Sequestering carbon dioxide into complex structures of naturally occurring gas hydrates

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Large amounts of CH_4 in the form of solid hydrates are stored on continental margins and in permafrost regions. If these CH_4 hydrates could be converted into CO_2 hydrates, they would serve double duty as CH_4 sources and CO_2 storage sites. We explore here the swapping phenomenon occurring in structure I (sI) and structure II (sII) CH_4 hydrate deposits through spectroscopic analyses and its potential application to CO_2 sequestration at the preliminary phase. The present 85% CH_4 recovery rate in sI CH_4 hydrate achieved by the direct use of binary $N_2 + CO_2$ guests is surprising when compared with the rate of 64% for a pure CO_2 guest attained in the previous approach. The direct use of a mixture of $N_2 + CO_2$ eliminates the requirement of a CO_2 separation/purification process. In addition, the simultaneously occurring dual mechanism of CO_2 sequestration and CH_4 recovery is expected to provide the physicochemical background required for developing a promising large-scale approach with economic feasibility. In the case of sII CH_4 hydrates, we observe a spontaneous structure transition of sII to sI during the replacement and a cage-specific distribution of guest molecules. A significant change of the lattice dimension caused by structure transformation induces a relative number of small cage sites to reduce, resulting in the considerable increase of CH_4 recovery rate. The mutually interactive pattern of targeted guest–cage conjugates possesses important implications for the diverse hydrate-based inclusion phenomena as illustrated in the swapping process between CO_2 stream and complex CH_4 hydrate structure.

clathrate | CO_2 sequestration | methane | swapping phenomenon | NMR

Because the total amount of natural gas hydrate was estimated to be about twice as much as the energy contained in fossil fuel reserves (1, ‖), many researchers have tried to find a way to exploit CH_4 hydrates deposited worldwide as a new energy source. For recovering them at various conditions in an efficient way, several strategies such as thermal treatment, depressurization, and inhibitor addition into the hydrate layer have been proposed (2). However, all of these methods are based on the decomposition of CH_4 hydrate by external stimulation, which can trigger catastrophic slope failures (3). Furthermore, if CH_4 hydrate decomposes rapidly, it is also possible that the CH_4 released from the hydrate could transfer to the air and significantly accelerate the greenhouse effect (4).

Recently, the replacement of CH_4 hydrate with CO_2 has been suggested as an alternative option for recovering CH_4 gas. When CO_2 itself is put under certain pressure, a solid CO_2 hydrate can be formed according to the stability regime (5). In addition, the formation condition of CO_2 hydrate is known to be more stable than that of CH_4 hydrate. Therefore, the swapping process between two gaseous guests is considered to be a favorable approach toward long-term storage of CO_2. It not only enables the ocean floor to remain stabilized even after recovering the CH_4 gas, because CH_4 hydrate maintains the same crystalline structure directly after its replacement with CO_2, but also makes the swapping process more viable by enhancing its economical efficiency. Of course, a variety of external variables such as injection depth, salt concentration, and initial droplet size of liquid CO_2 may affect the fundamental dynamics of hydrate formation (6–9). Accordingly, intense investigations concerning the effect of external factors and the realization of the process have been performed. Using *in situ* Raman spectroscopy, Komai *et al.* (10) measured the replacement rate between CO_2 and CH_4 occurring in the CH_4 hydrates and found that CO_2 hydrates reform at both the surface and inside of both CH_4 hydrate samples and ice crystals appear, coexisting with the hydrate phase as well.

