

## Effect of gas composition on dissociation heat of mixed-gas hydrate composed of methane and ethane

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Structure I and II gas hydrates, composed of methane and ethane, were observed in the same sediment cores in Kukuy K-2 mud volcano, Lake Baikal (Kida *et al.*, 2006). Enormous amount of latent heat generates/absorbs at the formation/dissociation process of gas hydrates and controls their thermal condition themselves. Although Handa (1986) obtained the dissociation heat of pure methane/ethane hydrate, little attention has been given to natural gas hydrate (mixed-gas hydrate). Hachikubo *et al.* (2008) reported the dissociation heat of methane and ethane mixed-gas hydrate, but gas composition of the sample was not uniform due to preferential consumption of ethane into hydrate phase in a batch-type reactor. We supposed that the change of crystal structure affects to a hydration number and a dissociation heat of the hydrate. In this study we investigated the effect of ethane concentration on dissociation heat of mixed-gas (methane and ethane) hydrate by an improvement of sample preparation.

Samples of mixed-gas hydrate were formed in a pressure cell with an agitation system. 2g of pure water was put into the cell and pressurized by nine different composition of methane and ethane mixed-gas at 274K. After well agitation of gas and water, a nucleation occurred by an artificial vibration. The residual gas and the hydrate were sampled and their gas compositions were determined by GC. Ethane in the hydrate phase was enriched from the gas phase and its compositions were 1.2%, 1.6%, 3.7%, 10.9%, 17.5%, 21.2%, 30.1%, 55.1% and 63%. The hydrate samples were ground up well in liquid nitrogen and then put into a Tian-Calvet type heat-flow calorimeter (BT2.15; Seraram Instrumentation) and their dissociation heat were measured. Inside the calorimeter was pre-cooled at 93K. The internal pressure, temperature and a heat flow to/from the sample were monitored. The sample was heated from 93K to 298K at the rate  $0.15 \text{ K min}^{-1}$  to dissociate gas hydrate. Dissociation heat was calculated by an integration of the peak of heat flow and the amount of dissociated gas.

Thermograph of the mixed-gas hydrates showed some complicated behavior: some samples dissociated rapidly at the last stage and some other samples formed two peaks. These results indicate that a **self-preservation** like effect appeared in their dissociation process and secondary generation of ethane-rich gas hydrate simultaneously with the dissociation process (Hachikubo *et al.* (2008). Dissociation heat of the mixed-gas hydrate was within the range between those of pure methane and ethane hydrates and increased with ethane concentration.