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Experimental Verification of Methane Replacement in Gas Hydrates by Carbon Dioxide

Yongwon Seo*[a], Seungmin Lee[b], Jaehyoung Lee[c]

[a]School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology, Ulsan 689-798, Republic of Korea
[b]Offshore Plant Resources R&D Center, Korea Institute of Industrial Technology, Busan 618-230, Republic of Korea
[c]Petroleum & Marine Resources Division, Korea Institute of Geoscience & Mineral Resources, Daejeon 305-350, Republic of Korea
ywseo@unist.ac.kr

If the conversion of methane hydrate to carbon dioxide hydrate with the net recovery of methane could occur, this would be quite attractive as an innovative method of both methane production and carbon dioxide storage. In this study, the swapping phenomenon occurring in gas hydrates and its potential application to carbon dioxide sequestration was demonstrated through stability condition measurements and ^{13}C NMR spectroscopic analysis. The hydrate phase equilibria for the ternary CH_4 + CO_2 + water mixtures were measured to determine the hydrate stability conditions of the mixed gas hydrates. Through ^{13}C NMR measurements, it was found that carbon dioxide has a preference for the large cages in the sI hydrate and carbon dioxide is a relatively poorer guest when carbon dioxide competes with methane in occupying the small cages of the sI hydrate. From the NMR spectra and direct dissociation, it was confirmed that about 70% of methane is recoverable after reaction with carbon dioxide.

1. Introduction

Gas hydrates are solid inclusion compounds in which guest molecules of suitable size and shape are incorporated into hydrogen-bonded water frameworks. These compounds exist in three distinct crystal structures, sI, sII and sH, which consist of various cages with different sizes and shapes (Sloan and Koh, 2008). Gas hydrates are of particular interest in the gas and oil industry as well as in relation to greenhouse gas sequestration (Sloan and Koh, 2008). Naturally occurring gas hydrates, which contain mostly methane (CH_4) and are found in the permafrost regions and deep ocean sediments, have great potential as future energy resources due to their huge quantities and wide geographical distribution(Sloan and Koh, 2008). Furthermore, carbon dioxide (CO_2) produced from fossil fuel-fired power plants can be sequestered as solid gas hydrates in the deep ocean (Tajima et al., 2004). Recent investigations suggest the possibility of exchanging CH_4 with CO_2 in natural gas hydrates, which has the advantage of both CO_2 sequestration and CH_4 recovery (Hirohama et al., 1996; Lee et al., 2003; Park et al., 2006). Molecular dynamic simulations revealed that the substitution of CH_4 with CO_2 in sI hydrate cages has a negative free energy (Dorman, 2007). This indicates that CO_2 spontaneously replaces CH_4 from sI hydrates, causing the release of CH_4. With the replacement of CH_4 with CO_2, the naturally occurring gas hydrates can function as both CH_4 sources and CO_2 storage sites.
Several studies on the CH_4-CO_2 swapping process, covering both spectroscopic and kinetic approaches, have recently been reported and have demonstrated notable success (Lee et al., 2003; Park et al., 2006). However, little attention has been paid to the complex phase behavior of the mixed CH_4-CO_2 gas hydrates and its direct relation to guest distribution in CH_4-CO_2 swapping. A complete understanding of the complex phase behavior and guest distribution is essential for revealing the CH_4-CO_2 replacement mechanism. The phase behavior can offer stability conditions of the mixed gas hydrates and thus is very important in determining the pressure and temperature conditions of CO_2 being injected into the CH_4 hydrate layer. In addition, the guest distribution is closely related to the extent of CO_2 replacement in the CH_4 hydrate.

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Therefore, in this study, the complex phase behavior of mixed CH_4-CO_2 gas hydrates was intimately connected to ^{13}C NMR spectroscopic results in order to explore the guest distribution and the extent of CO_2 replacement and, furthermore, to reveal the CH_4-CO_2 swapping mechanism. For this purpose, the three-phase equilibria (hydrate (H) – liquid water (L_W) – vapor (V)) for ternary CH_4 + CO_2 + water mixtures were measured at CO_2 compositions of 20 and 60 % in order to meet changeable stability conditions in the CH_4-CO_2 swapping process. Based on the three-phase equilibrium conditions, the pressure-composition diagram at a specified temperature was obtained in order to estimate the guest composition in the hydrate phase after swapping. Solid-state NMR spectroscopy was used to examine the distribution of CH_4 over the two cage sites of the mixed CH_4 + CO_2 hydrates. From the pressure-composition diagram linked to the distribution of CH_4 in the hydrate cages, the CO_2 concentration in the hydrate phase after replacement could be accurately predicted and was compared with the actual value measured by gas chromatography.

