Thermodynamic Stability of Structure II Methyl Vinyl Ketone Binary Clathrate Hydrates and Effects of Secondary Guest Molecules on Large Guest Conformation

Yun-Ho Ahn,† Hyery Kang,† Minjun Cha,‡ Kyuchul Shin,*§ and Huen Lee*†‡

1Department of Chemical and Biomolecular Engineering (BK21+ Program), KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea
2Department of Energy and Resources Engineering, Kangwon National University, 1 Kangwondaehak-gil, Chuncheon-si, Gangwon-do 24341, Republic of Korea
3Major in Applied Chemistry, School of Applied Chemical Engineering, Kyungpook National University, 80 Daehak-ro, Buk-gu, Daegu 41566, Republic of Korea

ABSTRACT: Clathrate hydrates have received massive attention because of their potential application as energy storage materials. Host water frameworks of clathrate hydrates provide empty cavities that can capture not only small molecular guests but also radical species induced by γ-irradiation. In this work, we investigated structure II methyl vinyl ketene (MVK) binary clathrate hydrates with CH₄, O₂, and N₂, and the effects of secondary guest species on MVK conformation in the cavity of hydrate and on the thermodynamic stability of unirradiated and γ-irradiated hydrate phases. The present findings provide meaningful information to understand the nature of guest–host interactions in γ-irradiated clathrate hydrates and to open up practical applications for hydrate-based nanoreactors.

1. INTRODUCTION

Clathrate hydrates are nonstoichiometric crystalline compounds that are stabilized by host–guest molecular interactions. Numerous guest molecules that vary in type and size have been reported to be enclathrated in the host frameworks of water cages.1 Because of their capability to accommodate gas molecules, clathrate hydrates have been considered to be the media for gas storage and separation. Hydrate pelletizing for natural gas transportation and hydrate-based carbon dioxide separation from precombustion gases are examples of utilizing clathrate hydrates as gas storage media.2,3 For these utilizations, the thermodynamic stability of clathrate hydrates is one of the most important factors. In particular, the pressure and temperature conditions for stable storage of gases are the key issues to evaluate the potential of gas storage materials.

There are three widely known structures of clathrate hydrates, structure I (sI, cubic Pm3m), structure II (sII, cubic Fd3m), and structure H (sH, hexagonal P63/mmc), usually depending on the molecular sizes and geometries of guest molecules.1 Small gaseous molecules below 4.2 Å such as O₂, N₂, or H₂ form sI clathrate hydrates solely under considerably high-pressure conditions, and slightly larger molecules such as CH₄ or CO₂ form sII clathrate hydrates solely under low-pressure conditions. Adding organic molecules such as tetrahydrofuran (THF) or tert-butylamine to a water solvent can dramatically reduce the formation pressures of binary sII clathrate hydrates of organic guests and small gases, even though partial occupation of cages by the organic guests leads to a decrease in the storage capacity.1–6

In a recent study, it has been reported that γ-irradiation to sII methyl vinyl ketene (MVK) + CH₄ hydrate induces an intracavity conformational change in MVK guest molecules and increases the dissociation temperature of the hydrate phase. Although the exact mechanism for delaying the dissociation has not been revealed, enhancement of the thermodynamic stability of clathrate hydrates by γ-irradiation might provide important information for the application of hydrates to storage materials.7 Some studies on irradiation of clathrate hydrates have been reported. Bednarek et al. published two studies on the appearance and disappearance of trapped electrons in X-irradiated tetramethylammonium hydroxide (Me₄NOH) clathrate hydrates,8,9 and Lee and co-workers reported the existence of superoxide ions and ionic host–guest interactions in a γ-irradiated Me₄NOH + O₂ clathrate hydrate.10–12

Some studies have focused on atomic hydrogen generation in irradiated clathrate hydrates. Yeon et al. reported that γ-irradiation of THF + H₂ hydrate creates hydrogen atomic radicals from the enclathrated hydrogen molecules.13 Shin et al.
demonstrated that hydrogen atomic radicals can be generated from a water framework when the ionic clathrate hydrate containing N\textsubscript{2} guest molecule is \gamma-irradiated.\textsuperscript{14} Koh et al. suggested two additional hydrogen radical generation pathways from the anions of the host lattice and ionic guest molecules in a \gamma-irradiated semicladtrate hydrate system.\textsuperscript{15}

Studies on the \gamma-irradiation of canonical clathrate hydrates such as methane, ethane, ethylene, or tert-butylamine hydrates were performed by Ohgaki and co-workers.\textsuperscript{16–19} They also reported a hydrogen picking phenomenon between guest molecules in adjacent cages in \gamma-irradiated propane hydrate, methane + propane mixed hydrate, and isobutane hydrate.\textsuperscript{20–22} The hydrogen picking is a kind of chain reaction: induced \textit{\alpha}-propyl or isobutyl radical attacks \textit{\alpha}-hydrogen of propane or isobutane molecule in neighboring cages, and other radical species are produced. When \beta-hydrogen is attacked, isopropyl or tert-butyl radicals are produced, and then, the chain reaction is terminated because they have thermally stable stereostructures. As the temperature increases, the population of thermally favored radical species (isopropyl radical in the propane hydrate and tert-butyl radical in the isobutane hydrate) increases. The structural changes in propyl or butyl radicals induced by the intermolecular hydrogen-picking phenomenon resemble the intracavity conformational change in MVK molecules occurring in the \gamma-irradiated MVK + CH\textsubscript{4} clathrate hydrate; however, there has been no additional investigation on the thermodynamic stability of \gamma-irradiated clathrate hydrates showing intercavity proton transfer after the irradiation.

