

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/259933117>

# Hydrogen storage in clathrate hydrates: Current state of the art and future directions

ARTICLE *in* APPLIED ENERGY · JANUARY 2014

Impact Factor: 5.61 · DOI: 10.1016/j.apenergy.2014.01.063

CITATIONS

56

READS

312

## 3 AUTHORS:



**Hari Prakash Veluswamy**

National University of Singapore

14 PUBLICATIONS 154 CITATIONS

SEE PROFILE



**Rajnish Kumar**

CSIR - National Chemical Laboratory, Pune

84 PUBLICATIONS 1,704 CITATIONS

SEE PROFILE

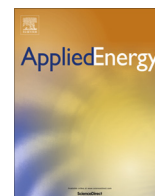


**Praveen Linga**

National University of Singapore

92 PUBLICATIONS 1,774 CITATIONS

SEE PROFILE



# Hydrogen storage in clathrate hydrates: Current state of the art and future directions



Hari Prakash Veluswamy<sup>a</sup>, Rajnish Kumar<sup>b,\*</sup>, Praveen Linga<sup>a,\*</sup>

<sup>a</sup> Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117 576, Singapore

<sup>b</sup> Chemical Engineering and Process Development Division, CSIR – National Chemical Laboratory, Pune, India

## ARTICLE INFO

### Article history:

Received 23 July 2013

Received in revised form 24 November 2013

Accepted 29 January 2014

### Keywords:

Gas hydrates

Hydrogen storage

Clathrates

Hydrogen hydrates

Promoters

Storage capacity

## ABSTRACT

Hydrogen is looked upon as the next generation clean energy carrier, search for an efficient material and method for storing hydrogen has been pursued relentlessly. Improving hydrogen storage capacity to meet DOE targets has been challenging and research efforts are continuously put forth to achieve the set targets and to make hydrogen storage a commercially realizable process. This review comprehensively summarizes the state of the art experimental work conducted on the storage of hydrogen as hydrogen clathrates both at the molecular level and macroscopic level. It identifies future directions and challenges for this exciting area of research. Hydrogen storage capacities of different clathrate structures – sI, sII, sH, sVI and semi clathrates have been compiled and presented. In addition, promising new approaches for increasing hydrogen storage capacity have been described. Future directions for achieving increased hydrogen storage and process scale up have been outlined. Despite few limitations in storing hydrogen in the form of clathrates, this domain receives prominent attention due to more environmental-friendly method of synthesis, easy recovery of molecular hydrogen with minimum energy requirement, and improved safety of the process.

© 2014 Elsevier Ltd. All rights reserved.

## Contents

1. Introduction	113
2. sII hydrates of hydrogen	114
2.1. Pure hydrogen hydrates	114
2.2. sII hydrates with promoters	115
2.2.1. Tetrahydrofuran (THF)	115
2.2.2. Cyclopentane	116
2.2.3. Cyclohexanone	117
2.2.4. Furan and tetrahydrothiophene	117
2.2.5. Other notable sII promoters	117
2.2.6. Gas phase promoters	118
3. Semi-clathrates of hydrogen	118
3.1. Alkylammonium and alkylphosphonium salts	118
3.1.1. Tetrabutyl ammonium bromide (TBAB)	118
3.1.2. Tetrabutyl ammonium fluoride (TBAF)	119
3.1.3. Tetrabutyl ammonium chloride (TBAC) and tetrabutyl phosphonium bromide (TBPB)	119
3.1.4. Tetrabutyl ammonium nitrate (TBANO <sub>3</sub> )	120
3.2. Other semi-clathrate hydrate promoters	120
3.3. Atomic hydrogen from semiclathrates	120
4. sH hydrates of hydrogen	120
5. sI hydrates of hydrogen	121
6. sVI clathrates storing hydrogen	122

\* Corresponding authors. Tel.: +65 66011487 (P. Linga).

E-mail addresses: [krajnish@ncl.res.in](mailto:krajnish@ncl.res.in) (R. Kumar), [praveen.linga@nus.edu.sg](mailto:praveen.linga@nus.edu.sg) (P. Linga).

7.	Organic and inorganic compounds forming hydrogen hydrates .....	122
7.1.	Organic clathrates of hydrogen .....	122
7.2.	Inorganic clathrates of hydrogen .....	123
8.	Polymeric materials storing hydrogen clathrates .....	123
9.	Hybrid storage of hydrogen .....	123
9.1.	Chemical hybrid clathrates .....	123
9.2.	Clathrate mediated adsorption for increased hydrogen storage .....	124
10.	Multiple hydrogen occupancy .....	124
11.	Tuning effect observed in hydrogen hydrates .....	125
12.	Energy analysis for hydrate based hydrogen storage process .....	126
13.	Future directions .....	128
14.	Conclusion .....	129
	Acknowledgements .....	129
	References .....	129

## 1. Introduction

Hydrogen is the lightest, simplest and the most abundant element on earth. Hydrogen is termed as 'green fuel' and the 'fuel of the future' as it is a 'clean energy' carrier which on combustion yields only water vapor contributing to near zero emission. Despite numerous benefits of hydrogen, the storage and delivery of hydrogen has been a severe bottleneck and there have been considerable efforts in finding novel materials for developing new processes to increase the hydrogen storage capacity.

Hydrogen being the lightest element in nature has a very low density; hence creates huge problems during storage, as it requires more volume for a given amount of energy. Conventional methods of hydrogen gas storage include compression and liquefaction. Compressing hydrogen gas to high pressures of around 300 bars poses safety risk during transportation and storage. Compressed gas is able to store 15 g/l at 35 MPa [1]. Cryogenic cooling or liquefying the hydrogen gas to temperature of around 20 K is highly energy intensive and equivalent to 30% of the energy stored is expended in achieving such low temperature. Other storage methods include physical adsorption of hydrogen gas to solid material support; interaction between the host material and smaller H<sub>2</sub> molecule is dominated by weak Van der Waals interactions, which limits the storage capacity under ambient conditions [2–4]. Chemical storage of hydrogen in the form of metal hydrides and nitrides seem to be promising considering relative high hydrogen storage [5–7]. However, release of hydrogen from such compounds requires high temperature which is additional energy requirement. Carbon nanotubes, graphenes and metal organic frameworks are the novel materials being researched for hydrogen storage [8–16]. Relatively new and promising material for hydrogen storage is the cage compound or clathrate hydrate [17–20].

Clathrate hydrates are inclusive compounds where the guest gas molecules are trapped in host water molecules [21–24]. There is no chemical reaction, the gas is held inside the cavities only by physical bonds. Gas hydrate or clathrate hydrate research has progressed over several decades from a mere academic curiosity to being a nuisance to the oil and gas industry for flow assurance. Gas hydrate formation continues to have an impact on flow assurance due to the ever progressing deep offshore oil and gas exploration activities making it more favorable to appear in the pipelines and offshore facilities [21,25]. Later in 1960s after the discovery of naturally occurring hydrate deposits, there has been considerable interest among the research community spanning across disciplines of chemical engineering, mechanical engineering, civil and environmental engineering and chemists to understand the energy and environmental impact of these hydrate deposits [26–33]. Over the recent decades, several researchers have been applying this gas hydrate phenomena to develop innovative novel technologies for

natural gas storage and transportation [34,35], carbon dioxide capture, storage & sequestration [36–43], refrigeration [44–46], desalination [47], gas separations [48–50] and hydrogen storage [17–20]. This review will focus on one such technological application, i.e. hydrogen storage in clathrate hydrates.

Despite the recent discovery (in the 90s) there have been considerable research efforts in improving the clathrate process for hydrogen storage. Continued interest in exploring the clathrate hydrates for hydrogen storage is due to its inherent advantages which include – (i) clathrate process is environmentally benign as it uses only water and very low concentration of promoters for improving the operating conditions (ii) hydrogen is stored in its molecular form, for ready utilization just by depressurization or minimal thermal stimulation (iii) Moderate temperature and pressure conditions for storage (in the presence of low concentration of promoters) (iv) Relative high hydrogen content per unit mass/volume [1] and (v) it is non-explosive in nature. However, there are few challenges encountered in storing hydrogen as clathrates such as (i) slower formation kinetics of hydrogen hydrates (ii) stability of hydrogen hydrates at ambient conditions (iii) low hydrogen storage capacity when used along with promoters (the promoters occupy hydrate cages preventing hydrogen gas from occupying the cages). Research efforts in overcoming the above challenges and making hydrogen clathrates as a storage medium are on-going. Struzhkin et al. [1] were the first to present a comprehensive review on hydrogen clathrates, they had discussed the history of hydrogen hydrates, different clathrate structures of hydrogen hydrates, explained the characterization techniques for studying the hydrogen clathrates, theoretical models and calculations available for studying the hydrogen clathrates along with the challenges encountered in theoretical studies.

Strobel et al. [51] evaluated the hydrogen storage properties of different clathrate hydrate structures including sII formed by hydrogen/THF mixed hydrates, semi-clathrates formed using TBAB and Jeffrey's structures. Evaluation was based on theoretical calculations as well as experimental volumetric gas release measurements and Raman spectroscopy. Maximum hydrogen storage in the available clathrate hydrate structures and Jeffrey's structures were calculated by using suitable assumptions and valid correlations. One representative compound for each hydrate structure was considered and the hydrogen storage capacity was worked out. Maximum of around 7.2 wt% was predicted for sVI hydrogen hydrate with six molecules of hydrogen occupying the large cages in sVI structure [51]. However, extreme conditions of pressure and temperature are required for achieving high hydrogen storage which may not be feasible at large scale considering the associated energy requirement. It is possible to bring the temperature and pressure requirements to a milder condition if a co-guest is used for hydrate formation along with hydrogen. However, it is very

## Nomenclature

MD	molecular dynamics	SDS	Sodium dodecyl sulphate
PXRD	powder X-ray diffraction	CP	cyclopentane
XRD	X-ray diffraction	THT	tetrahydrothiophene
PND	powder neutron diffraction	DXN	1,4 dioxane
NMR	nuclear magnetic resonance spectroscopy	SF <sub>6</sub>	sulphur hexafluoride
THF	tetrahydrofuran	MTBE	methyl tert-butyl ether
TBAB	tetrabutylammonium bromide	MCH	methylcyclohexane
TBAF	tetrabutylammonium fluoride	DMCH	1,1-dimethylcyclohexane
TBAC	tetrabutylammonium chloride	TMB	trimethylbutane
TBPB	tetrabutylphosphonium bromide	DD3R	DecaDodecasil 3R
TBANO <sub>3</sub>	tetrabutylammonium nitrate	SGT	SigmaTwo
TMA	trimethyl amine	polyHIPE	polymerized high internal phase emulsion material
TBAPA	tetrabutylammonium polyacrylate	PSA	poly(acrylic acid) sodium salt
TIAPA	tetraisoamylammonium polyacrylate	HQ	hydroquinone
TBABh	tetrabutylammonium borohydride	CGC	critical guest concentration
AOT	aerosol-OT [sodium bis(2-ethylhexyl sulfosuccinate)]	DOE	department of energy

difficult to achieve high capacity because the co-guest being larger in size preferably occupies the large cavities thus only small cages are available for hydrogen molecules which significantly reduces the storage capacity. Research is now focused on processes/procedures that can result in increased hydrogen storage at moderate conditions of temperature and pressure (closer to ambient conditions), exploration for thermodynamic promoters that can reduce the hydrate formation conditions and kinetic promoters that can result in increased hydrate formation rate. Strobel et al. [52] further provided a comprehensive review of promoters forming mixed hydrogen hydrates. Dynamics of hydrogen in clathrate cavities had been discussed in detail along with a novel hybrid method for storing hydrogen in both guest and host.

Since the earlier reviews, there have been several new promoters reported for storing hydrogen as clathrates. New polymeric materials that aid in hydrogen hydrate formation have been studied. Different hydrate formation procedures have been formulated to increase the hydrogen storage capacity. Kinetic studies on hydrogen clathrates were conducted. Combining hydrate formation with other processes like adsorption for increased hydrogen storage was attempted. New hybrid materials that store hydrogen both in the guest as well as the hosts were discovered. This review aims to discuss the progress in experimental work in the area of storage of molecular hydrogen as clathrates. However, it is noted that molecular dynamic (MD) simulation studies throw light on the microscopic properties of the hydrogen clathrates. Forces and interactions existing between the atoms of the host water cages and the guest hydrogen molecules can be calculated using such simulation studies. Simulation studies thus complement the experimental studies, and help in predicting the optimal experimental conditions for high hydrogen storage. However, the accuracy of these results may vary with simulation techniques, models and methods used for the study. MD simulation studies on hydrogen hydrates [53–71] are available in the literature. This review attempts to provide a comprehensive overview of the current state of the art experimental work in the area of hydrogen hydrates and future directions. Different promoters forming hydrogen hydrates have been discussed and the hydrogen storage capacity achieved in the presence of these promoters has been summarized. A section on the energy analysis of the hydrogen hydrate process is presented. In addition, two major topics on the hydrogen hydrates, namely the multiple-cage occupancy and the tuning effect are discussed in detail. Possible challenges and opportunities for further

improving hydrogen storage capacity and future directions are highlighted.

## 2. sII hydrates of hydrogen

### 2.1. Pure hydrogen hydrates

It was presumed that hydrogen being the smallest molecule cannot stabilize the hydrate cages until Vos et al. [72] reported the first hydrogen clathrates at high pressures between 0.75 and 3.1 GPa at 295 K wherein the hydrogen gas was trapped in water cages having ice II structure. However, there has been a theoretical study by Lunine and Stevenson [73] as early as 1985 predicting inclusion of hydrogen in hydrate cages due to high pressure and low temperature conditions occurring in planetary bodies. Hydrogen molecule forming hydrates was very significant however the high pressure required for hydrate formation was not attractive for applying the process for hydrogen storage. Further, Dyadin et al. [74] experimented and reported that hydrogen hydrates are similar to ice II structures. Mao et al. [20] performed Raman, Infra-red, X-ray and Neutron diffraction studies and showed that hydrogen forms classical sII structure with two hydrogen molecules occupying small cages and four molecules of hydrogen occupying the large cages of sII structure.

Further study on hydrogen hydrates by Mao and Mao [75] showed an increase in potential of storing hydrogen as hydrates, about 5.3 wt% of hydrogen could be stored in the hydrates synthesized at 200–300 MPa and 240–249 K. Effect of the low temperature in improving hydrogen storage was demonstrated in their work. It was found that by reducing temperature to 77 K, hydrogen hydrates were stable at atmospheric pressure. They calculated gravimetric and volumetric energy densities of hydrogen stored to be 1.8 kW h/kg and 1.5 kW h/l respectively [75]. These values are promising and capable of achieving 2015 hydrogen storage targets set forth by DOE. However, due to the extreme conditions of hydrate formation it may not be feasible to be implemented on a commercial scale. They also formed ice filled hydrogen hydrates at 2300 MPa and 300 K. These hydrates were found to be stable till 500 MPa and 77 K. They calculated the amount of hydrogen stored to be around 11.2 wt%. Lokshin et al. [76] reported a faster method of forming hydrogen clathrates. The formation of hydrogen clathrates from water (pressurization at room temperature followed by cooling to 100–260 K) took longer time, only 70% of water

was converted to hydrates after 20 h and full conversion was not observed even after 5–10 days of synthesis. However, when powdered ice Ih was pressurized with hydrogen, the hydrogen hydrate formation was observed in less than 10 min under same operating conditions.

Though the kinetics of pure hydrogen hydrate can be increased by forming hydrates with hexagonal ice powders, it still requires significantly higher pressure for hydrate formation. For practical hydrogen storage applications, an alternative preparation method which is kinetically favorable, not requiring significantly high pressure for formation and having significant storage capacity is required. A novel approach was tried in a recent paper by Kumar et al. [77], in which a reactive form of ice was identified and with clever experimentation pure sII hydrogen hydrates were synthesized at significantly lower pressure of 15–18 MPa. Most of the synthesized material was identified as H<sub>2</sub> filled ice-Ic, which was found to have a theoretical H<sub>2</sub> capacity of 10 wt% which is much higher than classical sII hydrate. The kinetics of this H<sub>2</sub> filled ice Ic was found to be very favorable and an experiment done at 15–18 MPa and 140 K for a period of 30 min yielded a material with 2.7 wt% H<sub>2</sub>. This material was found to be stable at 77 K and ambient pressure. Quantification of H<sub>2</sub> was done by using a combination of analytical techniques ranging from NMR spectroscopy, powder pattern and Raman spectra. It was concluded that the potentially large H<sub>2</sub> capacity of ice Ic (10 wt% if fully loaded) prepared by this route suggests that ice Ic could be a viable hydrogen storage material.

It has been conclusively proven that hydrogen does form classical hydrate structure and occupies significant portion of the solid hydrate phase. However, conflicting reports have been made in the literature regarding the hydrogen occupancy of the small/large cavities in the hydrate phase [78–80]. The question of single versus multiple occupancy of the hydrate cages is very important in the context of the total hydrogen storage capacity of the clathrate and hence is addressed separately at the end of the paper in section 10.0, as it also involves the presence of promoters.

## 2.2. sII hydrates with promoters

### 2.2.1. Tetrahydrofuran (THF)

Udachin et al. [81] studied hydrogen forming mixed clathrates with THF and hexafluorophosphoric acid at high pressures of 350 MPa and 700 MPa. Hydrogen was found to occupy 91% of the small cavities when it formed binary clathrates with THF at 350 MPa. An important breakthrough for hydrogen storage as clathrate hydrates was reported by Fluoresse et al. [82] that reduced the hydrogen hydrate formation pressure from order of 300 MPa to just 5 MPa (around 60 times reduction) at 279.6 K with the inclusion of THF molecule as a co-guest in hydrate cages. This proved that hydrogen hydrates can be formed at moderate operating conditions of temperature and pressure by including molecules called ‘promoters’ which help to modify the hydrate forming conditions. This opened up the research front for the search of other promoters which can store hydrogen at improved conditions (closer to ambient temperature and moderate pressure). One notable drawback with the addition of promoter molecules is the drop in hydrogen storage capacity of such hydrates due to favorable inclusion of promoter molecules in the hydrate cages. Though promoter molecules favor moderate hydrate formation conditions they offset the storage capacity. Thus finding a suitable promoter and optimizing the concentration of promoter for maximizing hydrogen storage capacity at milder temperature and pressure conditions is still a challenge. Later, Lee et al. [78] showed that it is possible to increase the amount of hydrogen by lowering the concentration of THF from stoichiometric composition (5.56 mol%) to about 0.1 mol% at 12 MPa. Maximum hydrogen storage capacity of

4.03 wt% was observed for 0.15 mol% of THF concentration. This ‘tuning effect’ was characterized by partial occupancy of large cages of sII structure by THF with space for hydrogen molecules occupying remaining large cages in sII structure accounting for high hydrogen storage of 4.03 wt%. Though the study was quite impressive, the observed results was contradicted by an elaborate study done by Strobel et al. [83] that showed maximum hydrogen storage of only 1 wt% when THF concentration was lowered from 5.56 mol% to 0.5 mol% even at 13.8 MPa. There was no significant increase in storage capacity in the entire range of concentration tested. There have been studies reporting ‘tuning effect’ observed in mixed hydrogen hydrates [78,84–88], whereas few other studies refute such a claim [83,89–91]. Tuning effect being an unresolved issue has been addressed separately in section 11.0. Ogata et al. [92] reported a hydrogen storage capacity of 1.05 wt% at 85 MPa and 277.15 K. They studied two different methods of hydrate formation using Raman spectroscopy – (i) formation of mixed hydrates from compressed hydrogen gas and THF aqueous solution (ii) isothermal pressure swing adsorption using THF hydrates at 277.15 K. There are also studies available showing increased hydrogen storage by using different method of mixed hydrate formation [88] and reduction of induction time using porous medium for the mixed hydrate formation [93].