Although numerous hydrate studies, covering both macroscopic and microscopic approaches, have recently been conducted for a variety of purposes, and to a certain extent have yielded notable success, little attention has been paid to cage dynamics exploring guest distributions within the sensitive host–guest networks. Moreover, the complex hydrate behavior occurring under strong attacks of external guest molecules to the existing cages has not yet been fully considered, and no detailed study exists even at a very fundamental level. In our previous work (11, 12), we explored the replacement mechanism of CH_4 hydrate with CO_2 by using spectroscopic methods and found that, when a CH_4 hydrate is exposed to gas mixtures containing CO_2, CH_4 is replaced by CO_2 mainly in the large cages. If the CH_4 hydrates could be converted into CO_2 hydrates, they would serve double duty as CH_4 sources and CO_2 storage sites. Here, we further extend our investigations to consider the occurrence of CO_2 replacement phenomena on structure II (sII) hydrate, which is thought to exist in the seabed. Using this point of view, we present an interesting conclusion reached by inducing a structure transition. A microscopic analysis was conducted to examine the real swapping phenomena occurring between CO_2 guest molecules and sII hydrate through spectroscopic identification, including solid-state NMR spectrometry and Fourier transform-Raman spectrometry. More importantly, we also investigated the possibility of direct use of a binary N_2 and CO_2 gas mixture for recovering CH_4 from the hydrate phase, which showed a remarkably enhanced recovery rate by means of the cage-specific occupation of guest molecules because of their molecular properties.

Results and Discussion

Direct Sequestration of CO_2 and N_2 Mixtures into Structure I (sI) CH_4 Hydrates. In previous work (11, 12) we verified that the CH_4 amount that could be recovered by replacing sI CH_4 hydrate with CO_2 could reach ≈64% of the hydrate composition. CO_2 molecules only preferably replaced CH_4 in large cages, whereas

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Abbreviations: sI, structure I; sII, structure II; MAS, magic angle spinning.

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CH_4 molecules in small cages remained almost intact. Because of such a preferential cage occupation of guest molecules, the recovery rate of CH_4 was limited to the maximum value of 64%. This swapping process accomplished by the direct attacks of external guests is considered to be a favorable method for long-term storage of CO_2. It also enables the ocean floor to remain stabilized even after recovering the CH_4 gas, because the sI CH_4 hydrate maintains the same crystalline structure directly after its replacement with CO_2. Is it possible to completely achieve the spontaneous exchange by extracting CH_4 molecules and substituting any other guest molecules to most of the small cages already existing in sI CH_4 hydrate? We first attempted to examine the real swapping phenomenon occurring between binary guest molecules of N_2 and CO_2 and crystalline sI CH_4 hydrate through spectroscopic identification. In accordance with the idealized cage-specific pattern of multiple guests, N_2 molecules attack CH_4 molecules occupying small cages (sI-S) and eventually take the sites, whereas CO_2 molecules specifically play an active role in replacing most of the CH_4 molecules in large cages (sI-L). Such a unique cage occupancy behavior might be attributed to molecular details of the participating guests. CO_2 has a molecular diameter almost identical with the small cage diameter of sI hydrate, and a certain degree of distortion in small cages should be required to accommodate CO_2 molecules. Accordingly, we sufficiently expect that CO_2 molecules could be more stably encaged in sI-L under a favorable host–guest interaction. On the other hand, N_2 is known as one of the smallest hydrate formers and its molecular size almost coincides with CH_4. Although N_2 itself forms pure sII hydrate with water (13), the relatively small size of N_2 molecules leads to the preference of sI-S over other cages and, moreover, the stabilization of the overall sI hydrate structure when N_2 directly participates in forming the hydrate. Accordingly, CH_4 and N_2 are expected to compete for better occupancy to sI-S, whereas CO_2 preferentially occupies only sI-L without any challenge from other guests. Thus, the capacity of these two external guests, N_2 and CO_2, in extracting original CH_4 molecules would make it possible for diverse CO_2 streams to be directly sequestrated into natural gas hydrate deposits.

To verify several key premises mentioned above we first identified the ternary guest distribution in cages by means of Raman and ^{13}C NMR spectra. First, for a qualitative description of cage occupancy enforced by N_2 molecules, we measured the Raman spectra of the ternary $CH_4 + N_2 + CO_2$ hydrates formed from several different compositions (Fig. 5, which is published as supporting information on the PNAS web site). These Raman peaks confirm that the approaching N_2 molecules have sufficient ability to expel CH_4 molecules already existing in cages and be stabilized in the host lattice. On the other hand, the NMR spectrum shown in Fig. 1*a* provides clear evidence that CO_2 molecules are distributed only in sI-L, whereas CH_4 molecules remained in both sI-S and sI-L even after completion of replacement as shown in Fig. 1*b*. The qualitative information of cage dynamics in sI-S and sI-L concerning CO_2 molecules could be obtained by analyzing the ^{13}C cross polarization NMR spectral shape of the mixed hydrate. For CO_2 entrapped in hydrate cages, an anisotropic chemical shift is induced by asymmetry in the immediate environment of molecules and is sensitively affected by the guest distribution in hydrate cages (14). As the sI-S produces pseudospherical symmetry, which causes molecular motions to be isotropic, only a sharp peak at an isotropic chemical shift of ≈123 ppm is observed for CO_2 (15, 16). For hydrate samples prepared after replacement, no clear isotropic line appeared and thus CO_2 molecules were not observed in sI-S, as can be seen in Fig. 1*a*. However, a powder pattern having an anisotropic chemical shift of −55.8 ppm was observed, and this spectral shape reflects the anisotropic motion of CO_2 molecules in asymmetric sI-L. The anisotropic chemical

