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Phase Equilibria for H_2 + CO_2 + Tetrahydrofuran + Water Mixtures Containing Gas Hydrates

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Isothermal phase equilibria (pressure−composition in the gas phase) for the quaternary system of H_2 + CO_2 + tetrahydrofuran + water have been measured in the presence of gas hydrate phase. The lowest three-phase equilibrium pressure is obtained under the condition that the mole fraction of tetrahydrofuran in water is 0.056. The Raman spectroscopy results show that the H_2 and CO_2 molecules competitively occupy the S-cage of structure-II (i.e., the H_2 molecule is enclathrated in the hydrate cages with a small amount of tetrahydrofuran at considerably low pressure).

Introduction

The purification of H_2 from gas mixtures is one of the most important techniques for developing a new society sustained by H_2 energies. An option of H_2 separation would be an application of gas hydrates (i.e., impurities in the gas mixtures are removed from the H_2 stream by generating gas hydrates where impurities are selectively entrapped in the hydrate cages). It is well-known that the pure H_2 hydrate is generated only in extremely high-pressure regions.[1,2]

In a previous paper,[3] we have investigated the phase equilibria for the ternary mixtures of H_2 + CO_2 + water. The isothermal equilibrium pressure of three-phase coexistence (gas hydrates, aqueous solution, and gas phase) has increased in proportion with the H_2 composition in the gas phase. It has been also shown that the isothermal equilibrium pressure can be estimated under a constant fugacity of CO_2 from the assumption of pure CO_2 hydrate formation.

In the present study, a quaternary mixture including tetrahydrofuran (THF) has been investigated at the same temperature with the aim of reducing operation pressures. The dependence of THF composition in the aqueous solution has been also investigated near the stoichiometric THF composition. Finally, the cage occupancy of the H_2 molecules has been discussed briefly by use of Raman spectroscopy.

Experimental Section

Experimental Apparatus. The experimental apparatus for the phase equilibrium measurements is the same as the previous one[3] except for the charge line for THF aqueous solution. The inner volume and maximum working pressure of the high-pressure cell are 150 cm^3 and 10 MPa, respectively. The cell has a set of windows for visually observing the phase behavior. All of them are immersed in a temperature-controlled water bath. The contents are agitated using an up-and-down mixing bar driven by an exterior permanent magnetic ring.

The high-pressure optical cell for the Raman spectroscopic analysis has a pair of quartz (highly pure) windows on both the upper and lower sides. The thermostated water was circulated constantly in the exterior jacket of high-pressure optical cell. A ruby ball was enclosed to agitate the contents by the vibration from outside.

Table 1. Isothermal Phase Equilibrium Data for the H_2 (1) + CO_2 (2) + THF (3) + Water Mixed System in the Presence of Hydrate Phase at 280.1 K at the THF Mole Fractions of 0.030, 0.056, and 0.080[a]

y_1	p/MPa
$x_3 = 0.030$	
0.000	0.32
0.157	0.40
0.201	0.52
0.255	0.65
0.439	0.79
0.570	0.92
0.661	1.06
0.723	1.17
0.795	1.44
0.810	1.71
0.855	2.08
0.875	2.30
0.887	2.51
0.905	2.82
0.934	3.46
$x_3 = 0.056$	
0.000	0.22
0.186	0.38
0.194	0.33
0.230	0.37
0.237	0.38
0.259	0.44
0.363	0.41
0.431	0.44
0.495	0.50
0.569	0.55
0.569	0.59
0.657	0.64
0.705	0.68
0.728	0.71
0.808	0.97
0.832	1.02
0.840	1.11
0.864	1.25
0.879	1.37
0.881	1.39
0.898	1.64
0.904	1.95
0.945	2.32
0.960	2.81
0.985	3.61
$x_3 = 0.080$	
0.000	0.23
0.183	0.34
0.253	0.45
0.591	0.61
0.752	0.80
0.794	1.00
0.849	1.26
0.874	1.43
0.925	2.00
0.946	2.47
0.967	3.10

[a] x_3 represents the composition of THF solution.

