Cage Occupancy of Hydrogen in Carbon Dioxide, Ethane, Cyclopropane, and Propane Hydrates

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Abstract: We have already reported the cage unoccupancy of hydrogen in the CO_2 hydrate from the Raman spectroscopic analysis and the thermodynamic analysis using Soave - Redlich - Kwong equation of state. On the other hand, at the low temperatures, Kim and Lee (*Journal of American Chemical Society*, vol. 127, pp. 9996-9997, Jul. 2005) claimed that hydrogen is enclathrated in the CO_2 hydrate. In the present study, the cage unoccupancy of hydrogen in the CO_2 hydrate was reconfirmed clearly by in situ Raman spectroscopy for single crystal of gas hydrates. Isothermal phase equilibria (pressure - composition) and Raman spectra for three ternary systems of hydrogen + hydrocarbon (ethane, cyclopropane, propane) + water with same experimental procedures as hydrogen + CO_2 + water system were measured at 276.1 K in the pressure range up to 5 MPa. In addition, the released gas from hydrates was analyzed to confirm the occupancy or unoccupancy of hydrogen at the temperature. All analyses arrive at the single conclusion that hydrogen is enclathrated in only propane hydrate under the present experimental conditions.

INTRODUCTION

Gas hydrates are stabilized by guest species in the cavity of cages composed of the hydrogen-bonded water molecules. Three types of hydrate cages are well-known, pentagonal dodecahedron (5^{12}, Small-cage (hereafter, S-cage)), tetrakaidecahedron ($5^{12}6^2$, Middle-cage (M-cage)) and hexakaidecahedron ($5^{12}6^4$, Large-cage (L-cage)). The combination of two S-cages and six M-cages builds the structure-I (s-I) hydrate lattice (cubic, *Pm3n*), and that of sixteen S-cages and eight L-cages builds the structure-II (s-II) hydrate lattice (cubic, *Fd3m*). Gas hydrates have potential for versatile applications, due to some characteristic properties of gas storage, chemical stability, lightness and so on.

The separation, storage, and transportation of H_2 are one of the most important techniques for developing a new society sustained by H_2 energies. The generation of pure s-II H_2 hydrate requires a high pressure of 100 - 360 MPa at ambient temperatures [1]. The hydrate cages are multiple occupied with a cluster of two H_2 molecules in the S-cage and four H_2 molecules in the L-cage, respectively [2]. The mixed-gas hydrate systems containing H_2 and suitable additives enable us to perform the H_2 storage at much lower pressure conditions than the pure H_2 hydrate. Tetrahydrofuran (hereafter, THF) is the most familiar of such additives [3-8]. In addition, quaternary ammonium salts [6, 9-12], cyclic hydrocarbons [13] and so on have been reported.

In our previous study, phase equilibria containing gas hydrate, aqueous and gas phases for the ternary system of H_2 + CO_2 + water have been investigated at 274.3 - 281.9 K up to 10 MPa [14]. The s-I CO_2 hydrate generated from the mixture cannot entrap the H_2 molecule. The additional

Raman spectroscopic result also supports it. However, the intensity of Raman spectra indicated in our previous paper [14] has been somewhat weak due to the effect of the combination between window material and wavelength of laser. Such weak peak may lead to confusion and misinterpretation about the results of H_2 unoccupancy in the CO_2 hydrate. On the other hand, at the low temperatures of 120-180 K, Kim and Lee [15] claimed that H_2 is enclathrated in CO_2 hydrate, which contradicts the results at the relatively high temperatures of 274.3-281.9 K in our previous paper. It is necessary to reconfirm our results.

Zhang, Chen, Ma, Yang, and Guo [16] and Klauda and Sandler [17] have reported that H_2 may partially fill the hydrate cages with other guest species. Recently, Skiba, Larionov, Manakov, Kolesov, and Kosyakov [18] have reported that the H_2 molecules are not detected in the hydrate generated from H_2 + CH_4 mixtures at a pressure up to 250 MPa. The information for the cage occupancies of guest species and the thermodynamic stability of mixed gas hydrate for H_2 + other gas mixed hydrate systems, however, are insufficient.

In the present study, at first, the cage unoccupancy of H_2 in the CO_2 hydrate was reconfirmed clearly by in situ Raman spectroscopy for single crystal of gas hydrates. Subsequently, isothermal phase equilibria (pressure - composition) and Raman spectra for three ternary systems of H_2 + hydrocarbon (ethane, cyclopropane, propane) + water with same experimental procedures as H_2 + CO_2 + water system were measured at 276.1 K in the pressure range up to 5 MPa.

