CLATHRATES OF HYDROGEN WITH APPLICATION TOWARDS HYDROGEN STORAGE

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ABSTRACT

In the current work we present a significant advancement in the area of hydrogen storage in clathrates: hydrogen storage from both enclathrated molecular hydrogen as well as storage from the clathrate host lattice. We have investigated the hydrogen storage potential in all of the common clathrate hydrate structures with techniques such as gas evolution, X-ray / neutron diffraction, and NMR / Raman spectroscopy. We have determined that the common clathrate structures may not suffice as H_2 storage materials, although these findings will aid in the design and production of enhanced hydrogen storage materials and in the understanding of structure-stability relations of guest-host systems. In view of current storage limitations, we propose a novel chemical – clathrate hybrid hydrogen storage concept that holds great promise for future materials.

Keywords: hydrogen storage, hydrogen clathrate hydrate, hydroquinone

INTRODUCTION

Clathrate hydrates are inclusion compounds formed from water and small molecules. Clathrate hydrates crystallize into three common structures: structure I (sI), structure II (sII), and structure H (sH). All structures are composed of polyhedral water cavities; however, the size, shape and distribution of these cavities vary between structures. The type of cavities comprising each structure is denoted by A^xB^y, where x and y represent the number of A and B sided faces per cavity. The type of structure that forms largely depends on the size of the guest molecule [1].

Small molecules such as argon form sII hydrates $[8(5^{12}6^4)\cdot16(5^{12})\cdot136H_2O]$, whereas larger molecules like methane form sI $[6(5^{12}6^2)\cdot2(5^{12})\cdot46H_2O]$. Even larger molecules like tetrahydrofuran (THF) form sII. The largest hydrate guests (~7-9 Å) form sH hydrate $[1(5^{12}5^8)\cdot2(4^35^66^3)\cdot3(5^{12})\cdot34H_2O]$ with the help of a smaller molecule like methane.

Storing hydrogen with an energy density comparable to current fossil fuel based media has proved to be a great challenge and it is generally accepted that novel approaches must be taken to develop materials that can meet hydrogen storage

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standards. Due to the inherent ability of clathrate hydrates to concentrate gas molecules, these materials have been proposed as an alternative storage material.

REVIEW OF HYDROGEN HYDRATES

Historically the hydrogen molecule was considered to be too small to contribute to the stability of clathrate hydrates [2]. In 1999 Dyadin *et al*. [3] formed the first pure hydrogen hydrate and presented a phase diagram. In 2002 Mao *et al*. [4] performed high pressure diamond anvil cell studies on the hydrogen + water system. The simple H_2 clathrate hydrate structure was confirmed to be sII with a lattice parameter of 17.047 Å. Additionally, Raman spectroscopic measurements confirmed the presence of H_2 in the hydrate phase.

In 2004, Lokshin *et al*. [5] performed neutron diffraction studies on simple D_2 hydrate. They determined that one hydrogen molecule occupied the small cavities of the sII hydrate. The large cavity occupancy was found to vary between two and four molecules depending on pressure and temperature conditions. Additionally, Lokshin *et al*. [5] determined a tetrahedral arrangement of hydrogen quadruply occupied in the large cavities, with a D_2-D_2 distance of 2.93 Å. This distance suggests unique intermolecular forces, as the distance between molecules in solid hydrogen is 3.78 Å at atmospheric pressure and 4.2 K [6]. This fascinating feature suggests potential for clathrates as hydrogen storage materials, as the local density of H_2 molecules can be unusually high.

Simple hydrogen hydrate has several advantages as a material for H_2 storage. Firstly, the storage material is pure water. When the hydrogen is released and the structure decomposes, the only byproduct is pure water. Secondly, the formation and decomposition kinetics can be very fast. Hydrogen hydrate has been shown to form from powdered ice on the order of minutes, and from one gram of solid ice on the order of hours [7]. Additionally, the hydrogen is stored in molecular form. This means that, no chemical reactions are required for the hydrogen release. Finally, water is abundant and cheap. However, the clear disadvantage to using hydrogen hydrate as a storage material is the high pressure (or low

temperature) required for formation (~200 MPa at 273 K) [3].