2. Experimental

The gas mixtures of CH_4 + CO_2 (20 and 60 %) were supplied by PSG Gas Co. (Republic of Korea). Double distilled deionized water was used. The experimental apparatus for the hydrate phase equilibria was specially designed to measure the hydrate dissociation pressures and temperatures accurately. The equilibrium cell was made of 316 stainless steel and had an internal volume of about 250 cm^3. The cell content was vigorously agitated by an impeller-type stirrer. The experiment for hydrate-phase equilibrium measurements began by charging the equilibrium cell with about 80 cm^3 of ultra high purity water. After the equilibrium cell was pressurized to the desired pressure with gas mixtures of CH_4 + CO_2, the main system was slowly cooled to a temperature lower than the expected equilibrium value. Due to thermal contraction, the cell pressure was slightly decreased by decreasing the temperature at a cooling rate of 1 K /h. An abrupt pressure depression was subsequently observed at the stage of hydrate crystal growth after nucleation. When the pressure depression due to hydrate formation reached a steady-state condition, the temperature was increased in 0.1 K increments with sufficient time of 90 min, and accordingly, the cell pressure increased with gas hydrate dissociation. After all the hydrates were dissociated with increasing temperature, the cell pressure again increased slightly due to thermal expansion. The three-phase (H – L_W – V) equilibrium points at each vapor composition were determined as the intersection between the hydrate dissociation and thermal expansion lines.

To measure the compositions of the vapor and hydrate phases, a sampling valve (Rheodyne, Model 7010, USA) with a loop volume of 20 μl was installed and connected to a gas chromatograph (Agilent 7890, USA) through a high-pressure metering pump (Eldex, USA). A thermal conductivity detector (TCD) and a Porapak Q column (Supelco, USA) were used as the detector and the column, respectively. For each experimental run, after nucleation, the equilibrium cell with an excess of water and vigorous agitation was left for 24 h to reach a state of equilibrium at a specified temperature. The vapor phase composition was then analyzed by gas chromatography, after the vapor phase was circulated through a sampling line with a high-pressure metering pump to equilibrate both compositions of the cell and loop for more than 10 min. The corresponding composition of the hydrate phase was also measured by gas chromatography after the vapor phase was evacuated under cooling of the cell in a liquid nitrogen vessel, and the entire hydrate phase was then dissociated at 298.15 K.

A Bruker 400 MHz solid-state NMR spectrometer was used to identify the hydrate structure and guest distributions in the mixed CH_4 + CO_2 hydrates. The NMR spectra were recorded at 243 K and atmospheric pressure by placing the clathrate hydrate samples in a 4 mm o.d. Zr rotor that was loaded into a variable-temperature (VT) probe. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with magic angle spinning (MAS) between 2 and 4 kHz. A pulse length of 2 μs and pulse repetition delay of 10 s under proton decoupling were employed when a radio frequency field strength of 50 kHz corresponding to 5 μs 90^o pulses was used. The downfield carbon resonance peak of adamantane, which was assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference. More detailed description of the experimental methods can be found in previous papers (Cha et al., 2010; Lee et al., 2012).

3. Results and Discussion

The three-phase H – L_W – V equilibria for ternary CH_4 + CO_2 + water mixtures with two different CO_2 concentrations of 20 and 60 % were experimentally measured in order to understand the complex phase behavior of the mixed gas hydrates and to meet changeable stability conditions of the CH_4-CO_2 swapping process. The equilibrium measurements for the mixed gas hydrates were undertaken over wide

temperature and pressure ranges, depending on the vapor phase CO_2 concentrations and the results are presented in Figure 1. The H – L_W – V lines of the ternary CH_4 + CO_2 + water mixtures exist between those of the binary CH_4 + water and CO_2 + water mixtures. Both CH_4 and CO_2 are known to form sI hydrates and to occupy both small and large cages of the hydrate structure (Sloan and Koh, 2008). However, due to the relatively larger molecular size of CO_2, CO_2 hydrate is thermodynamically more stable than CH_4 hydrate, and accordingly, the H – L_W – V lines of the CH_4 + CO_2 + water mixtures generally appear nearer to that of the binary CO_2 + water mixture than that of the binary CH_4 + water mixture.

