Effect of low concentration hydrogen sulfide on cage occupancy during hydrate formation

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Near-surface gas hydrate beneath the sea floor encages not only light hydrocarbons but also hydrogen sulfide. Microbial community produces hydrogen sulfide in the layer of anaerobic oxidation of methane (AOM) using methane ascending from deeper sediment layer and sulfate supplied from sea water. In the case of methane and hydrogen suflide mixed-gas hydrate, hydrogen sulfide decreases its equilibrium pressure and stabilize the hydrate crystal. The system of methane and hydrogen sulfide, gas hydrate forms the cubic structure I. It is known that hydrogen sulfide induces guest-host interaction rather than methane. Therefore, hydrogen sulfide may affect the cage occupancy of large and small cages and change its hydration number. In this study, we focused on the cases of low concentration of hydrogen sulfide and synthesized methane and hydrogen sulfide mixed-gas hydrate in order to check the ratio of cage occupancy between large and small cages for methane and hydrogen sulfide.

Hydrate samples were synthesized in a pressure cell (volume: 30mL) at 273.2K and retrieved the crystals at the temperature of liquid nitrogen. Concentration of hydrogen sulfide in the hydrate-bound gas was controlled less than several percent. Hydrate-bound and residual gases were obtained and their gas compositions were determined using a gas chromatograph. Raman spectra of the crystals were obtained at 123 K in the range 2,800-3,000 cm^{-1} and 2,500-2,700 cm^{-1} for the C-H stretching peaks of methane and the S-H stretching peaks of hydrogen sulfide, respectively. The Raman peaks were fitted using a Voigt function to obtain the integrated intensities of the two peaks corresponding to methane and hydrogen sulfide encaged in the large and small cages of the cubic structure I.

The cage occupancy ratio of large to small cages for methane slightly increased with the concentration of hydrogen sulfide, whereas that for hydrogen sulfide was smaller than that for methane. These results indicate that hydrogen sulfide molecules prefer to be encaged in small cages and molecules of methane tend to encage in large cages.

Keywords: gas hydrate, hydrogen sulfide, cage occupancy, Raman spectroscopy

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