Sugahara et al. [88] reported a storage capacity of 3.4 wt% in hydrogen/THF hydrate formed by using powdered ice and solid THF at 255 ± 2 K and pressure of approximately 60 MPa. They observed tuning effect similar to results of Lee et al. [78] below the eutectic composition of THF (1.06 mol%). Maximum storage of 3.4 wt% was observed for 0.5 mol% of THF. Based on Raman and PXRD analysis, only one hydrogen molecule was present in small cages unlike the observations of Lee et al. [78] where two hydrogen molecules were present in all the small cages. Sugahara et al. [88] reported that the fractional occupancy of hydrogen in large cages is a function of concentration of THF and the amount remains constant for about a week due to the method of hydrate formation adopted.

Saha et al. [93] studied mixed hydrogen/THF hydrate formation in porous media of different sizes 49, 65, 100 and 226 Å. Induction time for mixed hydrate formation in 49 Å porous media of silica gel was only 27 min which was about 6–22 times faster (3–10 h) than the formation of mixed hydrates from bulk ice. However, the induction time increased with the increase in particle size. Maximum of 1 wt% hydrogen at 65 bar and 270 K was reported to be stored in their study. Talyzin [94] evaluated the hydrogen storage capacity of mixed hydrogen/THF hydrates. The study focused on mixed hydrate formation from bulk ice and from dispersed THF solution in polyurethane foam. Gravimetric method using magnetic suspension balance was considered for the study, there was less than 0.1 wt% of hydrogen stored in the bulk hydrogen/THF sample at around 140 bar and 272 K even after 6 days of exposure to hydrogen gas. Polyurethane foam was used as a support and about 1/3rd of the pores were filled with THF solution. Increased storage of around 0.2 wt% of hydrogen was calculated at similar experimental conditions of bulk ice. It took longer time to observe hydrogen release from mixed hydrates formed in polyurethane foam because escaping hydrogen gas bubbles get attached in the porous network thus making dissociation of hydrates time consuming.

Grim et al. [95] found that rapid hydrogen hydrate growth occurred when preformed seeds of THF + H<sub>2</sub> hydrate were quenched to liquid nitrogen temperatures in presence of unconverted ice. Such a growth was observed only in presence of seeds of preformed hydrates and unconverted ice, and the hydrogen was found to occupy large cages of sII hydrate. Profio et al. [96] formulated a new nanotechnology based approach for storing hydrogen in the form of clathrates. Water-in-oil nanoemulsion with monolayer of amphiphile molecules (surfactants) was dispersed in bulk organic



solvent. This innovative method was patented [97] and the authors demonstrated the technology using isooctane as bulk organic solvent, Aerosol OT surfactant (AOT), THF as co-former (promoter) and water.

0.1 M AOT in 200 ml of isooctane was prepared first, to which suitable quantity of water was added such that stable nanoemulsion without phase separation was obtained. Then suitable amount of THF (co-former) depending on the partition equilibrium between water and organic phase was added. Iso-octane exhibited higher solubility for hydrogen than the water which resulted in faster induction time for THF/hydrogen mixed hydrates. Further the added AOT surfactant maximized the surface contact between water and the hydrogen gas resulting in increased hydrogen forming hydrates. The contents were stirred and pressurized with hydrogen for hydrate formation. 1 wt% of hydrogen was reported to be stored. This method reduced the mass transfer limitation and resulted in improved hydrogen storage. Authors also demonstrate the hydrogen storage with other co-formers – tetrahydrothiophene and cyclopentane. Cyclopentane serves as both bulk organic phase as well as co-promoter in forming binary hydrogen hydrates.

The literature data on phase equilibrium of mixed sII hydrates of hydrogen and THF [78,90,91,98,99] is shown in Fig. 1 at different concentrations of THF and at different temperature and pressure conditions. As can be seen in the figure, there is a comprehensive data bank on the thermodynamics of hydrogen/THF hydrates for a range of THF concentrations, temperature and pressure conditions.

Although sufficient experimental data is available on equilibrium of hydrogen/THF hydrates, only few studies have thrown light on the kinetics of mixed hydrate formation which is very important considering scaling up and applying the process commercially for hydrogen storage. Effects of pressure, temperature and particle size of solid THF hydrates in the formation of mixed hydrogen/THF hydrates were studied by Nagai et al. [100]. As expected formation kinetics was favored by smaller sized THF hydrate particles at lower temperature and higher pressures. For a sample size of 10 g, maximum of around 0.28 wt% of hydrogen storage was achieved at optimal conditions of formation. Study by Veluswamy and Linga [101] showed the effect of operating pressure and concentration of THF in the formation of mixed hydrogen hydrates from aqueous THF solution. The study conducted in stirred tank reactor showed variation in induction time of hydrates even at higher driving force and high THF concentration. There has been no effect of Sodium Dodecyl Sulphate (SDS) surfactant observed in improving the

kinetics of hydrate formation unlike the other mixed hydrate systems known. The kinetic challenges encountered during the scale up of hydrate process for hydrogen storage were highlighted.

THF, the well-known sII promoter for hydrogen storage has been studied exhaustively and there have been quite a number of studies [78,82,83,88,90–94,98,100–102] on thermodynamics, kinetics and different methods of hydrate formation in improving the hydrogen storage. Despite a number of promising studies on THF, there is still a strong interest for identifying new thermodynamic promoters that yield mixed hydrogen hydrates of increased stability, increased hydrogen storage capacity and improved formation methods at moderate operating conditions. The following sections discuss some of these promoters that form mixed hydrogen hydrates.

Fig. 2 provides the variation of ratio of mole of hydrogen/mole of water as a function of the experimental pressure (operating pressure). This ratio was calculated using the experimental data available in the literature. Literature data containing the sample size were only plotted as the required ratio could be computed based on sample size taken for hydrate formation. 0.312 mol of hydrogen/mol of water at 60 MPa was the highest value reported so far by Sugahara et al. [103] for THF/hydrogen mixed hydrates wherein the authors had adopted a new method for formation of hydrogen hydrates. Also 0.342 mol of hydrogen/mol of water was reported by using acetone as promoter at 255 K. Both the samples considered were of 1 g.

Fig. 3 provides the plot of hydrogen storage capacity against the concentration of THF. Hydrogen storage capacity values reported in the literature were considered for the plot. The storage values from 2.4 mol% to 5 mol% were calculated from the gas uptake data reported by Veluswamy and Linga [101]. Multiple values available for a particular concentration of THF was averaged and error bars were calculated for these values. The lower concentration (0.2 mol%) show high storage capacity due to the tuning effect reported by Lee et al. [78], which has been debated as researchers were not able to replicate the results. Storage of 3.4 wt% with 0.5 mol% THF was reported by Sugahara et al. [88] for the mixed hydrogen/THF hydrates. This plot does not include the formation pressure of mixed hydrogen/THF hydrates but presents an overview of the storage capacity attained for hydrogen/THF hydrates.

### 2.2.2. Cyclopentane

Cyclopentane is another notable compound that forms sII mixed hydrate structure with hydrogen. Cyclopentane is immiscible in water and forms a layer above the water and serves as an

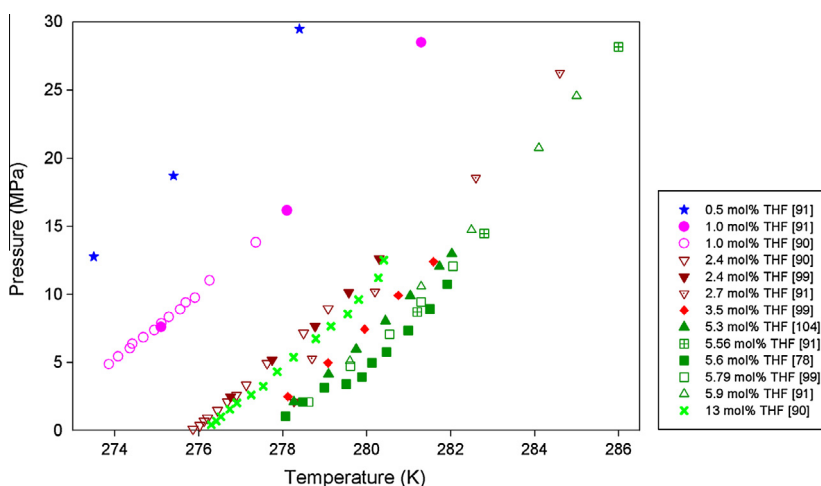


Fig. 1. Plot showing phase equilibrium data for THF + Hydrogen + water available in the literature.

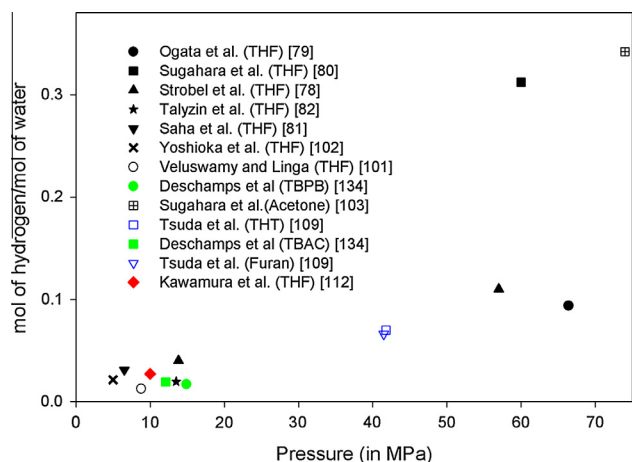


Fig. 2. Plot showing hydrogen uptake (mole of hydrogen stored per mole of water) vs experimental pressure using different promoters.

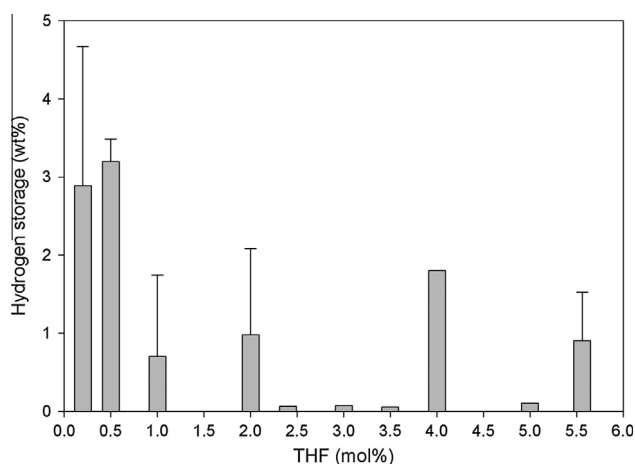


Fig. 3. Plot of hydrogen storage capacity with variation of THF concentration available in the literature. The data presented in the figure was compiled from the literature [78,83,88,91,92,94,100,101,187].

interface between gas and water. The first equilibrium study on hydrogen/CP/water system was performed by Zhang et al. [104]. Their study was performed at pressures between 2.7–11.1 MPa and at temperatures of 280.7–283.7 K. Dissociation temperatures of hydrogen/CP hydrates were found to be greater than that of hydrogen/THF hydrates. Other equilibrium studies on hydrogen/CP mixed hydrate system include that of Komatsu et al. [105] and Du et al. [106]. Komatsu et al. [105] studied and characterized the mixed CP hydrates using Raman spectroscopy. Du et al. [106] performed the equilibrium study at higher pressures up to 33 MPa. Deng et al. [107] studied the hydrogen storage capacity by forming mixed hydrogen hydrates starting from water–cyclopentane mixture and powdered cyclopentane hydrates at 275.15 K and pressures in the range of 10–18 MPa. 0.27 wt% of hydrogen storage was the maximum capacity achieved using powdered cyclopentane hydrates in the experimental conditions studied.

### 2.2.3. Cyclohexanone

Strobel et al. [108] reported the first sII hydrate formation of cyclohexanone with hydrogen. Cyclohexanone does not form hydrates on its own. It is one of the largest size molecule (7.3 Å) forming sII hydrate structure with hydrogen. Powder Neutron

Diffraction (PND) studies showed that despite larger size hydrate cages (due to the size of cyclohexanone), the hydrogen occupancy in cyclohexanone mixed hydrates are lower than that of occupancy of hydrogen in cages of mixed THF hydrate.

### 2.2.4. Furan and tetrahydrothiophene

Compounds structurally similar to THF like furan and tetrahydrothiophene (THT) were studied as candidates for hydrogen storage. Tsuda et al. [109] investigated these two compounds and studied their phase equilibrium for forming mixed hydrates with hydrogen. Hydrates of furan and tetrahydrothiophene were formed first at 270 K, hydrates were crushed at 263 K, kept in reactor at 275.1 K and pressurized with hydrogen. Phase equilibrium curve of hydrogen/THT system shifted by 2 K to the left of equilibrium curve of hydrogen/THF system. For hydrogen/furan system, the equilibrium curve shifted by only 0.5 K to the left of mixed THF hydrate curve. Both these hydrates were stable at slightly lower temperatures compared to THF system. Absorption of hydrogen to the furan or THT hydrates was faster and was completed within 3 h compared to THF hydrates which took more than 10 h. Hydrogen storage of 0.6 wt% was reported for both these compounds at 41.8 MPa and 275.1 K. Storage capacities were found to be similar to THF under the tested experimental conditions.

### 2.2.5. Other notable sII promoters

Treuba et al. [110] did an elaborate work investigating five compounds that were forming sII hydrates on their own. These compounds were studied for formation of mixed hydrates with hydrogen, the phase equilibrium curve for the formed mixed hydrates were determined. Stability of the mixed hydrates formed was also assessed. The five compounds that were studied included cyclopentane (CP), furan, 2,5-dihydrofuran, 1,3-dioxalane and tetrahydropyran in pressure range of 2–14 MPa and temperature range of 269–285 K. Fig. 4 shows the phase equilibrium data of different sII promoters (excluding THF) reported in the literature.

All the organic compounds studied were insoluble in water except 1,3-dioxalane which had only 3 phases in equilibrium (hydrate phase, water rich phase and gas phase) whereas other compounds had 4 phases in equilibrium with an additional organic liquid phase to the above three phases listed. Dipole moment of the promoters was not found to affect the stability of hydrates; predominantly molecular size and geometry played an important role in the stability of mixed hydrates.

Yoon et al. [111] reported that 1,4 dioxane (DXN) forms hydrates with hydrogen. X-ray diffraction, solid-state NMR and Raman spectroscopy conducted on the mixed hydrates showed that they are of characteristic sII structure. DXN concentration was varied and experiments were conducted. The stoichiometric composition (5.56 mol%) yielded around 0.4 wt% hydrogen storage at 12 MPa and 233 K. Increased storage of hydrogen in the mixed hydrates was observed at DXN concentration less than 1 mol% till 0.2 mol%. Maximum of around 1.1 wt% was reported at 0.2 mol% DXN concentration at 12 MPa and 233 K. Kawamura et al. [112] studied enclathration of hydrogen in hydrates using acetone and four cyclic ethers–propylene oxide, 1,3-dioxalane, 2,5-dihydrofuran and 1,4-dioxane. PXRD and Raman analysis were performed on the mixed hydrogen hydrates of the above compounds formed at 253 K and 12 MPa. All the mixed hydrates formed at stoichiometric composition of the above compounds were sII structures. Amount of hydrogen stored in these mixed hydrates was measured by reducing pressure from 10 MPa to atmospheric pressure at 233 K. 0.027–0.029 mol of hydrogen/mol of water was stored in all the mixed hydrates except for the 1,3 dioxalane mixed hydrate where only 0.014 mol of hydrogen/mol of water was observed.

Sugahara et al. [103] observed interesting results when they studied hydrogen storage using the following promoters – THF,

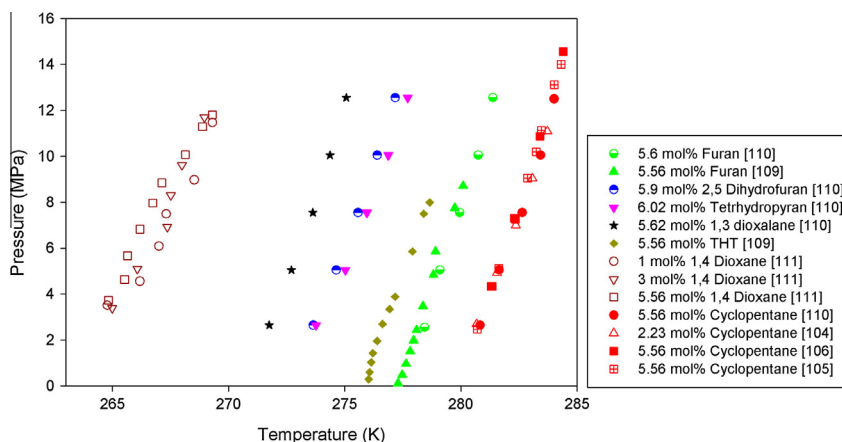


Fig. 4. Plot showing phase equilibrium data for different sII promoters + hydrogen + water available in the literature.

acetone, cyclohexanone and methyl cyclohexane at  $255 \pm 2$  K and till pressures around 70 MPa. Raman spectroscopy, XRD and volumetric gas release measurements were used to analyze the mixed hydrates, it was found that hydrogen was found to occupy large cages in mixed clathrates of THF, Acetone and cyclohexanone at suitable pressure and promoter concentrations. Maximum storage of around  $3.6 \pm 0.1$  wt% was observed for hydrogen/acetone hydrate formed using 0.0058 mol fraction of acetone at 74 MPa and  $255 \pm 2$  K. The storage capacity was similar to that of THF promoter under same operating conditions.