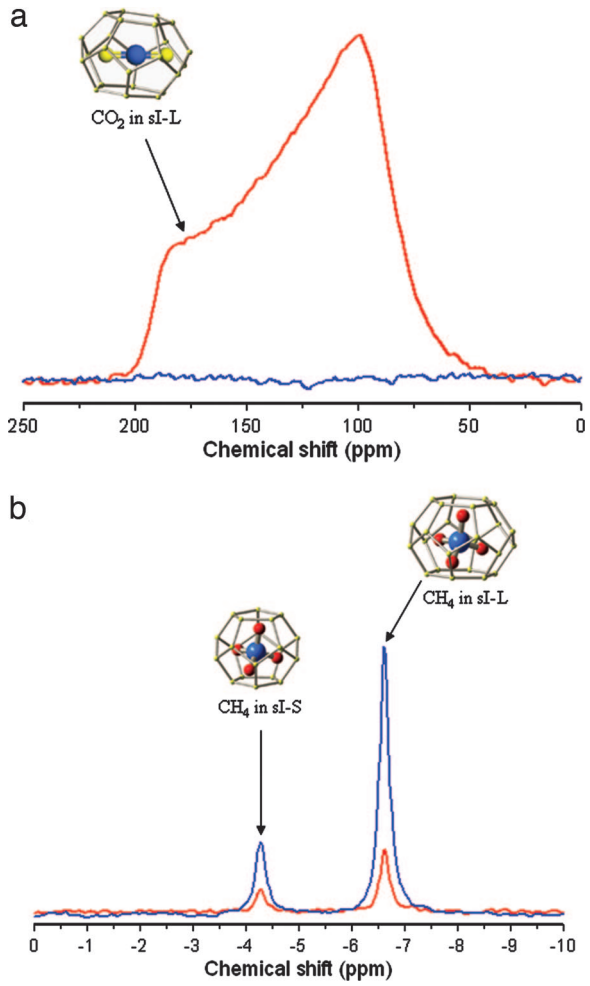

Fig. 1. The $N_2 + CO_2$ mixture consists of 20 mol% CO_2 and balanced N_2. ^{13}C NMR spectra of CH_4 hydrates replaced with $N_2 + CO_2$: blue line, before replacement; red line, after replacement. (*a*) ^{13}C cross-polarization NMR spectra for identifying replaced CO_2 molecules in CH_4 hydrates. (*b*) ^{13}C MAS NMR spectra for identifying residual CH_4 molecules in CH_4 hydrates.

shift is defined as $\Delta = \delta_{iso} - \delta_{zz}$, (15, 16) where $\delta_{iso}(= (2\delta_{xx} + \delta_{zz})/3)$ is the isotropic chemical shift, and δ_{xx} (= 99.6 ppm) and δ_{zz} (= 183.3 ppm) are the *xx* and *zz* components of the chemical shift tensor in Fig. 1*a*, respectively. However, for CH_4 molecules, the ^{13}C magic angle spinning (MAS) NMR spectra (Fig. 1*b*) were taken at conditions before/after replacement and two peaks were clearly identified as representing CH_4 in sI-S and sI-L, respectively. Here, we note that the CH_4 in sI-S was replaced mainly with N_2, whereas CO_2 replaced CH_4 in sI-L. However, further spectroscopic evidence might be required before the pattern of N_2 cage occupancy is more definitively established.

