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In Situ X-ray Diffraction Measurements of the Self-Preservation Effect of CH_4 Hydrate

Satoshi Takeya,* Wataru Shimada, Yasushi Kamata, Takao Ebinuma, Tsutomu Uchida, Jiro Nagao, and Hideo Narita

National Institute of Advanced Industrial Science and Technology (AIST), 2-17 Tukisamu Higashi Toyohira-ku, Sapporo 062-8517, Japan

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In situ observations of CH_4 hydrate dissociation using X-ray diffraction were carried out at atmospheric pressure and at both 168 and 189 K. Dissociation rates of the hydrate and the rate of transformation into hexagonal ice were measured using time-resolved energy-dispersive X-ray diffraction. The dissociation of CH_4 hydrate had an initially fast regime followed by slower dissociation. Thus, the data support a previously suggested two-step process. In addition, we observed dynamic behavior of the X-ray diffraction intensities of ice Ih, which implies a transient crystal structure at the beginning of the dissociation. Our analyses indicates that the first step, which lasted several tens of minutes, was the formation of an ice Ih layer around the CH_4 hydrate, and the second step was relatively slow because the CH_4 had to diffuse through the thickening ice layer. This second step determined the hydrate lifetime. The resulting diffusion coefficients were estimated at 2.2×10^{-11} m^2/s at 189 K and 9.6×10^{-12} m^2/s at 168 K.

Introduction

Gas hydrates are ice-like inclusion compounds formed from water and gas molecules at high pressures. Such hydrate formation is a nuisance when it plugs up offshore oil wells and gas pipelines. But it could also prove useful; recently it has been suggested as an important new energy storage and transport medium. Gudmundsson et al.[1] argued that the hydrate is more suitable for large-scale transport of natural gas over long distances than liquid natural gas (LNG) for the following two reasons. (1) The gas density stored in gas hydrates at temperatures near 273 K is nearly that of LNG below 113 K. (2) Gas hydrates are fairly stable under relatively low nonequilibrium pressures below 273 K.

The gas storage density is due to the crystallographic structure of gas hydrate crystals. Their crystalline structures are either Stackelberg's structure I, specifically, 12- and 14-hedra with a space group of *Pm*3*n*, or Stackelberg's structure II, specifically, 12- and 16-hedra with a space group of *Fd*3*m*.[2,3] The lattice constants of structures I and II hydrate are about 12.0 and 17.3 Å, respectively.[4] Each polyhedra is a cage that can hold up to one gas molecule. The high stability under nonequilibrium conditions is thought to be caused by a layer of ice from dissociated hydrate; this layer coats the hydrate and seals it from further dissociation. The effect is called the "self-preservation" of gas hydrates.[5,6] However, due to the difficulty of quantifying this kinetic phenomenon and visually observing thin coatings of ice, little is known about the self-preservation effect.

To understand the dissociation and the self-preservation mechanism of gas hydrates, we observed the dissociation process of CH_4 hydrate crystals in situ using time-resolved X-ray diffraction.

Experimental Section

CH_4 hydrate crystals with an average diameter of about 20−50 μm were prepared by grinding up 0.5- to 1.0-mm ice grains in a high-pressure cell that was compressed with CH_4 gas. After about 1 day at 5.8 MPa and 267 K, the ice transformed into CH_4 hydrate. The hydrate was put into the X-ray system described below, and then the temperature and pressure were lowered such that the hydrate dissociated as shown in Figure 1.

CH_4 hydrate particles were put in a quartz glass capillary cell (Hilgenberg; ϕ 1.5 mm, 0.01-mm thick) that was put on top of the goniometer. By immersing them in liquid N_2, the hydrate crystals were compacted such that they occupied 40% of the total capillary volume. Just before the dissociation measurements the volume ratios of the samples were measured at 120 K using an X-ray diffraction method. The only samples that were used were those that had a volume ratio of CH_4 hydrate to total solid of over 0.95.

