Structure and Guest Distribution of the Mixed Carbon Dioxide and Nitrogen Hydrates As Revealed by X-ray Diffraction and ^{13}C NMR Spectroscopy

Yu-Taek Seo and Huen Lee*

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea

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In this contribution, X-ray diffraction and ^{13}C NMR spectroscopy were used to identify structure and guest distribution of the mixed $N_2 + CO_2$ hydrates. X-ray diffraction results of the mixed $N_2 + CO_2$ hydrates confirmed that the unit cell parameter was ∼11.8 Å over the gas mixture composition range of 3−20 mol % CO_2 and the formed hydrates were identified as structure I. When the composition of the gas mixture was reduced to 1 mol % CO_2, the structure of the mixed hydrate was transformed to structure II showing the unit cell parameter of 17.26(2) Å. ^{13}C cross-polarization (CP) NMR spectroscopy was used to examine the distribution of carbon dioxide molecules in small 5^{12} and large $5^{12}6^2$ cages of structure I. From NMR spectra of the mixed $N_2 + CO_2$ hydrate formed from gas mixture of 20 and 10 mol % CO_2, powder patterns having chemical shift anisotropy of −54.5 and −53.8 ppm were observed, respectively. There was no clear isotropic line indicating carbon dioxide molecules in the small 5^{12} cages of structure I. These NMR spectra showed that the carbon dioxide molecules occupied mainly the large $5^{12}6^2$ cages of structure I when the mixed $N_2 + CO_2$ hydrate was formed at a vapor-phase composition range of 10−20 mol % CO_2. In addition, from the analysis of the gases collected from a dissociating hydrate sample, the amount of carbon dioxide in the mixed $N_2 + CO_2$ hydrates increased greatly with a small increase of carbon dioxide in the vapor phase. Accordingly, the carbon dioxide molecules seemed to occupy both the small and large cages of structure I above the vapor-phase composition of 33.3 mol % CO_2.

Introduction

Gas hydrates are a general class of crystalline compounds formed by the physically stable interaction between water and relatively small guest molecules.[1] Under suitable temperature and pressure conditions, water molecules are connected by hydrogen bonding and form polyhedral cages. Low-molecular-weight gas molecules such as methane, carbon dioxide, and nitrogen could be contained in these cages. Although gas guest molecules are physically enclosed within the cages, no actual chemical union exists between the guest and host water molecules. These nonstoichiometric crystalline compounds are divided into three distinct structures, I, II, and H, which differ in cavity size and shape.[2] Besides these three structures, structure T, a more complex structure, containing two unusually shaped cages, was also newly observed in the presence of dimethyl ether.[3] It is clear that many of the physical attributes of gas hydrates remain unknown and thus have to be identified in more detail.

Gas hydrates are of particular interest in energy and environmental fields because of the emerging possible applications of hydrates in the storage of natural gas,[4] sequestration of carbon dioxide on the ocean floor,[5] and separation of greenhouse gas from flue gas.[6] The literature contains a number of experimental and theoretical works to understand the macroscopic phase behavior and structural characteristics[7−10] of pure and mixed hydrates. In particular, recently, a powerful hydrate equilibrium prediction program called as CSMGem was developed by the Colorado School of Mines, which basically incorporates the

hydrate fugacity model with the Gibbs energy minimization techniques.[11] However, only a few studies have been focused on the mixture of carbon dioxide and nitrogen despite its industrial importance in greenhouse gas separation. Kang et al.[6] developed the basic concept for separating carbon dioxide from power plant flue gas using the mixed hydrate formation of nitrogen and carbon dioxide. They measured hydrate equilibrium conditions of the mixed hydrates and analyzed hydrate phase compositions to verify the feasibility of a hydrate-based gas separation process; however, they did not provide any precise experimental results revealing the structure of the mixed hydrate and distribution of guest molecules in the hydrate cages. Thus, in the present study, X-ray diffraction was used to confirm the structure of mixed $N_2 + CO_2$ hydrates, and NMR spectroscopy was used to identify the distribution of carbon dioxide in both small and large hydrate cages. In addition, the corresponding hydrate phase compositions were also measured as macroscopic approaches to complement the NMR spectroscopic results.

