CH$_4$ Nanobubbles on the Hydrophobic Solid−Water Interface Serving as the Nucleation Sites of Methane Hydrate

Yong Guo,[†,‖] Wei Xiao,[‡,§,‖] Wanfen Pu,[†] Jun Hu,[§] Jinzhou Zhao,[*,†] and Lijuan Zhang[*,§]

[†]State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, 610500 Chengdu, China

[‡]School of Minerals Processing & Bioengineering, Central South University, Changsha 410083, China

[§]Key Laboratory of Interfacial Physics and Technology, Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

ⓢ *Supporting Information*

ABSTRACT: The surface hydrophobicity of solid particles plays a critical role in the nucleation of gas hydrate formation, and it was found that the hydrophobic surface will promote this nucleation process, but the underlying mechanism is still unveiled. Herein, we proposed for the first time our new theory that the formation of methane nanoscale gas bubbles on the hydrophobic surface provides the nuclei sites for further formation of methane hydrate. First, we studied the effect of hydrophobicity of particles on the nucleation of hydrate. It was found that the hydrophobic graphite and silica particles would promote the nucleation of hydrate, but the hydrophilic silica particles did not promote the methane hydrate nucleation. Then, we designed the atomic force microscopy experiment to explain this mechanism from a nanometer scale. The results showed that the methane nanobubbles were formed on the hydrophobic highly ordered pyrolytic graphite surface, but they were hard to form on the hydrophilic mica surface. These results indicated that the methane nanobubbles on the hydrophobic surface could provide the gas hydrate nucleation sites and may induce a rapid nucleation of methane hydrate.
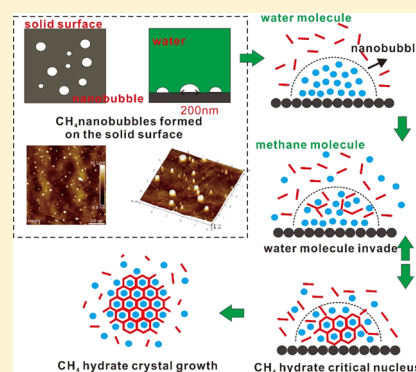
INTRODUCTION

Gas hydrates are inclusion compounds formed from small gas molecules being trapped in a water lattice.[1] Because of the weak interaction between the gas molecule and the water lattice, and the relatively strong hydrogen bond, the gas hydrate has a high thermodynamic stability under low temperature and high pressure.[2] However, the full description of the molecular mechanism of gas hydrate formation is still an important issue to research; it is tremendously beneficial for the development of hydrate-based technologies, for example, energy storage and recovery, gas separation, carbon sequestration, seawater desalination, and refrigeration.[3]

Hydrate nucleation has been studied by many researchers.[4−14] Actually, solid surfaces such as the reactor wall, agitator, and impurities in water can act as the nucleation sites in a typical hydrate formation process; thus, the heterogeneous nucleation is the most likely pathway in a practical situation. Many researches have been known to study the gas hydrate formation using additives, including fumed silica, graphite, and carbon nanotube.[15−18] Cha et al. inferred that the solid surface might serve as a nucleation site because they found that the bentonite surface could thermodynamically and kinetically promote the methane hydrate formation.[19] Kaschiev and Firoozabadi calculated the work required for the formation of clusters of a new phase in heterogeneous environments and found that in a practical case, hydrate nucleation preferentially occurred on the solid substrates in solution.[20] The surface of a solid particle played a critical role in the promotion effect, but the underlying mechanism is still elusive. Thus, the mechanism research about gas hydrate heterogeneous nucleation became interesting and important.

Recently, the research on gas nanobubbles at the solid/water surface, surface nanobubbles, is becoming a very hot topic because of their significance in environmental, biological, and nanotechnological sciences.[21−24] It was reported that surface nanobubbles preferably form and absorb on hydrophobic surfaces.[25−27] Their absorption on a solid surface might have an important influence on a lot of processes, such as folding of protein, efficiency of sensors, slippage, and so forth.[28−30] How about the role of methane in the nucleation of methane hydrate if methane forms nanoscale gas bubbles?

In this paper, we presented for the first time that methane nanobubbles formed on a hydrophobic surface might be a great driving force for the nucleation of hydrate. First, we studied the kinetics of heterogeneous nucleation of methane hydrate using additives as suspended solid particles (graphite, silica) to study the influence of the hydrophobicity of the particles on the nucleation. It was found that the hydrophobic

graphite particles promoted the nucleation remarkably, but the hydrophilic silica particles did not promote the nucleation. Remarkably, our further research showed that the methane nanobubbles preferably formed on the hydrophobic graphite [highly ordered pyrolytic graphite (HOPG)] surface instead of forming on the hydrophilic surface of mica. We proposed the hypothesis that the methane nanobubbles on the hydrophobic interface may serve as the methane hydrate nucleation sites and induce a rapid nucleation of methane hydrate.

