

# GROWTH PATTERNS OF XENON HYDRATE ON SURFACES WITH VARYING WETTABILITY

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## ABSTRACT

The gas hydrate is an emerging energy resource, while the blockage of pipelines caused by hydrate is of utmost concern. To investigate the formation properties of hydrate, visual experiments of xenon hydrate formation were carried out on the modified aluminum sheets with contact angles of 61.5°, 90.0°, and 123.6°, which were marked as hydrophilic, untreated and hydrophobic surfaces respectively. The microscopic results show that the hydrate growth behavior and the crystal morphology of the xenon hydrate depend on the wettability. On hydrophilic surfaces, the hydrate grows outside the original water boundary, i.e., halo effect. For the untreated surface, the phenomenon of halo still appeared. The finally formed halo was smaller with a slower growth rate, while the hydrate layer was thicker and rougher. In addition, there was no halo on the surface of hydrophobic. The hydrate shell was firstly smooth, but depressed in 30 minutes. The study is instructive for the wettability treatment of surfaces, and then provide some reference in the efficient application of hydrate.

**Keywords:** gas hydrate, hydrophilic, hydrophobic, wettability, crystal growth, morphology

## 1. INTRODUCTION

Natural gas hydrate, an ice-like non-stoichiometric crystal, is an important clean energy source. Hydrate can be applied in natural gas storage and transportation[1], seawater desalination[2], greenhouse gas sequestration[3], etc. At the same time, the hydrate has a certain extent of harm in the oil and gas industries, the blockage of oil and gas pipelines caused by hydrate formation and growth bring flow assurance problems[4]. Thus, the study of the nucleation and growth of the hydrate is necessary, which can improve the production

efficiency in hydrate application technology and avoid the blockage of hydrate in oil and gas pipelines.

It is generally known that the surface effect is one of the key factors affecting hydrate nucleation and growth[5, 6]. When a surface exists, it changes the local structure of water molecules and gas distribution near liquid-solid interfaces, thus alter the mechanism and dynamics of gas hydrate nucleation[5]. Previous hydrate studies have shown that the growth processes of hydrate in varying wettability would be different[7-12]. The wettability of the surface is usually divided into hydrophilicity and hydrophobicity. Hydrate grow along the hydrophilic surfaces, which is a phenomenon known as the halo effect[7-9]. It was observed that the halos spread faster on hydrophilic glass compared to that of untreated, an effect attributed to the quantity of water present on the substrate[7]. Also, the methane hydrate was reported to propagate on glass and the hydrate film formed on the advancing the front of water, possibly through capillarity[8]. Moreover, hydrophobic surfaces are generally considered to promote the formation of hydrate[10-12]. The existence of interfacial gas enrichment at hydrophobic surfaces plays an important role in promoting the formation of hydrate[10]. In addition, methane nanobubbles on the hydrophobic surface may provide the sites of gas hydrate nucleation and induce rapid nucleation of methane hydrate[11].

In summary, the surface wettability is related to the nucleation and growth of hydrate. As mentioned above, a considerable amount of studies have been carried out on the growth of hydrophilic or hydrophobic surfaces, but there are few studies on the growth of hydrate from hydrophilic surfaces to hydrophobic surfaces. Thus, in this work, the effects of hydrophilic, untreated and hydrophobic surfaces on the growth and morphology of hydrate were respectively studied. We aim to identify

the growth patterns of hydrate by visual observations of the hydrate growth and crystal morphology at different wettability surfaces. Also, we make efforts to reveal the influence mechanism of the wettability on hydrate growth, and then provide some reference in the application of hydrate technology and prevention of hydrate blockage.

