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Kinetics of Methane Hydrate Replacement with Carbon Dioxide and Nitrogen Gas Mixture Using in Situ NMR Spectroscopy

Minjun Cha,[†] Kyuchul Shin,[‡] Huen Lee,[§] Igor L. Moudrakovski,^{||, #} John A. Ripmeester,^{||} and Yutaek Seo^{*, †, ‡}

[†]Department of Energy and Resources Engineering, Kangwon National University, 1 Kangwondaehak-gil, Chuncheon-si, Gangwon-do 200-701, Republic of Korea

[‡]Department of Applied Chemistry, Kyungpook National University, 80 Daehak-ro, Buk-gu, Daegu, Gyeongsangbuk-do 702-701, Republic of Korea

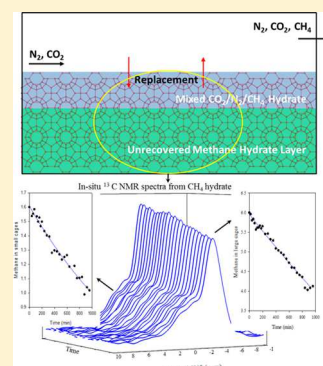
[§]Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon, Chungcheongnam-do 305-701, Republic of Korea

^{||}National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

^{*}Ocean Systems Engineering Division, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon, Chungcheongnam-do 305-701, Republic of Korea

S Supporting Information

ABSTRACT: In this study, the kinetics of methane replacement with carbon dioxide and nitrogen gas in methane gas hydrate prepared in porous silica gel matrices has been studied by in situ ¹H and ¹³C NMR spectroscopy. The replacement process was monitored by in situ ¹H NMR spectra, where about 42 mol % of the methane in the hydrate cages was replaced in 65 h. Large amounts of free water were not observed during the replacement process, indicating a spontaneous replacement reaction upon exposing methane hydrate to carbon dioxide and nitrogen gas mixture. From in situ ¹³C NMR spectra, we confirmed that the replacement ratio was slightly higher in small cages, but due to the composition of structure I hydrate, the amount of methane evolved from the large cages was larger than that of the small cages. Compositional analysis of vapor and hydrate phases was also carried out after the replacement reaction ceased. Notably, the composition changes in hydrate phases after the replacement reaction would be affected by the difference in the chemical potential between the vapor phase and hydrate surface rather than a pore size effect. These results suggest that the replacement technique provides methane recovery as well as stabilization of the resulting carbon dioxide hydrate phase without melting.



INTRODUCTION

Gas hydrates are crystalline host–guest compounds composed of hydrogen-bonded networks of host water molecules and encaged guest molecules, such as methane, nitrogen and carbon dioxide.¹ Recently, natural gas hydrates have received considerable attention because of their potential as a future energy resource.^{1–3} Recent studies have focused on the efficient recovery of methane from natural gas hydrate deposits located offshore in marine sediments and under the permafrost in the Arctic region.^{4–7} However, exploiting methane from hydrate deposits as a fuel may result in increasing the concentration of CO₂ in the atmosphere, since currently methane is used mostly as a fuel. From the perspective of the global carbon cycle, the sequestration of CO₂ needs to be considered, along with the production of methane to avoid the portion of global warming that may be caused by anthropogenic CO₂ emission.

Recovering methane from the natural gas hydrate deposits through the injection of CO₂ into the hydrate layers, called the replacement technique, has been widely studied as a promising option for producing methane and sequestering CO₂

simultaneously.^{8–12} Recent studies include thermodynamic measurements, spectroscopic analysis, and molecular dynamic simulations to understand the replacement process. On the basis of ¹³C NMR spectroscopic analysis, Lee et al. suggested that the direct injection of carbon dioxide into methane hydrate layers could provide both methane gas recovery and CO₂ sequestration with about 64% methane recovery.¹³ From a combination of thermodynamic studies and ¹³C NMR spectroscopic measurement, Seo et al. estimated a replacement ratio of 67% when exposing methane hydrate to CO₂.¹⁴ Schicks et al. observed slow changes in hydrate composition during the replacement reaction and obtained a maximum methane replacement in the hydrate phase of 50% using in situ Raman spectroscopic measurements.¹⁵ They suggested three stages of replacement, step (1) disturbing the hydrate–gas equilibrium by

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changing vapor composition, step (2) decomposition of hydrate and reformation of a transient mixed hydrate at the surface of the original hydrate particle, and step (3) the achievement of a new equilibrium. The in situ Raman and Powder X-ray Diffraction (PXRD) results suggested that the replacement process is diffusion controlled and therefore is inherently slow.

The magnetic resonance imaging (MRI) technique has been applied to monitor the spontaneous replacement of methane with CO₂ within the hydrate structure formed in Bentheim sandstone, and suggested that large-scale melting of hydrate did not occur during the replacement process at 277 K.¹² By monitoring the heat flow in a high pressure microdifferential scanning calorimeter (DSC), Lee et al. also found that there were no thermal events attributable to dissociation or formation of gas hydrate during the replacement process.¹⁶ Molecular dynamics simulations performed under constant temperature 280 K and pressure 60 bar were used to investigate the replacement mechanism, depending on the rigidity of the water cages, and suggested that the replacement could take place without melting of water molecules in the host network.¹⁷ However, another simulation result obtained at constant temperature 270 K and pressure 20 bar suggested a two-step process for the replacement, where the melting of methane hydrate formed some residual hydrate structures inducing subsequent formation of the amorphous layer of CO₂ hydrate.¹⁸ Both simulations ran on a microsecond time scale (up to 0.18 μ s¹⁷ and up to 20 μ s¹⁸), and both simulation temperatures were above the melting temperature of methane hydrate and below the that of carbon dioxide hydrate, thus these results clearly indicate further experimental results are required to advance the simulation of the replacement process.

