Functionalized Nanoparticles for the Dispersion of Gas Hydrates in Slurry Flow

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Abstract: Gas hydrates are crystals that can form in oil and gas production. Their agglomeration in flowlines may disrupt the normal production. One current strategy ofhydrate management is to inject an anti-agglomerant, a type of low-dosage hydrate inhibitor that prevents hydrate agglomeration. Concerns in the use of these chemicals include their toxicity, cost, and environmental impacts. In this study, we exploited functionalized nanoparticles in place of anti-agglomerants to produce hydrate slurry, with the potential benefit of nanoparticles to be more environmentally friendly and conveniently recyclable. We coated 256 nm spherical silica nanoparticles with different hydrophobicity and evaluated their performance for the hydrate dispersion at atmospheric and high pressure. Nanoparticles with moderate hydrophobicity stabilized oil-in-water (O/W) or water-in-oil (W/O) emulsions. Direct visualization of the cyclopentane hydrate formation from the nanoparticle-stabilized emulsions revealed different morphologies of hydrate particles depending on whether the nanoparticles prevented agglomeration. We also measured the apparent viscosity of a hydrate–nanoparticle mixture using a high-pressure rheometer. Nanoparticles with moderate hydrophobicity during hydrate formation slowed the viscosification, reduced the maximum viscosity, increased the water conversion, and ultimately helped to maintain a low steady-state viscosity. Increasing nanoparticle or salt concentrations also improved the gas hydrate dispersion. Our study demonstrated the great potential of using nanoparticles in preventing agglomeration of gas hydrates under realistic pipeline flow conditions.

1. Introduction

Gas hydrates are solid crystalline compounds where small guest molecules are contained in cages of water molecules.1 Gas hydrate formation usually requires relatively high pressure and low temperature. At constant pressure, a hydrate forms when the temperature drops below the hydrate equilibrium temperature. Depending on the composition and formation condition, hydrates in nature have been considered potential energy sources2,3 and hydrate-based technologies have been proposed and tested for gas storage,4−6 gas separation,7 and water treatment.8

In the oil and gas industry, hydrate formation is often undesirable because it can bring detrimental consequences to hydrocarbon production.9,10 For example, hydrates can increase the fluid viscosity and the pressure drop along the flowline and in the worst scenario block the flowline. Hydrate agglomeration can lead to production interception, economic loss, and safety hazards. Therefore, hydrate management has been a crucial component in the flow assurance of hydrocarbon production. Traditionally, the industry uses thermodynamic hydrate inhibitors such as methanol and monoethylene glycol to prevent hydrate formation by keeping the pressure-temperature conditions out of the hydrate forming region. In recent years, the industry has turned the focus on a more cost-effective method, that is, using low-dosage hydrate inhibitors such as anti-agglomerant (AA) chemicals that do not inhibit hydrate formation but prevent hydrate aggregation.11 In recent years, a few field tests using AAs have been reported with promising results.12 Appropriately designed AAs can form a transportable hydrate slurry, effectively reducing or eliminating the hydrate blockage risks and ensuring a continuous production stream.

AA chemicals consist of a wide variety of compounds. While most of the currently used AAs have proprietary trademarks, a generic class of chemicals, that is, quaternary ammonium salt surfactants, has shown to be effective although the mechanisms are not well understood.11 The surfactant-type AAs typically showed much better performance when the head group contains n-butyl, n-pentyl, or i-pentyl structures.13 One hypothesis is that these alkyl groups can penetrate into the open cages on existing hydrate surfaces, preventing further growth of hydrate and reducing agglomeration. Molecular
Table 1. Summary of the Experiments Performed

| system | NPs | comments |
|--------|-----|----------|
| SEM, FTIR, TGA, gel-trapping method | 0X, 0.25X, 0.5X, 1X, 2X, 4X, 8X | NP characterization |
| glass vial | 0X, 0.25X, 0.5X, 1X, 2X, 4X, 8X, 1XS\(^a\) | emulsion stability |
| microscope | 1X, 2X | cyclopentane hydrates under static conditions |
| microscope | 0X, 0.25X, 0.5X, 1X, 2X, 4X, 8X | methane/ethane gas hydrates; effect of NP hydrophobicity |
| rheometer | 1XS\(^a\) | effect of NP concentration; effect of salt concentration |

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Besides molecular surfactants, solid nanoparticles (NPs) are known to promote dispersion and stabilize emulsions, that is, the Pickering emulsions.\(^{18}\) Appropriately functionalized NPs tend to be adsorbed at the oil/water interface, forming a protective layer that prevents the coalescence of emulsion droplets. Therefore, it is possible that such a particulate layer reduces or prevents the agglomeration of hydrate particles during the formation of hydrates from Pickering emulsions. In fact, some previous studies are supportive to this hypothesis. Min et al.,\(^{19}\) Cha et al.,\(^{20}\) and Baek et al.\(^{21}\) reported that the silica-NP-laden oil/water interface was less penetrable by hydrate particles and the activated carbon NPs could kinetically prevent hydrate formation by preventing the seeding hydrate penetration into the water phase. The results suggested that the NPs may prevent the coalescence between liquid water droplets and hydrate particles. Hydrate formation from Pickering emulsions has also been reported by others.\(^{16,17}\)

One interesting observation by Wang et al.\(^{16}\) and Farhang et al.\(^{22}\) is that hydrates that formed a Pickering emulsion have lower water conversion and ultimately assist the formation of a hydrate slurry even without addition of surfactants.\(^{16,17}\)

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2. RESULTS

Table 1 shows a summary of the NP characterization and the hydrate formation and dispersion experiments. After surface functionalization, we characterized the NPs using SEM (NP shape, size), FTIR, TGA (coated silane molecule amount), and gel-trapping method (contact angle at water--n-decane interface). We tested the stability of Pickering emulsions in glass vials. We then conducted static cyclopentane hydrate formation tests using optical microscopy and dynamic gas hydrate formation tests in the high-pressure rheometer.