Another important aspect of the present research was to explore the cage-specific distribution of N_2, CO_2, and CH_4 and their kinetic behavior during the replacement process. Two peaks representing CH_4 in sI-S (2,914 cm^{-1}) and CH_4 in sI-L (2,904 cm^{-1}) continuously decreased during a replacement period of 750 min, but subsequently no noticeable change occurred in the peak intensity (Fig. 2*a*). This kinetic pattern can also be confirmed by cross checking them with the corresponding Raman peaks of N_2 and CO_2 (Fig. 2 *b* and *c*). The quantitative analysis revealed that 23% of CH_4 in hydrate is replaced with N_2 whereas 62% of CH_4 is replaced with CO_2. Accordingly, ≈85% of CH_4 encaged in saturated CH_4 hydrate is recovered. This recovery rate is expected to change with variations of external

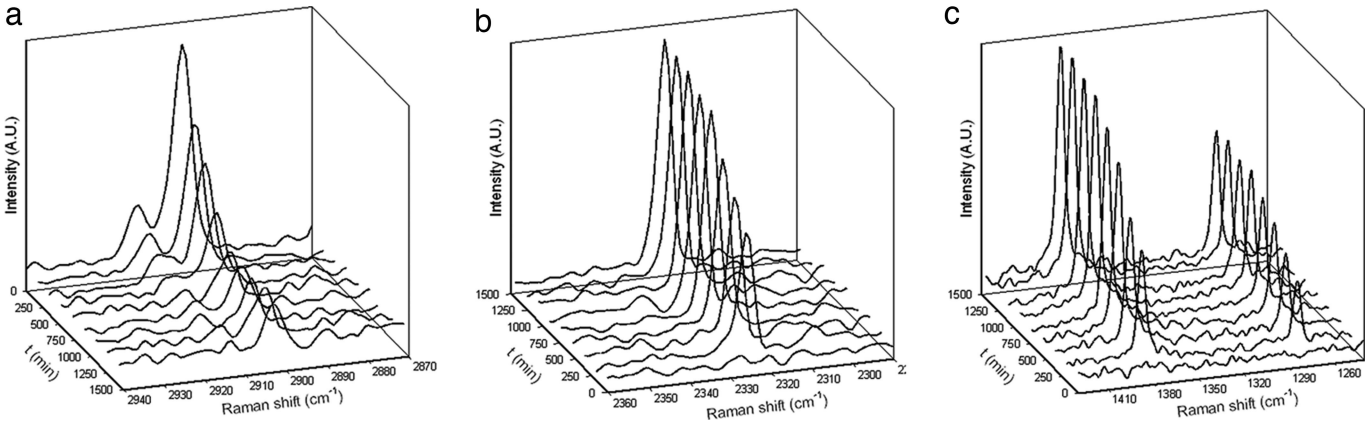

Fig. 2. *In situ* Raman spectra of CH_4 hydrate replaced with N_2 + CO_2 (80 mol% N_2 and 20 mol% CO_2) mixture. (*a*) C–H stretching vibrational modes of CH_4 molecules in the replaced CH_4 hydrate. (*b*) N–N stretching vibrational modes of N_2 molecules in the replaced CH_4 hydrate. (*c*) C=O stretching and bending vibrational modes of CO_2 molecules encaged in the large cages of the replaced CH_4 hydrate.

variables such as pressure, temperature, and hydrate particle size. The overall kinetic results (Fig. 6, which is published as supporting information on the PNAS web site) led us to conclude that the replacement of CH_4 with N_2 + CO_2 proceeds more effectively in crystalline hydrate than in the case of using only pure CO_2, because N_2 molecules are confirmed to offer the excellent cage–guest interaction in an unusual configuration. Even for the simple hydrate systems assessed in the present work, the unique cage dynamics drawn from spectroscopic evidence should offer insight into the inclusion phenomena, particularly,