To observe the changes of diffraction profiles during hydrate dissociation, an energy-dispersive X-ray diffraction method was used. White X-rays generated by a W-target (40 kV, 350 mA; Rigaku model Rint-2000) was radiated to the sample and the energy dispersive spectra were measured with a Si solid-state detector (Amptec model XR-100-CR). As spectra continuously accumulated, data were retrieved every 500 s. Usually, the 2θ angle was fixed at 12.50°. However, this angle was changed to 17.50° to observe higher-order crystal planes. The capillary cell was rotated 180° about the θ-axis during each measurement to include many crystals.

These in situ measurements of CH_4 hydrate dissociation process were done at atmospheric pressure with temperatures at 189 and 168 K. The temperature of the sample was controlled to ±1.0 K by blowing cold, dry N_2 gas around it. This also prevented frost formation, regulated the pressure, and removed the CH_4 gas. The evaporation of the sample was negligible because X-ray diffraction intensities of ice sample with an

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* Corresponding author. Fax: +81-11-857-8993. E-mail: s.takeya@aist.go.jp.

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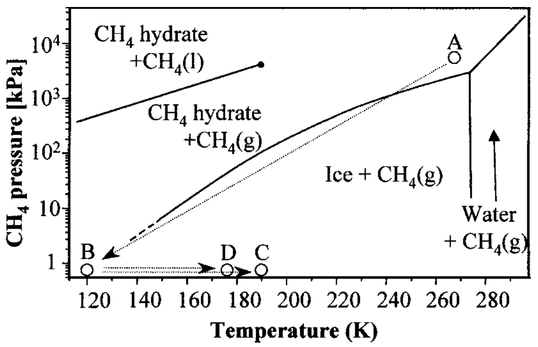


Figure 1. Phase diagram for the CH_4-H_2O system and experimental conditions. Point A indicates the synthesis condition of sample CH_4 hydrate. The temperature and methane pressure were then reduced to point B to make initial X-ray measurements for estimating the volume ratio of CH_4 hydrate to total sample solid, and then the temperature was raised to either 189 K (point C) or 168 K (point D) for the dissociation measurements.

average diameter of about 20−50 μm did not decrease over two weeks by blowing the N_2 gas.

Results and Discussion

Figure 2, parts a and b, show the changes of X-ray diffraction profiles from CH_4 hydrate, structure I, to hexagonal ice (Ih). The initial profile is that of CH_4 hydrate at 120 K. After setting the temperature to 168 or 189 K, several diffraction peaks from Ih appeared and generally increased with time, whereas the CH_4 hydrate diffraction peak heights decreased with time. This indicates that the amount of hydrate decreased and the amount of ice increased. Because the only source of water molecules in the system is the hydrate, the dissociated CH_4 hydrate likely transformed into ice Ih as it released CH_4 gas.

The relative intensity changes of each crystal plane of CH_4 hydrate and Ih versus time are plotted in Figure 3 parts a and b. Each data point in Figure 3, parts a and b, was calculated by integrating the intensity over each peak in Figure 2, parts a and b. Because the integrated intensity of X-ray diffraction is proportional to the crystal volume, their rates of change are measures of volume transformation rates. Figure 3a shows that the initial dissociation rate of CH_4 hydrate was very fast within the first several tens of minutes, and then became relatively slow. We argue below that the initial growth of ice is due to nucleation and lateral growth that coats the hydrate with a nearly uniform coating of ice, the slower part of the growth occurs after the particle is completely coated with ice. This two-step model of hydrate dissociation was first reported by Handa.[5] He measured the pressure rise caused by the dissociation of Kr hydrate; it also appeared that the hydrate contained a large crystal that remained until the temperature rose to the melting temperature of ice. The relatively fast increase of the ice signals in the beginning supports the hypothesis that the particles are coated with ice. The CH_4 evaporates from the surface first, thus leaving only pure water that should crystallize into ice Ih; any surface region that is not coated, would quickly lose CH_4 and become coated with ice. Sintering of the particles is unlikely to slow the transformation rate because the temperatures are too cold for significant sintering.

