Molecular dynamics simulation of CH4-CO2 mixed hydrate

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The molecular dynamics (MD) method was applied to CH4-CO2 mixed hydrate (structure I, Pm3n) in order to reproduce and predict the compositional dependence of crystallographic and thermodynamic properties.

The following three types of mixed hydrate crystals were prepared for the simulation:

1) The CH4 is completely partitioned into S-cage, and CO2 into M-cage.

2) The CH4 and CO2 are evenly distributed to S- and M-cages (Disordered structure).

3) The CO2 is completely partitioned into S-cage, and CH4 into M-cage.

The system contains 216 gas molecules (= 54 in S-cage + 162 in M-cage) and 1242 H2O molecules. The interatomic potential model employed in this study is an empirical one, which can reproduce the dielectric constant, diffusion coefficient, and density for H2O, the vibration spectrum, density, and structure for CH4 and CO2. The MD calculation was carried out under constant temperature and pressure conditions with the step time of 0.4 fs. In each MD run a sufficient long period of aging (more than 100000 steps) was performed in order to establish steady state of the system. After this, the subsequent period of 50000 steps was carried out to calculate time-averaged lattice parameter and molar enthalpy.

The characteristic results are as follows:

1) The compositional dependence of lattice parameter

The lattice parameter varies systematically with the CO2 concentration [= CO2 / (CH4 + CO2)] in M- and S-cages. The lattice parameter of CO2 hydrate is 0.1 % (100 K, 0.01 GPa) or 0.3 % (300 K, 0.01 GPa) larger than that of methane hydrate. The concentration of CO2 in S-cage largely affects the lattice parameter.

2) The compositional dependence of molar enthalpy

The excess molar enthalpy is shown in Figure 1. The structure with the enrichment of CO2 into M-cage is more stable than the disordered structure, where CH4 and CO2 are evenly distributed to both cages. This is consistent with the result of cage occupancy measurements by use of Raman spectroscopy (Nakano and Ohgaki, 2000).

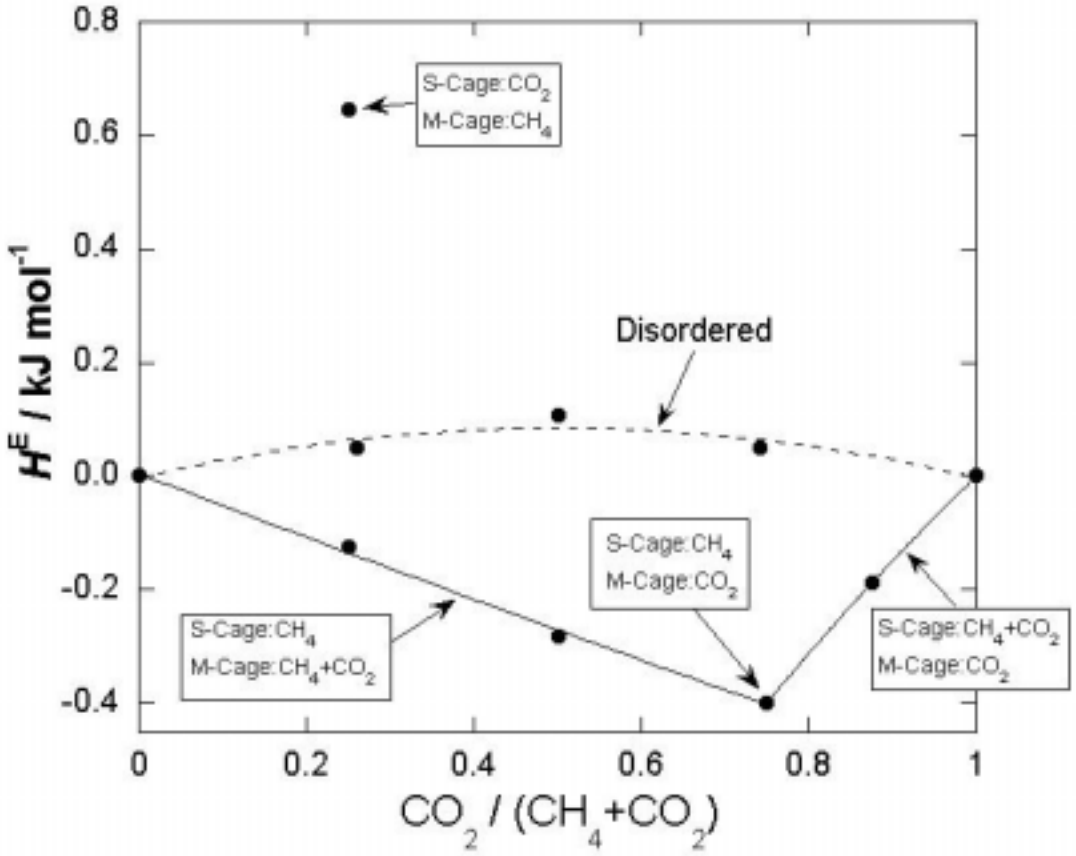

Fig. 1. MD-simulated excess molar enthalpy of CH4-CO2 mixed hydrate (8/46)(CH4,CO2)・H2O (structure I) at 250 K, 0.01 GPa. Solid line: In case CH4 is completely partitioned into S-cage, and CO2 into M-cage. Dashed line: In case CH4 and CO2 are evenly distributed to S- and M-cages.