2.1. Particle Characterization. Figure 1a shows the SEM image of unmodified (0X) and modified silica NPs (1X). It can be seen that the surface modification does not noticeably change the particle size and the NP diameter was determined
two weight loss events, our conclusions about the increasing trend of weight loss with increasing silane amount in the modification, however, do not change if we choose 200 or 250 °C as the starting point. The weight loss from 150 to 600 °C increases with the silane amount used in the conjugation reaction. The weight loss, however, was smaller than the expected silane amount, indicating that the reaction did not proceed stoichiometrically.

Based on the TGA measurement, we can calculate the mass ratio of coated silane to the NPs and the number of silanes coated on the NPs based on the following formula

\[
\text{weight loss} \% = \frac{m_{C_{18}H_{37}}}{m_{\text{NP}} + m_{C_{18}H_{37}Si_3}} \times 100\%
\]

where the weight loss % is the relative weight loss percentage from 150 to 600 °C compared to the 0X NPs, \(m_{\text{NP}}\) is the mass of one pristine silica NP, \(m_{C_{18}H_{37}Si_3}\) is the total mass of silane molecules attached on the surface of one modified NP, and \(m_{C_{18}H_{37}}\) is the mass of the C_{18}H_{37} functional groups on the same NP. Based on the mass ratio, we can further calculate the number of silane molecules coated per unit surface area by assuming that the surface area occupied by one silane molecule is 0.13 nm². Table 2 summarizes the average weight loss of each NP batch relative to the unmodified NPs and the calculated silane molecules per nm². The detection limit of the TGA equipment is approximately 0.001% in this study. The results overall show that the number of silane molecules per unit surface area increased with the amount of silane molecules used in the conjugation reaction. However, with the large standard deviations (SDs), the relative weight losses of the 0.25X and 0.5X NPs were insignificant, suggesting that the TGA could only partially quantify the silane amount and the wettability. Much convincing evidence of the successful silane coupling and the different wettability of the 0.25X and 0.5X NPs was reported by the three-phase contact angle measurement and the emulsion stability tests discussed later.

Since particle wettability can be very important in governing the stabilization of water-in-oil droplets and gas hydrates, we further characterized the three-phase contact angle (θ) of silica NPs at the water–n-decane interface by using the gel-trapping method, as described in the Materials and Methods section. Figure 2a shows a schematic representation of the position of a modified silica NP embedded in the PDMS in two scenarios: θ > 90° and θ < 90°. The height of protrusion \(h\) can be determined from the contact radius \(d\) and particle radius \(r\) via the geometric relationship. When θ < 90°, we can measure \(d\) accurately from the SEM images of the NPs embedded in PDMS. However, it is difficult to be determined

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Figure 1. Characterization of the functionalized NPs. (a) SEM images of NPs before modification (0X) and after modification (1X). (b) FTIR spectra. (c) TGA results.

Table 2. Amount of Silane Molecules Coated on the NP Surface Based on TGA Results

| NPs | relative weight loss (%) | number of silane molecules per nm² |
|-----|--------------------------|----------------------------------|
|     | average | SD   | average | SD   |
| 0.25X | 0.0026 | 0.0037 | 0.47   | 0.66   |
| 0.5X  | 0.0025 | 0.0028 | 0.46   | 0.51   |
| 1X    | 0.0045 | 0.0035 | 0.82   | 0.64   |
| 2X    | 0.0081 | 0.0016 | 1.47   | 0.30   |
| 4X    | 0.0181 | 0.0032 | 3.30   | 0.61   |
| 8X    | 0.0269 | 0.0003 | 4.99   | 0.06   |

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as 256 ± 14 nm. The FTIR spectra of the NPs in Figure 1b show peaks at 2917 and 2849 cm⁻¹ resulting from −CH₂− asymmetric stretching and indicate successful coupling of octadecylsilane onto the NPs. The peak intensities became stronger as a higher amount of silane molecules was used.

The attachment of silanes can be further confirmed by the TGA results shown in Figure 1c. In our experiments, the weight-loss events result from the loss of absorbed moisture and trapped solvent (at relatively low temperature), the silanol dehydration, and the pyrolysis of the alkyl chains for silane-functionalized NPs (at relatively high temperature). To exclude the weight loss from the absorbed moisture and the solvent, we only counted the weight loss from 150 to 600 °C. The initial fast weight loss from room temperature in fact at 150 °C, indicating the end of the solvent vaporization. The weight loss stabilizes at 600 °C, indicating the end of the pyrolysis of the alkyl chains. Although the choice of 150 °C may appear arbitrary, as there is no clear distinction between the two weight loss events, our conclusions about the increasing trend of weight loss with increasing silane amount in the modification, however, do not change if we choose 200 or 250 °C as the starting point. The weight loss from 150 to 600 °C increases with the silane amount used in the conjugation reaction. The weight loss, however, was smaller than the expected silane amount, indicating that the reaction did not proceed stoichiometrically.

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Figure 2. Three-phase contact angles of functionalized silica NPs at water–n-decane interface. (a) Schematic representation of the position of a modified silica NP embedded in the PDMS for θ > 90° and θ < 90°. (b) Measured heights of protrusion h and contact angles θ of modified silica NPs (0.25X, 0.5X, 1X, 2X, 4X, 8X).

from SEM when θ ≥ 90° unless we tilt the sample by a very large angle. Therefore, we also used AFM to directly measure the height of protrusion.