Experimental Section

The X-ray powder diffraction pattern was recorded at 113 K on a Rigaku Geigerflex goniometer diffractometer, using graphite monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å) in the $\theta/2\theta$ scan mode. Samples were scanned over a range of $10° < 2\theta < 60°$, with a scan speed of 0.5° per minute at an increment of 0.05° in 2θ, rendering a total acquisition time of approximately 2 h for each sample.

The ^{13}C cross-polarization (CP) NMR spectra were recorded on a Bruker DSX 400 NMR spectrometer at a Larmor frequency of 100.6 MHz. The powder samples were placed in a 4 mm

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o.d. zirconia rotor loaded into a variable temperature probe. The pulse length for protons was 5 μs and a pulse repetition delay of 3 s was employed when a contact time of 1.0 ms was used. The downfield carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference. The hydrate samples were prepared in a mechanically stirred reactor having the volume of 150 cm³ and formed from finely pulverized ice particles crushed in a mortar and pestle. The reactor, which maintained a constant temperature of 272.1 K, was filled with 10 g of powdered ice particles and then pressurized with a gas mixture to a higher pressure than the corresponding three-phase equilibrium pressure at the same temperature. A sufficient amount of gas molecules was supplied to minimize the possible effect of the ice/gas molar ratio on the hydrate phase composition. A mechanical stirrer agitated the ice particles during the entire formation process to provide a fresh surface to participate in the formation of gas hydrates. The formation and dissociation steps were repeated at least four times to avoid the possible appearance of metastable structures. After completing the formation process, the mixed hydrate was sampled and transported to the Zr-rotor, which was inserted into the precooled NMR probe.

The hydrate compositions were measured by analyzing the gases encaged in the hydrate structures. For composition measurement of dissociated gases from the hydrate phase, a sampling valve with a loop volume of 1 μL was installed and connected to a gas chromatograph on-line. The gas chromatograph used a thermal conductivity detector (TCD) with a PORAPAK-Q packed column and was preliminarily calibrated for carbon dioxide and nitrogen. Instead of liquid water, finely pulverized ice was used as the starting material to form the mixed $N_2 + CO_2$ hydrates. During vigorous stirring of the ice particles under the desired pressure, the hydrate nucleated and grew, and the system pressure continuously decreased due to the introduction of gas molecules into hydrate cages. When the system pressure reached a steady state, the vapor phase was vacuumed at 243.1 K. Then, the valve was quickly closed to isolate the system, and the temperature was increased to 272.1 K, inducing the complete dissociation of the hydrate phase. The evolving gases were analyzed several times by a gas chromatograph directly attached to the reactor to eliminate any error that could occur during the sampling procedure and to confirm the reproducibility of the data. The experimental composition deviations were found to be within ±0.1%.

Results and Discussion

CO$_2$ Dynamics in Hydrate Cages. X-ray diffraction was adopted as one of the fundamental approaches to determine the crystal structure of gas hydrates. The guest dynamics in hydrate cages was determined by the NMR spectroscopic analysis of hydrate samples, so it is imperative to establish the mutual consistency between the structures by X-ray diffraction and the dynamics by NMR spectroscopy to obtain the structural characteristics of pure and mixed hydrates. Therefore, for the preliminary reference, these two powerful methods were used to analyze polycrystalline samples of pure CO_2 hydrates, which provide the unit cell parameters and more importantly the guest dynamics of carbon dioxide molecules in the small and large cages of structure I.

