

Effects of Water Soluble Guest on Clathrate Hydrate Crystal Growth

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Abstract: This study reports on the visual observations of the crystal growth behavior and the crystal morphology of clathrate hydrate in liquid water presaturated with the tetrahydropyran (THP) and the methane gas. THP is the partially water soluble guest substance. It was observed that the crystal growth behavior of the hydrate in methane + THP + water system greatly changed compared to those in methane + water system, and also those in the mixed gas + water soluble ionic guest substance + water system. The hydrate was initially formed at the water – THP interface. The formed hydrate was grew to a certain size and then detached from the water - THP interface. The water – THP interface was maintained and then the hydrate formation was continually repeated.

Key words: Clathrate hydrate, crystal growth, crystal morphology, tetrahydropyran.

1. Introduction

Clathrate hydrate (hereafter hydrate) is the crystal formed with the cages composed of water molecules by hydrogen bonding and different molecules (guest molecules) wrapped up inside the cages. Hydrates have properties such as the large gas storage capacity, the guest molecules selectivity, and the large heat of formation and decomposition. It is considered that hydrates can be used for gas separation [1]-[4], gas storage and transportation [5]-[7], and thermal energy storage [8]-[10] using those properties. Crystal morphology (size and shape) and crystal growth behavior were dynamic characteristics required for the process design of these technologies. Understanding the crystal morphology and the crystal growth behavior leads to design the method for the reducing pressure loss on hydrate transportation, changing the hydrate decomposition rate, and improving the efficiency of the hydrate formation.

The gas separation technology using hydrate formation and decomposition has been proposed. The gas selectivity depends on the guest molecules. Therefore, the specific gas can be separated from the mixed gas by repeating hydrate formation and decomposition.

Generally, hydrates are formed under the low temperature and the high pressure condition. For this reason, the moderating equilibrium temperature and the pressure of hydrates are required for industrial technology using hydrates. It has been reported that the hydrate equilibrium condition could be moved to lower pressure and higher temperature condition by adding large molecule guest substances (LMGS). Because the crystal structure of hydrates changed and became thermodynamically stable. Therefore, adding LMGS is a useful method to use hydrate on industrial technology. It is reported that if the LMGS has

a water solubility, the greater hydrate formation rate can be obtained [11]. Because the hydrate formation and decomposition are repeated in hydrate technology, using LMGS with water solubility can improve the hydrate formation rate.

According to the previous study [12], CH_4 + tetrahydropyran (THP) hydrate is useful for the gas hydrate separation of methane gas and carbon dioxide gas such as coal bed methane gas. THP is LMGS with partial water solubility.

As mentioned above, the crystal morphology and the crystal growth behavior are necessary for considering the process design of hydrate technologies. Tetrahydrofuran (THF) is LMGS with water solubility. The crystal growth behavior with THF has already been observed [13] and it is different from CH_4 hydrate crystal growth behavior [14]. However, THF has toxicity and it was regulated in the specific area. Therefore, the industrial use of THF is difficult. Thus THP has been proposed as a new LMGS for hydrate technology. THP has less toxicity than THF and it is LMGS with partial water solubility. Although it is dissolved in water, they are not completely miscible. However, the crystal morphology and the crystal growth behavior added LMGS with partial water solubility have not been reported.

The physical properties, the crystal morphology, and the crystal growth behavior of hydrate depend on the chemical species of the guest substance. The appropriate hydrates for each hydrate technology would be realized by using the appropriate guest substances. The efficiency of each hydrate technology would be improved by using appropriate hydrate. It is necessary to understand the influence of guest on the thermal physical properties, the crystal morphology, and the crystal growth behavior. It is the objective of this study to understand the crystal growth behavior and the crystal morphology of CH_4 + THP hydrate.