■ MATERIALS AND METHODS

Materials and Reagents. The chemically pure graphite particles and silica particles (hydrophilic/hydrophilic) with a diameter of 1 μm were obtained from Aladdin Company and used in this study without further purification. Deionized water with a conductivity of 18.2 MΩ (Millipore Corp., Boston, M A) was used, and methane (99.99%) was purchased from Kelong Company. The graphite particles, silica particles, and pure water were measured by using a Mettler Toledo (XS-105) accurate analytical balance. Mica and HOPG were from S&J Trading Co. (NY) and used as the substrates for the formation of methane nanobubbles. They were freshly cleaved before the experiment.

Experiment of Methane Hydrate Formation. The schematic diagram of the gas hydrate formation experimental apparatus is shown in Figure 1. The reactor of 350 mL is manufactured with SUS316 to
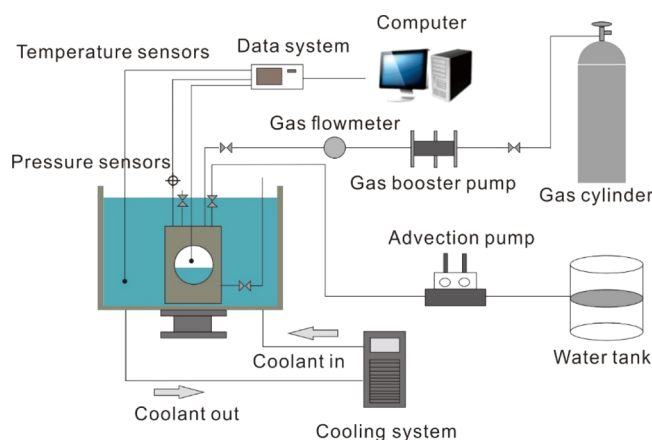

Figure 1. Schematic diagram of the gas hydrate formation experimental apparatus.

endure a pressure of over 10 MPa and salt corrosion. A stirrer with variable speeds was installed in the vessel to agitate the fluids. All the experiments were conducted with a fixed speed of 400 rpm/s. The reactor was immersed in a constant temperature bath (water + ethylene glycol), to maintain the temperature inside at a desired level. One copper-constantan thermocouple was used to measure the gas phase temperature inside the reactor, and one pressure sensor was used to measure the pressure inside the reactor. Quartz glasses with a diameter of 30 mm were installed at the front and rear sides of the reactor to check the gas hydrate formation. A data logger acquisition system was used to record their average values for 5 s.

At first, water or aqueous solution containing solid particles was poured into the reactor. Then, methane gas was injected until the final pressure reached 8.5 MPa at 293.15 K. Then, the cooling system was turned on, and its temperature was adjusted to 275.15 K. When the electromotor was turned on, data recording was started. The methane hydrate formation experiment was repeated three times for each system under the same condition. Table S1 in the Supporting Information shows the result of the repeated experiment.

Formation of Methane Nanobubbles. Nanobubbles were prepared using the method shown in Figure 2. First, the deionized water was degassed in the sealed container for 3 h at a pressure of
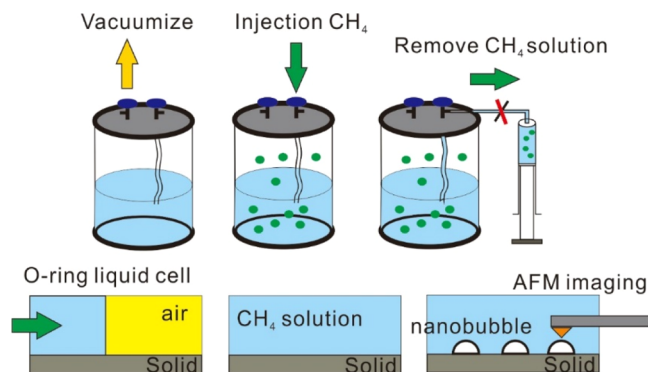

Figure 2. A schematic diagram of nanobubbles' formation on the solid surface.

−0.1 atm. Second, the methane gas was injected into the degassed water at an atmosphere and room temperature. Third, the methane solution was injected into the liquid cell with an O-ring using a glass syringe. The nanobubbles will be formed on the HOPG or mica surface and were imaged by a PeakForce Quantitative Nano-Mechanics mode atomic force microscope.[31−33] Force-volume mode atomic force microscopy (FV-AFM) was used to obtain the force curves on the nanobubble.

