CH4 Hydrate Formation on the Surface of a Gas Bubble in Simulated Deep Water Environment with Different Depth

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ABSTRACT

Seabed methane seepage is a ubiquitous phenomenon in deep-sea environments and on continental margins, affecting the ocean and global carbon cycle. As one of the world's largest methane reservoirs, natural gas hydrate (NGH) is an important barrier for methane capture. However, the formation of hydrate shells on the surface of CH4 bubbles seeping into the water column may also assist in the migration of methane to the shallow sea and even into the atmosphere. Therefore, it is necessary to reveal the formation characteristics of hydrate film on the surface of CH4 bubble. In this work, the evolution of CH4 hydrate formation on a bubble surface and the dissolved CH4 concentration in the surrounding aqueous phase were simulated in different simulated ocean depth environments by using the suspended bubble method. The results showed that higher subcooling for hydrate formation leaded to smoother initial hydrate film, and the hydrate bubble was prone to flexible collapse due to faster gas consumption. In contrast, for dense and thick hydrate films, the occurrence of pressure difference between the internal and external of the film can lead to brittle collapse of the hydrate shell. The Raman measurement results basically corresponded to the morphological evolution phenomenon. In addition, it was found that the formation of hydrate film on the bubble surface weakened the mass transfer from the gas phase to the liquid phase, making the CH4 dissolution rate almost equivalent in different pressure environments. This work can provide important fundamentals for assessing the flux of methane leakage into shallow water in the marine environment.

Keywords: CH4 hydrate, gas bubble surface, subcooling, morphology, Raman

1. INTRODUCTION

Methane is an important fuel for human activities and the second most vital greenhouse gas contributing to global warming [1]. Seabed methane seeps are found everywhere on continental margins and are an momentous source of methane to the atmosphere. Preliminary estimates suggest that methane released from the seafloor accounts for 5-10% of the current global atmospheric input [2]. The study of the fate of seafloor methane seepage processes is an important basis for understanding the ocean and global carbon cycle.

Natural gas hydrates (NGH) are ice-like substances that form at high pressures and low temperatures, and are also known as methane hydrates because methane is their main gas component. NGH is mainly distributed in permafrost zones and submarine sediments around the world [3], among them, the formation/decomposition of NGH in the marine environment is closely related to the sequestration and evolution of seeping methane. On the one hand, as one of the largest methane reservoirs in the world, NGH formation in seafloor sediments is a special process that blocks the free emission of methane from the seafloor [4]; On the other hand, for CH4 bubbles leaking into the ocean, a CH4 hydrate shell may form on its surface within the CH4 hydrate stability domain, which may reduce the diffusion of its gaseous methane into the surrounding water phase during the bubble's ascent, thus allowing the methane to reach shallower depths in the water column or even the atmosphere before it is heavily dissolved[5]. It has been shown that the formation of hydrate shells can slow down the transport of methane from the bubbles to seawater by up to 80%[6]. Therefore, it is important to study the formation evolution of methane bubble surface hydrate and its influence law to explore the transport process of methane in the water column.

During the migration of seeping methane bubbles from the seafloor to shallow waters, the driving force for their conversion to methane hydrate changes gradually due to the changing temperature and depth of their environment. Due to different propulsion conditions, the properties of the hydrate film formed on the surface of methane bubbles will change accordingly. Therefore, it is important to investigate the evolution of methane bubble surface hydrate formation by the driving force corresponding to different depths of the ocean environment in order to reveal the oceanic and global methane fate. However, previous studies involving hydrate formation on the surface of methane bubbles have mainly focused on the formation of hydrates with subcooling below Conditions of 2 K [7, 8]. There are major differences with the conditions of high subcooling of hydrate formation in the marine environment, especially in the deep sea.

Cold seep is a geological phenomenon that methane-rich fluid overflows from the seabed sediment interface, is direct evidence of methane seepage from the seafloor. "Haima" cold seep is a typical active cold seep with the water depth of 1200-1400 m, which is firstly discovered in the Western area of the northern slope of the South China Sea in 2015 [9]. In this paper, we investigated the generation-evolution characteristics of CH4 bubble surface hydrate in different ocean depths in the cold spring area of "Haima" using Raman spectroscopy-optical microscopy. The results of this study can provide fundamental data for the investigation of the evolution of methane leakage from the seafloor.