In this study, we investigated the thermodynamic stabilities of binary MVK clathrate hydrates before and after \gamma-irradiation. The crystal structures of binary MVK + O\textsubscript{2} and MVK + N\textsubscript{2} hydrates were identified using a synchrotron high-resolution powder diffracation (HRPD) pattern analysis. The liquid water (L\textsubscript{W})–hydrate (H)–vapor (V) phase equilibrium curves of three binary MVK clathrate hydrates with CH\textsubscript{4}, O\textsubscript{2}, and N\textsubscript{2} were obtained. To measure the dissociation temperature at which the secondary gaseous guests are released, Raman spectra of the binary MVK hydrates before and after \gamma-irradiation were also obtained at various temperatures. The secondary guest dependence of the intracavity conformational change phenomenon occurring in the \gamma-irradiated MVK clathrate hydrates was also investigated using Raman spectroscopy.

2. RESULTS AND DISCUSSION

2.1. Structure Identifications of MVK + Gaseous Guest Hydrates. In our previous study, the crystal structure of MVK + CH\textsubscript{4} clathrate hydrate was identified as cubic Fd\textit{\textdagger}m (lattice parameter \textit{a} = 17.1959(3) Å at 80 K), usually called s\textsubscript{II} hydrate, through a HRPD pattern analysis. Although the calculated molecular size of \textit{s-cis} MVK (8.36 Å) is slightly larger than a suitable size (below 7.5 Å) to fit into s\textsubscript{II} large cavity, which is suggested in the literature,\textsuperscript{4} the incorporation of the MVK molecule is allowed by the flexibility of the hydrogen bonded water framework. The lattice parameter of MVK + CH\textsubscript{4} hydrate in this work is significantly larger than the values \textit{a} = 17.138 Å (at 77 K) for CH\textsubscript{4} + C\textsubscript{3}H\textsubscript{8} hydrate (molecular size of C\textsubscript{3}H\textsubscript{8}: 6.28 Å)\textsuperscript{23} and \textit{a} = 17.107 Å (at 90 K) for CH\textsubscript{4} + C\textsubscript{2}H\textsubscript{6} hydrate (molecular size of C\textsubscript{2}H\textsubscript{6}: 5.5 Å)\textsuperscript{24} but slightly smaller than the value \textit{a} = 17.240 Å (at 77 K) for CH\textsubscript{4} + tetrahydropyran hydrate (molecular size of tetrahydropyran: 6.95 Å).\textsuperscript{25} Smaller lattice parameter of MVK hydrate than that expected from its molecular size could be due to the hydrogen bonding ability of the MVK molecule, which allows shorter distances between host H\textsubscript{2}O and MVK guests.

To additionally identify the structures of binary MVK + O\textsubscript{2} and N\textsubscript{2} hydrates, HRPD patterns of both hydrates were obtained and analyzed. As shown in Figure 1, most reflections in both patterns for MVK + O\textsubscript{2} and MVK + N\textsubscript{2} hydrates are well-matched to a cubic Fd\textit{\textdagger}m structure (green ticks of both patterns), and a small fraction of hexagonal ice (P\textit{\textdagger}6\textsubscript{3}/mmc; blue ticks) exists. The lattice parameters are \textit{a} = 17.1931(5) Å for MVK + O\textsubscript{2} and \textit{a} = 17.2312(0) Å for MVK + N\textsubscript{2} hydrates. Therefore, it is concluded that the MVK molecule is a s\textsubscript{II} hydrate former with small gaseous molecules as help guests.

2.2. Phase Equilibria of MVK + Gaseous Guest Hydrates. After the crystal structures of the binary MVK clathrate hydrates were identified, the phase equilibria of MVK + CH\textsubscript{4}, O\textsubscript{2}, and N\textsubscript{2} clathrate hydrates were measured at the temperature ranges of 280–292, 273–281, and 271–279 K and in the pressure ranges of 5–21, 7–20, and 7–20 MPa, respectively, with various MVK concentrations (3.0, 5.6, and 8.0 mol %). The phase boundary curves are presented in Figure 2 for MVK + CH\textsubscript{4} hydrates, in Figure 3 for MVK + O\textsubscript{2} hydrates, and in Figure 4 for MVK + N\textsubscript{2} hydrates, and each figure contains the phase boundary curve for pure CH\textsubscript{4}O\textsubscript{2}, or N\textsubscript{2} hydrates from the literature for comparison.\textsuperscript{25–27} The detailed experimental data are shown in Tables 1–3.

