Hydrogen Storage

Clathrate Hydrogen Hydrate—A Promising Material for Hydrogen Storage

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Hydrogen is viewed as a promising clean fuel of the future. A low-cost hydrogen storage technology that provides a high storage capacity and fast kinetics is a critical factor in the development of a hydrogen economy for transportation. The technologies to store hydrogen can be classified into three types: compression, liquefaction, and storage in a solid material.[1,2] Compressing hydrogen requires a very high pressure to obtain enough hydrogen fuel for a reasonable driving cycle of 400–500 km, which in turn leads to safety issues related to tank rupture in case of accidents.[2] The large amount of energy consumed during liquefaction and the continuous boil-off of hydrogen limit the possible use of liquid-hydrogen storage technology.[1] Therefore, attention is currently focused on solid storage materials.

In general, the storage of hydrogen in solid materials is achieved by one of two processes: chemical reactions, in which the hydrogen reacts with the solid material to form new compounds, and adsorption, in which the hydrogen is adsorbed on the solid material. Materials for the storage of hydrogen through chemical reactions include metals,[3] complex hydrides,[4] and nitrides.[5] Materials with relatively high hydrogen storage capacities usually have a hydrogen-releasing temperature of over 100°C (some even higher than 200°C) as a consequence of the high energy needed to break chemical bonds. On the other hand, the release temperature of hydrogen is usually low if hydrogen is stored in a solid material by adsorption,[6,7] however, such materials have lower storage capacities.

A new type of hydrates, namely the clathrate hydrogen hydrates, were recently reported,[8–12] opening a new direction for hydrogen storage. Storage of H$_2$ in this type of material is carried out by capturing the hydrogen in H$_2$O cages rather than through chemical reaction or adsorption.

Hydrogen-bonded H$_2$O frameworks can generate polyhedron cages around guest molecules to form solid clathrate hydrates.[13–15] There are three common types of gas hydrate structures: 1) the sI hydrate, which consists of 46 water molecules that form two pentagonal dodecahedron (512) and six tetrakaidecahedron (51266) cages in a unit cell; 2) the sII hydrate, which consists of 136 water molecules that form sixteen 512 and eight 51266 cages in a unit cell; and 3) the sH hydrate, which consists of 36 water molecules that form three 512, two 4568, and one 51266 cages in a unit cell. The type of crystalline structure that forms depends on the size of the guest molecule; for example, CH$_4$ and C$_2$H$_6$ generate the sI hydrate, C$_3$H$_8$ gives rise to the sII hydrate, and the larger guest molecules, such as cyclopentane in the presence of methane, result in the sH hydrate.[15]

In contrast to other gases, the hydrogen molecule with its diameter of 2.72 Å was initially thought to be too small to support a clathrate structure. However, this point of view was challenged by recent experimental results.[8–12] Mao et al. reported that mixtures of H$_2$ and H$_2$O can crystallize into an sII clathrate with a molar ratio of H$_2$ to H$_2$O of approximately 1:2.[9] When a mixture of H$_2$ and H$_2$O was compressed at a pressure of 180–220 MPa and cooled to 249 K, a single solid compound was formed. Furthermore, energy-dispersive X-ray diffraction (EDXD) measurements indicated that the solid compound has a face-centered cubic unit cell with $a = 17.047 ± 0.010$ Å, in excellent agreement with the archetypal sII clathrate.[16]

As the H$_2$/H$_2$O ratio in the hydrate is 0.45 ± 0.05, the 24 cages must be multiply occupied by H$_2$ clusters to accommodate 61 ± 7 molecules of H$_2$. By comparing the size of the H$_2$ clusters and the volume of the cage cavities, Mao et al. proposed that two molecules of H$_2$ were located in each of the 512 cages and four molecules of H$_2$ were located in each of the 51266 cages (Figure 1A).[9] This means that the hydrogen hydrate can reversibly store about 5.3 wt% hydrogen (excluding the hydrogen atoms of H$_2$O).[9]

Raman spectroscopy showed that the roton peaks for hydrogen in the clathrate were similar in frequency to those of pure hydrogen, indicating that the hydrogen molecules in the clathrate cages were still in free rotational states.[9] This indicates that the hydrogen molecules in the clathrate remain unbound to each other or to water. However, a substantial softening and splitting of the vibron peaks of hydrogen indicate some intermolecular interactions.