## 2. MATERIALS AND METHODS

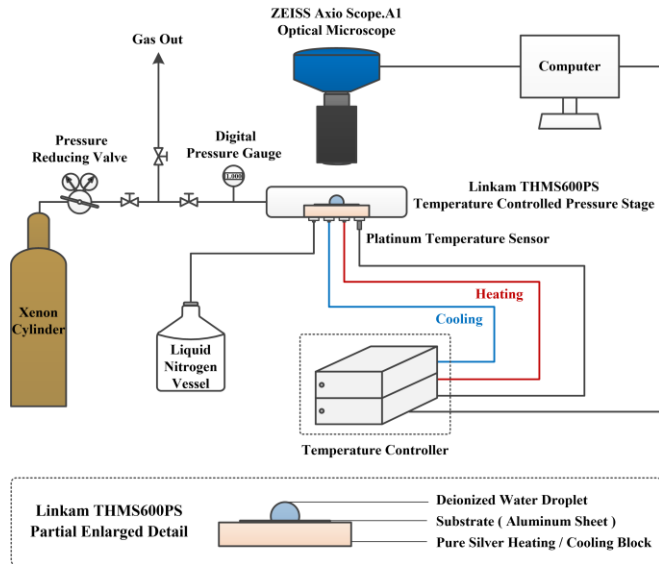


Fig 1 Schematic diagram of experimental apparatus.

### 2.1 Materials

In this experiment, the aluminum sheet (16mm diameter, 0.5mm thick) was selected as the experimental substrate. The surface was firstly modified by 3mol/L hydrochloric acid for 7min, then immersed in the fluoroalkyl silanes for 30min, and dried at 150°C for 60 min to obtain a hydrophobic surface. Next, plasma cleaning machine was applied, and the surface was turned to a hydrophilic one by a treatment time of 5min. The untreated aluminum sheet was invoked as a contrast experiment in this study.

### 2.2 Characterization

The growth process of xenon hydrate on the surfaces was observed using an optical microscope (Scope A1; Zeiss) coupled with a high definition camera. The water contact angles on different surfaces were measured at ambient temperature using a contact angle measuring system (OCA25; Dataphysics) and the droplet volume was 3 $\mu$ L.

### 2.3 Experiment.

To observe the growth process of xenon hydrate on the surfaces with varying wettability, the droplets (5 $\mu$ L, deionized water) were placed on a temperature controlled pressure stage (THMS-PS 600; Linkam). When the surface temperature of the substrate was cooled from ambient temperature to -5°C at a rate of 20°C/min, xenon gas was injected into the cell to a pressure of 1.2MPa. Then, the xenon hydrate growth process was recorded by the high definition camera of the optical microscope, and the growth mode of xenon hydrate could be identified based on the hydrate morphology.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Hydrate Growth Behavior

The sequence images of typical hydrate xenon growth from water droplets on hydrophilic, untreated, and hydrophilic surfaces are shown in Fig 2. The moment when the hydrate is in the process of being generated but not yet generated is defined as  $t=0s$ . Nucleation points were random. Nucleation occurred in the gas-liquid-solid interface on the hydrophilic surface (Fig 2 (1b)). And the point of nucleation observed within the field of vision on the untreated surface was located at the interior of the water droplet (Fig 2 (2b)). The hydrophobic surface was nucleated at a certain point in the lower hemisphere. But the nucleation site was not accurately observed due to the observation from a bird's-eye view (Fig 2 (3b)).

During the growth process of hydrate on the hydrophilic surface, the hydrate shell grew along the surface of the water droplet. At the same time, the hydrate propagated beyond the edge of the water droplet, which is known as halo effect[7, 9] (Fig 2 (1c, 1d)). After 10 minutes of hydrate nucleation, the halo extended to almost the entire surface of the substrate. On the untreated surface, the growth process of hydrate is similar to that of the hydrophilic surface, and the halo effect also occurred (Fig 2 (2c, 2d)). Moreover, the time of which the hydrate covered the water droplet was almost the same. However, the halo coverage of the untreated surface was smaller than that of the hydrophilic surface, and the growth rate of halo was slower. The formation of the hydrate shell on the hydrophobic surface was a process of smooth growth from the bottom of the cross-section of the water drop to the top. Then the hydrate gradually wrapped the water drop. The initial hydrate shell was thinner at first but thickened over time. The diameter of the water droplet on the hydrophobic surface was slightly larger than that before hydrate formation, but its cross-section

