



Investigating the partial structure of the hydrate film formed at the gas/water interface by Raman spectra



Xin-Yang Zeng^{a,1}, Jin-Rong Zhong^{a,1}, Yi-Fei Sun^a, Sheng-Li Li^b, Guang-Jin Chen^a, Chang-Yu Sun^{a,*}

^a State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

^b The college of construction engineering, Jilin University, Changchun 130012, China

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ABSTRACT

The morphology and structure of hydrate films of pure methane and methane+ethane mixtures were studied by suspending a single gas bubble in liquid water. The methane+ethane gas mixtures, containing 20 mol% or 81–89 mol% methane, were used to form hydrate films with different crystal structures. Polyhedral structures appeared on the background of uniform polycrystalline hydrate films formed by gas mixtures with a high methane mole fraction of 0.81–0.82. Some of the polyhedral structures are holes, and others are separated structure II polyhedral hydrate crystals. However, for pure methane, a gas mixture with a lower CH₄ mole fraction of 0.2, or a gas mixture with a higher CH₄ mole fraction of 0.89, the morphology is uniform through the whole hydrate film. The crystal structures in the hydrate film were determined using in situ Raman spectra. The results show that both pure methane and the gas mixture with a lower CH₄ mole fraction of 0.2 form a hydrate film with structure I. The single polyhedral crystal appeared in the background of the uniform polycrystalline hydrate film formed by gas mixtures with a high methane mole fraction of 0.81–0.82 as a structure II CH₄-C₂H₆ double hydrate crystal. The hole is mainly gas with an initial small amount of structure I hydrate, and that hole will be filled with structure II hydrate after a certain time. The experimental methods and the new findings presented in this work should be significant for the further research of hydrate growth kinetics.

1. Introduction

Gas hydrates are nonstoichiometric crystalline solids containing guest molecules within the cages formed by the host hydrogen-bonded water molecules at low temperatures under high pressure conditions (Sloan and Koh, 2007). Three common clathrate hydrate structures have been identified: cubic structure I (sI), cubic structure II (sII) and hexagonal structure H (sH) (Koh et al., 2012). Hydrates have been of increasing interest, mainly because huge amounts of natural gas hydrate deposits have been found in oceanic and arctic sediments and are considered a potential new energy resource (Koh et al., 2012; Li et al., 2012; Joskow, 2013; Reagan et al., 2014; Song et al., 2014; Bhade and Phirani, 2015). However, gas hydrates have drawn attention in the natural gas and oil industries since the 1930s because it had been recognized that hydrate formation might lead to plugging of gas pipelines (Jamaluddin et al., 1991; Peng et al., 2012; Zha et al., 2012; Joshi et al., 2013; Sami et al., 2013; Yan et al., 2014; Osfouri et al., 2015). Understanding the kinetic behaviour of gas hydrate

formation is fundamental to both the utilization of hydrates and the prevention of hydrate plugging. In general, gas hydrate formation is initiated at the water/guest-fluid interface. Once a hydrate crystal forms at the interface, that crystal grows in the lateral and vertical directions at the interface, thereby forming a hydrate film with a certain thickness between the water and the guest fluid (Freer et al., 2001; Mori, 2001; Lee et al., 2005; Mochizuki and Mori, 2006; Peng et al., 2007; Sun et al., 2007; Lehmkuhler et al., 2008; Turner et al., 2009; Liang and Kusalik, 2011; Li et al., 2014a, 2015).

The morphology and growth rate of the hydrate film at the water/guest-fluid interface are significant for the overall study of hydrate formation kinetics. For a hydrate film formed from pure methane, ethane, and carbon dioxide at the gas/water interface (Freer et al., 2001; Taylor et al., 2007; Davies et al., 2010), on the surface of a gas bubble suspended in water (Peng et al., 2007; Sun et al., 2007; Li et al., 2013), or at a water drop interface (Uchida et al., 1999, 2002; Daniel-David et al., 2015; Li et al., 2015), the hydrate morphologies were usually uniform, and no heterogeneous morphology was observed,

* Corresponding author.

E-mail address: cysun@cup.edu.cn (C.-Y. Sun).

¹ These authors contributed equally to this work.

although mesoporous structures for the migration of gas molecules or water molecules within these pores exist (Hirata and Mori, 1998; Davies et al., 2010; Li et al., 2015). The morphology of hydrate film is influenced by factors such as subcooling, composition of the gas/liquid, and additives. The morphologies of hydrates formed with a methane+ethane+propane mixture in bulk liquid water were studied (Watanabe et al., 2011), and the degree of subcooling and the methane mole fraction in the gas mixture were found to affect the morphology of the hydrate crystals. Saito et al. (2010) also studied the morphologies of hydrates formed with methane+ethane+propane gas mixture on the surface of a water droplet. The crystal size was found to decrease with increasing methane concentration in the gas mixtures. In addition, the crystal size for the hydrate formed from the gas mixture was smaller than the crystal size from simple methane hydrates.