In 2004 Florusse *et al*. [8] established that by forming a binary hydrate with hydrogen and THF, the formation pressure is reduced by almost two orders of magnitude. Although Udachin *et al*. [9] previously synthesized this binary hydrate, pressures of 350 MPa and greater were used. Florusse *et al*. [8] demonstrated the stability of the binary H_2/THF at more favorable conditions of temperature and pressure (~5 MPa at 280 K). Reducing the formation pressure conditions of hydrogen hydrate is a critical initial step towards realization of a practical storage material.

In 2005, Lee *et al*. [10] used Raman measurements to show that the stoichiometric THF/H_2 hydrate (formed from 5.6 mol% THF solution) contained two hydrogen molecules per small cavity. Lee et al. [10] also introduced the concept of "tuning," where the THF concentration was decreased to create vacant large cavities in which hydrogen could reside. Following this approach, Lee *et al*. [10] claimed to form a binary hydrate formed from a 0.15 mol% THF solution and the hydrate was reported to contain about 4.0 wt% hydrogen at only 12.0 MPa and 270 K.
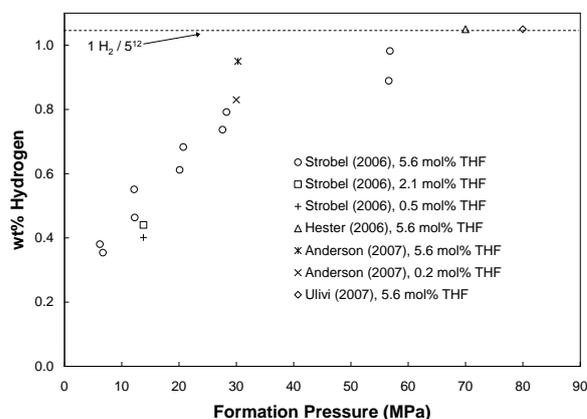
Figure 1. Hydrogen content in THF+H_2 hydrate as a function of pressure for several studies using different techniques and different THF concentrations.

In contrast to the double-occupation suggestion by Lee at al., several recent studies have suggested that the maximum hydrogen occupancy in the small cavity of the THF+H_2 hydrate is only one hydrogen molecule, and that hydrogen storage is independent of THF composition over the same range of formation conditions [11-14]. Figure 1

shows the hydrogen content of THF+H_2 hydrate as a function of pressure for several different studies and various THF concentrations. Strobel et al. [11] formed THF+H_2 hydrate from crushed THF particles. Hester et al. [12] used high resolution neutron diffraction experiments to determine the H_2 occupancy of stoichiometric THF+H_2 hydrate formed at 70 MPa. Anderson et al. [13] formed THF+H_2 hydrate from a liquid phase aqueous mixture and degassed the formed hydrate to determine the hydrogen content. After forming THF+H_2 hydrate at 80 MPa for inelastic neutron measurements, Ulivi et al. [15] used thermodynamic gas release measurements to determine the H_2 content. As demonstrated in Figure 1, all of these studies showed that the maximum hydrogen content of THF+H_2 hydrate is about 1 wt%, consistent with single occupancy of the small dodecahedral cavity.

In addition to THF+H_2 hydrate, various other binary sII hydrates have been formed with hydrogen and a second larger guest. Rovetto et al. [16] have synthesized these hydrates with various furan type molecules. Additionally, molecules like propane have also been used [17]. One particularly interesting binary sII hydrate formed with hydrogen used cyclohexanone (CHONE) as a second large guest [18].
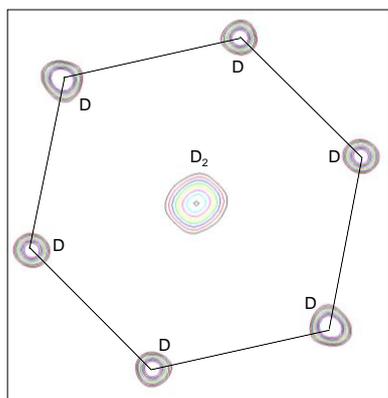
Figure 2. Fourier observed nuclear density map centered in small cavity for sII CHONE+H_2 hydrate.