A normal NP probe with the spring constant of the cantilever of 0.32 N/m (Digital Instruments Veeco Metrology Group) was used to image the formed nanobubbles. All the imaging was carried out at room temperature.

■ RESULTS AND DISCUSSION

Effect of Solid Particles on the Methane Hydrate Nucleation. Hydrate formation is divided into the "nucleation" and "growth" stages. During the nucleation stage, hydrate nuclei are generated in a supersaturated aqueous solution; the hydrate process ends with the appearance of a critical-sized, stable hydrate. In the growth stage, the hydrate nuclei grow to solid hydrate crystals.[34] "Induction time" is defined as the duration of the nucleation stage and is a parameter of a supersaturated system to remain in the state of metastability.[20] The induction time can be detected by a pressure drop or temperature rise in the vessel showed in Figure 3; a detailed description is given in Supporting Information S1. In this work, the induction time was used to evaluate the difficult degree of methane hydrate nucleation.

This experiment was designed to find out the difference of induction time between the hydrophobic particle system and hydrophilic particle system. Graphite particles were chosen as the typical hydrophobic particles. We compared the methane hydrate formation in a pure water−gas system and in the presence of graphite particles. The solution containing graphite particles (15 mL, 10% (v/v)) of about 150 mL was injected into the reactor. The experimental temperature was 275.2 K and initial pressure was 8.5 MPa. The obtained pressure−time and temperature−time profiles are plotted in Figure 3a,b. It was shown that methane hydrate was formed with a sharp drop in pressure and a slight increase in temperature. The pressure drop was because of the consumption of the methane molecules in the gas phase, which were trapped by a water lattice; the methane hydrate nucleation was an exothermic reaction that caused a slight temperature rise. On the basis of the data, the induction time of the graphite system was about 7500 s, which was remarkably shorter than that of the pure water system (about 24 000 s). The results demonstrated that graphite particles promoted the nucleation remarkably, which
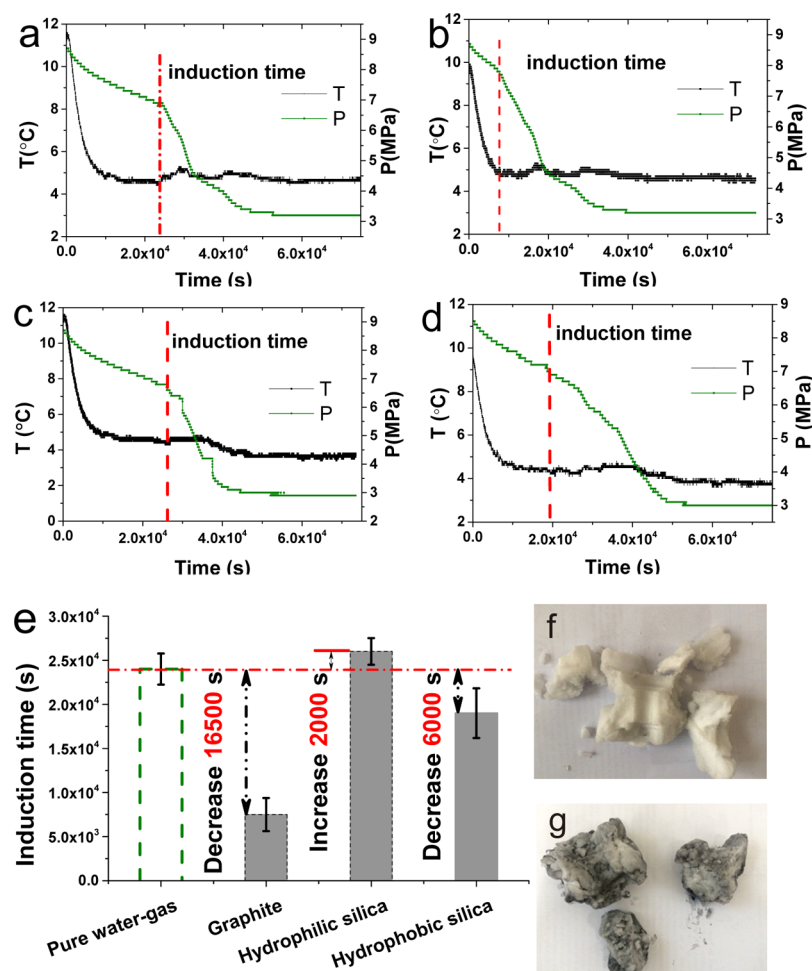
Figure 3. $P-t$ and $T-t$ profiles of methane hydrate formation at a target temperature of 275.15 K and initial pressure of 8.5 MPa: (a) in the presence of pure water; (b) in the presence of the graphite particles; (c) in the presence of the hydrophilic silica particles; (d) in the presence of the hydrophobic silica particles; (e) column diagram of the effect of solid particles on the methane hydrate nucleation; (f) methane hydrate formed in the pure water−gas system; (g) methane hydrate formed in the presence of graphite particles.