#### 2.2.6. Gas phase promoters

Apart from the listed liquid phase promoters forming sII hydrates with hydrogen, there have been studies on gas phase promoters forming sII hydrates with hydrogen. Zhang et al. [113] explored the phase equilibrium of mixed hydrates of hydrogen (at varied concentration) with hydrocarbon gases like methane, ethane and propane with the intention of applying the same for hydrogen gas separation wherein the enrichment of hydrocarbon gases in hydrates was focused. Propane was found to form sII hydrate with hydrogen. Propane hydrogen mixed hydrate (sII structure) was found to be favorable for storing hydrogen with 0.33 wt% storage capacity achieved at 120 bar and 270 K [114]. Skiba et al. [115] studied hydrogen/propane mixed hydrates varying the composition of hydrogen (40–80 mol%) and obtained decomposition curves for mixed hydrates till pressures of around 250 MPa.

Abbondondola et al. [116] studied hydrogen storage in pre-formed propane hydrates with ice grains at two different pressures. About 50 g of ice grains sieved through 250  $\mu$ m mesh was pressurized with 0.38 MPa of propane at 272.2 K to form propane hydrates for three days. Gas uptake measurement show around 67% of propane enclathrated after three days. The hydrate containing cell was then set at 263 K and 0.12 MPa (corresponding to vapor pressure of propane hydrate at 263 K), pressurized with hydrogen gas to either 0.67 MPa or 1.5 MPa and left for 2–4 days for stabilization. Absorption of hydrogen in first 30 min was the highest in both cases and considerable reduction of pressure was possible till 2 h after which the rate of absorption was very slow. Hydrogen cage occupancy of 2.1% and 4.5% was observed at the pressure conditions considered corresponding to 0.02 and 0.04 wt% of hydrogen respectively.

Park et al. [117] examined  $\text{SF}_6 + \text{H}_2$  gas mixtures and obtained equilibrium data of gas mixtures with hydrogen composition varying from 0% to 90%. The equilibrium conditions for 90% hydrogen and 10%  $\text{SF}_6$  are well below the THF (5.56 mol%) +  $\text{H}_2$  system at

279–282 K. They reported the ability of  $\text{SF}_6$  gas promoter to stabilize hydrogen in hydrate cages at operating conditions better than THF.

### 3. Semi-clathrates of hydrogen

Semi-clathrates are another interesting group of inclusion compounds (clathrates) that are being researched for their hydrogen storage properties. Semi-clathrates are typically ionic, the cationic part occupies the cages of hydrate structure like a guest molecule and the anionic part takes part in the lattice formation along with water. Hence the name semi-clathrates as part of the compound is involved in hydrate cage formation whereas the remaining part occupies the cages of the hydrate structure. Characteristic features of these compounds are their stability and ease of hydrate formation close to room temperature and at nominal pressures compared to sI and sII hydrates. Tetraalkylammonium/phosphonium compounds are typical semi-clathrate forming compounds. Fowler and his team [118] were the first to report the quaternary ammonium salts that dissolved in water had the ability to form hydrates.

#### 3.1. Alkylammonium and alkylphosphonium salts

##### 3.1.1. Tetrabutyl ammonium bromide (TBAB)

Tetrabutyl ammonium bromide (TBAB) is the most exhaustively studied semi-clathrate promoter for different gas systems including  $\text{CO}_2$ ,  $\text{CO}_2/\text{H}_2$ ,  $\text{CH}_4$  and  $\text{H}_2$ . Equilibrium study conducted by Hashimoto et al. [119] reported that hydrogen/TBAB mixed semi-clathrates are stable at 8 K greater than hydrogen/THF mixed hydrates which illustrate that semi-clathrates require milder conditions for storing hydrogen compared to sII hydrate promoters. However, the Raman spectroscopic studies showed that occupancy of hydrogen in small cages of semi-clathrates is lesser than occupancy of hydrogen in small cages of sII structure speculating a low hydrogen storage capacity of hydrogen in TBAB semi-clathrate. Phase equilibrium was determined using stoichiometric composition of 3.7 mol% TBAB.

Arjmandi et al. [120] determined the equilibrium data for hydrogen/TBAB mixed hydrates at 0.1 and 0.43 weight fraction of TBAB (0.60 mol% and 4.0 mol% respectively). It was found that the stability of hydrates increases with the increase in TBAB concentration. A and B types of TBAB hydrates were observed by Shimada et al. [121,122] and Oyama et al. [123]. Type A TBAB hydrate has hydration number of 26 and is reported to be tetragonal structure. Type B TBAB clathrate is orthorhombic having hydration number of 38. Difference in the crystal structure arises due to the



variation in concentration of TBAB solutions [122,123]. Type A TBAB hydrate was observed to be more stable at TBAB mole fraction greater than 0.014 and Type B TBAB hydrate was stable at TBAB mole fraction lower than 0.014. Hashimoto et al. [124] studied the equilibrium behavior of non-stoichiometric TBAB solutions forming semi-clathrates with hydrogen. The equilibrium study was conducted at 0.006 mole fraction (representative for type B TBAB clathrate), 0.02 (representative for type A TBAB clathrate) and at 0.07 (greater than stoichiometric composition of TBAB). Raman spectroscopy analysis performed on different hydrogen/TBAB semi-clathrates demonstrated that neither the difference in concentration (mole fraction) nor the difference in TBAB hydrate type was found to affect cage occupying selectivity of hydrogen. Hydrogen molecule was found to occupy only the small empty cages of TBAB semi-clathrates.

Storbel et al. [51] observed hydrogen storage capacity of 0.22 wt% for 2.6 mol% TBAB solution at 279.5 K and 13.8 MPa. TBAB hydrates were first formed at 275 K, crushed using mortar and pestle under liquid nitrogen and then sieved to size less than 250  $\mu\text{m}$ . Hydrates were loaded in reactor and pressurized with hydrogen gas to experimental pressure. Phase equilibrium data on hydrogen/TBAB mixed semi-clathrates [119,120,124–127] are presented in Fig. 5. As inferred from the figure, exhaustive experimental data is available on the phase equilibria of hydrogen/TBAB hydrates at varying compositions of TBAB. The data for 2 mol% TBAB and 3.7 mol% extends up to 140 MPa [126] is not presented in the figure due to pressure scale chosen in order to avoid overlapping of data points.

Treuba et al. [128] studied the effect of pressure, TBAB concentration and method of hydrate formation on hydrogen/TBAB mixed hydrates and storage capacity of the formed hydrates. Kinetics of hydrate was favorable at higher pressure and high TBAB concentration. The highest hydrogen storage reported in this study was 0.046 wt% at 16 MPa and 281.15 K for 3.7 mol% TBAB. 2.6 mol% TBAB solution in this study yielded 0.031 wt% hydrogen storage at 16 MPa and 281.15 K. Hydrogen storage observed was quite less compared to that reported by Strobel et al. Authors attributed the low hydrogen storage capacity to the mass transfer resistance encountered in stirred tank vessel, less contact area between gas and liquid phase, difficulty for gas to diffuse into liquid phase than to the hydrate phase.

### 3.1.2. Tetrabutyl ammonium fluoride (TBAF)

TBAF hydrates were found to exist at room temperature. TBAF hydrates were thus found to be more stable than TBAB hydrates.

Sakamoto et al. [129] conducted phase equilibrium study for hydrogen/TBAF mixed hydrates. TBAF solutions of mole fractions 0.018 and 0.034 were employed for phase equilibrium study. Hydrogen/TBAF hydrates formed from 0.034 mole fraction TBAF solution were stable at 23 K greater than hydrogen/THF hydrates. This is the most stable hydrates formed at room temperature. However, the storage capacity of hydrogen was found to be less than that of hydrogen/THF mixed hydrates. Two structures of TBAF hydrate are observed – cubic structure with hydration number of 28.6 and tetragonal structure with hydration number of 32.3. Cubic structure was found to be more stable than the tetragonal structure. Also with 0.018 mole fraction of TBAB solution there was characteristic slope change in three phase equilibrium curve at about 9 MPa indicating a structural change in hydrates.

Treuba et al. [130] performed kinetic studies on hydrogen/TBAF hydrates and studied the effect of pressure, TBAF concentration and hydrate formation method on formation kinetics of mixed hydrogen/TBAF hydrates. High concentration of TBAF and high pressures (high driving force) resulted in increased formation of hydrogen/TBAF hydrates. Maximum of 0.024 wt% (or 12 mmol) hydrogen was reported using 3.4 mol% TBAF at 13.0 MPa. Raman spectroscopic analysis of hydrogen/TBAF hydrates showed that solubility of hydrogen in TBAF solution was higher than hydrogen solubility in TBAB solution. Thus despite the presence of more number of small cavities (hydrogen occupies small cavities) in hydrogen/TBAB hydrates, hydrogen storage was higher for hydrogen/TBAF hydrates at same experimental pressure of 13.0 MPa.

### 3.1.3. Tetrabutyl ammonium chloride (TBAC) and tetrabutyl phosphonium bromide (TBPB)

TBAC semi-clathrates were reported to form the following structures – TBAC $\cdot$ 24H $_2$ O, TBAC $\cdot$ 30H $_2$ O, and TBAC $\cdot$ 32H $_2$ O [131]. Equilibrium study on hydrogen/TBAC hydrates was first conducted by Makino et al. [132] at stoichiometric composition of 3.23 mol% TBAC. There was no structural transformation observed in hydrogen/TBAC clathrates under studied conditions. Equilibrium study on TBPB mixed clathrates with hydrogen was carried out by Fujisawa et al. [133] at 2.6 mol% TBPB solution having a hydration number of 37.5. There was no structural transition observed during phase equilibrium study and hydrogen was found to occupy only small cages in semi clathrates till pressure of 170 MPa.

Hydrogen hydrates of tetrabutylammonium chloride (TBAC) and tetrabutylphosphonium bromide (TBPB) were studied by Deschamps et al. [134] using Differential Scanning Calorimetry (DSC). They calculated amount of hydrogen stored in hydrates in terms of

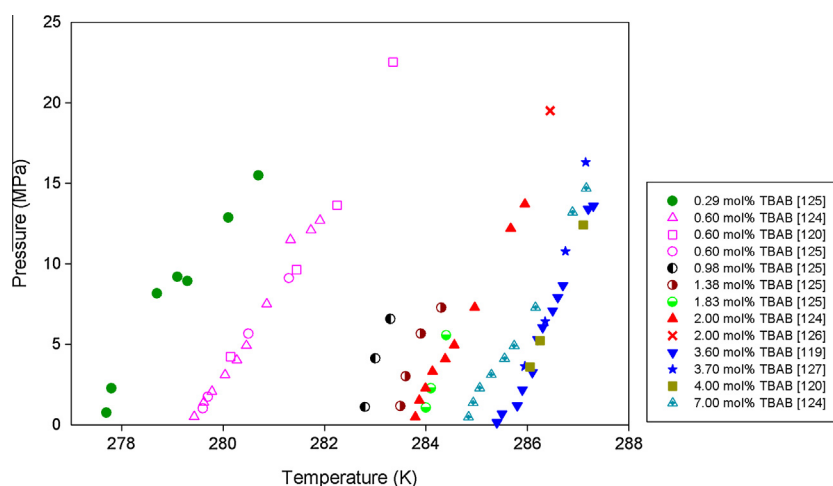


Fig. 5. Plot showing phase equilibrium data for TBAB + hydrogen + water available in the literature.

ratio of moles of hydrogen to water obtained from dissociation enthalpies and equilibrium data. Thermal stability of mixed hydrogen/TBAC hydrates was higher than hydrogen/TBAB mixed hydrates. Hydrogen/TBPB hydrates showed slightly less thermal stability than hydrogen/TBAB hydrates. However in terms of hydrogen stored, both TBPB and TBAC mixed hydrates exhibit almost two times hydrogen/water mole ratio compared to TBAB mixed hydrates at around 15 MPa and temperature range of 282–291 K. TBPB and TBAC mixed hydrates store 0.16 wt% and 0.14 wt% hydrogen respectively.

### 3.1.4. Tetrabutyl ammonium nitrate (TBANO<sub>3</sub>)

The latest reported equilibrium study of mixed hydrogen semi-clathrates is that of Tetrabutyl ammonium nitrate conducted by Du et al. [135] using 3.7 mol% and 3 mol% of TBANO<sub>3</sub> corresponding to stoichiometric composition of TBANO<sub>3</sub>·26H<sub>2</sub>O and TBANO<sub>3</sub>·32H<sub>2</sub>O respectively. It was found that equilibrium pressure for TBANO<sub>3</sub>·32H<sub>2</sub>O was higher than TBANO<sub>3</sub>·26H<sub>2</sub>O at any given temperature. The latter hydrate was found to be more stable than the former in experiments conducted in pressure range of 9–32 MPa and 282–285 K. Compared to other semi-clathrate formers, equilibrium pressure in the range of 282–285 K considered for stoichiometric composition of TBANO<sub>3</sub> was high. With regards to stability, hydrogen/TBANO<sub>3</sub> mixed hydrate is slightly less stable than hydrogen/TBPB mixed hydrate. No data is available on the extent of hydrogen storage in TBANO<sub>3</sub>. Fig. 6 shows phase equilibrium data of different semi-clathrates (excluding TBAB) reported in the literature.

### 3.2. Other semi-clathrate hydrate promoters

Other semi-clathrates which have been studied for hydrogen storage include trimethyl amine (TMA) [136], tetrabutyl ammonium polyacrylate (TBAPA) [137,138] and tetraisoamyl ammonium polyacrylate (TIAPA) [138]. Ogata et al. [136] performed equilibrium and Raman spectroscopic studies on hydrogen/TMA hydrates. All the available small cages were occupied by hydrogen and no increase in hydrogen occupancy was observed at pressures greater than 80 MPa. No change in hydrate structure or cage occupancy was observed with change in TMA concentration. Tetrabutyl ammonium polyacrylate and tetraisoamyl ammonium hydrates stabilized with hydrogen were observed to be more stable and decomposition temperature of such mixed clathrates was higher compared to pure semi-clathrates. Skiba et al. [138] measured

the amount of hydrogen stored in TBAPA hydrate to be about 0.1 wt% (10.5 ml of hydrogen was stored in 1 g of TBAPA hydrate).

### 3.3. Atomic hydrogen from semiclathrates

Apart from molecular storage of hydrogen in semi-clathrates, there has been a recent study by Koh et al. [139] wherein the production of atomic hydrogen from semi-clathrates has been discussed. Guest based and host based atomic hydrogen generation were explored and maximizing the production of hydrogen radicals using suitable semi-clathrate former was presented. This will be a significant step in the development of proton conducting materials and hydrate to energy devices in the future.

Fig. 7 shows the plot of hydrogen storage capacity reported for different semiclathrate hydrate formers. So far for the semi-clathrates, the maximum hydrogen storage capacity reported is for tetrabutyl ammonium borohydride (TBABh).

## 4. sH hydrates of hydrogen

sH structure for hydrates were discovered in 1987 by Ripmeester's group [140]. sH hydrate structure consists of three pentagonal dodecahedrons (5<sup>12</sup>) “small cages”, two irregular dodecahedrons (4<sup>3</sup>5<sup>6</sup>6<sup>3</sup>) “medium cages”, and one icosahedron (5<sup>12</sup>6<sup>8</sup>) which is the “large cage”. 34 molecules of water form a unit sH hydrate structure [21].

Two research groups simultaneously reported the formation of first sH hydrogen hydrates experimentally [141,142]. Strobel et al. [141] reported that hydrogen could be stabilized in the small cavities of sH hydrates along with a larger guest molecule. Authors studied sH hydrate formation using methyl tert-butyl ether (MTBE), methylcyclohexane (MCH), 2,2,3-trimethylbutane (2,2,3-TMB), and 1,1-dimethylcyclohexane (1,1-DMCH) in stoichiometric composition of 2.9 mol%. They predicted 40% increase in hydrogen storage capacity (by weight) compared to binary hydrogen sII hydrates. This was based on single occupancy of hydrogen in small and medium cages with large guest molecules occupying large cages completely. Duarte et al. [142] reported phase equilibrium data of hydrogen along with each of MTBE, MCH and DMCH forming sH hydrates. DMCH was found to form hydrates at pressure of 60 MPa and 274.7 K showing higher stability than other two promoters. This study also theoretically showed 40% increase by weight in storing hydrogen by sH hydrates compared to sII binary hydrogen hydrates. Further a number of liquid hydrocarbon sH

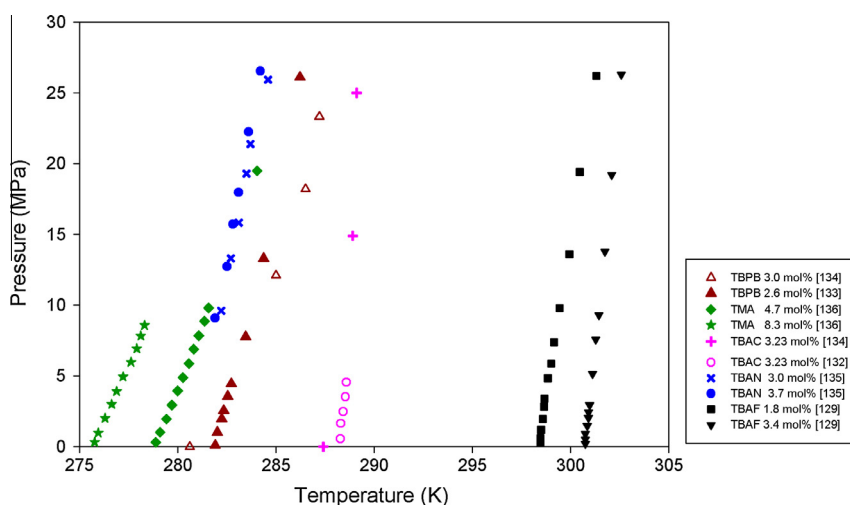


Fig. 6. Plot showing phase equilibrium data for different semiclathrate promoters + hydrogen + water available in the literature.