Figure 3, parts a and b, also show the dynamic behavior of X-ray diffraction intensities of Ih. The relative intensity ratios of the Ih (10−10), (10−12), and (20−20) planes are all nearly equal, whereas the ratios of Ih (10−11) and (11−20) planes are larger than the other Ih crystal planes at the beginning of the dissociation. The influence of preferred orientation was dissolved by capillary rotation in this experiment. Therefore, it is possible that a transient crystal structure of ice Ih forms from the hydrate, epitaxial growth of ice Ih on the hydrate surface, or the ice Ih grows with different crystal habits[7] after the nucleation of ice crystals. The ice should coat the hydrate surface completely because an uncoated hydrate surface would be an easier dissociation point of hydrate. After the ice crystals grow and coat the hydrate particles, the dynamic behavior of X-ray diffraction intensity will disappear because further free growth of each ice crystal will be prevented.

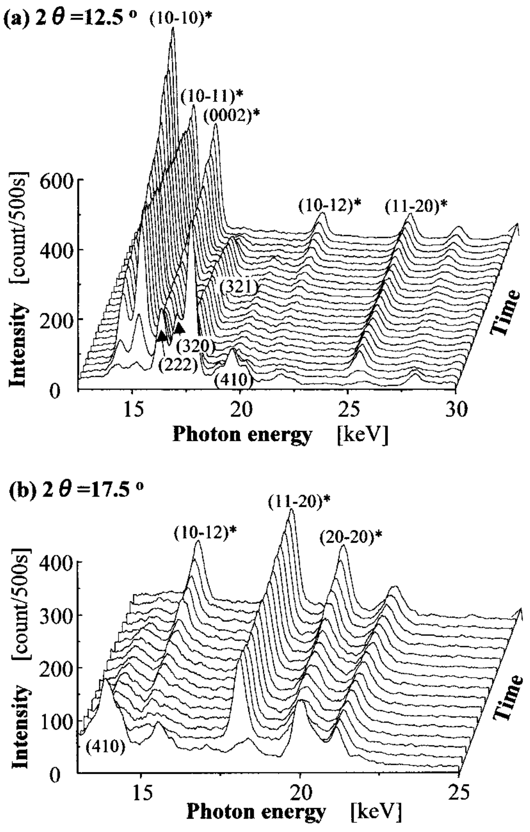


Figure 2. In situ, time-resolved, energy-dispersive X-ray diffraction profiles during the transformation of CH_4 hydrate to ice Ih at 189 K. Indices of the crystal planes are labeled on the diffraction peaks. The 4-numeral indices with asterisks are crystal planes of ice Ih. Each scan is separated by 500 s.

After this initial growth, either the dissociation reaction of CH_4 hydrate or the subsequent diffusion of CH_4 gas through the ice Ih layer controls the rate of hydrate dissociation. For the dissociation-limiting case of spherical crystals, the decreasing rate of its radius should be constant. Figure 4 shows that the rate at each temperature was not constant. So, we assume that the rate-determining process in this second stage of growth, and hence the rate-determining process for the entire dissociation process, is the diffusion of CH_4 gas through the Ih layer. Thus, we formulated a diffusion-limited hydrate dissociation model below 273 K for each hydrate grain. The geometry of this model is in Figure 5.

The Ih layer increases its thickness by the recombination of H_2O molecules from the hydrate crystal to the Ih crystal. The released CH_4 gas should have a pressure about equal to the dissociation pressure of CH_4 hydrate because it compresses the hydrate to near equilibrium; this pressure would be maintained because the gas diffuses through the Ih layer to the atmosphere at a relatively slow rate. A diffusion-limiting rate should cause the ice layer to have a uniform thickness because a thicker region