is consistent with the report that carbon nanotubes promoted the methane hydrate formation by Park and Kim[35] Figure 3f,g shows the pictures of the methane hydrate formed in the absence and presence of graphite particles, respectively. The graphite particles were distributed in the bulk methane hydrate more uniformly, which indicated that the graphite particles may induce the nucleation of methane hydrate.

However, the question is whether all solid particles could promote the nucleation process or not. Then, we chose the hydrophilic silica particles (15 mL, 10% (v/v)) as the studied system. As shown in Figure 3c, the induction time was about 26 000 s after the adding of silica particles, which was longer than that of the pure water−gas system, about 24 000 s. That is to say, the hydrophilic silica particles did not promote the nucleation process. The experimental results were also consistent with the data of molecular dynamics simulation obtained from Bai et al.[36] They noticed that surface hydrophilicity had a strong effect on the induction time and proposed that there will be a structure mismatch between the hydrate lattice and an amorphous ice-like layer-inhibited nucleation, when the surface is hydrophilic.

Effect of the Hydrophilic/Hydrophobic Properties of Solid Particles on the Methane Hydrate Nucleation. As we discussed in the previous section, the hydrophobicity of

solid particles might influence the nucleation of the hydrate. In this section, we compare the difference of induction time of hydrophobic and hydrophilic silica particles (15 mL, 10% (v/v)) for the nucleation of the hydrate. Figure 3c,d shows that the induction time of hydrophobic silica was about 19 000 s, which was much shorter than that of hydrophilic silica particles, 26 000 s. The promotion effect of the hydrophobic silica particles was better than that of the hydrophilic silica particles.

We summarized the induction time of the studied solid particles as shown in Table 1. It should be noted that the real promotion effect of hydrophobic silica might be under-estimated because we found that most of the hydrophobic silica particles floated on the water surface, even during the agitating process. The effects of three solid particles on the

Table 1. Induction Time of Methane Hydrate Formation in Different Environments

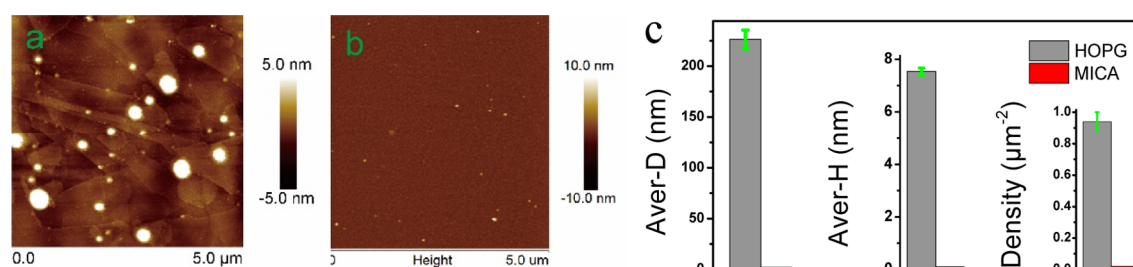| systems	induction time (s)
pure water−gas	24 000
graphite	7500
hydrophilic silica	26 000
hydrophobic silica	19 000

Figure 4. AFM images of methane nanobubbles on the (a) HOPG surface and (b) mica surface. (c) Methane nanobubbles' average diameter (nm), average height (nm), and density (μm^{-2}) on the HOPG and mica surfaces. Scan sizes: (a,b) 5 μm × 5 μm.
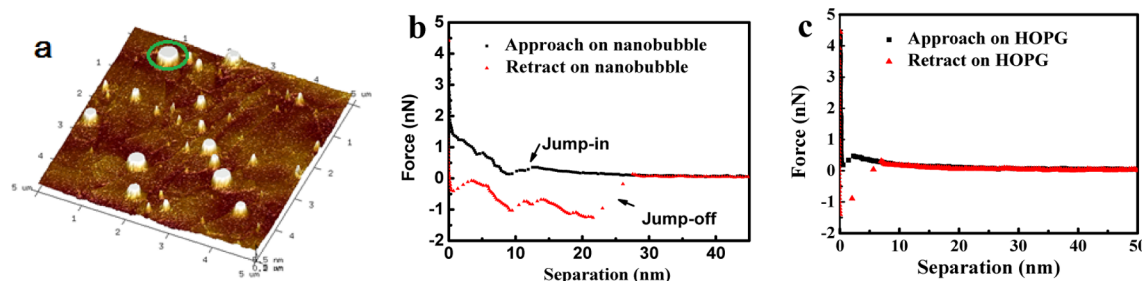

