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Transformation of Methane Hydrate to Carbon Dioxide Hydrate: In Situ Raman Spectroscopic Observations

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An in situ Raman spectroscopy study on the guest replacement of methane hydrate with carbon dioxide at high pressures is presented. The surface shielding of carbon dioxide hydrate formed in the outer layer plays a key function, retarding dissociation of methane hydrate in the core. A thorough investigation of Raman spectra of the vibration modes of water molecules enables us to understand the phenomena of the coexistence of methane and carbon dioxide hydrates and water phase for guest replacement reactions. These results should aid further efforts in the study of guest stability of clathrate hydrate as well as future technological applications.

I. Introduction

An important practical feature of gas hydrates is that vast quantities of methane in the form of the gas hydrate exist in the permafrost zone and the subsea sediment.[1] To develop a method for commercially producing natural gases from methane hydrate layers, the environmental and safety issues, which are of particular importance, should be first clarified. In the case of carbon dioxide hydrate, the disposal of global warming gases, mainly carbon dioxide, on the ocean floor using the hydrate formation process has been carefully studied.[2] Several field experiments were conducted to test and prove ideas for carbon dioxide ocean disposal by in situ hydrate formation.[3] Hence, for both purposes, a new application for relatively safe and environmentally harmless exploitation of methane gas from the methane hydrate reservoir by guest replacement method could emerge. We note that a complete understanding of the mechanism of guest replacement is key to the scale-up task.

It is now possible to closely monitor the exchange process of guest molecules of gas hydrate with other hydrate formers. Neutron diffraction experiments have enabled recent success in studying guest replacement, especially accompanying structural transition, and provide information for equilibrium exchange between guest molecules in the hydrate and free molecules in the surrounding phase.[4] The results showed that the reaction kinetics were dominated by the diffusion of the hydrate former through the outer hydrate layer and into the surrounding phase. It should be noted, however, that this technique has a drawback for guest replacement by hydrate formers in the same structure, as would be expected. Since Raman spectroscopy has been widely used for determining the structural identification, cage occupancy, and formation kinetics of gas hydrates,[5] it may give promising results for guest replacement experiments on gas hydrate, regardless of the hydrate structure. A fascinating feature of Raman spectroscopy is that the OH stretching intensity observed in Raman spectra of water in hydrate, ice, or liquid phases demonstrates the wide variety of hydrogen-bonding environments experienced by water molecules.[6] Here we document favorable exchange between carbon dioxide and methane hydrate by replacement reactions from in situ Raman spectroscopy at high pressures. The substitution rates are monitored in situ by observing the change in relative intensity of Raman spectra for methane and carbon dioxide molecules in the hydrate cavities.

II. Experimental Section

A Raman spectrometer with a triple monochromator of 1600 grooves/mm grating and a CCD detector were used in this work. An Ar-ion laser source emitting a 514.5 nm line was used with a power of 200 mW. The scattered radiation was collected at 180° geometry with a slit width of 250 μm.

Powdered methane hydrate with an average diameter of about 100−250 μm was used as the starting material. The methane hydrate powder was prepared by grinding ice grains in a high-pressure cell with methane gas under the conditions of 270 K and 15 MPa for about 10 days. The reaction was monitored by carefully recording the system pressure using a pressure transducer during sample fabrication. After completion of the formation reaction, we checked for the presence of unreacted ice in the samples by X-ray diffractometry using synchrotron radiation on BL-18C at the Photon Factory, High Energy Accelerator Research Organization (KEK).[7] Thus, it was confirmed that this material consists of almost pure methane hydrate and contains a maximum of a few volume percent of ice. Small and large hydrate particles were removed with 100 and 250 μm sieves, respectively, in liquid nitrogen.

For the replacement reaction, the hydrate samples were inserted into a high-pressure cell under liquid nitrogen and sealed instantly by the sapphire window. For complete conversion of remaining ice in the hydrate particles due to incomplete conversion or possible partial decomposition during sample treatment, the system temperature and pressure were increased to 275 K and 7 MPa by high-pressure methane gas. Complete conversion of the remaining ice to methane hydrate is then obtained by keeping the sample in the vessel for approximately 24 h. Our preliminary measurements using a high-pressure DSC indicate that this process allows us to confirm that the amount