EXPERIMENTAL APPARATUS

The experimental apparatus is the same as the previous one [14]. The inner volume and maximum working pressure of the high-pressure cell were 150 cm^3 and 10 MPa, respectively. The cell had a set of windows for visually observing the phase behavior. All parts of the high-pressure cell were immersed in a temperature-controlled water bath. The con-

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tents were agitated using an up-and-down mixing bar driven by an exterior permanent magnetic ring.

The high-pressure optical cell for the Raman spectroscopic analyses had a pair of quartz (highly pure) windows on both the upper and lower sides. This high-pressure optical cell is the same as previous one [14] except for the window material. In our previous study [14], the ordinary sapphire windows were used. However, very intensive and broad fluorescence peak derived from the impurities of sapphire window was overlapped with the H_2 vibration peaks. We have been forced to use He-Ne laser (generation power is 35 mW) near at hand. Nevertheless, the undesirable peaks are detected as shown in Fig. (**1a**). To get the information of H_2 occupancy in greater detail, in the present study, the windows made of quartz (highly pure), which do not have bothering peaks in a relevant wavenumber range around 4100 cm^{-1} as shown in Fig. (**1b** and **1c**), were adopted. The thermostated water was circulated constantly in the exterior jacket of the high-pressure optical cell. A ruby ball was enclosed into the high-pressure optical cell. The contents were agitated by the ruby ball, which is rolled around by the vibration of vibrator from outside.
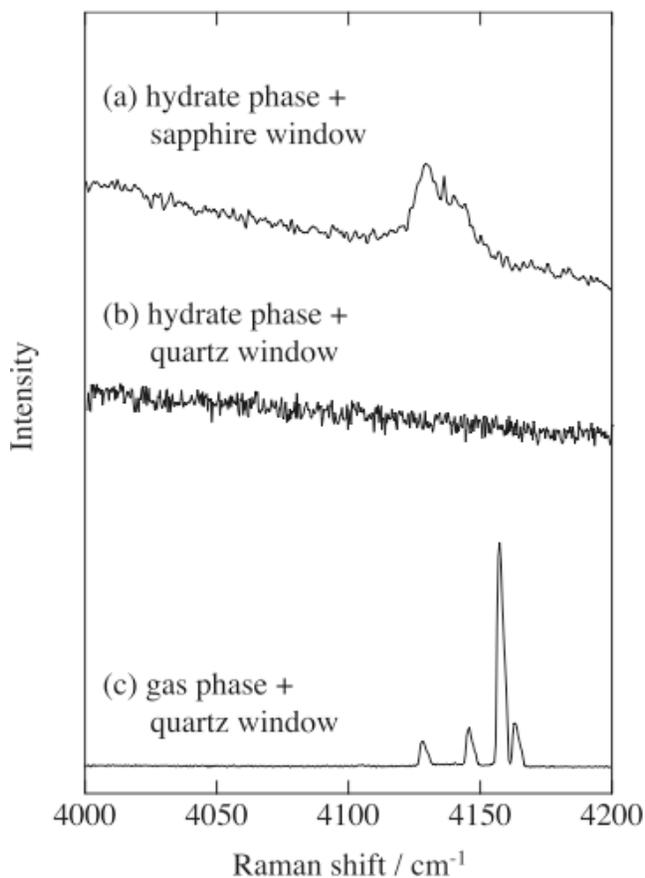

Fig. (1). Raman spectra around 4100 cm^{-1} in the hydrate generated from H_2 + CO_2 + water mixed system (**a**) with sapphire windows by use of He-Ne laser (15.2 MPa and 274.6 K) [14], and (**b**) with quartz windows by use of Ar ion laser (11.2 MPa and 276.5 K). The spectrum (**c**) of gas phase was obtained by use of quartz window and Ar ion laser at 11.2 MPa and 276.5 K.

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 defined by ITS-90. The system pressure was measured by a pressure gage (Valcom VPRT) calibrated by RUSKA quartz Bourdon tube gage (Direct Reading Pressure Gage, series 6000) with an estimated maximum uncertainty of 0.01 MPa.