The system temperature was measured within an uncertainty of ± 0.02 K using a thermistor probe (Takara D-632), which was inserted into a hole in the cell wall. The probe was calibrated with a Pt resistance thermometer. The system pressure was measured by the pressure gauge (Valcom VPRT) calibrated by RUSKA quartz Bourdon tube gauge with an estimated maximum uncertainty of ± 0.01 MPa.

Experimental Procedures. The THF aqueous solution prepared at a desired composition was introduced into the evacuated high-pressure cell. The THF molecule generates the structure-II hydrate, and the stoichiometric mole fraction is 0.056 for the pure THF hydrate formation.[4−6] In the present study, the THF mole fractions of 0.030, 0.056, and 0.080 were adopted. The contents were pressurized up to a desired pressure by supplying the H_2 + CO_2 mixture at a desired composition and then were continuously agitated using the mixing bar. After the formation

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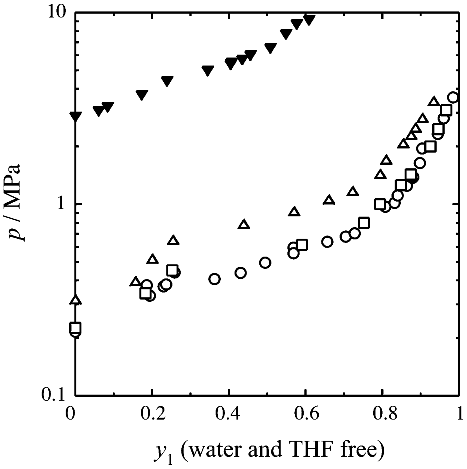

Figure 1. Isothermal phase equilibrium (pressure−composition) relations for the H_2 (1) + CO_2 (2) + THF (3) + water mixed system in the presence of hydrate phase at 280.1 K at the THF mole fraction of 0.030, 0.056, and 0.080; ▼, no additive (Sugahara et al.[3]); △, $x_3 = 0.030$; ○, $x_3 = 0.056$; □, $x_3 = 0.080$.

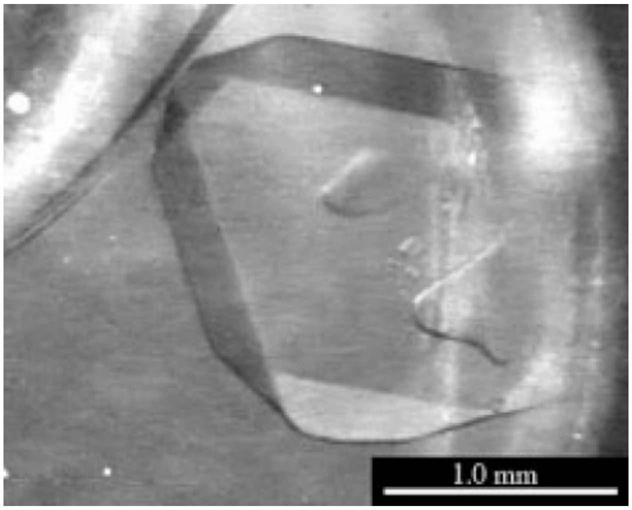

Figure 2. Photo of the hydrate single crystal for the H_2 + CO_2 + THF mixed hydrate.

of gas hydrates, the system temperature was kept constant to establish the three-phase coexisting state of hydrate + aqueous solution + gas. The phase behavior was observed directly through the window. After reaching the equilibrium state of three-phase coexistence, a small amount of gas phase was sampled for composition analysis. The equilibrium composition of gas phase was analyzed for H_2 and CO_2 by the TCD-gas chromatography (TCD-GC, Shimadzu GC-14B) as the water and THF composition of gas phase is negligibly small under the present experimental conditions.