The role of nitrogen as an additional replacement agent has been studied to try to improve the replacement ratio, and 85% recovery of methane from the hydrate layer was obtained. The higher recovery efficiency has been considered to be due to the ability of nitrogen, which can easily drive out methane from the small cages, but recent simulation studies reported that nitrogen enclathration in small cages of sI hydrates through the substitution of methane has a positive free energy,^{19–22} which would predict the kinetic promotion of nitrogen in the replacement mechanism rather than the thermodynamic effect, because nitrogen is more mobile in the hydrate lattice than carbon dioxide. The prevention of a possible blockage problem by carbon dioxide, which can occur when it is solely injected into the high pressure condition of deep sea sediment, is an additional role of nitrogen. Recently, the injection of a CO₂/N₂ gas mixture into a methane hydrate layer was field-tested on the North Slope of Alaska.²³ The CO₂/N₂ gas mixture (23 mol % CO₂ and 77 mol % N₂) was injected into hydrate deposits to prevent significant CO₂ hydrate build-up around the injection well, which may occur in the case of pure CO₂ injection. After injecting 210 mscf of a CO₂/N₂ gas mixture, most of the 162 mscf of injected N₂ was collected during the production stages; however, more than half of the 48 mscf injected CO₂ remained in the formation. This field test has successfully demonstrated the feasibility of injecting the CO₂/N₂ gas mixture into a hydrate layer with simultaneous recovery of methane, and suggesting that the replacement technology may be commercially viable.

Although the kinetics of replacement between methane and CO₂/N₂ gas mixtures is central to understanding the replacement mechanism, there have been few results on the

study of the kinetics of methane hydrate replacement with a CO₂/N₂ gas mixture. In this study, we investigate the replacement characteristics of methane hydrate when exposing it to a CO₂/N₂ gas mixture (20 mol % of CO₂ and 80 mol % of N₂) using in situ NMR spectroscopy. Because the structural characteristics of silica gel as a porous media can represent a natural analogue of the geologic formation environments, methane hydrate was formed inside silica gel pores in this study. ¹H NMR spectra were monitored to observe the replacement of methane in hydrate cages by CO₂ and N₂ molecules, as well as to observe the possible occurrence of a free water phase upon decomposition of the methane hydrate. ¹³C NMR spectra were obtained during the experiment, which follows the replacement process of methane molecules in small and large cages of methane hydrates. Hydrate formed in a conventional high pressure cell was used to measure methane, CO₂, and N₂ content in the hydrate phase after completing the replacement reaction to confirm the overall replacement rate.

■ EXPERIMENTAL SECTION

Materials. CH₄ gas with a stated minimum purity of 0.9999, an N₂ and CO₂ gas mixture with a desired composition (80 mol % of N₂ + 20 mol % of CO₂ and 60 mol % of N₂ + 40 mol % of CO₂) were supplied by Special Gas (Korea). Compositions of N₂ and CO₂ gas mixtures were confirmed by gas chromatography. Silica gels having nominal pore diameters of 15 and 30 nm with a particle size distribution from 40 to 75 μ m were purchased from Silicycle (Canada). Silica gel having a nominal pore diameter of 6 nm with a particle size distribution from 35 to 75 μ m was purchased from Sigma-Aldrich Inc. Ultrahigh purity water was obtained from a Millipore purification unit. Silica gels were first dried at 373 K for 24 h before water sorption. Water pore saturated silica gel was prepared by placing the dried material in a desiccator containing degassed and distilled water, evacuating the desiccator, and allowing it to stand for more than 5 days. The total amount of adsorbed water in the silica gel pores was confirmed by measuring the mass of silica gel before and after saturation and was found to be almost identical with the reported pore volume for each silica gel.

NMR Spectroscopic Analysis. The replacement process of methane hydrate with a CO₂/N₂ gas mixture was monitored with a Bruker 400 MHz solid state NMR spectrometer (magnetic field 9.4 T, resonance frequencies 400 and 100.6 MHz for ¹H and ¹³C, respectively). The experiments were performed with a specially designed static high pressure cell similar to the one previously reported.²⁴ The detection cell of the probe was custom-built around a 7 mm O.D. sapphire tube and connected to a gas handling system. Supporting Information (SI) Figure S1 shows the schematic diagram of the gas handling system connected to the NMR spectrometer. Methane hydrate was formed in silica gel pores at 276 K and 140 bar for 1 day. The temperature of the experiments was controlled using a Bruker BVT 3000 temperature control unit.

After confirming the formation of methane hydrate, methane gas was removed under vacuum and a CO₂/N₂ gas mixture was charged into the cell to a pressure of 100 bar with the gas handling system. ¹H NMR spectra were recorded to follow the replacement reaction and to observe the possible occurrence of a free water phase. In addition, ¹³C NMR spectra were obtained to observe the changes of the methane resonance intensity, indicating the number of methane molecules in cages of the hydrate structure as a function of time. Both ¹H NMR and ¹³C

NMR spectra for the replacement reaction are collected at 273 K.