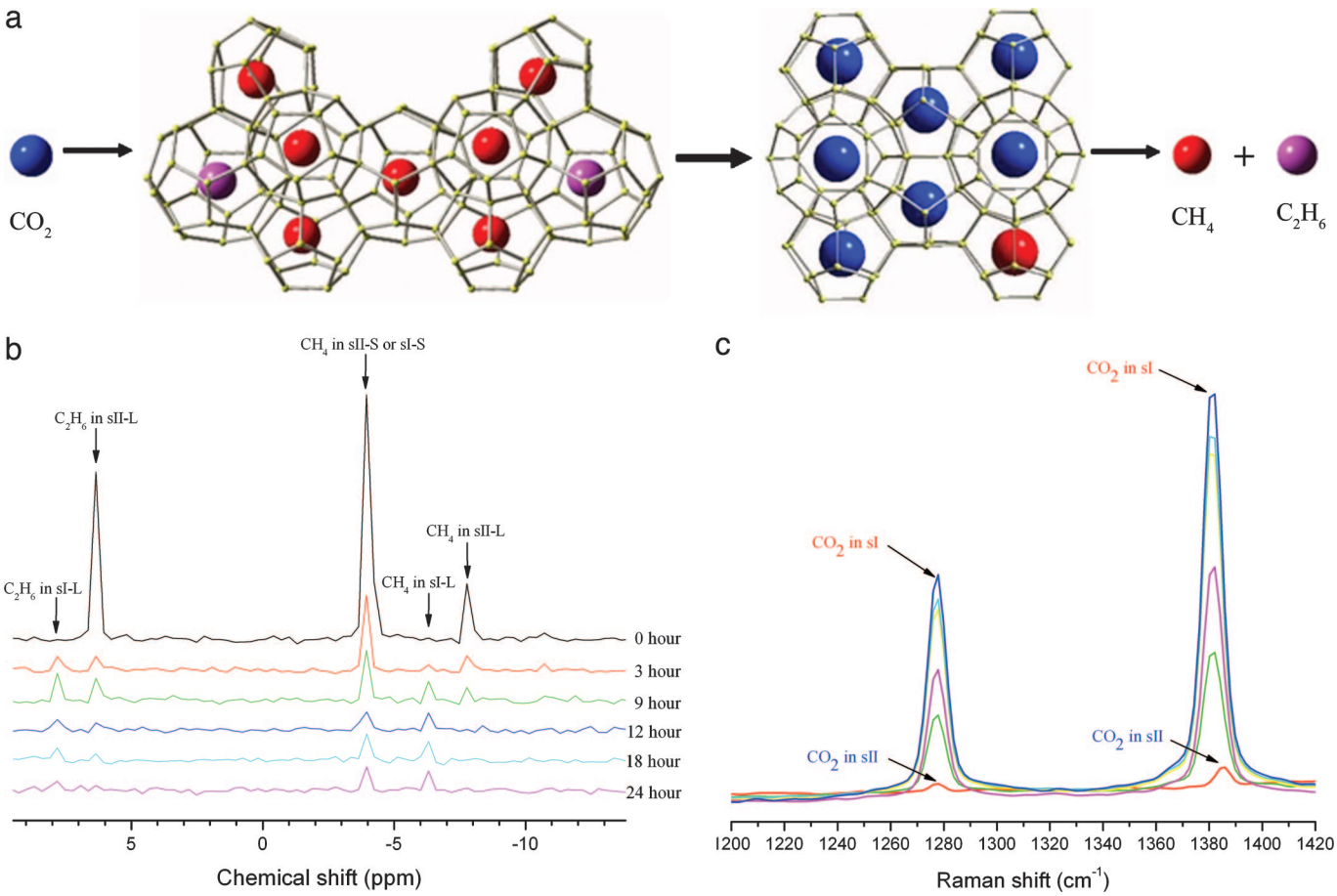

Fig. 3. Replacement of the sII Ch_4 + C_2H_6 hydrate with CO_2. (*a*) Schematic diagram of CH_4 + C_2H_6 hydrate replaced with CO_2. Before the swapping phenomena occurred, all of the sII-S and most of the sII-L cages were occupied by CH_4 (red balls). After the replacement was fully achieved, structure changed from sII to sI, and most of the CH_4 and C_2H_6 (purple balls) molecules were replaced by CO_2 (blue balls). (*b*) The ^{13}C high-power decoupling MAS NMR of mixed CH_4 + C_2H_6 hydrate replaced with CO_2. The samples were measured at 203 K. (*c*) The Raman spectra of the mixed CH_4 + C_2H_6 hydrate replaced with CO_2 at 123 K. The peak intensity of CO_2 symmetric stretching and bending vibration increases as the hydration goes to completion.

the host lattice–guest molecule interaction and the guest–guest replacement mechanism.

