Structural properties of methane and butane mixed-gas hydrates

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HIGHLIGHTS

- NMR is a useful way to identify guest and solid/liquid components in C_1–C_4 hydrates.
- NMR measurements reveal guest distribution in C_1–C_4 hydrate crystals with sII.
- PXRD shows occurrence of lattice expansion depending on the guest composition.
- The lattice expansion acts to lower the hydrate density.

ARTICLE INFO

ABSTRACT

Solid-state ^{13}C NMR and powder X-ray diffraction measurements were conducted on mixed gas hydrates including methane and butane (*i*-butane and *n*-butane) to investigate the effect of guest composition in the hydrate lattice on the lattice parameters and density. The guest molecules were quantitatively analyzed by ^{13}C NMR spectroscopic techniques without the influence of uncaged components. The ^{13}C NMR measurements showed that the large cages in the structure II hydrate framework were almost fully occupied by methane and butane. Furthermore, small cage occupancies decreased with increasing butane composition as butane molecules preferentially occupied the large cages of structure II. The powder X-ray diffraction profiles showed that the lattice constant of structure II hydrate crystals increased with increasing butane composition, suggesting that the variation in guest distribution in the methane–butane systems contributes to the lattice expansion. The hydrate densities were estimated using the lattice parameters from the powder X-ray diffraction profiles and cage occupancies from ^{13}C NMR spectra, and the results obtained suggested that the lattice expansion contributes to lowering the hydrate density. The resultant structural properties of the mixed gas hydrates will be useful for designing novel gas hydrate technologies.

1. Introduction

Gas hydrates are crystalline inclusion compounds that have guest gas molecules incorporated in the host structure which is constructed by hydrogen-bonded water molecules under low-temperature–high-pressure conditions. Natural gas hydrate deposits in marine or permafrost environments are potential natural gas resources, and gas production using these deposits has been attempted (Dallimore et al., 2008). Gas hydrates have characteristics such as high gas storage capacity, gas trapping selectivity and heat of formation/dissociation, which make them promising for applications in natural gas storage/transportation (Gudmundson and Borrehaug, 1996), gas separation (Tajima et al., 2004), and thermal storage technologies using a hydrate-water slurry (Fournaison et al., 2004; Delahaye et al., 2008).

The crystal structures of gas hydrates are classified as either structure I (sI), structure II (sII), or structure H (sH), depending on the guest composition (Sloan, 2003). Natural gas components such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and isobutane (*i*-C_4H_{10}) are representative simple sI or sII hydrate formers (Sloan, 2003). Crystal structures of multi-component gas hydrate systems are more complex. For example, although both simple CH_4 and C_2H_6 hydrates are sI, it has been confirmed that CH_4–C_2H_6 mixed gases can form both sI and sII hydrates in natural and artificial systems, depending on the mixing ratio (Subramanian et al., 2000;

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Uchida et al., 2002; Takeya et al., 2003; Kida et al., 2006, 2007, 2009). Although simple n-butane (n-C_4H_{10}) does not form a hydrate structure, it has the potential to form a hydrate structure when combined with a help gas such as CH_4 or xenon (Sloan and Koh, 2007a). Gas hydrates with sI and sII are cubic crystals with $Pm3n$ and $Fd3m$ space groups, respectively, in which guest gas molecules occupy the two different cavities formed from polyhedral cages of water molecules (Jeffrey, 1984). The typical lattice parameter of a cubic crystal (a) is 1.2 nm for sI and 1.73 nm for sII (Sloan, 2004), suggesting that guest composition affects hydrate lattice parameters (Sloan and Koh, 2007b). Although there is significant difference in the lattice constant between various gas hydrate crystals with same crystal structure in many literatures (Hester et al., 2007), the effect of gas composition on hydrate lattice parameter remains poorly understood.

In recent times, it was reported that the lattice constants of simple i-C_4H_{10} and CH_4-i-C_4H_{10}/n-C_4H_{10} mixed hydrates with sII were significantly higher than those of simple C_3H_8 or sII mixed gas hydrates including CH_4, C_2H_6, C_3H_8, or small amounts of i-C_4H_{10}/n-C_4H_{10} (Takeya et al., 2014). Gas hydrate density is a fundamental property for gas hydrate technologies, such as gas storage/transportation or thermal storage using a slurry including hydrate particles, and can be precisely estimated by the lattice parameter and guest composition (cage occupancies of guest molecules) of gas hydrate crystals. A better understanding of the effect of guest composition on the hydrate lattice parameters is crucial not only from a fundamental aspect, but also from the viewpoint of engineering applications for gas hydrate technologies. However, in a synthetic hydrate system including gas components with relatively low fusing and high boiling points, such as i-C_4H_{10} or n-C_4H_{10}, the guest gas composition is masked by unreacted (uncaged) components coexisting with the gas hydrate phase (Takeya et al., 2014). Therefore, separation of the guest gas from unreacted components is required. Solid-state ^{13}C NMR spectroscopy is a powerful tool for the identification of guest molecules and unreacted components (Dec et al., 2006; Moudrakovski et al., 2008). However, in a multi-component gas hydrate system including heavier hydrocarbons, spectra can have complexly overlapping peaks from guest or coexisting, uncaged, heavier hydrocarbons (Lu et al., 2007; Moudrakovski et al., 2008). This implies that coexisting guest and uncaged components in a synthetic hydrate system including heavier hydrocarbons make it difficult to analyze the guest components. Therefore, detailed signal identification of ^{13}C NMR spectra is required for reliable qualitative and quantitative analyses of guest components. In this study, structural analyses were conducted using solid-state ^{13}C NMR spectroscopic techniques to identify the guest and unreacted components and reveal the relationship between guest composition and cage occupancies for CH_4-i-C_4H_{10}/n-C_4H_{10} double hydrates. Furthermore, hydrate lattice parameters were measured using powder X-ray diffraction (PXRD) techniques. Herein, we report the effect of guest composition on the hydrate lattice parameters and hydrate density of double hydrates.