Compositional Analysis. The composition of the vapor and hydrate phases after completion of the replacement reaction was measured using a high pressure cell with a total volume of 100 cm³ and a gas chromatograph (HP 6890). The experiment began by charging the cell with about 25 g of silica gel containing pore water. After the reaction cell was pressurized to the desired pressure with methane (140 bar), the cell was cooled slowly to 276 K. When the pressure reduction due to hydrate formation reached a steady-state, the cell conditions were maintained for at least 1 day. Then the free methane gas was discharged completely and a CO₂/N₂ gas mixture of the desired composition was introduced at a pressure of 100 bar. In this study, two gas mixtures of 20 and 40 mol % of CO₂ in N₂ were used. The reaction cell conditions were kept for 60 h to allow the replacement reaction between methane hydrate and CO₂/N₂ gas mixture to reach a steady state. The composition of the vapor phase was measured, then the vapor phase was discharged completely to initiate the dissociation of the hydrate phase. The cell temperature was increased to 293 K to facilitate the dissociation. The composition of the released gas from the hydrate phase was analyzed after it was confirmed that the dissociation of the hydrate phase was complete. The details of the apparatus have been presented in our previous work.²⁵ The composition of the evolved gas was analyzed several times by a gas chromatograph attached directly to the reaction cell to eliminate possible errors that might arise during the sampling procedure and to confirm the reproducibility of the data.

RESULTS AND DISCUSSION

Replacement Process from ¹H and ¹³C NMR Spectra.

CH₄ hydrate was formed for 1 day in silica gel pores having a pore size of 15 nm with a particle size distribution from 40 to 75 μm at 276 K and 140 bar. SI Figure S2 shows the ¹H NMR spectra recorded during this time. The peak intensity from free water is seen to decrease during the formation of hydrate, which can be ascribed to hydrate formation, the signal from hydrate being invisible in our experiment because of the short *T*₂ values. The more shielded signal next to that of free water is the peak from methane gas. From the ¹H NMR spectra, we confirmed that 81% of the water was converted to hydrate. Fitting the experimental data in SI Figure S2 with a single-exponential decay function, $y = y_0 + A \exp(-k_1 x)$, provides an average formation rate constant of $k_1 = 0.05 \text{ min}^{-1}$.

Once it was confirmed that the formation had reached a steady state, methane hydrate was exposed to a gas mixture of CO₂/N₂ (20 mol % CO₂ and 80 mol % N₂) at 100 bar and 273 K. One should note that these temperatures and pressures were carefully chosen to be inside the stable hydrate region for the CO₂/N₂ mixture. The ¹H NMR spectra were then used to follow the replacement reaction and to estimate the amount of CH₄ replaced by the CO₂/N₂ gas mixture. Figure 1(a) indicates the results obtained from the ¹H NMR data as a function of time after CH₄ hydrate in silica gel was exposed to the mixture gas of 20 mol % CO₂, balance N₂. The peak intensities of the CH₄ ¹H NMR signal, shown in Figure 1(b) reveal the number of CH₄ molecules in hydrate cages, the change in peak intensity from CH₄ signals indicates the number of CH₄ molecules remaining in the hydrate cages. In Figure 1, we can observe two representative signals from the ¹H NMR spectra. The chemical shift around −0.1 ppm represents CH₄ molecules in cages of sl

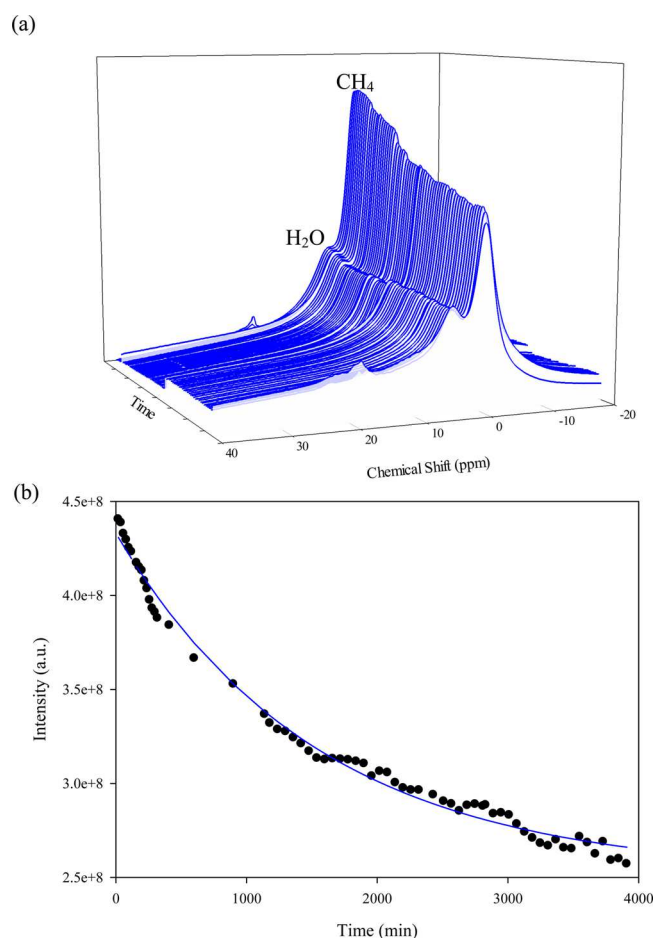


Figure 1. (a) Series of ¹H NMR spectra as a function of time, and (b) time-dependence of the integrated intensity change of the ¹H NMR spectrum for H₂O when CH₄ hydrate in silica gel is exposed to 20 mol % of CO₂, balance N₂, gas mixture at 273 K and 100 bar.

