Gas-Phase Synthesis and Characterization of CH$_4$-Loaded Hydroquinone Clathrates

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A CH$_4$-loaded hydroquinone (HQ) clathrate was synthesized via a gas-phase reaction using the α-form of crystalline HQ and CH$_4$ gas at 12 MPa and room temperature. Solid-state ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR and Raman spectroscopic measurements confirm the incorporation of CH$_4$ molecules into the cages of the HQ clathrate framework. The chemical analysis indicates that about 69% of the cages are filled by CH$_4$ molecules, that is, 0.69 CH$_4$ per three HQ molecules. Rietveld refinement using synchrotron X-ray powder diffraction (XRD) data shows that the CH$_4$-loaded HQ clathrate adopts the β-form of HQ clathrate in a hexagonal space group $R3$ with lattice parameters of $a = 16.6191$ Å and $c = 5.5038$ Å. Time-resolved synchrotron XRD and quadrupole mass spectroscopic measurements show that the CH$_4$-loaded HQ clathrate is stable up to 368 K and gradually transforms to the α-form by releasing the confined CH$_4$ gases between 368−378 K. Using solid-state ^{13}C CP/MAS NMR, the reaction kinetics between the α-form HQ and CH$_4$ gas is qualitatively described in terms of the particle size of the crystalline HQ.

Introduction

Clathrates are inclusion compounds that are formed by entrapping guest molecules into three-dimensional host frameworks.[1] The clathrate features a variety of crystal structures depending on the type of the host lattice and the guest molecules used. Gas hydrates, whose host frameworks are made of water molecules, are one of the most popular families in the clathrate compounds. Because huge amounts of natural gases are known to exist in nature in the form of the gas hydrates, many researchers have investigated fundamentals of the gas hydrates to exploit and develop them as new energy media of the future.[2,3] Most gas hydrates are, however, unstable at ambient conditions, and therefore, recent interests have been put on a certain class of organic clathrates that are stable at ambient conditions.

Among these, hydroquinone (HQ) has been recognized as one of the most promising clathrate formers.[3,4] HQ clathrates crystallize into three distinct forms, designated as α-, β-, and γ-forms. The α-form is stable at room temperature and can be converted into the β-form to create vacant cages accessible for a variety of gas species.[3−8] On the other hand, the γ-form is known to be formed by sublimation or rapid evaporation of HQ solution in ether.[9] We note that the energy difference between the α- and β-forms is only 0.13 kcal/mol.[10] This indicates that the β-form HQs may have a natural tendency to be converted into the α-form spontaneously at room temperature. Because Palin and Powell reported enclathration of HCl, HCN, and SO$_2$

in the β-form HQ,[8] extensive structural investigations have been performed to demonstrate that other guest species, including Ar, Kr, Xe, N$_2$, O$_2$, CO$_2$, and CH$_4$, can also form organic clathrates with HQ.[3] In addition, Ripmeester et al.,[11] Ripmeester,[12] and Burgiel[13] analyzed molecular behaviors of guest species in HQ clathrates using solid-state nuclear magnetic resonance (NMR) and far-infrared spectroscopy. Zubkus et al.[14,15] explained the observed enclathration of the β-form HQ in the energy stability point of view by performing molecular dynamics (MD) simulations for various guest substances. Furthermore, Daschbach et al.[16] postulated the possibility of hydrogen enclathration based on their MD simulation.

Conventionally, the preparation of HQ clathrates has involved the recrystallization and evaporation processes from a solvent, which inherently limits the practicality of the HQ synthesis.[3,9] In this study, a gas-phase synthesis of the CH$_4$-loaded β-form HQ was attempted, and the as-prepared samples were characterized by a suite of diffraction and spectroscopic measurements, including synchrotron powder X-ray diffraction (XRD), mass spectroscopy (MS), solid-state ^{13}C NMR, and Raman spectroscopy. Furthermore, the storage capacity of the occluded CH$_4$ molecules was evaluated on the basis of chemical analysis. Such a direct and facile synthesis method can be applied to the preparation of other organic clathrates, in general, for future applications in energy storage.

