SWAPPING CARBON DIOXIDE FOR COMPLEX GAS HYDRATE STRUCTURES

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ABSTRACT

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. Herein, we report the swapping phenomena between global warming gas and various structures of natural gas hydrate including sI, sII, and sH through ^{13}C solid-state nuclear magnetic resonance, and FT-Raman spectrometer. The present outcome of 85% CH_4 recovery rate in sI CH_4 hydrate achieved by the direct use of binary N_2 + CO_2 guests is quite 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 and sH CH_4 hydrates, we observe a spontaneous structure transition to sI during the replacement and a cage-specific distribution of guest molecules. A significant change of the lattice dimension due to 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 on the diverse hydrate-based inclusion phenomena as clearly illustrated in the swapping process between CO_2 stream and complex CH_4 hydrate structure.

Keywords: gas hydrate, clathrate, CO_2 sequestration, methane, swapping phenomenon, NMR

INTRODUCTION

There are currently two urgent global issues that should be resolved, global warming effects and future energy sources. In order to effectively control atmospheric CO_2 levels, CO_2 needs to be sequestered to appropriate sites on a large scale. Several suggested methods that entail injecting CO_2 into the ocean involve producing relatively

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pure CO_2 at its source and transporting it to the injection point [1]. In particular, when CO_2 is injected in seawater below a certain depth, a solid CO_2 hydrate can be formed according to the stability regime [2].

On the other hand, naturally-occurring gas hydrates are deposited on the continental margin and its permafrost regions and are scattered all over the world [3]. The total amount of natural gas hydrate over the world is estimated to be about twice as much as the energy contained in fossil fuel reserves [4, 5]. In order to recover CH_4 efficiently, several strategies such as thermal treatment, depressurization, and inhibitor addition into the hydrate layer have been proposed [6]. However, all these methods are based on the decomposition of CH_4 hydrate by external stimulation and could potentially trigger catastrophic slope failures [7]. It thus needs to be recognized that the present natural gas production technologies have inherent limitations in terms of their adoption for the effective recovery of natural gas hydrates. As such, the safest and most economically feasible means should be developed with full consideration of environmental impacts.

Recently, the replacement technique for recovering CH_4 from CH_4 hydrate by using CO_2 has been suggested as an alternative option for recovering CH_4 gas [8, 9]. This swapping process between two gaseous guests is considered to be a favorable approach toward long-term storage of CO_2. It also 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. 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 sII, and sH hydrate. In this point of view, we present an interesting conclusion reached by inducing a structure transition. A microscopic analysis is conducted in order to examine the real swapping phenomena occurring between CO_2 guest molecules and various types of hydrate through spectroscopic identification, including solid-state Nuclear Magnetic Resonance (NMR) spectrometry and FT-Raman spectrometry. More importantly, we also investigate the possibility of direct use of binary N_2 and CO_2 gas mixture for recovering CH_4 from the hydrate phase, which shows a remarkably enhanced recovery rate by means of the cage-specific occupation of guest molecules due to their molecular properties.

RESULTS AND DISCUSSION

The recoverable amount of CH_4 by replacing sI CH_4 hydrate with CO_2 could reach around 64% of hydrate composition because CO_2 molecules only preferably replace CH_4 in large cages, while CH_4 molecules in small cages remain almost intact [8]. This swapping process between two gaseous guests is considered to be a favorable way as a long-term storage of CO_2 and enables the ocean floor to remain stabilized even after recovering the CH_4 gas because sI CH_4 hydrate maintains the same crystalline structure directly after its replacement with CO_2. We first attempted to examine real swapping phenomenon occurring between binary guest molecules of N_2 and CO_2 and crystalline sI CH_4 hydrate through spectroscopic identification. For CO_2 its molecular diameter is the same as the small cage diameter of sI hydrate, and thus only a little degree of distortion in small cages exists to accommodate CO_2 molecules. Accordingly, we sufficiently expect that CO_2 molecules can be more stably encaged in sI-L under 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, the relatively small size of N_2 molecules leads to the preference of sI-S over other cages and moreover the stabilization of overall sI hydrate structure when N_2 directly participates in forming hydrate.
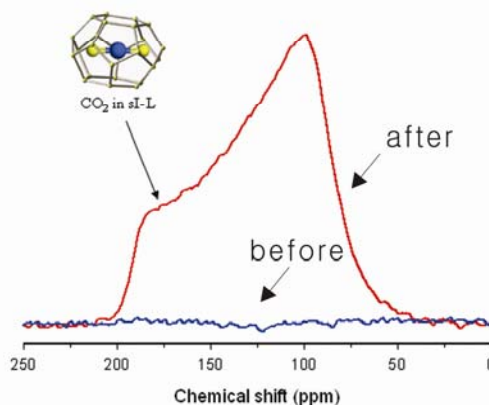