hydrate.²⁶ Near a chemical shift of 3.5 ppm, there is a shoulder on the ¹H NMR spectra from the water molecules that did not participate in hydrate formation and remained as free water in the porous media.²⁷ No significant change in this peak intensity was observed during the replacement reaction, which indicates that there is spontaneous conversion of CH₄ hydrate to a mixed gas (likely N₂/CO₂ and CH₄) hydrate when CH₄ hydrate is exposed to the gas mixture. However, as the reaction time increases, we can clearly observe the decrease in CH₄ intensity at around −0.1 ppm. As the number of CH₄ molecules in the cages of sl hydrate decreases, the peak intensity of CH₄ molecules in the ¹H NMR spectra also decreases. This phenomenon implies that the CH₄ is replaced steadily by the gas mixture of 20 mol % CO₂, balance N₂. The change in CH₄ peak intensity was monitored in order to identify the amount of CH₄ recovered from hydrate cages. When the experiment ran for 65 h, it was confirmed that 42 mol % of CH₄ was replaced. These results indicate that CH₄ in hydrate cages can indeed be replaced when the hydrate is exposed to CO₂/N₂ gas mixtures even at concentration of CO₂ as low as 20 mol %. The replacement reaction was faster at earlier stages until about 25% of CH₄ was replaced over 17 h, but slowly reached 42% of replacement in the following 48 h. Moreover, the decrease in CH₄ line intensity in the ¹H NMR spectra can be described by an exponential decay function as shown in Figure 1(b). It gives a replacement rate constant of $k_1 = 0.0007 \text{ min}^{-1}$, indicating

that the replacement reaction is much slower than the formation of methane hydrate from ice. Eventually, the replacement ratio of CH_4 in hydrate phase reached 42% after 65 h of exposing to CO_2/N_2 gas mixture.

From the ^1H NMR spectra, we observed that the fastest replacement reaction occurred in the first 17 h of experimental time, but the detailed mechanism of the substitution behavior of CH_4 through the injection of the mixture gas of 20 mol % CO_2 balance N_2 is still not clear. Therefore, in order to gain additional insight, we have observed the ^{13}C NMR spectra of CH_4 in hydrate cavities and the changes in occupancy of CH_4 in small and large cages of structure I hydrate, ^{13}C NMR spectra were monitored during the replacement reaction, as shown in Figure 2. The results indicate that 36% of CH_4 in

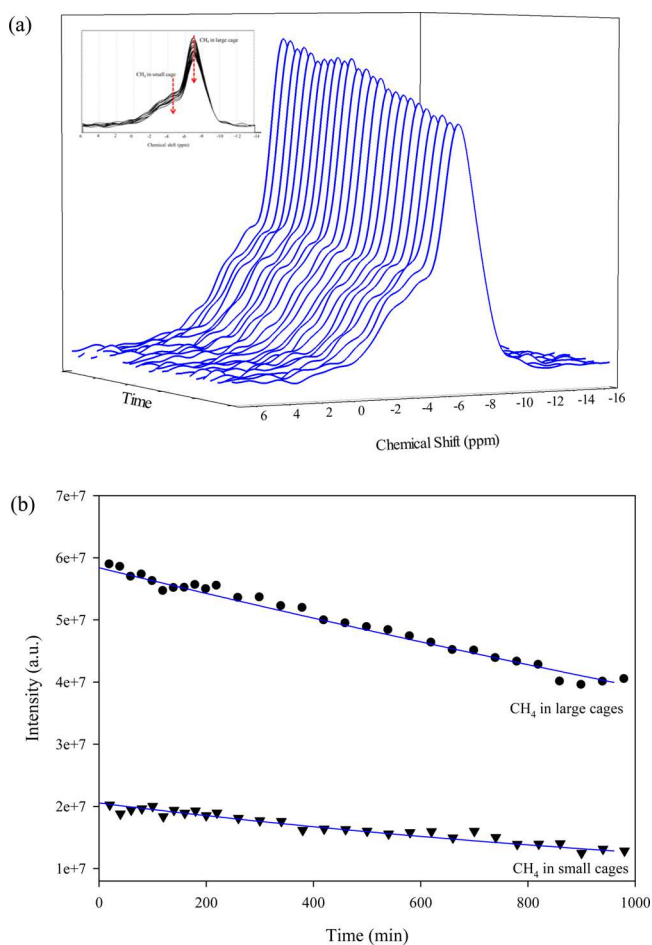


Figure 2. (a) ^{13}C NMR spectra as a function of time (inset: stacked NMR spectra). (b) Time-dependence integrated intensity change of ^{13}C NMR spectra when CH_4 hydrate in silica gel is exposed to 20 mol % of CO_2 and balance N_2 gas mixture at 273 K and 100 bar.

small cages was replaced with k_1 of 0.0007 min^{-1} , while 31% of CH_4 in large cages was replaced during 17 h with k_1 of 0.0002 min^{-1} (Figure 2). This is in a good agreement with ^1H NMR data as the amount of replaced methane is 25% during 17 h. As the large cages outnumber the small cages by a factor of 3 in structure I hydrate, the amount of replaced CH_4 should be much larger in large cages than small cages.

