

IN SITU NMR STUDIES OF HYDROGEN STORAGE KINETICS AND MOLECULAR DIFFUSION IN CLATHRATE HYDRATE AT ELEVATED HYDROGEN PRESSURES

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ABSTRACT

Clathrate hydrates can be reasonable choices for high-density hydrogen storage into compact host media, which is an essential task for hydrogen-based future society. However, conventional storage scheme where aqueous solution is frozen with hydrogen gas was impractically slow for practical use. Here we propose a much faster scheme where hydrogen gas was directly charged into hydrogen-free, crystalline hydrate powders. The storage kinetics was observed in situ by nuclear magnetic resonance (NMR) spectroscopy in a pressurized tube cell. At pressures up to 20 MPa the storage was complete within 80 minutes, as observed by growth of stored-hydrogen peak into the hydrate. Since the rate-determining step of current storage scheme is body diffusion of hydrogen within the crystalline hydrate media, we have measured the diffusion coefficient of hydrogen molecules using the pulsed field gradient NMR method. The results show that at temperatures down to 250 K the stored hydrogen is highly mobile, so that the powdered hydrate media should work well even in cold environments. Compared with more prevailing hydrogen storage media such as metal hydrides, the clathrate hydrate could offer even more advantages: It is free from hydrogen embrittlement, more chemically durable, more environmentally benign, as well as economically quite affordable.

Keywords: hydrogen storage, clathrate hydrates, NMR, diffusion, pressure

INTRODUCTION

Efficient storage of high-density hydrogen into compact host media is an essential challenge for hydrogen society in future [1, 2]. Hydrates can be reasonable choices, since structure II hydrogen clathrate hydrate is thermodynamically stable phase at elevated pressure [3-7]. The reported maximum capacity for hydrogen is 5.3 wt.%,

which is enough large as an alternative storage media, although the required pressure to store this amount of H₂ into the hydrate is excessively high [8]. Subsequently the storage pressure was reduced down to ca. 10 MPa, by blending in another guest species, that can act as a hydrate promoter. Tetrahydrofuran (THF) [4-6] and quaternary ammonium salts (QAS) [6, 7] are representative

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water-soluble promoters. Their aqueous solution and pressurized hydrogen gas are frozen together into hydrogen-bearing double clathrate (or semi-clathrate) hydrates. The promoters occupy part of the cages to stabilize the hydrate structure, so that there is a trade-off for hydrogen capacity to be reduced. The latest reports [9-11] showed that the THF hydrate gave smaller capacity than previous expectations [5], although this will depend on the details of the synthetic conditions, while the newly proposed QAS semi-hydrate gave larger capacity [7].

The other key issue for the hydrate storage than its hydrogen capacity is practical scheme for efficient hydrate synthesis. Conventional scheme where aqueous promoter solution is frozen with hydrogen gas often takes a week or more, which is of course impractically slow. Here we need to distinguish between hydrogen hydrate that crystallizes in bulk from solution contacting with hydrogen gas, and the hydrogen hydrate that converts from hydrogen-free hydrate powders through absorption of hydrogen gas. In the first case, the hydrate has to nucleate at the contact of mutually insoluble liquid and gas phases. The rate-determining step is then ascribed to the hydrogen diffusion through hydrogen-filled hydrate film growing at the interface. It was reported that to disperse the aqueous solution on a planar support, which makes the averaged diffusion length shorter, was found to be effective in accelerating this slow reaction [5]. However, such a support with additional weight is not practical. Therefore, we employ the reaction of finely-powdered hydrate crystals with pressurized hydrogen gas, into which the diffusion is comparably short. In this case, the hydrate crystal growth has already completed and the rate-determining step is hydrogen diffusion into empty cages in the hydrate structure. We have comprehensively analyzed both the kinetics and the diffusion relevant to this storage reaction. We employed in situ nuclear magnetic resonance (NMR) spectroscopy at high hydrogen gas pressure, which we believe is the best approach to study both macroscopic kinetics and microscopic diffusion all at once.

EXPERIMENTAL METHODS

Fully-deuterated THF (THF-d₈, 99.5 atom % D, ISOTEC) was dissolved in heavy water (D₂O, 99.9 atom% D) and then frozen at -30 °C to give a stoichiometric structure II THF clathrate hydrate (THF•17D₂O). The hydrate was ground into a fine

powder (2~300 μm in size) in a liquid N₂ Dewar and stored again for more than two weeks at -30 °C to ensure complete hydrate crystallization. The powder was tightly packed by hand into a sapphire tube cell of 10 mm O.D. and 7 mm I.D which sustains gas pressure up to 20 MPa [12]. A glass rod of 6 mm O.D. was also used to fill the dead space in the tube, which is effective for reducing the intense NMR signal from hydrogen gas.

