Evaluation of Hydrogen Storage in Clathrate Hydrates: Review of Recent Advances

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ABSTRACT

Clathrate hydrates have significant advantages as gas-storing materials, which render them as possible candidates for storing hydrogen. In this study we perform a review of published experimental and computational work that examined hydrogen storage in clathrate hydrates. While significant progress has been made, additional work is required to improve the hydrogen uptake of hydrates, in order to meet the required gas-storage capacity for mobile applications.

Keywords: hydrogen storage, clathrate hydrates, simulation, experiments

1 INTRODUCTION

The adoption of “Hydrogen Route” is considered as a promising alternative to meet our long-term energy needs. In this approach energy is stored/transferred and used in the form of hydrogen. Hydrogen is a versatile molecule and can be a fuel for direct combustion, a means of producing electricity in fuel cells for stationary use and transport, and a medium for the temporary storing of energy. However, significant scientific, technological and socio-economic barriers need to be surpassed before the transition from the “carbon-based” to the “hydrogen-based” economy is successfully completed. Moving towards the so-called “Hydrogen Economy” requires the secure supply of large amounts of hydrogen. Significant progress has been achieved towards hydrogen-production issues. However, a major research issue that has not yet been solved, in a satisfactory manner, is the temporary storage (and recovery) of hydrogen.

As a result of their capacity to store large volumes of gas, hydrates have been considered as an alternative material for storing and transporting hydrogen [1]. Gas hydrates are a class of crystalline, non-stoichiometric, inclusion compounds. They are composed of a framework of hydrogen bonded water molecules that forms cavities/ cages where small gas molecules can be enclosed (“enclathrated”). The empty cages are unstable and the guest molecules provide stability to the cages [2].

Depending on their crystal structure and the type and number of cavities present in the hydrate unit cell, different hydrate structures are known to exist in nature. The most common structures (depicted in Figure 1) are sI, sII and sH [3].

Clathrate hydrates can be considered a special kind of nanoporous materials (with pores of diameter 0.7-1.2 nm) that mainly consist of water. The major advantages of hydrates as hydrogen-storage materials, comparatively to other materials investigated for the same purpose, include complete reversibility, improved kinetics and life cycle, low cost, almost not any environmental hazards, and operational safety (in terms of toxicity and flammability).

The current study is a review. The main objective of this work is to evaluate the hydrogen storage capacity of hydrates based on the progress achieved in the recent years. All available experimental and simulations studies are reviewed in order to delineate the possible range of applications for which storing hydrogen in hydrates would be suitable. A detailed discussion is presented regarding the possible use of sII, sH, and sI hydrates for hydrogen storage. The issue of “hydrate tuning” is also revisited in light of the recent experimental findings.

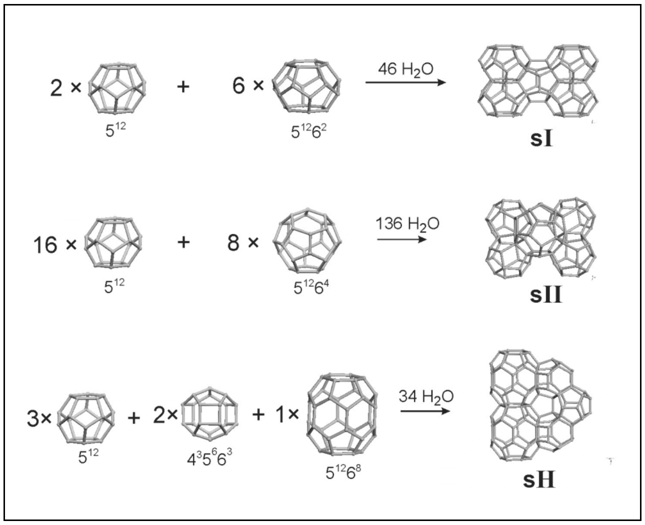

Figure 1: Schematic and notation of the empty water cavities and the most common resulting hydrate structures.