Figure 5. (a) 3D image of methane nanobubbles on the surface of the HOPG; (b) force curve of the nanobubble (marked by the green circles in (a)); (c) force curve of the bare HOPG surface.

nucleation are also summarized in Figure 3e. The hydrophobic graphite and silica promoted the nucleation process, but the hydrophilic silica did not promote the nucleation. The results demonstrated that the surface hydrophobicity could dominate the methane hydrate nucleation, but how the hydrophobic solid surface promotes the nucleation process needs to be further explored at the nanometer scale.

Formation of Methane Nanobubbles on the Hydrophobic Surface. According to the above results, we found that the hydrophobic surface could promote the nucleation process remarkably. We further studied the formation of methane nanobubbles on the hydrophobic HOPG surface. Mica was used as the hydrophilic surface for comparison.

In Figure 4a, it could be seen that the methane nanobubbles were formed and located randomly on the HOPG surface, but they were hardly found on the mica surface (Figure 4b). Figure 4c shows that the average diameter of the nanobubbles on the HOPG surface was 223.4 nm with the average height of 7.5 nm, and the number density of nanobubbles in the HOPG surface was about 0.91 μm^{-2}.

In order to confirm that the formed nanobubble-like domains were gas nanobubbles, we performed the force measurements on the nanobubbles by FV-AFM. First, the AFM image was obtained by AFM topographic imaging as shown in Figure 5a. Then, FV-AFM was performed to obtain the corresponding force curves of one nanobubble (marked by green circles in Figure 5a). From Figure 5b, we could find a small jump-in (snap-in or jump-to contact) during the approach but a long-range attraction force during retraction; jump-off occurs at a larger separation distance than the jump-in, leading to an obvious hysteresis behavior, which is similar to the force curve of the nanobubble reported by Wang et al.[37] The force curves of the bare HOPG surface is also shown in Figure 5c; the approach curve was quite different from that of the nanobubble. The above characteristic behaviors of the approaching force curves obtained from methane nanobubbles

proved that the formed nanobubble-like domains are gas nanobubbles inside.

On the basis of the results, we proposed a hypothesis that the methane nanobubbles on the hydrophobic solid−water interface provide the methane hydrate nucleation sites. This might the reason why the hydrophobic surface can promote the nucleation of hydrate during the nucleation process. The result was in agreement with the hypothesis proposed by Maeda[38] and the molecular simulation result from He et al.[39]

CONCLUSIONS

In summary, the process of methane hydrate nucleation with graphite particles and hydrophobic/hydrophilic silica particles in pure water under high pressure was investigated in this paper. The influence of the hydrophobicity of the solid particles on this nucleation was further explored. The results demonstrated that the hydrophobic surface could promote the methane hydrate nucleation but the hydrophilic surface failed to promote the nucleation. We then designed the nanobubble experiments to explore this mechanism. More interestingly, we found that a lot of methane nanobubbles could be formed on the hydrophobic HOPG surface but not on the hydrophilic mica surface. We further proved that the formed nanobubble-like domains are indeed gas inside by measuring the force−volume curves. Finally, we proposed our new mechanism to explain why the hydrophobic surface would promote the nucleation of hydrate. That is, methane first formed the nanobubbles on the hydrophobic solid−water interface, which further provides the nucleation sites for the formation of methane hydrate. These results will be very helpful to explain the mechanism of the hydrophobic surface promoting the nucleation of methane hydrate. For convenient AFM observation and suitable imaging, we used the surface of the HOPG-replaced graphite particles. However, the surface of hydrophobic graphite may not necessarily be smooth; the rough surface promoting the nanobubble formation has been

proved,[40−42] but the impact on the methane nanobubble will be further studied.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhaojz@swpu.edu.cn (J.Z.).
*E-mail: zhanglijuan@sinap.ac.cn (L.Z.).

ORCID Ⓘ

Yong Guo: 0000-0003-0517-4299
Wei Xiao: 0000-0001-5245-4926
Jun Hu: 0000-0002-7282-2316
Lijuan Zhang: 0000-0001-9829-2918

Author Contributions

‖Y.G. and W.X. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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