

## Complex Structure Transition Induced by Swapping Process Occurring in Natural Gas Hydrate Layer

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### ABSTRACT

In this study, we examine the swapping pattern occurring between two external guest molecules, N<sub>2</sub> and CO<sub>2</sub>, and crystalline (sI and sII) CH<sub>4</sub> hydrate. For sI methane hydrate, the spectroscopic result shows that N<sub>2</sub> molecules mainly attack CH<sub>4</sub> molecules occupying small cages while CO<sub>2</sub> molecules play an active role in replacing most of CH<sub>4</sub> molecules in large cages. In the other case for sII and sH methane hydrates, we observe the spontaneous structure transition of sII to sI during replacement and cage-specific distribution of guest molecules. We present here that under strong attacks of external CH<sub>4</sub> guest molecules the sII and sH methane hydrates are structurally transformed to the crystalline framework of sI, leading to favorable change of the lattice dimension of the host-guest networks.

**KEY WORDS:** clathrate hydrate, methane, CO<sub>2</sub>, ethane, sI, sII, sH, structure transition, cage specific swapping, NMR

### INTRODUCTION

Although numerous hydrate studies, covering both macroscopic and microscopic approaches, have recently been conducted for a variety of purposes, and to a certain extent have yielded notable success, little attention has been paid to cage dynamics exploring guest distributions within the sensitive host-guest networks. Moreover, the complex hydrate behavior occurring under strong attacks of external guest molecules to the existing cages has not yet been fully considered, and no detailed study exists even at a very fundamental level. In our previous study, we explored the replacement mechanism of CH<sub>4</sub> hydrate with CO<sub>2</sub> using spectroscopic methods and found that when a CH<sub>4</sub> hydrate is exposed to gas mixtures containing CO<sub>2</sub>, CH<sub>4</sub> is replaced by CO<sub>2</sub> in mainly of the large cages (Lee, H., 2003). If the CH<sub>4</sub> hydrates could be converted into CO<sub>2</sub> hydrates, they would serve double duty as CH<sub>4</sub> sources and CO<sub>2</sub> storage sites. Here, we further extend our investigations to consider the occurrence of CO<sub>2</sub> replacement phenomena on sII hydrate, which is thought to exist in the seabed. In this point of view, we present an interesting conclusion reached by inducing a structure transition. More importantly, we also investigate the possibility of direct use of binary N<sub>2</sub> and CO<sub>2</sub> gas

mixture for recovering CH<sub>4</sub> from the hydrate phase, which shows a remarkably enhanced recovery rate by means of the cage-specific occupation of guest molecules due to their molecular properties.

In addition, the structure transition observed during the replacement between external CH<sub>4</sub> gas and internal (CH<sub>4</sub>-rich +C<sub>2</sub>H<sub>6</sub> or isopentane/methylcyclohexane) guests is examined and spectroscopic evidence is put forth that establishes the preponderant occurrence of sI over sII and sH in natural methane hydrate deposits. A microscopic analysis is conducted in order to examine the real swapping phenomena occurring between external guest molecules and hydrates through spectroscopic identification, including solid-state Nuclear Magnetic Resonance (NMR) spectrometry.

### RESULTS and DISCUSSIONS

#### 1. sI hydrate with CO<sub>2</sub>+N<sub>2</sub>

We first attempted to examine the real swapping phenomenon occurring between binary guest molecules of N<sub>2</sub> and CO<sub>2</sub> and crystalline sI CH<sub>4</sub> hydrate through spectroscopic identification. In accordance with the idealized cage-specific pattern of multiple guests, N<sub>2</sub> molecules attack CH<sub>4</sub> molecules occupying small cages (sI-S) and eventually take the sites, while CO<sub>2</sub> molecules specifically play an active role in replacing most of the CH<sub>4</sub> molecules in large cages (sI-L). Such a unique cage occupancy behavior might be attributed to molecular details of the participating guests. CO<sub>2</sub> has a molecular diameter almost identical with the small cage diameter of sI hydrate, and thus only a slight degree of distortion in small cages exists to accommodate CO<sub>2</sub> molecules. Accordingly, we sufficiently expect that CO<sub>2</sub> molecules could be more stably engaged in sI-L under a favorable host-guest interaction. On the other hand, N<sub>2</sub> is known as one of the smallest hydrate formers and its molecular size almost coincides with CH<sub>4</sub>. Although N<sub>2</sub> itself forms pure sII hydrate with water (Sloan, 1988), the relatively small size of N<sub>2</sub> molecules leads to the preference of sI-S over other cages and, moreover, the stabilization of the overall sI hydrate structure when N<sub>2</sub> directly participates in forming the hydrate. Accordingly, CH<sub>4</sub> and N<sub>2</sub> are expected to compete for better occupancy to sI-S, while CO<sub>2</sub> preferentially occupies only sI-L without any challenge from other guests. Thus, the capacity of these two external guests, N<sub>2</sub> and CO<sub>2</sub>, in extracting original CH<sub>4</sub> molecules would make