Experimental Methods

Material and Sample Preparation. Pure HQ (α-form) with nominal purity of 99 mol % was supplied by Sigma-Aldrich Chemicals Co., and CH$_4$ gas with minimum purity of 99.995 mol % was purchased from World Gas Co. (Korea). These materials were used without further purification or treatment in the present study. To prepare the CH$_4$-loaded HQ samples, pure

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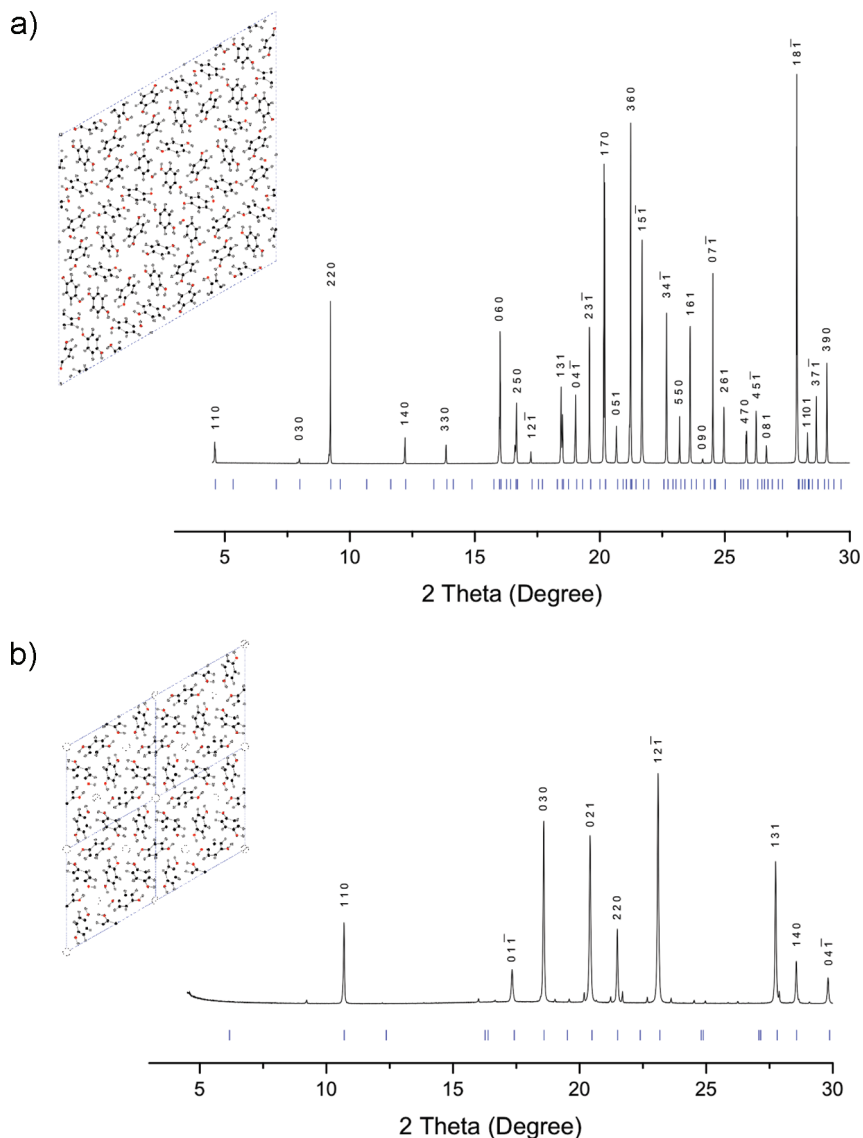‖ Methane Hydrate Research Center, AIST.
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Figure 1. Synchrotron powder XRD patterns of (a) the α-form and (b) the CH$_4$-loaded β-form clathrate of HQ compounds. Vertical ticks represent the positions of calculated reflections. Insets show the unit cell structures viewed along the (001) direction. For the CH$_4$-loaded β-form HQ, the striped circles in the unit cells indicate the channel cages occupied by CH$_4$ molecules.