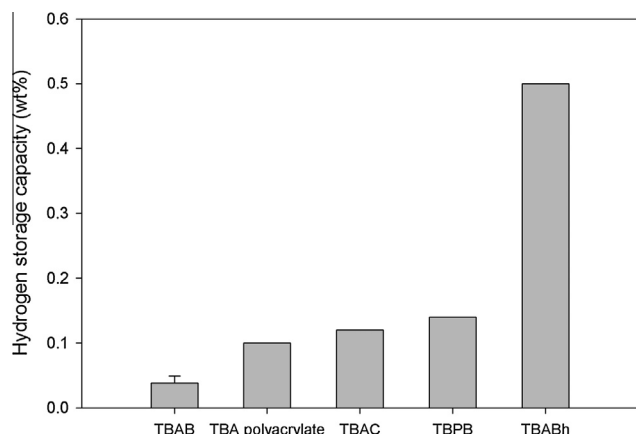


Fig. 7. Plot showing hydrogen storage capacity of different semi-clathrate formers.

promoters were studied by Duarte et al. [143]. They found that the equilibrium pressure of mixed hydrogen-sH hydrate promoters lie in the range of 60–100 MPa at 269–275 K. Fig. 8 shows phase equilibrium plots of hydrogen-hydrocarbon promoters studied by Duarte et al. [143]. The hydrocarbons included in their study covered a wide range and are listed in Table 1.

Martin et al. [144] proposed a thermodynamic model for predicting hydrogen storage capacity as well as cage occupancy of hydrogen and promoter molecules in cages of sH hydrates. This model was able to predict results of experiments conducted with MCH, MTBE and DMCH. Hydrogen storage capacity was found to be between 0.85% and 1.05 % by weight under the experimental conditions of sH hydrate formation. Babae et al. [145] devised a thermodynamic model to incorporate sH promoting effect of alkanes, alkenes, alkynes, cycloalkanes or cycloalkenes in storing hydrogen. 50–57% of volume of unit hydrate cell was occupied by hydrogen in all the cases. These models will help in studying the performance of new sH promoters for increased hydrogen storage in the hydrate cages.

Theoretical investigation in sH hydrate structure for storing hydrogen by Vardes et al. [146] showed that single molecule occupancy of hydrogen was favored in small and middle cages of sH hydrate structure and double molecule occupancy in the large cage of sH hydrate was favored. Promoters (typically molecules >7 Å) can only occupy larger cavities, favoring hydrogen to occupy small and medium size cavities. Very high pressure (of the order of around 0.1 GPa and low temperature of around 273 K) is required to form sH hydrates despite the high hydrogen storage capacity

Table 1

List of available sH promoters for storing hydrogen.

Promoter type	Compounds
Alkanes	2,2,3-Trimethylbutane
	2,2-Dimethylbutane
	3,3-Dimethylpentane
	2,3-Dimethylbutane
	2,3-Dimethyl-1-butene
Alkenes	3,3-Dimethyl-1-butene
	3,3-Dimethyl-1-butyne
Alkyne	Methylcyclohexane
Cycloalkanes	1,2-Dimethylcyclohexane
	1,1-Dimethylcyclohexane
	Methylcyclopentane
	Cycloheptene
Ether	Methyl tert-butyl ether

which makes the practical application of using sH promoters for hydrogen storage difficult. Present research is focused on the search of new sH hydrate formers that could form hydrates in moderate operating conditions similar to the available sH promoters for storing hydrogen. In the wake of recent understanding that it is possible to push multiple hydrogen in the small cages of these hydrate structures, it is important to revisit some of these studies done on sH hydrates of H<sub>2</sub>.

Fig. 9 shows the schematic of the temperature and pressure regions of the existence of different hydrogen hydrates discussed so far for illustrative purposes. Pure hydrogen hydrates occur predominantly in extreme pressure conditions (>250 MPa) at temperatures greater than 270 K. sH hydrogen hydrates are stable in the range of 50–100 MPa at temperatures of 267–279 K. sH hydrogen hydrates are stable at lower pressures (<30 MPa) and lower temperatures (265–285 K). Semiclathrate hydrogen hydrates are the most stable occurring at lower pressures (<30 MPa) and towards the ambient temperature conditions (285–300 K).

## 5. sH hydrates of hydrogen

Presence of hydrogen in the small cages of sH hydrate was first reported by Kim and Lee [147]. It was reported that the small cages of hydrogen/CO<sub>2</sub> mixed hydrate were occupied by two hydrogen molecules. In a separate work, Kumar et al. [79] quantified the cage occupancy of H<sub>2</sub> and CO<sub>2</sub> in sH mixed hydrate which was synthesized at a moderate pressure of 8 MPa and 253 K. In one such sample reported in this work, small cages were occupied by single as well as two hydrogen molecules and the large cages were filled with CO<sub>2</sub>. Hydrogen molecules existed in the form of two-spin

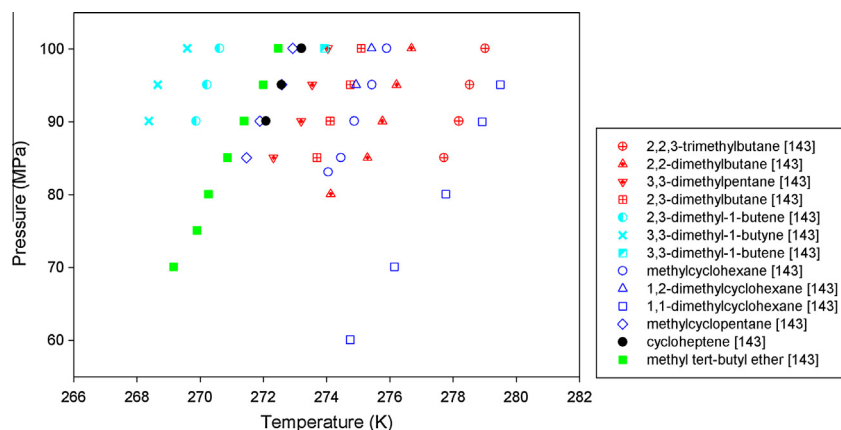


Fig. 8. Plot showing phase equilibrium data for different sH promoters + hydrogen + water available in the literature.

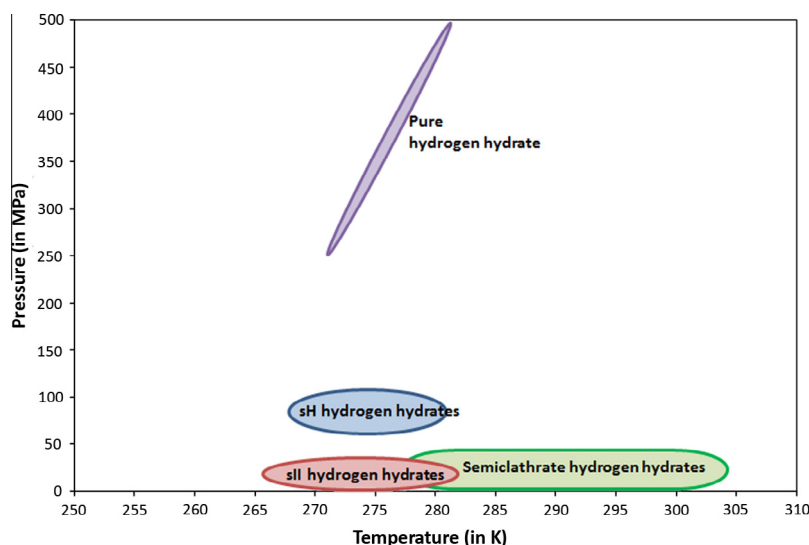


Fig. 9. Schematic plot showing temperature and pressure conditions for existence of different hydrogen hydrate structures.

isomers ortho- and para- hydrogen, with only the ortho-isomer observed by proton NMR. This work presented the ratio of doubly occupied cages to singly occupied small cages without commenting on the overall quantity of  $H_2$  in the mixed hydrates of  $CO_2$  and  $H_2$ .

A recent study conducted by Grim et al. [148] showed the possibility of storing hydrogen in small and large cavities of sI hydrate structure. They initially formed sI hydrates of  $CO_2$  and  $CH_4$ , later pressurized the system with hydrogen gas allowing hydrogen to occupy both large and small cavities of sI hydrates. They used evidences of Raman spectroscopy and powder X-ray diffraction to justify the hydrogen occupancy in large cavities of sI. Though the amount of hydrogen stored in large cavity of sI hydrates might be low compared to that stored in pure sII hydrogen hydrate, this study drives the fact that it is possible to promote guest molecules to occupy the cages of different hydrate structures that cannot be usually formed by the guest molecule. Here hydrogen, a sII hydrate former was found to occupy small and large cages of sI hydrate that had been already formed by  $CO_2$  or  $CH_4$ . This study throws open research arena in increasing the amount of hydrogen stored to greater than 4 wt% (maximum theoretical storage predicted for pure hydrogen in sII hydrate). Authors put forth that about 3.2–7.2 wt% hydrogen storage can be possible if the same procedure (applied for sI hydrate) works for sVI hydrates formed from tert-butyl amine.

First principle electrostatic calculations by Willow et al. [62] showed that maximum of around 10 wt% of hydrogen was possible in sI hydrate with five molecules occupying dodecahedron cages ( $5^{12}$ ) and seven molecules occupying tetrakaidecahedron ( $5^{12}6^2$ ) cages. While such a high possible occupancy of  $H_2$  molecules was made based on theoretical calculations, it is yet to be proven or validated experimentally. Main reason for low occupancy of hydrogen in sI was observed to be the release of hydrogen through hexagonal faces of hydrate lattice; the release was blocked by coating hydrate lattice with larger size molecules like methane which resulted in improved hydrogen storage [62].

## 6. sVI clathrates storing hydrogen

Tert-butyl amine was reported to form mixed hydrate with hydrogen for the first time by Prasad et al. [149]. Tert-butyl amine formed a distinct sVI structure hydrate containing two types of cages 8-hedra ( $4^45^4$ ) and 17-hedra ( $4^35^96^27^3$ ). Theoretical

calculations showed that sVI clathrates are capable of storing maximum hydrogen compared to other hydrates due to the size of the cages in the sVI hydrate structure. 6 wt% of hydrogen could be stored in sVI mixed hydrate of hydrogen/tert-butyl amine assuming full occupancy in small cages and about 90% occupancy in large cages. Theoretical predictions for other structures were also presented in their work.

Experimental study using different concentrations of tert-butyl amine from 0.98 to 9.31 mol% at 13.8 MPa and 250 K was performed. Powder X-ray Diffraction (PXRD) and Raman spectroscopy showed that there was a transformation from sVI structure to sII structure observed at high pressures of hydrogen. Volumetric gas release measurements showed that only 0.07 wt% hydrogen was stored at 8.86 mol% tert-butyl amine concentration corresponding to the stoichiometric composition of sVI hydrate. However, an increased storage of around 0.7 wt% was observed at 5.56 mol% tert-butyl amine concentration corresponding to the stoichiometry of sII hydrates.

Equilibrium studies on hydrogen/tert-butyl amine were performed by Du et al. [150] using different mole fractions of tert-butyl amine–0.0556, 0.0886, 0.0975 and 0.130 in the temperature range of 268.4–274.7 and pressure of 9.54–29.95 MPa. Hydrogen/tert-butyl amine hydrates were stable at lower temperatures compared to mixed hydrogen hydrates formed using THF, cyclopentane, TBAB and TBAF promoters. 0.0975 mol fraction of tert-butyl amine hydrate showed the highest stability of mixed hydrates among the concentrations tested.

## 7. Organic and inorganic compounds forming hydrogen hydrates

### 7.1. Organic clathrates of hydrogen

Minoru Yagi's patent [151] shows an exhaustive list of organic compounds of different categories/groups that form hydrogen clathrates. Organic compound dissolved in suitable solvent was brought in contact with hydrogen gas at pressures suitable for enclosing the hydrogen molecule in the clathrate cages of the organic compound. Other method studied by Minoru was pressurizing the host organic compound directly with hydrogen gas for the hydrogen hydrate formation. Measured weight of the organic compound (0.1–1 g) was taken in 25 ml test tube. Test tube was then filled with helium gas for checking the air tightness, after which



**Table 2**

Hydrogen storage capacity in different organic compounds.

Organic compound	Wt (in g)	Exp P (in MPa)	Retained time (in hrs)	Hydrogen stored (in g)	Hydrogen storage (in wt%)
1,1-Bis(4-hydroxyphenyl)cyclohexane	0.5602	4.7436	1	0.000263	0.0469
1,1-Bis(4-hydroxyphenyl)cyclohexane	0.2361	8.9985	8	0.001602	0.2860
9,9'-Bianthryl	0.5897	7.8390	1	0.000144	0.0244
1,1,2,2-Tetrakis (4-hydroxy phenyl) ethylene	0.5230	7.9153	1	0.000261	0.0498
1,1,2,2-Tetraphenyl ethane	0.6150	7.8587	1	0.000491	0.0799
Bis-dicyclohexylamidofumarate	0.6442	7.9172	1	0.000137	0.0213
Cellulose	0.6570	8.2599	1	0.000162	0.0246
Chitosan	0.6725	8.1704	1	0.000342	0.0508
Hydroquinone	0.7029	7.8462	1	0.000586	0.0834
Urea	0.3482	7.9120	1	0.000137	0.0392
Acetylene dicarboxyl acid	0.8880	7.8874	1	0.000203	0.0229
B-Cyclodextrin	0.8967	7.8767	1	0.000465	0.0517
Methyl gallate	0.7383	7.9817	1	0.000234	0.0317

the test tube was depressurized and vacuumed using a rotary pump. Then the sample was maintained at 25 deg C using temperature control bath. After this the test tube was pressurized with hydrogen gas and retained for suitable time till the pressure balanced. Hydrogen storage capacity was then calculated. Table 2 summarizes hydrogen storage capacity of selected compounds studied by Minoru Yagi [151]. For the quantity of organic compound sample taken, the hydrogen storage achieved at maximum experimental pressure is provided.

## 7.2. Inorganic clathrates of hydrogen

Few of the group 14 elements (Si, Ge, Sn) have been reported to form inorganic clathrate structures. In these structures, group 14 elements formed the host cages and guest molecules were alkali/alkaline earth metals. These compounds were earlier researched for their thermoelectric properties. Neiner et al. [152] reported the formation of hydrogen encapsulating inorganic silicon clathrates having structure similar to conventional si hydrate. The formed hydrate was observed to be stable at room temperature and pressure.  $\text{Na}_{5.5}(\text{H}_2)_{2.15}\text{Si}_{46}$  hydrate was formed by reaction between NaSi and  $\text{NH}_4\text{Br}$  under vacuum at 300 deg C. Solid state NMR analysis performed on the sample showed presence of sodium and hydrogen inside the clathrate cages. Sodium completely filled small cages and was deficient in the large cages, hydrogen was observed to be present in large cages of the silicon clathrate framework. Continuing their work, Neiner et al. [153] reported the formation of silicon clathrate of type I structure containing potassium,  $\text{K}_7(\text{H}_2)_3\text{Si}_{46}$  similar to the previously formed sodium based silicon clathrate. The characterization showed potassium deficient in large and small cages of clathrate structure unlike the sodium based clathrate. The potassium crystal structure was stable till 650 deg C unlike the sodium based clathrate cages which decomposed at the same experimental conditions.

Silica ( $\text{SiO}_2$ ) was found to form similar structures like clathrate hydrates and were commonly referred as 'clathrasils'. Clathrasils (including zeolitic clathrates) were studied for their ability to store hydrogen. Van Den Berg [154] reported the encapsulation of hydrogen during the formation of clathrasils. Major differences between conventional clathrates and clathrasils pointed by Van Den Berg include (i) clathrasil formation is an irreversible process unlike clathrate hydrate formation and (ii) pressure has no influence in the formation of clathrasil and they can exist even in absence of gas unlike clathrate hydrates. Possibility of extracting hydrogen without destroying the clathrasil cages and the stability of clathrasils are favoring these materials as candidates for hydrogen storage, however hydrogen encapsulation being not required for clathrasil formation could result in incomplete filling of cages resulting in transport limitations. DecaDodecasil 3R (DD3R) and SigmaTwo (SGT) were synthesized at 50 bar pressure of hydrogen

and characterized subsequently. This was an attempt to examine the encapsulation of hydrogen during clathrasil formation. These compounds had the smallest cage structures encapsulating hydrogen, considerable part of  $5^{12}$  cages of DD3R contain hydrogen unlike SGT wherein the  $4^{356}$  cages were empty after the synthesis. Hydrogen release was very difficult and was possible only above 1150 K.

## 8. Polymeric materials storing hydrogen clathrates

Very interesting study conducted by Su et al. [155] showed a new polymerized high internal phase emulsion material (polyHIP-E) support based on polystyrene capable of improving the kinetics of hydrogen/THF mixed hydrate formation at 11.6 MPa and 270 K. Maximum storage of around 0.4–0.5 wt% hydrogen was predicted from volume release measurements which is comparable to storage observed by Strobel et al. [83]. Hydrogen gas uptake in the successive run after dissociation increased and then stabilized and yielded reproducible results for next 3 runs conducted by authors. This is very important finding because mixed hydrates formed from crushed and frozen water-THF system (that yield high hydrogen storage) showed rapid drop in kinetics after the first decomposition cycle due to melting. Such polyHIPE based materials may be considered for practical application due to the improved kinetics and reproducible storage capacity of hydrogen for at least 3 cycles. However, further research is required in improving the hydrogen storage capacity in such promising materials.

Further, Su et al. [156] found a novel hydrogel for improving kinetics as well as hydrogen storage capacity in comparison to polyHIPE based material studied earlier. Particulate hydrophilic water-swelling polymer networks based on poly(acrylic acid) sodium salt (PSA) was used in this work. About 1 g of PSA can be treated with around 20 g of THF-Water solution, after dispersion the polymer swelled up. The swelled gel did not agglomerate and melt when undergoing the dissociation process, thus yielded reproducible high hydrogen storage compared to ground ice particles and polyHIPE tested earlier. Use of PSA was advantageous as the weight of the supporting material was less compared to silica beads and other polymeric supports. Though PSA showed less storage initially compared to polyHIPE, it finally demonstrated approximately double the hydrogen content under the experimental conditions of 270 K and 12 MPa.

## 9. Hybrid storage of hydrogen

### 9.1. Chemical hybrid clathrates

Strobel et al. [157] proposed a new alternative to improve the hydrogen storage in clathrates by storing hydrogen in both guest and host molecules i.e. both in clathrate cavities and in the host



lattice. Hydroquinone was used as proof of concept to demonstrate this idea. Hydroquinone was observed to form clathrate at 70 MPa at 296 K and the formation pressure can be lowered further by operating at lower temperature.  $\alpha$ -phase hydroquinone is stable at atmospheric pressure and at room temperature. Thermodynamically favorable  $\beta$ -phase hydroquinone was found to form clathrates enclosing gas molecules like hydrogen and methane. Raman spectroscopy showed that hydrogen enclosed in hydroquinone clathrate did not rotate freely unlike hydrogen observed in other mixed hydrates. One hydrogen molecule per cavity of hydroquinone resulted in 0.61 wt% storage, the host lattice was dehydrogenated by oxidizing hydroquinone to benzoquinone (though hydrogen was not recovered in its molecular form). Considering the entire host lattice being dehydrogenated and including the hydrogen stored in cages, around 2.43 wt% of hydrogen could be stored in  $\beta$ -phase hydroquinone clathrates.

