Structure Identification and Dissociation Enthalpy Measurement of the CH_4 + C_3H_8 Hydrate Replaced by CO_2

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The CH_4-CO_2 replacement occurring in natural gas hydrates has attracted significant attention due to its double function for CH_4 recovery and CO_2 sequestration. This study examined the influence of the CH_4-CO_2 replacement occurring in the CH_4 (90%) + C_3H_8 (10%) hydrate on the hydrate structure and dissociation enthalpy (ΔH_d). The crystalline structure of gas hydrates before and after replacement using CO_2 was investigated using powder X-ray diffractometer (PXRD). In addition, ^{13}C NMR was adopted in order to identify the cage-dependent guest molecule distribution in the gas hydrates before and after replacement with CO_2. The composition of the hydrate phase was measured using a gas chromatograph. A gradual increase in the extent of the replacement was observed as the driving force (ΔP_{CO2}) increased. A high-pressure micro-differential scanning calorimeter (HP μ-DSC) revealed that the ΔH_d values of the hydrates after replacement with CO_2 were decreased with large variation depending on ΔP_{CO2}, comparing with those of initial CH_4 + C_3H_8 hydrates.