Unlike THF, propane, or other various furan type sII forming molecules, CHONE is incapable of stabilizing a sII hydrate on its own. Due to the large size of CHONE, a second "help-gas" molecule is required for stability [19]. This second molecule is thought to add stabilization through interactions with the small cavity to help off-set unfavorable distortions to the large cavity caused

by the presence of the large molecule [20]. Figure 2 shows the observed Fourier nuclear density profile for the small cage of the CHONE+D_2 hydrate. The formation of CHONE+D_2 hydrate suggests that the stabilizing interactions of hydrogen are analogous to more common hydrate forms like methane. This has many implications to the formation of other types of clathrate structures with hydrogen.

Another interesting feature of the CHONE+D_2 hydrate is the small cavity occupancy. Table 1 shows the small cage D_2 occupancy for TDF+D_2 [12] hydrate and CHONE+D_2 [11] hydrate both formed and measured at the same conditions.

Table 1. Occupancy and lattice parameters for TDF+D_2 and CHONE+D_2 hydrates formed at 70 MPa and 265 K, measured at atmospheric pressure and 20 K

Hydrate	lattice parameter a (Å)	D_2 occupancy in 5^{12} cage
sII TDF+D_2	17.06	1.005(16)
sII CHONE+D_2	17.28	0.828(24)

Although both hydrates were formed and measured under the same experimental conditions, the occupancy of the TDF+D_2 hydrate is about 20% greater than that of the CHONE+D_2 hydrate. This suggests that there may be an ideal cavity size for hydrogen in order to maximize hydrogen content while minimizing the required formation pressure. By calculating the small cavity volumes though geometrical considerations [21], the 1.3% larger CHONE+D_2 lattice corresponds to a 4.8% increase in available small cavity volume. Assuming a spherical small cavity, the CHONE+D_2 small cavities are calculated to be 1.6% larger in radius. This shows that small perturbations in cavity size can have a large impact on cavity filling. This concept has also been applied towards carbon based hydrogen storage materials where the carbon interlayer distance for ideal hydrogen interactions has been calculated to be about 6 Å [22]. Tailoring hydrate cavities to the ideal size for increased hydrogen interactions may provide a valuable path for clathrate based hydrogen storage materials closer to ambient conditions.

In addition to the CHONE+D_2 hydrate, recent work has demonstrated that hydrogen can stabilize another hydrate structure where a second guest is

required for stability: sH [23, 24]. Figure 3 shows a powder X-ray diffraction pattern for sH methylcyclohexane (MCH)+H_2 hydrate formed at 150 MPa and 250 K. sH hydrate offers a potential increase in storage of 40% by weight when compared with binary sII hydrates.
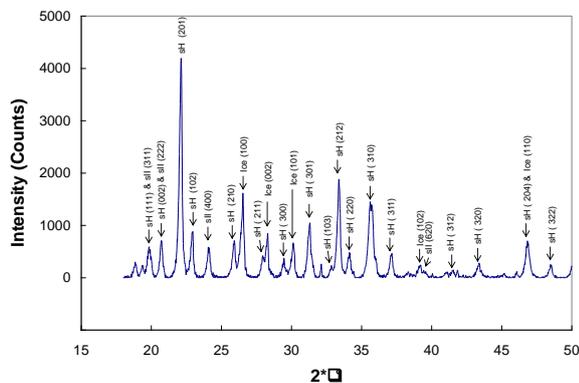
Figure 3. PXRD pattern for MCH+H_2 hydrate a=12.18(1) c=9.94(3).

The formation of sH hydrate with hydrogen demonstrates that hydrogen can be stored within all three of the common clathrate hydrate structures. Additionally, experimental evidence for hydrogen contained within the small cavities of a semi-clathrate with TBAB has been reported [25, 26]. Depending on the formation conditions and available components, hydrogen may multiply occupy large sII cavities, or singly occupy the small cavities of other structures, providing several different hydrogen storage materials.