Figure 1a represents the X-ray diffraction pattern of pure CO_2 hydrate at 113 K, which was known to form structure I, along with the calculated angles of structure I. All of the diffraction lines of pure CO_2 hydrate were attributed to structure I and assigned as Miller indices at corresponding angles.[12] It has been
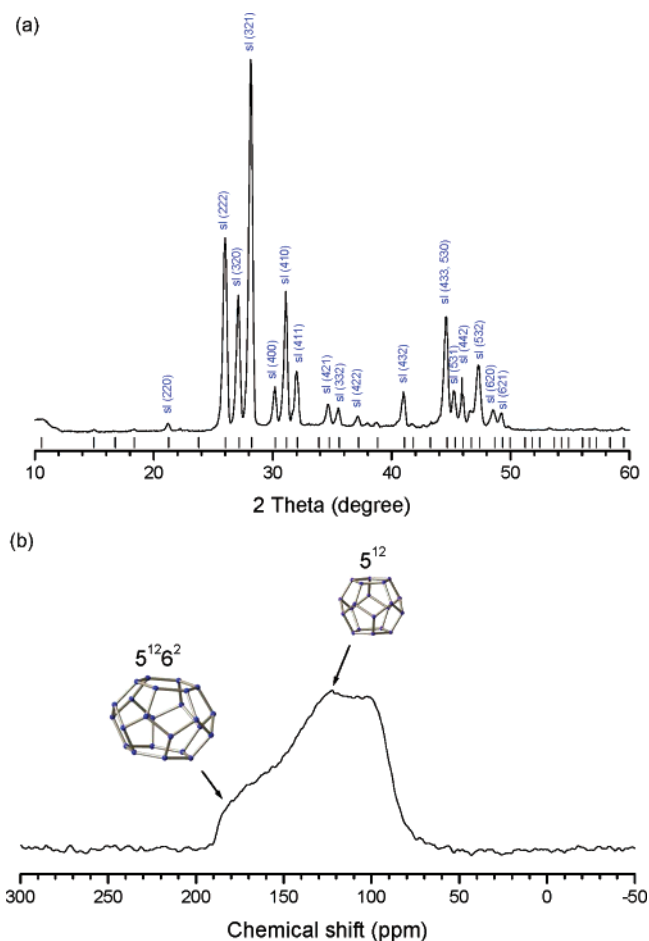
Figure 1. (a) X-ray diffraction of the pure CO_2 hydrate forming structure I and (b) ^{13}C CP NMR spectrum of pure CO_2 hydrate at 243 K.

noted that the (110), (200), (210), and (211) diffraction peaks appearing at low angle ranges showed weak relative intensities compared to other peaks appearing from 25° to 60°. From these Miller indices and 2θ values, the unit cell parameter for the polycrystalline sample of pure CO_2 hydrates that formed structure I was 11.89(3) Å. With the results of other structure I samples, all of the values were compared and confirmed to be in a high level of agreement.[13,14]