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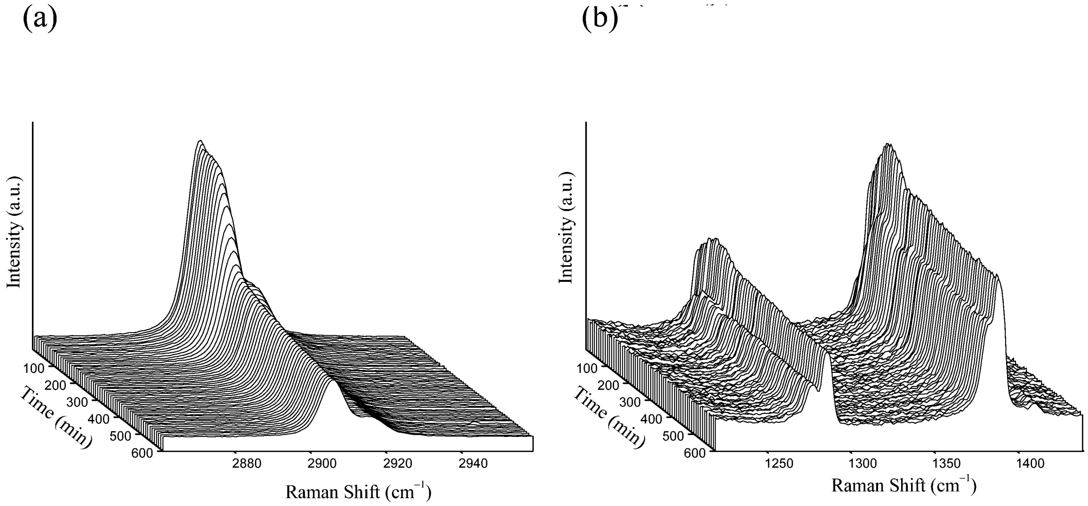

Figure 1. Time-resolved Raman spectra for the C−H stretching mode of CH_4 molecules encaged into hydrate (a) and for CO_2 molecules encaged into the large cavity of hydrate (b). The experimental conditions for guest replacement are 281 K and 4 MPa (CO_2).

of unreacted ice in the samples is very negligible. Next, the system temperature and pressure were decreased to 270 K and 3 MPa to minimize an abrupt melting of the hydrate surface during exchange of the gas phase. Isobaric exchange of the methane gas phase with carbon dioxide, and then a quick increasing of temperature and pressure up to the experimental condition, led to initiation of guest replacement of methane hydrate. For the replacement reaction, the gas phase is continuously refreshed with carbon dioxide using a pressure control unit and a metering valve, and it is monitored by Raman spectroscopy to confirm complete removal of methane gas generated by dissociation of methane hydrate.

III. Results and Discussion

Figure 1 shows the time-resolved Raman spectra for guest replacement of methane hydrate by carbon dioxide at 4 MPa and 281 K. The initial replacement rate of methane hydrate was very fast within 200 min, and then became relatively slow. In particular, a sharp increase in the Raman peaks of carbon dioxide hydrate was observed for the initial 100 min, but the relative intensity change does not depend on the elapsed time after 100 min. This suggests that the replacement by carbon dioxide stops when the thickness of the carbon dioxide hydrate layers is enough to become a strong barrier against the diffusion of carbon dioxide, which is consistent with the formation of clathrate hydrates on the surface of ice observed by using hyperpolarized xenon.[8] The effect of methane molecules released from the hydrate core on the formation of carbon dioxide hydrate layers would also not be negligible. It should be noted, however, that complete replacement of methane hydrate by carbon dioxide hydrate is expected to take considerable time, even if a high partial pressure of carbon dioxide is maintained on the sample.

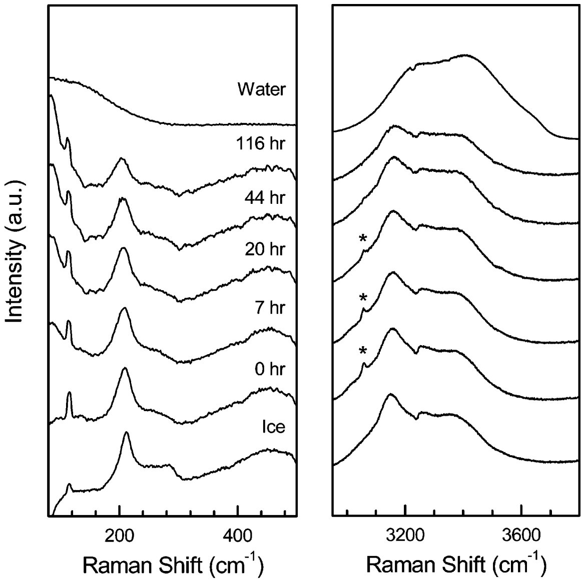

Figure 2. Raman spectra of lattice vibrations and O−H vibrations around 100−400 and 3000−4000 cm^{-1}, respectively, of sI hydrate. The asterisks denote characteristic Raman peaks for weak C−H vibration of methane molecules in the cages of the sI hydrate discussed in the text. For comparison, the intensity for hydrate samples is reduced in a same scale, even though it is given in arbitrary units. The experimental conditions for replacement are 278 K and 3 MPa (CO_2).