Table 2. Hydrogen content in common structures.

Structure	Max. H_2 Storage	Required Pressure
Single sII[a]	3.8 wt%	~200 MPa
Binary sH[b]	1.4 wt%	~100 MPa
Binary sII[b]	1.0 wt%	~50 MPa[c]
Binary sI[b]	0.4 wt%	~50 MPa[c]

a – 1 H_2 / 5^{12}, 4 H_2 / $5^{12}6^4$
b – large guest resides in large cavity, one H_2 in small cavities
c – higher pressure than incipient formation required for adequate hydrogen filling

Table 2 summarizes the hydrogen content in all three common structures as well as the required pressure to obtain these hydrogen contents. It is apparent that a balance exists between the hydrogen content and formation pressure.

Over the past six years the paradigm has shifted as to the role that hydrogen plays in clathrate science and technology. Going from a molecule that was thought not to enter the clathrate phase to a molecule that is capable of stabilizing all three common structures as well as semi-clathrates certainly redefines the perception of the interactions between small molecules like hydrogen and clathrate cavities. Although the hydrogen storage values listed in table 2 appear too low, and the pressure conditions are too high to be considered as functional hydrogen storage materials, the diversity of clathrate structures formed with hydrogen suggests potential for other inclusion compound structures. In order for clathrates to be considered for hydrogen storage, compounds with increased hydrogen content and improved formation and operating conditions must be developed.

NOVEL CLATHRATE MATERIALS
For any hydrogen storage material, the determining factor in the amount of hydrogen stored will be the ratio of hydrogen to storage substance. In many current technologies this storage substance is comprised of metal atoms, carbon lattices and other types of molecules. For clathrate phases, molecular hydrogen is trapped within cavities formed from a host lattice. This host lattice has not yet been thought capable of contributing to the energy content of the storage material. The concept of chemical – clathrate hybrid technology is to combine molecular hydrogen contained within the clathrate phase with the hydrogen that is chemically bound to the host lattice. A schematic illustration of this process is given in Figure 4.
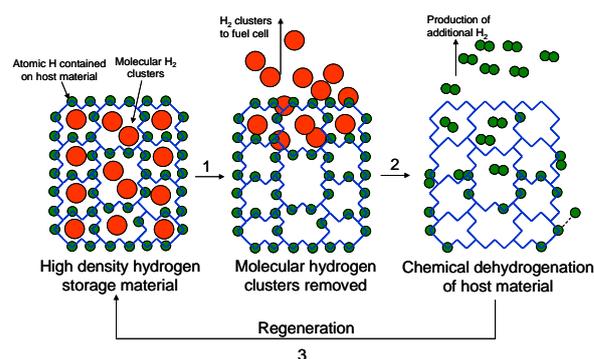
Figure 4. Representation of chemical – clathrate hybrid storage.

Proof-of-principle of this concept has been demonstrated using hydroquinone (HQ) clathrate. HQ is a known clathrate former with guest molecules such as methane or xenon [27, 28]. The clathrate phase (β phase) of HQ has cavities

composed of six hydroquinone molecules terminated at the top and bottom by rings of six hydroxyl groups (Figure 5). These cavities have a radius of about 4.5 Å.
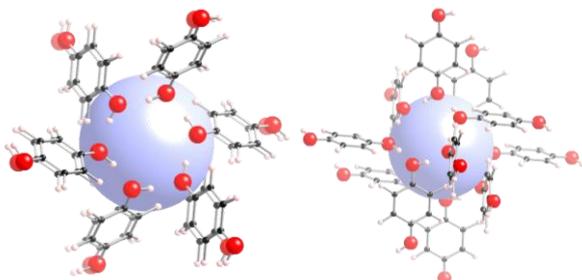
Figure 5. Hydroquinone clathrate. Clathrate cavity represented by sphere r = 4.5 Å.