For the MVK + CH\textsubscript{4} clathrate hydrates, their phase equilibrium curves are shifted to relatively less stable regions (i.e., lower temperatures at any pressure and higher pressures at any temperature) than that of the pure CH\textsubscript{4} hydrates.\textsuperscript{26} More concentrated systems have relatively unstable pressure–temperature phase equilibrium conditions. The MVK seems to act as a thermodynamic inhibitor in the MVK + CH\textsubscript{4} clathrate hydrate system. On the other hand, for the binary MVK + O\textsubscript{2} or MVK + N\textsubscript{2} hydrate systems, their phase equilibrium curves are shifted to more stable regions than those of the pure O\textsubscript{2} or N\textsubscript{2} hydrates (Figures 3 and 4).\textsuperscript{25–27} The stoichiometric concentration for large cages (5\textsuperscript{\textdagger}6\textsuperscript{\textdagger}6\textsuperscript{\textdagger}6\textsuperscript{\textdagger}6) of s\textsubscript{II} clathrate hydrate, 5.6 mol % MVK, represents the most stable phase boundary condition for both the O\textsubscript{2} and N\textsubscript{2} cases. At this
stage, we should consider that the crystal structures of pure O$_2$ and N$_2$ hydrates are cubic Fd$ar{3}$m (i.e., sII hydrates), whereas those of pure CH$_4$ hydrate are cubic Pm$ar{3}$m (i.e., sI hydrate).\(^1\) All three binary MVK clathrate hydrates of CH$_4$, O$_2$, or N$_2$ are sII hydrates, as described above. Therefore, it is concluded that the MVK, a sII hydrate former, acts as a thermodynamic promoter of sII hydrates. For the methane case, the hydrogen bonding ability of an MVK molecule can make MVK act as a thermodynamic inhibitor similar to many antifreezes. Outside of the clathrate hydrate phase, MVK destabilizes pure sI methane hydrate, and thus, the phase equilibrium curve of MVK + CH$_4$ hydrate might exist at a more stable region than that of sI methane hydrate, which is being inhibited by MVK in solution.

2.3. Large Guest Conformation in MVK + Gaseous Guest Hydrates. In nature, there are two conformers of s-cis and s-trans MVKs (molecular sizes: 8.36 Å for s-cis and 7.53 Å for s-trans forms), and their existence ratio depends on the temperature.\(^26–28\) In our previous report, it was confirmed that the s-cis form of MVK is the preferred molecular geometry in the S$^6$ cage of MVK + CH$_4$ sI hydrate in spite of its larger size and that an intracavity conformational change from the s-cis to s-trans form of MVK can be induced by $\gamma$-irradiation using an annealing process.\(^7\) The relative energy difference between the two conformers is 0.6 kJ/mol obtained by DFT calculation using the B3LYP model and 6-311++G(d,p) basis set, and the torsional energy barrier from s-cis to s-trans is 6.56 kJ/mol.\(^29\) Lee et al. suggested that only one favorable conformation for the enclathrated guest exists when the energy

---

**Figure 2.** Phase equilibrium curve of the pure CH$_4$ and MVK (3.0, 5.6, 8.0 mol %) + CH$_4$ hydrates. Data points for CH$_4$ + water are adapted with permission from the original publishers (ref 26, copyright 1997, Elsevier).

**Figure 3.** Phase equilibrium curve of the pure O$_2$ and MVK (3.0, 5.6, 8.0 mol %) + O$_2$ hydrates. Data points for O$_2$ + water are adapted with permission from the original publishers (ref 27, copyright 2003, American Chemical Society).

**Figure 4.** Phase equilibrium curve of the pure N$_2$ and MVK (3.0, 5.6, 8.0 mol %) + N$_2$ hydrates. Data points for N$_2$ + water are adapted with permission from the original publishers (ref 26, copyright 1997, Elsevier).

**Table 1.** Experimental Equilibrium (H$_L$−L$_W$−L$_{MVK}$−V) Data of MVK + CH$_4$ at Various Concentrations (Pressure Accuracy: ±0.02% and Temperature Accuracy: ±0.05%)

| CH$_4$ + MVK | MVK (8.0 mol %) | MVK (5.6 mol %) | MVK (3.0 mol %) |
|--------------|----------------|----------------|----------------|
| T (K) | P (MPa) | T (K) | P (MPa) | T (K) | P (MPa) |
| 281.3 | 5.94 | 280.9 | 5.51 | 280.7 | 5.47 |
| 283.5 | 7.98 | 283.6 | 7.92 | 283.3 | 7.55 |
| 285.3 | 10.32 | 285.8 | 10.74 | 284.9 | 9.49 |
| 286.7 | 12.90 | 287.1 | 13.16 | 286.7 | 12.01 |
| 288.0 | 15.34 | 288.3 | 15.89 | 288.3 | 14.95 |
| 289.1 | 18.14 | 289.6 | 18.89 | 289.4 | 17.91 |
| 289.8 | 20.72 | | | 290.8 | 21.16 |