2. Materials and methods

Mixed gas hydrates of CH_4-i-C_4H_{10} and CH_4-n-C_4H_{10} were synthesized by a contact reaction between 20 g of ice particles (≤ 1.0 mm) and the corresponding gas mixtures in a high-pressure vessel (1×10^{-3} m³) at 263 K. The gas mixtures were prepared from CH_4 ($\geq 99.9\%$, Sumitomo Seika Chemicals Co. Ltd.), i-C_4H_{10} ($\geq 99.9\%$, Takachiho Chemical Industrial Co. Ltd.), and n-C_4H_{10} ($\geq 99.95\%$, Takachiho Chemical Industrial Co. Ltd.). The CH_4-i-C_4H_{10} hydrates were formed from CH_4/i-C_4H_{10} ratios of 97.86/2.14 (initial feed pressure: 1.1 MPa), 97.10/2.90 (initial feed

pressure: 2.1 MPa), and 94.61/5.39 (initial feed pressure: 1.1 MPa). The CH_4-n-C_4H_{10} hydrates were synthesized from CH_4/n-C_4H_{10} ratios of 98.92/1.08 (initial feed pressure: 2.1 MPa), 98.88/1.12 (initial feed pressure: 1.4 MPa), and 98.14/1.86 (initial feed pressure: 1.7 MPa). All samples were recovered from the vessel by quenching with liquid nitrogen after completion of the hydrate reaction of approximately half of a day. The recovered samples were ground to a powder at liquid nitrogen temperature for homogenization of sample, and kept in the refrigerator at 128 ± 5 K and atmospheric pressure to remove unreacted i-C_4H_{10}. A fraction of the sample was stored at liquid nitrogen temperature.

For qualitative identification of guest and unreacted i-C_4H_{10}/n-C_4H_{10} in a sample, solid-state ^{13}C NMR measurements were carried out for the hydrate sample formed from gas mixtures with ratios of CH_4/i-C_4H_{10}=94.61/5.39 and CH_4/n-C_4H_{10}=98.88/1.12 and stored at liquid nitrogen temperature. The single-pulse/magic angle spinning (SP-MAS) and cross-polarization/magic angle spinning (CP-MAS) spectra of the samples were measured using an NMR spectrometer (JNM-AL400, 100 MHz; JEOL) at 122 and 162 K. The temperature used for the measurements was calibrated using the ^{207}Pb chemical shift of lead(II) nitrate (Bielecki and Burum, 1995). A 90° pulse length, 50 s pulse delay, 20 or 24 acquisitions, 3.5 kHz spinning rate at the magic angle for SP-MAS and CP-MAS spectra, and 10 ms contact time for CP-MAS spectra were used. The pulse delay time permits the complete relaxation of all the nuclei in the samples. For quantitative analyses of guest CH_4, i-C_4H_{10}, and n-C_4H_{10} molecules, the SP ^{13}C NMR spectra of samples stored at 128 ± 5 K were measured using an NMR spectrometer (100 MHz, Avance III 400; Bruker BioSpin, Bruker Corp.). The temperature used for measurements was 171 K, which was calibrated using the ^{79}Br chemical shift of potassium bromide (Thurber and Tycko, 2009). The SP ^{13}C NMR spectra was obtained under the following conditions: 90° pulse length, 50 s pulse delay, 8–24 acquisitions, and 3.0 kHz spinning rate at the magic angle. The chemical shift values of all ^{13}C NMR spectra in the present study were determined using adamantane as an external reference material, with the methine carbon peak set at 29.472 ppm at 298 K (Hayashi and Hayamizu, 1991).

The PXRD profiles of CH_4-i-C_4H_{10} and CH_4-n-C_4H_{10} hydrate samples stored at 128 ± 5 K were obtained at a constant temperature of 83 K using a low-temperature chamber (TTK 450; Anton Paar GmbH) and an X-ray diffractometer with Cu Kα radiation (45 kV, 200 mA, SmartLab; Rigaku Corp.). The PXRD profiles were obtained using a step width of 0.01° and scanning speed of 4.0°/min. The phase identification and lattice parameter calculations were conducted using a whole-powder-pattern fitting method with a commercial software package (PDXL; Rigaku Corp.).

3. Results and discussion

The gas hydrates were formed from mixed gases with CH_4/i-C_4H_{10}=94.61/5.39 and CH_4/n-C_4H_{10}=98.88/1.12 and stored in liquid nitrogen. The SP-MAS and CP-MAS ^{13}C NMR spectra of these hydrates are shown in Fig. 1. As shown in the SP-MAS spectrum of the CH_4-i-C_4H_{10} hydrate sample at 162 K in Fig. 1(a), four ^{13}C NMR signals were detected. These can be attributed to guest CH_4 and i-C_4H_{10} molecules incorporated in the sII hydrate framework and unreacted i-C_4H_{10}, which are comparable to previous literature reports (Davidson et al., 1986; Lu et al., 2007; Moudrakovski et al., 2008; Seo et al., 2009). The unit cell of the sII hydrate framework consists of 136 H_2O molecules, composed of 16 small cages with 12 pentagonal faces and eight large cages with 12 pentagonal and four hexagonal faces. The ^{13}C NMR signals at 26.6, 25.2, 23.7, and -4.4 ppm were attributed to the methyl carbons of i-C_4H_{10} in the large cages of sII, methyl carbons of liquid i-C_4H_{10}, methine carbon