The stability of type sII hydrogen clathrate was investigated using a statistical mechanical model in conjunction with statistical mechanical model in conjunction with...
with first-principle quantum chemistry calculations. It was found that the stability of the hydrogen clathrate is mainly due to the dispersive interactions between the molecules of H₂ and the water molecules that form the cage walls. Furthermore, the theoretical analysis showed that the hydrogen molecules undergo essentially free rotations inside the clathrate cages consistent with the experimental results provided by Raman spectroscopy.

A limitation of this example is that the hydrogen clusters can be stabilized in a clathrate hydrate only at extremely high pressures (typically 220 MPa at 249 K). To store H₂ at lower pressures, Sloan and co-workers introduced a second guest component into the hydrogen hydrate. They found that by introducing tetrahydrofuran (THF) into the larger cavities, the clathrate could be stabilized at pressures of 5 MPa at 279.6 K as compared to 300 MPa at 280 K for pure H₂ hydrate. This observation is a very meaningful result and challenges the current theory, which suggests that hydrogen is excluded from the clathrate framework in the presence of a second guest component.

X-ray powder diffraction (XRPD) data showed that the H₂/THF hydrate has the crystalline structure of the sII hydrate; that is, it has the same structure as reported for the pure H₂ hydrate by Mao et al. Furthermore, on the basis of Raman spectroscopy measurements Sloan and co-workers suggested that all or most of the large cages of the binary clathrate hydrate are filled with THF. In contrast, the H₂ molecules most likely occupy to a significant extent only the small cages. Although the inclusion of THF molecules, which almost completely fill the larger cavities, decreases considerably the synthesis pressure, their presence also leads to a significant decrease in the capacity of hydrogen storage.

In another study, Lee et al. found by tuning the H₂/THF composition that the hydrogen guest can enter both in the larger and the smaller cages, thus increasing the hydrogen storage capacity to approximately 4 wt% at modest pressures. Lee et al. carried out a number of experiments at a H₂ pressure of 12 MPa and temperature of 277.3 K. When the THF concentration was in the range of 2.0 to 5.56 mol%, H₂ and THF molecules occupied the smaller and larger cages, respectively, leading to a storage capacity of 2.09 wt% H₂. However, a further decrease in the concentration of THF was found to enhance the H₂ capacity, such that a maximum storage capacity of about 4 wt% H₂ was finally reached at a concentration of 0.15 mol% THF. In this case, H₂ occupied not only all the small cages but also some of the larger ones (Figure 1C).

Other additives, such as 1,3-dioxolane, 2,5-dihydrofuran, and tetrahydropyran, can have similar effects on the formation of hydrogen hydrate as THF, but none of these performs as well as THF.

In summary, the successful synthesis of hydrogen hydrates is a breakthrough in the development of materials for hydrogen storage. While very different from conventional hydrogen storage materials, the hydrogen hydrates, which are neither flammable nor corrosive, provide a safe and environmentally friendly material to store hydrogen. However, it still remains a challenge to employ hydrogen hydrates as practical materials for hydrogen storage. The synthesis of hydrogen hydrates mentioned above is a relatively slow process because their formation is controlled by diffusion through a bulk solid phase. The slow kinetics may create difficulties to recharge hydrogen onboard for fuel cell vehicles. However, an extremely fast method of clathrate synthesis was recently reported that allows the formation of hydrogen hydrate to be completed in minutes. Permanent cooling, which is necessary to keep hydrogen hydrates stable, may be another issue. When the cooling fails, the material will release large amounts of hydrogen in a rather short time, which may lead to safety problems. Another challenge is to increase the hydrogen capacity of the hydrogen hydrates. The maximum hydrogen capacity is 5.3 wt% for the sII structure of the hydrogen hydrate at a high synthesis pressure and 4 wt% at a modest pressure. Thus, to achieve higher capacities, new structures of hydrogen hydrates are required.

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