The knowledge of molecular dynamics in small and large cages of structure I could be obtained from the analysis of the ^{13}C NMR spectral shape of a pure CO_2 hydrate. If carbon dioxide molecules were isolated, it shows no chemical shift anisotropy, and therefore, gaseous carbon dioxide molecules contribute to the isotropic shift. For carbon dioxide enclathrated into hydrate cages, a chemical shift anisotropy has been induced by asymmetry in the immediate environment of the molecules making the chemical shift anisotropy a very sensitive probe of guest distribution in hydrate cages.[15] The ^{13}C CP NMR spectrum of pure CO_2 hydrate is shown in Figure 1b. Since the small 5^{12} cages of structure I produced pseudospherical symmetry, causing the molecular motions to be isotropic, only a sharp line at the isotropic chemical shift of 123.1 ppm was observed. For carbon dioxide in the large $5^{12}6^2$ cages of structure I, the powder pattern was observed due to the asymmetric shape of the $5^{12}6^2$ cages and reflected the anisotropic motions of carbon dioxide molecules. The chemical shift anisotropy could be defined as $\Delta = \delta_{iso} - \delta_{zz}$,[15] where δ_{iso} is the isotropic chemical shift and δ_{zz} is the zz component of the chemical shift tensor; then the observed chemical shift anisotropy value was −55.3 ppm. The symmetry
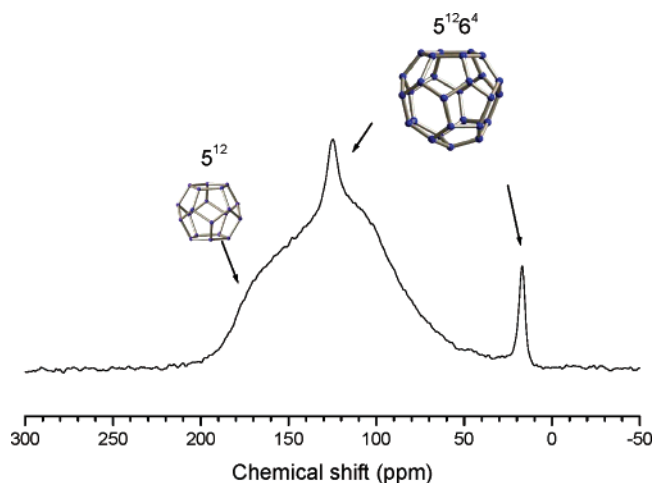
Figure 2. ^{13}C CP NMR spectra of the mixed CO_2 + C_3H_8 hydrate formed from 80 mol % CO_2 and balanced C_3H_8 gas mixture.

of small 5^{12} and large $5^{12}6^4$ cages of structure II was contrary to that of the structure I cages.

To investigate the CO_2 molecular dynamics in the cages of structure II, the mixed CO_2 + C_3H_8 hydrate was formed from 80 mol % CO_2 and a balanced propane gas mixture, where the structure of the mixed hydrate was known to be structure II. The resulting ^{13}C CP NMR spectrum of the mixed CO_2 + C_3H_8 hydrate is shown in Figure 2. Although the carbon dioxide spectrum in Figure 2 is similar to the spectrum observed for structure I, there are clear differences in chemical shift data. The isotropic line observed at a chemical shift of 124.6 ppm indicates that carbon dioxide molecules occupy the pseudo-spherical large $5^{12}6^4$ cages. The powder pattern was associated with carbon dioxide molecules in small 5^{12} asymmetric cages, and the observed chemical shift anisotropy was -42.2 ppm, slightly lower than that of large cages of structure I. The two propane ^{13}C resonance lines are not resolved and are observed as a single peak at 16.8 ppm. The ^{13}C NMR spectra shown in Figures 1 and 2 clearly suggest that the cage symmetry could be used as an effective indicator for determining the guest distribution in hydrate cages. Thus, with cross-exploration of X-ray diffraction and the ^{13}C CP NMR spectra, it becomes possible to elucidate the structure and guest distribution of mixed hydrates containing carbon dioxide.
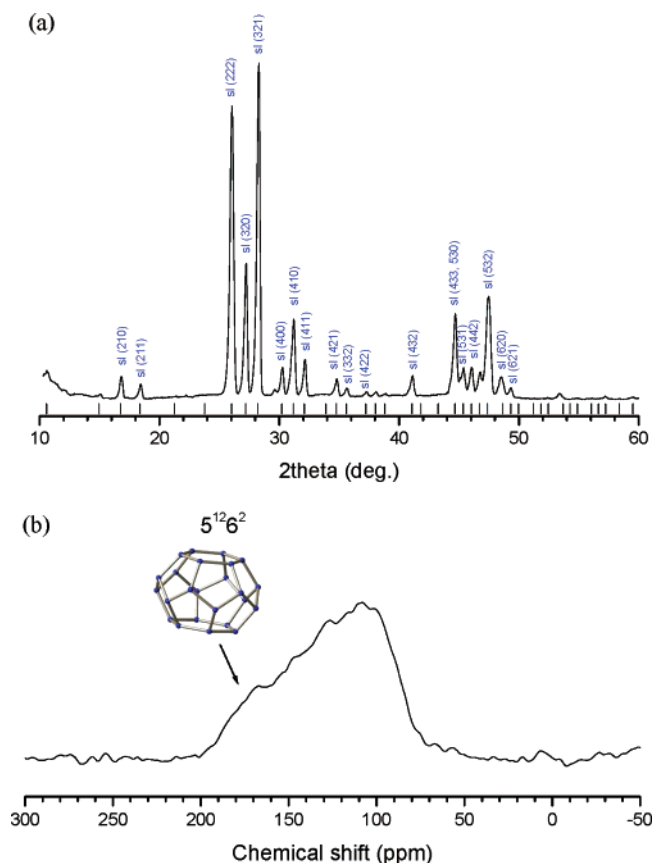
Structure and Guest Distribution of the Mixed N_2 + CO_2 Hydrates. Nitrogen is one of the smallest formers of gas hydrate when existing as a single guest. Davidson et al.[16] suggested that nitrogen stabilized small cages of structure II and also occupied all of the large cages, while carbon dioxide forms structure I. Only judging from the relative size difference between a carbon dioxide molecule and a small cage of structure I, the small cages might remain essentially unoccupied. However, recent studies revealed that carbon dioxide molecules occupied both small and large cages of structure I, where the large cages were fully occupied and the small cages were partially occupied at a level of an occupancy of 0.71.[14,15] Therefore, when the mixed N_2 + CO_2 hydrate forms, carbon dioxide and nitrogen molecules compete with each other for better occupancy in the hydrate cages, and the resulting structure of mixed hydrates was influenced by guest distribution in hydrate cages. In this study, the mixed N_2 + CO_2 hydrates were formed from various compositions; the structure and guest distribution were checked through the cross-examinations of X-ray diffraction and NMR spectroscopy.