Figure 3(a),(b) shows the amount of methane in large and small cages, respectively, which was obtained from the integrated intensities in Figure 2 and the unit cell composition

of structure I methane hydrate. The methane hydrate composition can be written in terms of the unit cell contents: $(2S) \cdot (6L) \cdot 46\text{H}_2\text{O}$, where L is the large cage occupancy, and S is the small cage occupancy. Our previous works indicated the small cages occupancy was 0.8 and the value for large cages was close to 1.0, usual values needed to stabilize the cage structure.¹³ Accordingly, we estimated the amount of methane in large and small cages considering the unit cell formula of structure I, $(1.6S) \cdot (6.0L) \cdot 46\text{H}_2\text{O}$, and cage occupancies of methane in both cages. Figure 3(a) suggests the methane in large cages decreases from 6.0 to 4.1 while the methane in small cages decreases from 1.6 to 1.0, as seen in Figure 3(b). The final methane composition of hydrate unit cell would be $(1.0S) \cdot (4.1L) \cdot 46\text{H}_2\text{O}$. The ratio of methane in small to large cages ($I_{\text{small}}/I_{\text{large}}$) is calculated from Figure 3(a),(b) and is shown in Figure 3(c). It is worth noting that the initial ratio was 0.27 when commencing the replacement process, and shows only slight change to 0.25, suggesting the methane composition in hydrate follows the average unit cell composition of structure I methane hydrate. This is interesting result considering that the small cages are well isolated from each other, with the large cages forming stacks in three dimensions, thus the direct exchange between gaseous CO_2 or N_2 and CH_4 in the small cage is impossible, and the exchange process in small cages needs to involve the large cages.

For a simplified model of the replacement reaction in the hydrate phase, the overall kinetics of replacement should be dependent upon at least two parameters: the rate of the replacement reaction at the hydrate gas interface and the transport of the CO_2/N_2 gas through the mixed hydrate layer already formed at the gas–hydrate interface. ^1H and ^{13}C NMR spectra in Figures 1 and 2 suggest that the spontaneous replacement reaction seems to occur on the surface of methane hydrates once the methane hydrates are exposed to the CO_2/N_2 gas mixture. Methane hydrate at the surface of the hydrate becomes unstable when methane gas is replaced by the CO_2/N_2 gas mixture, thus decomposing the surface hydrate layer. From the ^1H NMR spectra, there was no indication of increased amounts of free water, thus it is expected that the decomposed surface hydrate layer transforms rapidly into a mixed hydrate. The thickness of the mixed hydrate layer will increase as the time progresses; therefore, the diffusion of CO_2 and N_2 molecules through the mixed hydrate phase as well as the diffusion of methane out of the hydrate through the mixed layer is likely to be the rate determining stage for replacement reaction in the bulk hydrate. In ^1H NMR spectra, from 0 to 17 h the replacement rate constant k_1 is evaluated as 0.002 min^{-1} , while the constant k_1 from 17 to 65 h is calculated as 0.00015 min^{-1} . Therefore, the total replacement rate constant of $k_1 = 0.0007 \text{ min}^{-1}$ is dominantly affected by this later replacement stage between 17 and 65 h, implying that the diffusion of CO_2/N_2 gas mixture after 17 h into interaction has significantly slowed. This reaction kinetics showed quite a similar trend of the formation of hydrate-shells on the surface of water droplets also showing a two-step process, (1) surface reaction, and (2) bulk reaction processes.^{28,29} In addition, the formation of a mixed hydrate layer on the methane hydrate would reduce the chemical potential difference between gas and hydrate phases, which reduces the driving force for the transport of the CO_2/N_2 gas through the mixed hydrate layer. As the replacement front moves forward into the methane hydrate, these two processes—transportation of CO_2/N_2 gas into a mixed hydrate layer and diffusion of CO_2/N_2 molecules thorough the mixed

