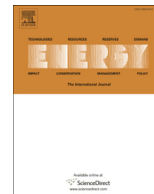




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# Raman analysis on methane production from natural gas hydrate by carbon dioxide–methane replacement

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## ABSTRACT

Using CO<sub>2</sub>–CH<sub>4</sub> (carbon dioxide–methane) replacement to produce CH<sub>4</sub> from NGH (natural gas hydrate) is not only a new CH<sub>4</sub> production technology but also a direct way to disposal CO<sub>2</sub> by CO<sub>2</sub> hydrates. Although there are many studies focusing on the mechanism of CH<sub>4</sub> replacement in hydrates by CO<sub>2</sub>, the mechanism of the replacement is still not clear. In this work, the replacement process and hydrate structure change are tracked and investigated by Raman and NMR (nuclear magnetic resonance) spectra. By comprehensively analyzing the Raman and NMR spectra, we infer the mechanism of the replacement and the hydrate structures. Conclusions are drawn as, on one hand, CH<sub>4</sub> molecules are fully replaced with the gas–solid interface, but partly replaced in deeply inner hydrates by CO<sub>2</sub> molecules; on the other hand, the CO<sub>2</sub> hydrate and CH<sub>4</sub> hydrate coexist in a type of structure I (sI) and there is no structure transformation during the replacement. The research results are important to further confirm the mechanism of the replacement and reveal factors restraining efficiency of the CH<sub>4</sub> production.

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## 1. Introduction

People are facing two difficult problems. One is the decrease of nonrenewable fossil energy like oil, coal and natural gas, the other is the continually growing demand for energy. As a result, people are devoting themselves to concerning about the projects of the sustainable energy supply. NGHs (Natural gas hydrates), scattering in sea floor and permafrost regions, contain plenty of carbon resources. In the light of a conservative estimate, the carbon resources are nearly twice as many as that of the proven fossil on the Earth [1,2]. Moreover, the estimated natural gases in the form of clathrate hydrates are up to 50 times of the conventional petroleum reserves, with as much as 2500–2000 trillion cubic meters of methane being available [3]. Thus, the NGH is considered as an alternative energy for the future.

Since the early 1990s, producing methane from the NGHs has been widely investigated. There are three conventional

technologies of CH<sub>4</sub> production from the NGH, (1) thermal stimulation [4,5], injecting hot water, steam, or hot brine to heat the hydrate reservoir to more than the hydrate dissociation temperature, (2) depressurization [6–8], extracting to free gas from the hydrate reservoir to lower the reservoir pressure below the equilibrium pressure, (3) chemical inhibitor stimulation [9], injecting chemical inhibitors such as methanol or ethylene glycol into the hydrate reservoir to shift the hydrate equilibrium conditions. Recently, a new technology combined thermal stimulation and depressurization has been developed to improve CH<sub>4</sub> recovery and gas production rate [10]. The application of all these technologies is based on shifting the natural gas/water/NGH (three-phase) equilibrium conditions into the NGH dissociation side. However, the dissociation of NGH might destruct the geology, resulting in seriously environmental and geological disasters. Therefore, researchers devote themselves to developing a safer production technology. Meanwhile, the plentifully manmade emissions of CO<sub>2</sub> cause the continuous rise of greenhouse gas in the atmosphere with the use of the fossil fuels [11]. Thus, it is pressing to reduce the carbon emission. The IPCC (Intergovernmental Panel on Climate Change) reported that CCS (carbon capture and sequestration) is one likely technical protocol for the carbon emission reduction [12]. Producing CH<sub>4</sub> from the NGH by CO<sub>2</sub>–CH<sub>4</sub> replacement is based on the difference of thermodynamic stability between CH<sub>4</sub> and CO<sub>2</sub>

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hydrates. The method provides a way for CH<sub>4</sub> recovery and long-term storage of CO<sub>2</sub> simultaneously. In addition, the method potentially benefits to stabilize the ocean floor and the permafrost zones during the production. The destruction resulted from the CH<sub>4</sub> production from NGH by the CO<sub>2</sub>–CH<sub>4</sub> replacement can be neglected because there are negligible changes in the structures between CH<sub>4</sub> hydrates and CO<sub>2</sub> hydrates [13].