The storage of hydrogen started with instant filling of desired pressure of hydrogen into the tube cell, while the release started with the evacuation of hydrogen. NMR spectra were obtained at various stages of the storage reaction.

RESULTS

Analysis of NMR spectra

Figure 1 shows representative NMR spectra during the hydrate synthesis and decomposition reaction at a specific hydrogen pressure (10.6 MPa). From the analysis of the observed spectra series, we have identified three different ¹H species. These are residual HDO in that make up the hydrate cages (C), the hydrogen atmosphere (A), and hydrogen stored in the hydrate (S), respectively.

We have observed the C peak throughout the experiments, the A peak whenever the hydrogen atmosphere was filled, and the S peak gradually growing and decaying after the hydrogen filling and the evacuation. These observations led us the unique assignments of the peaks. The sharp Lorentzian profile of the S peak comes from liquid-like mobility of the hydrogen molecules within the solid crystalline hydrate, otherwise a broad Gaussian profile must have emerged [13]. This is a surprising observation, but in fact it was what we expected because a sharp NMR peak arising from mobile hydrogen guests already has been observed for hydrogen hydrates of different structures those crystallize at much higher pressures [14, 15]. Such a mobile nature of hydrogen is in stark contrast from methane or other guests in their hydrates. This unique nature of hydrogen in the hydrates is a useful principle for designing future applications of hydrogen hydrates, such as purification of hydrogen from gas mixtures [16], as well as for designing the scheme of hydrogen storage.

Figure 2 shows examples of real-time evolution of the S peak during the storage taking place. At all pressures to 20 MPa the hydrogen storage was complete within 80 minutes, as seen in the Figure. The hydrogen release was also complete within comparable but slightly shorter timescale. This

accelerated kinetics is consistent with the observed highly-mobile nature of the hydrogen within the hydrate crystals. Thus the powdered clathrate hydrate has been demonstrated as appropriate for practical purposes, even though its hydrogen capacity is reduced by blending the hydrate promoter to keep the storage media always being frozen.

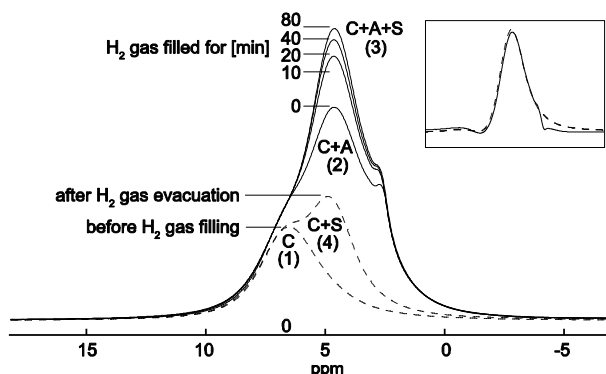


Figure 1 Static solid-state high resolution ^1H NMR spectra obtained along with the synthesis of THF- H_2 double hydrate at 10.6 MPa hydrogen pressure and at 260 K. Solid lines show the spectra when the hydrogen gas was filled into the tube cell, while broken lines show the spectra when the hydrogen gas was not filled or evacuated. The storage reaction occurred as follows: (1) Before the hydrogen gas was filled, only the C (cage) peak at 4.3 ppm was identified which came from the hydrogen-free hydrate powders. (2) After the hydrogen gas was filled, the A (atmosphere) peak immediately appeared at ~ 2 ppm; see the spectrum for "H $_2$ gas filled for 0 min". (3) Along with the storage reaction was taking place, the S (stored) peak at ~ 2 ppm had gradually growing up. Finally the storage was completed; see the spectrum for "H $_2$ loading for 80 min". (4) When the hydrogen gas was released, the A peak immediately had disappeared but the C and S peaks still remained. Then the S peak gradually decreased its intensity with time (not shown). The inset compares two calculated profiles of the pure S peak; the solid line shows the difference between (3) and (2), while the broken line shows the difference between (4) and (1). These two profiles are identical, demonstrating that the above assignment is unique and reasonable. All the spectra were obtained at NRC Magnetic Resonance Facility using a Bruker Avance 200 spectrometer, and a microimaging probe equipped with 10 mm

resonators for ^1H and with a pulsed field gradient coil up to 1 Tesla/m for z axis. A typical $\pi/2$ pulse length was 12 μs . The chemical shift axis was defined by the position of the C peak at 4.3 ppm[4].

