

Discrete Thermal Patterns of Hydrogen and Deuterium Molecules Enclathrated in Confined Hydrate Cages

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Recently, two unique swapping and tuning phenomena that naturally occur in the nanocages of clathrate hydrates were confirmed. Such cage-specific phenomena can be applied to a variety of energy and environmental fields, such as gas storage materials, carbon dioxide sequestration, and future energy resources;^{1–4} however, most of the fundamental cage dynamics and unique host–guest interacting patterns appearing in the complex hydrate structures remain unanswered. In particular, the tuning mechanism of the hydrogen clathrate hydrate was investigated in order to determine the stable storage conditions for it as compared to other materials.⁴ It was noted that the empty cages can be used for guest molecules to exist by themselves, considering the possible interactions with the surrounding host and guest molecules. In this case the engaged guest molecules are in a very small volume where they can bounce around. A sufficiently hydrophobic guest molecule has a tendency to occupy the empty site without significant host–guest interactions. It thus acts as an isolated free molecule. However, hydrogen molecules can also very easily pass through the holes in the host networks, leading to the failure of the guest imprisonment. Eliminating the chemisorption involvement of guests on the host frameworks, the intermolecular interaction between the water-soluble liquid guest and other gaseous guest molecules leads to total energy lattice stabilization. A clear understanding of such guest-dynamic behavior occurring in solely confined nanosized cages has often been achieved through the neutron diffraction technique together with other spectroscopic methods. However, the incoherent scattering exhibited by hydrogen generates a background signal that makes it difficult to detect the coherent Bragg scattering from the sample. For this reason, two recent neutron diffraction studies regarding hydrogen hydrates used deuterium as an equivalent substitute of hydrogen.^{5,6} However, it must be recognized that deuteration is an inevitable option, but might significantly lead to erroneous conclusions in terms of revealing the real neutron powder diffraction (NPD) nature of fully hydrogenous materials as well as the hydrogen molecules that exist in the hydrate cages.⁷

Accordingly, we attempted to synthesize the two different clathrate hydrates of THF + H₂ and THF + D₂ and for the first time to directly determine and compare their neutron diffraction patterns. First, 5.56 mol % THF (THF-*d*8, 99.5 atom % D) and deuterated water (D₂O, 99.9 atom % D) solutions were frozen at 243 K for 1 day. They were then ground to a fine powder (~120 μm). The powdered solid placed in the cell was then exposed to H₂ or D₂ gas and maintained at 120 bar and 268 K for 1 day. When the hydrate reaction was completed, after venting the residual H₂ and D₂ gas in the cell, the mixed hydrogen hydrate powders were packed into a neutron sample holder (thin vanadium cylinders with 3 cm³ volumes) which was cooled in liquid nitrogen. Neutron

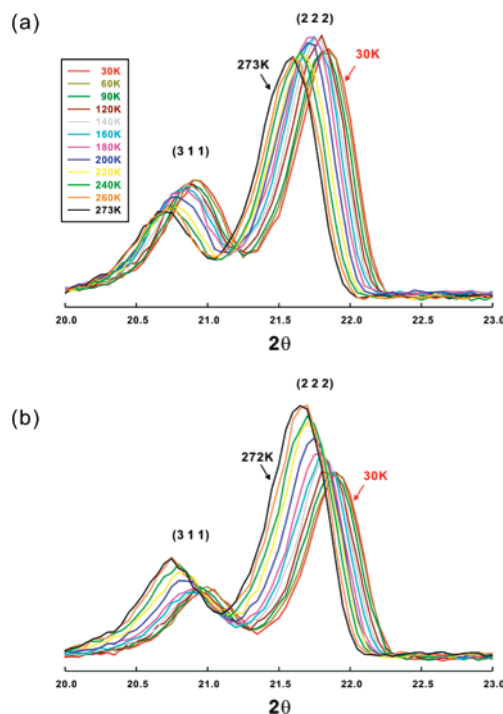


Figure 1. Neutron powder diffraction patterns of (a) THF + H₂ and (b) THF + D₂ clathrate hydrates from 30 to 273 K. The (311) and (222) in the range of 20.0° < 2θ < 23.0° are shown. An opposite tendency of intensity changes of two hydrates appears as the variance of temperature.

diffraction experiments were then performed on a high-resolution powder diffractometer installed at the 30 MW reactor “HANARO” of the Korea Atomic Energy Research Institute.

Molecular hydrogen is a mixture of the ortho- and para-hydrogen. The neutron scattering lengths of the *o*-H₂/D₂ and the *p*-H₂/D₂ differ greatly from each other, and those of molecular hydrogen (H₂, D₂) also differ entirely from atomic hydrogen (H, D). These peculiar characteristics of H₂ and D₂ in terms of neutron scattering make data analysis a nontrivial task. At this stage, it is important to note that the H₂ molecule exists as freely isolated molecule without any chemical bonding linked to the surrounding frameworks, and that it must be distinguished from the hydrogen contained in the hydrogenous compounds. The direct use of H₂ without resort to D₂ must provide a more reliable understanding of the hydrogen (H₂) enclathration and dissociation processes within the H₂ (rather than the D₂) clathrate hydrate; furthermore, it plays an important role in analyzing hydrogen hydrate-based applications.