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, ethane, cyclopropane, and propane (mole fraction purity 0.9999, 0.999, 0.995, and 0.9999, respectively) were obtained from the Takachiho Tradings Co., Ltd. The distilled water was obtained from the Wako Pure Chemicals Industries, Ltd. All of them were used without further purifications.

EXPERIMENTAL PROCEDURE

Phase Equilibrium Measurements

The gas mixture of H_2 and hydrocarbon prepared at a desired composition was introduced into the evacuated high-pressure cell. The content was pressurized up to the desired pressure by supplying water successively and then continuously agitated using the mixing bar. After the formation 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 hydrocarbon by the TCD-Gas Chromatography (TCD-GC, Shimadzu GC-14B) as the water mole fraction of gas phase is negligible under the present experimental conditions.

Raman Spectroscopic Analysis

Under the three-phase equilibrium state, the single crystal of gas hydrates was analyzed through a quartz window by in situ Raman spectroscopy using a laser Raman microprobe spectrophotometer with multi-channel CCD detector. The argon ion laser beam (spot diameter: 2 μm, 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}. All Raman spectra in hydrate phase are obtained from the hydrate single crystal that can be completely distinct from gas phase at microscopic field, under the three-phase equilibrium state (gas + aqueous solution + hydrate phases). In order to secure the laser focus on the hydrate crystal, Raman spectrum of H-H vibration mode was measured simultaneously at the focal position where the characteristic spectra corresponding to the CO_2 or hydrocarbon in hydrate crystal can be detected.

THERMODYNAMIC ANALYSIS

In the hydrocarbon + water binary system without H_2, the fugacity of hydrocarbon in the gas phase can be evaluated at a given temperature as:

$$f_2 = \varphi_2\left(P_2^e\right) P_2^e \tag{1}$$

where f_2 and φ_2 are the fugacity and fugacity coefficient of hydrocarbon at three-phase (gas + aqueous solution + hy-

drate) equilibrium pressure P^e_2, respectively. In the present study, the fugacity coefficient of pure hydrocarbon was calculated by use of Soave - Redlich - Kwong equation of state [19].

In the H_2 + hydrocarbon + water ternary system, the equilibrium fugacity of hydrocarbon in the gas phase can be evaluated as:

$$f_2 = y_2 \, \varphi_2\big(y_2, P^e\big) P^e \tag{2}$$

where y_2 is equilibrium composition of hydrocarbon in the mixed gas phase and P^e stands for the three-phase (gas + aqueous solution + hydrate) equilibrium pressure.

Supposing that the generated gas hydrate is the pure hydrocarbon hydrate, that is, H_2 is not enclathrated in hydrate cages, the fugacity of hydrocarbon calculated from equations (1) and (2) should coincide with each other. That is, the hydrocarbon hydrate cannot be generated until the fugacity of hydrocarbon in the gas mixture exceeds the equilibrium fugacity of pure hydrocarbon hydrate system.

The equation (3) is derived from equations (1) and (2).

$$P^e = \frac{\varphi_2\big(P^e_2\big)}{\varphi_2\big(y_2, P^e\big)} \frac{P^e_2}{y_2} \tag{3}$$

At a given gas-phase composition, the equilibrium pressure is obtained by the trial and error method from equation (3) on the assumption that the equilibrium fugacity of hydrocarbon in gas mixture is equal to that of pure hydrocarbon hydrate system in the whole composition range. The fugacity coefficient of hydrocarbon in the gas mixture was calculated by Soave - Redlich - Kwong equation of state [19] with the ordinary mixing rule (binary parameter $k_{12} = 0.1867$ for H_2 + ethane, 0.0 for H_2 + cyclopropane, 0.2359 for H_2 + propane) [20]. The applicable binary parameter for H_2 + cyclopropane under the present experimental condition could not be found, therefore, the value of $k_{12} = 0.0$ for H_2 + cyclopropane is compelled to be used. The critical constants of hydrocarbon and H_2 and other parameters were obtained from the reference [21].

RESULTS AND DISCUSSION

Reconfirmation of H_2 Unoccupancy in the CO_2 Hydrate by Raman Spectroscopy Using Quartz Windows

In order to reconfirm the cage unoccupancy of H_2 in the CO_2 hydrate, Raman spectra for single crystal of gas hydrates were measured at 276.5 K. As mentioned above, the quartz windows were used instead of ordinary sapphire windows in the present study. In order to secure the laser focus on the hydrate crystal, Raman spectrum of H-H vibration mode was measured simultaneously at the focal position where the characteristic spectra corresponding to CO_2 in hydrate crystal can be detected. The Raman spectra obtained in the present study are shown in Fig. (**2**). As well as the results in our previous paper [14], Raman peaks of H-H vibration are detected in only gas phase, while those of CO_2 are detected in both gas and hydrate phases.