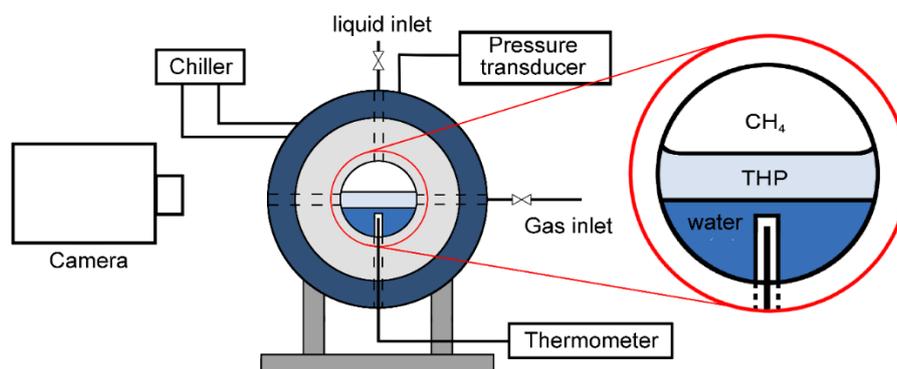


Fig. 1. Schematic diagram of the experimental apparatus.

2. Experiment Details

The fluid samples used in the experiments were methane (99.99 vol %, Takachiho Chemical Industrial Co.), THP (99 mass %, Aldrich Chemical Co.) and liquid water, which was deionized and then distilled.

A schematic diagram of the experimental apparatus used in this study is shown on Fig. 1. The test cell is a cylindrical vessel made of stainless steel. The inner space of the test cell was 25 mm in diameter and 20 mm in axial length. The test cell has a pair of glass windows. The formation and growth of the hydrate crystals were observed through the window. The system temperature T was controlled by circulating ethylene glycol solution as refrigerant through a brass jacket covering the test cell. T was measured with a platinum resistance thermometer inserted in a port at the bottom of the test cell into the bulk of the liquid-water phase inside the test cell. The system pressure P was controlled by supplied methane gas from high-pressure cylinder through a pressure-regulating valve. P was measured with a strain-gauge pressure transducer. The formation and the growth of the hydrate crystals were observed and recorded using a CMOS camera (Fortissimo Co., Ltd. model CMOS130-USB2) and a microscope (Edmund Optics Co.).

Firstly, 2.5 cm³ of liquid water, 2.0 cm³ of THP and methane gas were charged in the test cell and three phases were formed. The test cell was left for several hours so as to be saturated each phase. After each phase was saturated, T was decreased to experimental temperature T_{ex} to form hydrate. The time was started to count after a hydrate was first confirmed. When CH₄ + THP hydrate was formed, experiments were run at the range from T_{ex} from 274 K to 288 K and P from 1.5 MPa to 2.0 MPa, to avoid the formation of CH₄ hydrate.

The subcooling ΔT_{sub} is defined as the difference between T_{ex} and the equilibrium temperature T_{eq} of CH₄ + THP hydrate ($\Delta T_{\text{sub}} \equiv T_{\text{eq}} - T_{\text{ex}}$). ΔT_{sub} was used as index for the driving force of crystal growth.

3. Results and Discussion

Sequential images of the formation and growth of the methane + THP hydrate at $\Delta T_{\text{sub}} = 6$ K are shown in Fig. 2. The elapsed times are shown below each image. The water - THP interface formed a concavity by the meniscus. The site of hydrate growth was in the water phase. The hydrate crystal was initially and preferentially formed at the water - THP interface (Fig. 2a). The formed hydrate grew toward the bulk of water phase (Fig. 2b). It grew to a certain size and then detached from the water - THP interface a few minutes after the confirmation of the hydrate crystal formation and sank into the bottom of the reactor (Fig. 2c). The major part of water phase was apparently converted into hydrates by the repetition of hydrate formation and detaching from the water - THP interface (Fig. 2d). This crystal growth behavior is different from that in the CH₄ + water system [14] and in the mixed gas + tetrabutylammonium bromide (TBAB) + water system [15].