Figure 1 shows the two different neutron powder diffraction patterns (20.0 < 2θ < 23.0) of the THF + H₂ and the THF + D₂ clathrate hydrates measured at a temperature range of 30 to ~273

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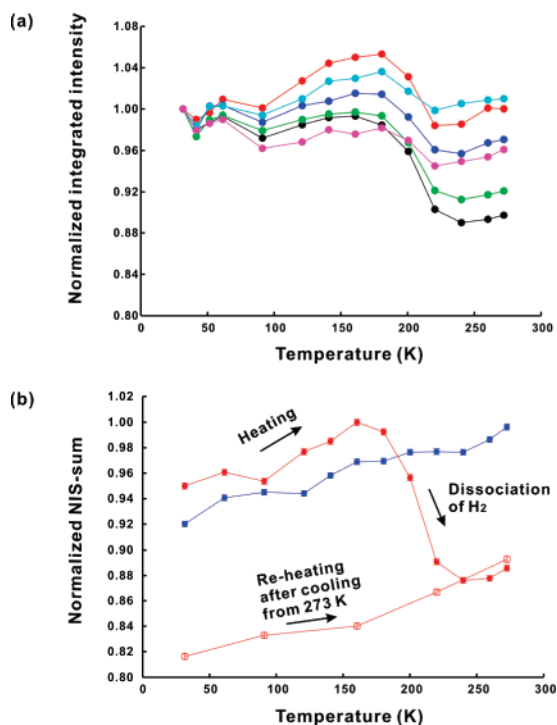


Figure 2. (a) Integrated intensities of the THF + H₂ neutron diffraction patterns: (111) red, (400) cyan, (331) blue, (422) green, (333) black, and (440) pink. (b) Summation of the neutron incoherent scattering (NIS) intensities of the THF + H₂ and THF + D₂ clathrate hydrates. The NIS summation ($13^\circ < 2\theta < 15^\circ$) shows an abrupt decrease in the range of 150 to ~ 250 K: THF + H₂ (red) and THF + D₂ (blue).

K. Over the entire temperature range, both clathrate hydrates were preserved as sII structures, even during H₂ and D₂ dissociation according to the temperature evolution. The temperature dependence of (311) and (222) clearly indicates the different tendency of the dissociation progress for the two hydrates with the H₂ and D₂ molecules. As shown in Figure 1, there is an opposite tendency of intensity change as the temperature varies. This can be explained by the opposite signs of the neutron scattering lengths of H₂ (negative) and D₂ (positive). Scattering intensities from the reflection planes containing the center of the small cages (or the hydrogen molecules) will show the opposite tendencies when the negative scatter (H₂) or the positive scatter (D₂) disappears as the temperature increases. In order to observe the effect of the hydrogen dissociation on the diffraction patterns, it is necessary to carefully examine the integrated intensities of the neutron diffractions, particularly for low index peaks such as (111), (400), (311), (422), (333), and (440), as shown in Figure 2a. As shown in Figure 1a, the hydrogen dissociation might start slowly in a macroscopic scale from 120 K in a H₂ hydrate system, and then at the temperature range of 180 to ~ 210 K, as shown in Figure 2a, most, but not all, of the H₂ gas is degassed. For a quantitative approach for the H₂ gas during degassing, a summation of the neutron incoherent scattering (NIS) intensities of the THF + H₂ and THF + D₂ clathrate hydrates following the degassing was accomplished, and the results are shown in Figure 2b. The 2θ range of this summation is from 13° to 15° of the background to avoid any Bragg-peak contribution. The rapid decrease in the NIS sum of the H₂ clathrate hydrate around 180 K indicates that the dissociation of encaged hydrogen molecules actively commences from this temperature. However,

for the THF + D₂ clathrate hydrate, the sum of NIS increased monotonically as the temperature increased, which is a consequence of the increased thermal motion of the lattice. At 180 K, the difference in the NIS-sums between the THF + H₂ and THF + D₂ clathrate hydrates is considered to have resulted from the considerable difference of the incoherent scattering cross sections (x_{inc}) between H₂ (19.93 b) and D₂ (< 4.2 b).⁸ In particular, the H₂-depleted clathrate hydrate was again cooled to 30 K and then gradually heated to 273 K for a confirmation of H₂ release pattern. The abrupt decrease in the NIS summation of THF + H₂ observed in the range of 150–250 K suggests a unique on/off-like pattern of hydrogen dissociation in the confined cages, which might prove to be useful information for H₂ charge–discharge applications. The directly released amount of H₂ and D₂ were approximately 14% (H₂, 180 K), 9% (D₂, 180 K), 55% (H₂, 250 K), and 28% (D₂, 250 K).

In this study, the dissociation behaviors of H₂ and D₂ on the clathrate hydrate system of THF + H₂ (D₂) were investigated by analyzing the neutron diffraction patterns under varying temperatures. The direct usage of H₂ gas confined in a cage without a chemical bond was successfully performed, showing stable backgrounds through the incoherent scattering length of the H₂. In addition, the distinct thermal behavior of H₂ and D₂ in a THF hydrate system in terms of the difference in the physical properties of H and D was observed. The major differences in the neutron scattering lengths as well as the masses between the H₂ and the D₂ molecules are considered to be the key reasons for the quite different dissociation behavior; thus it is necessary to measure the neutron scattering from the H₂-hydrate instead of from the D₂-hydrate to obtain the real physics of the H₂-hydrate. The present results will make the direct use of a neutron diffraction analysis of hydrogen gas possible in the development of hydrogen storage media and they present the basic information needed for obtaining the precise value in structural analyses.

Acknowledgment. This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the National Research Lab. Program funded by the Ministry of Science and Technology (No. M20511000052-05B0200-05210) from Nuclear R&D Program of the Ministry of Science & Technology, also partially supported by the Brain Korea 21 Project. We thank the Korea Atomic Energy Research Institute for granting beam time and support.

Supporting Information Available: Sample preparation, experimental procedure, and neutron powder diffraction patterns details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0674441