ラマン分光分析によるメタン・エタン混合系ガスハイドレートの自己保存効果の検証

Validation of self-preservation effect of methane and ethane mixed-gas hydrate by Raman spectroscopy

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Methane hydrate can be stored long time under atmospheric pressure below 273.2K, even though their P-T conditions is unstable, namely "self-preservation effect". On the contrary, Takeya and Ripmeester (2008) reported that ethane hydrate shows no self-preservation. In natural condition, methane and ethane mixed-gas hydrates have been found at Lake Baikal, however, there is no information for the mixed-gas system. In the last JpGU meeting we report self-preservation effect for mixed-gas hydrate, but the conditions of samples are not uniform. Because the size of crystals affect rate of survival at higher temperature, we controlled the specific surface of area of gas hydrate samples in this study.

We put 0.7 g of fine ice balls (diameter: 0.108-0.180 mm) into a pressure cell (volume: 30 mL) and mixed-gas of methane and ethane was introduced. Hydrate crystals formed at 273.2 K. The gas hydrate sample was degased and recovered at the temperature of liquid nitrogen. We controlled the ethane composition of hydrate-bund gas from 0% to 100%, covering the area of methane-rich structure I, ethane-rich structure I, and their intermediate structure II. We measured compositions of methane and ethane by a gas chromatograph (GC-2014, Shimadzu Corporation). Gas hydrate samples were placed on a temperature-controlled device and kept at 80 K. Raman spectra of hydrate samples were obtained using a Raman spectrometer (RMP-210, JASCO Corporation). We checked the Raman spectra of C-H stretching mode at 83 K, and then increased the sample temperature every 10 K until complete dissociation. We calculated the Raman peak area for C-H stretching mode of methane and ethane around 2900 cm^{-1} by a peak fitting method and obtained the survival rate of gas hydrate samples with temperature.

Pure methane hydrate survived well, more than 20% of hydrate still remained at 263 K, whereas pure ethane hydrate completely dissociated at around 200 K. These results agree well with our previous report. As for mixed-gas hydrate composed of methane and ethane, the rates of survival of structure I were lower than that of pure methane hydrate, but the crystals remained till 253 K, suggesting self-preservation. That of structure II well remained at 83-183 K, but quickly disappeared at 213 K. Therefore, it is possible that the survival rate of mixed-gas hydrate composed of methane and ethane depends on not only gas composition but also crystallographic structure.

Reference

Takeya S, Ripmeester JA (2008) Dissociation behavior of clathrate hydrates to ice and dependence on guest molecules. Angew Chem Ed 47: 1276-1279

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