Figure 1 ^{13}C cross-polarization NMR spectra for identifying replaced CO_2 molecules in sI CH_4 hydrate.

Accordingly, CH$_4$ and N$_2$ are expected to compete for better occupancy to sI-S, while CO$_2$ preferentially occupies only sI-L without any challenge of other guests. Thus, the successful role of these two external guests of N$_2$ and CO$_2$ in extracting original CH$_4$ molecules makes it possible for diverse flue gases to be directly sequestrated into natural gas hydrate deposits.
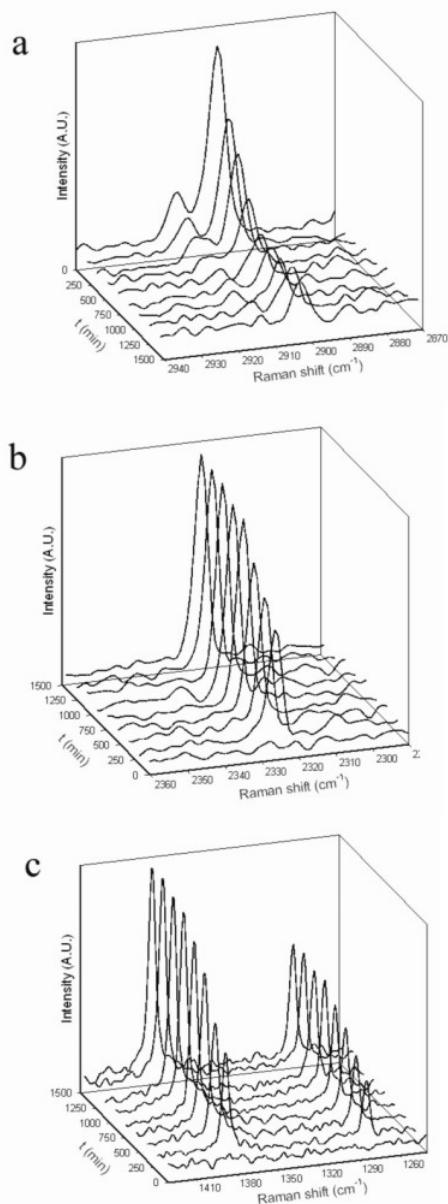

Figure 2 *In-situ* Raman spectra of sI CH$_4$ hydrate replaced with N$_2$ + CO$_2$ (80 mol% N$_2$ and 20 mol% CO2) mixture. (a) C-H stretching vibrational modes of CH$_4$ molecules, (b) N-N stretching modes of N$_2$ molecules, (c) C=O stretching and bending vibrational modes of CO$_2$ in clathrate hydrate cages.

