Peculiarity of CO_2/H_2 Hydrate Decomposition: The Equilibrium Decomposition Temperature Seems to be Affected by Different H_2 Molecule Occupation

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ABSTRACT

It is well known that H_2 molecule can more easily migrate between hydrate cages and realize multiple molecule occupation due to its small molecular diameter. In this work, several splitting DSC endothermic peaks for CO_2/H_2 hydrate decomposition in constant pressure and 29.5% CO_2 + 70.5% H_2 gas composition were unexpectedly found through a high pressure micro-differential scanning calorimeter (HP μ-DSC). These DSC decomposition peaks have the typical characteristics with several different hydrates coexisting. The dissociation temperatures corresponding to these peaks showed obvious regularity that the temperatures for those first peaks and last peaks are almost close to the equilibrium decomposition temperature of the CO_2/H_2 hydrate with the similar gas phase component and pure CO_2 hydrate respectively. We speculate that the occurrence of this peculiar phenomenon may be mainly due to the different occupation of H_2 molecules in CO_2/H_2 hydrate cages. This led to the metastable change of hydrate equilibrium conditions, and therefore resulted into the delayed decomposition. Raman spectra confirmed the various occupation of H_2 molecules in CO_2/H_2 hydrate cages under this experimental conditions. The finding in this study may provide some new insights into the deeper understanding of the physical/chemical properties behind clathrate hydrates in the future.

Keywords: CO_2/H_2 hydrate, splitting DSC endothermic peaks, metastable hydrate equilibrium conditions, different H_2 molecule occupation

1. INTRODUCTION

Gas hydrate is a non-stoichiometric crystalline compound formed by host hydrogen-bonded water molecules and small gas molecules under certain temperature and pressure conditions [1]. In addition to CH_4, C_2H_6, C_3H_8 and other natural gas, hydrate can also be the reservoir for smaller H_2 molecules [2].

Although it is difficult for H_2 to stabilize the cage structure of clathrate hydrate alone due to the small molecule diameter [3], however, it is also this small diameter that determines the special properties of H_2 in the hydrate formation. For example, a single hydrate cage can be occupied by several H_2 molecules simultaneously even under some mild conditions [4, 5], and H_2 molecule is easier to transfer between hydrate cages [6, 7]. These properties are hard to be possessed by larger gas molecules such as CH_4 and CO_2.

As we all known that clathrate hydrate stability is directly related to the guest to cavity size ratio, and there is a one-to-one relationship between hydrate decomposition temperature and system pressure with constant gas phase composition [1]. In this work, however, it was unexpectedly found that the DSC thermograms for CO_2/H_2 hydrate dissociation have the typical decomposition characteristics of multiple hydrates, and the highest decomposition temperature was even close to pure CO_2 hydrate. In situ Raman spectroscopy were used for analyzing the H_2 molecular occupation in hydrate cages. We consider that the appearance of these phenomena should be related to the small molecule properties of H_2.

2. EXPERIMENTAL SECTION

2.1 Materials

The CO_2/H_2 mixed gases and CO_2 gas with a purity of 99.99% were supplied by the Beijing Beifen Gas Industry Corporation. The quartz sands were purchased from Yifeng Quartz sands Co. Deionized water with a conductivity less than 10^{-4} S· m^{-1} was used.

2.2 Experimental apparatus and procedures

A high pressure micro-differential scanning calorimeter (HP μ-DSC7 Evo, Setaram Inc.) and a Raman spectrometer were used. The schematic diagram of the DSC is shown in Fig. 1. More information about the apparatus were detailed elsewhere in literatures [8, 9].
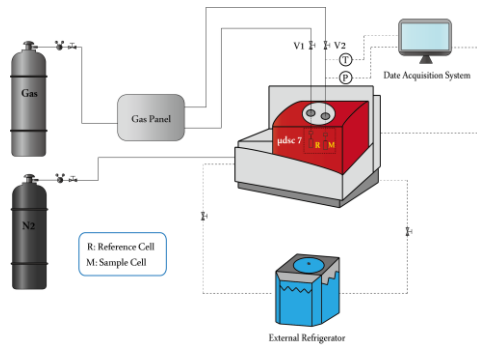
Fig. 1. Schematic diagram of DSC setup