For the first time we have successfully synthesized HQ+H_2 clathrate by recrystallization from a saturated ethanol solution in the presence of hydrogen. Figure 6 shows a powder X-ray diffraction (PXRD) pattern of the novel HQ+H_2 clathrate.
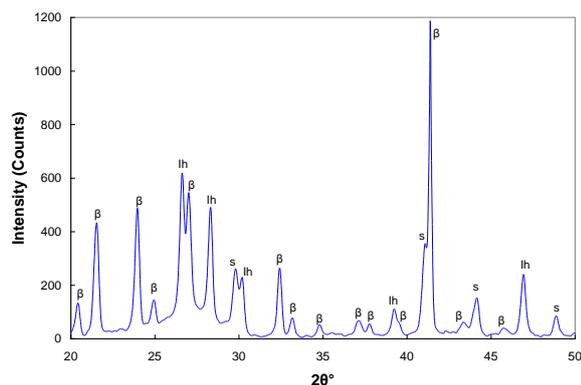
Figure 6. XRD pattern (90 K, 0.1 MPa) confirming the formation of clathrate phase β with H_2.

In addition to the structural information from the PXRD data, Raman spectroscopic data confirms the presence of H_2 contained within β-HQ clathrate lattice. Figure 7 shows Raman spectra for both pure H_2 fluid (100 K) and the β-HQ+H_2 clathrate (77 K). At these cold temperatures hydrogen exhibits two Raman peaks in the region for H_2 vibration. These two bands are a result of the two lowest rotational energy states (J=0 and J=1) being populated, and are labeled $Q\Delta v(J)$ where v and J are the vibrational and rotational quantum numbers respectively.

The frequencies of both the $Q_1(0)$ and $Q_1(1)$ bands are significantly red-shifted, about 50cm^{-1}, from

that of the free fluid phase. This decrease in H_2 stretching frequency is induced by interactions with the clathrate cavity lattice, and is consistent with the enclathration of hydrogen molecules.
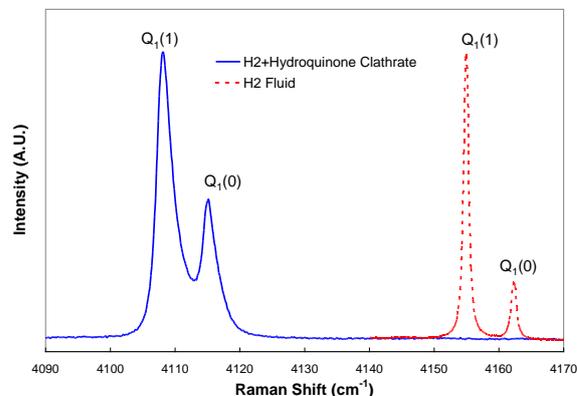
Figure 7. Raman spectra for gaseous H_2 (red dashed) and HQ+H_2 clathrate (blue solid).

Preliminary tests demonstrated enhanced stability of the β-HQ+H_2 clathrate when compared with the H_2O+H_2 clathrate hydrate. After ten minutes of exposure to ambient conditions, the β-HQ+H_2 clathrate maintained significant H_2 Raman peak intensity. In the case of H_2O+H_2 clathrate hydrate, exposure to ambient conditions resulted in the immediate dissociation of the clathrate and release of all contained hydrogen. Although preliminary results suggest superior stability for the β-HQ+H_2 clathrate, the detailed phase behavior has yet to be measured.

The large cages of sII clathrate hydrate have a radius of about 4.7 Å and have been experimentally shown to contain up to four hydrogen molecules. Given that the cavities of β-HQ have a radius of 4.5 Å, the possibility of the enclathration of four hydrogen molecules seems very reasonable. With four H_2 molecules per cavity this novel clathrate would contain about 2.4 wt% hydrogen, counting only molecules contained within the cavities (excluding atomic hydrogen in the host framework).