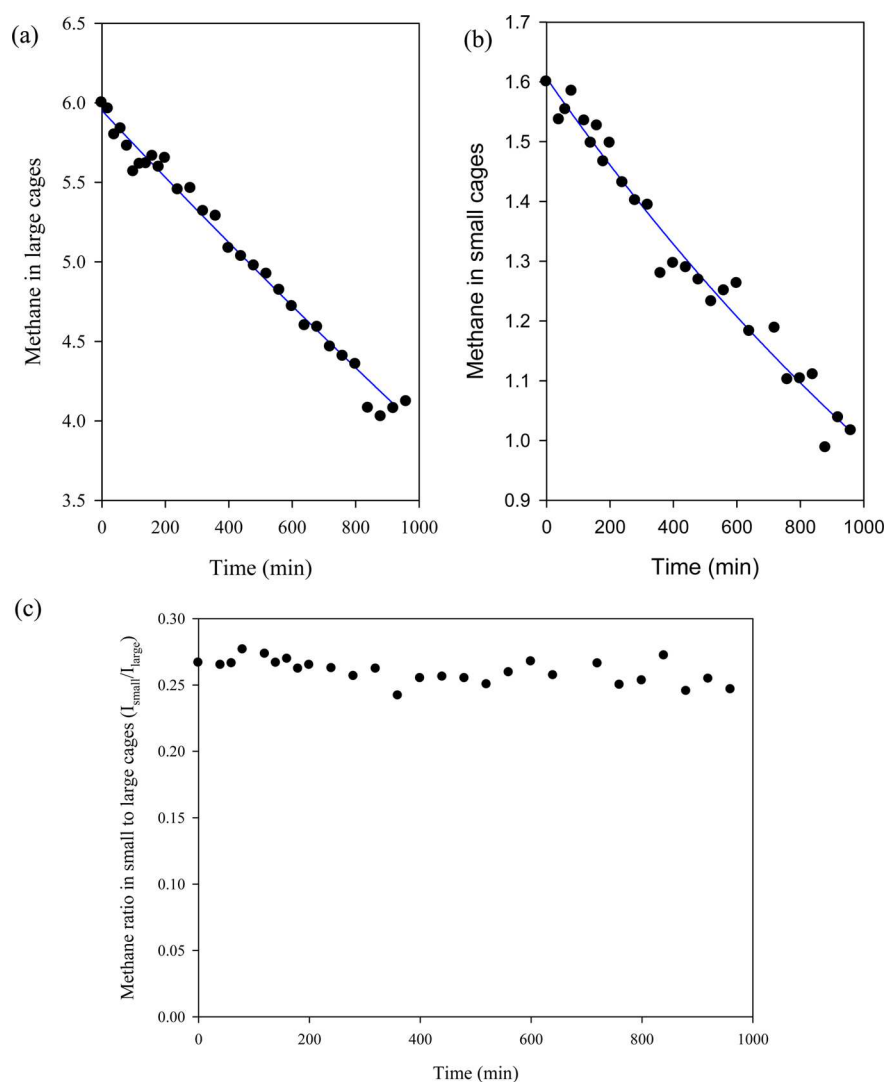


Figure 3. Time dependence of methane in hydrate unit cell, (a) methane in large cages from ^{13}C NMR spectra, (b) methane in small cages, and (c) the ratio of methane in small to large cages from ^{13}C NMR spectra during the replacement process in silica gel pores of nominal size 15 nm at 273 K and 100 bar.

hydrate layer will become an obstacle for continuation of the replacement reaction.

Stationary ^{13}C NMR spectrum of the CO_2 molecules in the hydrate cages (SI Figure S3) reveals an axially anisotropic powder pattern reflecting the anisotropic motion of CO_2 trapped in the large cages of structure I hydrate after 17 h of the replacement. However, it is not possible to confirm unambiguously that CO_2 molecules are also present in the small cages of structure I hydrate, because the chemical shift of CO_2 in the gas phase and the small cages of hydrate is almost identical, and the signal from the CO_2 molecules in the small cages is expected to show no anisotropy. While we confirm the displacement of the methane with the CO_2 molecules in the large cages of structure I hydrate, the ^{13}C NMR spectra cannot provide the exact composition of the hydrate. Therefore, the direct measurement of the composition of gas released from the hydrate phase was carried out. The effect of pore size in silica gel was also investigated using silica gel materials with different pore sizes.

Composition Analysis of Gas and Hydrate Phases.

Even though pure N_2 usually forms structure II hydrate, the CO_2/N_2 gas mixture forms a structure I hydrate.¹ The

molecular sizes of N_2 and CO_2 are significantly different, so the role of the CO_2/N_2 gas molecules during the replacement reaction will be different. The inclusion of CO_2 in hydrate cages after the replacement reaction was confirmed by our ^{13}C NMR results (SI Figure S3), but our NMR results could not reveal the occupancy of N_2 in hydrate cages. In addition, through the microscopic approach, we obtained 42% of CH_4 recovery by using a N_2 and CO_2 gas mixture. Therefore, the question remains as to which of the two molecules replaces CH_4 in the hydrate cages.

In order to investigate the composition of hydrates after the replacement process, a macroscopic approach was used to measure the vapor and hydrate phase compositions. We prepared pore water-containing silica gels having different pore sizes (average pore sizes of 6, 15, and 30 nm) through solid–vapor equilibrium processes in desiccators. Prepared in this fashion, water-containing silica gels were placed in a high pressure cell, and pressurized with CH_4 up to 140 bar. After confirming hydrate formation in silica gel pores, CH_4 hydrates in the different pore-sized silica gels were contacted with a CO_2/N_2 gas mixture at 100 bar for 60 h. After that, the compositions of both vapor and hydrate phases were measured.