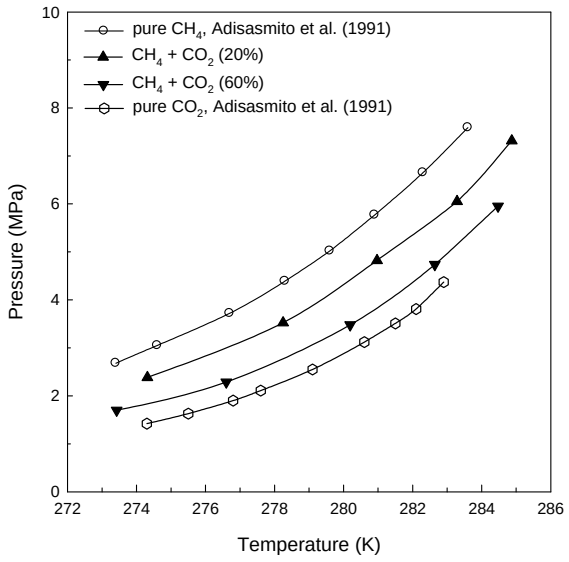

Figure 1. Gas hydrate phase equilibria of the CH_4 + CO_2 + water mixtures

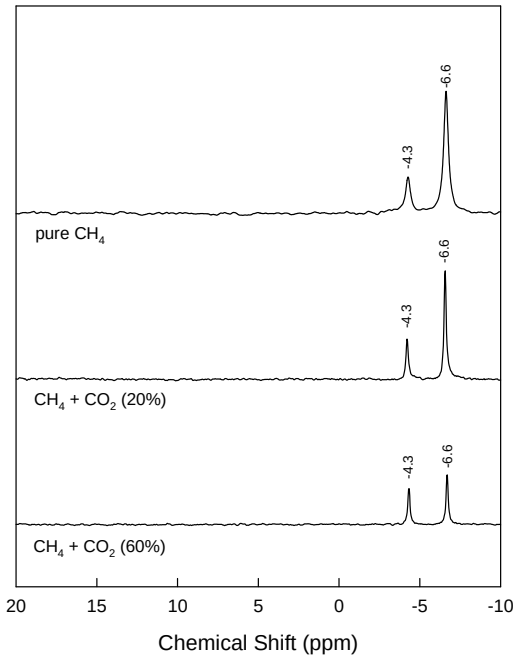

Figure 2.^{13}C MAS NMR spectra of sI hydrates prepared using CH_4 + CO_2 gas mixtures

The pure CH_4 hydrate and mixed CH_4 + CO_2 hydrates were analyzed via ^{13}C MAS NMR in order to investigate guest distributions and preferential occupation of each guest in the hydrate cages. The cage dependent ^{13}C MAS NMR chemical shift for captured CH_4 molecules can be effectively used to determine

the structure types of the mixed gas hydrate formed and to examine the distribution of CH_4 over the two different cage sites (Ripmeester and Ratcliffe, 1999). Figure 2 shows a stacked plot of the ^{13}C MAS NMR spectra of the pure CH_4 hydrate and CH_4 + CO_2 hydrates with two different CO_2 compositions (20 and 60%). The spectrum of the pure CH_4 hydrate, known to form sI hydrate, has two signals at -4.3 and -6.6 ppm. The peak at -4.3 ppm can be assigned to CH_4 molecules captured in the small 5^{12} cages and the peak at -6.6 ppm to CH_4 molecules in the large $5^{12}6^4$ cages, considering the ideal stoichiometric ratio (1 : 3) of the small 5^{12} to the large $5^{12}6^4$ cages in the unit cell of the sI. With increasing CO_2 concentration in the gas mixture, the peak area at -6.6 ppm relatively declines. The decrease in the peak area ratio with increasing CO_2 is attributed to the preferential occupation of CO_2 in the large $5^{12}6^4$ cages due to the difference in the molecular size of CH_4 and CO_2. The molecular diameter of CO_2 is larger than that of CH_4 and is almost identical to the cavity diameter of the 5^{12} cages in the sI hydrate (Sloan and Koh, 2008). Therefore, when CO_2 competes with CH_4 for occupying the small 5^{12} cages, CO_2 is a relatively poorer guest for the 5^{12} cages even though CO_2 can also occupy both small and large cages of the sI hydrate. The lower fractional occupancy of CO_2 in the small 5^{12} cages results in a higher hydration number ($CO_2 \cdot 6.3H_2O$) when compared with the hydration number of CH_4 hydrates ($CH_4 \cdot 6.0H_2O$) (Sloan and Koh, 2008).