First, the mixed N_2 + CO_2 hydrates were formed at specific compositions of gas mixture according to the flue gas type of
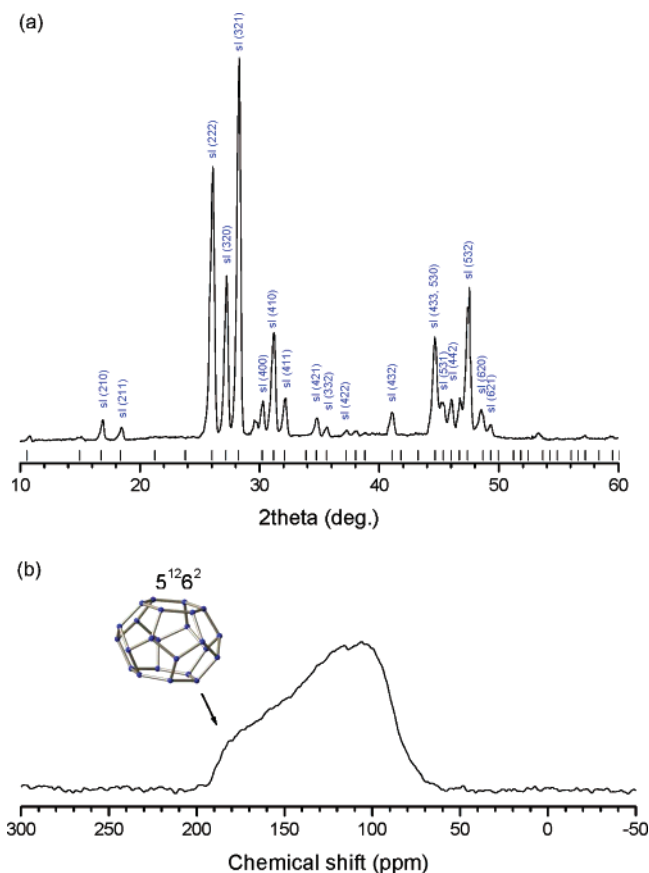
Figure 3. (a) X-ray diffraction of mixed N_2 + CO_2 hydrate formed from 20 mol % CO_2 and balanced N_2 and (b) ^{13}C CP NMR spectra of mixed N_2 + CO_2 hydrate formed from 20 mol % CO_2 and balanced N_2.