HQ was allowed to react with CH$_4$ gas in a high pressure reactor. The reactor was made of 316 stainless steel and has an internal volume of approximately 200 cm^3. Before loading, HQ powders were ground and filtered to particle sizes less than 45 μm to promote the reaction with CH$_4$ gas. After loading the fine HQ powders, the reactor was purged with CH$_4$ gas at least five times to remove residual air and pressurized with CH$_4$ gas up to 12 MPa. The pressurized mixture was kept for 5 days in room temperature. The product was then collected by slowly releasing pressure for microscopic analysis.

Analytical Methods. HQ samples were analyzed by a series of microscopic analysis. First, high-resolution synchrotron X-ray powder diffraction data were measured at beamline 8C2 at the Pohang Accelerator Laboratory (PAL) in Korea. The incident X-rays were vertically collimated by a mirror and monochromatized to the wavelength of 1.5496(1) Å using a double-crystal Si(111) monochromator. The detector arm of the vertical scan diffractometer is composed of seven sets of soller slits, flat Ge(111) crystal analyzers, antiscatter baffles, and scintillation detectors, with each set separated by 20°. The powdered sample of about 0.2 g CH$_4$-loaded HQ was prepared by flat plate side loading method to avoid preferred orientation, and the sample

was then rotated about the normal to the surface during the measurement to increase sampling statistics. Step scan was performed at room temperature from 4.5° in 2θ, with a 0.005° increment, and 2° overlaps to the next detector bank up to 126.5° in 2θ. For the estimation of cage occupancy of CH$_4$ molecules using the XRD data, the Rietveld refinement was performed using the RIETAN-2000 program.[17] The initial crystallographic model for the host structures composed of HQ molecules was introduced from the previously reported models of X-ray diffraction data of the α-form[5] and β-form.[6] Because the measured diffraction patterns revealed that the samples were mixtures of the α-form and β-form, multiphase refinement was performed. Additionally, rigid-body constraint of HQ molecule was used to solve the host structure of β-form HQ clathrate.

Time-resolved XRD-MS experiments were performed at beamline X7B at the National Synchrotron Light Source (Brookhaven National Laboratory) in the U.S.A. A MAR345 Imaging Plate (IP) detector was employed for the data collection and the data were integrated using the FIT2D suite of programs.[18,19] The beam was monochromatized using Si(111) crystal to a wavelength of 0.9212 Å and a Pt/Rh/Si mirror was used to focus the beam to a size about 0.6 × 0.6 mm. A small

amount of powdered sample (~2 mg) was inserted into a flow-through cell (sapphire capillary tube with a radius of ~1 mm) and glass wool plugs were placed in both sides of the sample ends to prevent it from moving.[20] Heating wire (resistance heater) was wrapped outside of the sapphire tube and a thermocouple was placed close to the sample for temperature measurements. Temperature was programmed to increase linearly from room temperature to 573 K in 4 h. The IP was repeatedly exposed for 100s during the heating. Simultaneously, the outlet gases from the sample were allowed to flow through a quadrupole mass spectrometry (QMS) and the relative amounts of various gaseous products were calculated.

For the solid-state ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR measurements, a Bruker DSX400 NMR spectrometer in the National Instrumentation Center for Environmental Management (NICEM) of Seoul National University (Korea) was used. The spectra were collected at ambient temperature by placing samples within a 4 mm o.d. Zirconia rotor. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with MAS at 9 kHz. A pulse length of 2 μs and pulse repetition delay of 10s under proton decoupling were employed when the radio frequency field strengths of 50 kHz corresponding to 5 μs 90° pulses were used. The downfield carbon resonance peak of adamantine, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference.

A Raman spectrometer (Jobin Yvon Ramanor T-64000) with a triple monochromator of 1800 grooves/mm grating and a CCD detector was used for HQ compounds. An Ar-ion laser source emitting a 514.5 nm line was used at the power of 100 mW. The scattered radiation is collected at 180° geometry with a slit width of 50 μm, and spectra are collected with a 0.5 cm^{-1} scanning step and a 0.05 s integration time/step.