Figure 3 presents the ^{13}C MAS NMR spectra of the pure CH_4 hydrate (before replacement) and the mixed CH_4 + CO_2 hydrate (after replacement). In the ^{13}C MAS NMR spectra presented in Figure 3, the peak areas at -4.3 and -6.6 ppm are quantitatively proportional to the amount of CH_4 molecules captured in the small 5^{12} and the large $5^{12}6^4$ cages, respectively. The area ratio of CH_4 molecules in large and small cages (A_L/A_S) for the pure CH_4 hydrate is 3.27, which indicates the hydrate composition of $CH_4 \cdot 6.03H_2O$. Meanwhile, the A_L/A_S for the mixed gas hydrate after CO_2 replacement is 1.44, which is clearly caused by predominant occupation of CO_2 in the large $5^{12}6^4$ cages.

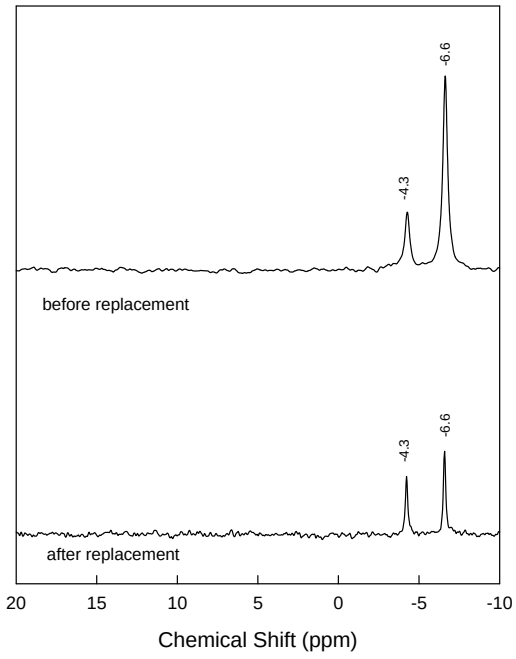

Figure 3. ^{13}C MAS NMR spectra of a sI hydrate before and after CO_2 replacement

From Figure 2, it can be found that the A_L/A_S value of 1.44, which results from CO_2 replacement, corresponds to a feed CO_2 concentration of 60 %. If this value of the feed CO_2 concentration is applied to the pressure-composition diagram shown in Figure 4, the corresponding CO_2 composition in the hydrate phase can be predicted. In Figure 4, the equilibrium CO_2 compositions of the hydrate and vapor phases, which were experimentally measured at 276.15 K, are depicted with calculation results. Compositions and cage occupancies of each component at equilibrium were calculated in the process of predicting equilibrium pressure at a specified temperature.

The equilibrium criteria of the hydrate-forming mixture are based on the equality of fugacities of the specified component *i* in all phases that coexist simultaneously

$$\hat{f}_i^H = \hat{f}_i^L = \hat{f}_i^V (= f_w^I) \quad (1)$$

where *H* denotes for the hydrate phase, *L* for the water-rich liquid phase, *V* for the vapor phase, and *I* for the ice phase.

In the model given here, for hydrate equilibrium calculations, the fugacities are calculated by SRK-EOS (Soave-Redlich-Kwong equation of state) incorporated with the modified Huron-Vidal second order mixing rule for fluid phases, and by statistical thermodynamics for the hydrate phase at the same pressure. The optimized Kihara potential parameters used in this study and more details of the model description were given in previous papers (Seo et al., 2002).

In the case of a feed CO_2 concentration of 60%, the corresponding CO_2 composition in the hydrate phase is 67% at 2.2 MPa as can be predicted from Figure 4. Here, 67% CO_2 in the hydrate phase means that 67% recovery of CH_4 can be achieved with CO_2 injection into the CH_4 hydrates. Assembling the results presented here, the A_L/A_S ratio of 1.44 after CO_2 replacement derived from Figure 3 implies that approximately 67% of CH_4 in the hydrate was replaced by CO_2. This is consistent with a previous result that at least 64% of CH_4 should be recoverable by replacement of CO_2 (Lee et al., 2003). In addition, the result is also almost identical to the CO_2 composition of 68 ± 2% which was measured directly by dissociation of the replaced hydrate sample. Based on both hydrate phase compositions and cage occupancy of each guest calculated from the combination of ^{13}C NMR spectra, pressure-composition relation, and phase equilibrium modeling, the chemical formula for the mixed gas hydrate after CO_2 replacement was found to be $5.03CO_2 \cdot 2.51CH_4 \cdot 46H_2O$.