Figure S1 shows the SEM images of functionalized silica NPs embedded in PDMS. Before SEM imaging, 2 min of gold sputtering was performed to make the PDMS-particle surface more conductive. The effective contact radii d’s for 0.25X, 0.5X, 1X, 2X, 4X, and 8X silica NPs embedded in PDMS were 105 ± 6, 114 ± 10, 103 ± 8, 107 ± 9, 86 ± 6, and 88 ± 10 nm, respectively. Since d’s for 0.25X, 0.5X, 1X, and 2X NPs were relatively similar and close to the particle radius, it is possible that their contact angles were close to 90°; therefore, we further used AFM to measure their protrusion heights h directly, which are shown in Figure S2. The open-source software Gwyddion was used to process the images. Briefly, a line was first drawn across the center of the silica NP, then the height profile along this line was obtained, line correction function was applied to flat the baseline, and the height of protrusion h was obtained by comparing the height difference between the peak and the baseline. Once we determined the height of protrusion h, we can calculate the three-phase contact angle θ = arccos (1 − h/r). Figure 2b shows the measured and calculated heights of protrusion and three-phase contact angles for functionalized NPs with different amounts of silanes. It shows that, when they were placed at the water–n-decane interface, 0.25X, 0.5X, and 1X silica NPs have contact angles smaller than or close to 90°; however, 2X, 4X, and 8X silica NPs have contact angles larger than 90°.

2.2. Emulsion Stability. After the characterization of particles, we further examined the stability of emulsions decorated by the NPs. Although a stable W/O emulsion prior to hydrate formation is not a necessary condition for hydrate dispersion, it is generally considered a positive factor for generating a flowable hydrate slurry. To examine the emulsion stability, a mixture of water, n-decane, and NPs was homogenized at 13500 rpm for 2 min. The water/decane ratio is 20/80 vol %, and the NP concentration is 1 wt % based on the water amount.

Figure 3a shows that the NP hydrophobicity influences the emulsion types. 0.25X NPs yielded O/W emulsions due to their relatively small contact angle, while 0.5X, 1X, and 2X NPs yielded stable W/O emulsions. Both 4X and 8X NPs yielded W/O emulsions but with a noticeable amount of free water since they were highly hydrophobic. Figure 3b,c shows the microscopic images of these two types of emulsions. Interestingly, the O/W emulsions were spherical, while irregular and nonspherical shapes were observed for the W/O emulsions. The irregular emulsion droplets are not uncommon since they have been reported in the literature, which are usually due to either jamming of the trapped colloidal particles at the liquid–liquid interface or the buckling and crumpling of the particle layer.

Regardless of their types, the emulsions decorated by 0.25X, 0.5X, 1X, and 2X NPs remained stable for weeks, similar to the stable Pickering emulsions reported in the literature. The average sizes of all emulsion droplets measured from optical images are summarized in Table S1. Those stabilized by 0.5X, 1X, and 2X NPs were of similar sizes, while the O/W emulsions stabilized by 0.25X and W/O emulsions stabilized by 4X NPs were much smaller and larger, respectively, indicating their very different hydrophobicity, which was confirmed by our contact angle measurement. The time for silane coating did not affect much the particle hydrophobicity and the emulsion stability. For example, the W/O emulsions stabilized by 1X NPs, that is, the particles coated by 1X silane molecules for 1 h instead of 24 h, remained stable after four weeks (Figure S3).

2.3. Cyclopentane Hydrates Stabilized by NPs. Based on the emulsion stability test, we chose 1X and 2X NPs to study their impacts on the stabilization of cyclopentane hydrates using optical microscopy since both types of particles form stable water-in-decane (W/O) emulsions. We put the emulsions in a customized cooling cell filled by a mixture of cyclopentane and decane (20/80 vol %) and followed the temperature change protocol illustrated in Figure 10b. In brief, we first converted the W/O Pickering emulsions into ice particles at −15 °C. We then melted and converted them into cyclopentane hydrates at 0.5 °C. Finally, the hydrates were dissociated at 10 °C. We formed hydrates from melted ice because the hydrate formation time is shorter than directly from the W/O emulsion.

Figure 4 shows the microscopic images of the emulsions decorated by 1X NPs at different temperatures. The emulsion...
droplets were first added in the cooling cell at 21 °C (Figure 4a). The temperature was then decreased to −15 °C (Figure 4b). Water droplets started to crystallize within 10 min, and most of the emulsion droplets converted into ice particles in ∼30 min, as evidenced by the change of light intensity from Figure 4a,b due to the refractive index difference between water and ice. During the ice formation, we did not observe any coalescence between neighboring droplets and the boundaries between them were sharp and clear (indicated by the red arrows in Figure 4e). The temperature was then increased to 0.5 °C (Figure 4c), ice melted, and cyclopentane hydrates formed gradually from the water−oil interface. Compared with ice particles, the hydrate particles were visually more transparent but rougher on the surfaces (Figure 4f). Again, during the hydrate formation, we did not observe any coalescence between neighboring droplets. 30 min after the hydrate formation, we used a glass fiber with a ∼5 μm tip to disturb the hydrate particles and confirmed that they were separated from each other without any noticeable aggregation (Movie S1). When we raised the temperature to 10 °C, the hydrates dissociated and most of the emulsions remained in their shapes (Figure 4d). Coalescence of the emulsion droplets was very limited. We also observed the appearance of small oil droplets within the water phase of the emulsion (Figure 4f). Since n-decane is immiscible with water, these oil droplets were likely the trapped cyclopentane from hydrate dissociation. This explanation was further confirmed by the observation of no trapped oil droplets by replacing the oil to pure n-decane and applying the same temperature change. Clearly, 1X NPs showed excellent anti-agglomeration properties for W/O emulsion droplets, ice crystals, and cyclopentane hydrates at different temperatures.

