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## Raman Spectroscopic Study on Hydrate-based Carbon Dioxide Separation from Fuel Gas in the Presence of THF

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### Abstract

Carbon dioxide (CO<sub>2</sub>) capture via clathrate hydrate is a promising method for reducing carbon emission. In this work, the water-solubility (tetrahydrofuran (THF)) was adopted to capture CO<sub>2</sub> and recover hydrogen (H<sub>2</sub>) from fuel gas via clathrate hydrate at 274.15 K and 4.00 MPa. In order to understand hydrate nucleation and crystallization well from view of macroscopic morphology and microscopic structure, the CO<sub>2</sub> concentration in the gaseous phase was measured by GC, the morphology of the hydrate formation was filmed by camera, and the structure changes of compounds in and around the gas/liquid interface was monitored by *in-situ* Raman spectrometer. The experimental results shows that the hydrate formation is completed in 5 hours in view of CO<sub>2</sub> separation and macroscopic morphology, however, the compounds transition and hydrate formation are still in process from view of microscopic structure. The hydrate initially occurs in the gas/liquid interface due to the enough contact between CO<sub>2</sub> and THF solution. With the hydrate formation, the hydrate nucleation interface is moving from the gas/liquid interface towards the THF aqueous solution. Finally, the THF-CO<sub>2</sub> binary hydrate are subsided into the bulk solution in the form of hydrate layer. The aggregate state of water molecules around the gas/liquid interface is beneficial to construct the framework of the hydrate. It might be related to the original structures in the initial hydrate nucleation process.

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## 1. Introduction

Gas hydrate is the inclusion compound formed by water molecules (host) and guest molecules under high pressure and/or low temperature. Water molecules crystallize different cavities by the hydrogen bonding, and guest molecules can be encapsulated into the cavities via van der waal force.[1] Because of the great selectivity of CO<sub>2</sub> and gas uptake capacity, the hydrate-based CO<sub>2</sub> separation process is regarded as a promising method for recovering CO<sub>2</sub> from flue gas, fuel gas and biogas.[2, 3] However, the thermal condition and the hydrate formation rate limit its utilization.[4, 5] In order to moderate the thermal condition, accelerate the hydrate formation rate and enhance the CO<sub>2</sub> separation efficiency, thermodynamic hydrate promoter tetrahydrofuran (THF) is widely investigated. Zhong et al. [6] adopted THF combining with cyclohexane (CH) to separate CO<sub>2</sub> from CO<sub>2</sub>/H<sub>2</sub> gas mixture via hydrate process. The thermal state was moderated and the CO<sub>2</sub> selectivity was enhanced by adding 1.0 mol% THF and 10 vol% CH. Veluswamy et al.[7] investigated the macroscopic kinetics of the semi-clathrate hydrate (TBAB) and sII hydrates (THF and cyclopentane (CP)) for H<sub>2</sub> storage via hydrate. THF was superior to accelerate the THF/H<sub>2</sub> hydrate formation rate in comparison with TBAB and CP. Lee et al. [8] separated CO<sub>2</sub> in the 1.0 mol% THF solution and proved that the CO<sub>2</sub> can be concentrated up to 88.0 mol%. After optimizing the condition, CO<sub>2</sub> concentration can be reduced down to 8.9 mol% with bubbling. [9] Such hydrate-based CO<sub>2</sub> separation refers to the hydrate promoter, the gas/liquid contact, etc. However, its mechanism still fails to be clear.

Therefore, micro-structure analysis methods, such as x-ray power diffraction (XRD), Raman spectroscopy, nuclear magnetic resonance (NMR) and the simulation methods are introduced to understand the CO<sub>2</sub> hydrate formation process. For example, Xia et al. [4] adopted gas solvent (dimethyl sulfoxide, DMSO) combining with TBAB as the synergic additive to capture CO<sub>2</sub> from fuel gas and determined the hydrate structures using Raman spectrometer. It was testified that DMSO failed to participate the hydrate formation and only had impact on gas dissolution and gas diffusion from gaseous phase to bulk solution. Chazallon et al. [10] adopted in-situ Raman spectrometer to understand the structure changes of semi-clathrate hydrate containing CO<sub>2</sub>. Velaga et al. [11] calculated the potential energy surface between water and CO<sub>2</sub> to predict the cage occupancies using quantum mechanical method and molecular dynamics simulations. However, little experimental micro-structure changes of compounds near the gas/liquid interface and nucleation information can be found. In this work, the morphology and structure of compounds near the gas/liquid interface and in the bulk solution were investigated. In addition, the CO<sub>2</sub> concentration in gaseous phase was measured by gas chromatography (GC). The experiments were carried out in the 1.0 mol% THF solution at 274.15 K and 4.00 MPa.

## 2. Experimental section

### 2.1. Materials

The CO<sub>2</sub>/H<sub>2</sub> gas mixtures with CO<sub>2</sub> 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, was used to prepare all solution.

### 2.2. Procedure

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. [12] After the crystallizer was cleaned and dried, the solution containing water (CO<sub>2</sub> saturated water) and water-soluble promoter was added into the crystallizer. Then, the temperature of the jacket filled with water and ethylene glycol aqueous solution was controlled by the refrigeration system with the temperature of 274.15 K. When the temperature was constant, the gas was introduced into the crystallizer and pressurized up to 4.00 MPa. All the experiments were

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