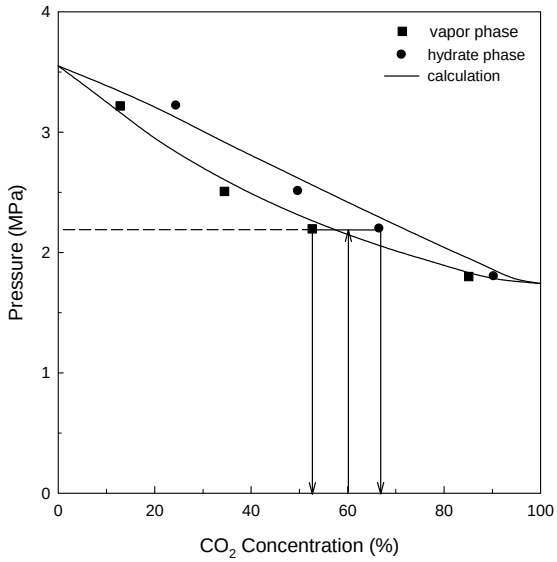

Figure 4. Pressure-composition diagram for the CH_4 + CO_2 + water mixtures at 276.15 K

4. Conclusions

In this study, the replacement of CH_4 by CO_2 in naturally occurring gas hydrates was investigated as an innovative and efficient method of both sequestering a global warming gas and harvesting a future energy source. The experimental results presented here indicate that at least, in a laboratory setting, the replacement of CH_4 by CO_2 is favored and thus, CO_2 is possibly sequestered into the CH_4 hydrate layer. In particular, through thermodynamic equilibrium studies linked to the spectroscopic approach on replacement of CH_4 by CO_2, the CO_2 composition in the hydrate phase and the chemical formula of the mixed gas hydrate after replacement can be easily estimated if the information about the area ratio of the ^{13}C MAS NMR resonance lines of CH_4 molecules in large and small cages is provided. However, for actual CO_2 replacement in natural gas hydrate deposits, a variety of factors such as reaction kinetics, sediment environment, mass transfer, and hydrate particle size should be further considered.

References

Adisasmito, S.; Frank, R. J.; Sloan, E. D. 1991, Hydrates of carbon dioxide and methane mixtures. J. Chem. Eng. Data, 36, 68-71.

Cha, I.; Lee, S.; Lee, J. D.; Lee, G.-W.; Seo, Y. 2010, Separation of SF_6 from gas mixtures using gas hydrate formation. Environ. Sci. Technol., 44, 6117-6122.

Dornan, P.; Alavi, S.; Woo, T. K. 2007, Free energies of carbon dioxide sequestration and methane recovery in clathrate hydrates. J. Chem. Phys., 127, 124510.

Hirohaman, S.; Shimoyama, Y.; Wakabayashi, A.; Tatsuya, S.; Nishida, N. 1996, Conversion of CH_4-hydrate to CO_2-hydrate in liquid CO_2. J. Chem. Eng. Jpn., 29, 1014-1020.

Lee, H.; Seo, Y.; Seo, Y.-T.; Moudrakovski, I.; Ripmeester, J. A. 2003, Recovering methane from solid methane hydrate with carbon dioxide. Angew. Chem. Int. Ed., 42, 5048-5051.

Lee, S.; Lee, Y.; Park, S.; Kim, Y.; Lee, J. D.; Seo, Y. 2012, Thermodynamic and spectroscopic identification of guest gas enclathration in the double tetra-n-butylammonium fluoride semiclathrates. J. Phys. Chem. B, 116, 9075-9081.

Park, Y.; Kim, D.-Y.; Lee, J.-W.; Huh, D.-G.; Park, K.-P.; Lee, J.; Lee, H. 2006, Sequestering carbon dioxide into complex structures of naturally occurring gas hydrates. Proc. Natl. Acad. Sci. USA, 103, 12690-12694.

Ripmeester, J.A.; Ratcliffe, C.I. 1999, On the contributions of NMR spectroscopy to clathrate science. J. Struct. Chem., 40, 654-662.

Seo, Y.; Lee, H.; Uchida, T. 2002, Methane and carbon dioxide hydrate phase behavior in small porous silica gels: three-phase equilibrium determination and thermodynamic modeling. Langmuir, 18, 9164-9170.

Sloan, E. D.; Koh, C. A. 2008, Clathrate Hydrates of Natural Gases, 3rd Ed.; CRC Press: Boca Raton, U.S.A.

Tajima, H.; Yamasaki, A.; Kiyono, F. 2004, Continuous formation of CO_2 hydrate via a kenics-type static mixer. Energy Fuels, 18, 1451-1456.