**, *8*, 6−748, using EXPGUI. (c) Toby, B. H. *J. Appl. Crystallogr.* **2001**, *34*, 210−213. It was impossible to distinguish between the propsed tetragonal space groups *P*4/*m* (ref 33) and *P*4 (ref 26).

(38) For the TBABh sample, 0.3 wt % NaOH solution was used to prevent a premature hydrolysis reaction. The 0.3 wt % is the minimum concentration of NaOH that the gas bubbles were not observed during TBABh dissolution. From DSC result, the added NaOH is considered to exist as an impurity with some water molecules (Figure 4).

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(40) This capacity indicates 2.4 H_2 per one TBA^+. The ideal capacities for tetragonal and orthorhombic structure are 2.0 H_2 and 3.0 H_2 per one TBA^+, respectively. The experimental capacity result implies the coexistence of two phases (refs 19 and 34).

(41) Because one drop of HCl solution can completely hydrolyze 1 g of TBABh solution, the hydrogen capacity reduction caused by adding HCl is quite small.

(42) The production of H_2, the consumption of BH_4^-, and the appearance of BO_2^- after hydrolysis were confirmed by gas chromatography and IR spectroscopy. See the Supporting Information.

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