Research paper

Thermal expansivity of γ-irradiated clathrate hydrate with intracavity conformational change

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A B S T R A C T

The lattice expansion and thermal behavior of γ-irradiated unstable clathrate hydrates are explored to understand the complex physicochemical properties of clathrate hydrates. A previous study revealed that enclathrated methyl vinyl ketone molecules show a peculiar conformational change via a ketyl radical anion after γ-irradiation with an annealing process. We measured the lattice parameters of γ-irradiated binary methyl vinyl ketone + CH_4, O_2, and N_2 hydrates at various temperatures. We observed that induced radical affects the lattice expansion behavior, and the thermal expansion coefficients of γ-irradiated hydrates highly depend on the types of secondary gaseous guest molecules.

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1. Introduction

Clathrate hydrates are non-stoichiometric inclusion compounds basically composed of a hydrogen-bonded host water framework and entrapped guest molecules. There are two general categories of clathrate hydrates depending on the types of guest species: nonionic clathrate hydrates having normal gas or organic guests and ionic clathrate hydrates consisting of ions incorporated into the host water lattice with enclathrated counterions [1,2]. In order to comprehend the complex physicochemical properties of clathrate hydrates such as thermodynamic stability, tuning behavior, formation kinetics, discrete magnetic behavior, and proton conductivity, the interaction between the guest and host lattice should be extensively investigated [3–9]. In particular, lattice parameters of various clathrate hydrates, which can provide clear evidence to undeverstand the host-guest interaction, have been explored to date. Takeya et al. reported that guest occupancy does not affect the lattice parameter of structure I (sI) hydrates, but affects that of structure II (sII) hydrates due to the different host-guest or guest-guest interaction occurring in different crystal structures [10]. They also reported unique expansion behavior of structure H (sH) hydrates with various large guest molecules: the icosahedron ($5^{12}6^8$) cavities easily expand in the a-axis rather than in the c-axis [11]. The thermal expansion of clathrate hydrates also

has been investigated in many previous studies. Thermal expansion of sI ethylene oxide hydrate is larger than that of hexagonal ice, resulting in relatively smaller thermal conductivity of the hydrate, and this could be explained by larger anharmonicity from the interaction between the host water and guest molecules [12]. Also, Hester et al. synthesized various nonionic sI and sII hydrates and showed that the thermal expansivity of clathrate hydrates shows guest-independent and structure-dependent correlations [13]. In contrast, Shin et al. suggested that the lattice expansion of ionic clathrate hydrates by thermal stimulation is affected by the types of ionic guest species because of different host-guest charge interactions [14]. Park et al. and Koh et al. also observed plastic-like deformation of binary THF + gas hydrates [15,16]. Recently, the thermal expansion of the water cavity was correlated with the reference chemical potential in accurately predicting the hydrate equilibria [17].

In this study, the lattice parameter of a γ-irradiated clathrate hydrate in a temperature range of 93–193 K was examined for the first time. Some previous studies induced radical species in clathrate hydrate media by using γ-irradiation and investigated their peculiar characteristics such as stably entrapped hydrogen radicals [18–20] and a hydrogen picking phenomenon [21,22]. However, the lattice parameter of γ-irradiated clathrate hydrates has not been explored yet, even though it might shed light on the host-guest interaction occurring in these hydrates. We investigated the thermal expansivity of γ-irradiated binary methyl vinyl ketone + gas hydrates with their lattice parameters obtained by the high resolution powder diffraction (HRPD) patterns. Among the aforementioned studies,

some adopted neutron powder diffraction instead of X-ray powder diffraction in order to avoid incoherent X-ray scattering caused by the interaction of X-ray photons with electron clouds [14–16]. Also, the X-ray may induce radical species from the enclathrated guest species, leading to unreliable results [23]. However, since certain radical species already exist in the γ-irradiated clathrate hydrate media, unexpected radical production caused by HRPD measurements is not a critical factor that must be considered. Here, we investigated the abnormal thermal expansivity of γ-irradiated MVK binary clathrate hydrates.

2. Experimental section

2.1. Materials and sample preparations

Methyl vinyl ketone (hereafter MVK) was purchased from Sigma-Aldrich Inc. and used without further purification. CH_4 (99.95 mol%), O_2 (99.95 mol%), and N_2 (99.90 mol%) gases were supplied by Special Gas (Korea). Deionized water with ultrahigh purity was supplied by Merck (Germany).

For sample preparation, 10 g of 5.0 mol% MVK solution was initially loaded into a stirring cell, which was a bolted closure-type high-pressure reactor made of 316-stainless steel. The internal working volume was around 50 ml. The stirring cell had a vertical magnetic drive agitator so that continuous stirring could be applied during the binary (MVK + gas) hydrate formation. After loading the solution, the reactor was assembled, and the air present inside the reactor was flushed out by continuously injecting gaseous guest species (CH_4, O_2, and N_2), which were selected as help-gas molecules to form binary hydrates. The reactor was then quenched in a refrigerated ethanol circulator (RW-2025G, Jeio Tech Co., Ltd., Republic of Korea) for temperature control. The gas was pressurized up to around 120 bar by using a microflow syringe pump (Teledyne, ISCO 260D). The temperature was then slowly lowered (−1 K/min) to the hydrate formation starting points, where a sudden pressure drop was detected. The reactor was kept at 258 K for at least three days for the complete conversion of the binary hydrate. In order to recover the synthesized binary hydrate samples, the reactor was quenched in liquid nitrogen for a few minutes and then the gas was vented. The recovered samples were ground (∼200 μm) in a mortar at liquid nitrogen temperature and then stored in a liquid nitrogen tank for γ-irradiation. The samples were irradiated at a 90 kGy dose (15 kGy per 1 h) by a ^{60}Co γ-ray source at KAERI in Jeongeup, Korea. The samples were immersed in liquid nitrogen during the irradiation to avoid dissociation. The irradiated samples were used for HRPD analyses.