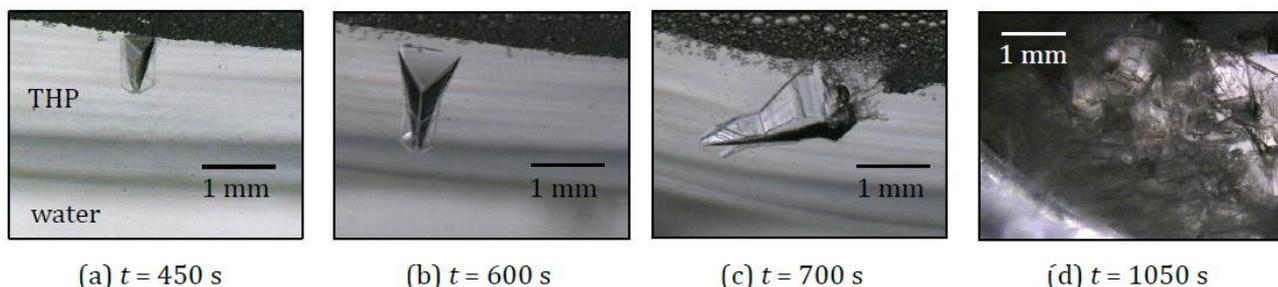


Fig. 2. Crystal growth behavior of CH₄ + THP hydrates when $\Delta T_{\text{sub}} = 6$ K, $T_{\text{ex}} = 284$ K, $P = 1.8$ MPa.

The hydrate crystal growth behavior in CH₄ + water system was previously observed in detail [14]. At this system, the hydrate crystal initially formed at the methane - water interface and then grew into the thin film between the methane gas and the liquid water. Subsequently the hydrate crystal grew toward water phase from the water side surface of the hydrate film covering methane - water interface. The hydrate crystal growth behavior in mixed gas + TBAB + water system was also previously observed [15]. TBAB is the water soluble ionic guest. In this system, the hydrate crystal initially formed at the gas - liquid interface and then immediately detached from the gas - liquid interface and sank into the bulk of the aqueous phase. This crystal growth behavior is similar to that in the system with the surfactant [16], [17]. Hayama *et al.* [15] explained that the formed hydrate crystal in gas + TBAB + water system was more wettable with liquid compared to the gas + water system. It is inferred that the hydrate crystal in CH₄ + THP + water system was more wettable with liquid compared to the gas + water system, however, it was less wettable with liquid compared to gas + TBAB + water system. As a result, the formed hydrate crystal in methane + THP + water system detached from the water - THP interface after it grew to a certain size. These results suggest that it would be possible to maintain the interface without applying external force and controlling the size of the hydrate crystals in hydrate formation system by adding LMGS with partial water solubility.

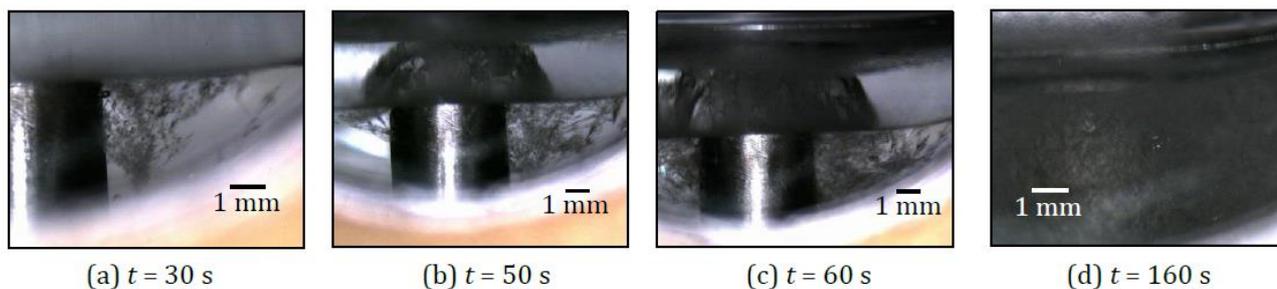


Fig. 3. Crystal growth behavior of $\text{CH}_4 + \text{THP}$ hydrates when $\Delta T_{\text{sub}} = 10 \text{ K}$, $T_{\text{ex}} = 279 \text{ K}$, $P = 1.6 \text{ MPa}$.