Similarly, Shin et al. [158] reported tetra-*n*-butyl ammonium borohydride semiclathrate as a hybrid material for storing hydrogen. Tetra-*n*-butyl ammonium borohydride semiclathrate was found to store around 0.5 wt% of hydrogen at 70 MPa and 253 K. Volume release measurement show  $73 \pm 3$  ml of hydrogen per 1 g of TBABh hydrate. This is the physically stored hydrogen in the clathrate. When TBABh undergoes hydrolysis in presence of HCl catalyst it releases hydrogen stored in hydride group, thus  $197 \pm 4$  mL of hydrogen was released from 1 g of TBABh hydrate after hydrolysis, resulting in around 1.35 wt% of hydrogen. Chemically bonded hydrogen was substantially high compared to physically stored hydrogen in TBABh semiclathrate. Further research into such hybrid compounds can further improve the hydrogen storage capacity.

Han et al. [159] recently reported a faster and reversible method for storing hydrogen in hydroquinone clathrates. CO<sub>2</sub> loaded hydroquinone clathrate (solid gas phase reaction) was formed at 20 to 80 deg C and 4 MPa. Later the hydrates were kept in atmospheric pressure and 65 deg C to remove the CO<sub>2</sub> from Hydroquinone clathrate framework. Complete removal of CO<sub>2</sub> was ascertained by XRD, solid state NMR and Raman spectroscopy. Following this uptake of hydrogen by guest free hydroquinone clathrate was carried out using gravimetric method. Hydrogen storage of 0.19 wt% at 10 MPa and 0.38 wt% at 35 MPa was reported to be observed at the temperature of 298 K. Ideal storage capacity of HQ clathrate was calculated to be 0.61 wt%, thus around 62% of cages are occupied at 298 K and 35 MPa. The key advantage of hydrogen stored in HQ clathrate was the rapid adsorption and desorption from the cages. It took only 2 s for the entire hydrogen to be stored or released and the cages were only marginally degraded even after 10 cycles of repeated uptake and release. This is the fastest uptake and release for hydrogen reported so far.

## 9.2. Clathrate mediated adsorption for increased hydrogen storage

Hydrogen storage by adsorption is well known and various forms of carbon (carbon nanotubes, nanofibers, activated carbon, carbon monoliths etc.) have been studied for increased hydrogen uptake. Saha et al. [160] put forth a study on increased adsorption in mesoporous carbon through clathrate formation. THF/water mixture having stoichiometric composition (5.56 mol% THF) was doped to carbon adsorbent in three different weight ratios of 1 wt%, 0.75 and 0.5 wt%. Enhanced adsorption of hydrogen was observed due to formation of mixed hydrates of hydrogen/THF at 270 K and 163 bar. 0.5 wt% loaded THF/water mixture on carbon adsorbent demonstrated higher hydrogen storage equivalent to 0.747 wt%. 1 wt% loading of THF/water mix did not show increased hydrogen capture under the experimental conditions, whereas for 0.5 wt% and 0.75 wt% improved performance was observed only after 90 bar and 130 bar respectively. Only in these pressure

conditions, the mixed hydrogen/THF clathrates started forming which resulted in improved adsorption performance. Below these pressures, performance of doped adsorbents was less than undoped adsorbent due to the occupancy of water/THF mixture in pores preventing adsorption of hydrogen. Though the study yielded less hydrogen storage, the idea of using clathrate process for hydrogen storage along with other hydrogen storage methods like adsorption to increase the total amount of hydrogen stored has brighter prospects for meeting DOE target for hydrogen storage. However, sufficient effort is required in pursuing such combination studies for storing hydrogen.

## 10. Multiple hydrogen occupancy

It has been conclusively proven that H<sub>2</sub> does form classical hydrate structure and occupies significant portion of solid hydrate phase in simple or binary hydrates (e.g. THF/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> hydrate). However, conflicting reports have been made in the literature regarding the hydrogen occupancy of the small/large cavities in the hydrate phase [19,78–80,89,161]. The question of single versus multiple occupancy of the hydrate cages is very important in the context of the total hydrogen storage capacity of the clathrate, since it changes stoichiometric H<sub>2</sub>/H<sub>2</sub>O mass ratio in the hydrate phase. Mass ratio of H<sub>2</sub> to that of non-hydrogen element is critical for the practical application of clathrates as a hydrogen storage medium. Generally NMR spectroscopy is the tool of choice for quantifying the cage occupancy values in the solid hydrate phase. However, H<sub>2</sub> exists in two-spin isomer and one of which is not detected by NMR, thus quantifying the amount of ortho and para hydrogen inside the hydrate cages is a first step towards correct quantification of H<sub>2</sub> in the hydrate cages. At ambient condition hydrogen molecules exist in the form of two-spin isomers, ortho- and para- hydrogen (in the ratio 3:1) [162] with only the ortho-isomer being observable by proton NMR. However, at liquid nitrogen temperatures the ratio of ortho hydrogen to para hydrogen is close to 1:1 [163]. NMR measurements done at liquid nitrogen temperature probably quantifies only the 50% of the total hydrogen present in the solid hydrate phase.

Multiple occupancy of hydrogen in simple hydrogen hydrate has only been observed at high pressure of the order of >200 MPa. Multiple occupancy of hydrogen in binary clathrate has been reported in the literature [78,79]. It is important to note that insitu-NMR done at lower temperature and higher pressure should be able to accurately quantify the cage occupancy of simple and mixed hydrate if ortho and para corrections are done accurately. Significant and interesting work by Lu et al. [164] showed that multiple occupancy of hydrogen is possible both in small and large cages at pressure of 15 MPa and 243 K. The formation procedure was different from the conventional hydrogen hydrate formation process. They initially formed nitrogen hydrate at 20 MPa and 253 K. Approximately 2 g of nitrogen hydrate with ice was pressurized with hydrogen gas at 15 MPa and 77 K and the pressure cell was stored in freezer at 243 K for four days. Due to the chemical potential difference (due to absence of nitrogen in the gas phase), some of the nitrogen got replaced by hydrogen resulting in mixed hydrate of N<sub>2</sub> and H<sub>2</sub>. Resultant hydrate sample was analyzed by Raman spectroscopy and powder X-ray diffraction (PXRD). Double occupancy of hydrogen was observed in small cages and maximum of four molecule occupancy of hydrogen was observed in the large cages. However, samples obtained were not homogeneous; varied occupancy of hydrogen was observed in the large cages.

It is difficult to quantify the exact hydrogen content in clathrate structures using Raman spectroscopy alone. Kumar et al. [79] have previously reported that Raman spectroscopy cannot determine

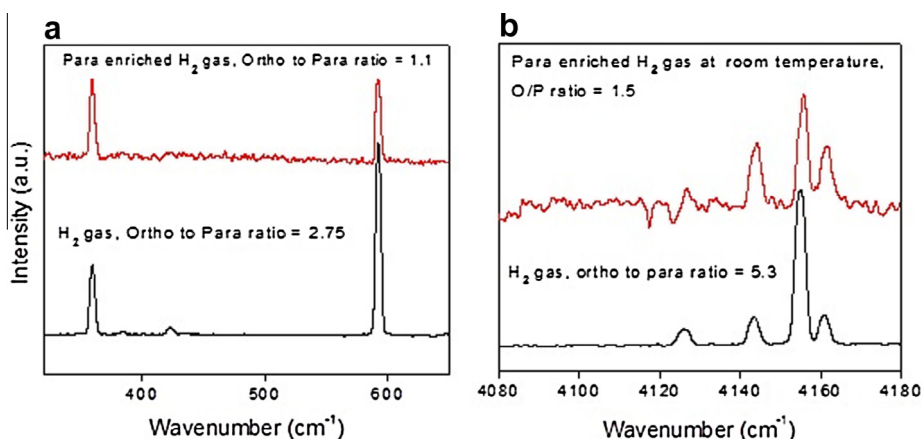
whether hydrogen is present as single molecule or as a cluster of two molecules in the small cages of resultant hydrate structures. Lee et al. [78] reported 2.09 wt% of hydrogen stored in hydrogen/THF binary hydrate with formation pressure of 16 MPa. Strobel [80] considers this an error arising due to application of Raman spectroscopy for quantification of hydrogen, considering two hydrogen molecules occupying each of small cages of hydrate structure and failure to provide external calibration to be used in conjunction with Raman band intensities. This suggestion of Strobel is quite relevant; a brief discussion presented in this work [80] clearly demonstrates the complications of using Raman spectroscopy for quantification of hydrogen in the gas hydrates. A detailed account of Raman spectroscopy for characterizing hydrogen hydrates has been provided by Strobel et al. [165]. Fig. 10 shows Raman spectra in the hydrogen vibron and rotational bands when hydrogen gas is equilibrated for sufficient time at different temperature. As discussed before, under ambient conditions hydrogen exist in two spin state, para- state of hydrogen (total nuclear spin of zero) and ortho- state of hydrogen (total nuclear spin of 1). As seen from the figure, at ambient condition the ratio of ortho- to para-hydrogen is  $\sim 3:1$ , a larger ortho- peak at  $590\text{ cm}^{-1}$  (rotational band) compared to para- peak at  $360\text{ cm}^{-1}$  (rotational band) is observed. However, at liquid nitrogen temperature, the ratio of ortho hydrogen to para hydrogen is close to 1:1 and as observed in this study (Fig. 10a), ortho to para ratio in the  $\text{H}_2$  gas changes and shows more para compared to that at ambient condition with an ortho to para ratio of 1:1. A para enriched  $\text{H}_2$  gas was obtained by passing  $\text{H}_2$  gas through  $\text{Fe}_2\text{O}_3$  at liquid nitrogen temperature for several hours. Presence of  $\text{Fe}_2\text{O}_3$ , which is a paramagnetic compound, catalyzes the rate of ortho to para conversion and hence results in a para enriched  $\text{H}_2$  gas at relatively faster rate. The Raman spectra of this para enriched gas were obtained at dry ice temperature ( $\sim -75^\circ\text{C}$ ). H-H stretch of hydrogen gas at ambient conditions shows four visible peaks  $Q_1(0)$ ,  $Q_1(1)$ ,  $Q_1(2)$ , and  $Q_1(3)$  which appear at  $4161$ ,  $4155$ ,  $4144$ , and  $4126\text{ cm}^{-1}$  respectively. It is important to note that the ratio of these peaks also change at liquid nitrogen temperature.

$\text{H}_2$  signals from the solid hydrate phase appears as two separate rotational bands one for ortho hydrogen in the hydrate phase at  $585\text{ cm}^{-1}$  and other at  $355\text{ cm}^{-1}$  for para hydrogen. For the stretching mode,  $\text{H}_2$  signal appears as a peak doublet with maxima at  $4120\text{ cm}^{-1}$  and  $4126\text{ cm}^{-1}$ . This peak doublet has been identified as  $\text{H}_2$  occupying the small cages of resultant sII hydrate [1]. During one such work in our group, a mixed hydrate of hydrogen/THF was synthesized at moderate pressure, with 6 mol% THF-water solution.  $\text{H}_2$  is expected to occupy only the small cages of resultant

sII hydrate, the change in intensity of the two rotational bands and area under each spectrum compared to THF peak suggests that,  $\text{H}_2/\text{THF}$  hydrate is quite stable at liquid nitrogen temperature. However, ortho  $\text{H}_2$  converts to para  $\text{H}_2$  upon storage in liquid nitrogen. It was concluded that the conversion of ortho to para is catalyzed by some  $\text{O}_2$  impurity in the hydrate structure as well as some  $\text{O}_2$  impurity in the liquid nitrogen where hydrates were stored for analysis at a later date. We believe it is possible to track the change in the nuclear spin of hydrogen gas through Raman spectroscopy and thus Raman spectroscopy along with NMR spectroscopy might be useful for quantifying  $\text{H}_2$  content in the hydrate phase.

## 11. Tuning effect observed in hydrogen hydrates

Another important topic of discussion pertaining to hydrogen hydrates is the tuning effect that is being observed at certain low concentrations of the promoter. When mixed hydrogen hydrates form in the presence of a promoter, the promoter molecule preferably occupies large cages stabilizing the hydrate structure thereby making it difficult for hydrogen molecules to enter and occupy the large cages. Hydrogen occupies only small cages in sII hydrate due to which the storage capacity is low compared to that of pure hydrogen hydrates. Theoretically, if we assume that 4 hydrogen molecules occupy the large cages and two hydrogen molecules occupy the small cages, the theoretical hydrogen capacity in sII would be 5.0 wt%. If we add a promoter like THF and assume that all the large cages of sII are occupied by the guest THF and if two hydrogen molecules occupy each of the small cages, the hydrogen storage capacity reduces from 5.0 wt% to 2.07 wt%. However, at certain low concentrations of promoter it has been reported that hydrogen also occupies a fraction of the large cages contributing to an increased hydrogen storage. This is referred as the 'tuning effect' wherein the concentration of the promoter is tuned or adjusted in order to achieve the maximum hydrogen storage. Lee et al. [78] were the first to report tuning effect when forming mixed hydrogen hydrates in presence of THF promoter. At concentrations between 0.15–1 mol% of THF (well below the stoichiometric composition of 5.56 mol%), they observed that hydrogen occupied large cages through NMR and Raman spectroscopy. For 0.15 mol% THF at 120 bar and 270 K, the hydrogen to THF ratio in hydrate cages was estimated to be as high as 23 and the hydrogen storage capacity was around 4 wt%. The hydrogen to THF ratio was only 4 at the stoichiometric composition of THF. Hydrogen storage capacity in hydrogen/THF mixed hydrates was comparable to the maximum of 5 wt% hydrogen achieved in pure sII hydrogen



**Fig. 10.** Raman spectra of  $\text{H}_2$  gas measured at room temperature and dry ice temperature showing  $\text{H}_2$  rotational band and vibrational band. Para enriched gas was obtained at liquid nitrogen temperature, however Raman measurement was done at dry ice temperature.

**Table 3**  
Enthalpy of dissociation for pure and binary hydrogen hydrates.

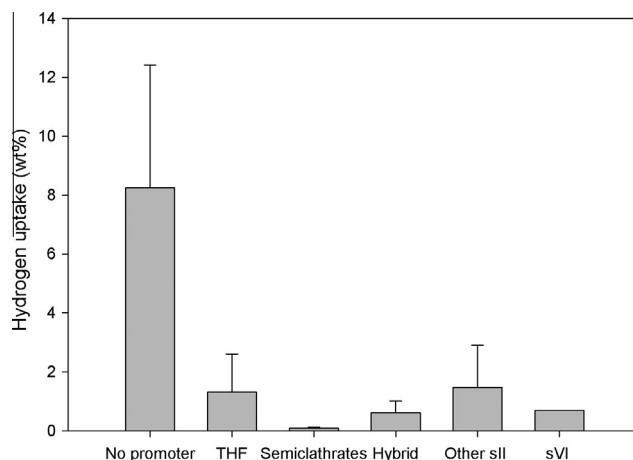
S. no.	System	Hydrate structure	Enthalpy of dissociation (in kJ/mol)	Refs.
1	Hydrogen + water	sII	11.42	Nakayama et al. [170]
2	Hydrogen + THF (5.3 mol%) + water	sII	212	Komatsu et al. [105]
3	Hydrogen + CP (5.6 mol%) + water	sII	220	Komatsu et al. [105]
4	Hydrogen + furan (5.61 mol%) + water	sII	329.23	Treuba et al. [110]
5	Hydrogen + tetrahydropyran (6.02 mol%) + water	sII	343.57	Treuba et al. [110]
6	Hydrogen + 2,5 dihydrofuran (5.9 mol%) + water	sII	343.62	Treuba et al. [110]
7	Hydrogen + TBAB (0.29 mol%) + water	Semi-clathrate	287.26	Treuba et al. [110]
8	Hydrogen + TBAB (0.62 mol%) + water	Semi-clathrate	233.56	Du et al. [135]
9	Hydrogen + TBAB (2 mol%) + water	Semi-clathrate	382.96	Du et al. [135]
10	Hydrogen + TBAB (3.7 mol%) + water	Semi-clathrate	577.91	Du et al. [135]
11	Hydrogen + TBAB (3.7 mol%) + water	Semi-clathrate	316.70	Du et al. [135]
12	Hydrogen + TBAB (7 mol%) + water	Semi-clathrate	326.06	Deschamps et al. [134]
13	Hydrogen + TBAC (3.26 mol%) + water	Semi-clathrate	615.86	Du et al. [135]
14	Hydrogen + TBPB (3.04 mol%) + water	Semi-clathrate	333.68	Deschamps et al. [134]
15	Hydrogen + TBANO <sub>3</sub> (3 mol%) + water	Semi-clathrate	318.72	Deschamps et al. [134]
16	Hydrogen + TBANO <sub>3</sub> (3.7 mol%) + water	Semi-clathrate	340.23	Du et al. [135]
17	Hydrogen + TBAF (1.8 mol%) + water	Semi-clathrate	322.53	Du et al. [135]
18	Hydrogen + TBAF (3.4 mol%) + water	Semi-clathrate	448.50	Du et al. [135]
19	Hydrogen + TMA (4.7 mol%) + water	Semi-clathrate	508.02	Du et al. [135]
20	Hydrogen + TMA (8.3 mol%) + water	Semi-clathrate	401.53	Du et al. [135]
21	Hydrogen + methylcyclohexane + water	sH	430.02	Duarte et al. [143]
22	Hydrogen + 2,2,3-trimethylbutane + water	sH	65.0	Duarte et al. [143]
23	Hydrogen + 2,2-dimethylbutane + water	sH	81.8	Duarte et al. [143]
24	Hydrogen + 2,3-dimethyl-1-butene + water	sH	55.7	Duarte et al. [143]
25	Hydrogen + 1,2-dimethylcyclohexane + water	sH	86.1	Duarte et al. [143]
26	Hydrogen + 3,3-dimethylpentane + water	sH	65.8	Duarte et al. [143]
27	Hydrogen + methyl tert-butyl ether + water	sH	58.9	Duarte et al. [143]
28	Hydrogen + 1,1-dimethylcyclohexane + water	sH	66.2	Duarte et al. [143]
29	Hydrogen + methylcyclopentane + water	sH	60.7	Duarte et al. [143]
30	Hydrogen + 2,3-dimethylbutane + water	sH	64.6	Duarte et al. [143]
31	Hydrogen + cycloheptene + water	sH	69.4	Duarte et al. [143]
32	Hydrogen + 3,3-dimethyl-1-butyne + water	sH	57.7	Duarte et al. [143]
			47.5	Duarte et al. [143]

hydrate (2 hydrogen molecules occupying each of small cages and 4 hydrogen molecules occupying each of the large cages). However, other experimental works [1,83,89–91] could not achieve such high capacity and only a maximum of around 1 wt% equivalent to hydrogen stored in small cages were reported [83,91].