Results and Discussion

Pure HQ is in the stable α-form at atmospheric pressure and room temperature, while it changes to the β-form after capturing CH$_4$ molecules at high pressure. Figure 1 represents synchrotron XRD data for HQ samples before and after reacting with CH$_4$ gas. As seen in this figure, the diffraction pattern of the pure HQ is significantly different from that after reaction with CH$_4$. These XRD patterns are indexed to the α- and the β-form, respectively. For the α-form HQ, the lattice parameters are calculated to be $a = 38.5361(1)$ Å and $c = 5.6641(1)$ Å in the space group $R3$, and for the β-form HQ clathrate, $a = 16.6191(1)$ Å and $c = 5.5038(1)$ Å in the space group $R3$. These values show good agreement with previously reported ones in the literature ($a = 38.46(2)$ Å and $c = 5.650(3)$ Å for the α-form, and $a = 16.650(1)$ Å and $c = 5.453(1)$ Å for the β-form).[5,6]

To identify the structural change and the incorporation of CH$_4$ molecules into the HQ host framework, solid-state ^{13}C CP/MAS NMR analysis was performed. As shown in Figure 2, the ^{13}C NMR spectra between 100 and 160 ppm show the characteristics of the HQ molecules in both the α-form and the CH$_4$-loaded β-form HQ compounds. Because there are three structurally inequivalent carbon atoms in the β-form HQ clathrate with a centro-symmetric $R3$ structure, the ^{13}C NMR spectra reveal only three resonance lines. The chemical shift of the carbon atoms (C$_1$) attached hydroxyl groups is obtained clearly at 148.8 ppm, whereas the line splitting is attributed to the crystallographically inequivalent two hydroxyl nonsubstituted carbon atoms (C$_2$ and C$_3$ at 118.3 and 116.7 ppm, respectively). The difference (1.6 ppm) in the chemical shift
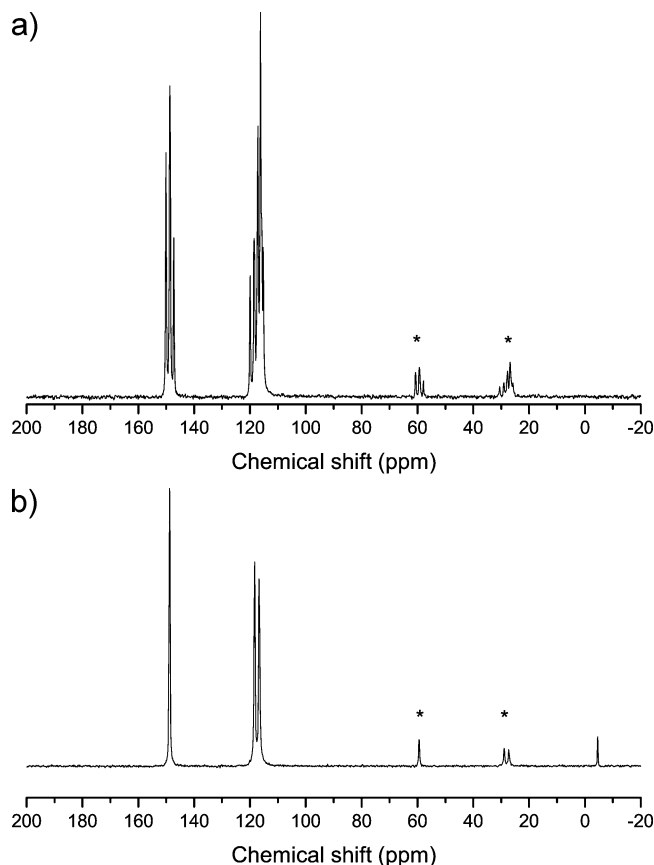

