CP-MAS 13C-NMR Studies on the Crystallographic Structure of Natural Gas Hydrate

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A natural gas hydrate is present in natures at the bottom of sea or inside of permafrost layer. Natural gas hydrates are expected as natural gas resources since the amounts of that have been estimated to be a lot. A gas hydrate is an ice-like substance, which encaged gas molecules in the polyhedral cages consist of hydrogen-bonded water molecules. Three types of gas hydrate structures, structure I, structure II and structure H are known to be present in nature. The structures are dependent on kind of encaged natural gas components and vary the gas volume densities. Therefore, it is important to clarify the structures of natural gas hydrates for estimating the amount of resources.

It has been known that 13C-NMR technique is a very powerful tool to determine the structure of gas hydrates containing hydrocarbons. In the present work, we applied 13C-NMR technique to reveal relations between gas compositions and structures of artificially prepared multi-components hydrate samples. And then, 13C-NMR measurements on the natural gas hydrate samples obtained from the Okhotsk Sea and Lake Baikal were performed.

The binary gas hydrates containing CH4, CH4 + C2H6, CH4 + C3H6 and CH4 + CO2 were artificially prepared from ice particles and the corresponding gas mixture with appropriate compositions using a Milling-type high-pressure vessel at 263 K. Natural gas hydrate samples of the Okhotsk Sea were obtained from five locations of the Okhotsk Sea Offing of northeast Sakhalin. The sampling was performed as a part of KOMEX (Kurili-Okhotsk Marine EXperiment) Project 2002 and CHAOS (Hydro-Carbon Hydrate Accumulations in the Okhotsk Sea) Project 2003. Lake Baikal sample was obtained from south of Lake Baikal.

13C-NMR measurements were carried out using a NMR apparatus (JEOL model JNM-AL400, 400 MHz). 13C-NMR spectra were measured with CP-MAS technique at 163 – 183 K. The decomposition gases from the artificially prepared samples and the natural samples were analyzed by gas chromatograph (SHIMADZU model GC-14B).

Artificially prepared pure CH4 forms structure I (sI) hydrate and shows two peaks at –1.80 ppm (P1) and –4.18 ppm (P2), where P1 and P2 are attributed to CH4 in small cages (12-hedron) and in large cages (14-hedron), respectively. In the case of a mixed gas hydrate sample with 66.8 % of CH4 and 33.2 % of C2H6, P2 was observed at the position with lower chemical shift value than pure CH4 hydrate. On the other hand, almost no appreciable shift was observed on P1. Pure C2H6 hydrate is of sI and shows only a peak at 10.06 ppm (P3) due to C2H6 in large cages of 14-hedron. In the sample with 66.8 % of CH4 and 33.2 % of C2H6, P3 position sifted to 8.55 ppm. These changes in chemical shift values towards lower value for CH4 and C2H6 in large cages indicate the change in the size of large cage from 14-hedral cage to 16-hedral cage. Namely, the crystallographic structure of the mixed hydrate was clearly shown to be structure II (sII). The chemical shifts to the lower values were observed in the range of approximately 20 – 40 % of ethane, indicating that CH4+C2H6 hydrates in the range are of sII.

For CH4+C3H8 system, structural change depending on the gas composition was not observed, where all CH4+C3H8 hydrates were of sII hydrates. For CH4+CO2 mixtures, the structures of all CH4+CO2 samples were found to be sI. Thus, the crystallographic structures of the mixed hydrates are sensitive to the gas components and gas compositions.

For analyzed natural gas hydrates, only CH4 peaks were observed at same positions as artificial pure CH4 hydrate. No other peaks from higher hydrocarbons were observed. The decomposition gas fraction of all natural hydrate samples by gas chromatography was over 95 vol % of CH4, less than 5 vol % of CO2, less than 3000 ppm of H2S and less than 100 ppm of C2H6 and C3H8.

Thus, it is revealed that these natural gas hydrates are of sI, and the principal component is CH4.