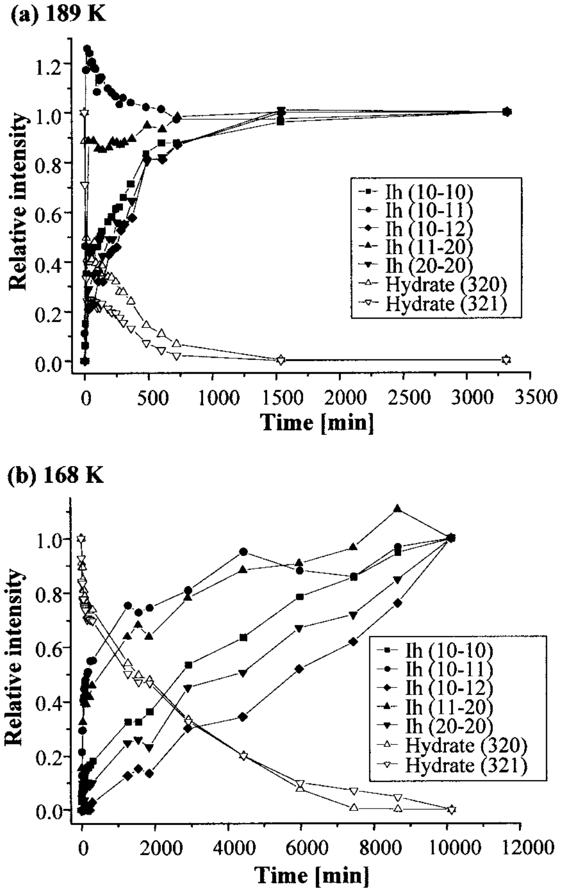


Figure 3. The integrated intensity of each crystal plane as a function of time for (a) 189 K, and (b) 168 K. Each hydrate curve was scaled such that initial intensity equaled unity. Each ice curve was scaled such that it equaled unity when the intensity of the (321) plane of CH_4 hydrate became zero at 1583 min at 189 K and at 10134 min at 168 K. The trends in the curves indicate the trends in the dissociation rates of CH_4 hydrate and the growth rates of ice Ih.

of ice would have a slower rate of diffusion and hence a slower rate of growth.

Using the above assumptions, the volume change of a spherical hydrate crystal in steady state is[8]

$$\frac{dV_h}{dt} = -4\pi D\frac{r_i r_h}{r_i - r_h}\left(\frac{C_d(T) - C_a}{C_0 - C_a}\right) \qquad (1)$$

Here t is reaction time, $V_h = (4/3)\pi r_h^3$ is the volume of CH_4 hydrate, D is the diffusion coefficient of CH_4 through ice, r_i is the radius of the entire particle, and r_h is the hydrate radius. Thus, $r_i - r_h$ is the thickness of the ice layer (see Figure 5). $C_d(T)$ is the density of CH_4 gas in the gas phase at the dissociation pressure of CH_4 hydrate at temperature T, C_o is the CH_4 density in the hydrate, and C_a is the CH_4 density in the surrounding atmosphere. Assuming that the external radius of Ih is equal to that of initial hydrate and that the external radius of the entire particle is constant, $r_i = r_{ho}$, integration of eq 1 yields

$$3(1 - R^2) + 2(R^3 - 1) = \frac{6D}{r_{ho}^2}\left(\frac{C_d(T) - C_a}{C_0 - C_a}\right)t \qquad (2)$$

Here, R is the scaled radius of the hydrate, $R = r_h/r_{ho}$. Therefore, if our assumptions about diffusion being the rate-limiting step are valid, a plot of $3(1 - R^2) + 2(R^3 - 1)$ vs t would be a straight line with slope equal to the factors of t on the right side of eq 2.

