Experimental Verification of Structural Transition and Dissociation Enthalpy Change during CH_4 Recovery Induced by CO_2 Injection into CH_4 + C_3H_8 hydrate

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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. In this study, CO_2 was injected into the CH_4 + C_3H_8 hydrate to identify the influence of the replacement on the hydrate structure and dissociation enthalpy (ΔH_d). The shift of the three-phase (H-L_W-V) equilibrium line after CO_2 injection indicated that a significant portion of CH_4 and C_3H_8 in the initial hydrate was replaced with CO_2. The extent of the replacement was measured using a gas chromatograph, and was gradually increased as the driving force (ΔP_{CO2}) increased. The NMR confirmed that the CH_4 + C_3H_8 hydrate is structure II and no structural transition was observed after the replacement. The influence of the replacement on ΔH_d was examined using a high-pressure micro-differential scanning calorimeter (HP μ-DSC). During the replacement, there was no significant heat flow associated with the hydrate dissociation or formation. This study revealed that the CH_4 recovery induced by CO_2 injection into CH_4 + C_3H_8 hydrate could be achieved in a sII isostructural system without significant hydrate cage destruction.