2 LITERATURE REVIEW

2.1 Structure II (sII) Hydrates

Until recently, the hydrogen molecule was considered too small to stabilize the hydrate cavities and, therefore, incapable of forming hydrate by itself. This picture changed dramatically with the synthesis of pure hydrogen hydrate, initially by Dyadin et al. in 1999 [4], and subsequently by Mao et al. [5] in 2002. The synthesis of pure H_2 hydrate was considered a breakthrough in the hydrogen storage research. Hydrogen hydrate was found to be of cubic sII structure, with H_2 content up to approximately 5 wt. % (which is very close to the specifications required by the automobile industry for applications of hydrogen in transportation).

The unit cell of the sII hydrate (cubic *Fd3m* space group) consists of 136 water molecules that form two types of cavities: the small, a pentagonal dodecahedron (5^{12}), and the large that is formed by twelve pentagons and four hexagons ($5^{12}6^{4}$). There are sixteen small and eight large cavities per unit cell and it was estimated by Mao et al. [5] that more than one H_2 molecule can enter the same cavity (up to two molecules per small cavity and up to four per large). Patchkovski and Tse [6] used Density Functional Theory (DFT) in conjunction with first-principles quantum chemistry calculations and confirmed the double occupancy of the small cavities and the quadruple occupancy of the large cavities. Alavi et al. [7] used Molecular Dynamics simulations and reported single occupancy of the small cavities and quadruple occupancy of the large cavities. Lokshin et al. [8] conducted neutron diffraction studies of the deuterium (D_2) clathrate hydrate and while confirming that up to four D_2 molecules enter the large cavities, they reported single D_2 occupancy in the small cavities.

The number of hydrogen molecules inside the cavities is a crucial factor that would determine the total storage capacity of the hydrate (e.g. 5.0 wt. % H_2 with double occupancy of the small cavities, while 3.9 wt. % H_2 with single occupancy, assuming quadruply occupied large cavities). If hydrates are to be used as hydrogen-storage materials, specific storage capacity targets should be met [9]. In addition, the storing conditions should be moderate, especially in case hydrates are to be used in everyday applications (e.g. hydrogen storage for automotive applications). However, for the stability of pure H_2 hydrates, very high pressures are required (200 MPa at 280 K) [5]. On the other hand, hydrogen hydrate can be stable at ambient pressure (0.1 MPa) for temperatures lower than 140 K [1, 5]. Both these cases can be regarded as extreme for practical applications.

Florusse et al. [10] managed to produce hydrogen hydrates at low pressures (down to 5 MPa) by adding a hydrate promoter. Hydrate promoters are substances that assist in stabilizing the hydrate structure at moderate conditions, by occupying some of the available cavities, allowing H_2 molecules to enter the remaining. Obviously, the presence of the promoter reduces the storage capacity of the material. Tetrahydrofuran (THF) was found to be the most effective promoter. If all eight large cavities of the sII structure are occupied by THF and assuming that two H_2 molecules enter each small cavity, the maximum hydrogen content of the hydrate would be 2.1 wt. %. On the other hand, the maximum hydrogen content would be 1.05 wt. % with single hydrogen occupancy of the small cavities. The occupancy of the small cavities of H_2-THF hydrate remains an open issue, as there is no consensus among the experimental data [5, 8,10-13].

Furthermore, Lee at al. [11] and Kim et al. [12] suggested that by adjusting the THF concentration in the formation solution, one can "tune" how many of the large cavities would be occupied by THF, with the rest of them remaining available to H_2 molecules. They found a critical value for the THF concentration of about 0.15 mol %, which led to a binary H_2-THF hydrate having 4.1 wt. % H_2, stable at 12 MPa. Similar effect was later observed in other binary hydrates [14] and the recent work of Sugahara et al. [15]. Alavi et al. [16] used Molecular Dynamics to study binary H_2-THF hydrates with different H_2:THF ratios and reported that the substitution of H_2 molecules by THF molecules in the large cavities results in lower configurational energies and enhances the stability of the hydrate.