In addition to the Raman spectroscopic analysis, direct gas release method was performed. The hydrates prepared from H_2 + CO_2 gas mixtures at 274.3 K were quenched and

taken out from the high-pressure cell at 243 K. After the dissociation of gas hydrate, gas sample was analyzed by use of the TCD-Gas chromatography. The mole fraction of H_2 (water free) in hydrate phase is 0.007 at 274.3 K and 5.06 MPa. We conclude that H_2 molecules adsorb on the hydrate surface rather than that H_2 is enclathrated in hydrate cage. At the moment the reason for the discrepancy between our and other results [15] about the capability of H_2 occupancy is unclear, but we speculate that the existence of aqueous phase (instead of ice solid phase) with hydrate phase may affect the H_2 occupancy and that crystal lattice defects may be increased, caused by the difference between the preparation methods of hydrate sample (we have never prepared the hydrate samples from powder ice + gas mixtures).
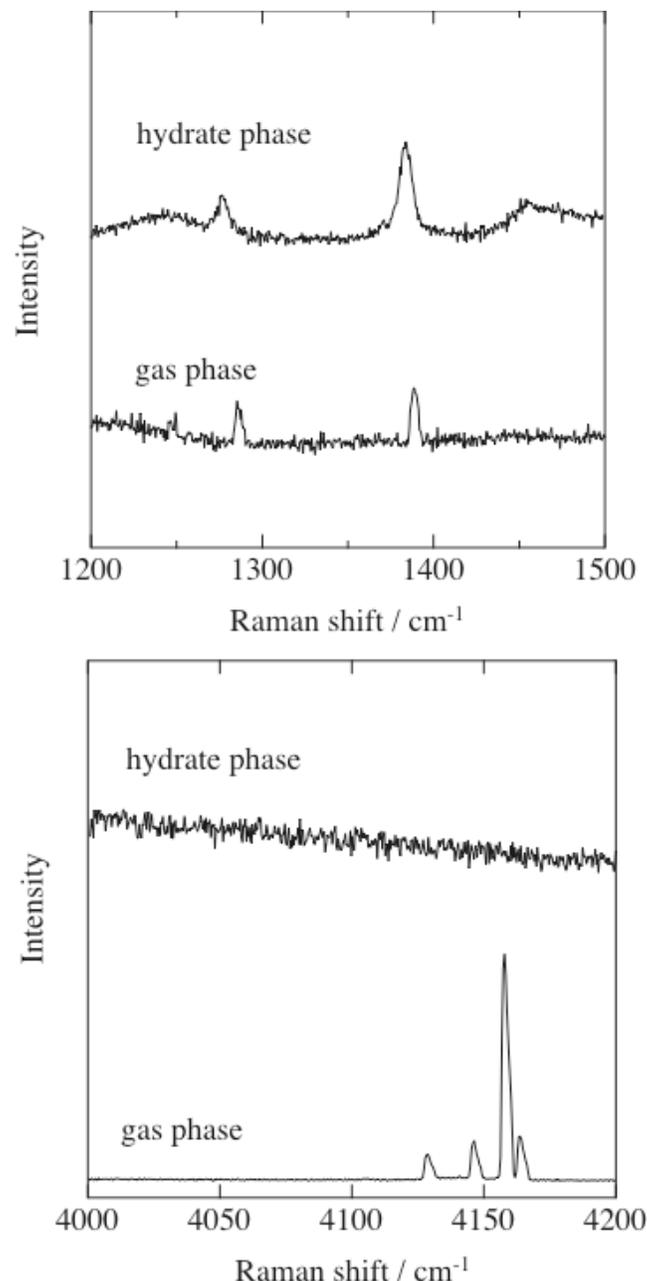

Fig. (2). Raman spectra in the gas and hydrate phases for the H_2 + CO_2 + water mixed system with quartz windows by use of Ar ion laser at 11.2 MPa and 276.5 K. Equilibrium mole fraction of H_2 in gas phase (y_1) is about 0.80.