In the DSC experiments, only a small amount of deionized water (0.02 g) was loaded into the sample cell to maintain the almost constant gas phase composition after hydrate formation. The two cells were vacuumed and injected with CO_2/H_2 mixed gas to specified pressure for hydrate formation. In the hydrate formation process, a multicycle mode of cooling-heating was employed for the complete conversion of water to hydrate, as is illustrated in Fig. 2. In the multicycle, the temperature was cooled to 263.15 K (1.0 K/min) for water freezing and heated to 275.15 K (1.0 K/min) for ice melting. The DSC heat flow change with temperature is shown in Fig. 2a. The positive and negative heat flow values corresponding to heat release and absorption respectively. Therefore, the gradually diminishing exothermic and endothermic peaks indicates the progressive transformation of water to hydrate. After the complete conversion, the temperature was heated to 293.15 K (0.5 K/min) for the hydrate decomposition. The equilibrium dissociation temperature and dissociation enthalpy of hydrates can be determined by the DSC endothermic peak, as is displayed in Fig. 2d. For a single endothermic peak, the decomposition

temperature of hydrates is generally identified by DSC onset temperature, which has been proved the high accuracy [10, 11]. Interestingly, however, there were multiple splitting DSC decomposition peaks for CO_2/H_2 hydrate obviously, which has the typical characteristics with several different hydrates coexisting.

In the Raman experiment, the same experimental steps were used. In addition, to avoid gas phase interference, the hydrates compositions were measured in water phase.
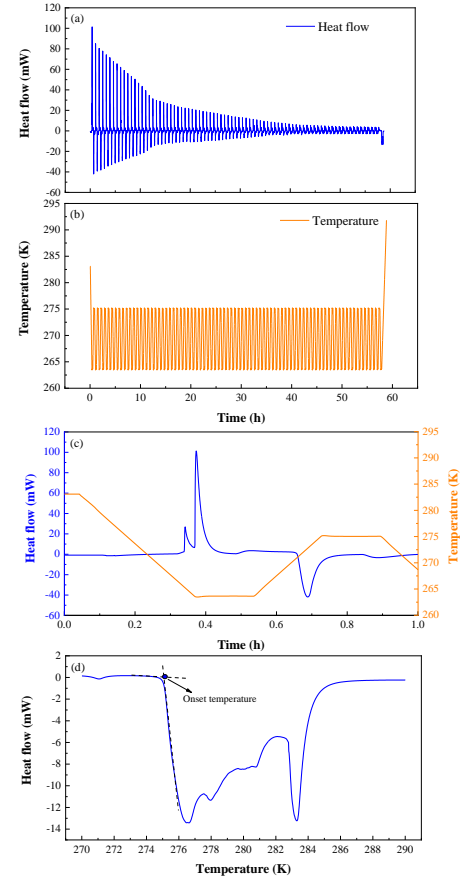
Fig. 2. Typical DSC thermograms of cooling-heating multicycle for CO_2/H_2 hydrate formation and decomposition in Run 3. (a) DSC thermogram in the whole process, (b) temperature change in the whole process, (c) changed temperature and corresponding DSC thermogram during the first cycle, (d) DSC endothermic thermogram during the last heating process for CO_2/H_2 hydrate decomposition, in which the onset temperature was determined as the hydrate dissociation temperature for a single DSC endothermic peak

3. RESULTS AND DISSCUTION

3.1. Peculiarities of DSC thermograms for CO_2/H_2 hydrate dissociation

Generally, there is only one DSC decomposition peak for one hydrate in their decomposition process. In the case where multiple different hydrates coexist

simultaneously, the DSC thermogram will show multiple splitting endothermic peaks due to the decomposition temperature differences. Curiously, the hydrate formed by the CO_2/H_2 mixed gas also presented more than one obvious DSC decomposition peak during its decomposition, as shown in Fig. 2d. The decomposition temperature corresponding to the last DSC peak was even much higher than the equilibrium temperature of the possibly formed pure CO_2 hydrate in the system. Consequently, we had a comparison of the DSC thermograms for the decomposition of CO_2/H_2 binary hydrate with simple CO_2, binary CO_2/N_2 and CH_4/H_2 hydrates, as illustrated in Fig. 3. It can be found that the temperature span of dissociated CO_2/H_2 hydrate in the DSC thermogram was extremely wide and multiple DSC endothermic peaks occurred. In particular, the last peak was extremely obvious. For the CO_2/N_2 system, there were also two obvious splitting DSC peaks, while for the CH_4/H_2 and pure CO_2 systems, they mainly presented a single DSC endothermic peak.