CO_2 Sequestration into sII CH_4 Hydrates. The sII hydrate, which is known to be formed by the influence of thermogenic hydrocarbon and mainly includes oil-related C_1–C_4 hydrocarbons (13), was discovered at a shallow depth in sea floor sediment in a few sites such as the Gulf of Mexico outside the Caspian Sea (17, 18). Among major hydrocarbons, C_2H_6 is specially selected to form a hydrate with CH_4. We note that both CH_4 and C_2H_6 form simple crystalline sI hydrates with water. However, when they are mixed within the limits of specific concentrations, they act as binary guests causing the formation of a sII double hydrate (19). For experimental convenience we only treated C_2H_6 exclusive of propane and butanes; otherwise the use of multiguests makes spectroscopic identification much too complicated. Accordingly, in the present work, replacement of the mixed CH_4 + C_2H_6 hydrate with CO_2 was performed to investigate the swapping phenomena on sII CH_4 hydrate. Fig. 3*b* shows the ^{13}C high-power decoupling MAS NMR spectra of mixed CH_4 + C_2H_6 hydrates that are replaced with CO_2 molecules at 274.15 K and 35 bar just below the equivalent CO_2 vapor pressure. The same swapping test was carried out at the higher pressure of 42 bar at which the CO_2 exists as a liquid phase. The resulting NMR spectra appear to be essentially identical with those measured at 35 bar, recovering 90% for CH_4 and 97% for C_2H_6 as shown in Figs. 7 and 8, which are published as supporting information on the PNAS web site. Three peaks representing CH_4 in sII-S, CH_4 in sII-L, and C_2H_6 in sII-L appeared at chemical shifts of −3.95, −7.7, and 6.4 ppm, respectively. Interestingly, during the swapping process, the external guest CO_2 molecules attack both small and large cages for better occupancy, which causes the structure transition of sII to sI to continuously proceed. Within 24 h the sII peaks almost disappeared and instead only a very small amount of CH_4 in sI-S and sI-L and C_2H_6 in sI-L was detected at chemical shifts of −4.0, −6.1, and 7.7 ppm, respectively (19). From a structural viewpoint, it is speculated that the hydrate lattices are slightly adjusted to accommodate the three guests of CH_4, C_2H_6, and CO_2 in highly stabilized hydrate networks.

A Raman study was also performed to confirm the molecular distribution of CO_2 and assess the spontaneous exchange by extracting CH_4 and C_2H_6 and substituting CO_2 molecules; the resulting spectra are shown in Fig. 3*c*. The Raman spectra of CO_2 in vapor phase have Fermi diads of symmetric stretching (1,286 cm^{-1}) and bending vibration (1,389 cm^{-1}) with hot bands (1,266 and 1,410 cm^{-1}). However, when CO_2 molecules are enclosed by hydrate networks, the Fermi diads are broadened and red-shifted, and the hot bands become undistinguishable (20). As the hydration is completed, the CO_2 peaks of symmetric stretching and bending vibration assigned as sII cages of 1,278 and 1,386 cm^{-1} grew and shifted to sI cages of 1,277 and 1,382 cm^{-1}, respectively. The cage-specific behavior revealed by CO_2 is expected according to its molecular dimension over a small cage. Thus, the approaching CO_2 competes only with CH_4 and C_2H_6 in sII-L at the initial stage of swapping. The CH_4 and C_2H_6 expelled from sII-L provoke a loss of sustainability of sII phase by exceeding the limit of critical guest concentration. The reestablishment process of guest molecule distribution in the hydrate network induces the hydrate structure to alter and ultimately adjusts the lattice dimension for sI. Another important feature noted from this complex host–guest inclusion phenomenon is that CO_2 molecules are capable of filling the sI-S under a fresh crystal configuration. Meanwhile, for a simple swapping process between CO_2 and sI CH_4 hydrate, only a few CO_2 guests occupy the sI-S, weakening the actual CO_2 storage capacity from an ocean sequestration point of view. According to previous work (11, 12), CO_2 replacement occurs only at sI-L, but CH_4 molecules in sI-S remain barely intact. At the present stage, we focus specifically on guest distributions of sI and sII hydrates that have ideally stoichiometric formulae of 2 D·6 T·46 H_2O and 16 D·8 H·136 H_2O in a unit cell, respectively (21), where D is cage of 5^{12}, T is cage of $5^{12}6^2$, and H is cage of $5^{12}6^4$. However, when considering the equivalent number of water molecules in both hydrates, sI hydrate has a revised formula, represented by 5.9 D·17.7 T·136 H_2O. Regardless of whether the transition of sII to sI occurs coercively or spontaneously, the structure transformation leads to a reduction of total sI-S sites by 10.1 in the dimension of a unit cell and induces CH_4 molecules in cages to be more readily recovered.