Figure 2. ^{13}C CP/MAS NMR spectra for (a) the α-form and (b) the CH$_4$-loaded β-form clathrate of HQ compounds. Asterisks indicate spinning side bands for carbon atoms of the HQ molecules.
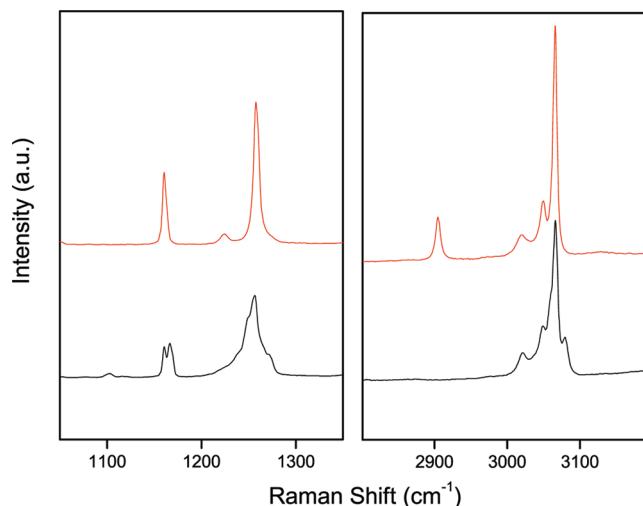

Figure 3. Raman spectra for the α-form (black lines) and the CH$_4$-loaded β-form (red lines) of HQ compounds.

between C$_2$ and C$_3$, which normally depends on the nature of the guest and the degree of cage occupancy, is similar to the value from the H$_2$S-loaded β-form HQ clathrate.[11] We note that a new ^{13}C line observed at −4.4 ppm should be attributed to the CH$_4$ molecules trapped in the β-form cages of the HQ clathrate, which is similar to that of CH$_4$ molecules trapped in the small 5^{12} (sI and sII) cages of the clathrate hydrates.[21] On the other hand, the α-form HQ shows many line splitting, attributed to the complicated orientations of the crystallographically independent HQ molecules.[11,12] The hydroxyl substituted carbon atoms generate three lines at around 150 ppm and the
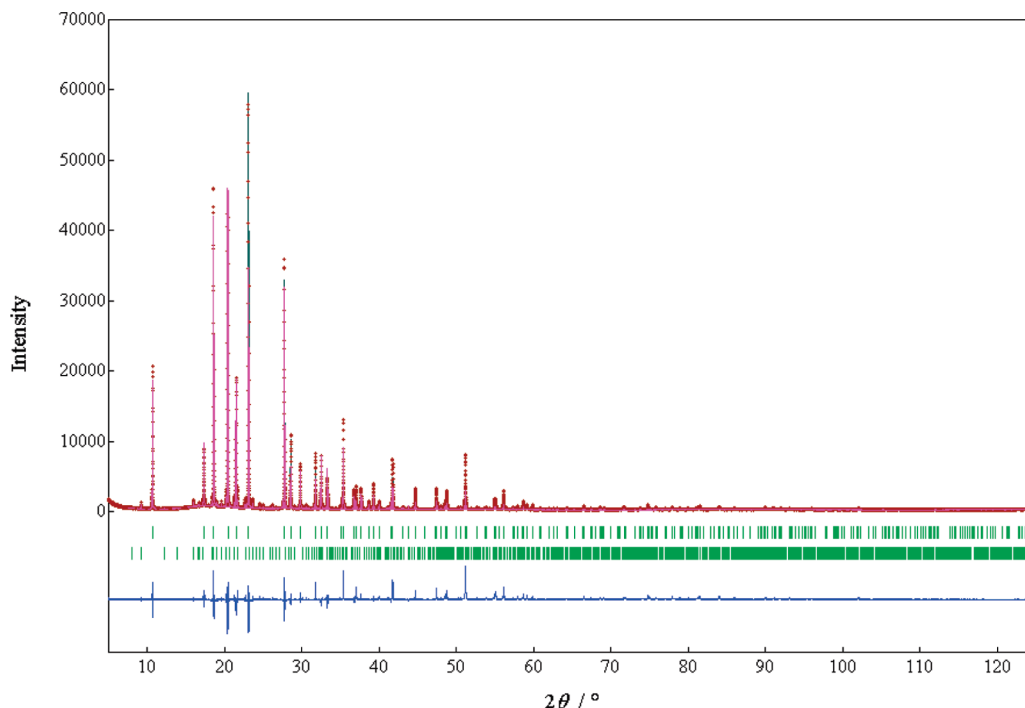
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Figure 4. Rietveld refinement for the CH$_4$-loaded β-form HQ clathrate: observed data (crosses), calculated profile (solid line), and difference (lower blue line). Vertical ticks represent the positions of calculated reflections for the CH$_4$-loaded β-form clathrate (upper ticks) and the α-form (lower ticks) of HQ compounds.
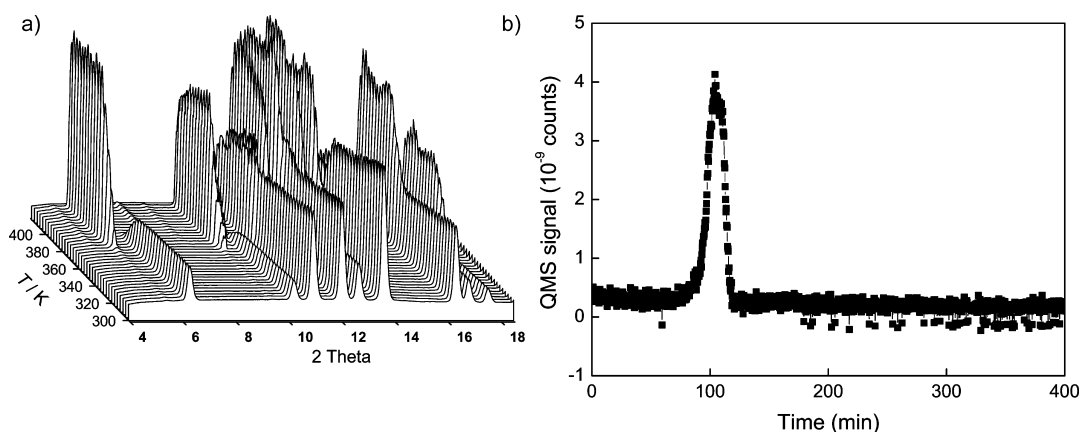