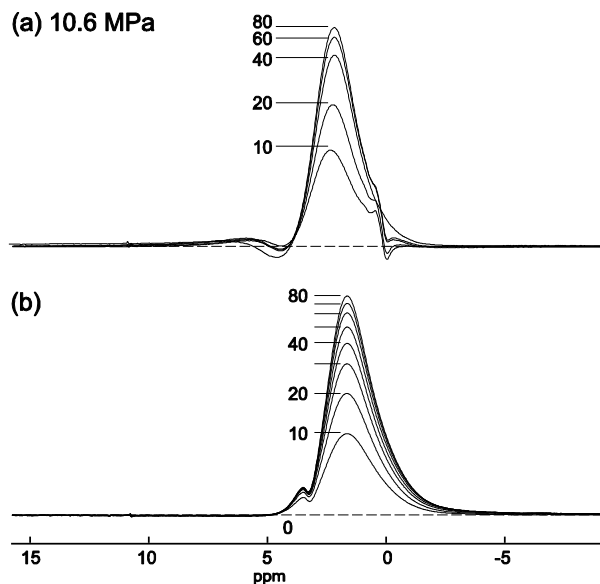


FIG. 2. Observed growth of the S peak profile during the storage reaction. (a) at 10.6 MP hydrogen pressure and at 260 K. (b) at 13.4 MPa hydrogen pressure and at 260 K. The numbers denote reaction times for the hydrogen storage in minutes.

Diffusion measurements

A detailed analysis of body diffusion of hydrogen within the hydrate crystals is obviously very important, as this enables a prediction of the reaction time for storage and release of hydrogen in the hydrate at various practical conditions. To measure the diffusion coefficient, we applied a pulsed-field gradient NMR method [17]. The sample at each specific temperature and pressure was first kept in equilibrium with the pressurized hydrogen gas. The gas induces the strong A (atmosphere) peak to interfere with the weaker S (stored) peak (Figure 1). To eliminate the interferences from the A and also from the C (cage) peaks, we employed the principle of diffusion-ordered spectroscopy [18]. By using a diffusion coefficient axis in addition to the chemical shift axis to give a two-dimensional NMR spectrum, the S peak was completely separated to enable accurate measurements of the

diffusion coefficient D_S . Figure 3 shows an example of the data regression for the diffusion measurement.

Figure 4 shows the results as a function of the hydrogen pressure and temperature. It gives comparable values to the self diffusion coefficients of viscous molecular liquids such as glycerin [17], which again reinforces the mobile character of stored hydrogen in the hydrate. The calculated diffusion length of hydrogen in the hydrate for $t = 80$ minutes is $\sqrt{D_S t} \sim 100$ μm , which is consistent with the grain radii of the powder (100 to 150 μm).

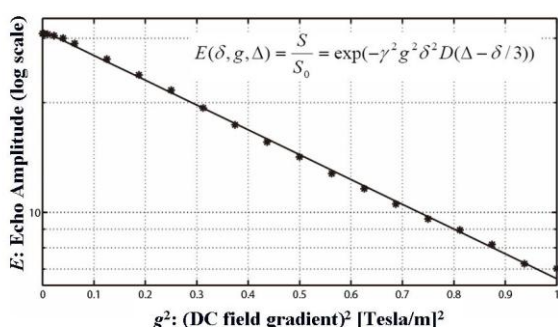


Figure 3 An example of diffusion measurement of hydrogen molecules in the hydrate crystals. This measurement was made at 6.0 MPa hydrogen pressure and at 265 K. The length of pulsed field gradient was $\delta = 20$ ms. The duration between π and $\pi/2$ pulses was $\Delta = 22.5$ ms. The D_S was obtained by log-linear fitting of the observed echo amplitude E against square of the DC field gradient g^2 . The results gave $D_S = 3.5 \times 10^{-8}$ cm^2/s .