Critical Guest Concentration (CGC) is defined as the liquid promoter concentration at which maximum occupancy of smaller guest gaseous molecules in large cages is achieved, this term was introduced by Kim et al. [87]. Highest hydrogen storage capacity is achieved at CGC (lowest possible liquid promoter concentration) under chosen conditions of hydrate formation. Decreasing liquid promoter concentration below the CGC either results in lowering of gaseous guest in large cages or makes the hydrate formation difficult due to very less liquid promoter concentration. Kim et al. [87] used solution theory to substantiate that tuning effect is a general phenomenon observable by adjusting partial pressures of gaseous guests and concentration of liquid phase promoters. Experimental verification of the tuning effect by forming hydrogen/THF mixed hydrates and methane/t-butyl amine mixed hydrates were performed and results were reported. They highlighted the application of ‘tuning effect’ in improving hydrogen storage capacities of mixed hydrogen hydrates. Recent work by Koh et al. [86] showed tuning effect observed in using water soluble sH hydrate formers resulting in multiple occupancy of hydrogen in large cages. However this was specific only to one of the water soluble sH hydrate former studied, 1-methylpiperidine. Of other promoters, 2-methylpiperidine showed weak tuning effect, 3-methylpiperidine did not show any tuning effect and 4-methylpiperidine did not form hydrates. Also 1-methylpiperidine showed change in hydrate structures with varying concentration; at 2.9 mol% only sH hydrates were formed; at 1 and 2 mol% concentrations, mixture of both sII and sH hydrates were observed and at 0.5 mol% only sII hydrates are observed. This showcases that tuning effect of hydrogen is

dependent on the hydrate forming promoter and is more prominent for sII clathrate structure.

Tuning effect observed using other liquid promoters with methane gas has also been reported in the literature [84,85]. They also exhibit similar trend as that of hydrogen gas with water soluble liquid promoters. It is noted that at the macroscopic level, kinetics of hydrate formation for different systems have been reported to have an optimum hydrate growth rate and gas uptake at a particular promoter concentration [166–168]. Though the concept of ‘tuning effect’ seems to be promising to achieve higher hydrogen storage capacities, these results have to be confirmed experimentally by other researchers at the molecular level. The concept of using both NMR and Raman simultaneously to analyze hydrogen



**Fig. 11.** Hydrogen storage capacities (in wt%) of different groups of promoters.

**Table 4**

Hydrogen storage capacity in hydrates using different promoters.

S. no.	Promoter and concentration	Pressure (MPa)	Temp. (K)	Sample size	Amount of hydrogen stored (wt%)	Characteristics of hydrates/method of preparation	Refs.
1	Hydrogen without promoter	300	249		5.3	sII hydrogen hydrate	Mao et al. [75]
2	Hydrogen without promoter	2300	300		11.2	Hydrogen filled in C2 ice	Mao et al. [75]
3	Hydrogen without promoter	15–18	140	2 g	2.7	Hydrogen filled in reactive ice	Kumar et al. [77].
4	THF/5 mol%	5	279.6			sII mixed hydrogen hydrates	Fluoresse et al. [82]
5	THF/5.56 mol%	12	270		2.09	THF solution was cooled and freezed to form THF hydrates and powdered hydrates were subjected to hydrogen pressurization	Lee et al. [78]
6	THF/0.15 mol%	12	270		4.03		
7	THF/1 mol%	13.8	265–270	5 g	0.43	Powdered THF hydrate/ice	Strobel et al. [83]
8	THF/5.56 mol%	57	270–278	5 g	0.98	Powdered THF hydrate	Strobel et al. [83]
9	THF/0.2 mol%	30	270		0.83	Formed from Ice/THF hydrate	Anderson et al. [91]
10	THF/5.6 mol%	30	283		0.95	Formed from liquid THF solution	
11	THF/0.5 mol%	60	255 ± 2	1 g	3.4	Powdered ice and solid THF	Sugahara et al. [88]
12	THF/5.56 mol%	6.5	266.7	10 g	0.28	Powdered THF hydrate pressurized with hydrogen	Nagai et al. [100]
13	THF/5.56 mol%	66.4	277.15	3 g	0.835	Powdered THF hydrate pressurized with hydrogen	Ogata et al. [92]
14	THF/5.56 mol%	195	277.15		1.05	THF solution super cooled and pressurized with hydrogen	Ogata et al. [92]
15	THF/1 mol%	13.1	272	1 g	0.1	THF/ice sample	Talyzin [94]
16	THF/2 mol%	13.5	272	1 g	0.2	THF solution dispersed in polyurethane foam	
17	THF/5.56 mol%	6.5	270		1	THF solution in porous media	Saha et al. [93]
18	THF/5.56 mol%	5.0	265.1	7.36 g	0.19	Powdered THF hydrates pressurized with hydrogen	Yoshioka et al. [102]
19	THF/0.5 mol%	74	255 ± 2	1 g	3.4	Hydrates formed from solid promoter and powdered ice	Sugahara et al. [103]
20	THF/5 mol%	8.8	278	190 ml solution	0.12	Hydrates formed from THF solution in stirred tank reactor	Veluswamy and Linga [101]
21	Cyclopentane (CP)	10–18	275.15		0.27	Powdered CP hydrates pressurized with hydrogen	Deng et al. [107]
22	1,4 Dioxane/0.2 mol%	12	233		1.1	Powdered Dioxane hydrates	Yoon et al. [111]
23	Furan/5.6 mol%	41.8	275.1	3 g	0.6	Powdered Furan hydrates pressurized with hydrogen	Tsuda et al. [109]
24	Tetrahydrothiophene/5.6 mol%	41.5	275.1	3 g	0.6	Powdered THT hydrates pressurized with hydrogen	Tsuda et al. [109]
25	Acetone/0.58 mol%	74	255 ± 2	1 g	3.6 ± 0.1	Hydrates formed from solid promoter and powdered ice	Sugahara et al. [103]
26	Propane (gas promoter)	12	270		0.33	Powdered propane hydrates pressurized with hydrogen	Park et al. [114]
27	Tetrabutylammonium (TBA) polyacrylate (cross linking ratio of 0.5%)	12.5	259.15	1 g	0.1	TBA polyacrylate hydrate pressurized with hydrogen	Aladko et al. [138]
28	Tetrabutylammonium chloride (TBAC)/3.26 mol%	14.9	288.9		0.12	Hydrates formed from TBAC solution	Deschamps et al. [134]
29	Tetrabutylphosphonium bromide (TBPB)/3.04 mol%	12.9	285		0.14	Hydrates formed from TBPB solution	Deschamps et al. [134]
30	Tetrabutylammonium bromide (TBAB)/2.6 mol%	16	281.15		0.031	Hydrates formed from TBAB solution	Treuba et al. [128]
31	Tetrabutylammonium bromide (TBAB)/3.7 mol%	16	281.15		0.046	Hydrates formed from TBAB solution	Treuba et al. [128]
32	Tetrabutylammonium bromide (TBAB)/2.71 mol%	13.8	279.5	5 g	0.214	Powdered TBAB hydrates pressurized with hydrogen	Strobel et al. [51]
33	Tetrabutylammonium Fluoride (TBAF)/1.8 mol%	13	294.15		0.009	Hydrates formed from TBAF solution	Treuba et al. [130]
34	Tetrabutylammonium Fluoride (TBAF)/3.4 mol%	13	294.15		0.024	Hydrates formed from TBAF solution	Treuba et al. [130]
35	Tertbutylamine/5.56 mol%	13.8	250		0.7	Powdered tertbutyl amine hydrates pressurized with hydrogen	Prasad et al. [149]

(continued on next page)



Table 4 (continued)

S. no.	Promoter and concentration	Pressure (MPa)	Temp. (K)	Sample size	Amount of hydrogen stored (wt%)	Characteristics of hydrates/method of preparation	Refs.
36	Tetrabutylammoniumborohydride (TBABh)/2.54 mol% (without acid hydrolysis)	70	253	1 g	0.5	TBABh semiclathrate pressurized with hydrogen gas	Shin et al. [158]
37	Tetrabutylammoniumborohydride (TBABh)/2.54 mol% (with acid hydrolysis)	70	253	1 g	1.35	TBABh semiclathrate pressurized with hydrogen gas	Shin et al. [158]
38	Hydroquinone clathrate	35	298		0.38	CO <sub>2</sub> loaded hydroquinone clathrates formed first, then CO <sub>2</sub> removed by controlled heating followed with pressurization with hydrogen	Han et al. [159]
39	THF along with adsorption on mesoporous carbon (0.5 wt% of carbon loaded with 5.56 mol% THF solution)	16.3	270		0.747	THF solution dispersed in carbon and then pressurized with hydrogen	Saha et al. [160]
40	THF (5.56 mol%) along with polymerized high internal phase emulsion material as support	11.6	270	20 g of THF solution with 3 g of polyHIPE material	0.4–0.5	THF solution dispersed in polyHIPE material	Su et al. [155]
41	THF with polyacrylic sodium salt (PSA)	11.5	270	20 g of THF solution with 1 g of PSA	0.3	THF solution dispersed in PSA	Su et al. [156]

present in hydrates will help in resolving ambiguity of the 'tuning effect' phenomenon.

## 12. Energy analysis for hydrate based hydrogen storage process

It has been known that hydrates have high volumetric density – the volume of gas stored per unit volume of hydrate is quite large and thus possess high energy density. Apart from being the source of energy, hydrates also find their application in cold storage. Large heat of dissociation (melting), phase change temperature being above the freezing point of water, ability of hydrate slurries to remain in fluid state are features of hydrates that aid in the application of hydrates in cold storage application [44–46,169]. Comparison of hydrogen hydrates with other hydrogen storage technologies in terms of energy and cost associated was performed by Profio et al. [96]. They have calculated energy content in hydrogen hydrate to be 6 MJ/kg gravimetrically and 4979 MJ/m<sup>3</sup> volumetrically. The ratio of spent energy to stored energy in hydrogen hydrates was reported to be 9%. These numbers are comparable with other methods of storing hydrogen. Profio et al. [96] summarize that despite a maximum theoretical 5.6 wt% possible, storing hydrogen as hydrates has added advantages including intrinsic safety, environmentally benign and comparably low process cost.

Nakayama et al. [170] have conceptually designed a hydrogen hydrate based plant for hydrogen uptake of 500 Nm<sup>3</sup>/h and 3000 Nm<sup>3</sup>/h for small scale and large scale applications respectively. They consider pure hydrogen hydrate formation at 35 MPa and 120 K as well as hydrogen/THF mixed hydrate formation at 30 MPa and 223 K. Despite the drastic conditions used for the formation of pure hydrogen hydrates, cost estimation reveals that for the same hydrogen uptake considered, cost for hydrogen/THF mixed hydrate plants is 40–60% higher than pure hydrogen hydrate plant. The reason was attributed to large number of ice makers required for making THF hydrate and more binary clathrate forming reactors compared to pure hydrogen hydrate forming ice makers and reactors. The reduced hydrogen storage capacity in hydrogen/THF mixed hydrates required more quantity of ice and THF hydrates to achieve the same hydrogen uptake as that of pure hydrogen hydrates. Further Shibata et al. [171] made conceptual designs for different types of underground silos for handling the

hydrogen hydrates and computed energy requirement for the designs proposed. Though hydrogen hydrate process is yet to be proven on a large scale, these studies have made a preliminary forecast and have given conceptual design for commercial scale hydrogen hydrate production along with the energy requirement for the entire process. Improvement of hydrogen storage capacity and kinetics of hydrogen hydrate formation will foster the development of hydrogen hydrates on a large scale.

Heat of dissociation data for different hydrogen hydrates reported so far is presented in Table 3. From the heat of formation/dissociation data in Table 3, it can be seen that pure hydrogen hydrates have the least stability, thus requiring the least heat of dissociation (11.42 kJ/mol). Following this, sH hydrates have heat of dissociation ranging from 47.5–86 kJ/mol. Hydrogen/THF mixed hydrates have heat of dissociation to be 212 kJ/mol and other sII promoters forming mixed hydrogen hydrates have higher heat of dissociation as reported in Table 3. Mixed hydrogen semiclathrates have the highest heat of dissociation ranging from 233.56–615.86 kJ/mol, thus inferring the greatest stability. Low heat of dissociation for pure H<sub>2</sub> hydrate clearly shows that its utilization at room temperature is certainly not possible. Higher heat of dissociation as in the case of H<sub>2</sub>/THF mixed hydrate or mixed hydrogen semiclathrates, merely points to the fact that such hydrates are very stable and can be utilized at room temperature, however hydrogen content in such hydrates are quite low. Structure I (sI) has lesser number of water molecules in a unit cell and a mixed hydrate of methane and hydrogen might have lesser heat of dissociation (compared to sII) and would be favorable in terms of energy stored per unit mass of hydrate. Such a combination of hydrogen–methane fuel is called as “Hythane” [172].

## 13. Future directions

Fig. 11 shows the hydrogen storage capacities of different group of promoters reported in the literature. From the figure, it is quite clear that hydrogen storage capacity without using any promoter is the highest; however such storage is possible only under extreme pressure (2300 MPa) and temperature conditions. Addition of promoter drastically reduces the storage capacity, however the pressure and temperature conditions are moderate, thus favoring clathrates as a medium for storing hydrogen on a commercial



scale. sII promoters have shown the best hydrogen storage capacity in comparison to sVI promoters, semiclathrates and hybrid storage methods reported so far. The hydrogen storage capacities reported in this plot are provided in Table 4.

Samples considered for mixed hydrogen hydrate formation studies reported in the literature vary between 1–20 g (Table 4) except for the studies by Veluswamy and Linga [101] and Treuba et al. [128,130], wherein they considered larger samples of order of 100 g. In these studies, the hydrogen storage capacity achieved was low in the order of 0.1 wt% despite high driving force and continuous stirring employed. Mass transfer limitation when considering large sample sizes and high energy cost involved due to continuous stirring were highlighted in the listed studies. This poses a serious challenge when considering the scale up of clathrate process for storing hydrogen commercially. As seen from the literature data (Table 4), potential exists (reported based on small scale measurement), and the immediate focus should be to scale-up one of the potential method and study the kinetics. Several works in the literature have been promising in employing a fixed bed configuration with silica gel, silica sand or hollow silica as medium to enhance the kinetics of hydrate formation particularly for the capture of carbon dioxide and methane storage [173–179]. While for the case of hydrogen storage as clathrates such an approach might not be useful unless the medium used has a very low density. One such medium that has very low density is polyurethane foam. Babu et al. [180] recently reported that polyurethane foam as a medium can significantly enhance the kinetics of hydrate formation for the clathrate process. Other possible methods to enhance the kinetics of hydrogen hydrate formation could be to use “dry water” [181,182] or aluminum foam [183,184] or multi-wall carbon nanotubes [185,186] which have been reported to enhance methane hydrate kinetics. Additionally, H<sub>2</sub> being one of the lightest material known, it would be futile to expect that a physical adsorption can happen at temperature closer to zero degrees (low thermal motion for H<sub>2</sub> is needed to bind through some physical bonds). Probably the best approach would be to work at temperatures lower than zero degree, and focus on improving the kinetics by better mass transfer/heat transfer protocol. Challenges encountered during scaling up of the processes that report high hydrogen storage using small sample size are not known and have to be explored for improving and applying such processes for storing hydrogen on a large scale.

## 14. Conclusion

There have been considerable research efforts put forth in storing hydrogen as clathrates in the past few years. Quite a number of new promoters for storing hydrogen in the form of hydrates have been reported. Modifying the hydrate formation procedure for increasing the hydrogen storage capacity has been attempted. Kinetic studies focusing on development of clathrate process on a large scale were also pursued. Novel hybrid materials that use simultaneously two processes for hydrogen storage (hydrogen hydrates along with adsorption) have been identified and evaluated. Some of the major challenges that need to be addressed are to increase the storage capacity of hydrogen in clathrates when employing promoters and to overcome the kinetic challenges at the macro level for process scale up. There is scope of improvement in all the listed areas and we believe it will be possible to develop the clathrate process for hydrogen storage on a commercial scale in the foreseeable future.

## Acknowledgements

The financial support from the Ministry of Education's AcRF Tier 1 (R-279-000-386-112) and the National University of Singapore is

greatly appreciated. R.K. would like to thank the Council of Scientific and Industrial Research (CSIR) for the financial support (CSC-0102). P.L. and R.K. would like to specially thank Dr. John Ripmeester and Professor Peter Englezos for the valuable discussions they had with them over the years. The authors thank John Ripmeester and National Research Council of Canada, Ottawa for permitting the use of the facilities for obtaining the data presented in Fig. 10.