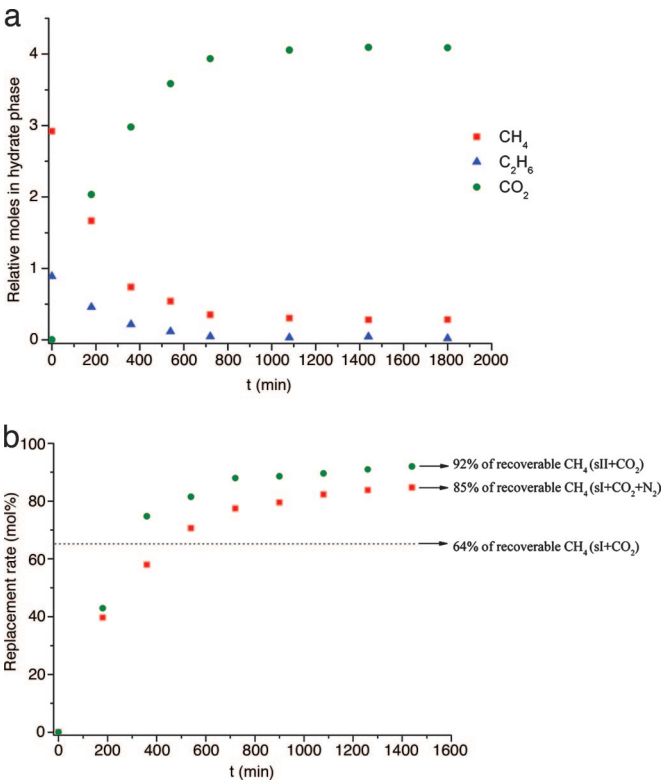

Fig. 4. Replacement kinetics of guest molecules in the sI and sII hydrates. (*a*) Relative moles in the sII CH_4 + C_2H_6 hydrate replaced with CO_2 measured by gas chromatography. (*b*) Replacement rate of CH_4 molecules encaged in sI CH_4 hydrates by N_2 + CO_2 mixture (square) and in sII CH_4 hydrate by pure CO_2 (circle). The recovered CH_4 is 85% for the N_2 + CO_2 mixture and 92% for sII CH_4 hydrate with CO_2. The dotted line represents the 64% recovery rate of CH_4 obtained during the swapping process between sI CH_4 hydrate and pure CO_2.

The effect of a substantial small-cage reduction on CH_4 recovery rate was checked by the GC analysis; the results are shown in Fig. 4*a*. During the swapping process, the CH_4 and C_2H_6 molecules in hydrate phase continuously decrease until they reach the recovery rate of 92% for CH_4 and 99% for C_2H_6. Both the NMR and GC results imply that most of the CH_4 molecules in sI-L and sI-S were displaced by CO_2 molecules. The externally approaching CO_2 guests attack and occupy most of the sII-S and sII-L cages, accompanying structure transition of sII to sI as illustrated in Fig. 3*a*. We note again that CO_2 molecules possess a sufficient enclathration power to be entrapped in sI-S during change of sII to sI, whereas the CO_2 occupancy to sI-S of pure CH_4 hydrate is very difficult to occur. The 30% or more CH_4 recovery enhancement in sII and >64% in sI is caused by structure transition totally altering the host–guest interactions during swapping. Furthermore, the naturally occurring sII hydrates contain more CH_4 than the laboratory-made sII hydrates used in these experiments (18, 22, 23) and thus the actual limitation of recoverable CH_4 in sII hydrate would be higher