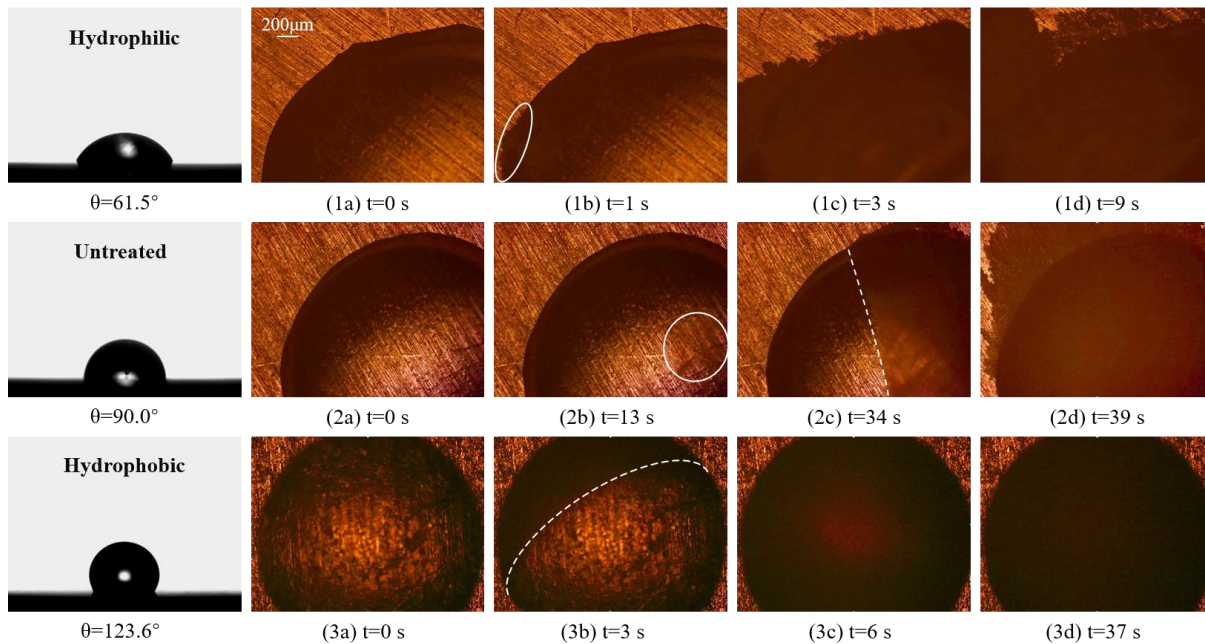


Fig 2 Sequence images of typical hydrate xenon growth from water droplets on hydrophilic, untreated, and hydrophilic surfaces. (a) Before hydrate growth, (b) beginning of the growth (c) when the hydrate film had mostly covered the original water droplet, (d) hydrate extended beyond the water droplet boundaries (halo) on hydrophilic, and untreated surfaces, but not on hydrophilic.  $P=1.2\text{Mpa}$ ,  $T=268\text{K}$ .

remained round. Also, no hydrate grew beyond the edge of the water droplet, that is, halo effect did not occur (Fig 2 (3c, 3d)).

In summary, the experimental results show that there are two types of characteristic behaviors occur for xenon hydrate on surfaces with varying wettability, which are along-surface growth and off-surface growth. When the surface was hydrophilic ( $61.5^\circ$ ) or untreated ( $90.0^\circ$ ), the adhesion force of the surface is greater than the cohesive force, and the capillary force causes the water migration so that the hydrate will grow outside the edge of the water droplet. With a smaller surface contact angle, the connection between the water droplet and the surface of the substrate is more sufficient. With a stronger adhesion, the growth rate of halo gets faster and the range gets wider. On the hydrophobic surface ( $123.6^\circ$ ), the adhesion force of the surface was weaker

than the cohesive force. In the process of hydrate formation, the water droplet tended to maintain the original shape, which means that no halo appeared. Due to the low adhesion of hydrate on hydrophobic surfaces, it can be beneficial for application in oil and gas pipeline to inhibit the deposition of hydrate.