The single crystal of gas hydrate prepared from the H_2 + CO_2 + THF + water mixtures was analyzed through a quartz window by in situ Raman spectroscopy using a laser Raman microprobe spectrophotometer with multichannel CCD detector. The argon ion laser beam (wavelength 514.5 nm, power 100 mW) from the object lens was irradiated to the sample through the upper quartz window. The backscatter of the opposite direction was taken in with the same lens. The spectral resolution was about 1 cm^{-1}.

Materials. Research grade H_2 (mole fraction purity 0.999999) was obtained from the Neriki Gas Co., Ltd. The maximum impurity was 0.2 ppm of nitrogen. Research grade CO_2 (mole fraction purity 0.9999) was obtained from the Takachiho Tradings Co., Ltd. Research grade THF (mole fraction purity 0.997) was obtained from Yashima Pure Chemicals Co., Ltd. The distilled water was obtained from the Yashima Pure Chemicals Co., Ltd. All of them were used without further purifications.

Results and Discussion

The isothermal phase equilibrium (p−y) relations for the H_2 + CO_2 + THF + water mixed system (the mole fraction of THF in water is 0.030, 0.056, and 0.080) containing gas hydrate at 280.1 K are summarized in Table 1 and shown in Figure 1. In the present study, it is assumed that the mole fraction of THF in the gas phase can be neglected. In comparison with the previous one,[2] the most remarkable change is a large depression of equilibrium pressure, which is caused by the addition of a small amount of THF. This pressure depression is the greatest at the THF mole fraction of 0.056, which is stoichiometric for the pure THF hydrate. The degree of pressure depression

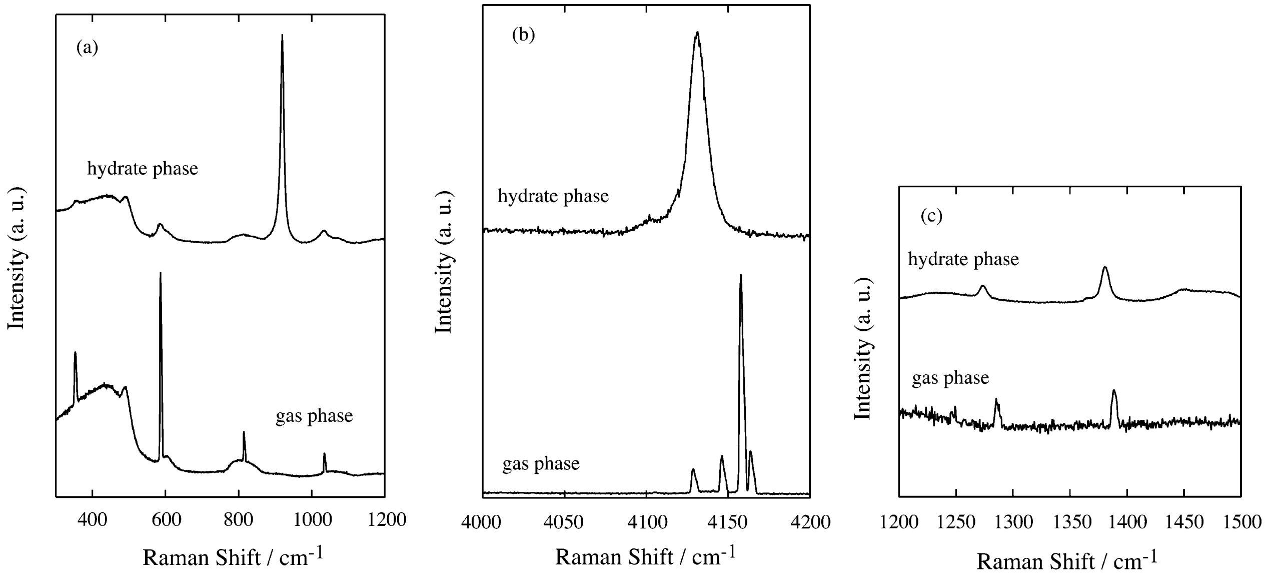

Figure 3. (a) Raman spectra of the intramolecular vibration for THF in the gas and hydrate phases. Panel contains the spectra corresponding to the rotation of H_2. The high baseline less than 520 cm^{-1} is due to the quartz windows of high-pressure optical cell. (b) Raman spectra of the intramolecular vibration for H_2 in the gas and hydrate phases. (c) Raman spectra of the intramolecular vibration for CO_2 in the gas and hydrate phases.

depends on the additive composition (i.e., the additional THF depresses the equilibrium pressure till the THF composition comes up to the stoichiometric mixture). The THF composition exceeding the stoichiometric ration does not depress the equilibrium pressure any more.