For the next step of the chemical-clathrate hybrid process, the host material must be chemically dehydrogenated. For our proof-of-principle hydroquinone system, we have targeted the hydroxyl hydrogens as they may be removed in solution by a mild oxidation reaction to form benzoquinone and aqueous protons. These aqueous protons may then be reduced to form

gaseous hydrogen. This simple redox reaction scheme is shown in equations 1 and 2.

$$+ \; 2Ag^+ \longrightarrow \quad + \; 2H^+ \; + \; 2Ag \quad (1)$$

$$2H^+ \; + \; Zn \longrightarrow H_2 \; + \; Zn^{2+} \quad (2)$$
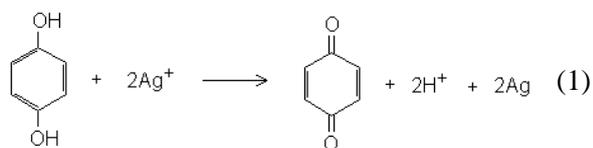
In the first reaction step (Eq. 1), hydroquinone is oxidized by silver ions to produce benzoquinone and hydrogen ions. In the second reaction step (Eq. 2) the hydrogen ions are reduced by zinc to evolve hydrogen gas.

We have successfully demonstrated the feasibility of dehydrogenation of the hydroquinone molecule by the above reaction scheme (Eq. 1-2). Figure 8 (left) shows large hydrogen bubbles produced from a 1M hydroquinone solution in a test tube. Figure 8 (right) depicts a gas chromatogram of the gas in the head-space of the test tube. The head space was not purged so a large fraction of air remains present. However, H_2 gas was undoubtedly produced.
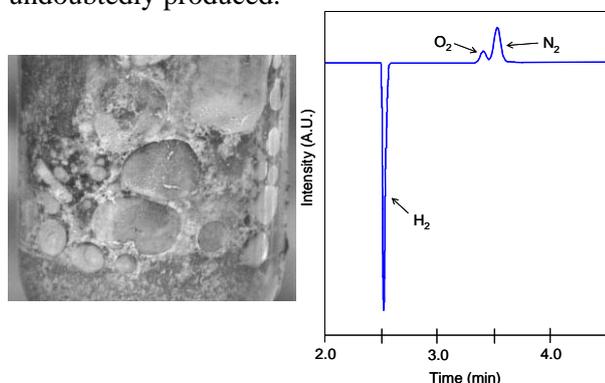
Figure 8. Large hydrogen bubbles produced from hydroquinone solution (left). Gas chromatogram showing hydrogen productions (right).

The proof-of-principle H_2-hydroquinone chemical-clathrate hybrid system is not yet optimized for ideal hydrogen storage. Nevertheless, this is the first direct evidence that molecular and chemical hydrogen storage can be used concurrently to raise the capacity of a hydrogen storage material. Table 3 shows the hydrogen storage values for this clathrate at a given cavity occupancy, as well as the storage values combined with the chemical hydrogen storage.

Table 3. Storage capacity of HQ+H_2 clathrate and hybrid process

H_2 per cage	clathrate H_2 wt%	hybrid H_2 wt%	% increase
1	0.61	2.43	298.4
2	1.21	3.01	148.8
3	1.80	3.60	100.0
4	2.38	4.17	75.2
5	2.96	4.74	60.1

If each of the clathrate cavities in the structure were to contain four hydrogen molecules, and the redox scheme were to react to completion, the hydrogen storage capacity of this material would be about 4.2 wt%. Compared with the maximum storage of 3.8wt % for clathrate hydrates (pure sII), this storage scheme appears promising, and many other chemical components may prove favorable when compared with hydroquinone.

CONCLUSIONS
In the current work we present a significant advancement in the area of hydrogen storage in clathrates: hydrogen storage from both enclathrated molecular hydrogen as well as storage from the clathrate host lattice. We have investigated the hydrogen storage potential in all of the common clathrate hydrate structures with techniques such as gas evolution, X-ray / neutron diffraction, and NMR / Raman spectroscopy. Although the small dodecahedral cavity may only contain one hydrogen molecule, the degree of filling is highly dependent on the cage radius. An ideal radius may exist where lower pressures are required for complete occupancy. We have determined that the common clathrate structures may not suffice as H_2 storage materials, although these findings will aid in the design and production of enhanced hydrogen storage materials and in the understanding of structure-stability relations of guest-host systems. The proposed novel chemical – clathrate hybrid hydrogen storage concept holds great promise for future materials.

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