In comparison, Figure 5 shows the microscopic images of the W/O emulsions decorated by 2X NPs. While the emulsions were also stable at 21 °C (Figure 5a), they aggregated during the conversion into ice particles (Figure 5b,e). When we attempted to disturb them using the glass fiber, we found that the aggregates typically consist of 2−8 ice particles (Movie S2). Note that the surfaces of the ice particles also appeared hairy. When the temperature was increased to 0.5 °C, ice particles melted and cyclopentane hydrates started to form (Figure 5c). The aggregation between hydrate particles became more severe as necks formed between neighboring particles (Figure 5f and Movie S3). The formation of necks
likely resulted from the ice and hydrate crystallization process where liquid water protruded out of droplets and bridged with neighboring droplets.

The degree of agglomeration between two contacting hydrate particles can be quantitatively characterized as in Figure 5g by the parameter \( \beta = L / (r_1 + r_2) \), where \( L \) is the length and \( r_1 \) and \( r_2 \) are the radii of two particles. As the actual particles were not perfectly circular, we avoided the minority of the extreme irregular particles and used the effective radius for each particle \( r_{\text{eff}} = \sqrt{S / \pi} \), where \( r_{\text{eff}} \) is the effective radius and \( S \) is the area of the particle in the 2D optical images. As a comparison, \( \beta = 0.036 \pm 0.061 \) for 27 pairs of hydrate particles stabilized by 1X NPs, while \( \beta = 0.23 \pm 0.12 \), 1 order of magnitude larger, for 22 pairs of hydrate particles stabilized by 2X NP. This qualitative method showed again that the 2X NPs did not prevent hydrate agglomeration as effective as the 1X.

Span 80 is a common nonionic surfactant used to stabilize W/O emulsions. We also tested the W/O emulsions stabilized with Span 80 to see whether such an emulsion can help reduce hydrate agglomeration at static conditions. The tested Span 80 concentration was adjusted to be 1 wt % based on the water amount. Representative images of the emulsions at different temperatures are shown in Figure S4. Compared with Pickering emulsions stabilized by NPs, the Span 80 emulsions were smaller (34.33 ± 10.40 \( \mu \)m) and they were not as stable as the Pickering emulsions at 21 °C. At −15 °C, severe aggregation between ice particles can be seen. Hydrate particles were also fused together at 0.5 °C. As hydrates dissociated at 10 °C, the W/O emulsions became unstable and the droplet sizes increased to 48.90 ± 14.06 \( \mu \)m.

2.4. Rheology of Methane/Ethane Gas Hydrate Stabilized by NPs. Our observations using optical microscopy revealed the striking difference between 1X and 2X NPs for stabilizing the cyclopentane hydrates under static conditions. Whether they behave differently in gas hydrates under dynamic shear conditions is the next question that we aimed to address. We used a high-pressure rheometer to induce shear flow and studied the impacts of NP hydrophobicity, NP concentration, and salt concentration on dispersing gas hydrates. Different from the optical microscopy experiments, we did not pre-form Pickering emulsions. Instead, the mixture of water or brine (10 mL), n-decane (15 mL), methane/ethane (75/25 mol %), and variable amounts of NPs was subjected to a constant rotation rate of the impeller (200 rpm) at 70 bar and 8 °C with a subcooling of 8.5 °C. Considering the stochastic nature of hydrate formation, we adjusted the time zero to be the onset time of hydrate formation, the moment when the torque experienced by the rheometer increased rapidly.

Figure 6 shows the apparent viscosity of the mixture of gas hydrates and NPs (2.5 wt % based on the water amount) coated by different amounts of silanes. The apparent viscosity is a good indicator of hydrate aggregation. As expected, when we did not add any NP, the system viscosity increased so quickly that the rheometer reached its maximum torque (0.2 N m) ~15 min after the onset of hydrate formation, indicating severe hydrate agglomeration. Interestingly, the addition of unmodified hydrophilic NPs (0X) significantly delayed the catastrophic increase of viscosity. The system remained dispersed and flowable for 2 h before it eventually jammed the rheometer. On the other hand, the systems with 0.25X, 0.5X, and 1X NPs exhibited a finite viscosity rise (spikes around 1–3 h) after the onset of hydrate formation. The viscosities, however, then decreased dramatically and reached much lower values at the steady state, suggesting that hydrates were well dispersed in the oil phase and formed a flowable slurry. Comparing the steady-state viscosity, 1X NPs showed a better performance than 0.5X and 0.25X NPs. At 6 h, the apparent viscosity of the 1X-NP system was 330 cP, whereas those of the 0.25X- and 0.5X-NP systems were 10450 and 3692 cP, respectively. When more silanes were coated on the NPs (2X, 4X, and 8X), the system viscosity again increased rapidly and was jammed within 30 min. Our results here are consistent with our previous observations that 1X NPs stabilized cyclopentane hydrates very well but 2X NPs did not prevent hydrate agglomeration.