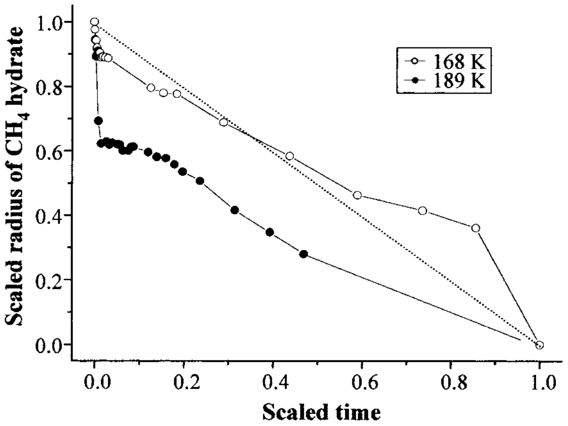


Figure 4. The radius of spherical CH_4 hydrate as a function of scaled time. The scaled radius of the hydrate is defined as r_h/r_{h0} where r_{h0} is the initial radius of the hydrate and r_h is the hydrate radius. The scaled time is the time ratio to the total reaction time of hydrate dissociation. The dotted line indicates constant reduction of the radius.

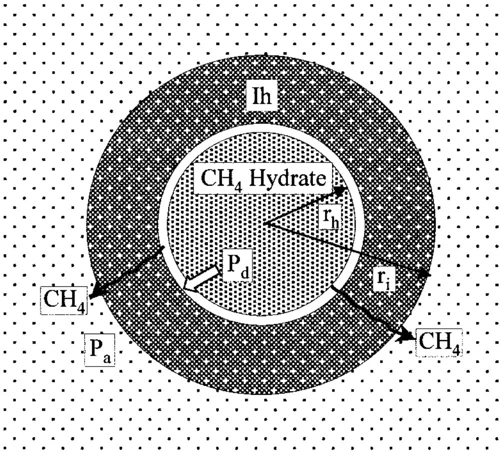


Figure 5. A sketch showing our assumed model for the transformation of CH_4 hydrate to ice Ih at one atmosphere. Here r_i is the external radius of the Ih layer and r_h is the external radius of the hydrate grain.

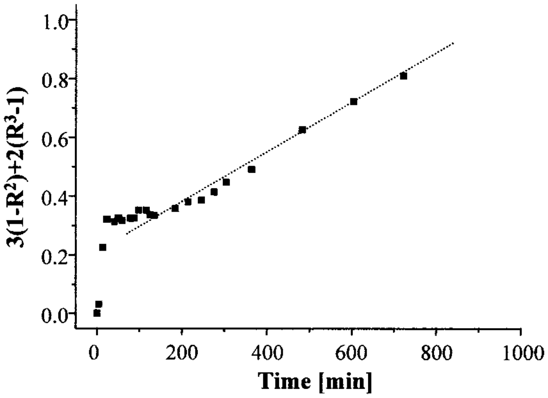
We assumed that the hydrate (321) signal was proportional to the hydrate volume, and then computed $3(1 - R^2) + 2(R^3 - 1)$ from the data of Figure 3, parts a and b. Figure 6, parts a and b, show that these data give straight lines except at the beginning, and thus they indicate that the diffusion of CH_4 gas is the rate-determining process of CH_4 hydrate dissociation in the second stage of growth. However, Figure 6a shows that the initial dissociation is not on the straight line fit to the later times. This supports the hypothesis of a two-step dissociation process mentioned above.

The diffusion constant was estimated from the slope as follows. We assumed that the initial hydrate radius was $r_{ho} \sim 35\ \mu m$, the density of CH_4 gas in the surrounding gas was negligible $C_a \sim 0$, and the CH_4 density in CH_4 hydrate was $C_o \sim 7.54 \times 10^{-3}\ mol/m^3$. The latter was calculated at 267 K and 5.8 MPa[9] assuming a 12.0 Å lattice constant. The dissociation density of CH_4 gas C_d was then calculated assuming the ideal gas law and the dissociation pressure of CH_4 hydrate

$$p_d(T) = \exp(15.517 - 2105.16/T)\ [kPa] \qquad (148.8-262.4\ \text{K}) \qquad (3)$$

This equation is based on the experimental results of Falabell[10]