Other experimental studies [17-20] that attempted to confirm the feasibility of the tuning process of H_2-THF hydrate, produced results refuting the suggestions by Lee at al. [11], and Kim et al. [12]. The new experimental studies, based on various experimental techniques (gas release measurements [17, 18], NMR spectroscopy [17] and Raman spectroscopy [19, 20]), showed a fixed THF content in the hydrate, independent of its concentration in the initial solution. The reported hydrogen content values vary from 0.3 up to 1.05 wt. % (see Figure 2). These values are far from the requirements for the practical use of this material in mobile applications (hydrogen storage) [21].

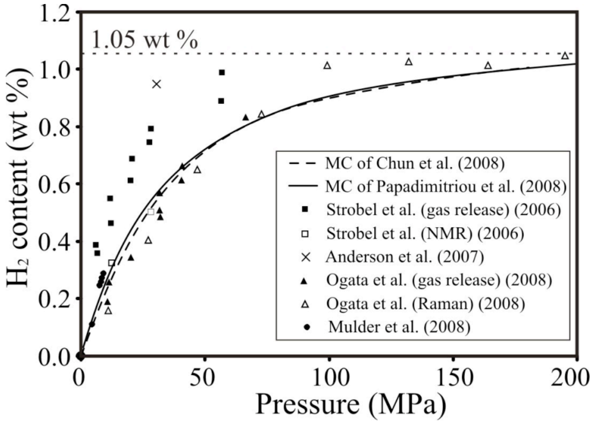

Figure 2: Hydrogen content for the sII binary H_2-THF hydrates. Comparison between experiments and Monte Carlo simulations. The dashed line (at 1.05 wt %) denotes the case when all small cavities are occupied by a single H_2 molecule.

Katsumasa et al. [22] used Grand Canonical Monte Carlo (GCMC) simulations to study pure H_2 sII hydrates and calculate hydrogen occupancies in both type of cavities of the sII hydrate, while Chun and Lee [23] used GCMC to study the binary H_2-THF hydrate. Papadimitriou et al. [24] have employed GCMC simulations to calculate the cavity occupancies for pure H_2 and binary H_2–THF sII hydrates. They reported that the storage capacity of pure H_2 hydrate could reach 3.0 wt. % only at pressures above 380 MPa (at 274 K). Also, the H_2 storage capacity of the binary H_2-THF hydrate, at temperatures close to ambient, was estimated to be lower than 1.1 wt. %. The previous three studies [22-24] are in very good agreement, and reported single occupancy of the small cavities.

2.2 Structure H (sH) Hydrates

An important advancement in H_2-hydrate science and technology is the synthesis of sH binary H_2 hydrates in early 2008, by Strobel et al. [25], and Duarte et al. [26], using several organic promoters including methyl-cyclohexane (MCH), 1,1-dimethyl-cyclohexane (DMCH), and methyl-*tert*-butyl ether (MTBE). The new binary hydrates were found to be stable in the pressure range 60–100 MPa at close-to-ambient temperatures (269 – 280 K) [25]. The sH hydrate crystal contains three small (5^{12}), two medium ($4^3 5^6 6^3$) and one large ($5^{12} 6^8$) cavity per unit cell that consists of 34 water molecules [2]. The promoter molecules occupy the large cavities and H_2 molecules can enter both the small and the medium ones. The size of the small (3.91 Å) and medium (4.06 Å) cavities of the sH hydrate is approximately the same as the size of the small cavity of the sII hydrate (3.91 Å) [2]. The small cavity of the sII hydrate has been found to accommodate one H_2 molecule at most [16, 17], although there is some evidence that double occupancy can also occur [5, 11]. If one assumes that the small and medium cavities of the sH hydrate can also be occupied by a single H_2 molecule at most, sH hydrates can reach a H_2 uptake of 1.42 wt % (when MTBE is used as the promoter). This value is by 35% higher than the corresponding value of binary sII hydrates (1.05 wt %, with THF as the promoter); however, it remains relatively low if hydrates are to be considered as hydrogen-storage materials for practical applications. The volumetric H_2 content is also increased (13.1 kg/m^3 for sH hydrate compared to 10.5 kg/m^3 for sII hydrate, i.e., an increase of 25%).