It is also notable characteristic that the unusual behavior comes into existence on the $p-y$ curve for the quaternary mixtures including THF. A stepwise increase in the equilibrium pressure appears around 0.2 in the H_2 mole fraction of gas phase (y_1) for every aqueous solution of different THF mole fractions. It is reasonable to guess that the H_2 molecule starts to occupy the S-cage of structure-II in the CO_2 + THF mixed gas hydrate at y_1 = (nearly) 0.2, although we could not obtain clear evidence of non-occupation with H_2 in the composition range of $y_1 < 0.2$. It would be a further study to make sure a physical meaning of the above discontinuous point by use of X-ray and/or neutron diffraction analyses. To confirm the existence of H_2 in the hydrate phase, the single crystals of H_2 + CO_2 + THF mixed gas hydrate were prepared in the higher composition region than $y_1 = 0.2$. The photo of a single crystal of H_2 + CO_2 + THF mixed hydrate is shown in Figure 2. The Raman spectroscopy for the above single crystal gives the characteristic signals of THF, H_2, and CO_2. The Raman shifts obtained in the present study are shown in Figure 3. The mole fraction of THF is 0.056, and the mole fraction of the gas mixture is 0.90 of H_2. As shown in Figure 3a, the single peak detected at 919 cm^{-1} corresponds to the ring breathing mode of the THF molecules enclathrated in the hydrate phase. In addition, the triplet peak corresponding to the H_2 rotation in the gas phase is observed at around 350, 590, and 820 cm^{-1}. The weak and broad peaks are also detected at the similar position in the hydrate phase. Figure 3c indicates that the split peaks by Fermi resonance effect corresponding to C═O symmetric stretching vibration mode of CO_2 are detected at 1286 and 1389 cm^{-1} in the gas phase and at 1274 and 1381 cm^{-1} in the hydrate phase. These peaks are consistent with the previous one.[3] As shown in Figure 3b, the peaks corresponding to the H−H stretching vibration mode of H_2 are observed at 4129, 4146, 4159, and 4165 cm^{-1} in the gas phase and at 4131 cm^{-1} in the hydrate phase. These sharp peaks in the gas phase and the broad and single peak in the hydrate phase corresponding to the H−H stretching vibration mode of the H_2 molecule are consistent with the reference data.[7] These findings reveal that the THF molecules occupy L-cages and that the H_2 and CO_2 molecules are competitively enclathrated in the S-cages.

Sugahara et al.[3] have claimed that the hydrate generated in the ternary system of H_2 + CO_2 + water (without THF) can be regarded as the pure CO_2 hydrate crystal (structure-I) from Raman spectroscopic study. They have also tried to estimate the equilibrium curve under the constant fugacity of pure CO_2. The gas hydrate crystal generated in the present study is the structure-II. The S-cage of structure-II is somewhat smaller than that of structure-I.[8] Therefore, it is possible that the H_2 molecule occupies the S-cage to generate the H_2 + CO_2 + THF mixed hydrate crystal.

Conclusion

Phase equilibria for the H_2 + CO_2 + THF + water mixed system were measured. The results reveal that the equilibrium pressure considerably reduces with a small amount of THF. The largest pressure depression is obtained when the THF concentration is the stoichiometric composition for the pure THF hydrate formation. In the hydrate single crystal generated from H_2 + CO_2 + THF + water mixtures, the H_2 and CO_2 molecules are competitively enclathrated in the S-cages of structure-II hydrate while the THF molecules occupy L-cages.

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