To verify several key premises mentioned above we first identified ternary guest distribution in cages through the ^{13}C NMR and Raman spectra. As shown in Figure 1. the NMR spectra provide a clear evidence such that CO$_2$ molecules are distributed only in sI-L. For qualitative description of cage occupancy enforced by N$_2$ molecules, we measured the Raman spectra of the sI CH$_4$ hydrates replaced with N$_2$ + CO$_2$ mixture. Two peaks in Figure 2a representing CH$_4$ in sI-S (2914 cm^{-1}) and CH$_4$ in sI-L (2904 cm^{-1}) continuously decreased during the replacing period of 750 min, but after that no noticeable change occurred in peak intensity. This kinetic pattern can be also confirmed by crosschecking them with the corresponding Raman peaks of N$_2$ and CO$_2$ (Figures 2b and 2c). The quantitative Raman analysis revealed that, 23% of CH$_4$ in hydrate is replaced with N$_2$, while 62% of CH$_4$ is replaced with CO$_2$. Accordingly, approximately 85% of CH$_4$ encaged in saturated CH$_4$ hydrate is recovered and, of course, this recovery rate might be expected to more or less change with variations of external variables such as pressure, temperature and hydrate particle size. The overall kinetic results lead us to make a clear conclusion that the replacement of sI CH$_4$ hydrate with N$_2$ + CO$_2$ mixture proceeds more effectively in crystalline hydrate than using only pure CO$_2$ because N$_2$ molecules is confirmed to possess the excellent cage-guest interaction in an unusual configuration. Even for simple hydrate systems focused in the present work the unique cage dynamics drawn from spectroscopic evidences might be expected to offer the new insight for better understanding of inclusion phenomena, particularly, host lattice-guest molecule interaction as well as guest-guest replacement mechanism.

However, sII and sH hydrates, which are known to be formed by the influence of thermogenic hydrocarbon and mainly includes oil-related C$_1$-C$_7$ hydrocarbons, were discovered at shallow depth in sea floor sediment in a few sites such as the Gulf of Mexico or Cascadian margin [10-12]. Thus, it is also required to verify the swapping phenomena occurring on sII or sH type clathrate hydrate. For sII hydrate, C$_2$H$_6$ is specially selected to form the hydrate with CH$_4$. We note that both CH$_4$ and C$_2$H$_6$ form simple crystalline sI hydrates with water. But, when they are mixed within the limits of specific concentrations, they act as binary guests causing to form the stable sII double hydrate [13]. Figure 3 shows the ^{13}C HPDEC MAS NMR spectra of

mixed CH_4 + C_2H_6 hydrates that are replaced with CO_2 molecules. Three peaks representing the 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 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 hours 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.
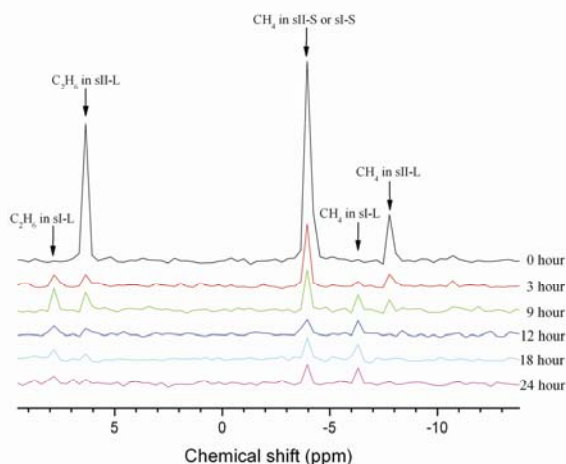

Figure 3. The ^{13}C HPDEC MAS NMR spectra of sII CH_4 + C_2H_6 hydrate replaced with CO_2.
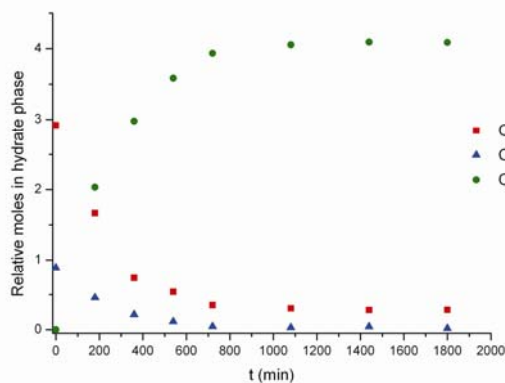

Figure 4. Relative moles in the sII CH_4 + C_2H_6 hydrate replaced with CO_2 measured by gas chromatography.