**Table 2.** Experimental Equilibrium (H$_L$−L$_W$−L$_{MVK}$−V) Data of MVK + O$_2$ at Various Concentrations (Pressure Accuracy: ±0.02% and Temperature Accuracy: ±0.05%)

| O$_2$ + MVK | MVK (8.0 mol %) | MVK (5.6 mol %) | MVK (3.0 mol %) |
|--------------|----------------|----------------|----------------|
| T (K) | P (MPa) | T (K) | P (MPa) | T (K) | P (MPa) |
| 273.7 | 7.78 | 273.8 | 7.80 | 273.1 | 7.65 |
| 275.5 | 9.89 | 275.5 | 9.85 | 274.8 | 9.68 |
| 276.9 | 12.11 | 276.9 | 11.88 | 276.7 | 12.13 |
| 278.0 | 13.99 | 278.1 | 14.06 | 277.8 | 13.82 |
| 279.0 | 16.08 | 279.1 | 16.02 | 279.2 | 16.54 |
| 279.9 | 18.00 | 278.0 | 18.02 | 279.9 | 18.32 |
| 280.5 | 19.88 | 280.9 | 20.31 | 280.4 | 19.97 |

**DOI:** 10.1021/acsomega.7b00264

ACS Omega 2017, 2, 1601–1607
The difference between the two conformers is approximately 10 kJ/mol; therefore, the relative energy difference and the torsional energy barrier can be overcome by the thermal annealing process in the presence of electron transferring.

To check the conformation of enclathrated MVK molecules in unirradiated and γ-irradiated MVK + O2 or N2 clathrate hydrates, we obtained the Raman spectra of those samples at various temperatures (Figures 5 and 6). As we used a 5.0 mol % solution of MVK, which is slightly less concentrated than the stoichiometric concentration for sII hydrate (5.6 mol %), it was assumed that most MVK molecules were included in the clathrate phases for all samples. Enclathration of O2 or N2 in sII hydrates can be confirmed from the symmetric stretching modes observed at frequencies of 1546 cm$^{-1}$ (for O2) and 2322 cm$^{-1}$ (for N2) (Figures 5a and 6a). Although a portion of 51264 cavities could be occupied by the O2 or N2 guest in the MVK concentrations of this work, the vibration frequency of O2 or N2 in the 51264 cavity is not distinguishable from that in the 512 cavity in Raman spectroscopy. For the MVK enclathration, two peaks at 1626 cm$^{-1}$ (for C=O stretching mode) and 1692 cm$^{-1}$ (for C=O stretching mode), which implies the s-cis form in the 51264 cavity, were observed at 93–153 K (Figures 5a and 6a). As in the case of acetone, the hydrogen bonding between C=O functional group of the enclathrated MVK molecule and host water framework might exist, but it is difficult to observe any certain lines of evidence for the host–guest hydrogen bonding in the Raman spectra of this work. Similar to the MVK + CH4 clathrate hydrate, the s-cis form is the geometrically favored conformer for the sII MVK + O2 or N2 hydrate. As the temperature increased, both MVK clathrate hydrates started to dissociate and released MVK molecules.

### Table 3. Experimental Equilibrium (H−LW−LMVK−V) Data of MVK + N2 at Various Concentrations (Pressure Accuracy: ±0.02% and Temperature Accuracy: ±0.05%)

| N2 + MVK | MVK (8.0 mol %) | MVK (5.6 mol %) | MVK (3.0 mol %) |
|----------|----------------|----------------|----------------|
| T (K)    | P (MPa)        | T (K)          | P (MPa)        |
| 271.2    | 7.87           | 271.3          | 7.91           |
| 272.7    | 9.95           | 272.9          | 9.90           |
| 274.2    | 11.98          | 274.3          | 11.87          |
| 275.4    | 13.88          | 275.5          | 13.79          |
| 276.4    | 16.05          | 276.6          | 15.94          |
| 277.3    | 17.72          | 277.4          | 17.61          |
| 278.1    | 19.64          | 278.3          | 19.66          |

Figure 5. Raman spectra of (a) nonirradiated MVK + O2 hydrate and (b) γ-irradiated MVK + O2 hydrate measured at various temperatures.

Figure 6. Raman spectra of (a) nonirradiated MVK + N2 hydrate and (b) γ-irradiated MVK + N2 hydrate measured at various temperatures.
from the clathrate phases that existed as solvated solid phases.\(^7\) At 173 K, two additional peaks at 1618 cm\(^{-1}\) (for C\(=\)C stretching) and 1672 cm\(^{-1}\) (for C\(=\)O stretching), which implies solvated \(\text{s-trans}\) MVK solid by water, were observed (Figures 5a and 6a). The temperature (173 K) at which the dissociation of MVK + O\(_2\) or N\(_2\) hydrate was observed is slightly higher than that of MVK + CH\(_4\) hydrate (153 K)\(^7\) even though the equilibrium curves for the three binary MVK clathrate hydrates (Figures 2–4) show that the MVK + CH\(_4\) hydrate is the most thermodynamically stable at the region from 7 to 20 MPa. The Raman spectroscopic results presented in Figures 5a and 6a, thus, imply that the binary MVK + O\(_2\) and N\(_2\) hydrates are more stable than the MVK + CH\(_4\) hydrate at the ambient pressure.