Ohgaki et al. [14] first proposed the conception of CH<sub>4</sub> production from the NGH by the CO<sub>2</sub>–CH<sub>4</sub> replacement in 1996. In their study, a new three-phase (gas–water–hydrate) equilibrium system (containing CO<sub>2</sub>/CH<sub>4</sub> gas, H<sub>2</sub>O and hydrate) spontaneously formed after the CO<sub>2</sub> was injected into the CH<sub>4</sub>–H<sub>2</sub>O–hydrate three-phase system. In the new system, CO<sub>2</sub> molecules competed against CH<sub>4</sub> molecules with occupying the large hydrate cavities, resulting in the release of CH<sub>4</sub>. Hirohama et al. [15] and Komai et al. [16] agreed with the conception and carried out the relative work to support the conception. Nakano et al. [17] successfully recovered the ethane (C<sub>2</sub>H<sub>6</sub>) from C<sub>2</sub>H<sub>6</sub> hydrate by CO<sub>2</sub> replacement. Yezdimer et al. [18] and Geng et al. [19] proved the thermodynamic feasibility of CO<sub>2</sub>–CH<sub>4</sub> replacement in hydrate by MD (molecular dynamics) simulation. The Gibbs free energy ( $\Delta G$ ) of  $-3.49 \text{ kJ mol}^{-1}$  of the CO<sub>2</sub>–CH<sub>4</sub> replacement reaction in the conditions of 275.2 K and 3.25 MPa was obtained by Ota et al. [20], and it indicates the replacement is a spontaneous reaction. Presently, pure CO<sub>2</sub> [21,22], liquid CO<sub>2</sub> [23] and CO<sub>2</sub> emulsion [24,25] are used to replace CH<sub>4</sub> from methane hydrate by CO<sub>2</sub>–CH<sub>4</sub> replacement. The common conclusions were drawn as follow: one, the CH<sub>4</sub> recovery rate obtained in the studies is quite low; the other, the displacement reaction rate at the initial stage is significantly faster than that at the mid or later stage. Uchida et al. [26] and Ota et al. [27] established different kinetic models to investigate the restraint of the replacement based on the experimental data. Uchida et al. [26] considered a CH<sub>4</sub> recovery as a function of time ( $t$ ), and CH<sub>4</sub> recovery increased with  $t$ . However, in the later stage of the real replacement reaction, CH<sub>4</sub> recovery had few changes with  $t$ . Ota et al. [27] thought the displacement reaction included two processes, CH<sub>4</sub> hydrate dissociation and CO<sub>2</sub> hydrate formation. In Ota et al.'s model, CH<sub>4</sub> recovery was a function of the difference of fugacity between CH<sub>4</sub> and CO<sub>2</sub> in the gas and hydrate phases. Therefore, the dissociation of CH<sub>4</sub> hydrate and the diffusion of CO<sub>2</sub> in the system were defined as the two crucial factors in the CH<sub>4</sub> recovery. Nevertheless, the micromechanism and the hydrate structures during the replacement were still not clear.

Thus, in order to deeply reveal the mechanism of the CO<sub>2</sub>–CH<sub>4</sub> displacement reaction, Raman and NMR (nuclear magnetic resonance) are employed to investigate the hydrate structures and components in this paper. Through the analysis of the spectra, the mechanism of the CO<sub>2</sub>–CH<sub>4</sub> displacement and the hydrate structures are inferred.