Figure 5. (a) Temperature-dependent XRD profiles showing the transformation pattern of the CH$_4$-loaded β-form HQ clathrate to the α-form HQ. (b) Quadrupole mass spectrometric (QMS) detection for CH$_4$ gases released from the CH$_4$-loaded β-form HQ clathrate during the transformation.

partially resolved lines at around 120 ppm are attributed to the C$_2$ and C$_3$ atoms.

Figure 3 shows the Raman spectroscopic measurements for the α-form and the CH$_4$-loaded β-form HQ compounds. The dominant peaks between 3000−3100 cm^{-1}, similarly observed from both samples, indicate the C−H vibrational mode of HQ molecules. However, a relatively small peak at 2905 cm^{-1} is observed only for the CH$_4$-loaded β-form HQ clathrate, indicating that this peak represents the symmetrical C−H stretching of the CH$_4$ molecules trapped in the β-form cages of the HQ clathrate. It should be noted that the peak position is very similar to that observed for the CH$_4$ molecules trapped in the large $5^{12}6^2$ (sI) and $5^{12}6^4$ (sII) cages of the clathrate hydrates.[22,23] A clear difference in the spectra of the C−O stretching of the host HQ molecules at ∼1600 cm^{-1} is attributed to the different dimensionality of the hydrogen bonding networks between the α- and the β-form HQ structures.[24,25]

The unit cell of the CH$_4$-loaded β-form HQ clathrate consists of nine HQ molecules and three cages, which are capable of