Figures 5b and 6b show the Raman spectra of \(\gamma\)-irradiated samples of MVK + O\(_2\) and N\(_2\) hydrates at various temperatures, respectively. In Figure 5b, two peaks at 1620 and 1674 cm\(^{-1}\), indicating the signals of \(\text{s-trans}\) MVK enclathrated in the hydrate cavity, appear at 133 K. Thus, as with the case of the \(\gamma\)-irradiated MVK + CH\(_4\) hydrate, an intracavity conformational change from s-cis to s-trans form is observed in the irradiated MVK + O\(_2\) hydrate. In our previous report,\(^8\) the \(\gamma\)-irradiated MVK + CH\(_4\) hydrate shows a change in the MVK conformation at 133 K (the Raman peaks of s-trans MVK in the hydrate cavity appear), returning the s-trans to s-cis form in the hydrate cavity at 153 K (the peaks of s-trans MVK in the cavity disappear) and the commencement of hydrate phase dissociation at 173 K (the peaks of s-trans MVK solvated appear). The dissociation temperature (173 K) of the \(\gamma\)-irradiated MVK + CH\(_4\) hydrate is higher than that of the unirradiated sample (153 K). A different aspect of the O\(_2\) case is that the dissociation of \(\gamma\)-irradiated MVK + O\(_2\) hydrate is observed from 153 K, a lower temperature than that before irradiation (Figure 5). From this result, the return of s-trans to s-cis form in the cavity of the MVK + O\(_2\) hydrate (i.e., peak disappearance of s-trans MVK enclathrated at 153 K) cannot be confirmed in the Raman spectra because the peaks of solvated s-trans MVK already appear at 153 K (Figure 5b). The temperature at which enclathrated O\(_2\) and MVK molecules is completely released from the hydrate phase (173 K) is also lower than that of the unirradiated MVK + O\(_2\) hydrate (193 K, Figure 5).

In contrast to the MVK + O\(_2\) hydrate, there is no significant observation for intracavity conformational change in the Raman spectra of the \(\gamma\)-irradiated MVK + N\(_2\) hydrate (Figure 6b). Even though the temperature was increased from 93 to 173 K, no signal for enclathrated s-trans MVK was observed. At 193 K, the dissociation of the hydrate phase is first detected, accompanied by the appearance of the Raman peak of solvated s-trans MVK. Complete dissociation of the \(\gamma\)-irradiated MVK + N\(_2\) hydrate phase was observed at 223 K, which is substantially higher temperature than that observed for the unirradiated case (193 K).

From the comparison of three binary MVK clathrate hydrates with and without \(\gamma\)-irradiation, it was found that the phenomenon of intracavity conformational change induced by irradiation was observed in the CH\(_4\) and O\(_2\) hydrates and that the elevation of the dissociation temperature after irradiation was observed in the CH\(_4\) and N\(_2\) hydrates. The conformational changes in the MVK guest and the thermodynamic stability change in hydrate phases might be independent phenomena relative to each other. The plausible mechanism of the intracavity conformational change involves an electron transfer between cavities,\(^7\) and thus, how secondary guests or their radical derivatives can stabilize electrons inside of the hydrate phases induced by \(\gamma\)-irradiation might determine the occurrence of this phenomenon. Properties such as molecular electron affinity are important factors for this case.\(^7\) It is still difficult to suggest the mechanism underlying the change in thermodynamic stability of binary MVK hydrate phases caused by \(\gamma\)-irradiation in this work, and further investigation of this phenomenon is needed.

### 3. CONCLUSIONS

In this work, we confirmed that the binary MVK clathrate hydrates with secondary guests, O\(_2\) and N\(_2\), have a \(\text{Fd3m}\) crystal structure and investigated the thermodynamic stability of MVK + CH\(_4\), O\(_2\), and N\(_2\) clathrate hydrates. The \(\gamma\)-irradiation may affect the thermodynamic stability of binary MVK hydrates and the direction of the effect, whether stabilization or destabilization, induced by irradiation depended on the secondary guests. The intracavity conformational change from s-cis to s-trans forms of the MVK guest was also observed in the \(\gamma\)-irradiated MVK + O\(_2\) or CH\(_4\) hydrate, whereas the irradiated MVK + N\(_2\) hydrate did not exhibit any conformational changes. The present findings show that the physicochemical properties of \(\gamma\)-irradiated binary clathrate hydrate depend on the characteristics of secondary guest species; selection of a proper secondary guest species is a key factor for the design of functionalized clathrate hydrate materials.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials and Sample Preparations.

Deionized water of ultrahigh purity was supplied by Merck (Germany). MVK was supplied by Sigma-Aldrich Inc. and used without further purification. CH\(_4\), O\(_2\), and N\(_2\) gases were purchased from Special Gas (Korea) with stated minimum purities of 99.95, 99.95, and 99.9 mol %, respectively.