Figure 7 shows the impacts of NP and salt (NaCl) concentrations on the apparent viscosity of the gas hydrates. These experiments were performed at 70 bar with a methanol/ethane (75/25 mol %) mixture. The temperatures were held at 1 and 10 °C, resulting in a subcooling of 15.5 and 6.5 °C, respectively. The NPs investigated were coated by 1X silanes for 1 h, that is, 1XS NP. As before, the time zero in these figures was adjusted to the onset time of hydrate formation when the torque increased rapidly. The systems tested with NaCl and NP jammed at 1 °C but remained flowable at 10 °C. When no salt or NPs were added (Figure 7a,d), the system viscosity increased rapidly indicating hydrate formation and agglomeration. The initial increase in apparent viscosity was more rapid at 1 °C than at 10 °C, reflecting that hydrate formation is positively correlated to the subcooling. At 1 °C, the apparent viscosity increased so fast that the system stopped within approximately 10 min. At 10 °C, the system eventually jammed the rheometer ~1.7 h after the onset. By contrast, for the system at 1 °C with 5.0 wt % 1XS NPs, it plugged at a longer time after the hydrate onset, indicating that the NPs might have slowed the agglomeration and the viscousification. For the system with 1XS NPs at 10 °C, we also observed spikes in viscosities that indicated significant hydrate formation. The viscosities eventually decreased to the steady values of 149 and 233 cP for 2.5 and 5.0 wt % NPs, respectively. This confirms the NP abilities in dispersing hydrates under realistic hydrate formation conditions.

In addition to the apparent viscosity, another parameter of interest from these experiments is the water conversion. With 0, 2.5, and 5.0 wt % NPs at 10 °C and no NaCl, the water conversion reached 51, 50, and 54% at 2 h, respectively. The 50% water conversion at the jamming point for 0 wt % NP
agrees well with the previous study.\textsuperscript{43} The water conversion appeared to approach a plateau after \(\sim 2\) h, while the apparent viscosity kept decreasing until \(6\) h. These results suggested that, during the later stage of the hydrate formation, the hydrate particles redistributed in size under shear and the apparent viscosity further reduced with little additional hydrate formation.

At 10 °C, however, adding 1 mM NaCl (Figure 7e) led to about a 2-fold increase compared to the no-salt system in the apparent viscosity during hydrate formation (2–6 h after the onset), but the steady-state apparent viscosity remained small. The water conversion of 1 mM NaCl systems at 2 h was approximately 50%, similar to the no-salt system. More interestingly, the presence of 10 mM NaCl in water reduced the viscosities of all systems dramatically (Figure 7f). Even the one without any addition of NPs at 10 °C could maintain its apparent viscosity at a finite level (2806 cP at 8 h). The salt also helped to improve the performance of NPs as the spikes in the apparent viscosity were much smaller. At 10 mM NaCl and 10 °C, the apparent viscosities at 8 h were 23 and 50 cP at 2.5 and 5.0 wt % NPs, respectively. Compared to that without NaCl, the apparent viscosities at 8 h were 160 and 180 cP at 2.5 and 5.0 wt % NPs, respectively. Consistent with previous cases, the water conversion of the 10 mM NaCl systems was \(\sim 50\%\) after 2 h. Clearly, there appeared a synergistic effect between NPs and high concentration of NaCl. Similar experiments at 1 °C (subcooling of 15.5 °C) showed the same salt effect; that is, the flowability increased with increasing NaCl concentration (Figure 7a–c). The system with 10 mM NaCl and 5.0 wt % NP remained flowable rather than jamming. This series of experiments demonstrated that NPs can effectively prevent hydrate agglomeration especially at

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure7.png}
\caption{Apparent viscosity and water conversion of the gas hydrates and 1XS NPs. Temperature: (a–c) at 1 °C, (d–f) at 10 °C. NaCl concentrations: (a,d) 0, (b,e) 1, (c,f) 10 mM.}
\end{figure}
high salt concentrations, which is typical in oil and gas production pipelines.

The maximum apparent viscosity can represent the moment when hydrate agglomeration is the most severe. Figure 8 summarizes the maximum apparent viscosity at different NP and salt concentrations of 10 °C IXS-NP experiments.

![Figure 8](image)

**Figure 8.** Maximum apparent viscosities of gas hydrates measured at different NP and salt concentrations of 10 °C IXS-NP experiments.

3. DISCUSSION

In this study, we investigated the potential of using functionalized NPs as colloidal dispersants for hydrates. We performed a series of experiments in three different types of tests: the vial tests for emulsion stability, the optical microscopic tests for cyclopentane hydrates, and the high-pressure rheometer tests for methane-ethane gas hydrates. We also investigated the impact of NP hydrophobicity, NP concentration, and salt concentration on the stabilization of hydrate particles. Overall, our results suggest that the addition of properly functionalized NPs can greatly reduce the extent of hydrate agglomeration, leading to much improved hydrate particles. Overall, our results suggest that the addition of properly functionalized NPs can greatly reduce the extent of hydrate agglomeration, leading to much improved hydrate particles.

Based on our results, here, we propose a possible mechanism for the NPs to prevent ice and hydrate agglomeration. Overall, the particle hydrophobicity increased from the 0X to the 8X NPs. As shown in Figure 9a, NPs with different hydrophobicity prefer different relative positions at the oil–water interface and resulted in different stability of the emulsions.18 NPs with proper functionalization and intermediate hydrophobicity, that is, 0.5X, 1X, and 2X NPs, can result in the best dispersive effect in terms of liquid emulsions. NPs with too little silane coatings, such as 0X and 0.25X NPs, or too much silane coatings, such as 4X and 8X NPs, cannot form stable W/O emulsions. As depicted in Figure 9b,c, before hydrate formation, the mixing of the oil, water, and NPs can result in stable W/O Pickering emulsions, while water droplets without any NP or AA will be unstable. At the beginning of hydrate formation, the guest molecules (cyclopentane or gas) diffuse onto the water droplets, gradually converting water into hydrates from the oil–water interface. Since there is still a significant amount of unconverted water droplets in the system, if without NPs, the water can easily attach to hydrates or other droplets via collision especially under shear. Even at the latter stage of hydrate formation, a thin layer of wetting water on the surface of hydrate particles can result in very strong capillary attractions between hydrates and causes their agglomeration (Figure 9d). The NPs, however, reduce the agglomeration by forming a physical coating (Figure 9e). They may not only stay at the water–oil interface but can also remain at the solid–liquid interface after hydrate formation. The reduced adhesion force between water droplets and hydrates or between hydrates themselves was also reported by Min et al.19