Table 1. DSC experimental conditions and results for CO_2/H_2 hydrate dissociation with different gas component at various pressure

Runs	Gas component (CO_2/H_2)	Pressure (MPa)	First onset [a] temperature (K)	Last onset [a] temperature (K)	ΔH_d (J/g water)
1		6.51	274.43	282.41	457.02
2		7.29	275.37	282.75	441.91
3	0.295/0.705	8.00	275.95	282.8	446.92
4		8.87	276.4	282.9	455.19
5		10.05	277.15	283.23	459.09

[a] There were multiple endothermic peaks in the DSC thermograms of CO_2/H_2 hydrate decomposition, in which the first and last onset temperatures correspond to the first and last endothermic peaks respectively
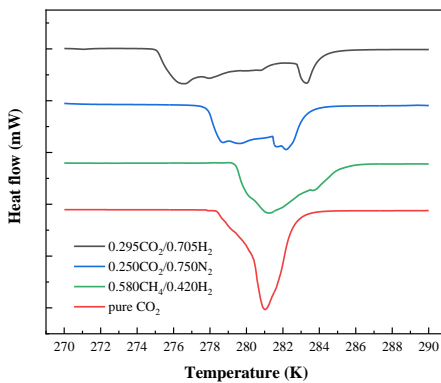

Fig. 3. Comparison of DSC peaks for hydrate dissociation in 29.5% CO_2 + 70.5% H_2 gas system at 8.0 MPa, 25.0% CO_2 + 75.0% N2 gas system at 9.05 MPa, 58.0% CH_4 + 42.0% H_2 gas system at 12.0 MPa and pure CO_2 gas system at 2.4 MPa respectively

To prove the universality of the peculiar phenomenon, the hydrate decomposition under different system pressures were investigated. The experimental conditions and results are listed in Table 1. The DSC thermograms of dissociated CO_2/H_2 hydrate in 29.5 % CO_2 + 70.5% H_2 mixed gas system at different pressures is displayed in Fig. 4. It can be found that the hydrates decomposed at each pressure showed multiple endothermic peaks, while the shape and size of the endothermic peaks were distinctly different. For the pressure at 6.51 MPa, the multiple peaks phenomenon

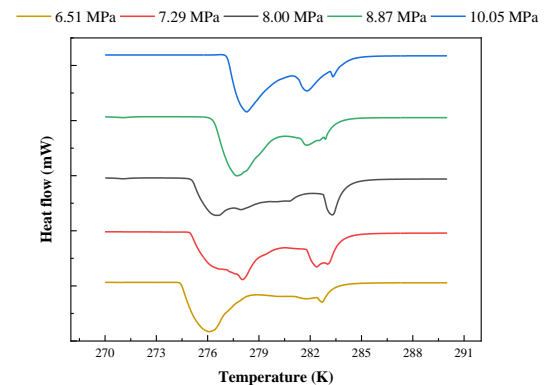was the weakest. However, it does not show increasing diversity trend with the increased pressure.

Fig. 4. DSC endothermic peaks for dissociated CO_2/H_2 hydrate at various pressure of 29.5% CO_2 + 70.5% H_2 mixed gas

3.2. The stability condition of CO_2/H_2 hydrate discriminated by DSC decomposition peaks

Fig. 5 presents the temperatures and pressures corresponding to the first and last peaks in the DSC thermograms of dissociated CO_2/H_2 hydrates in Fig. 4. It can be found that the temperatures and pressures for the first peaks are approximately consistent with the equilibrium decomposition conditions of the CO_2/H_2 hydrates formed by the similar gas component reported in the literature, which confirms the formation of the same hydrates. Surprisingly, the temperatures and pressures corresponding to the last DSC peaks under