2. MATERIAL AND METHODS

2.1 Materials

Methane gas with a purity of 99. 99% was supplied by Guangdong Yuejia Gas Co. Ultrapure water was supplied by Waters Technology (Shanghai) Co.

2.2 Experimental apparatus and procedures

The experimental system used in this study is shown in Figure 2. The effective volume of the reactor used in the experiment is 10.0 mL, and the maximum load pressure is 25 MPa. A more detailed description of the reactor can be found in our previous study [10]. This experiment was extended to investigate the changes of hydrate film on the surface of bubbles by the suspended bubble method[8, 10]. However, because of the high subcooling conditions involving hydrate formation, the suspended bubbles were not brought into contact with the top gas-liquid interface to avoid severe downward pressure at the top. In all experiments, 5.0 mL of deionized water was first injected into the reactor. Then, the system temperature was cooled to 277.15 K and kept constant. After that, the reactor was evacuated and CH4 gas was injected from the top to make the system pressure much higher than the hydrate formation pressure to accelerate hydrate nucleation. After the formation of CH4 hydrate at the gas-liquid interface the system was depressurized to decompose the hydrate and to repeat the memory effect of the excited water several times. Subsequently, CH4 gas is injected from the bottom of the reactor and suspended in bubbles at the lower injection port and a hydrate film is formed. Afterwards, the hydrate film evolution over time was measured and recorded by Raman spectroscopy and optical microscopy.



Fig. 1 Schematic diagram of the experimental setup

3. RESULTS AND DISCUSSION

In this study, three sets of experiments on the evolution of CH4 hydrate film formation on the bubble surface under different subcooling degrees were conducted, and their corresponding ocean gradient environments and hydrate formation driving forces are shown in Figure 2. It should be noted that the effect of subcooling is more obvious compared to the effect of temperature variation on hydrate formation, so in this study, the temperature is kept constant and the pressure conditions are only changed to achieve the simulation of hydrate film formation evolution on the surface of CH4 bubbles at different depths of the ocean environment.

study				
Runs	Gas component	Т(К)	P(MPa)	$ riangle T_{sub}(K)$
1	CH₄	277.15	6.00	2.17
2		277.15	10.00	6.17
3		277.15	14.00	10.17

Table 1 Experimental investigation conditions in this study



Figure 2 Ocean gradient and CH4 phase equilibrium diagram

3.1 Evolution of CH4 hydrate film morphology on the bubble surface

Figure 3 shows the effect of different subcooling conditions on the morphological evolution of the CH4 hydrate film on the bubble surface. From the comparison of the initial morphology, it can be found that the larger the subcooling degree, the smoother the hydrate film on the bubble surface is. For the 14 MPa condition, the CH4 hydrate film can even reflect the optical microscope head, indicating that the initial hydrate particles on the surface of the film are extremely fine. Observing the changes of hydrate film with time under each condition, it can be found that the hydrate film depresses inward at different pressures as the hydrate film gradually thickens, and the depression time shortens with the increase of subcooling degree. For the subcooling degree of 10.17 K, the obvious depression of hydrate bubbles appeared only 3 min, and by 35 min, the suspended hydrate bubbles collapsed from the bottom. The more rapid inward depression of the hydrate bubble is mainly related to the faster gas depletion rate inside the bubble. The gas depletion inside the hydrate bubble leads to the pressure disparity between the inner and outer sides of the hydrate film, and the pressure on the outer side is greater than that on the inner side, which leads to the depression. In contrast, the hydrate vesicle morphology only shows a relatively slight change at 6.17 K subcooling, indicating that the average gas consumption rate inside and outside the hydrate vesicle is similar at this condition. It is noteworthy that at 2.17 K subcooling, the change is very weak until 20 min, while at 36 min, the hydrate film shows a local "seismic" collapse. This collapse may be mainly related to the more dense hydrate film microscopic morphology. Unlike the depression at higher pressures, this collapse leads to the appearance of a large number of new gasliquid interfaces, which is beneficial to the overall hydrate growth rate, but also to the transport of free gas through the newly formed thin hydrate film and its dissolution in the surrounding water phase.



