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Experimental investigation into gas recovery from CH_4-C_2H_6-C_3H_8 hydrates by CO_2 replacement

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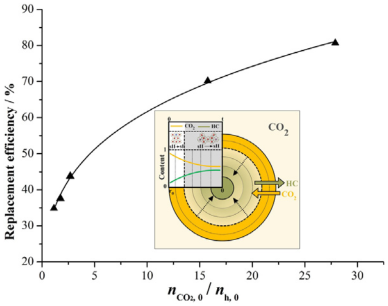
HIGHLIGHTS:

- The replacement of CH_4-C_2H_6-C_3H_8 ternary hydrates by gaseous and liquid CO_2 is experimentally investigated.
- CH_4, C_2H_6 and C_3H_8 are recovered heterogeneously from gas hydrates by CO_2 replacement.
- There is a structural transformation followed by an isostructural conversion in sII hydrate replacement.
- The spatial distribution of gas compositions in the replaced hydrates is obtained based on shrinking-core model.
- A power function relation was found to exist between the replacement efficiency and mole ratio of CO_2 to hydrate.

GRAPHICAL ABSTRACT

Schematic illustration of the swapping process in CH_4-C_2H_6-C_3H_8 ternary hydrates by CO_2.



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ABSTRACT

The replacement of CH_4-C_2H_6-C_3H_8 ternary hydrates in sandy sediments by gaseous and liquid CO_2 was studied to explore the gas recovery from structure II (sII) gas hydrate reservoirs. It was found that the swapping pattern in sII mixed hydrates is significantly different from that in the pure methane hydrate, which is a structure I (sI) hydrate. CH_4, C_2H_6 and C_3H_8 can be recovered heterogeneously from the mixed hydrates by CO_2 replacement. The results showed CH_4 was the easiest to replace in all of the experimental runs. In addition, there was a preferential release of C_3H_8 over C_2H_6 with higher mole ratio of CO_2 to initial hydrate. The guest-to-cavity size ratio was used to qualitatively study the gas exchange kinetics in the mixed hydrates. It was proposed that the isostructural conversion and structural transition coexisted in the mixed hydrates replacement. The spatial distribution of multiple components in the replaced hydrate particles was obtained by coupling gas production measurements with compositional analysis of the hydrate dissociation. It was found that further hydrate structure-transition from sII to sI occurred in deeper layers of the hydrate particles in replacement with higher mole ratio of CO_2 to initial hydrate. A power function relation was found to exist between the replacement efficiency and mole ratio of CO_2 to hydrate. These results are of significance for guiding successful sII hydrate recovery and CO_2 sequestration.

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1. Introduction

Gas hydrates, or simply hydrates, are nonstoichiometric crystalline compounds formed when guest molecules are entrapped in host frameworks of water molecules. Hydrates are found in three distinct structures: (1) structure I (sI) made up of pentagonal dodecahedron (5^{12}) and tetrakaidekahedron ($5^{12}6^2$) cages; (2) structure II (sII) composed of pentagonal dodecahedron and hexakaidecahedron ($5^{12}6^4$) cages; and (3) structure H (sH) including pentagonal dodecahedron [1]. Hydrates formed from pure CH_4, C_2H_6, or CO_2 are usually found to be sI. Gas mixtures containing larger guest molecules such as C_3H_8 and C_4H_8 readily form sII hydrates. Natural hydrates that form from methane, or a gas predominantly CH_4, are also usually sI. However, natural occurrences of sII hydrates have also been observed. These sII hydrates, which are formed from thermogenic hydrocarbons and mainly include C_1–C_4 hydrocarbons [2], were discovered in several places on the Earth; including the Gulf of Mexico and the Caspian Sea [3,4], Lake Baikal [5,6], the Qilian Mountain permafrost of China [7–9], and the Pearl River Mouth Basin of the South China Sea [10,11].

Natural gas hydrates have recently received considerable attention as a promising future energy source [12]. Current methods for gas hydrate production include depressurization [13], thermal stimulation [14], and inhibitor injection, which are all based on decomposition of clathrate crystals through external stimulations [15]. As the decomposition of gas hydrate may lead to destabilization of sediments, due to the removal of solid hydrate phase, and subsequent seafloor subsidence [16], the CO_2 replacement method has recently emerged as a promising method of recovering natural gas without hydrate dissociation. It also has the benefit of simultaneously sequestering CO_2 in the hydrate reservoir [17]. Since the idea of swapping CO_2 for CH_4 in gas hydrates was first proposed by Ohgaki et al. [18], extensive researches have been conducted around thermodynamic [19], heat/mass transfer [20], microscopic conditions [21], kinetics [22] and other aspects [23]. Most of the studies focus on the behavior related to the replacement of sI hydrates [24] due to their more common occurrence in nature. In these cases, the CH_4 hydrate goes through an isostructural replacement by CO_2, since CO_2 and any mixture composed of CO_2 and CH_4 form sI hydrates. The recovery efficiency of CH_4 is limited due to the preferentially replacement of CH_4 molecules in large cages by CO_2 molecules [25]. More recently, a binary CO_2-N_2 gas mixture was studied because of an enhanced replacement of the CH_4 molecules entrapped in the small cages by substitution with N_2 molecules [26]. This indicates the hydrate structure and the swapping pattern of multiple guests molecules play an important role in gas exchange process.