2.2. Synchrotron high resolution powder diffraction (HRPD) analyses

The HRPD patterns were recorded at the HRPD beamline (9B) facility of the Pohang Accelerator Laboratory (PAL) in Korea. During the measurements, the θ/2θ 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 γ-irradiated hydrate sample powder stored in liquid nitrogen was quickly transferred to the pre-cooled sample stage, and the experiment was carried out at various temperatures from 93 K to 193 K. In order to determine the crystal structures and obtain the lattice parameters of the samples, the obtained patterns were analyzed by the Le Bail fitting method using the profile matching of Fullprof Program [24].

3. Results and discussion

In our previous study, we synthesized three binary (methyl vinyl ketone (MVK) + CH_4, O_2, and N_2) clathrate hydrates and analyzed their HRPD patterns using the Le Bail fitting method [24]. The three HRPD patterns were consistent with the unique diffraction pattern of the cubic $Fd\bar{3}m$ structure II (sII) hydrate. As with the other reported sII hydrate forming agents [3,25], MVK was confirmed as a sII hydrate former that can occupy the large cavity with the help of small gaseous guest molecules [26,27]. Furthermore, the conformational change of enclathrated MVK molecules was observed by Raman spectroscopic measurement when the MVK + CH_4 or O_2 hydrate was annealed [26,27]. In nature, there are two MVK conformers, s-cis and s-trans MVK, having different molecular diameter (the largest end-to-end distance of s-cis MVK = 8.36 Å and that of s-trans MVK = 7.53 Å) [26], and the distortion of enclathrated MVK molecules cannot be avoided for the isomers to fit the $5^{12}6^4$ cavities of the sII hydrate because of their relatively larger size than the cavity diameter. At this stage, there must be an expansion or shrinkage of the hydrate cavity while the intracavity conformational change occurs. To elucidate the effect of radical species and intracavity conformational change on the lattice expansion, we measured HRPD patterns of three γ-irradiated binary (MVK + CH_4, O_2, and N_2) hydrates with application of an annealing process.

Figs. 1–3 present the HRPD patterns of γ-irradiated binary MVK + CH_4, O_2, and N_2 hydrates, respectively, measured in a temperature range of 93–193 K. Even after γ-irradiation, binary MVK + CH_4, O_2, and N_2 hydrates maintained their crystal structures of cubic $Fd\bar{3}m$ (red tick marks in Figs. 1–3). Since we used a 5.0 mol% MVK solution, which is less concentrated than the stoichiometric concentration of 5.6 mol%, in order to minimize the amount of excluded MVK, a small amount of ice impurity was also observed in the diffraction pattern of the hexagonal ice structure of hexagonal $P6_3/mmc$ (blue tick marks in Figs. 1–3). As the temperature rose, the peak intensities of the three γ-irradiated sII hydrates decreased, whereas those of the ice phase increased with partial dissociation of the hydrate phases. Furthermore, we observed a small peak shift of the sII hydrate phase to the left side, and this implied hydrate lattice expansion caused by thermal stimulation (Figs. 1–3). According to previous studies, γ-irradiation affects the thermodynamic stability of binary MVK + gas hydrates; γ-irradiation stabilizes binary MVK + CH_4 and N_2 hydrates but destabilizes binary MVK + O_2 hydrates, changing the dissociation temperature window [26,27]. Unfortunately, the exact dissociation temperature window of γ-irradiated binary MVK + CH_4, O_2, and N_2
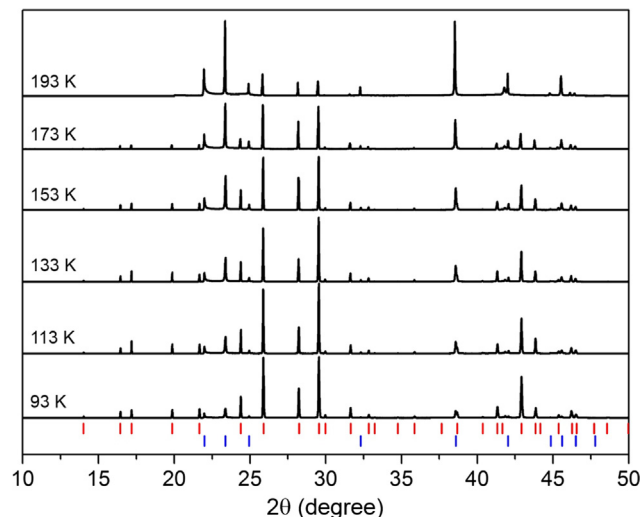

Fig. 1. HRPD patterns of γ–irradiated binary MVK + CH_4 hydrate at various temperatures.