power plant. The flue gas usually consists of $10-20$ mol % CO_2, $5-9$ mol % O_2, trace gases, and balanced N_2. After pretreatment steps, the flue gas might be simplified as a binary mixture of carbon dioxide and nitrogen. To make this study more practical and feasible, two gas mixture compositions of 10 and 20 mol % CO_2 were specially chosen to acquire their fundamental structure and guest distribution information. Accordingly, at first, the mixed hydrate was formed from a 20 mol % CO_2 and balanced N_2 gas mixture. The obtained X-ray diffraction is shown in Figure 3a, which agrees with that of pure CO_2 hydrate in an overall range of 2θ values. All of the diffraction lines of the mixed N_2 + CO_2 hydrates were attributed to structure I, and the assigned Miller indices at the corresponding angles were similar to those of the pure CO_2 hydrate. The unit cell parameter of the cubic cell was 11.83(2) Å, which suggests that the lattice structure of the mixed hydrate was similar to that of pure CO_2 hydrate; however, the relative intensities changed from those observed at the lower angle range. It should be noted that from the Rietveld refinements the relative intensities of diffraction peaks in the lower 2θ angles are sensitive to guest molecules occupying the small cages of structure I because their electron densities induced a change of relative intensities of those diffraction peaks. Although there were only weak diffraction peaks in the lower 2θ angles of the pure CO_2 hydrate, the (210) and (211) diffraction peaks appeared when the mixed N_2 + CO_2 hydrate formed, suggesting that the change of guest distribution occurs mainly in the small cages of structure I. The distribution of carbon dioxide molecules in hydrate cages was represented by the ^{13}C NMR spectrum as shown in Figure 3b. The powder pattern having a chemical shift anisotropy of -54.5 ppm was observed, and this spectrum

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(a)

(b)

Figure 4. (a) X-ray diffraction of mixed N$_2$ + CO$_2$ hydrate formed from 10 mol % CO$_2$ and balanced N$_2$ and (b) ^{13}C CP NMR spectra of mixed N$_2$ + CO$_2$ hydrate formed from 10 mol % CO$_2$ and balanced N$_2$.

TABLE 1: ^{13}CO$_2$ Chemical Shift Data of Pure and Mixed Hydrates

system	hydrate structure	cage type	δ^{iso} (ppm)	Δ (ppm)
pure CO$_2$	structure I	5^{12}	123.1	0
		$5^{12}6^2$	127.8	- 55.3
CO$_2$ + C$_3$H$_8$ (80 mol % CO$_2$)	structure II	5^{12}	128.3	- 42.2
		$5^{12}6^4$	124.6	0
N$_2$ + CO$_2$ (20 mol % CO$_2$)	structure I	$5^{12}6^2$	127.6	- 54.5
N$_2$ + CO$_2$ (10 mol % CO$_2$)	structure I	$5^{12}6^2$	127.3	- 53.8

TABLE 2: Hydrate Phase Compositions of the Mixed N$_2$ + CO$_2$ Hydrates Measured at the Corresponding Vapor Phase Compositions

formation condition (K, bar)	vapor phase composition (mol % of CO$_2$)	hydrate phase composition (mol % of CO$_2$)
272.1, 145	1.2	9.0
272.1, 130	3.3	14.6
272.1, 105	9.9	46.5
272.1, 77	18.4	58.8
272.1, 50	33.3	73.4
272.1, 41	49.9	85.9
272.1, 35	66.5	93.9
272.1, 32	84.7	96.5

CO$_2$ chemical shift data for different hydrate cages are summarized in Table 1.

