Effects of Na-montmorillonite on thermodynamic equilibria, guest distributions, and dissociation behaviors of CH_4 hydrates

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Natural gas hydrates are nonstoichiometric compounds that formed at high pressure and low temperature and have a large potential of future clean energy resources. Some gas hydrates show meta-stability, which means gas hydrates are not dissociated below thermodynamic equilibrium curves. This unusual behavior is called self-preservation effect. Recently, it was revealed that the presence of montmorillonite (MMT), one of marine clay components, can affect cage occupancy of CH_4 hydrate. However, the dissociation behavior has not been well studied. In this study, the effects of Na-saturated MMT on the thermodynamic equilibria, guest distributions, and dissociation behaviors of CH_4 hydrates were examined with different MMT concentrations (0, 10, and 50 wt%). The cage occupancy of CH_4 hydrates with MMT were analyzed using ^{13}C NMR. In addition, the hydrate dissociation behaviors in the presence of MMT were observed by temperature-dependent powder X-ray diffraction patterns. The results demonstrated that Na-MMT does not affect H-L-V equilibria of CH_4 hydrates, but can contribute to retarding the dissociation of CH_4 hydrates below 273.15 K.