different gas phase pressures also showed obvious regularity, and are close to the equilibrium decomposition conditions of pure CO_2 hydrate. It seems to indicate that there was indeed the formation of pure CO_2 hydrate. However, this interpretation is problematic. Because the pressure in Fig. 5 is the total gas phase pressure, while the partial pressure of the CO_2 gas phase is only aroud 2.0 MPa. So even if pure CO_2 hydrate was formed, it should decompose at significantly lower temperatures. In consideration of the relationship between hydrate stability and guest molecular diameter, we speculated that the various occupancies of H_2 molecules in CO_2/H_2 hydrate cages resulted in the different hydrate decomposition temperatures. For the last DSC endothermic peak corresponding to the highest temperature, it may be due to the co-occupation of H_2 and linear CO_2 molecule in $5^{12}6^2$ cages.
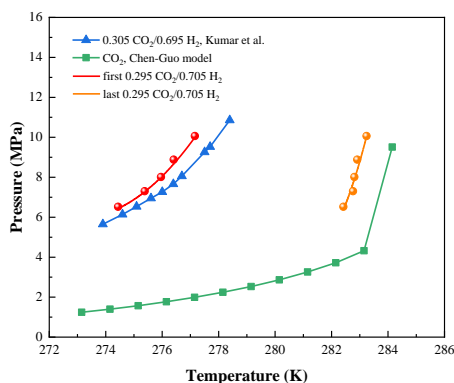

Fig. 5. Comparison of the DSC onset temperatures of the first and last peaks for dissociated CO_2/H_2 hydrates in this study with the equilibrium decomposition temperatures of CO_2 hydrate calculated from Chen-Guo model [12] and CO_2/H_2 hydrates measured by Kumar et al. [13]

3.3. Raman measurement on H_2 molecule occupation

Fig. 6 presents the H_2 gas Raman peaks and several typical Raman characteristic peaks for H_2 molecules in the hydrate formed by 29.5% CO_2 + 70.5% H_2 gas mixture. There are four Raman peaks for H_2 molecules in gas phase, of which the strongest peak locates in 4152 cm^{-1}. For the hydrate phase, the peaks at 4122 cm^{-1} and 4126 cm^{-1} correspond to the H_2 molecules in 5^{12} cages and $5^{12}6^2$ cages of sI hydrate respectively [14]. For the strong Raman peaks of 4152 cm^{-1} measured at some points, it may be due to the co-occupation of H_2 molecules and linear CO_2 molecules in the $5^{12}6^2$ cage. In addition, according to our limited knowledge, this study is also the first report about H_2 molecules occupying sI hydrate cages under such mild conditions.
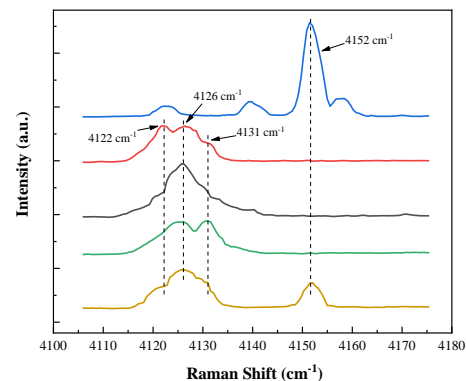

Fig. 6. H_2 gas (blue line) Raman peak and several typical Raman characteristic peaks for H_2 in CO_2/H_2 hydrate submerged in water phase

4. CONCLUSION

In this work, the multiple splitting DSC endothermic peaks for CO_2/H_2 hydrates decomposition with constant gas pressure and composition were unexpectedly found. These DSC peak shapes are completely different from the endothermic peak of single hydrate decomposition, but have the typical characteristics with several different hydrates coexisting. The dissociation temperatures corresponding to these peaks showed obvious regularity that the temperatures for those first peaks and last peaks are almost close to the equilibrium decomposition temperature of the CO_2/H_2 hydrate with the similar gas phase component and pure CO_2 hydrate respectively. We speculate that the occurrence of the peculiar phenomenon may be mainly caused by the different occupation of H_2 molecules in hydrate cages, which resulted in metastable hydrate state. The Raman experiment results confirmed the various occupation of H_2 molecules in CO_2/H_2 hydrate cages, and the co-occupation of H_2 molecules and linear CO_2 molecules in $5^{12}6^2$ cage may also be detected. This study may also be the first report showing that H_2 molecules can occupy sI hydrate cages under such mild conditions.

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