## References

- [1] Struzhkin VV, Militzer B, Mao WL, Mao HK, Hemley RJ. Hydrogen storage in molecular clathrates. *Chem Rev* 2007;107:4133–51.
- [2] Wang LF, Yang RT. New sorbents for hydrogen storage by hydrogen spillover – a review. *Energy Environ Sci* 2008;1:268–79.
- [3] Thomas KM. Adsorption and desorption of hydrogen on metal-organic framework materials for storage applications: comparison with other nanoporous materials. *Dalton Trans* 2009:1487–505.
- [4] Züttel A. Materials for hydrogen storage. *Mater Today* 2003;6:24–33.
- [5] Graetz J. New approaches to hydrogen storage. *Chem Soc Rev* 2009;38:73–82.
- [6] Biniwale RB, Rayalu S, Devotta S, Ichikawa M. Chemical hydrides: a solution to high capacity hydrogen storage and supply. *Int J Hydrogen Energy* 2008;33:360–5.
- [7] Schuth F, Bogdanovic B, Felderhoff M. Light metal hydrides and complex hydrides for hydrogen storage. *Chem Commun* 2004:2249–58.
- [8] Thomas KM. Hydrogen adsorption and storage on porous materials. *Catal Today* 2007;120:389–98.
- [9] Pumer M. Graphene-based nanomaterials for energy storage. *Energy Environ Sci* 2011;4:668–74.
- [10] Zhao D, Yuan D, Zhou H-C. The current status of hydrogen storage in metal-organic frameworks. *Energy Environ Sci* 2008;1:222–35.
- [11] Cheng H-M, Yang Q-H, Liu C. Hydrogen storage in carbon nanotubes. *Carbon* 2001;39:1447–54.
- [12] Darkrim FL, Malbrunot P, Tartaglia GP. Review of hydrogen storage by adsorption in carbon nanotubes. *Int J Hydrogen Energy* 2002;27:193–202.
- [13] Lee SM, Lee YH. Hydrogen storage in single-walled carbon nanotubes. *Appl Phys Lett* 2000;76:2877–9.
- [14] Wang L, Lee K, Sun Y-Y, Lucking M, Chen Z, Zhao JJ, et al. Graphene oxide as an ideal substrate for hydrogen storage. *ACS Nano* 2009;3:2995–3000.
- [15] Dillon AC, Heben MJ. Hydrogen storage using carbon adsorbents: past, present and future. *Appl Phys A* 2001;72:133–42.
- [16] Chambers A, Park C, Baker RTK, Rodriguez NM. Hydrogen storage in graphite nanofibers. *J Phys Chem B* 1998;102:4253–6.
- [17] Schuth F. Technology: hydrogen and hydrates. *Nature* 2005;434:712–3.
- [18] Hu YH, Ruckenstein E. Clathrate hydrogen hydrate – a promising material for hydrogen storage. *Angew Chem Int Ed Engl* 2006;45:2011–3.
- [19] Patchkovskii S, Tse JS. Thermodynamic stability of hydrogen clathrates. *Proc Natl Acad Sci* 2003;100:14645–50.
- [20] Mao WL, Mao HK, Goncharov AF, Struzhkin VV, Guo Q, Hu J, et al. Hydrogen clusters in clathrate hydrate. *Science* 2002;297:2247–9.
- [21] Sloan ED, Koh CA. Clathrate hydrates of natural gases. CRC Press; 2008.
- [22] Englezos P. Clathrate hydrates. *Ind Eng Chem Res* 1993;32:1251–74.
- [23] Davidson DW. Gas hydrates. In: Water: a comprehensive treatise. New York: Plenum Press; 1973.
- [24] Buffett BA. Clathrate hydrates; 2000. p. 477–507.
- [25] Hammerschmidt EG. Formation of gas hydrates in natural gas transmission lines. *Ind Eng Chem* 1934;26:851–5.
- [26] Makogon YF, Trebin FA, Trofimuk AA, Tsarev VP, Cherskii N. Detection of a pool of natural gas in a solid (hydrated gas) state. *Dokl Akad Nauk SSSR* 1971;196:203–6.
- [27] Makogon YF. Hydrates of natural gas. Tulsa: Penn Well Books; 1981.
- [28] Kvenvolden K. Potential effects of gas hydrate on human welfare. *Proc Natl Acad Sci USA* 1999;96:3420.
- [29] Rempel AW, Buffett BA. Formation and accumulation of gas hydrate in porous media. *J Geophys Res B: Solid Earth* 1997;102:10151–64.
- [30] Zatsepina OY, Buffett BA. Phase equilibrium of gas hydrate: implications for the formation of hydrate in the deep sea floor. *Geophys Res Lett* 1997;24:1567–70.
- [31] Wang Y, Li XS, Li G, Zhang Y, Li B, Feng JC. A three-dimensional study on methane hydrate decomposition with different methods using five-spot well. *Appl Energy* 2013;112:83–92.
- [32] Wang Y, Li XS, Li G, Zhang Y, Li B, Chen ZY. Experimental investigation into methane hydrate production during three-dimensional thermal stimulation with five-spot well system. *Appl Energy* 2013;110:90–7.
- [33] Li XS, Yang B, Duan LP, Li G, Huang NS, Zhang Y. Experimental study on gas production from methane hydrate in porous media by SAGD method. *Appl Energy* 2013;112:1233–40.
- [34] Mori YH. Recent advances in hydrate-based technologies for natural gas storage – a review. *J Chem Ind Eng (China)* 2003;54:1–17.
- [35] Gudmundsson JS, Parlaktuna M, Khokhar AA. Storing natural-gas as frozen hydrate. *SPE Prod Fac* 1994;9:69–73.
- [36] Duc NH, Chauvy F, Herri J-M. CO<sub>2</sub> capture by hydrate crystallization – a potential solution for gas emission of steelmaking industry. *Energy Convers Manage* 2007;48:1313–22.

- [37] Kang SP, Lee H. Recovery of CO<sub>2</sub> from flue gas using gas hydrate: thermodynamic verification through phase equilibrium measurements. *Environ Sci Technol* 2000;34:4397–400.
- [38] Linga P, Kumar R, Englezos P. The clathrate hydrate process for post and pre-combustion capture of carbon dioxide. *J Hazard Mater* 2007;149:625–9.
- [39] Lee S, Liang LY, Riestenberg D, West OR, Tsouris C, Adams E. CO<sub>2</sub> hydrate composite for ocean carbon sequestration. *Environ Sci Technol* 2003;37:3701–8.
- [40] Babu P, Kumar R, Linga P. Pre-combustion capture of carbon dioxide in a fixed bed reactor using the clathrate hydrate process. *Energy* 2013;50:364–73.
- [41] Tajima H, Yamasaki A, Kiyono F. Energy consumption estimation for greenhouse gas separation processes by clathrate hydrate formation. *Energy* 2004;29:1713–29.
- [42] Li XS, Xu CG, Chen ZY, Wu HJ. Tetra-n-butyl ammonium bromide semi-clathrate hydrate process for post-combustion capture of carbon dioxide in the presence of dodecyl trimethyl ammonium chloride. *Energy* 2010;35:3902–8.
- [43] Brewer PG, Friederich C, Peltzer ET, Orr FM. Direct experiments on the ocean disposal of fossil fuel CO<sub>2</sub>. *Science* 1999;284:943–5.
- [44] Fournaison L, Delahaye A, Chatti I, Petitot JP. CO<sub>2</sub> hydrates in refrigeration processes. *Ind Eng Chem Res* 2004;43:6521–6.
- [45] Xie Y, Li G, Liu D, Liu N, Qi Y, Liang D, et al. Experimental study on a small scale of gas hydrate cold storage apparatus. *Appl Energy* 2010;87:3340–6.
- [46] Obara S, Yamada T, Matsumura K, Takahashi S, Kawai M, Rengarajan B. Operational planning of an engine generator using a high pressure working fluid composed of CO<sub>2</sub> hydrate. *Appl Energy* 2011;88:4733–41.
- [47] Park K-N, Hong SY, Lee JW, Kang KC, Lee YC, Ha M-G, et al. A new apparatus for seawater desalination by gas hydrate process and removal characteristics of dissolved minerals (Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, B<sup>3+</sup>). *Desalination* 2011;274:91–6.
- [48] Cha I, Lee S, Lee JD, Lee GW, Seo Y. Separation of SF<sub>6</sub> from gas mixtures using gas hydrate formation. *Environ Sci Technol* 2010;44:6117–22.
- [49] Seo Y, Lee H. A new hydrate-based recovery process for removing chlorinated hydrocarbons from aqueous solutions. *Environ Sci Technol* 2001;35:3386–90.
- [50] Seo Y, Tajima H, Yamasaki A, Takeya S, Ebinuma T, Kiyono F. A new method for separating HFC-134a from gas mixtures using clathrate hydrate formation. *Environ Sci Technol* 2004;38:4635–9.
- [51] Strobel TA, Koh CA, Sloan ED. Hydrogen storage properties of clathrate hydrate materials. *Fluid Phase Equilib* 2007;261:382–9.
- [52] Strobel TA, Hester KC, Koh CA, Sum AK, Sloan ED. Properties of the clathrates of hydrogen and developments in their applicability for hydrogen storage. *Chem Phys Lett* 2009;478:97–109.
- [53] Alavi S, Ripmeester JA. Hydrogen-gas migration through clathrate hydrate cages. *Angew Chem Int Ed* 2007;46:6102–5.
- [54] Alavi S, Ripmeester JA, Klug DD. Molecular-dynamics study of structure II hydrogen clathrates. *J Chem Phys* 2005:123.
- [55] Alavi S, Ripmeester JA, Klug DD. Molecular-dynamics simulations of binary structure II hydrogen and tetrahydrofuran clathrates. *J Chem Phys* 2006:124.
- [56] Lokshin KA, Zhao Y, He D, Mao WL, Mao H-K, Hemley RJ, et al. Structure and dynamics of hydrogen molecules in the novel clathrate hydrate by high pressure neutron diffraction. *Phys Rev Lett* 2004;93:125503.
- [57] Patchkovskii S, Tse JS. Thermodynamic stability of hydrogen clathrates. *Proc Natl Acad Sci USA* 2003;100:14645–50.
- [58] Sluiter MHF, Belosludov RV, Jain A, Belosludov VR, Adachi H, Kawazoe Y, et al. Ab initio study of hydrogen hydrate clathrates for hydrogen storage within the ITBL environment. *Lect Notes Comput Sci* 2003;2858:330–41.
- [59] Sluiter MHF, Adachi H, Belosludov RV, Belosludov VR, Kawazoe Y. Ab initio study of hydrogen storage in hydrogen hydrate clathrates. *Mater Trans* 2004;45:1452–4.
- [60] Cao H, English NJ, MacElroy JMD. Diffusive hydrogen inter-cage migration in hydrogen and hydrogen-tetrahydrofuran clathrate hydrates. *J Chem Phys* 2013:138.
- [61] Zhang J, Kuo J-L, Iitaka T. First principles molecular dynamics study of filled ice hydrogen hydrate. *J Chem Phys* 2012;137:084505–84507.
- [62] Willow SY, Xantheas SS. Enhancement of hydrogen storage capacity in hydrate lattices. *Chem Phys Lett* 2012;525–526:13–8.
- [63] Pefoute E, Kemner E, Soetens JC, Russina M, Desmedt A. Diffusive motions of molecular hydrogen confined in THF clathrate hydrate. *J Phys Chem C* 2012;116:16823–9.
- [64] Mondal S, Ghosh S, Chattaraj PK. A molecular dynamics study on sl hydrogen hydrate. *J Mol Model* 2012:1–6.
- [65] Gorman PD, English NJ, MacElroy JMD. Dynamical cage behaviour and hydrogen migration in hydrogen and hydrogen-tetrahydrofuran clathrate hydrates. *J Chem Phys* 2012;136:044506–44507.
- [66] Alavi S, Ripmeester JA. Effect of small cage guests on hydrogen bonding of tetrahydrofuran in binary structure II clathrate hydrates. *J Chem Phys* 2012;137:054712–54717.
- [67] Wang JW, Lu HL, Ripmeester JA, Becker U. Molecular-dynamics and first-principles calculations of Raman spectra and molecular and electronic structure of hydrogen clusters in hydrogen clathrate hydrate. *J Phys Chem C* 2010;114:21042–50.
- [68] Papadimitriou NI, Tsimpanogiannis IN, Stubos AK. Computational approach to study hydrogen storage in clathrate hydrates. *Colloids Surf, A* 2010;357:67–73.
- [69] Nakayama T, Koga K, Tanaka H. Augmented stability of hydrogen clathrate hydrates by weakly polar molecules. *J Chem Phys* 2009:131.
- [70] Chun D-H, Lee T-Y. Molecular simulation of cage occupancy and selectivity of binary THF–H<sub>2</sub> sl hydrate. *Mol Simul* 2008;34:837–44.
- [71] Alavi S, Ripmeester JA, Klug DD. Molecular dynamics simulations of binary structure II hydrogen and methyl-tert-butylether clathrate hydrates. *J Chem Phys* 2006:124.
- [72] Vos WL, Finger LW, Hemley RJ, Mao HK. Novel H<sub>2</sub>–H<sub>2</sub>O clathrates at high pressures. *Phys Rev Lett* 1993;71:3150–3.
- [73] Lunine J, Stevenson D. Thermodynamics of clathrate hydrate at low and high pressures with application to the outer solar system. *Astrophys J Suppl Ser* 1985;58:493–531.
- [74] Dyadin YA, Larionov EG, Manakov AY, Zhurko FV, Aladko EY, Mikina TV, et al. Clathrate hydrates of hydrogen and neon. *Mendelev Commun* 1999:209–10.
- [75] Mao WL, Mao HK. Hydrogen storage in molecular compounds. *Proc Natl Acad Sci USA* 2004;101:708–10.
- [76] Lokshin KA, Zhao YS. Fast synthesis method and phase diagram of hydrogen clathrate hydrate. *Appl Phys Lett* 2006:88.
- [77] Kumar R, Klug DD, Ratcliffe CI, Tulk CA, Ripmeester JA. Low-pressure synthesis and characterization of hydrogen-filled Ice Ic. *Angew Chem* 2013;125:1571–4.
- [78] Lee H, Lee JW, Kim DY, Park J, Seo YT, Zeng H, et al. Tuning clathrate hydrates for hydrogen storage. *Nature* 2005;434:743–6.
- [79] Kumar R, Englezos P, Moudrakovski I, Ripmeester JA. Structure and composition of CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> hydrate in relation to simultaneous CO<sub>2</sub> capture and H<sub>2</sub> production. *AIChE J* 2009;55:1584–94.
- [80] Strobel TA. On some clathrates of hydrogen. Golden, Colorado: Colorado School of Mines; 2008.
- [81] Udachin KA, Lipkowsky J, Tkacz M. Double clathrate hydrates with helium and hydrogen. *Supramol Chem* 1994;3:181–3.
- [82] Florusse LJ, Peters CJ, Schoonman J, Hester KC, Koh CA, Dec SF, et al. Stable low-pressure hydrogen clusters stored in a binary clathrate hydrate. *Science* 2004;306:469–71.
- [83] Strobel TA, Taylor CJ, Hester KC, Dec SF, Koh CA, Miller KT, et al. Molecular hydrogen storage in binary THF–H<sub>2</sub> clathrate hydrates. *J Phys Chem B* 2006;110:17121–5.
- [84] Shin W, Park S, Ro H, Koh D-Y, Seol J, Lee H. Phase equilibrium measurements and the tuning behavior of new sl clathrate hydrates. *J Chem Thermodyn* 2012;44:20–5.
- [85] Seo Y, Lee J-W, Kumar R, Moudrakovski IL, Lee H, Ripmeester JA. Tuning the composition of guest molecules in clathrate hydrates: NMR identification and its significance to gas storage. *Chem Asian J* 2009;4:1266–74.
- [86] Koh D-Y, Kang H, Lee H. Multiple guest occupancy in clathrate hydrates and its significance to hydrogen storage. *Chem Commun* 2013;49:6782–4.
- [87] Kim D-Y, Park J, Lee J-W, Ripmeester JA, Lee H. Critical guest concentration and complete tuning pattern appearing in the binary clathrate hydrates. *J Am Chem Soc* 2006;128:15360–1.
- [88] Sugahara T, Haag JC, Prasad PSR, Warntjes AA, Sloan ED, Sum AK, et al. Increasing hydrogen storage capacity using tetrahydrofuran. *J Am Chem Soc* 2009;131:14616–7.
- [89] Mulder FM, Wagemaker M, van Eijck L, Kearley GJ. Hydrogen in porous tetrahydrofuran clathrate hydrate. *ChemPhysChem* 2008;9:1331–7.
- [90] Hashimoto S, Sugahara T, Sato H, Ohgaki K. Thermodynamic stability of H<sub>2</sub> + tetrahydrofuran mixed gas hydrate in nonstoichiometric aqueous solutions. *J Chem Eng Data* 2007;52:517–20.
- [91] Anderson R, Chapoy A, Tohidi B. Phase relations and binary clathrate hydrate formation in the system H<sub>2</sub>–THF–H<sub>2</sub>O. *Langmuir* 2007;23:3440–4.
- [92] Ogata K, Hashimoto S, Sugahara T, Moritoki M, Sato H, Ohgaki K. Storage capacity of hydrogen in tetrahydrofuran hydrate. *Chem Eng Sci* 2008;63:5714–8.
- [93] Saha D, Deng SG. Accelerated formation of THF–H<sub>2</sub> clathrate hydrate in porous media. *Langmuir* 2010;26:8414–8.
- [94] Talyzin A. Feasibility of H<sub>2</sub>H<sub>2</sub>–THF–H<sub>2</sub>O/H<sub>2</sub>O clathrate hydrates for hydrogen storage applications. *Int J Hydrogen Energy* 2008;33:111–5.
- [95] Grim RG, Kerkar PB, Sloan ED, Koh CA, Sum AK. Rapid hydrogen hydrate growth from non-stoichiometric tuning mixtures during liquid nitrogen quenching. *J Chem Phys* 2012:136.
- [96] Di Profio P, Arca S, Rossi F, Filippini M. Comparison of hydrogen hydrates with existing hydrogen storage technologies: energetic and economic evaluations. *Int J Hydrogen Energy* 2009;34:9173–80.
- [97] Arca S, Di profio P, Germani R, Savelli G. Method for the production of binary clathrate hydrates of hydrogen. WO patent 2,008,142,560; 2008.
- [98] Strobel TA, Koh CA, Sloan ED. Thermodynamic predictions of various tetrahydrofuran and hydrogen clathrate hydrates. *Fluid Phase Equilib* 2009;280:61–7.
- [99] Rovetto LJ, Shoonman J, Peters CJ. Phase behavior of low pressure hydrogen clathrate hydrate. In: *Proceedings of 5th international conference on gas hydrates*; 2005. p. 1644.
- [100] Nagai Y, Yoshioka H, Ota M, Sato Y, Inomata H, Smith RL, et al. Binary hydrogen–tetrahydrofuran clathrate hydrate formation kinetics and models. *AIChE J* 2008;54:3007–16.
- [101] Veluswamy HP, Linga P. Macroscopic kinetics of hydrate formation of mixed hydrates of hydrogen/tetrahydrofuran for hydrogen storage. *Int J Hydrogen Energy* 2013;38:4587–96.
- [102] Yoshioka H, Ota M, Sato Y, Watanabe M, Inomata H, Smith RL, et al. Decomposition kinetics and recycle of binary hydrogen–tetrahydrofuran clathrate hydrate. *AIChE J* 2011;57:265–72.

