Mechanism of CH_4 – CO_2 Replacement that Occurs in sH Hydrates as Revealed by Phase Behavior, ^{13}C NMR, and Molecular Dynamics Simulation

서용원†, 이요한, 주세훈, 곽상규
울산과학기술원
(ywseo@unist.ac.kr†)

In this study, the phase equilibria of the CH_4 + CO_2 + methylcyclopentane (MCP) hydrates were compared with those without MCP to elucidate the influence of MCP on the thermodynamic hydrate stability for the replacement. Also, to identify the structure of CH_4 + CO_2 + MCP hydrates depending on the CO_2 concentrations, and to examine the influence of replacement on the cage-specific guest distributions, the CH_4 + CO_2 + MCP hydrates and the replaced hydrate with CO_2 were analyzed using ^{13}C NMR spectroscopy. The hydrate phase behavior and 13C NMR spectroscopy results demonstrated that CO_2 functions as a co-guest of sH hydrates in CH_4-rich conditions and that the structural transition of sH to sI hydrates occurs in CO_2-rich conditions. Through the molecular dynamics simulation, it was verified that the structural transition involved the dissociation of initial sH hydrates and subsequent reformation of sI hydrates. The overall experimental and computational evidence can provide further insights into the exchange behavior of the guest molecules for the replacement mechanism occurring in sH natural gas hydrates.