## 2. Experimental section

### 2.1. Apparatus and materials

The experimental apparatus is shown in Fig. 1. The zone marked with a dash line shows a hydrate formation/dissociation reactor with an inner volume of 100 ml. The reactor is made of 316 stainless steels, and its maximum operating pressure is around 10 MPa. Two viewing quartz windows are mounted on front/back sides of the reactor. The reactor is wrapped by a water bath jacket which is full of EG (ethylene glycol) solution. The set of device containing the reactor and the jacket is designed by our team. The volume ratio of EG to water is approximately 1:3. The temperature of the water bath is controlled by a cooling system. The operating temperature of the water bath ranges from 253.15 K to 303.15 K. We carefully calibrate the temperature difference between the reactor and the water bath, and we find the temperature of the water bath is 1.5 °C higher than that of the reactor in the operating temperature range of 253.15 K–279.15 K. The temperature of the water bath is measured using a Pt1000 thermocouple (JM6081) with uncertainties of  $\pm 0.1 \text{ K}$ . The reactor directly connects CO<sub>2</sub> tank, CH<sub>4</sub> tank and air through three gas tubes, respectively. A Raman spectrometer (LabRam, Jobin Yvon) is employed to investigate the hydrate components and hydrate structures, and Raman spectra are obtained through a 50 $\times$  tele lens.

The CH<sub>4</sub> and CO<sub>2</sub> gases with a purity of 99.9% are supplied by Foshan Huate Gas Co., Ltd. The chemically pure EG is supplied by Jinan Kaijun Chemical Ltd. The de-ionized water with the resistivity of  $18.25 \text{ m}\Omega \text{ cm}^{-1}$  is produced with an ultra-pure water machine which is supplied by Nanjing Ultrapure Water Technology Co., Ltd.

### 2.2. Procedure

The de-ionized water of 60 ml is injected into the reactor, which is evacuated in advance. Then, the system temperature is reduced to 274.15 K by the cooling system. The CH<sub>4</sub> is continuously pumped from the CH<sub>4</sub> tank into the reactor to 4.0 MPa. In this experiment, no stirring is employed to mix the content. As the gas dissolves in water and forms CH<sub>4</sub> hydrate, the additional gas is supplied from the gas tank to maintain the pressure at 4.0 MPa. If there is no gas supplied into the reactor for more than 72 h, the hydrate formation completes. Then, the residue CH<sub>4</sub> in gas phase is released via the released valve to the atmosphere after the system temperature quickly drops down to 258.15 K. Then, the CO<sub>2</sub> is quickly pumped from the CO<sub>2</sub> tank into the reactor to recover the system pressure at 4.0 MPa. Meanwhile, the temperature quickly rises to 274.15 K. In the condition of 274.15 K and 4.0 MPa, CO<sub>2</sub> exists in liquid, and it fills most of the vacancy, leaving small space for residue CH<sub>4</sub> gas in the reactor. Then, CO<sub>2</sub> gradually displaces CH<sub>4</sub> from the hydrates. A rectangle lens-tube is employed to make the Raman spectrometer close to the visual window. Due to special requirement of the Raman spectrometer, the whole experimental equipment is placed in a closed and dark room where temperature and humidity are controlled by air conditioner and air humidifier, respectively. During the displacement process, Raman spectra of gas phase, liquid phase and hydrate phase are obtained every half an hour through the visual window mounted on the reactor. The Raman spectroscopy with a single monochromator of 1800 grooves/mm grating

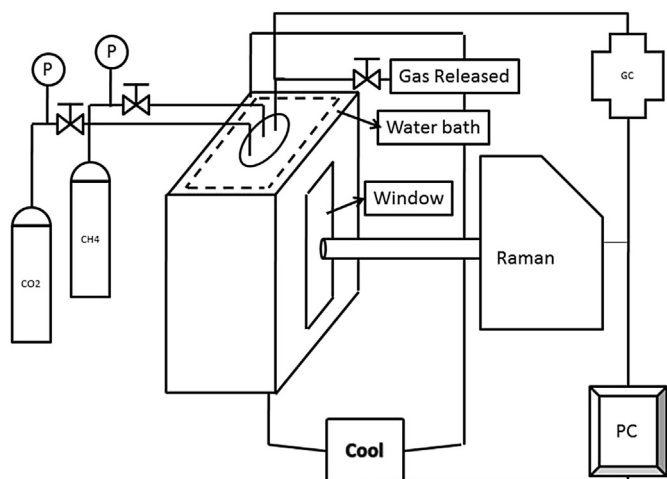


Fig. 1. Schematics of the experimental apparatus.

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