メタンエタン系混合ガスハイドレートの自己保存効果
Self-preservation phenomena of methane and ethane mixed-gas hydrates

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Gas hydrates are crystalline clathrate compounds composed of gas and water molecules, and stable under low temperature and high pressure conditions. In the case of methane hydrate, samples can be stored under atmospheric pressure below 273.2K, even though their P-T conditions is outside the zone of their stability. Researchers call this phenomena as "self-preservation effect". Takeya and Ripmeester (2008) clarified many kinds of guest gas and found that ethane hydrate has no self-preservation. In the retrieval process of near-surface gas hydrates on a research vessel, the structure I hydrates of methane-rich tends to remain under the atmospheric pressure, whereas the structure II hydrates of methane and ethane mixed-gas tends to dissociate quickly. In this study, we clarify the self-preservation effect of gas hydrate for methane-ethane system by using Raman spectroscopy.
As for sample preparation, we put 0.7g of fine ice powder into a pressure cell (volume: 30mL), introduced methane and ethane mixed-gas, and formed a gas hydrate at 273.2K. The gas hydrate sample was cooled and recovered at the temperature of liquid nitrogen. We controlled the ethane composition of hydrate-bund gas from 2% to 98%, 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. Gas hydrate samples were placed on a temperature-controlled device and kept at 123K for Raman spectroscopy. We measured their Raman spectra of C-H stretching mode (center: 2900cm^{-1}) and C-C stretching mode (center: 1000cm^{-1}) each for ten minutes, and then increased the sample temperature every 10K until complete dissociation. We calculated the Raman peak area for C-H stretching mode of methane and ethane around 2900cm^{-1} by a peak fitting method and obtained the decrease process of gas hydrate samples with temperature.
In the same conditions of increasing temperature, pure methane hydrate well survived, while pure ethane hydrate completely dissociated around 193K. In the case of mixed-gas system of methane and ethane, the rates of survive for most cases were plotted between those of pure hydrates. However, the rates of survive for samples of low ethane composition (2-5%) were rather larger than that of pure methane hydrate.

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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