Raman spectroscopic studies on carbon dioxide separation from fuel gas via clathrate hydrate in the presence of tetrahydrofuran

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HIGHLIGHTS

- Hydrate-based carbon dioxide separation was achieved in systems with and without gas supply.
- Hydrate formation interface and normal interface are generated.
- Raman peak intensity around interface is the weakest.
- Gas flux through the boundary layer around interface affects hydrate nucleation.
- Change of water molecules aggregation benefits for hydrate nucleation.

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ABSTRACT

Hydrate carbon dioxide (CO$_2$) separation is a promising method for reducing carbon emission. In this work, water-solubility of tetrahydrofuran (THF) was added into water to generate the single gas/liquid interface. In order to understand hydrate nucleation and crystallization well, CO$_2$ concentration in the residual gaseous phase was measured, morphology of the hydrate formation was filmed, and structure changes of compounds around the gas/liquid interface was monitored by in situ Raman spectrometer. Two groups of experiments were carried out at 274.15 K and 4.0 MPa in the systems with and without gas supply. The experimental results illustrate that hydrate formation is completed in 5 h according to CO$_2$ concentration, gas consumption and morphology, however, the compound transition and hydrate crystallization are still in process from the microstructure point of view. For the system with gas supply, the hydrates initially occur in the gas/liquid interface due to stable gas flux in the boundray layer, where Raman spectra change regularly at the beginning. Such stable gas flux has a positive impact on changing water aggregation. This change of water aggregation benefits for the original structures in the process of hydrate nucleation. With the hydrate formation, the hydrate nucleation interface is moving from the gas/liquid interface towards the THF solution. Otherwise, for the system without gas supply, no obvious hydrate was observed in the gas/liquid interface, and Raman spectra around the interface change with the saltation from gaseous phase towards the THF solution. For the two systems, THF hydrates form prior to the multi-hydrates and keep forming, and both intensity of Raman peaks around the interfaces is the weakest.

1. Introduction

Gas hydrate is a kind of ice-like inclusion compound formed by water molecules (host) and light hydrocarbon molecules (guest) under the sufficiently high pressure and/or relatively low temperature conditions. Water molecules constitute different cavities via hydrogen bonding, and guest molecules can be encapsulated into these cavities via van der waal force [1,2]. Generally, hydrate structure depends on the sizes of guest molecules. There are three prevalent hydrates, whose crystal texture include cubic structure I (sI), cubic structure II (sII) and hexagonal structure H (sH). Specifically, the sI hydrate is composed of two 12-hedra (5^{12}) and six 14-hedra ($5^{12}6^2$); the sII hydrate is

composed of sixteen 12-hedra (5^{12}) and eight 16-hedra ($5^{12}6^4$); and the sH hydrate is composed of three 12-hedra (5^{12}), two 12-hedra ($4^35^66^3$) and one 20-hedra ($5^{12}6^8$).

Based on the properties of environmental friendly, high gas capacity and different selectivity of gas molecules, various technological applications have been widely investigated, such as gas separation technology [3–6], gas storage technology [7–9], water desalination [10,11] and carbon dioxide (CO_2) sequestration [12–15]. For hydrated-CO_2 separation, because CO_2 molecules can encage into the hydrate cavities by controlling hydrate formation condition with mild pressure and suitable temperature, the CO_2 capture process via hydrates is a promising method for separating and recovering CO_2 from fuel, flue gas or biogas [16–20]. However, the hydrated-CO_2 separation technologies fail to be utilized in industry owing to low hydrate formation rate and poor separation efficiency.

In order to accelerate the hydrate formation rate and enhance the gas separation efficiency, two different ways are widely applied, including changing the gas-liquid contact [20], adding thermodynamic hydrate promoter and kinetics hydrate promoter [21–23]. For changing the gas-liquid contact, Liu et al. [24] separated CO_2 in water-in-oil (W/O) emulsions and adopted TBAB and CP as the synergistic thermodynamic promoter. It proved that CO_2 can be effectively entrapped into the hydrate with two-stage separation and H_2 concentration can be concentrated from 53.6 mol% to 84.6 mol%. Li et al. [25] concentrated CO_2 from 38.6 mol% to 93.0 mol% by adding the TBAB and CP. CO_2 concentration in the residual gaseous phase can be decreased from 40.0 mol% to 13.2 mol% in the 0.29 mol% TBAB solution with the scale-up equipment [26]. After optimizing conditions of the hydrate formation, it can be reduced down to 8.9 mol% [27]. By adding the hydrate promoters, Lee et al. [28] separated CO_2 in the 1.0 mol% THF solution and proved that CO_2 concentration was enhanced from 39.9 mol% up to 88.0 mol%. Babu et al. [17] separated CO_2 in the different TBAB solution and concentrated CO_2 from 63.5 mol% to 95.2 mol% in the 0.3 mol% TBAB solution. Tetrahydrofuran (THF) as an excellent thermodynamic hydrate promoter is widely adopted into the researches of CO_2 capture.[4,29–32] In the process of hydrate formation, THF molecules take part in the hydrate formation, resulting in reducing the hydrate formation pressures significantly [33]. In particular, THF molecules encage into large cavities of the hydrate with a priority, forming the sII THF hydrates, subsequently, CO_2 molecules or other small gas molecules entrap into small or large cavities to form the multi-hydrates [34]. As a result, THF shows an excellent character on both moderating the thermal condition and accelerating the hydrate formation rate. For CO_2 recovery from integrated gasification combined cycle (IGCC) syngas via hydrate process, Zhong et al. [4] adopted THF combining with cyclohexane (CH) as the mixed thermodynamic hydrate promoter to separate CO_2 from CO_2/H_2 gas mixture. By adding 1.0 mol% THF and 10 vol% CH, the thermal state of hydrate formation was moderated, and CO_2 selectivity from CO_2/H_2 gas mixture was enhanced. Although the hydrate formation rate and the CO_2 separation efficiency can be improved based on above-mentioned methods, the essential factors leading to these results fail to be reported.