### 3.2 Hydrate Crystal Morphology

Fig 3 shows the crystal morphology of the halo at different surfaces. On the hydrophilic surface, the distribution of hydrate crystal of the halo was not uniform. One part of the hydrate layer was relatively thin, and the texture of the aluminum substrate can still be seen. The other part of the hydrate layer was thicker and appeared dark grey in the field of view. However, both the hydrate crystallites were smaller and the growth was smoother. When halo was grown on an untreated surface, the final hydrate layer was thicker and rougher. According to Mori and Mochizuki's capillary permeability model[13], these microchannels were slowly transformed into hydrates, and the shallower microchannels (thinner membrane) were filled more rapidly than the deeper microchannels (thicker membrane). The surface with a low contact angle has higher surface energy. Under the action of capillary force, these microchannels were continuously generated and propagated to the growth front, resulting in thinner hydrate layer. However, due to the possibility of the

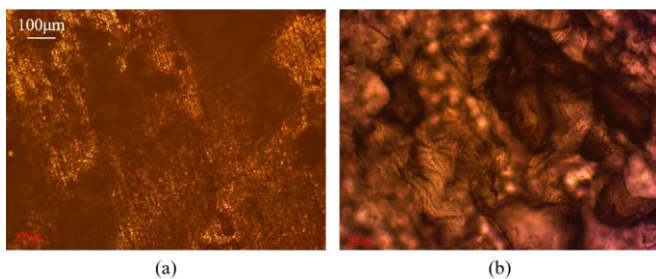


Fig 3 The crystal morphology of halo comparison between hydrophilic and untreated surfaces. (a) Hydrophilic, (b) untreated.

uneven capillary force action and different width of microchannels, the water aggregation could be formed in several parts, where the thickness of the transformed hydrate was greater. On an untreated surface with a large contact angle, the hydrate had a smaller propagation range and a slower growth speed, which may make the thicker hydrate layer.

Fig 4 shows the hydrate morphology within the droplet. On the hydrophobic surface, the hydrate film on the water droplet surface was smoother firstly, which could be attributed to the growth of larger grains instead of smaller ones, thus the grain boundary was eliminated. While the top of the water droplet was still distributed with micron fine grains. After about 30 minutes of hydrate formation, depression occurred in the hydrate shell, as shown in the white circle of Fig 4. This phenomenon is similar to the result of previous observation[9]. The reason may be that water molecules in the water droplet passed through the hydrate molecular layer to form hydrate with the gas.

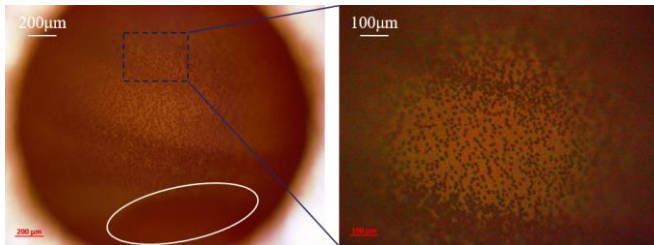


Fig 4 The hydrate morphology of water droplet on the hydrophobic surface.

## CONCLUSION

Visual experiments of xenon hydrate formation were carried out on the modified aluminum sheets with contact angles of  $61.5^\circ$ ,  $90.0^\circ$ , and  $123.6^\circ$ , marked as hydrophilic, untreated and hydrophobic surfaces respectively. The microscopic results show that the hydrate growth behavior and the crystal morphology of the xenon hydrate depend on the wettability. The halo that hydrate grows at the outside of the original water boundary occurs in hydrophilic surfaces. For the untreated surface, the phenomenon of halo effect still appeared. The final halo formed was smaller with a slower growth rate, while the hydrate layer was thicker and rougher. In addition, there was no halo on the surface of hydrophobic. And the hydrate shell was smooth firstly, but depression occurred in 30 minutes. The results suggest that the hydrophilic surfaces can be utilized to the application of hydrate technology to promote hydrate propagation, whereas hydrophobic

surfaces can help prevent hydrate deposition and blockage in the pipeline.

## ACKNOWLEDGEMENT

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