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EFFECT OF INJECTING N2/H2 ON METHANE HYDRATE DECOMPOSITION

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ABSTRACT

Injections of pressurized carbon dioxide in natural gas hydrates have attracted a number of attentions because it can simultaneously serve as a means of methane gas exploitation and greenhouse gas sequestration. It has been found that gas recovery could be significantly enhanced by adding small molecules gases such as nitrogen or hydrogen into injected gas mixture. In this work, the Raman spectroscopy, gas chromatography and charge coupled device were used to study the effect of injecting small molecule gases on the methane hydrate decomposition.

Keywords: Gas hydrates exploitation, decomposition, nitrogen, hydrogen.

1. INTRODUCTION

Gas hydrate is one of the backup energy resources which have raised wide attention [1]. This ice-like solid resource is distributed widely in all over the world, mainly in the seabed and permafrost zone. Many institutes are making substantial efforts in gas hydrate exploitation. CH_4-CO_2 replacement is a promising hydrate exploitation approach, because it could not only serve as a mean of continuously exploit clean gases, but also achieve the purpose of burying greenhouse gases [2]. This methane production approach could provide a stable reservoir for CO_2 sequestration in the deep see floor or permafrost zone, and avoid geologic hazards caused by the collapse of hydrate.

The exchange process between CO_2 and CH_4 hydrate has been studied in numerous laboratory experiments and computer simulations [3]. Many studied have confirmed the truth that the CH_4 recovery could be significantly improved by adding small molecules gases such as N_2 to injected CO_2 gas [4-6]. Sun et al. proposed a combined exploitation technology by integrating CO_2/H_2 injection and CH_4 production with in situ steam reformation of CH_4, in which the involved separation of CO2/H2 is much easier than that of CH_4/N_2 [7, 8]. Waage et al. studied the diffusion of gas mixtures in the sI hydrate using molecules simulation techniques [9]. They suggested that using a mixture of CO_2/H_2 as injection gases could boost the bulk diffusivities of both CH_4 and CO_2 in sI hydrate.

Precious studies have focused on the effects of injecting CO_2-containing mixtures on methane hydrate decomposition. However, few papers have reported on the roles of small molecular gases in the decomposition of methane hydrates. In this work, Raman spectroscopy and charge coupled device (CCD) were used to compare the effects of pure depressurization process and depressurization after H_2/N_2 injection on methane hydrate decomposition. At the same time, the change of gas composition in the high pressure optical cell (HPOC) was analyzed by gas chromatography.

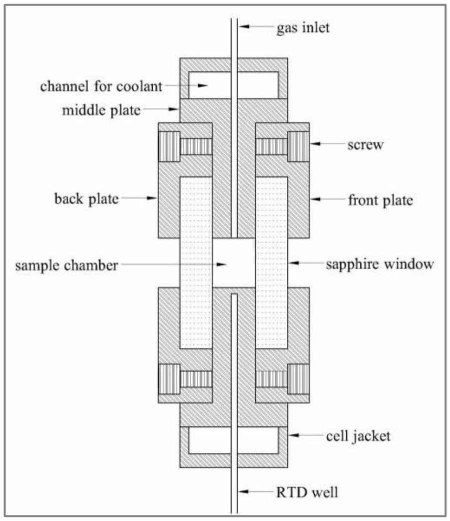


Fig. 1 Schematic of HPOC

2. EXPERIMETNAL SECTION

2.1 Material and methods

CH_4, N_2 and H_2 gas with a mole fraction purity of 99.99 % were both supplied by the Beijing Haipu Gas Company. LTD. The deionized water used was produced by a water distillation unit from Shanghai Yarong Biochemistry Instrument Factory.

Fig. 2 shows the schematic of experimental apparatus used in the work. The HPOC shows in the fig. 1 have been provided in our previous work [10]. A JYB pressure transducer (±0.02 MPa) installed on the gas inlet line was used to measure the pressure in the cell. A HORIBA XploRA Raman system equipped with a 1800 grooves·mm-1 grating and 20x microscope objective. A 532 nm wavelength laser, with excitation power of 20 mW, was focused on a fixed middle spot on the hydrate surface in all experiments, and the focused diameter was approximately 5 µm. The spectral resolution was 1 cm-1. The decomposition process was recorded by CCD. And the production gas was analyzed by the gas chromatography.

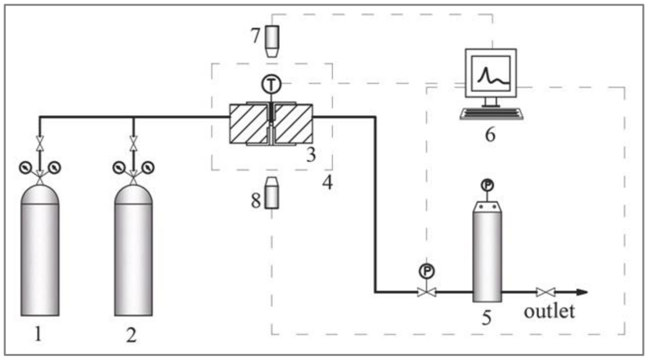


Fig. 2 Schematic graph of experimental apparatus includes:1 CH_4 cylinder, 2 injection gas cylinders, 3 HPOC, 4 water bath, 5 production gas cylinder, 6 computer, 7 Raman laser, 8 CCD.