At this moment, it is uncertain whether the structure II mixed hydrates should be formed from gas mixtures of carbon dioxide and nitrogen. The careful X-ray diffraction analysis was carried out at lower compositions of 6 and 3 mol % CO$_2$. The resulting diffraction patterns indicated that the mixed hydrates formed structure I, showing unit cell parameters of 11.81(1) and 11.78-(1) Å, respectively. However, in the case of the 1 mol % CO$_2$ gas mixture, the structure II hydrates eventually formed, showing a unit cell parameter of 17.26(2) Å under the conditions of our experiments. These results suggest that the stabilization of hydrate cages is mainly governed by carbon dioxide molecules occupying the large cages of structure I in compositions above 3 mol % CO$_2$. It must be noted, however, that below 1 mol % CO$_2$ the structure II hydrate was formed and stabilized by nitrogen molecules.

The previous microscopic approaches for hydrate phase analysis using X-ray diffraction and NMR spectroscopy provide valuable information on hydrate structure and carbon dioxide distribution in hydrate cages. However, the exact compositions of carbon dioxide and nitrogen occupying the hydrate cages could not be obtained because it is difficult to simultaneously analyze individual molecular distributions of carbon dioxide and nitrogen directly from the NMR spectra. Apparently, a macroscopic approach must be introduced to determine the guest compositions in hydrate cages. Thus, the compositions of gases collected from the dissociating hydrate samples were analyzed to determine the relative amount of carbon dioxide and nitrogen occupying the hydrate cages. Table 2 lists the resulting carbon dioxide compositions of the hydrate phase at the corresponding compositions of vapor phase and, as can be expected, shows a trend of increasing the carbon dioxide amount with the increase of carbon dioxide in the vapor phase. At a low carbon dioxide composition in the vapor phase of 1.2 mol % CO$_2$, the amount of carbon dioxide occupying the hydrate cages appeared to be 9.0 mol % CO$_2$. Accordingly, nitrogen molecules might be expected to occupy most of the small and large cages, while carbon dioxide molecules occupy only a small amount of large cages. However, the amount of CO$_2$ in the hydrate phase greatly

behavior reflects the anisotropic motion of carbon dioxide molecules in asymmetric $5^{12}6^2$ cages of structure I. There was no clear isotropic line identifying carbon dioxide molecules in pseudospherical 5^{12} cages of structure I. Both X-ray diffraction and the ^{13}C NMR spectrum indicate that structure I forms from a 20 mol % CO$_2$ gas mixture, and carbon dioxide molecules occupy mainly the large $5^{12}6^2$ cages of structure I.

Subsequently, the mixed N$_2$ + CO$_2$ hydrate was formed in a 10 mol % CO$_2$ and balanced N$_2$ gas mixture. As evident in Figure 4a, the obtained X-ray diffraction represents that the formed mixed N$_2$ + CO$_2$ hydrate was structure I. The Miller indices of the diffraction lines were similar to those of the mixed N$_2$ + CO$_2$ hydrate formed from the 20 mol % CO$_2$ gas mixture, and the resulting unit cell parameter was identical to the value of 11.83(2) Å. From the X-ray diffraction results, it is apparent that the mixed hydrates of structure I only form from the binary gas mixture of carbon dioxide and nitrogen in the composition range of 10−20 mol % CO$_2$. The ^{13}C NMR spectrum is shown in Figure 4b. The powder pattern having a chemical shift anisotropy of −53.8 ppm was obtained for the mixed N$_2$ + CO$_2$ hydrate formed from a 10 mol % CO$_2$ gas mixture, and there was no isotropic line of carbon dioxide molecules. It might be possible that the powder pattern of carbon dioxide in the large $5^{12}6^2$ cages overwhelmed the low intensity isotropic line of carbon dioxide in the small 5^{12} cages because of a relatively low concentration of carbon dioxide in the small 5^{12} cages. However, the recent NMR spectroscopic results clearly suggest that when the mixed N$_2$ + CO$_2$ hydrate is formed from the gas mixture of 10 and 20 mol % CO$_2$, carbon dioxide molecules primarily occupy the large $5^{12}6^2$ cages of structure I. The ^{13}-

increased by changing the hydrate structure from II to I above 3 mol % CO_2 in the vapor phase as listed in Table 2.

