Effects of CO_2 injecting pressure on the hydrate replacement behavior and gas production efficiency in sI and sH hydrates

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The gas hydrate replacement using CO_2 injection has been considered as a promising natural gas production technology which can function as both energy recovery and CO_2 sequestration. In this study, structure I and H hydrates were formed with CH_4 and CH_4 + methylcyclopentane (MCP), respectively. To examine the effect of the CO_2 injecting pressure on the replacement behavior, the replacement experiment was conducted at pressure ranges where pure CO_2 hydrate is thermodynamically stable and gaseous CO_2 is not liquefied. To identify the replacement efficiency of each experiment, the compositions of hydrate phase were measured by gas chromatography. In addition, Raman spectroscopy, ^{13}C NMR, and powder X-ray diffraction were used to observe the guest exchange behavior and structural information of gas hydrates during the replacement. In case of sH hydrate, the replacement efficiency was increased with increasing the CO_2 injecting pressure. However, for sI hydrate, the replacement efficiency was found to be almost constant irrespective of experimental pressure.