(a) 189 K



(b) 168 K

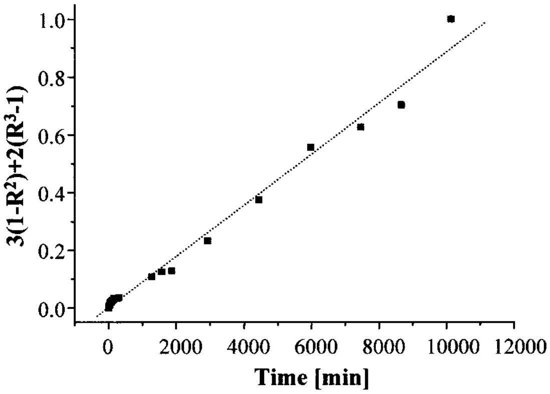


Figure 6. Diffusion-controlled dissociation of CH_4 hydrate. The ordinate is a function of the scaled hydrate radius R that appears in the diffusion eq 2. A straight line indicates that dissociation was controlled by CH_4 diffusion through a growing ice layer. Each data point was derived from the data of the (321) plane of CH_4 hydrate in Figure 2.

and Makogon et al.[11] The resulting densities are $C_d(189) = 5.07 \times 10^{-5}$ mol/m^3 and $C_d(168) = 1.42 \times 10^{-5}$ mol/m^3, which should represent upper limits to the possible gas pressures external to the hydrate. As a result, the diffusion coefficients of 2.2×10^{-11} m^2/s at 189 K and 9.6×10^{-12} m^2/s at 168 K were calculated using the slopes in Figure 6, parts a and b. The calculated diffusion coefficients depend on the radius size squared of the initial CH_4 hydrate, so we should include the size distribution for more precise estimates. In comparison, the estimated diffusion coefficients of N_2 and O_2 in ice Ih are reported to be about 10^{-19} m^2/s,[12] thus the diffusion coefficients of CH_4 should have a diffusion constant of about the same magnitude if the ice crystallinity was the same as that in the N_2 and O_2 experiments. The high diffusion coefficients in this experiment imply that the CH_4 does not diffuse through a solid Ih layer, but instead through pores or grain boundaries because the size distribution of the hydrate crystals with average diameter about 20−50 μm does not change the order of the coefficient. Such pores or grain boundaries could form because the water density in CH_4 hydrate is 796 kg/m^3 (assuming a lattice constant of 12.0 Å), which is significantly smaller than the 918 kg/m^3 density of ice Ih at atmospheric pressure.

The optical observations of Yakushev et al.[6] also indicated that pieces of massive, white, fine-porous gas hydrate crystals had dissociated after 2−14 days at 267 K and atmospheric pressure. They also mentioned that agglomerate ice−CH_4 hydrate crystals retained hydrate for about two years under the same conditions. The long lifetimes in their experiments might be explained if their crystals were larger than those in our experiments. Another difference between their study and ours is that their hydrate particles were coated with ice before dissociation began. This might have produced an ice layer that was thicker, and with less pores and grain boundaries than the ice in our study. Such an ice layer could explain the discrepancy with our results.

We studied the dissociation process of finely powdered CH_4 hydrate far below the melting temperature of ice Ih and showed the importance of diffusion through an ice layer. Additional observations at higher temperatures are needed to understand the self-preservation effect of CH_4 hydrate just below the melting temperature of Ih.

Conclusions

In these experiments, we clarified the transformation process of CH_4 hydrate into ice Ih under atmospheric pressure and at temperatures of 168 and 189 K. In situ observations of CH_4 hydrate dissociation using X-ray diffraction indicated that dissociation has two regimes. In the first, initial regime, the dissociation rate is faster, and the resulting ice Ih has relative X-ray diffraction intensity ratios that are larger for the (10−11) and (11−20) planes. The dissociation rate is slower in the second regime in which the hydrate decomposition follows a diffusion process that indicates that the hydrate is coated by an ice layer. The two-regime process agrees with an earlier study, but the rate of decomposition was much greater than previous experiments with larger hydrate particles. The inferred coefficients for diffusion of CH_4 through ice were 2.2×10^{-11} m^2/s at 189 K and 9.6×10^{-12} m^2/s at 168 K; these values suggest that the ice layers had pores or grain boundaries that allowed faster diffusion than would occur through an ideal ice lattice.

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