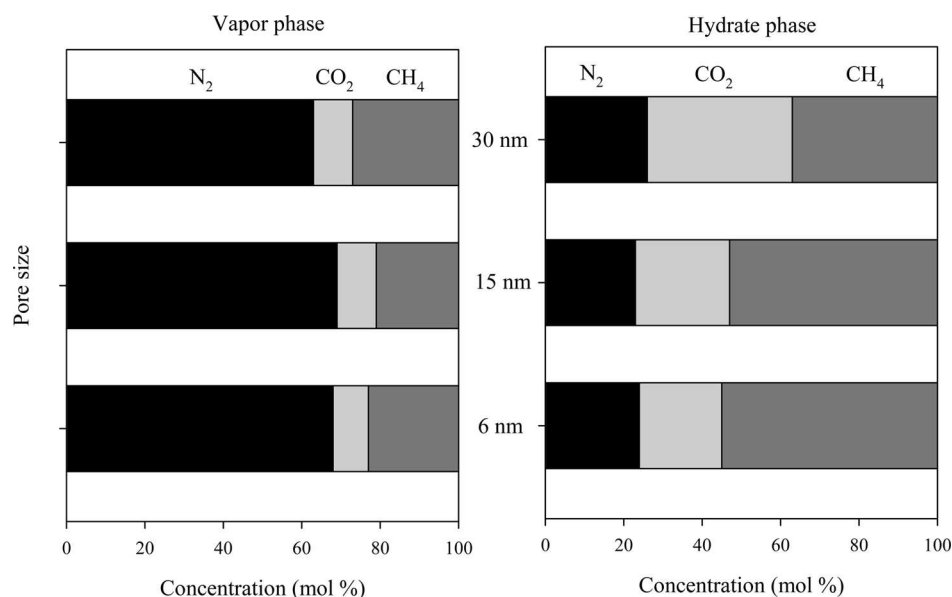


Figure 4. Vapor and hydrate phase composition after 3600 min of replacement reaction with 20 mol % CO₂ and balanced N₂ gas mixture in different pore sizes of silica gel.

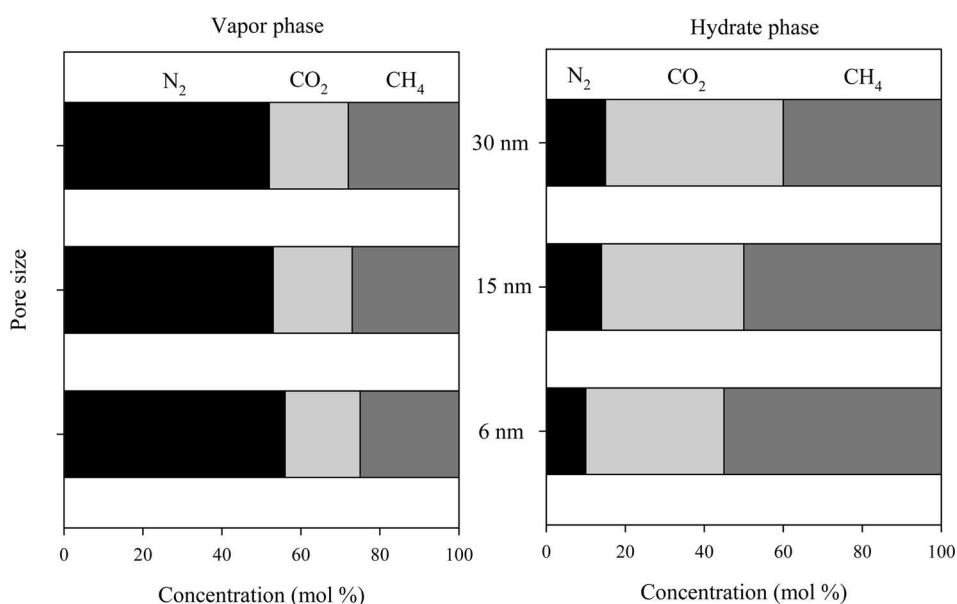


Figure 5. Vapor and hydrate phase composition after 3600 min of replacement reaction with 40 mol % CO₂ and balanced N₂ gas mixture in different pore sizes of silica gel.

The composition of the hydrate phase was obtained by measuring the composition of gas dissociated from the hydrate phase. The vapor and hydrate phase composition after the replacement reaction of CH₄ hydrate with the gas mixture (20 mol % for CO₂ and 80 mol % for N₂) are shown in Figure 4.

Figure 4 shows the composition of the vapor phase contacting the hydrate phase after the replacement reaction for CH₄ hydrate in silica gel having an average 15 nm pore size. The initial composition is 20 mol % of CO₂ and 80 mol % of N₂, but after 60 h of replacement reaction, the CO₂ and N₂ decreased to 10 and 69 mol %, respectively. It is noted that the CH₄ was detected as 21 mol %, which is assumed to have been released entirely from the hydrate phase due to the replacement. The initial mole ratio of N₂ to CO₂ was about 4, but this decreased to about 7. This gives us important

information about the replacement reaction, implying that there is preferential occupancy of CO₂ in the hydrate cavities. CO₂ can easily replace CH₄ in large cavities of sI hydrate due to favorable thermodynamic conditions of CO₂ hydrate and the molecular size of CO₂, and the number ratio of large to small cavities in the sI hydrate is three, and thus; preferential occupancy of CO₂ is reasonable.²² As the average pore size in silica gel changes, there is no significant change of the vapor phase composition. For the silica gel with the average pore size of 6 nm, the vapor phase concentrations of the CO₂ and N₂ after the replacement is complete are 9 and 68 mol %, and for the silica gel with the average pore size of 30 nm are 10 and 63 mol %, as shown in Figure 4 and SI Table S1. All vapor phases after the replacement reaction show similar CH₄ contents from

21 to 27 mol % and N_2/CO_2 ratios of ~ 7 regardless of the average pore size.