Li et al. (2014b) studied the growth kinetics of the hydrate film on the surface of methane-ethane bubbles suspended in water. A relationship between the gas composition and the hydrate morphology was studied and, when the methane mole fraction of the gas mixtures increased to 0.834 and even 0.923, the crystal morphology became leaf-like or dendritic, which is significantly different from hydrate films formed from pure ethane, pure methane, and mixtures with the methane mole fraction ranging from 0.190 to 0.620. The leaf-like morphology observed could possibly be attributed to the formation of sII methane-ethane double hydrates according to the research of Murshed and Kuhs (2009) and Subramanian et al., (2000a, 2000b). Another characteristic of hydrate films formed by gas mixtures with high methane mole fractions (0.834 and 0.923) observed by Li et al. (2014b) was the heterogeneous shapes. Li et al. observed the perfect polyhedral single crystals among the dendritic crystals formed by gas mixtures with the highest methane mole fraction of 0.923. The edges of these polyhedral crystals were very clear and similar to those of single crystals of pure methane hydrate. The single crystal was possibly pure methane sI hydrate. Li et al. (2014b) attributed this type of heterogeneous morphology to the coexistence of sI and sII hydrates and argued that the appearance of methane hydrate crystals might have been caused by the very high local concentration of methane near the main dendritic crystals due to the relatively faster consumption of ethane. However, they gave no direct proof to support their hypotheses. In this work, hydrate films of pure methane and methane+ethane mixtures were studied by suspending a single gas bubble in liquid water to investigate the possible heterogeneous morphology and structure. With a certain composition of methane+ethane mixtures, polyhedral structures, holes or separated polyhedral crystals were observed to appear on the background of the uniform polycrystalline hydrate film. The structural type of the hydrate crystals at different position of the hydrate film were determined using Raman spectra. The heterogeneous holes were also found to be different from mesopores in the hydrate film.

2. Method

2.1. Materials

Four groups of hydrate-forming gas mixtures, (20 mol% CH₄+80 mol% C₂H₆), (81 mol% CH₄+19 mol% C₂H₆), (82 mol% CH₄+18 mol% C₂H₆), and (89 mol% CH₄+11 mol% C₂H₆) used in this work were prepared in our laboratory. The purity of CH₄ and C₂H₆ used in the preparation was 99.99%, and both gases were purchased from Beijing Haipu Gas Co. Deionized water with a conductivity less than 10⁻⁴ S·m⁻¹ was used.

2.2. Experimental apparatus

A high-pressure cell, illustrated in Fig. 1(a), was manufactured and used in this work. The cell is composed of three stainless steel plates fixed together by screws, i.e., the front plate, the middle plate, and the

back plate. Channels were built in for coolant circulation and temperature control. The maximum work pressure and volume of the cell are 20 MPa and 10 mL, respectively. The cell contains two sapphire windows to permit laser light and an optical microscope to probe the hydrate film from its back and front sides, as shown in Fig. 1(a). The growth of the hydrate film can be observed by optical microscope and a Charge Coupled Device (CCD) camera recorder, and the structure types of hydrates can be confirmed via Raman spectroscopy. Details of the CCD camera were provided by Peng et al. (2007) and Li et al. (2013). A well, drilled in the bottom of the middle plate, allows for a temperature-sensing device (RTD) to be placed into the cell. One gas inlet at the top of the middle plate allows gas in the cell to connect to a pressure sensor. Another gas inlet at the bottom of the middle plate allows for gas flow into the sample cell to form a gas bubble.

The high-pressure cell is fixed on a three-dimensional spiral micrometer platform to cause laser light to accurately probe the desired point on the hydrate film, as shown in Fig. 1(b). The accuracy of the micrometer is 0.001 mm. The whole apparatus is shown in Fig. 2.

Raman spectra have been used successfully to determine the structure of the hydrate for pure gas and gas mixtures (Subramanian et al., 2000a, 2000b; Kumar et al., 2008; Ohno et al., 2009; Sun et al., 2010; Luzi et al., 2012; Seo et al., 2014; Chen et al., 2015; Zhou et al., 2016). The Raman spectrometer used in this work is a HORIBA XploRA multichannel fibre optic-based system equipped with a 1200 grooves/mm grating and a CCD detector. A 20× microscope objective on the probe focused the 532 nm wavelength laser onto the desired spot of the hydrate surface in all experiments, and the focused diameter was approximately 5 μm. The final excitation power at the sample was 20 mW. A spectral resolution of 1 cm⁻¹ was obtained. The spectrometer was interfaced with a computer to provide instrument and experimental control. Routine calibration of the monochromator was performed by using single-crystal silicon. The data acquisition time for one measurement was approximately 200 s, and the exposure time was 100 s for each accumulation. The spectra were averaged over two accumulations.

2.3. Experimental procedures

The procedure for formation of a gas bubble with a hydrate film is similar to our previous work (Peng et al., 2007; Sun et al., 2007; Li et al., 2014b). First, the sample compartment was loaded with 5 mL of deionized water. Then, the high-pressure cell and the entire pipeline was evacuated and purged several times with the desired hydrate-forming gas (CH₄ or CH₄+C₂H₆ gas mixture) to thoroughly displace air in the cell. The system temperature was then adjusted to a desired value. After the system temperature became stable, the hydrate forming gas was then introduced continuously into the cell through the needle at the bottom until the system pressure was significantly higher than the equilibrium pressure for hydrate formation. Subsequently, the gas was slowly discharged out of the cell from a top valve. Then, the cell was recharged with the gas to agitate the water phase, and this process of gas charging and discharging was continued to saturate the water phase until a hydrate layer formed atop the water phase. The cell was depressurized to completely dissociate the hydrate while the temperature of the coolant was kept constant. Then, the hydrate-forming gas was injected into the cell again and maintained at a desired pressure higher than the equilibrium value of hydrate formation at the specified temperature. Following the preparation procedure above, the hydrate film growth experiment started. A hydrate layer with a non-smooth surface was first formed at the bulk gas/liquid interface in the cell. A bubble of the same hydrate-forming gas was then injected slowly into the cell through the needle to produce a gas bubble. When the bubble just contacted the hydrate layer, the hydrate film growth on the suspended bubble started. The process of hydrate film growing on the bubble was recorded. At the same time, the cell was moved through the translational stage to allow for precisely

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