2.2 *Experimental procedure*

The procedure for hydrate formation was similar to that used in our previous work [10]. When the CH_4 hydrate sample was formed, the small molecule gases N_2/H_2 was slowly pressed into the HPOC from the injection gas cylinder until the experimental pressure was reached. The Raman spectra of the hydrate sample surface were measured at this time to observe whether the small molecule gases entered the methane hydrate cages. After gas injection, the pressure in the reactor would drop slightly. When the pressure in the HPOC was stable, slowly decrease the pressure until the methane hydrate began to decompose. The process of hydrate decomposition was recorded by CCD. The real-time temperature and pressure data of the sample-forming chamber were collected using a monitor and control generated system.

2.3 *Results*

2.3.1 Depressurization

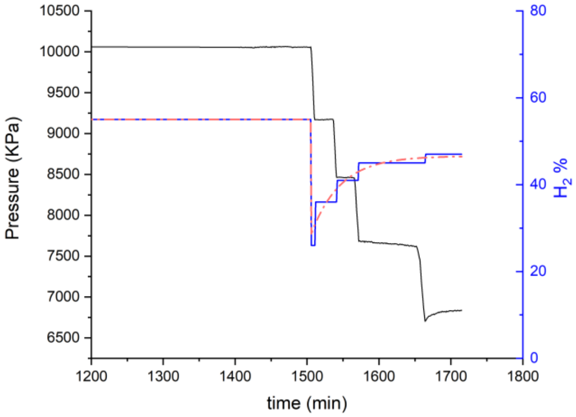


Fig. 3 Changes of pressure and H_2 content with time during depressurization

The CH_4 hydrate was formed at 4560 KPa and 275.15 K. H_2 was injected into the HPOC to 10080 KPa (CH_4:H_2 = 1:1.2). After 3 days, the pressure in HPOC was stable at 9800 KPa. Thereafter, the pressure in the HPOC was slowly decreased, and the production gas components were measured by gas chromatography.

The changes of pressure and H_2 content with time during the depressurization is shown in Fig. 3. At the initial stage of the depressurization, the H_2 content was much lower than the initial value. With the process of depressurization, the H_2 content in production gas increased gradually. When the CH_4 hydrate began to decompose, the depressurization was stopped. The final value of H_2 content was slightly lower than the initial value. It could be concluded that at the stage of injection H_2, the small molecule gas was absorbed by CH_4 hydrate, which caused the pressure decreased in the HPOC. In the process of depressurization, the small molecule gas escaped from the hydrate layer in the result from the main gas phase pressure gradually decreasing. The content of small molecule gas in the production gas increased.

As shown in Fig. 4, the peaks centered at 4130 cm^{-1} which corresponding to H-H stretching frequency in hydrate cages hadn't been measured, while the peaks centered at 4160 cm^{-1} which corresponding to H-H stretching frequency in gas phase had been measured. It meant that H_2 didn't enter the cages to form hydrate, while diffused in the form of gases in CH_4 hydrate.

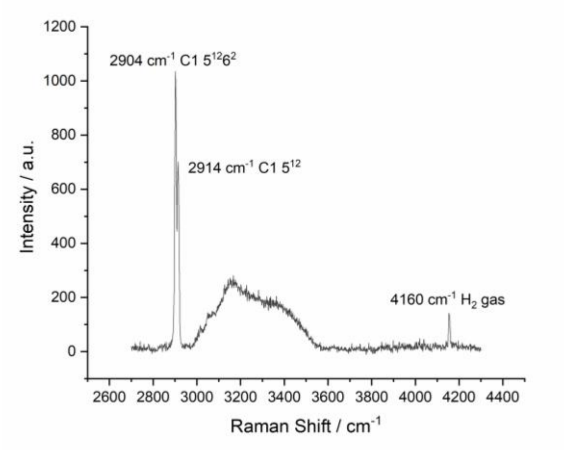
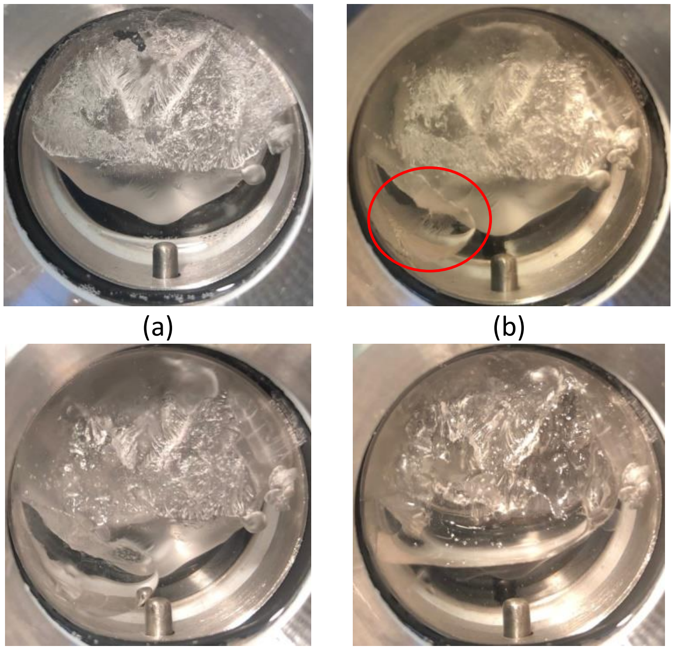