Table 1.   Phase Equilibrium Data for the H_2 (1) + Hydrocarbon (2) + Water Mixed Systems in the Presence of Gas Hydrate at 276.1 K

Systems	p / MPa	y_1
H_2 + cyclopropane + water	0.11	0.0
	0.16	0.33
	0.18	0.48
	0.21	0.58
	0.23	0.60
	0.26	0.65
	0.27	0.67
	0.28	0.68
	0.31	0.69
	0.33	0.71
	0.50	0.80
	0.71	0.84
	1.18	0.90
H_2 + ethane + water	0.67	0.0
	0.75	0.11
	0.82	0.20
	1.03	0.39
	1.55	0.54
	1.55	0.57
	1.70	0.58
	2.08	0.67
	2.50	0.73
	2.91	0.78
	3.32	0.79
	4.44	0.83
H_2 + propane + water	0.33	0.0
	0.35	0.23
	0.43	0.38
	0.46	0.41
	0.53	0.57
	0.59	0.55
	0.67	0.66
	0.74	0.66
	0.84	0.71
	1.00	0.72
	1.07	0.78
	1.19	0.82
	1.31	0.81
	1.38	0.83
	1.54	0.83
	1.78	0.88
	1.94	0.85
	2.03	0.86
	2.44	0.90
	2.91	0.89

Phase Equilibrium Measurements and Thermodynamic Analysis for H_2 + Hydrocarbon + Water Mixtures

The isothermal phase equilibrium data for three ternary systems of H_2 + ethane + water, H_2 + cyclopropane + water and H_2 + propane + water obtained at 276.1 K are summarized in Table **1** and shown in Fig. (**3**). All three-phase equilibrium pressures increase monotonically with the increase of composition of H_2. Each curve in Fig. (**3**) stands for the calculated values from equation (3) on the assumption that the equilibrium fugacity of each hydrocarbon in the gas mixture is equal to that of pure hydrocarbon hydrate system in the whole composition range.
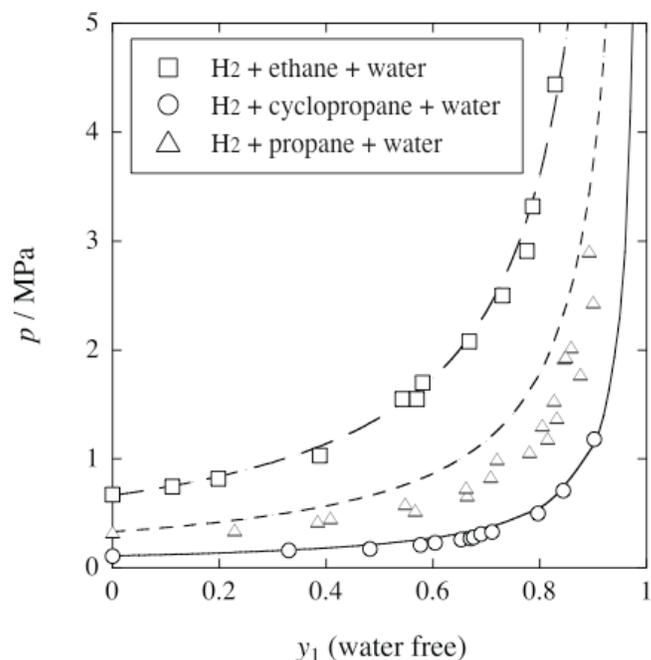

Fig. (3). Isothermal three-phase equilibrium (pressure-composition) relations for the H_2 (1) + each hydrocarbon (2) + water mixed systems at 276.1 K. The curves are estimated pressures by Eq. (3) on the assumption that the equilibrium fugacity of hydrocarbon in gas mixture is equal to that of pure hydrocarbon hydrate system in the whole composition range.

In both H_2 + ethane + water and H_2 + cyclopropane + water systems, the estimated pressures agree well with the experimental pressures as shown in Fig. (**3**). On the other hand, the experimental pressures shift to the high-temperature or low-pressure side of the estimated pressures in the H_2 + propane + water mixed system. This indicates that the hydrate phase would be changed from the pure propane hydrate to the mixed propane one. In other words, there is a possibility that H_2 can be enclathrated in the hydrate generated from H_2 + propane + water mixture.