Ten grams of 5.0 mol % MVK solution was initially loaded into the stirring cell. The stirring cell was a bolted closure-type high-pressure vessel made of stainless steel. The stirring cell has a vertical magnetic drive agitator so that continuous stirring is possible when making binary hydrates. After loading the solution, air existing inside of the cell was flushed out by continuous injection of gas, which acts as a help-guest molecule to form the binary MVK clathrate hydrate. After a few seconds, the gas was pressurized up to around 120 bar by using a microflow syringe pump (Teledyne, Isco 260D). The temperature of the stirring cell immersed in a circulating chiller bath (Jeo Tech, RW-2025G) was then slowly lowered until a sudden pressure drop caused by hydrate formation was detected. After the hydrate formation started, the cell was kept at 258 K for at least 3 days to complete the hydrate synthesis. To collect the synthesized sample, the stirring cell was quenched in liquid nitrogen for a few seconds, and then, the pressure was released to atmospheric pressure. The collected samples were ground (∼200 μm) in a mortar at liquid nitrogen temperature and then stored in a liquid nitrogen tank for HRPD and Raman analyses. Some samples were irradiated at 90 kGy dose (15 kGy per 1 h) using a \(^{60}\)Co \(\gamma\)-ray source at KAERI in Jeongeup, Korea. The samples were immersed in liquid nitrogen during the irradiation. The irradiated samples were also used for Raman spectroscopic analyses.
4.2. Structure Analysis Using Synchrotron High-Resolution Powder Diffraction. The HRPD patterns were recorded at the HRPD beamline (9B) facility of the Pohang Accelerator Laboratory (PAL) in Korea. During the measurements, the 0/20 scan mode with a fixed time of 2 s, a step size of 0.005° for 2θ = 5–125°, and the beamline with a wavelength of 1.497 Å were used for each sample. The sample powder stored in liquid nitrogen was quickly transferred to the sample stage and cooled to 80 K in air, and the experiment was carried out at around 77 K to minimize possible sample damage. To determine the crystal structures of the samples, the obtained patterns were analyzed using the Le Bail fitting method using the profile matching of FullProf Program. 68

4.3. Phase Equilibrium Measurements. The Lw−H−V phase equilibria of the binary MVK + CH4, O2, and N2 clathrate hydrates were measured using the P−T trace method in the mechanically stirred high-pressure vessel with an internal volume of 100 mL. First, the MVK aqueous solution (25 mL) was loaded into the cell. The cell was flushed out by a continuously injected and vented CH4 (or O2, N2) gas stream so as to remove the air inside of the cell and then was pressurized up to the target pressure using a microflow syringe pump (initial pressure condition: 5–21 MPa for CH4, 8–20 MPa for O2, and 8–20 MPa for N2). After the system was stabilized, the cell was cooled at −1 K/h until the hydrate was sufficiently formed, and then, the cell was slowly warmed up at 0.1 K/h, which was a sufficient rate to reach equilibrium in each case. During this hydrate formation−dissociation process, the pressure and temperature inside of the cell were sensed using a pressure transducer (Druck, PMP5073, ±0.02% accuracy) and a four-wire-type Pt100 Ω probe (±0.05% full-scale accuracy) and were automatically recorded using a data acquisition system. When the slope of a tangent line of the P−T curve suddenly decreased, the Lw−H−V phase equilibrium point was determined.

4.4. Characterization of Guest Molecules Using Raman Spectroscopy. The Raman spectra were recorded using a Horiba Jobin Yvon ARAMIS HR UV/vis/NIR high-resolution dispersive Raman microscope. A focused 514.53 nm laser was used as an excitation source, and its typical intensity was 30 mW. The scattered light was dispersed using a 1800 grating of a spectrometer and was detected using a CCD detector with electrical cooling (203 K). To control the sample temperature, a Linkam (THMS600G) unit was used, and at each temperature sufficient time was provided to reach the equilibrium state.

AUTHOR INFORMATION

Corresponding Authors
*E-mail: kyuchul.shin@knu.ac.kr (K.S.).
*E-mail: hlee@kaist.ac.kr (H.L.).

ORCID

Yun-Ho Ahn: 0000-0002-8886-7981
Kyuchul Shin: 0000-0002-2497-9589
Huen Lee: 0000-0003-0026-1756

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the support by a NRF grant (NRF-2015R1C1A1A02036607) funded by the Ministry of Science, ICT and Future Planning (MISP). HRPD experiments at PLS (Beamline 9B) were supported by POSTECH.