- [103] Sugahara T, Haag JC, Warntjes AA, Prasad PSR, Sloan ED, Koh CA, et al. Large-cage occupancies of hydrogen in binary clathrate hydrates dependent on pressures and guest concentrations. *J Phys Chem C* 2010;114:15218–22.
- [104] Zhang JS, Lee JW. Equilibrium of hydrogen plus cyclopentane and carbon dioxide plus cyclopentane binary hydrates. *J Chem Eng Data* 2009;54:659–61.
- [105] Komatsu H, Yoshioka H, Ota M, Sato Y, Watanabe M, Smith RL, et al. Phase equilibrium measurements of hydrogen–tetrahydrofuran and hydrogen–cyclopentane binary clathrate hydrate systems. *J Chem Eng Data* 2010;55:2214–8.
- [106] Du JW, Liang DQ, Li DL, Li XJ. Experimental determination of the equilibrium conditions of binary gas hydrates of cyclopentane plus oxygen, cyclopentane plus nitrogen, and cyclopentane plus hydrogen. *Ind Eng Chem Res* 2010;49:11797–800.
- [107] Deng C, Liang D, Li D. Formation of cyclopentane–hydrogen clathrate hydrates. *Shiyong Huagong/Petrochem Technol* 2009;38:951–6.
- [108] Strobel TA, Hester KC, Sloan ED, Koh CA. A hydrogen clathrate hydrate with cyclohexanone: structure and stability. *J Am Chem Soc* 2007;129:9544.
- [109] Tsuda T, Ogata K, Hashimoto S, Sugahara T, Moritoki M, Ohgaki K. Storage capacity of hydrogen in tetrahydrothiophene and furan clathrate hydrates. *Chem Eng Sci* 2009;64:4150–4.
- [110] Trueba AT, Rovetto LJ, Florusse LJ, Kroon MC, Peters CJ. Phase equilibrium measurements of structure II clathrate hydrates of hydrogen with various promoters. *Fluid Phase Equilib* 2011;307:6–10.
- [111] Yoon J-H, Han J, Park J, Choi S, Yeon S-H, Lee H. Spectroscopic identification, thermodynamic stability and molecular composition of hydrogen and 1,4-dioxane binary clathrate hydrate. *J Phys Chem Solids* 2008;69:1432–5.
- [112] Kawamura T, Takeya S, Ohtake M, Yamamoto Y. Enclathration of hydrogen by organic-compound clathrate hydrates. *Chem Eng Sci* 2011;66:2417–20.
- [113] Zhang SX, Chen GJ, Ma CF, Yang LY, Guo TM. Hydrate formation of hydrogen plus hydrocarbon gas mixtures. *J Chem Eng Data* 2000;45:908–11.
- [114] Park J, Lee H. Spectroscopic evidences of the double hydrogen hydrates stabilized with ethane and propane. *Korean J Chem Eng* 2007;24:624–7.
- [115] Skiba SS, Larionov EG, Manakov AY, Kolesov BA, Ancharov AI, Aladko EY. Double clathrate hydrate of propane and hydrogen. *J Incl Phenom Macrocycl Chem* 2009;63:383–6.
- [116] Abbondondola JA, Fleischer EB, Janda KC. Comparative study of hydrogen, argon, and xenon uptake into a propane hydrate. *AIChE J* 2010;56:2734–41.
- [117] Park DH, Lee BR, Sa JH, Lee KH. Gas-hydrate phase equilibrium for mixtures of sulfur hexafluoride and hydrogen. *J Chem Eng Data* 2012;57:1433–6.
- [118] Fowler DL, Loebenstein WV, Pall DB, Kraus CA. Some unusual hydrates of quaternary ammonium salts. *J Am Chem Soc* 1940;62:1140–2.
- [119] Hashimoto S, Murayama S, Sugahara T, Sato H, Ohgaki K. Thermodynamic and Raman spectroscopic studies on and tetra-n-butyl ammonium mixtures containing gas hydrates. *Chem Eng Sci* 2006;61:7884–8.
- [120] Arjmandi M, Chapoy A, Tohidi B. Equilibrium data of hydrogen, methane, nitrogen, carbon dioxide, and natural gas in semi-clathrate hydrates of tetrabutyl ammonium bromide. *J Chem Eng Data* 2007;52:2153–8.
- [121] Shimada W, Ebinuma T, Oyama H, Kamata Y, Takeya S, Uchida T, et al. Separation of gas molecule using tetra-n-butyl ammonium bromide semi-clathrate hydrate crystals. *Jpn J Appl Phys* 2003;42:129–L31.
- [122] Shimada W, Ebinuma T, Oyama H, Kamata Y, Narita H. Free-growth forms and growth kinetics of tetra-n-butyl ammonium bromide semi-clathrate hydrate crystals. *J Cryst Growth* 2005;274:246–50.
- [123] Oyama H, Shimada W, Ebinuma T, Kamata Y, Takeya S, Uchida T, et al. Phase diagram, latent heat, and specific heat of TBAB semiclathrate hydrate crystals. *Fluid Phase Equilib* 2005;234:131–5.
- [124] Hashimoto S, Sugahara T, Moritoki M, Sato H, Ohgaki K. Thermodynamic stability of hydrogen tetra-n-butyl ammonium bromide mixed gas hydrate in nonstoichiometric aqueous solutions. *Chem Eng Sci* 2008;63:1092–7.
- [125] Mohammadi AH, Eslamianesh A, Belandria V, Richon D. Phase equilibria of semiclathrate hydrates of CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, or H<sub>2</sub>+ tetra-n-butylammonium bromide aqueous solution. *J Chem Eng Data* 2011;56:3855–65.
- [126] Hashimoto S, Tsuda T, Ogata K, Sugahara T, Inoue Y, Ohgaki K. Thermodynamic properties of hydrogen + tetra-n-butyl ammonium bromide semi-clathrate hydrate. *J Thermodyn* 2010;20:1–5.
- [127] Chapoy A, Gholinezhad J, Tohidi B. Experimental clathrate dissociations for the hydrogen plus water and hydrogen plus tetrabutylammonium bromide plus water systems. *J Chem Eng Data* 2010;55:5323–7.
- [128] Trueba AT, Radović IR, Zevenbergen JF, Kroon MC, Peters CJ. Kinetics measurements and in situ Raman spectroscopy of formation of hydrogen–tetrabutylammonium bromide semi-hydrates. *Int J Hydrogen Energy* 2012;37:5790–7.
- [129] Sakamoto J, Hashimoto S, Tsuda T, Sugahara T, Inoue Y, Ohgaki K. Thermodynamic and Raman spectroscopic studies on hydrogen + tetra-n-butyl ammonium fluoride semi-clathrate hydrates. *Chem Eng Sci* 2008;63:5789–94.
- [130] Trueba AT, Radović IR, Zevenbergen JF, Peters CJ, Kroon MC. Kinetic measurements and in situ Raman spectroscopy study of the formation of TBAB semi-hydrates with hydrogen and carbon dioxide. *Int J Hydrogen Energy* 2013;38:7326–34.
- [131] Aladko LS, Dyadin YA, Rodionova TV, Terekhova IS. Clathrate hydrates of tetrabutylammonium and tetraisoamylammonium halides. *J Struct Chem* 2002;43:990–4.
- [132] Makino T, Yamamoto T, Nagata K, Sakamoto H, Hashimoto S, Sugahara T, et al. Thermodynamic stabilities of tetra-n-butyl ammonium chloride + H(2), N(2), CH(4), CO(2), or C(2)H(6) semiclathrate hydrate systems. *J Chem Eng Data* 2010;55:839–41.
- [133] Fujisawa Y, Tsuda T, Hashimoto S, Sugahara T, Ohgaki K. Thermodynamic stability of hydrogen + tetra-n-butyl phosphonium bromide mixed semiclathrate hydrate. *Chem Eng Sci* 2012;68:660–2.
- [134] Deschamps J, Dalmazzone D. Hydrogen storage in semiclathrate hydrates of tetrabutyl ammonium chloride and tetrabutyl phosphonium bromide. *J Chem Eng Data* 2010;55:3395–9.
- [135] Du JW, Wang LG, Liang DQ, Li DL. Phase equilibria and dissociation enthalpies of hydrogen semi-clathrate hydrate with tetrabutyl ammonium nitrate. *J Chem Eng Data* 2012;57:603–9.
- [136] Ogata K, Tsuda T, Amano S, Hashimoto S, Sugahara T, Ohgaki K. Hydrogen storage in trimethylamine hydrate: thermodynamic stability and hydrogen storage capacity of hydrogen + trimethylamine mixed semi-clathrate hydrate. *Chem Eng Sci* 2010;65:1616–20.
- [137] Aladko EY, Larionov EG, Manakov AY, Terekhova IS. Double clathrate hydrates of cross-linked tetrabutylammonium polyacrylate and noble gases at high pressures. *J Incl Phenom Macrocycl Chem* 2010;67:13–8.
- [138] Skiba SS, Terekhova IS, Larionov EG, Manakov AY. Incorporation of gas molecules into the frameworks of clathrate hydrates of ion-exchange resins in tetraalkylammonium form. *Mendelev Commun* 2008;18:126–7.
- [139] Koh DY, Kang H, Park J, Shin W, Lee H. Atomic hydrogen production from semi-clathrate hydrates. *J Am Chem Soc* 2012;134:5560–2.
- [140] Ripmeester JA, Tse JS, Ratcliffe CI, Powell BM. A new clathrate hydrate structure. *Nature* 1987;325:135–6.
- [141] Strobel TA, Koh CA, Sloan ED. Water cavities of sH clathrate hydrate stabilized by molecular hydrogen. *J Phys Chem B* 2008;112:1885–7.
- [142] Duarte ARC, Shariati A, Rovetto LJ, Peters CJ. Water cavities of sH clathrate hydrate stabilized by molecular hydrogen: phase equilibrium measurements. *J Phys Chem B* 2008;112:1888–9.
- [143] Duarte ARC, Shariati A, Peters CJ. Phase equilibrium measurements of structure sH hydrogen clathrate hydrates with various promoters. *J Chem Eng Data* 2009;54:1628–32.
- [144] Martin A, Peters CJ. Hydrogen storage in sH clathrate hydrates: thermodynamic model. *J Phys Chem B* 2009;113:7558–63.
- [145] Babaei S, Hashemi H, Javanmardi J, Eslamianesh A, Mohammadi AH. Thermodynamic model for prediction of phase equilibria of clathrate hydrates of hydrogen with different alkanes, alkenes, alkynes, cycloalkanes or cycloalkene. *Fluid Phase Equilib* 2012;336:71–8.
- [146] Valdes A, Kroes GJ. Theoretical investigation of two H-2 molecules inside the cages of the structure H clathrate hydrate. *J Phys Chem C* 2012;116:21664–72.
- [147] Kim DY, Lee H. Spectroscopic identification of the mixed hydrogen and carbon dioxide clathrate hydrate. *J Am Chem Soc* 2005;127:9996–7.
- [148] Grim RG, Kerkar PB, Shebouch M, Arias M, Sloan ED, Koh CA, et al. Synthesis and characterization of sl clathrate hydrates containing hydrogen. *J Phys Chem C* 2012;116:18557–63.
- [149] Prasad PSR, Sugahara T, Sum AK, Sloan ED, Koh CA. Hydrogen storage in double clathrates with tert-butylamine. *J Phys Chem A* 2009;113:6540–3.
- [150] Du J-W, Liang D-Q, Dai X-X, Li D-L, Li X-J. Hydrate phase equilibrium for the (hydrogen + tert-butylamine + water) system. *J Chem Thermodyn* 2011;43:617–21.
- [151] Yagi M. Method for storing hydrogen, hydrogen clathrate compound and production method thereof. Google Patents; 2007.
- [152] Neiner D, Okamoto NL, Condon CL, Ramasse QM, Yu P, Browning ND, et al. Hydrogen encapsulation in a silicon clathrate type I structure: Na-5.5(H-2)(2.15)Si-46: synthesis and characterization. *J Am Chem Soc* 2007;129:13857–62.
- [153] Neiner D, Okamoto NL, Yu P, Leonard S, Condon CL, Toney MF, et al. Synthesis and characterization of K8-x(H-2)(y)Si-46. *Inorg Chem* 2010;49:815–22.
- [154] Van den Berg AWC. Opportunities and limitations of hydrogen storage in zeolitic clathrates; 2006.
- [155] Su F, Bray CL, Tan B, Cooper AI. Rapid and reversible hydrogen storage in clathrate hydrates using emulsion-templated polymers. *Adv Mater* 2008;20:2663.
- [156] Su FB, Bray CL, Carter BO, Overend G, Cropper C, Iggo JA, et al. Reversible hydrogen storage in hydrogel clathrate hydrates. *Adv Mater* 2009;21:2382.
- [157] Strobel TA, Kim Y, Andrews GS, Ferrell JR, Koh CA, Herring AM, et al. Chemical-clathrate hybrid hydrogen storage: storage in both guest and host. *J Am Chem Soc* 2008;130:14975.
- [158] Shin K, Kim Y, Strobel TA, Prasad PSR, Sugahara T, Lee H, et al. Tetra-n-butylammonium borohydride semiclathrate: a hybrid material for hydrogen storage. *J Phys Chem A* 2009;113:6415–8.
- [159] Han KW, Lee Y-J, Jang JS, Jeon T-I, Park J, Kawamura T, et al. Fast and reversible hydrogen storage in channel cages of hydroquinone clathrate. *Chem Phys Lett* 2012;546:120–4.
- [160] Saha D, Deng SG. Enhanced hydrogen adsorption in ordered mesoporous carbon through clathrate formation. *Int J Hydrogen Energy* 2009;34:8583–8.
- [161] Hester KC, Strobel TA, Sloan ED, Koh CA, Huq A, Schultz AJ. Molecular hydrogen occupancy in binary THF–H<sub>2</sub> clathrate hydrates by high resolution neutron diffraction. *J Phys Chem B* 2006;110:14024–7.
- [162] Bonhoeffer KF, Harteck P. Experimente über Para- und Orthowasserstoff. *Naturwissenschaften* 1929;17:182.
- [163] Senadheera L, Conradi MS. Rotation and diffusion of H<sub>2</sub> in hydrogen–ice clathrate by 1H NMR. *J Phys Chem B* 2007;111:12097–102.



- [164] Lu HL, Wang JW, Liu CL, Ratcliffe CI, Becker U, Kumar R, et al. Multiple H-2 occupancy of cages of clathrate hydrate under mild conditions. *J Am Chem Soc* 2012;134:9160–2.
- [165] Strobel TA, Sloan ED, Koh CA. Raman spectroscopic studies of hydrogen clathrate hydrates. *J Chem Phys* 2009;130.
- [166] Lee HJ, Lee JD, Linga P, Englezos P, Kim YS, Lee MS, et al. Gas hydrate formation process for pre-combustion capture of carbon dioxide. *Energy* 2010;35:2729–33.
- [167] Linga P, Adeyemo A, Englezos P. Medium-pressure clathrate hydrate/membrane hybrid process for postcombustion capture of carbon dioxide. *Environ Sci Technol* 2008;42:315–20.
- [168] Li X, Xia Z, Chen Z, Yan K, Li G, Wu H-j. Gas hydrate formation process for capture of carbon dioxide from fuel gas mixture. *Ind Eng Chem Res* 2010;49:11614–9.
- [169] Chatti I, Delahaye A, Fournaison L, Petitot J-P. Benefits and drawbacks of clathrate hydrates: a review of their areas of interest. *Energy Convers Manage* 2005;46:1333–43.
- [170] Nakayama T, Tomura S, Ozaki M, Ohmura R, Mori YH. Engineering investigation of hydrogen storage in the form of clathrate hydrates: conceptual design of hydrate production plants. *Energy Fuels* 2010;24:2576–88.
- [171] Shibata T, Yamachi H, Ohmura R, Mori YH. Engineering investigation of hydrogen storage in the form of a clathrate hydrate: conceptual designs of underground hydrate-storage silos. *Int J Hydrogen Energy* 2012;37:7612–23.
- [172] Hythane Fuel. Hythane Company. <<http://hythane.net/hythane-fuel>>.
- [173] Yang M, Song Y, Jiang L, Zhu N, Liu Y, Zhao Y, et al. CO<sub>2</sub> hydrate formation and dissociation in cooled porous media: a potential technology for CO<sub>2</sub> capture and storage. *Environ Sci Technol* 2013;47:9739–46.
- [174] Seo Y-T, Moudrakovski IL, Ripmeester JA, Lee J-W, Lee H. Efficient recovery of CO<sub>2</sub> from flue gas by clathrate hydrate formation in porous silica gels. *Environ Sci Technol* 2005;39:2315–9.
- [175] Prasad PSR, Chari VD, Sharma DVSGK, Murthy SR. Effect of silica particles on the stability of methane hydrates. *Fluid Phase Equilib* 2012;318:110–4.
- [176] Linga P, Daraboina N, Ripmeester JA, Englezos P. Enhanced rate of gas hydrate formation in a fixed bed column filled with sand compared to a stirred vessel. *Chem Eng Sci* 2012;68:617–23.
- [177] Kumar A, Sakpal T, Linga P, Kumar R. Influence of contact medium and surfactants on carbon dioxide clathrate hydrate kinetics. *Fuel* 2013;105:664–71.
- [178] Kang S-P, Lee J-W. Kinetic behaviors of CO<sub>2</sub> hydrates in porous media and effect of kinetic promoter on the formation kinetics. *Chem Eng Sci* 2010;65:1840–5.
- [179] Babu P, Kumar R, Linga P. Medium pressure hydrate based gas separation (HBGS) process for pre-combustion capture of carbon dioxide employing a novel fixed bed reactor. *Int J Greenhouse Gas Control* 2013;17:206–14.
- [180] Babu P, Kumar R, Linga P. A new porous material to enhance the kinetics of clathrate process: application to precombustion carbon dioxide capture. *Environ Sci Technol* 2013;47:13191–8.
- [181] Wang W, Bray CL, Adams DJ, Cooper AI. Methane storage in dry water gas hydrates. *J Am Chem Soc* 2008;130:11608–9.
- [182] Carter BO, Wang W, Adams DJ, Cooper AI. Gas storage in “dry water” and “dry gel” clathrates. *Langmuir* 2009;26:3186–93.
- [183] Yang L, Fan S, Wang Y, Lang X, Xie D. Accelerated formation of methane hydrate in aluminum foam. *Ind Eng Chem Res* 2011;50:11563–9.
- [184] Fan S, Yang L, Lang X, Wang Y, Xie D. Kinetics and thermal analysis of methane hydrate formation in aluminum foam. *Chem Eng Sci* 2012;82:185–93.
- [185] Pasieka J, Coulombe S, Servio P. Investigating the effects of hydrophobic and hydrophilic multi-wall carbon nanotubes on methane hydrate growth kinetics. *Chem Eng Sci* 2013;104:998–1002.
- [186] Park SS, Lee SB, Kim NJ. Effect of multi-walled carbon nanotubes on methane hydrate formation. *J Ind Eng Chem* 2010;16:551–5.
- [187] Saha D, Deng S. Accelerated formation of THF–H<sub>2</sub> clathrate hydrate in porous media. *Langmuir* 2010;26:8414–8.