The performance of the NPs is related to their hydrophobicity, or equivalently, the three-phase contact angle. Only NPs with intermediate hydrophobicity may stabilize W/O emulsions, have enough penetration depth into water, stay at the solid–liquid interface, and reduce agglomeration. Our results also demonstrate that the ability to form stable W/O emulsions can be helpful for dispersing hydrates but is neither necessary nor sufficient for satisfactory anti-agglomeration, a phenomenon that has been observed for molecular AAs.16,17 Our in situ observation via optical microscopy shows the leakage of water and protrusion of solid out of the emulsions during both ice and hydrate formation, which eventually leads to the formation of necks between neighboring hydrates. This is likely related to the surface coverage and stability of NPs at the interface during hydrate formation whose conditions are typically quite different from the ambient conditions tested for emulsion stability.

The observed effects of the NP and salt concentrations may also be explained by the NP coverage and stability at the
water—oil or oil—water interfaces. Generally, a higher NP concentration can form a more compact layer at the interface with fewer voids, which helps in preventing the leakage of water and protonation of an ice/hydrate crystal from the interface. Studies have shown that the salt effect on Pickering emulsions is complex and its impact on hydrate stabilization is much less understood. Salts can affect the interactions between NPs. A moderate amount of electrolytes can reduce the electrostatic (between charges or dipoles) repulsion between NPs at the water—oil interface, making NPs more closely packed at the interface and increasing the stability of Pickering emulsions. It is possible that the 10 mM NaCl in this study yielded much better packing of NPs at the interface than without NaCl. However, to confirm this hypothesis, studies using confocal microscopy may be needed.

A high-pressure rheometer was used to study the formation and stabilization of gas hydrates, which provided us quantitative rheological measurement. There are, however, a few limitations in our measurement. First, due to the need to increase the mass transfer rate for gas hydrate formation, we used a hollow-vane impeller for which the shear rate profile is not well defined. Therefore, we obtained the torque—viscosity correlation using standard oil samples. This method assumes that the actual hydrate forming system would follow the same correlation. Second, when a high-pressure cell is used, it is often challenging to directly visualize the system inside and determine the distribution of different phases. For example, the apparent viscosity increase may be partially caused by the hydrate agglomeration on the impeller instead of the viscosification of hydrates themselves. Without confirming the distribution of hydrates, the apparent viscosity values reported here need to be treated with caution to avoid overexplanations. Last but not the least, the maximum torque tolerated by our rheometer sets the upper limit of our experimentally determined jamming state, making direct comparison among other jammed systems in the literature difficult.

It is interesting to notice that the dispersive effects of NPs on hydrates are different from those reported in the previous literature. Although the previous researchers did not intentionally study the dispersive effect, they observed severe agglomeration during hydrate formation from Pickering emulsions. Two possible reasons for the discrepancy can be the NP size and hydrophobicity. Both factors have been reported to significantly affect the properties of Pickering emulsions. Most previous studies used commercially available NPs around 10 nm, while NPs in this study are much larger (~256 nm). The energy of desorption of a particle from the interface scales with the particle surface area. Therefore, our particles will be much harder to desorb provided that the hydrophobicity of two particles is similar. In addition, previous studies did not attempt to tune the particle hydrophobicity over a wide range, which appears to be an important factor. Because of the different approaches used, currently it is difficult to make any direct comparison. Future studies need to address these issues to better understand the mechanism of NPs in preventing agglomeration of hydrates.

4. CONCLUSIONS

In this study, we have, for the first time, tested and demonstrated the promising potential of using NPs to disperse gas hydrates and reduce the tendency for hydrate agglomeration. The tested NPs were silica particles 256 nm in diameter coated with different amounts of hydrophobic alkyl chains. The performance of the NPs was tested in a customized cooling cell for cyclopentane hydrates at ambient pressure and a high-pressure rheometer for methane/ethane hydrates. The impacts of NP and salt concentrations on hydrate agglomeration were also investigated. We found that NPs with moderate hydrophobicity can significantly reduce the apparent viscosity of gas hydrates, increase water conversion, and help to form flowable hydrate slurries. Higher NP and salt concentrations further helped to reduce the steady-state apparent viscosity values of the gas hydrates.

Based on the experimental results, we further proposed a hypothesis of the underlying mechanism for the NPs in preventing hydrate agglomeration. NPs with moderate hydrophobicity can pack closely at the liquid—liquid and liquid—solid interfaces with a large particle-desorption energy barrier. As a result, they can stabilize the emulsion droplets before hydrate formation. Once hydrates are formed, the hydrophobic surfaces of the NPs can also help prevent the formation of a wetting water layer on hydrates, reducing the adhesion force between hydrate particles or free water droplets. Increased NP and salt concentrations may further limit the degree of hydrate agglomeration due to a dense packing of NPs with fewer voids at the interface. Our results show great potential of using functionalized NPs in the management of hydrates.

5. MATERIALS AND METHODS

5.1. Materials

The following materials and chemicals were used: n-octadecyltrimethoxysilane (OTMOS, C18H36O3Si, Gelest), silica nanoparticles (Fiber Optic Center Inc.), n-decane (n-C10H22, Sigma-Aldrich, anhydrous, ≥99%), deionized water, ethanol (C2H5OH, Sigma-Aldrich, ACS reagent, ≥99.5%), ammonium hydroxide solution (NH3 in H2O, Aristar, ACS reagent, 28–30 wt %), polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning), gelatin (from porcine skin, type A, Sigma-Aldrich), cyclopentane (C5H10, Sigma-Aldrich, ACS reagent, grade ≥98%), sodium chloride (NaCl, Sigma-Aldrich, ACS reagent, ≥99%), and methane/ethane gas mixture (75/25 mol %, General Air).