Compared with CH_4 hydrates, natural sII hydrates contain different cages and multiple guests with different sizes [1], which may lead to a unique swapping-pattern of sII hydrates. However, only a few reports have dealt with the swapping process of hydrocarbons with CO_2 in sII hydrates. Park et al. investigated the gas exchange in sII CH_4-C_2H_6 mixed hydrates using CO_2 and CO_2-N_2 gas mixtures. They observed a spontaneous structure-transition phenomenon of sII to sI during the replacement and a cage-specific distribution of guest molecules [26]. Schicks et al. studied the conversion of sII CH_4-C_2H_6 and CH_4-C_3H_8 mixed hydrates in CO_2 gas flow. Their results show that the more stable sII hydrate gradually converted into a less stable sI CO_2-rich hydrate, which should be induced by the chemical potential gradient between hydrate phase and the flow gas phase rather than pressure and temperature conditions [27]. Seo et al. reported an isostructural replacement of sII (C_3H_8 + CH_4) hydrate when a CO_2/N_2 (50:50) gas mixture was injected. They found that CH_4 in the small cages was replaced by N_2 and C_3H_8 in large cages was replaced by CO_2 [28]. Lee et al. [29] examined the CH_4-CO_2 replacement occurring in sII natural gas hydrates. Their results indicated that the initial sII hydrate underwent a structural transformation into sI hydrate as well as sII isostructural conversion and the portion of sI hydrate after replacement were closely related with the pressure of CO_2 injected. These reports show structural transformation and isostructural conversion may occur in the replacement of sII hydrates, which indicates the replacement mechanism in sII hydrates is significantly different from that in sI hydrates. However, the previous studies were mainly focused on binary hydrates of CH_4-C_2H_6 and CH_4-C_3H_8 mixed hydrates. There are no reports on the recovery of CH_4-C_2H_6-C_3H_8 ternary hydrates by CO_2 replacement even though multiple hydrocarbons exist in natural sII hydrates. Thus, the gas exchange behaviors of multiple hydrocarbons with CO_2 are not well understood. Although previous research showed that the state of CO_2 (gas versus liquid) had significant effect on the methane recovery for sI hydrate, the difference in sII hydrate replacement by gaseous and liquid CO_2 has rarely been examined. In addition, the hydrate replacement by CO_2 was found to be dominated by gas diffusion in hydrate phase [30,31], which led to a heterogeneous distribution of gas molecules in hydrate particles. However, the compositional evolution along the radial direction in hydrate particles was difficult to measure by traditional spectroscopic techniques.

The effects of factors such as pressure, temperature, particle size [32] on CO_2 replacement have been studied extensively. However, the majority of related research focused on qualitative analyses, and lack quantitative studies, especially regarding the replacement efficiency.

In this work, the replacement of $CH_4 + C_2H_6 + C_3H_8$ mixed hydrates by gaseous or liquid CO_2 is experimentally studied. Before the replacement, $CH_4 + C_2H_6 + C_3H_8$ ternary hydrates were synthesized in quartz sand sediments. During replacement, the guest-exchange behaviors of different hydrocarbons with CO_2 in mixed hydrates were examined by analyzing the compositional evolution of the fluid phase using gas chromatography (GC) to study the heterogeneous recovery of multiple components. After replacement, the dissociation of the replaced hydrates dissociated by depressurization was performed for further investigation, in which the spatial distributions of multiple components in the replaced hydrate particles were obtained by coupling gas production measurements with compositional analysis to study the gas exchange process in sII hydrate particles. Finally, the correlation between replacement efficiency and mole ratio of CO_2 to hydrate was analyzed.

2. Experimental section

2.1. Materials

Methane (99.99%), ethane (99.99%), propane (C_3, 99.99%) and CO_2 (99.99%) used in this study were all supplied by Beifang Special Gas Industry Corporation in China. The CH_4, C_2H_6, and C_3H_8 were then used in the preparation of (C_1-C_2-C_3) gas mixtures for forming the hydrates. Double-distilled and deionized water was used in experiments. The sediment was formed from 20 to 40 mesh quartz sands.

2.2. Experimental apparatus

A schematic of the experimental apparatus used in this work is shown in Fig. 1. The experimental apparatus consists of a high-pressure cell, a gas cylinder, a gas collector, and a data acquisition system. The high-pressure cell with an effective volume of 240 mL is a column made of stainless steel. The temperature is measured by secondary platinum resistance thermometer (type pt100). The pressure within the reactor was detected using a pressure transducer, and a target pressure is maintained by a back-pressure regulator. The uncertainties of pressure and temperature measurements in the system are ± 0.01 MPa and ± 0.1 K, respectively. Changes in the system temperature and pressure with respect to time are recorded and displayed on a computer.