The cross evaluations of both the macroscopic and microscopic results obtained from the X-ray diffraction, NMR spectra, and hydrate phase compositions make the specific analysis of the guest distribution in the hydrate cages possible. From the X-ray diffraction analysis, the mixed $N_2 + CO_2$ hydrate was found to form structure I at compositions above 3 mol % CO_2 in the vapor phase. If we consider the ideal occupation of nitrogen and carbon dioxide molecules in small and large cages $(2N_2 \cdot 6CO_2 \cdot 46H_2O)$, then the resulting composition of hydrate phase becomes 75.0 mol % CO_2. However, the obtained hydrate phase compositions varied from 14.6 to 96.5 mol % CO_2 at the corresponding compositions of vapor phase, indicating that the distribution of carbon dioxide molecules in the hydrate cages showed more complex behavior. For the mixed $N_2 + CO_2$ hydrate formed from 10 mol % CO_2, the NMR analysis confirmed that the carbon dioxide molecules occupy the large cages of structure I and the corresponding equilibrium composition of hydrate phase was 46.5 mol % CO_2. In accordance with cage behavior, if we consider the hypothetical structure I lattice composed of 8 small 5^{12} cages and 24 large $5^{12}6^2$ cages, we can expect that 15 $5^{12}6^2$ cages were filled with carbon dioxide molecules, while nitrogen molecules would occupy the small 5^{12} and remaining large $5^{12}6^2$ cages. As the vapor phase composition was increased to 20 mol % CO_2, carbon dioxide molecules still occupied 19 large $5^{12}6^2$ cages of structure I with a hydrate composition of 58.8 mol % CO_2. When the 50 mol % CO_2 in the vapor phase is in equilibrium with the 85.9 mol % CO_2 in the hydrate phase, the CO_2 composition of hydrate phase appeared to be higher than the ideal value of 75.0 mol % CO_2. Thus carbon dioxide molecules occupied all of the 24 large $5^{12}6^2$ cages and even 4 small 5^{12} cages, while nitrogen molecules occupied the other 4 small 5^{12} cages. When the amount of carbon dioxide in vapor phase increased, carbon dioxide molecules stabilize the overall hydrate cages, and therefore, as expected, more carbon dioxide molecules accumulated in the hydrate phase.

Recently, considerable research has been conducted regarding the hydrate structure, particularly in case of multiple guests, but most of it mainly focused on structural types of formed hydrates without addressing the guest participation in cages both qualitatively and quantitatively. In fact, the complete analysis of cage occupancy characteristics seems to be very difficult at the present stage even for the mixed hydrates involving only two guests, but more advanced analytical techniques might help resolve these problems.

Conclusions

In this study, we focused on identification of the structure and guest distribution of mixed $N_2 + CO_2$ hydrate at various compositions of gas mixtures. The crystal structure of mixed hydrates was identified as structure I from the resulting X-ray diffraction pattern at the gas mixture composition range of 3−20 mol % CO_2, while the structure of mixed hydrate seemed to be transformed to structure II when the gas mixture composition was reduced to 1 mol % CO_2. On the basis of ^{13}C CP NMR spectra for carbon dioxide, it was demonstrated that the carbon dioxide molecules occupied mainly the large cages of structure I. There was no clear isotropic line indicating the carbon dioxide molecules in small cages of structure I. The analysis of the gases collected from dissociating hydrate samples complements the NMR spectroscopic analysis and provides the carbon dioxide distribution in hydrate cages from the fact that the amount of carbon dioxide in mixed $N_2 + CO_2$ hydrates increased greatly with a small increase of carbon dioxide in the vapor phase. As the amount of carbon dioxide in the vapor phase increased, the role of stabilizing both small and large cages was transformed from nitrogen to carbon dioxide molecules, which is likely to prefer to stabilize the small and large cages of structure I.

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