5.2. Silica NP Functionalization and Characterization

The procedures for functionalization of the silica NPs were similar to those described in the literature. Briefly, the amorphous silica NP powders were dispersed into water under sonication for 30 min; silica NPs were then treated with 0.1 M NaOH aqueous solution 24 h for rehydroxylation. They were then mixed with OTMOS and NH4OH (as catalyst) in ethanol for 24 h to coat the silane molecules on their surfaces. The amount of OTMOS required to attach one silane molecule per nm2 of the silica NP surface was labeled as 1X. Accordingly, silica NP surfaces modified by other amounts of silane were labeled as 0.25X, 0.5X, 2X, 4X, and 8X. 0X referred to the pristine silica NPs treated by NaOH, which were highly hydrophilic due to abundant silanol functional groups on the particle surface. In a typical surface modification experiment (1X silica NPs), 40 mL of silica NPs in DI water suspension (0.05 g/mL) was mixed with 4.5 mL of 1 M NaOH aqueous solution in a 50 mL centrifuge tube. The tube was placed on a rotator to ensure good mixing for 24 h. After that, these silica NPs were cleaned three times via centrifugation (1800g, 20 min, IEC HT Centrifuge) with DI water to remove residual NaOH, and resuspended in 40 mL of ethanol. 128 μL of OTMOS in ethanol (10 v/v %) and 2 mL of ammonium hydroxide were added to the particle suspension. The tube was
placed on a rotator for 24 h. The surface-modified particles were cleaned three times via centrifugation (1800g, 20 min, IEC HT Centrifuge) with ethanol to remove residue reactants. Then they were cleaned one more time via centrifugation (1800g, 20 min, IEC HT Centrifuge) with n-decane and resuspended in n-decane to a final particle concentration of 0.1 g/mL.

Small fractions of the functionalized NPs were dried at room temperature (RT) for characterization, including scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). SEM images were obtained using a JEOL 7000F FE-SEM operated at 20 kV accelerating voltage. FTIR spectra were obtained with a Thermo Electron Nicolet 4700 FTIR spectrometer. A background measurement was taken before loading the NP sample. TGA was carried out under air using a Q50 TGA (TA Instruments). Measurements were obtained by adding 15 mg of NPs to a ceramic pan. The samples were heated from RT to 600°C at a rate of 10°C/min. The TGA measurements were run three times for each NP batch.

The three-phase contact angle of the modified silica NPs at the water—n-decane interface was measured with a gel-trapping technique. In brief, 12 mL of hot 2 wt % gelatin solution (50°C) and 10 mL of n-decane were sequentially added into a glass dish (80 mm in diameter). 100 μL of 1 mg/mL modified silica NPs in ethanol was then carefully added to the water—oil interface with a micropipette. The silica NPs spread over the water—oil interface as ethanol evaporates. The gelatin solution started gelling after cooling the glass dish to room temperature for 3 h, and the silica NPs were immobilized at the gel—oil interface. Then n-decane was gently removed, and a mixture of PDMS and curing agent (10:1 ratio, degassed in a vacuum chamber for 1 h) was poured over the gelatin gel. The PDMS was then peeled off the gel surface and immersed in a DI water bath at 50°C for 10 min to dissolve any residual gelatin. The PDMS was rinsed thoroughly with DI water and blow dry. A small piece of the PDMS sample was cut for FE-SEM and atomic force microscopy (AFM, tapping mode, Asylum Research) imaging. The contact radius d and the height of protrusion h of silica NPs at the interface were obtained.

The stabilization of oil/water emulsions by NPs was tested in glass vials. The emulsions were prepared by homogenizing a mixture of DI water, n-decane, and NPs. For a typical experiment, 2 mL of DI water, 7.8 mL of n-decane, 200 μL of modified NPs in n-decane suspension, and 40 μL of oil-soluble blue dye were added into a 22 mL glass vial. The mixture was vigorously stirred by an Ultra-Turrax homogenizer (IKA T25) at 13500 rpm for 2 min. The type of emulsion was then examined by adding one drop of the emulsions into n-decane and water. Oil-in-water (O/W) emulsions will remain as a drop in oil but disperse in water and vice versa.

5.3. Experimental Apparatus for Hydrate Testing. Figure 10 shows the customized cooling cell built for in situ observation of cyclopentane hydrate formation under an optical microscope. The cooling cell consisted of a 1/4 in. thick copper bar with a hole 1/2 in. in diameter. A clean 0.17 mm glass coverslip was glued at the bottom of this copper bar with epoxy. The cold side of a Peltier cooling plate (154 W) was attached to the copper bar to achieve fast cooling. An aluminum coolant block was integrated to the hot side of the Peltier, and a mixture of chilled ethylene glycol and water was circulated to remove the heat transferred to and generated by the Peltier plate. A resistance temperature detector (RTD) was inserted in the cooling cell to monitor the liquid temperature inside. The RTD, Peltier plate, and power supply were integrated with a temperature controller to maintain constant temperature inside the cell. The whole cooling cell was placed on the microscope stage for in situ observation.