than the present outcome of 92%. We also examined the swapping capacity of the N_2 + CO_2 mixture occurring in the mixed sII CH_4 + C_2H_6 hydrate and found that the recovery rates are 95% for CH_4 and 93% for C_2H_6 (Figs. 9 and 10, which are published as supporting information on the PNAS web site). Accordingly, with the better hope we might use the deep-ocean sII CH_4 hydrate layers for effectively sequestrating CO_2 without any loss of recoverable CH_4 amount.

Conclusion

First, we focused on the direct sequestration of gas mixtures containing CO_2 and N_2 into the preponderant sI naturally occurring CH_4 hydrate deposits. However, for ocean storage, recently proposed approaches require that injected CO_2 must be in a pure state, and thus an appropriate separation procedure of CO_2 from the mixed gas must be conducted. A spectroscopic analysis reveals that the external N_2 molecules specifically attack CH_4 molecules already entrapped in sI-S and play a significant role in substantially increasing the CH_4 recovery rate. On the contrary, during swapping the sII CH_4 hydrate structurally transforms to sI, which causes CH_4 molecules in sII-S to spontaneously be released through a continuous reduction of small cage sites. The cage-specific occupation accomplished by direct invasion of external guest molecules largely depends on their molecular details that appear to be so complex for visualization, but this mutually interactive pattern of targeted guest–cage conjugates might possess an important implication on the extensive hydrate-based applications as clearly illustrated in the swapping process between CO_2 stream and CH_4 hydrate. However, the swapping rate and total yield of the replacement reaction in actual natural gas hydrate deposits will depend on a variety of factors such as particle size and gas transport.

Materials and Methods

Sample Preparations and Swapping Procedures. CH_4, CO_2, N_2, and C_2H_6 were purchased from Praxair Technology (Danbury, CT), with a stated minimum purity of 99.995 mol%. The hydrate samples were prepared in a mechanically stirred reactor having the volume of 300 cm^3 and formed from finely pulverized ice particles crushed in a mortar and pestle. The reactor, which maintained a constant temperature of 274.15 K, was filled with powdered ice particles and then pressurized with gases 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 hydrate was sampled and transported to the sample holder.

After making CH_4 or CH_4 + C_2H_6 hydrate with a mechanically stirred high-pressure reactor, these hydrate samples were moved to another high-pressure reactor to experience the replacement with N_2 + CO_2 mixture or pure CO_2. During the movement of these hydrates into another reactor, sample treatment was performed in an atmosphere of liquid nitrogen to keep the prepared sample from dissociating. Immediately after putting the reactor in the water bath whose temperature, 274.15 K, was maintained by an external controller (RBC-20; JEIO Tech, Seoul, Republic of Korea), the N_2 + CO_2 gas mixture of 120 bar or pure CO_2 gas of 35 bar precooled at 274.15 K was introduced into the reactor.

NMR and Raman Analysis. To identify hydrate structure and guest distribution, a Bruker (Billerica, MA) AVANCE 400-MHz solid-state NMR spectrometer was used in this study. The powdered samples were placed in a 4-mm o.d. zirconia rotor loaded into a variable temperature probe. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with MAS at ≈5 kHz. The pulse length of 2 μs and pulse repetition delay of 15 s under proton decoupling were used with a radio frequency field strength of 50 kHz, corresponding to 5-μs 90° pulses. 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. For the mixed hydrate samples, $^{13}CO_2$ gas was used to obtain higher intensity CO_2 peaks. The RFS-100S Fourier transform-Raman spectrometer (Bruker) with a highly sensitive InGaAs detector cooled by liquid nitrogen was used. The excitation source was an air-cooled diode-pumped Nd;YAG laser. The scattered radiation was collected through a slit with 180° geometry at 300 μm. Spectra were collected with a resolution of 1 cm^{-1} scanning step, and typically 512 scans were averaged to obtain each spectrum. The high-pressure cell equipped with sapphire windows was also used for *in situ* Raman measurements.

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