We then investigated the intermediate phase between the methane and carbon dioxide hydrate layers. Figure 2 shows the time-resolved Raman spectra of two vibration modes in water molecules during the replacement of methane hydrate. The peaks between 100 and 500 cm^{-1} belong to lattice vibration modes of water in the hydrate, ice, or liquid phases. The relatively broad peaks for O−H vibrations can be observed between 3000 and 3700 cm^{-1}. As the reaction time increased, the relative intensity of the Raman peaks for gas hydrate (both methane and carbon dioxide hydrates) decreased, indicating that the total amount of gas hydrate decreased with increasing time. In contrast, the broad Raman baseline peak around 100 cm^{-1}, which is assigned to liquid water, steadily increased with increasing time. This was confirmed by cooling the sample back to 268 K and observing the decrease of the broad Raman peaks for water. Thus, we can conclude that, for the replacement reaction, the dissociation rate of methane hydrate is faster than the rate of formation of carbon dioxide hydrate layers. Notably, carbon dioxide hydrate in the crust layer plays a key role in significantly retarding the dissociation of methane hydrate in the core over a 100 h time scale. This retardation phenomenon would be of immense interest and increasing importance for future technological applications to transportation of natural gases by hydrate formation.

Of particular interest is that a new Raman band was found at 3060 cm^{-1}. This peak in the beginning was relatively strong, and then became weak, and finally not detectable. Our preliminary measurements indicate that two similar peaks of pure methane gas at 5 MPa could be observed at 3020 and 3070 cm^{-1}, respectively. Thus, these peaks can be assigned to weak

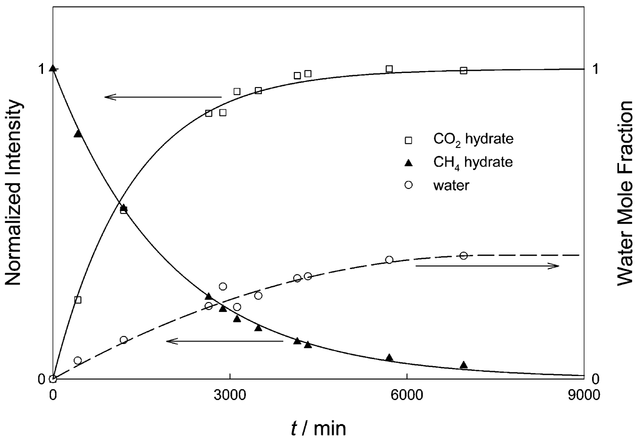

Figure 3. Normalized intensity of the Raman signal due to CH_4 and CO_2 molecules encaged into the cavity of the sI hydrate as a function of time. Water mole fraction is obtained from the intensity of the hydrate (CO_2 and CH_4 hydrates) Raman peaks at 205 cm^{-1}. The replacement conditions are 278 K and 3 MPa (CO_2).

Raman bands for the C−H stretching vibration of methane molecule in the vapor phase. The intensity and width of the new peak of methane hydrate at 3060 cm^{-1} are very similar to those of two peaks of pure methane gas. We note that this new peak was also observed for methane hydrate at 140 K and 1 atm, conditions at which methane hydrate is stable. However, when the measurements were performed with propane hydrate, we could not find any similar characteristic Raman band at the range of 3000−3100 cm^{-1}. This indicates that new small peaks should not be ascribed to the O−H vibrations of water molecules in the methane hydrate network. Hence, it is clear that the new peak observed at 3060 cm^{-1} could be assigned to a characteristic Raman peak for weak C−H vibrations of methane molecules in the cages of the sI hydrate. Prominent Raman bands for the C−H stretching vibration of methane in the sI hydrate cages have been observed at 2905 cm^{-1} for the large cage and 2915 cm^{-1} for the small cage as shown in Figure 1. As shown in Figure 2, there are no definitive conclusions for the split Raman band of methane hydrate at 3060 cm^{-1}, which indicates the occupation of both the large and small cages, as the intensity of new peaks is very small. However, we believe that the new Raman peaks observed in this work should be considered as a useful parameter for monitoring the formation or dissociation kinetics of methane hydrates. This requires a more complete understanding of Raman characteristics of new peaks by theoretical as well as experimental studies.