entrapping the CH$_4$ molecules. Therefore, the maximum stoichiometry for the CH$_4$-loaded β-form HQ clathrate must be 1 CH$_4$ molecules per three HQ molecules if we assume single occupancy of guest molecule per cage. The elemental analysis of the as-synthesized CH$_4$-loaded β-form HQ clathrate shows that 69% ($\pm$3%) of the cages in the HQ clathrate framework are filled by CH$_4$ molecules, leading to a β-form HQ clathrate, 0.69CH$_4$·3HQ. The calculated density of the CH$_4$-loaded β-form HQ clathrate is 1.29 g cm^{-3}, which is smaller than 1.33 g cm^{-3} for the α-form of crystalline HQ.[7,8] From these results, it is estimated that 1 L of the CH$_4$-loaded β-form HQ clathrate can store 63.9 L (42 g) of CH$_4$ gas at 298 K. The Rietveld refinement of the synchrotron XRD data suggests, however, higher cage occupancy of 0.84CH$_4$·3HQ (Figure 4). Moreover, the time-resolved synchrotron XRD measurements show that the CH$_4$-loaded HQ clathrate is stable only at temperatures lower than 368 K and gradually transforms to the α-form of crystalline HQ at temperatures in the range of 368−378 K, as shown in Figure 5a. Combining the time-resolved XRD and QMS
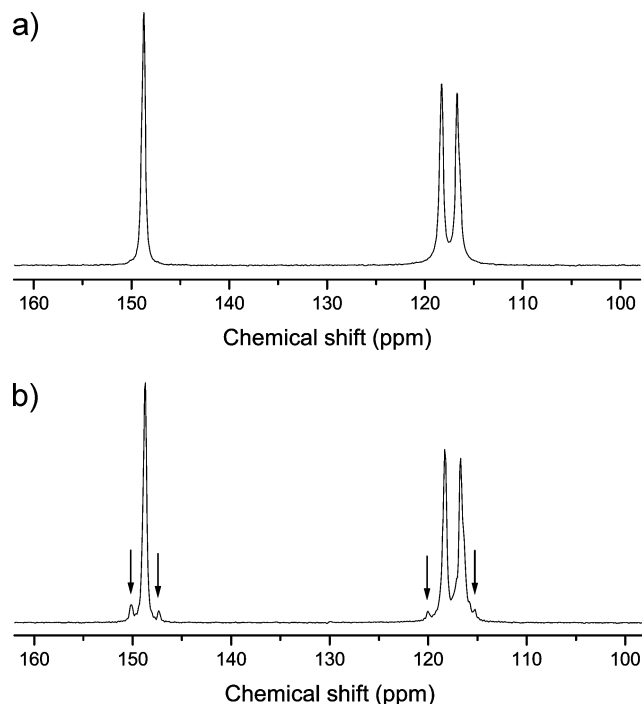
Figure 6. ^{13}C CP/MAS NMR spectra for the CH_4-loaded β-form HQ clathrates prepared from α-form HQ with particle sizes of (a) less than 45 μm and (b) less than 90 μm. Arrows represent NMR peaks from pure α-form HQ.

measurements, we confirm that the CH_4 gases are released from the CH_4-loaded HQ clathrate during the structural transformation (Figure 5b).

Figure 6 shows the effect of particle sizes of the α-form HQ on the conversion to the CH_4-loaded HQ clathrate, as measured by the ^{13}C CP/MAS NMR measurements. The α-form HQ with particle sizes less than 45 μm could be completely converted into the β-form HQ clathrate at 12 MPa and room temperature in 5 days, whereas the sample with particle sizes of 45−90 μm still contains unreacted α-form HQ. Works are in progress for more detailed description on the reaction kinetics between CH_4 and α-form HQ particles.

Conclusions

In the study, we have established a gas-phase reaction between pure (α-form) HQ and high pressure CH_4 gases to form the CH_4-loaded HQ clathrate. The as-synthesized samples were characterized systematically by means of diffraction and spectroscopic analysis. The crystal structure of the CH_4-loaded HQ clathrate was confirmed to be a β-form, and the incorporation of CH_4 molecules into the cages of the HQ clathrate frameworks was quantified using a combination of Raman spectroscopy and solid-state ^{13}C CP/MAS NMR. Combined time-resolved synchrotron XRD and QMS measurements indicated that the CH_4-loaded HQ clathrate

gradually transforms to the α-form at temperatures above 368 K by the release of the confined CH_4 gases. The effectiveness of the smaller particle sizes of the α-form HQ on the conversion rate to the CH_4-loaded HQ clathrate was investigated by the ^{13}C CP/MAS NMR measurements.

References and Notes

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