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Enclathration of CO_2 as a co-guest of structure H hydrates and its implications for CO_2 capture and sequestration

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HIGHLIGHTS

- We examine sH hydrates with $CO_2 + N_2$ + neohexane for CO_2 capture and sequestration.
- The structural transition occurs in the CO_2 (40%) + N_2 (60%) + neohexane system.
- CO_2 molecules are enclathrated into sH hydrates in the N_2-rich systems.
- CO_2 selectivity in sH hydrates is slightly lower than that in sI hydrates.
- ΔH_d values provide information on the structural transition of sH to sI hydrates.

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ABSTRACT

In this study, the thermodynamic behaviors, cage-specific guest distributions, structural transition, and dissociation enthalpies of sH hydrates with $CO_2 + N_2$ gas mixtures were investigated for their potential applications to hydrate-based CO_2 capture and sequestration. The stability conditions of the $CO_2 + N_2$ + water systems and the $CO_2 + N_2$ + neohexane (2,2-dimethylbutane, NH) + water systems indicated that the gas mixtures in the range of flue gas compositions could form sH hydrates, thereby mitigating the pressure and temperature required for gas hydrate formation. Structure identification using powder X-ray diffraction (PXRD) revealed the coexistence of sI and sH hydrates in the CO_2 (40%) + N_2 (60%) + NH system and the hydrate structure transformed from sH into sI as the CO_2 concentration increased. In addition, the Raman analysis clearly demonstrated that CO_2 molecules were enclathrated into the cages of sH hydrates in the N_2-rich systems. It was found from direct CO_2 composition measurements that CO_2 selectivity in the sH hydrate phase was slightly lower than that in the corresponding sI hydrate phase. Dissociation enthalpy (ΔH_d) measurements using a high-pressure micro-differential scanning calorimeter (HP μ-DSC) indicated that the ΔH_d values could also provide valuable information on the structural transition of sH to sI hydrates with respect to the CO_2 concentration in the feed gas. This study provides a better understanding of the thermodynamic and physicochemical background for CO_2 enclathration in the sH hydrates and its significance in gas hydrate-based CO_2 capture and sequestration.

1. Introduction

Clathrate hydrates, commonly referred to as gas hydrates, are non-stoichiometric inclusion compounds that can capture small-sized guest molecules in their hydrogen-bonded lattice structures under low temperature and high pressure conditions [1]. Gas hydrates generally exist in three different structures: cubic structure I (sI), cubic structure II (sII), and hexagonal structure H (sH). The structures are classified depending on crystal lattice parameters, and sizes and shapes of cages. In particular, it was once thought that the third hydrate structure, hexagonal sH, could be exclusively synthesized in the laboratory, but it has recently been reported that sH hydrates also exist in the natural environment [2,3]. Unlike sI and sII hydrates, sH hydrates require two kinds of guest molecules to stabilize each of the three differently sized and shaped cages; small gas molecules such as methane (CH_4) and nitrogen (N_2) occupy the small 5^{12} and medium $4^35^66^3$ cages, while larger hydrocarbon molecules such as neohexane (2,2-dimethylbutane, NH) and methylcyclopentane (MCP) occupy the large $5^{12}6^8$ cages [1]. Since these small gas molecules are indispensable for the enclathration of large hydrocarbons into

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the sH hydrates, they are called “help gases” [1]. However, very little attention has been paid to the precise nature and actual applications of sH hydrates despite their potential importance in gas storage and separation [4].

Recently, gas hydrate-based technologies have been regarded as one of the promising options for CO_2 capture and sequestration (CCS) [5–17]. CO_2 can be selectively captured from flue gas mixtures of $CO_2 + N_2$ into the gas hydrate lattices due to its lower hydrate equilibrium pressure at a given temperature when compared with N_2. However, the main drawback for this hydrate-based CO_2 capture is that it requires high pressure and low temperature conditions for gas hydrate formation [18–21]. Therefore, a great deal of effort has been put into reducing the equilibrium pressure or raising the equilibrium temperature by adding thermodynamic promoters such as tetrahydrofuran (THF) and cyclopentane (CP) [22–27]. Recent investigations have also shown that sequestration of CO_2 into the natural gas hydrate layers has potential advantages for both energy recovery and greenhouse gas storage [28–33]. The research on this CH_4–CO_2 replacement process has been conducted primarily focusing on the sI hydrate reservoirs even though naturally occurring gas hydrates in the deep ocean sediments were found to exist in sI, sII, and sH hydrates [34–36].

The hydrate-based CO_2 capture and sequestration in sH hydrates is attractive because sH hydrates can be formed at much milder conditions than sI or sII gas hydrates that enclose only a help gas, and can store a larger amount of gas in smaller cages than gas hydrates with thermodynamic promoters. Several researchers have reported that CO_2 can function as a help gas for sH hydrates in the presence of large hydrocarbons only at temperature ranges far below the freezing point of water due to the relatively large molecular size of CO_2 [37,38]. However, flue gas that is composed of $CO_2 + N_2$ is reasonably expected to be enclathrated in the cages of sH hydrates because CO_2 from CH_4-rich gas mixtures was found to be successfully captured in sH hydrates even at temperature ranges above the freezing point of water [39,40]. Therefore, the enclathration of CO_2 as a co-guest of sH hydrates is very important for sH hydrate-based CO_2 capture and sequestration.