Molecular Dynamics simulations by Alavi et al. [27] have shown that energy minimization is achieved when the small and medium cavities of the binary sH hydrate are singly occupied by H_2 molecules and all the large cavities occupied by the promoter (MTBE) molecules.

Papadimitriou et al. [28] have employed GCMC simulations to study pure and binary sH hydrates. They reported a maximum 1.4 wt % hydrogen uptake for the case of the sH binary H_2- MCH (Methyl-cyclo-hexane).

2.3 Structure I (sI) Hydrates

Kim and Lee [29] examined the possibility of using the binary gas mixture H_2–CO_2 to form hydrate, instead of using liquid organic promoters. Using X–ray diffraction (XRD) data they identified the formation of hydrate of structure I (sI). Using NMR they concluded that two H_2 molecules are found in the small cavities, however, their Raman studies were inconclusive on that issue. They also suggested that a number of binary H_2 hydrates of sI, sII, and sH may possibly form with various gaseous guests. Kumar et al. [30] and Linga et al. [31] conducted experiments for the H_2–CO_2 binary hydrate and the analysis of their results indicated the incorporation of H_2 into the hydrate. The idea of hydrogen enclathtration in the small cavities of the H_2–CO_2 binary hydrate has been questioned by Sugahara et al. [32, 33] based on Raman studies of single hydrate crystals. Sugahara et al. [33] examined also two additional cases of sI binary hydrates (i.e. H_2–ethane, H_2–cyclopropane) and concluded, again, that hydrogen is not incorporated in the small cages of sI hydrates. Skiba et al. [34] studied the H_2–CH_4 binary hydrate using XRD and identified the hydrate structure to be sI. Their Raman spectra could not detect any hydrogen encaged in the hydrate at pressures up to 250 MPa. In two recent studies Kumar et al. used NMR spectroscopy [35] and attenuated total reflection IR spectroscopy [36] in order to resolve the issue of cage occupancy for the sI binary H_2–CO_2 hydrate. Both studies concluded that CO_2 only occupies the large cavities and the small cavities either are occupied by H_2 or remain nearly empty with a very small amount of CO_2 (<2 %) in the small cages. Papadimitriou et al. [37] have employed GCMC simulations to study pure and binary sI hydrates. They reported a maximum 0.37 wt % hydrogen uptake for the case of the sI binary H_2- EO (ethylene oxide).

3 CONCLUSIONS

The following conclusions can be made from the examined computational and experimental studies:

It is evident, that hydrogen could be the second guest of a binary hydrate of all the common hydrate structures (i.e. sI, sII, and sH). However, the H_2 content of these hydrates, which is the decisive factor for their suitability as hydrogen-storage materials, still remains under discussion. Additionally, the case of semi-clathrates needs to be further examined.

Pure hydrogen hydrates require, either significantly high pressures, or very low temperatures in order to be stable, which are not very practical for every-day applications. In order to overcome the problem a hydrate promoter is required (i.e. a substance that occupies some of the hydrate cavities, thus offering stability to the hydrate at moderate pressure conditions, when compared to the pure gas hydrate). The use of a promoter, results in reducing the hydrate storage capacity. Improvements can be achieved with the method of hydrate "tuning", without, however consensus on the issue in the literature.

The number of guest hydrogen molecules in each cavity is the important factor that controls the amount of hydrogen stored in each hydrate structure. Single occupancy of the small cavities is reported in the majority of studies.

Papadimitriou et al. [38] presented a detailed discussion of the hydrogen storage capacity of sI, sII, and sH hydrates based on GCMC simulations. It is concluded that sH hydrates can store larger amount of hydrates than sI or sII hydrates.

Di Profio et al. [39] presented an energetic and economic evaluation of hydrogen hydrates and concluded that while far from been optimized, hydrogen hydrates may be competitive compared to other existing hydrogen storage technologies.

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