To understand the mechanism of CO_2 hydrate formation in the complicated systems with hydrate promoters, structure determination of the hydrates become the hot issue among the researchers. Microscopic structure analysis, such as power X-ray diffraction (PXRD), Raman spectroscopy, magnetic resonance imaging (MRI) and so on, are introduced into the studies on hydrate formation. For instance, Xia et al. [18] adopted gas solvent (dimethyl sulfoxide, DMSO) combining with TBAB as the synergic additive to capture CO_2 and recover H_2 from fuel gas and determined the hydrate structures using Raman spectrometer. It found that DMSO failed to participate the hydrate formation and only had the impact on gas dissolution and gas diffusion from gaseous phase to bulk solution. According to Raman spectra, Song et al. [35] also proved that the heavy metal ions also failed to participate the hydrate formation in the hydrate-based process for heavy metal

separation. In the system of THF and SDS, Yang et al. [36] investigated the thermodynamic and kinetic properties of hydrate formation and dissociation in the hydrate-based CO_2 separation from fuel gas via MRI. Meanwhile, they performed the hydrate formation and dissociation process using MRI in the silica gel and saline water system [37]. Besides, the simulation methods are also introduced to understand the CO_2 hydrate formation process in theory. Chazallon et al. [38] adopted in situ Raman spectrometer to understand the structure changes of semi-clathrate hydrate containing TBAB, CO_2 and N_2. Paweł and Joanna [39] calculated NMR properties of cages forming sI and sII clathrate hydrates of CO_2, and reported the intermolecular OH transmitted through hydrogen bonds H···O and the covalent H−O bonds. It supplied a useful method to figure out the properties of framework (host) constructed by water molecules via hydrogen bonds and the environment of CO_2 molecules (guest) encaged into the hydrate cavities. For CO_2 sequestration and CO_2 replacing the methane, Velaga et al. [40] calculated the potential energy surface between water and CO_2 to predict the cage occupancies using quantum mechanical method and molecular dynamics simulations. Martos-Villa et al. [41] evaluated the hydrate structures and behavior of the hydrate formation in the interlayer of Na-rich montmorillonite and beidellite smectite using molecular dynamics simulations. Besides the simulation calculation, little microscopic structure information near the gas/liquid interface and hydrate nucleation for hydrate-based CO_2 separation can be found in the lab.

In this work, in order to obtain microscopic structure information around gas/liquid interface and further understand the hydrate nucleation process well, the water-soluble hydrate promoter of THF was adopted to produce the single gas/liquid interface. Two different groups of experiments were achieved to generate two different interfaces, including hydrate formation interface and the normal interface. One group of experiments were carried out in the systems with continuous gas supply to keep the crystallizer pressure constant, generating the hydrate formation interface, and the other group were carried out in systems without gas supply in the constant volume, generating the normal interface. For each group, the gas composition in the residual gaseous phase were measured by gas chromatography (GC), the morphology of the hydrate formation was filmed by camera, the structures of the compounds near the gas/liquid interface, in the bulk solution and in the hydrates were monitored using in situ Raman spectrometer, and the hydrate crystals are determined by PXRD.

2. Experimental section

2.1. Material

The CO_2/H_2 gas mixtures with CO_2 concentration of 40.0 mol% was supplied by Foshan Huate Special Gas Co., Ltd., tetrahydrofuran (THF) with purity of 99.9%, supplied by Chengdu Best Reagent Co., Ltd. Distilled deionized water, produced by an ultrapure water system with a resistivity of 18.25 MΩ cm^{-1}, was used to prepare all solution.

2.2. Apparatus

The experimental apparatus was used in this work as shown in Fig. 1. It consists of a crystallizer with the inner volume of 115 mL, a water bath jacketing outside the crystallizer, a refrigeration system, a data-acquisition system, and a real-time Raman spectrometer. More details of apparatus can be found in our previous work. [42] All the experiments were carried out in four same crystallizer.

2.3. Procedure

In this work, two different groups of experiments were achieved in the same crystallizers. One group of experiments were carried out in the systems with continuous gas supply to keep the crystallizer pressure