Sequential images of methane + THP hydrate crystal growth at $\Delta T_{\text{sub}} = 10 \text{ K}$ are shown in Fig. 3. The process of hydrate formation and growth at $\Delta T_{\text{sub}} = 10 \text{ K}$ was similar to that at $\Delta T_{\text{sub}} = 6 \text{ K}$. The nucleation of hydrate crystal initially occurred at the water - THP interface (Fig. 3a). Number of hydrate crystals formed and they were covered the water - THP interface and sank into the bottom of the reactor (Fig. 3b, c). The major part of water phase was apparently converted into hydrates by the repetition of hydrate formation and detaching from the water - THP interface (Fig. 3d). This may be ascribed to the high frequency larger nucleation rate of the hydrate crystal and the growth rate of the hydrate crystal, due to the large subcooling, i. e, the large driving force for crystal growth.

The hydrate crystal morphology depending on the subcooling are shown in Fig. 4. At $\Delta T_{\text{sub}} = 3 \text{ K}$, the pyramidal crystals were observed (Fig. 4a). At $\Delta T_{\text{sub}} = 8 \text{ K}$, the needle crystals were observed (Fig. 4b). At $\Delta T_{\text{sub}} = 10 \text{ K}$, like the oligo - plate crystals were observed (Fig. 4c). The morphology of the hydrate crystal were changed by the dimension of the subcooling. The subcooling is difference of the temperature between at the bulk of the water phase and at the hydrate surface. The solubility depends on the temperature. The difference of the methane concentration to water between them became large when subcooling became large. The difference of solubility generated mass transfer of the methane from the bulk of water phase to the hydrate surface. The driving force of the hydrate crystal formation became large when mass transfer became large. The crystal growth rate varies by crystal plane. Because the difference of the crystal growth rate between each crystal plane was changed when the driving force of the hydrate crystal formation was changed, the morphology of the hydrate crystal was changed corresponding to the subcooling. Based on these results, it may be expected that the morphology of the hydrate crystals is controlled by subcooling.

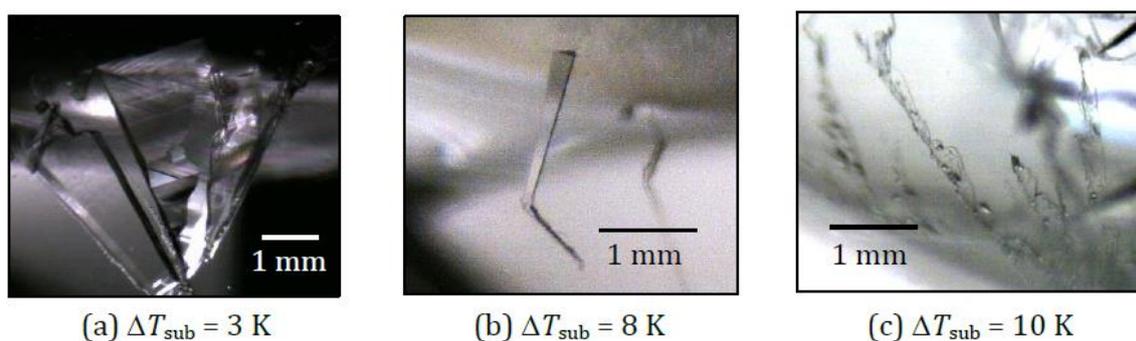


Fig. 4. Crystal morphology of $\text{CH}_4 + \text{THP}$ hydrates depending on ΔT_{sub} .

4. Conclusion

The crystal growth behavior and the crystal morphology of $\text{CH}_4 + \text{THP}$ hydrate were observed. The hydrate initially and preferentially formed at water - THP interface. The formed hydrate grew to a certain size and then detached from the water - THP interface. The crystal morphology changed from pyramid or

needle to oligo - plate crystal with increasing ΔT_{sub} . Based on these observational results, we may envision the enhancement of hydrate formation as well as the control of the hydrate crystal morphology by adding LMGs with partial water solubility.

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