Raman Spectroscopic Analysis for H_2 + Hydrocarbon + Water Mixtures

The Raman spectra obtained in the present study are shown in Figs. (**4**, **5**, and **6**). Fig. (**4a**) shows that the Raman peak corresponding to the intramolecular C-C stretching vibration mode of ethane is detected at 1000 cm^{-1} in the hydrate phase. The peak corresponding to the intramolecular C-C stretching vibration mode of ethane in the M-cage of s-I hydrate is detected at 1000 cm^{-1} [22]. As shown in Fig. (**5a**),

the Raman peak corresponding to the ring breathing mode of cyclopropane is detected at 1193 cm^{-1} in the hydrate phase, where it agrees well with that of the ring breathing vibration mode of cyclopropane in the M-cage of s-I hydrate [23]. As shown in Fig. (**4b**) and Fig. (**5b**), no peak of the intramolecular H-H stretching vibration of H_2 in the hydrate phase is detected in neither H_2 + ethane + water nor H_2 + cyclopropane + water systems (The peak should be detected around 4130 cm^{-1} if H_2 is entrapped in the S-cage). Hence, the hydrates generated from these mixed systems are s-I hydrate originated in the pure ethane or cyclopropane hydrates and H_2 cannot be entrapped with hydrate cages.
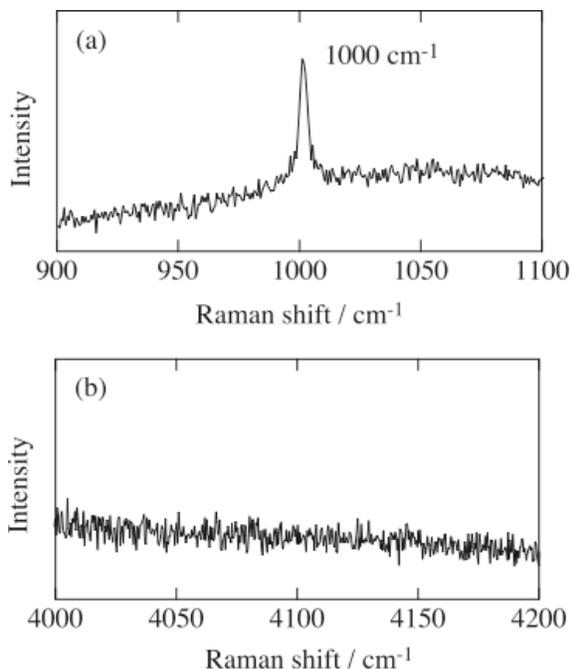

Fig. (4). Raman spectra of the intramolecular vibration for ethane around 1000 cm^{-1} (**a**), and around 4100 cm^{-1} (**b**) in the hydrate generated from the H_2 (1) + ethane (2) + water mixed system at 1.95 MPa, $y_1 = 0.62$, and 276.1 K.

Fig. (**6a**) shows that the Raman peak corresponding to intramolecular C-C stretching vibration mode of propane is detected at 877 cm^{-1} in the hydrate phase. It is known that the peak corresponding to the C-C stretching vibration mode of propane in the large cage (L-cage) of s-II hydrate is detected at 877 cm^{-1} [24]. Fig. (**6a**) also shows that the Raman peak derived from the H_2 rotation is detected around 581 cm^{-1} in the hydrate phase, which is the strongest peak corresponding to the H_2 rotation [25]. The peak derived from the H-H stretching vibration of H_2 is detected around 4131 cm^{-1} in the hydrate phase as shown in Fig. (**6b**). This Raman shift agrees with that of H_2 encaged in the S-cage of s-II hydrate [6, 7]. That is, H_2 can selectively occupy the S-cage of s-II hydrate generated from H_2 + propane + water mixture, while propane occupies the L-cage entirely.

The hydrates prepared from gas mixtures at 276.1 K were quenched and taken out from the high-pressure cell at 243 K. After the dissociation of gas hydrate, gas sample was analyzed by use of the TCD-Gas chromatography. The mole fractions of H_2 (water free) in the dissociation gas of the hydrate generated from H_2 + propane gas mixtures, in which the Raman peaks of H_2 are detected, is about 0.1 at 0.8 MPa