Fig. 4 Raman spectrum of H_2 in CH_4 hydrate

2.3.2 Decomposition



(a) (b)

(c) (d)

Fig. 5 The process of hydrate decomposition

As shown in Fig. 5, during the process of H_2 injection-depressurization, the part of hydrate which contacted with water decomposes first. During the decomposition, bubbles began to appear at the bottom of hydrate, as shown in Fig. 5(b). The Raman spectrum of bubbles is shown in Fig. 6, the bubbles contained large amounts of CH_4 and H_2 gas. The reason for this phenomenon is that the heat transfer coefficient at the bottom of the HPOC was large than other positions due to a part of water that wasn't converted into hydrate remained at the bottom of the HPOC. This means that the heat absorbed by the decomposition of this part of hydrate would soon be compensated.

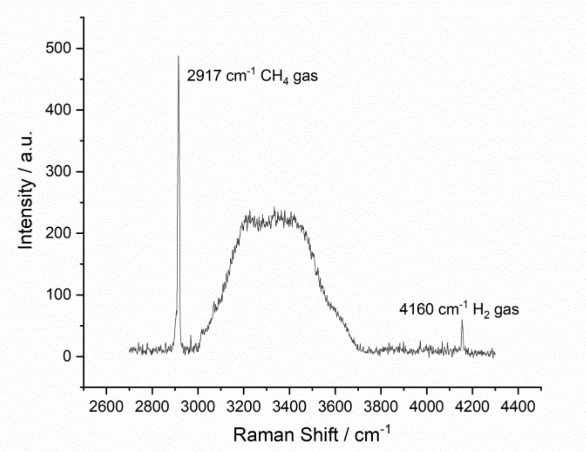


Fig. 6 Raman spectrum of bubbles

Different content of small molecule gases were injected into the HPOC. The decomposition pressures of different CH_4 content during the depressurization are shown in Fig. 7. For the CH_4 hydrates injected with different content of H_2, the higher the H_2 content, the lower the proportion of CH_4 in the HPOC, and the higher the decomposition pressure of CH_4 hydrate during depressurization. Meanwhile, the experiments of N_2 injection had the same trend.

Comparing the experiments of injection different types of small molecule gases, it was found that the decomposition pressures of H_2-injection were higher than N_2-injection. The diffusion process of H_2 and N_2 in CH_4 hydrate was measured by Raman spectroscopy, it was found that the diffusion factor of H_2 was larger than that of N_2.

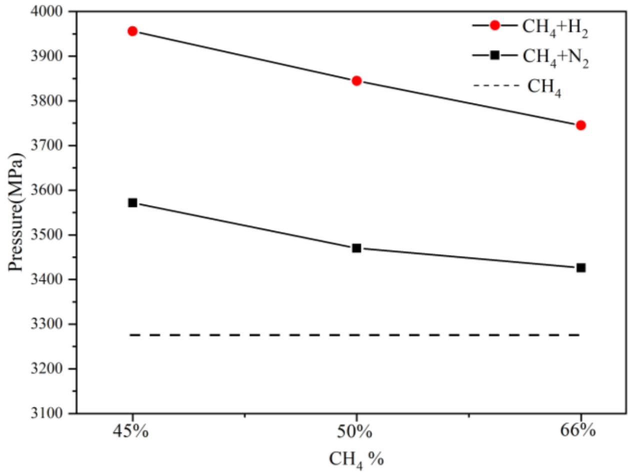


Fig. 7 Decomposition pressure of different CH_4 content

2.4 Discussion

In this work, the decomposition pressures of CH_4 hydrates which injected small molecule gases were found to be higher than that of CH_4 hydrate undergone the pure depressurization. Combining the changes of the small molecule gas content during the depressurization, it could be deduced that CH_4 hydrate absorbs a certain amount of small gas molecules, which resulted in a part of CH_4 hydrate located in the gas phase environment that the proportion of small molecule gases were higher than that in the main gas phase. As a result, the partial pressure of CH_4 in local hydrate reached the equilibrium pressure before that in main gas phase. Therefore, the decomposition pressures of hydrates which undergone injection-depressurization process were higher than pure depressurization.

2.5 Conclusions

Injection of small molecule gases such as H_2 or N_2 could promote the decomposition and increase the decomposition pressure of hydrate. Because the diffusion factor of H_2 in CH_4 hydrate is larger than that of N_2, the amount of H_2 absorbed in the hydrate is larger than N_2, so the promotion of H_2 to hydrate decomposition is stronger than N_2.

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