REFERENCES

(1) Sloan, E. D.; Koh, C. A. Clathrate Hydrates of Natural Gases, 3rd ed.; CRC Press (Taylor and Francis Group), 2008.
(2) Rehder, G.; Eckl, R.; Elgen, M.; Falenty, A.; Hamann, R.; Kähler, N.; Kuhls, W. F.; Osterkamp, H.; Windmeier, C. Methane Hydrate Pellet Transport Using the Self-Preservation Effect: A Techno-Economic Analysis. Energies 2012, 5, 2499–2523.
(3) Ho, L. C.; Babu, P.; Kumar, R.; Linga, P. HBGS (Hydrate Based Gas Separation) Process for Carbon Dioxide Capture Employing an Unstirred Reactor with Cyclopentane. Energy 2013, 63, 252–259.
(4) Seo, Y.-T.; Kang, S.-P.; Lee, H. Experimental Determination and Thermodynamic Modeling of Methane and Nitrogen Hydrates in the Presence of THF, Propylene Oxide, 1,4-Dioxane and Acetone. Fluid Phase Equil. 2001, 189, 99–110.
(5) Liang, D.-Q.; Du, J.-W.; Li, D.-L. Hydrate Equilibrium Data for Methane + tert-Butylamine + Water. J. Chem. Eng. Data 2010, 55, 1039–1041.
(6) Du, J.-W.; Liang, D.-Q.; Dai, X.-X.; Li, D.-L.; Li, X.-J. Hydrate Phase Equilibrium for the (Hydrogen + tert-Butylamine + Water) System. J. Chem. Thermodyn. 2011, 43, 617–621.
(7) Ahn, Y.-H.; Lim, H.-K.; Kang, H.; Kim, H.; Cha, M.; Shin, K.; Lee, H. Intracrystalline Conformational Changes in Clathrate Hydrates. J. Phys. Chem. C 2016, 120, 17190–17195.
(8) Bednarek, J.; Erickson, R.; Lund, A.; Slíck, S. The Return of the Trapped Electron in X-Irradiated Clathrate Hydrates. An ESR Investigation. J. Am. Chem. Soc. 1991, 113, 8990–8991.
(9) Bednarek, J.; Lund, A.; Slíck, S. Unstable Intermediates in X-Irradiated Clathrate Hydrates: ESR and Endor of Tetramethylammonium Hydroxide Pentahydrate (TMNOH). J. Phys. Chem. 1996, 100, 3910–3916.
(10) Cha, M.; Shin, K.; Kwon, M.; Koh, D.-Y.; Sung, B.; Lee, H. Superoxide Ions Entrapped in Water Cages of Ionic Clathrate Hydrates. J. Am. Chem. Soc. 2010, 132, 3694–3696.
(11) Shin, K.; Cha, M.; Lee, W.; Kim, H.; Jung, Y.; Dho, J.; Kim, J.; Lee, H. Superoxene Exchange Interaction of Encaged Molecular Oxygen in Nitrogen-Doped Water Cages of Clathrate Hydrates. J. Am. Chem. Soc. 2011, 133, 20399–20404.
(12) Shin, K.; Cha, M.; Lee, W.; Seo, Y.; Lee, H. Abnormal Proton Positioning of Water Framework in the Presence of Paramagnetic Guest within Ion-Doped Clathrate Hydrate Host. J. Phys. Chem. C 2014, 118, 15193–15199.
(13) Yeon, S.-H.; Seol, J.; Park, Y.; Koh, D.-Y.; Kang, Y. S.; Lee, H. Spectroscopic Observation of Atomic Hydrogen Radicals Entrapped in Icy Hydrogen Hydrate. J. Am. Chem. Soc. 2008, 130, 9208–9209.
(14) Shin, K.; Cha, M.; Kim, H.; Jung, Y.; Kang, Y. S.; Lee, H. Direct Observation of Atomic Hydrogen Generated from the Water Framework of Clathrate Hydrates. Chem. Commun. 2011, 47, 674–676.
(15) Koh, D.-Y.; Kang, H.; Park, J.; Shin, W.; Lee, H. Atomic Hydrogen Production from Semi-Clathrate Hydrates. J. Am. Chem. Soc. 2012, 134, 5560–5562.
(16) Takeya, K.; Nango, K.; Sugahara, T.; Ohgaki, K.; Tani, A. Activation Energy of Methyl Radical Decay in Methane Hydrate. J. Phys. Chem. B 2005, 109, 21086–21088.
(17) Takeya, K.; Nango, K.; Sugahara, T.; Ohgaki, K.; Tani, A.; Ito, H.; Okada, M.; Kasai, T. Electron Spin Resonance Study on γ-Ray-Induced Ethyl Radical in Ethane Hydrate. Jpn. J. Appl. Phys., Part 1 2007, 46, 3066–3070.
(18) Takeya, K.; Sugahara, T.; Ohgaki, K.; Tani, A. Electron Spin Resonance Study on γ-Ray-Induced Radical Species in Ethylene Hydrate. Radiat. Meas. 2007, 42, 1301–1306.
(19) Tani, A.; Koyama, S.; Urabe, Y.; Takato, K.; Sugahara, T.; Ohgaki, K. Blue-Colored tert-Butylamine Clathrate Hydrate. J. Phys. Chem. B 2014, 118, 13409−13413.

(20) Ohgaki, K.; Nakatsuji, K.; Takeya, K.; Tani, A.; Sugahara, T. Hydrogen Transfer from Guest Molecule to Radical in Adjacent Hydrate-Cages. Phys. Chem. Chem. Phys. 2008, 10, 80−82.