Figure 4 also shows the composition of the hydrate in silica gel with the average pore size of 15 nm, as the CH_4 is 53 mol % and the N_2 and CO_2 are 23, 24 mol %, respectively. This implies that both N_2 and CO_2 molecules participate in the replacement reaction, implying that when the N_2 and CO_2 gas mixture contact the CH_4 hydrate, both gas molecules replace CH_4 in hydrate cages. Notably, the amounts of CH_4 retained in the hydrate phases after the replacement reaction has decreased along with the increase in the average pore size from 15 nm (53 mol % CH_4) to 30 nm (37 mol % CH_4), while there was no detectable increase for the silica gels with the average pore sizes of 6 nm (55 mol %) and 15 nm (53 mol %). Considering the similar vapor compositions of three different pore size experiments, these results imply that the difference in the chemical potential between the vapor phase and hydrate surface is a more important factor for the driving force of the replacement reaction than any pore size effect. The in situ 1H NMR spectroscopic results above showed that 81% of free water was converted to a hydrate phase on 40–75 μm sized silica particles with 15 nm pore size. The values of hydrate conversion and the thickness of the formed hydrate solid might be different when the particle and pore sizes vary and thus, the retained CH_4 compositions might also be different from each other when the chemical potential difference between vapor and hydrate surface is reduced enough to approach the steady state. Additional experiments with different injection compositions of N_2 and CO_2 support this explanation (see below) but further study is needed for a more concrete conclusion.

Figure 5 and SI Table S2 show the vapor and hydrate phase composition when CH_4 hydrate is contacted with a 40 mol % CO_2 and N_2 gas mixture for 60 h at 274 K and 100 bar. The increased concentration of CO_2 in the injected gas mixture slightly elevates the amount of the released methane (25–28 mol %), but it is not very significant. However, the ratio of CO_2 to N_2 in the hydrate phase increased to ~ 3 from ~ 1 for the 20 mol % CO_2 and N_2 mixture injection. All three experiments in Figure 5 and SI Table S2 show similar vapor compositions (~ 2.7 N_2/CO_2 ratio and ~ 27 mol % CH_4) to each other. The amounts of retained CH_4 in the hydrate phases show similar trends to the ones for the 20 mol % CO_2 and N_2 mixture in Figure 4 and SI Table S1. These results suggest that the variation in injection gas composition rarely affects the replacement ratio, as this was between 44 and 62% for injection gases of two different CO_2 compositions. As already discussed above, the difference in the chemical potential in the vapor and hydrate phases is the driving force for the replacement reaction, and for the closed system studied it will decrease continuously because of the release of the methane from the hydrate phase into CO_2 and N_2 gas phase. We also note that the partial hydrate composition of the hydrate phase near the surface as well as the inner pore space may be different as the replacement reaction proceeds. Therefore, the replacement reaction slowly reaches a steady state as CH_4 is replaced near the surface. Eventually, the chemical potential of the vapor and hydrate phases will be in a pseudosteady state. Schicks et al. reported that that all of the CH_4 can be replaced by flowing pure CO_2 over CH_4 hydrate, but that the reaction is reversible, implying that the CO_2 hydrate can be converted to CH_4 hydrate with a steady stream of CH_4 . Therefore, in order to maintain the driving force, the vapor phase composition needs to be replenished with fresh

CO_2/N_2 mixture while recovering methane from the vapor phase. More studies are required for a better understanding of the driving force for replacement reaction and to find ways to maintain it over the course of replacement process.

As a preliminary approach to the application of the replacement technique, we have monitored the microscopic and macroscopic behavior of structure I methane hydrate in a course of CH_4 replacement by N_2 and CO_2 mixtures. The results suggest that the replacement reaction will be useful for enhancing the methane hydrate production already developed with the depressurization method. During the production of methane from the hydrate layer using depressurization, i.e., dissociation of the solid hydrate, the hydrate layer will experience endothermic cooling, and the production efficiency likely will decrease. At that moment, there will be free methane gas in the pore structure of the hydrate layer along with free water dissociated and ice from methane hydrate. Injection of a CO_2/N_2 gas mixture into this hydrate layer would produce more methane as free methane gas in the pore structure and methane replaced with CO_2/N_2 will be produced at the surface. Moreover, as the replacement reaction is not accompanied by a large scale melting of the hydrate phase and free water production, the hydrate layer structures remain intact and will be stabilized by the formation of a mixed hydrate layer. An additional benefit during this process is the permanent sequestration of CO_2 in the hydrate layer. Therefore, combining depressurization with the replacement technique will provide many benefits that can be adopted in field practices to produce the methane hydrate deposits.

■ ASSOCIATED CONTENT

● Supporting Information

Figure S1, (a) NMR spectrometer coupled with gas handling system and (b) high pressure cell for spectroscopic experiments. Figure S2, (a) 1H NMR spectra in 15 nm silica gel at 276 K and 140 bar and (b) the integrated intensity of the resonance of free water as a function of time. Figure S3, Full range spectra of ^{13}C NMR spectra after the replacement reaction is finished with 20 mol% of CO_2 and balance N_2 gas mixture at 273 K and 100 bar. Table S1, Composition of vapor and hydrate phases when CH_4 hydrate in silica gel is exposed to 20 mol% of CO_2 and balanced N_2 gas mixture at 273 K and 100 bar. Table S2, Composition of vapor and hydrate phases when CH_4 hydrate in silica gel is exposed to 40 mol% of CO_2 and balanced N_2 gas mixture at 273 K and 100 bar. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +82-42-350-1521; fax: +82-42-350-1510, e-mail: Yutaek.seo@kaist.ac.kr.

Present Address

#Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany

Notes

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