In this study, the thermodynamic behaviors, cage-specific guest distributions, structural transition, and dissociation enthalpies of sH hydrates with $CO_2 + N_2$ gas mixtures were investigated for their potential application to CO_2 capture and sequestration. The four-phase (hydrate (H)–liquid water (L_W)–liquid hydrocarbon (L_{HC})–vapor (V)) equilibria of the $CO_2 + N_2$ + NH + water systems were determined and compared with the three-phase (H–L_W–V) equilibria of the $CO_2 + N_2$ + water systems in order to verify thermodynamic stability and thermodynamic promotion due to the enclathration of NH. The accurate structure of the $CO_2 + N_2$ + NH systems at various compositions was analyzed via powder X-ray diffraction (PXRD) and Raman spectroscopy in order to confirm possible structural transitions depending on CO_2 concentrations. CO_2 compositions in the hydrate phase were also measured using gas chromatography because the preferential cage occupation of guest molecules depends on the hydrate structure. Furthermore, dissociation enthalpies of both $CO_2 + N_2$ and $CO_2 + N_2$ + NH hydrates were measured using a high-pressure micro-differential scanning calorimeter (HP μ-DSC) in order to understand the thermal behavior of the sI and sH hydrate systems.

2. Experimental investigation

2.1. Materials

The gas mixtures of CO_2 (10%, 20%, 40%, 60%, and 80%) + N_2 (balance) used for this study were supplied by MS gas Co. (Republic of Korea). Neohexane (2,2-dimethylbutane, NH) with a purity of 99.0% was purchased from Sigma–Aldrich (USA). Double-distilled and deionized water was used.

2.2. Stability condition measurements

A purpose-built equilibrium vessel was used to measure the four-phase (H–L_W–L_{HC}–V) equilibria of the gas hydrate systems. The equilibrium vessel had an internal volume of 250 cm^3 and was equipped with an impeller-type agitator to enhance the heat and mass transfer. A thermocouple was equipped into the vessel in order to measure the inner temperature, and calibrated using an ASTM 63 C thermometer (H-B Instrument Company, USA) with an accuracy of ±0.02 K. A pressure transducer (S-10, WIKA, Germany) was also calibrated using a Heise Bourdon tube pressure gauge (Ashcroft Inc. USA) with an accuracy of ±0.1% for the full-scale (0–10 MPa). The vessel was initially charged with 40 g of NH solution (3.0 mol%) and submerged into a water bath to control the temperature. In order to remove any residual air, the vessel was flushed with a $CO_2 + N_2$ gas mixture before pressurizing it to the desired pressure. An isochoric method (pVT) with step heating/cooling was adopted to determine the four-phase (H–L_W–L_{HC}–V) equilibria of the $CO_2 + N_2$ + NH hydrates. In this method, the temperature of the vessel was gradually decreased below the expected equilibrium temperature at a rate of 1.0 K/h to provide a sufficient driving force for gas hydrate formation. After the hydrate formation, which was confirmed by an abrupt pressure drop, the vessel was heated in increments of 0.1 K every 90 min until all of the hydrate crystals disappeared. The four-phase hydrate equilibrium points were determined by the intersection between the hydrate dissociation and the thermal expansion lines.

2.3. Microscopic analyses and gas composition measurements

In order to identify the structure of the $CO_2 + N_2$ + NH hydrates, the hydrate samples, which were prepared with the same apparatus used for the stability condition measurements, were analyzed via Raman spectroscopy and powder X-ray diffraction (PXRD). For the PXRD analysis, the hydrate samples were powdered into fine particles with a 100 μm sieve. The PXRD patterns of the $CO_2 + N_2$ + NH hydrates were collected using a Rigaku Geigerflex diffractometer with graphite-monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å) by step mode with a fixed time of 3 s and a step size of 0.02° for $2\theta = 10$–$55°$ at 133.15 K. The acquired patterns were analyzed using the Chekcell program. For the Raman measurement, the hydrate samples were finely powdered and then pelletized into a cylindrical shape (1 cm in diameter and 0.3 cm in height). The Raman spectra were obtained using a confocal Raman spectrometer (WItech alpha300 R, Germany) with a thermo-electric cooled CCD and an 1800 grooves/mm grating. The Raman spectrometer was equipped with a laser emitting at a wavelength of 532 nm and at a laser power of 35 mW. The samples were analyzed at 123.15 K by controlling the flow rate of liquid N_2 vapor under atmospheric pressure.

The gas hydrate samples for the composition analysis were prepared at a temperature of 275.15 K with a driving force of $\Delta P = 2.0$ MPa. After the completion of gas hydrate formation, the lower part of the pressurized vessel was submerged in a liquid nitrogen container for approximately 5 min to avoid any hydrate dissociation during the evacuation. Then, the vapor phase was evacuated with a vacuum pump to 0.005 MPa within 10 s, and the entire hydrate phase was dissociated at 293.15 K. The composition of gas retrieved from the hydrate phase was measured using a gas chromatograph (HP 5890II, USA) that was connected to the vessel. A high-pressure metering pump (Eldex, USA) was used to equilibrate the compositions between the connecting lines and the vessel and to transport the gas sample from the vessel