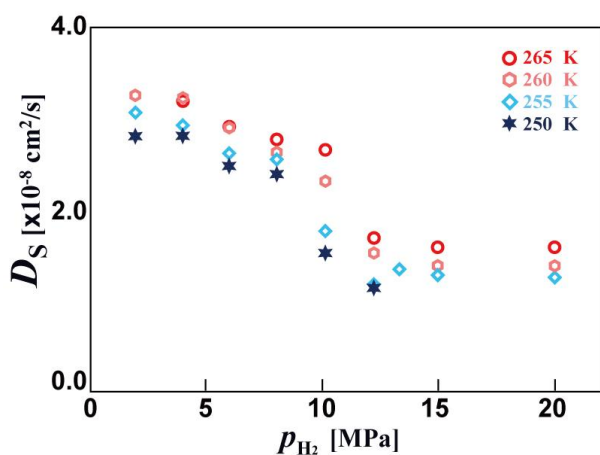


Figure 4 The diffusion coefficient of stored hydrogen in the structure II THF-hydrogen double

clathrate hydrate as a function of pressure and temperature. The temperature was between 250 K and 265 K where the hydrate was kept solid. Colour and shape of the symbols show the temperature, as indicated. At temperatures lower than 250 K echo signals from the stored hydrogen is not sufficient to give reliable results. We used pulsed field gradients $g = 1$ Tesla/cm in maximum strength and pulse length $\delta = 20$ ms. This long length was necessary to compensate the limited strength of the gradient. The second pulse occurred at $\Delta = 22.5$ ms after the beginning of the first pulse. Typical fitting residuals (1σ) for the regression of these diffusion coefficients, as seen in Figure 3, were 0.7 to 1% at 265 K and 2 to 3% at 250 K.

DISCUSSION

By taking the diffusion coefficient of hydrogen into account, we could design the reaction time of hydrate storage. When a powder with particles half the size is prepared, the storage is completed for a fourth part of the original reaction time; it is just 20 minutes in our case. If, instead, the powder of the larger size are prepared, the reaction becomes slower. Thus the efficiency of hydrogen storage and release can be tuned for specific purposes, either for a fast instant supply in a short time, or for a slow continuous supply in a long time. The powder must remain intact in the frozen state, otherwise hydrogen will be released all at once. Some hydrates have melting temperatures as high as 40 °C [7], so that keeping it frozen could not be a critical problem, although crystal sintering proceeds faster at such high temperatures. The sintering might be prevented by introducing polymer kinetic inhibitors which coat the surface of hydrates to keep the powders being separated. In situ micro-imaging techniques of crystal textures at high gas pressure [12] are necessary to be applied to investigate the problem of sintering, and therefore to further improve the hydrate storage scheme.

The D_S value gradually decreases with increasing pressure, or increasing hydrogen concentration in the hydrate [9] (Figure 4). This is because the transport of hydrogen molecules between the cages may proceed only when there is a vacant guest site in the neighboring cage [19], and diffusion is slower when a larger fraction of the guest sites is already filled. The D_S value weakly increases with increasing temperature, indicating

that the activation energy is small, being 3 ± 1 kJ/mol. The reaction energy of hydrogen molecule with the cage wall through van Der Waals interaction is even smaller than this value [20], so that the activation barrier should be the translation of hydrogen molecule between the two adjacent cages. Considering the structure of THF hydrate that the promoter molecules preoccupy all 16-hedral cages, the translation of hydrogen through pentagonal H₂O rings between two 12-hedral cages is the most likely barrier for the observed D_s . Modeling calculations [19] have indicated that such translation should be possible, although the calculated energy was much larger than the current observation. The presence of ring breathing modes, which was not considered, will significantly reduce the barrier as the case for H₂ in sodalite [21]. As well, the reorientation and diffusion of H₂O molecules in the cage wall [22] may further reduce the activation barrier. Further experimental and theoretical works are apparently necessary to find out the reason for very low activation barrier of the hydrogen diffusion in the hydrate.

CONCLUSIONS

We have demonstrated a much faster scheme of hydrogen storage into the hydrate where hydrogen gas was directly charged into the powders of crystalline structure II clathrate hydrate with partly empty cages. The storage kinetics and hydrogen diffusion into the hydrate was successfully observed by NMR in a pressurized tube cell. At pressures to 20 MPa the hydrogen storage was complete within 80 minutes for the hydrate powders with 200 to 300 μm in grain size. The accelerated kinetics is consistent with highly-mobile nature of hydrogen molecules within the hydrate crystals, which was demonstrated not only by NMR spectrum analysis but also by the diffusion measurements using a pulsed field gradient. Tiny effect of temperature on diffusion of hydrogen in the hydrate assures that the clathrate hydrate should work at low temperatures without warming up prior to the fuel storage or release. The small reaction enthalpy with the cage wall assures that the temperature of the media is always kept constant. Thus the powdered clathrate hydrate has been demonstrated as appropriate for practical purposes.

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