3.2 Changes in Raman spectra during hydrate film thickening

Figure 4 and Figure 5 exemplify the variation of Raman spectra on hydrate vesicles and their corresponding hydrate local morphology under experimental conditions of 6 MPa and 10 MPa, respectively. As can be seen from Fig. 4, the hydrate film is initially formed with a very strong CH4 gas phase peak, while almost no CH4 hydrate peak is visible. A weak hydrate peak can be measured until about 25 min, when the gas-phase CH4 peak is significantly weakened. By 54 min, the intensity of the hydrate relative to the gas phase had increased significantly, while the absolute intensity of the gas phase peak had decreased significantly. This indicates that for this pressure condition, the hydrate forms a denser hydrate within a relatively short period of 1 h, thereby reducing the density of pores on the membrane. In contrast, for the 10 MPa pressure condition in Figure 5, the weak CH4 hydrate peak is only detected at around 38 min of hydrate formation, and the intensity of the CH4 hydrate peak is almost constant by 63 min. The intensity of the gas phase peaks also remained almost unchanged during the experimental cycle. This Raman spectral phenomenon corresponds to some extent to the overall morphological evolution of the hydrate vesicles in Figure 3. In particular, the thicker and denser hydrate film at 6 MPa may be responsible for the collapse phenomenon in Figure 3.





Figure. 4 Variation of Raman spectra (a) and local morphology (b-d) at 6 MPa



Figure. 5 Variation of Raman spectrum (a) and local morphology (b-d) at 10 MPa

Figure 6 shows the relative content of dissolved CH4 in the aqueous phase adjacent to the hydrate bubble as function of time, as measured by Raman spectroscopy. It can be observed that the amount of dissolved methane in each system gradually increases with time. The increase in dissolved methane is probably due to both a small transfer of CH4 from the gas phase to the aqueous phase within the hydrate bubble and the decomposition of the CH4 hydrate film. This is because the dissolved methane content in the system is relatively low due to the low pressure of the system before the inlet gas reaches the target pressure. When the system pressure increases and hydrates are formed, CH4 is transferred from the gas phase as well as from the hydrate to the water phase in order to reach a three-phase gas-liquid-hydrate CH4 equilibrium. However, the rate of increase is very similar for different pressure conditions, rather than the faster methane dissolution rate at higher system pressures. This largely reflects the inhibition of gas-phase CH4 dissolution to the liquid phase by the formation of CH4 hydrate bubbles, allowing a shift from gas-liquid equilibrium driven CH4 dissolution to three-phase equilibrium driven CH4 dissolution. This is a good example of the role of methane bubble surface hydrate formation in controlling methane gas dissolution in a methane seeping marine environment.



Figure 6 Variation in the relative content of dissolved CH4 in the aqueous phase adjacent to the hydrate bubble

4. CONCLUSIONS

In this work, the evolution of hydrate formation on the surface of CH4 bubbles and the dissolved CH4 concentration in its surrounding water phase were investigated for different oceanic water depth environments. Experimental results show that subcooling differences in can affect hydrate morphological characteristics. Higher subcooling for hydrate formation resulted in a smoother initial hydrate film surface. In addition, the hydrate bubble was prone to flexible collapse due to relatively faster gas consumption inside the hydrate bubble. In the experiments with relatively low subcooling, the brittle collapse of the hydrate shell due to the thicker and film thickness happened. The denser Raman measurement results almost corresponded to the morphological evolution phenomenon, in which an inverse change in Raman intensity between the hydrate and gas occurred. In addition, it was found that the formation of hydrate films on the bubble surface attenuated the CH4 mass transfer from the gas phase to the aqueous phase, making the CH4 dissolution rates essentially equivalent in different pressure environments. This may be related to the shift in mass transfer driving force from the gas-liquid two-phase to the gas-liquid-hydrate three-phase.

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