and about 0.2 at 1.5 MPa. About five and ten percent of S-cages in the s-II hydrate are occupied by H_2 molecule at such mild condition, respectively. In the other systems of no Raman peak of H_2, the mole fraction (water free) of H_2 in the dissociation gas is less than 0.001.
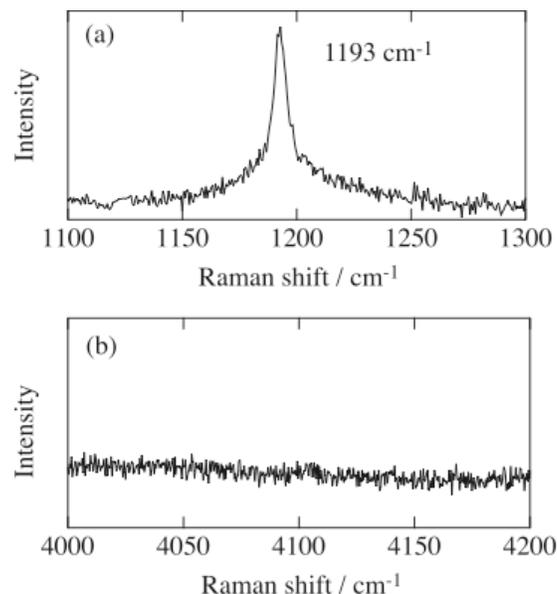

Fig. (5). Raman spectra of the intramolecular vibration for cyclopropane (**a**), and around 4100 cm^{-1} (**b**) in the hydrate generated from the H_2 (1) + cyclopropane (2) + water mixed system at 0.403 MPa, $y_1 = 0.71$, and 276.1 K.
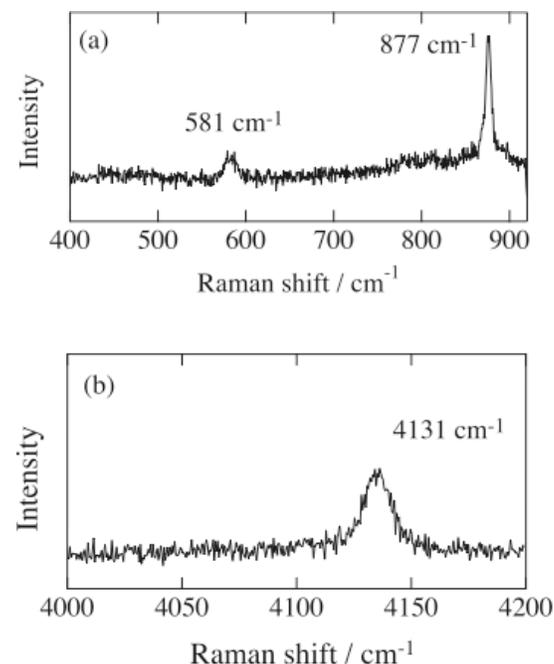

Fig. (6). Raman spectra of the intramolecular vibration for propane around 870 cm^{-1} (**a**), and H_2 (around 4150 cm^{-1}) (**b**) in the hydrate phase for the H_2 (1) + propane (2) + water mixture at 1.50 MPa, $y_1 = 0.82$, and 276.1 K. Panel (a) contains the Raman peak of 581 cm^{-1} corresponding to the rotation of H_2.

In the present study, the occupation of H_2 in the hydrate generated from H_2 + propane + water mixture has been confirmed by use of Raman spectroscopic analyses. The cage occupancy of H_2 in various mixed systems at relatively low-

pressure condition (up to 2 MPa) is summarized in Table **2**. The H_2 molecule can occupy the S-cage of s-II hydrate even at a few MPa, while it cannot occupy that of s-I hydrate at similar conditions. In the cases of ethane or cyclopropane additive, H_2 cannot be enclathrated in the hydrate despite the existence of empty S-cages. The S-cage of s-II is somewhat smaller than that of s-I [26], which may cause the variation of H_2 occupation depending on the difference between s-I and s-II.

Table 2. S-Cage Occupancy of H_2 at 276.1 K and up to 2 MPa. The Data CH_4, and THF were Obtained from the References [6, 18], Respectively

Additives	Hydrate Structure	S-Cage Occupancy of H_2
CO_2	I	-
CH_4 [18]	I	-
ethane	I	-
cyclopropane	I	-
propane	II	occupied
THF [6]	II	occupied

CONCLUSIONS

Isothermal phase equilibria for three hydrogen + hydrocarbon + water mixed systems containing gas hydrates were measured at 276.1 K. The present findings from phase equilibrium analysis and Raman spectroscopic study suggest that the hydrogen generates the mixed gas hydrate in the presence of propane. CO_2, ethane and cyclopropane do not play a role as the guest species of mixed gas hydrate containing hydrogen.

ACKNOWLEDGMENT

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