Figure 11 illustrates the experimental apparatus to test the effect of NPs on gas hydrate formation and dispersion in a high-pressure rheometer. The major components of the system include a rheometer (TA Instruments, HR-2), a syringe pump (Teledyne, USA), and a circulating chiller. The rheometer includes a high-pressure cell that is used for in situ hydrate formation. The cell is 57 mm in height and 28 mm in inner diameter. The total volume of the cell is 35 mL, while 25 mL of liquid is sufficient to cover the vanes of the impeller. The rheometer uses a customized hollow vane for stirring, which is 40 mm in height and 26 mm in diameter. The rationale for choosing a hollow vane is to promote shear force and increase gas—liquid mixing while minimizing hydrate accumulation in dead zones close to the shaft. The syringe pump has a capacity of 100 mL to maintain the system pressure constant up to 250 bar. The chiller is connected to the cooling jacket of the high-pressure cell to control the temperature ranging from −20 to 40°C.

5.4. Cyclopentane Hydrate Formation Tests. The NP performance was first evaluated through the in situ observation of cyclopentane hydrate formation with an optical microscope. A typical experiment started with adding 800 μL of a mixture...
of cyclopentane and n-decane (20/80 vol %) into the cooling cell followed by gently adding 50 μL of W/O Pickering emulsions stabilized by NPs. The emulsion droplets were spread on the bottom glass slide, and a coverslip was placed on top of the cell to minimize the evaporation of cyclopentane and n-decane. Static images were acquired using a color charge-coupled device (CCD) camera (Qimaging, Retiga 2000R) that was connected to an inverted microscope (IX71, Olympus). The agglomeration of hydrates was tested by attempting to disturb the hydrate particles with a glass fiber, and the process was recorded using a high-speed monochrome CCD camera (SV643M, EPiX) connected to the microscope.

Hydrate formation is a stochastic process, and direct conversion of liquid water into hydrates can take hours to days depending on the subcooling temperature, hydrate former, stirring speed, and purity of water. Figure 10b shows the protocol of temperature control to promote hydrate growth. The temperature in the cell was first lowered to −15 °C for 30 min to convert most of the water droplets into ice. Then the cell temperature was ramped up to 0.5 °C to melt the ice and induce hydrate formation and growth for 30 min. Finally, the cell temperature was raised to 10 °C for 10 min to dissociate the cyclopentane hydrate completely.

5.5. Rheological Measurement for Gas Hydrates. In the gas hydrate formation tests with the rheometer, a hollow-vane impeller was used for mixing and promoting the formation of gas hydrates. For such a kind of impeller, the shear profile is not well-defined, and as such, a torque–viscosity correlation was developed using standard silicone oils with known viscosity at 20 °C. The procedure for this calibration was previously reported. Briefly, 25 mL of standard silicone oil with different viscosities was measured in the pressure cell for different settings of the rotational speed of the impeller. The correlation obtained between the torque T (μN m) and viscosity μ (cP) is

\[
\log_{10} \mu = \left[ \log_{10} (T + 130.1) - 1.1216 \right]/0.8480
\]

for a rotational speed of 200 rpm. This correlation was used throughout this study to convert the measured torque to the reported apparent viscosity for gas hydrates.

The rheometer experiments were run at a constant pressure of 70 bar using a syringe pump. The hydrate gas former was chosen to be a methane/ethane (75/25 mol %) gas mixture. The hydrate equilibrium temperature was 16.5 °C (PVTSim Nova 3.1.117), and the expected hydrate structure was sI1. The experiments were run at 8 and 10 °C, giving 8.5 and 6.5 °C subcooling, respectively. Subcooling is defined as the difference between the running temperature and the hydrate equilibrium temperature, which characterizes the driving force for hydrate formation. Each set of experimental conditions was repeated three times to ensure reproducibility. The behavior of the hydrate formation was repeatable with major variation in the onset time for hydrate formation. At 1 and 10 mM sodium chloride (NaCl), the hydrate equilibrium temperature of the initial system is predicted to differ by less than 0.1 °C (as calculated by PVTSim Nova 3.1.117). Therefore, such depression in equilibrium temperature is negligible. Salts have been reported to change hydrate crystal growth morphology, but its impact on hydrate agglomeration has not been reported.

In each experiment, 15 mL of NP-n-decane suspension was mixed with 10 mL of DI water or brine solution, making the total liquid volume 25 mL in the rheometer, which was enough to immerse the vanes of the impeller. The system was then charged with the methane/ethane gas mixture. The syringe pump was started to maintain the pressure at 70 bar. The chiller was first started to maintain the cell temperature at 20 °C. The rotational speed of the impeller was set at 200 rpm throughout the experiments. However, if the torque experienced by the impeller remained close to a maximum of 0.2 N m for a prolonged time (e.g., 1 h) or goes beyond the maximum, it would cease to rotate to prevent mechanical damage to the rheometer. When the initial temperature and impeller rotational speed stabilized for 1 h, the chiller temperature was decreased to the set temperature (8 or 10 °C) to form gas hydrate. After hydrate formation, the impeller will either stop rotating because the torque reaches the maximum due to jamming by hydrates or rotate continuously with a constant shear.

During the experiments, the torque, pressure, temperature of the cooling jacket, ambient temperature, and the syringe pump volume were recorded. The gas consumed for hydrate formation was calculated from the above data. Assuming a hydration number of 6 (mol of water/mol of gas), the actual hydrate amount and water conversion could be obtained. The latter was defined as the percentage water that is converted into hydrate.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01806.

Average size of emulsions stabilized by different NPs; list of supporting movie files; SEM images of modified silica NPs embedded in PDMS; AFM height scan of modified silica NPs embedded in PDMS; images of the W/O emulsion stabilized by 1XS NPs; optical images of the W/O emulsions stabilized by Span 80 in a mixture of n-decane and cyclopentane (PDF). Dispersed hydrate particles with 1X NPs (AVI), Agglomerated ice particles with 2X NPs (AVI), Agglomerated hydrate particles with 2X NPs (AVI).

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**Notes**

The authors declare no competing financial interest.

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