The replacement experiments were carried out at 278 K and 3 MPa (CO_2) on a long time scale as shown in Figure 3.As previously mentioned, the gas phase is continuously refreshed with pure carbon dioxide to remove methane gas released from the hydrate core during the replacement reaction. Thus, the surrounding gas phase is always pure carbon dioxide for the entire reaction. One can see that the replacement reaction appears to be almost complete after a 150 h exposure of the methane hydrate samples to carbon dioxide. This indicates that it may be possible to expect favorable exchange between carbon dioxide and methane hydrate when the methane hydrate is replaced with carbon dioxide for sufficient reaction time, especially at temperatures above the ice point. When considering the kinetic behavior in Figure 3, it is clear that the water phase produced during the replacement reaction plays a key role in the relatively fast recovery of methane gas from methane hydrate, as it has much lower diffusion resistance than the solid phase. For instance, when the replacement reaction was carried out at 253 K and 0.8 MPa (CO_2), we could obtain only less than 10% conversion of methane hydrate after 20 h. Another aspect to be noted is that, from a microscopic point of view, a considerable volume change between the hydrate and water phases involves changing the sample morphology, such as the microfracture of the surface hydrate layer formed with carbon dioxide, which would allow the reaction to proceed rapidly by enhancing diffusion of both methane and carbon dioxide. It is worthwhile to note that the conversion of a fraction of methane hydrate to carbon dioxide hydrate can be balanced by the conversion of a portion of methane hydrate to water. For the replacement reaction investigated in this work, about 60% of methane hydrate can be transformed to carbon dioxide hydrate, provided the other 40% of methane hydrate melts. Incomplete conversion to carbon dioxide hydrate should be attributed to shielding effects of the surface layer.

IV. Conclusion

We presented experimental arguments for the guest replacement of methane hydrate with carbon dioxide using in situ Raman spectroscopy at high pressures. The surface shielding of carbon dioxide hydrate formed in the outer layer plays a key function of retarding the dissociation of methane hydrate in the core. However, the water phase produced during the replacement reaction allows the reaction to proceed rapidly by enhancing diffusion of both methane and carbon dioxide, resulting in complete and relatively fast recovery of methane gas from methane hydrate. These results may strongly encourage further efforts in the study of guest stability of clathrate hydrate and may provide useful applications for future technologies.

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References and Notes

(1) Kvenvolden, K. A. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 3420.

(2) Saito, T.; Kajishima, T.; Nagaosa, R. *Environ. Sci. Technol.* **2000**, *34*, 4140.

(3) Brewer, P. G.; Friederich, G.; Peltzer, E. T.; Orr, F. M., Jr. *Science* **1999**, *289*, 943.

(4) Halpern, Y.; Thieu, V.; Henning, R. W.; Wang, X.; Schultz, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 12826.

(5) Sum, A. K.; Burruss, R. C.; Sloan, E. D., Jr. *J. Phys. Chem. B* **1997**, *101*, 7371. Mao, W. L.; Mao, H.-K.; Goncharov, A. F.; Struzhkin, V. V.; Guo, Q.; Hu, J.; Shu, J.; Hemley, R. J.; Somayazulu, M.; Zhao, Y. *Science* **2002**, *297*, 2247. Chou, I. M.; Sharma, A.; Burruss, R. C.; Shu, J.; Mao, H. K.; Hemley, R. J.; Goncharov, A. F.; Stern, L. A.; Kirby, S. H. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 13484.

(6) Shimizu, H.; Hori, S.; Kume, T.; Sasaki, S. *Chem. Phys. Lett.* **2003**, *368*, 132. Chou, I. M.; Blank, J. G.; Goncharov, A. F.; Mao, H. K.; Hemley, R. J. *Science* **1998**, *281*, 809. Hemley, R. J.; Chen, L. C.; Mao, H. K. *Nature* **1989**, *338*, 638.

(7) Hirai, H.; Uchihara, Y.; Fujihisa, H.; Sakashita, M.; Katoh, E.; Aoki, K.; Nagashima, K.; Yamamoto, Y.; Yagi, T. *J. Chem. Phys.* **2001**, *115*, 7066.

(8) Moudrakovski, I. L.; Sanchez, A. A.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Phys. Chem. B* **2001**, *105*, 12338.