From structural viewpoint we think that the hydrate lattices are slightly adjusted to accommodate three guests of CH_4, C_2H_6 and CO_2 in the highly stabilized hydrate networks. The cage-specific behavior revealed by CO_2 can be sufficiently 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. CH_4 and C_2H_6 expelled from sII-L provoke losing sustainability of sII phase by getting out of the limit of critical guest concentration. The reestablishment process of guest molecule distribution in the hydrate network causes to alter and ultimately adjust the lattice dimension for structure transition to occur. The effect of a substantial small-cage reduction on CH_4 recovery rate was checked by the GC analysis and the results are shown in Figure 4. During the swapping process, the CH_4 and C_2H_6 molecules in hydrate phase continuously decrease until reaching the recovery rate of 92% for CH_4 and 99% for C_2H_6. Both the NMR and GC results imply that most of CH_4 molecules in sI-L as well as 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. We note again that CO_2 molecules possess a sufficient enclathration power to be entrapped in sI-S during change of sII to sI, while 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 over 64% in sI is caused by structure transition totally altering the host-guest interactions during swapping. Furthermore, the naturally-occurring sII hydrates contain more amount of CH_4 than the laboratory-made sII hydrates used in these experiments 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.
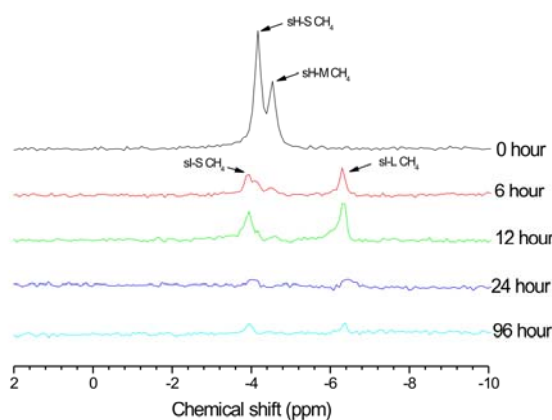

Figure 5. The ^{13}C HPDEC MAS NMR spectra of sH CH_4 + isopentane hydrate replaced with CO_2.

In case of sH CH_4 hydrate, structure transition was also occurred during the swapping process as shown in Figure 5. Before replacement, isopentane was entrapped in large cages of sH hydrate with CH_4 in both small and middle cages. However, external CO_2 gas provokes structure transition to sI type hydrate and finally sH phase disappeared. During the replacement, 92% of CH_4 was recovered. In addition, by using $N_2 + CO_2$ mixture exceeding 90% of recovered CH_4 readily achieved.

Type	Replaced with CO_2 (%)	Replaced with N_2+CO_2 (%)
sI (CH_4)	64%	85%
sII ($CH_4+C_2H_6$)	92%	95%
sH (isopentane+CH_4)	92%	90%

Table. 1. Recoverable CH_4 (mol%) in various types of gas hydrates

CONCLUSION

In this study, we investigated the swapping phenomena through flue gas mixtures of N_2 and CO_2 for efficiently developing gas hydrate in the deep ocean floor. The direct use of $N_2 + CO_2$ mixture enhanced CH_4 recovery as well as eliminated the CO_2 separation/purification process for sequestering CO_2. In addition, a spectroscopic analysis reveals that the external N_2 molecules attack CH_4 molecules already entrapped in sI-S and play a significant role in substantially increasing the CH_4 recovery rate. In particular, we performed the replacement experiment for naturally occurring sI, sII, sH hydrate. During the swapping the sII and sH CH_4 hydrate, structure transition to sI were observed. The utilization of this natural swapping phenomenon might greatly contribute to realizing both ocean storage of CO_2 and CH_4 recovery from marine deposits in a large scale.

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