Abnormal Structural Transition Induced by Cage-dependent Guest Exchange in CH4 + C3H8 Hydrates with CO2 Injection for Energy Recovery and CO2 Sequestration

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Abstract

This study investigated a structural transition induced by cage-dependent guest exchange in the CH4 + C3H8 hydrate with CO2 injection for CH4 recovery and CO2 sequestration. The influence of the CO2 replacement on the crystalline structure of initial CH4 + C3H8 hydrates and the cage-dependent distribution of guest molecules were quantitatively investigated using powder X-ray diffraction, 13C NMR spectroscopy, and gas chromatography. The quantitative analyses demonstrated that the CO2 occupation caused the depletion of C3H8 molecules in the large 51264 cages of sII hydrates, thereby resulting in the subsequent transformation into CO2-rich sI hydrates and the coexistence of sI and sII hydrates after the replacement. The guest-exchange behaviour observed from time-dependent Raman spectra indicated that the replacement rate was increased with an increase in PCO2 and that the extent of the replacement was enhanced at higher PCO2. Overall experimental evidence of the partial structural-transition replacement suggests that CO2 molecules first occupied sII hydrates predominantly with the rapid guest exchange at the surface and that the initial sII hydrates were subsequently converted to the CO2-rich sI hydrates from the surface to the inner side. Precise identification of the mechanism responsible for the partial structural transition occurring in the CH4 + C3H8 - CO2 replacement will be very helpful in developing a strategy for actual CO2 injection into sII gas hydrate reservoirs for energy recovery and CO2 sequestration

Keywords: *Gas hydrate, Replacement, CO2 sequestration, Structure II, Strucutral transition*