(21) Kobayashi, N.; Minami, T.; Tani, A.; Nakagoshi, M.; Sugahara, T.; Takeya, K.; Ohgaki, K. Intermolecular Hydrogen Transfer in Isobutane Hydrate. Energies 2012, 5, 1705−1712.

(22) Sugahara, T.; Kobayashi, Y.; Tani, A.; Inoue, T.; Ohgaki, K. Intermolecular Hydrogen Transfer between Guest Species in Small and Large Cages of Methane + Propane Mixed Gas Hydrates. J. Phys. Chem. A 2012, 116, 2405−2408.

(23) Hester, K. C.; Huo, Z.; Ballard, A. L.; Koh, C. A.; Miller, K. T.; Sloan, E. D. Thermal Expansivity for sI and sII Clathrate Hydrates. J. Phys. Chem. B 2007, 111, 8830−8835.

(24) Raw, C. J.; Rondinone, A. J.; Chakoumakos, B. C.; Marshall, S. L.; Stern, L. A.; Circone, S.; Kirby, S.; Jones, C. Y.; Toby, B. H.; Ishii, Y. Neutron Powder Diffraction Studies as a Function of Temperature of sII Hydrate Formed from a Methane + Ethane Gas Mixture. In Proceedings of the 4th International Conference on Gas Hydrates; Domestic Organizing Committee: Yokohama, Japan, 2002.

(25) van Cleeff, A.; Diepen, G. A. M. Gas Hydrates of Nitrogen and Oxygen. Rec. Trav. Chim. Pays-Bas 1960, 79, 582−586.

(26) Nixdorf, J.; Oellrich, L. R. Experimental Determination of Hydrate Equilibrium Conditions for Pure Gases, Binary and Ternary Mixtures and Natural Gases. Fluid Phase Equilib. 1997, 139, 325−333.

(27) Mohammadi, A. H.; Tohidi, B.; Burgass, R. W. Equilibrium Data and Thermodynamic Modeling of Nitrogen, Oxygen, and Air Clathrate Hydrates. J. Chem. Eng. Data 2003, 48, 612−616.

(28) Noack, K.; Jones, R. N. Conformational Equilibria in Open-Chain α,β-Unsaturated Ketones. Can. J. Chem. 1961, 39, 2225−2235.

(29) Durig, J. R.; Little, T. S. Conformational Barriers to Internal Rotation and Vibrational Assignment of Methyl Vinyl Ketone. J. Chem. Phys. 1981, 75, 3660−3668.

(30) Lee, J-W.; Lu, H.; Moudrakovski, I. L.; Ratcliffe, C. I.; Ohmura, R.; Alavi, S.; Ripmeester, J. A. 13C NMR Studies of Hydrocarbon Guests in Synthetic Structure H Gas Hydrates: Experiment and Computation. J. Phys. Chem. A 2011, 115, 1650−1657.

(31) Chazallon, B.; Champagnon, B.; Panczer, G.; Pauer, F.; Klapproth, A.; Kuhls, W. F. Micro-Raman Analysis of Synthetic Air Clathrates. Eur. J. Mineral. 1998, 10, 1125−1134.

(32) Sasaki, S.; Hori, S.; Kume, T.; Shimizu, H. Microscopic Observation and in Situ Raman Scattering Studies on High-Pressure Phase Transformations of a Synthetic Nitrogen Hydrate. J. Chem. Phys. 2003, 118, 7892−7897.

(33) Liu, C.-L.; Lu, H.-L.; Ye, Y.-G. Raman Spectroscopy of Nitrogen Clathrate Hydrates. Chin. J. Phys. Chem. 2009, 22, 353−358.

(34) Sugahara, K.; Tanaka, Y.; Sugahara, T.; Ohgaki, K. Thermodynamic Stability and Structure of Nitrogen Hydrate Crystal. J. Supramol. Chem. 2002, 2, 365−368.

(35) Alavi, S.; Susilo, R.; Ripmeester, J. A. Linking Microscopic Guest Properties to Macroscopic Observables in Clathrate Hydrates: Guest−Host Hydrogen Bonding. J. Chem. Phys. 2009, 130, 174501.

(36) Buch, V.; Devlin, J. P.; Monreal, I. A.; Jagoda-Cwiklik, B.; Uras-Aytemiz, N.; Cwiklik, L. Clathrate Hydrates with Hydrogen-Bonding Guests. Phys. Chem. Chem. Phys. 2009, 11, 10245−10265.

(37) Amtawong, J.; Guo, J.; Hale, J. S.; Sengupta, S.; Fleischer, E. B.; Martin, R. W.; Janda, K. C. Propane Clathrate Hydrate Formation Accelerated by Methanol. J. Phys. Chem. Lett. 2016, 7, 2346−2349.

(38) Rodriguez-Carvajal, J. Recent Advances in Magnetic Structure Determination by Neutron Powder Diffraction. Phys. B 1993, 192, 55−69.