The synergy of spiral agitation and nano-promoters significantly enhances hydrate formation under mild conditions

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Abstract

Sluggish hydrate kinetics and low methane storage capacity give rise to the limitation of the application of hydrate-based solidified natural gas (SNG) technology. Here, we prepared two nano-promoters of -SO3-@PSNS and -COO-@PSNS, with which, methane hydrate formation in a spiral-agitated reactor under mild conditions was evaluated. Excitingly, spiral agitation enhances hydrate nucleation and initial growth kinetics, while the nano-promoters improve hydrate later growth kinetics, and the synergy of them results in extraordinary hydrate formation kinetic under mild conditions. Large methane storage capacities of 147.28 V/V and 141.33 V/V were obtained in the systems of -SO3-@PSNS and -COO-@PSNS separately under the condition of 3.8 MPa, 275.15 K and 30 rpm, which increase by 85.07% and 77.59% comparing to that in pure water, respectively. The synergy performs better than that of spiral agitation and amino acids, and this may promote the application of SNG technology a step forward.

INTRODUCTION

As people pay more attention to environmental matters, the use of conventional fossil energy continues to decline, while clean energy, such as low-carbon natural gas, has been becoming popular. The question that follows is how to efficiently store and transport natural gas, especially for the remote areas lack of natural gas resource. Gas hydrates are non-stoichiometric compounds composed of water molecules and gas molecules under low-temperature and high-pressure conditions, where gas molecules are packed in the crystal lattices that consist of hydrogen-bonded water molecules[1]. The high storage capacity of about 170 V/V and extraordinary security of hydrates (can be long-term stored under 253.15 K and atmospheric pressure) endow it with great potential in natural gas storage and transportation[2–4]. This gives rise to a new technology, the so-called solidified natural gas (SNG),which was reported to be one of the most promising alternative for conventional technologies, such as liquefied natural (LNG) and compressed natural gas (CNG)[5]. However, it is difficult to generate another new phase (crystal nucleus) in a system, so hydrate nucleation generally requires a persistent induction period, which has great randomness and uncertainty especially when the driving force is feeble, and this stochastic nature of hydrate nucleation impedes the application of the SNG technology[6]. Meanwhile, hydrate growth kinetics is also sluggish, this would cause the storage capacity of natural gas in hydrates to be unsatisfactory[7]. Therefore, it is of significant importance to enhance hydrate nucleation and growth kinetics, while large storage capacity is also accessibility.

During the past few decades, surfactants have been widely used to improve hydrate formation by enhancing mass transfer and creating favorable morphology for sustained hydrate formation[8–13], such as sodium dodecyl sulfonate (SDSN), sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), etc.

Among these surfactants, SDS produces the most efficient promotion, which has been viewed as the most potential promoter[9,11]. It was reported that hydrate formation process could be shorten to 30 min by producing porous hydrates in SDS systems[14], and considerable methane storage capacity of 138 V/V can be obtained with the addition of 1000 ppm SDS[15]. However, the severe "climbing wall effect" during hydrate formation in SDS systems could decrease gas storage density[16], and substantial foam usually produces during hydrate dissociation[17], both of these two drawbacks are detrimental to its practical application. Another class of kinetics additive is amino acid[18–21], which promises to be comparable to SDS. Amino acid can significantly improve methane hydrate formation, and the absence of foam during degassing makes them attract attention[22,23]. However, amino acids are perishable, and its cost is relatively high, although the dosage of amino acids has been controlled to extremely low (0.3 mmol/L)[24], the question of economic feasibility for their large-scale industrial application is still open. Therefore, the design and preparation of high-efficiency promoters that could produce similar or better promotion as SDS and amino acids are required, while the defects of them should also be overcome. In our previous work[25–27], -SO_3^-(similar as the hydrophilic group of SDS) coated nano polymers (-SO_3^-@PSNS) had been successfully prepared, and methane storage capacity of 59 V/V-142 V/V can be obtained in -SO_3^-@PSNS systems, while there was no foam generated during hydrate dissociation. Since the preparation method is simple and cost is low, -SO_3^-@PSNS can be treated as one kind of potential alternative of SDS and amino acids.

In addition, take the excellent nature of mass and heat transfer into account, the promotion approach of mechanical stirring has been extensively applied, and enhanced hydrate nucleation and growth kinetics were commonly reported. Hydrate induction time and growth time are 230 min and 390 min separately under mild condition (5 MPa)[28], and the induction time even reduces to 2.33 min when pressure increases up to 10 MPa[22]. However, mass transfer would be significantly hindered when hydrate slurry is formed[29], so poor later performance in mechanical systems usually occurs. To overcome the drawback, the synergistic promotion of mechanical and chemical approaches appears, giving rise to improved hydrate nucleation and growth kinetics[30–33]. Hydrate induction time can be controlled within 10 min under the combined action of SDS (300 ppm) and spraying[32]. By introducing leucine into a stirring system, Veluswamy et al.[22]also founded that the stochasticity of hydrate nucleation significantly decreases. Moreover, hydrate growth rate was reported to increase approximately 4-fold with the presence of SDS (144.2 ppm) in a gas-inducing agitation reactor[34].

Recently, we proposed a novel spiral-agitated reactor[35], and fast hydrate nucleation was observed in pure water. Hydrate induction time is less than 4 min at 3.5 MPa and 60 rpm, suggesting excellent promotion of spiral agitation on hydrate nucleation, and this also guarantees fast hydrate growth rate in the original agitation stage. Clearly, compared with conventional stirring approaches, spiral agitation performs much better on enhancing hydrate nucleation and original growth kinetics under mild conditions (low-pressure and low-revolving speed). Therefore, it can be anticipated that more enhanced hydrate formation kinetics would be feasible under mild conditions by introducing chemical additives into the spiral-agitation systems. Excitingly, when amino acids were introduced[24], hydrate formation kinetics was significantly improved, and it was found that methane storage capacity in 2 mmo/L L-methionine system is up to 145.97 V/V under an extremely mild condition of 3.8 MPa, 275.15 K and 60 rpm.

Ultimately, the synergy of spiral agitation and chemical additives sheds light on high-efficiency hydrate formation, and this may pave the way on the application of SNG technology. However, due to the drawback of SDS and amino acids, economical and stable promoters are required, which also should cooperate well with spiral agitation. In this work, two nano-promoters were prepared by fixing -SO_3^- and -COO^- groups on the surface of polystyrene nanospheres, respectively. The synergy of the nano-promoters and spiral agitation on hydrate formation was evaluated. It is worth to highlight that when nano-promoters were introduced into the spiral-agitated reactor, enhanced hydrate formation kinetics was obtained even under extremely mild conditions, which is superior over the synergy of spiral agitation and amino acids.

EXPERIMENTAL SECTION

Materials

Methane with high purity (> 99.99%) was purchased from Heli Gas Co., Ltd. (Qingdao, China). The laboratory-made deionized water with a conductivity of 1.1 ± 0.1 µs/cm at 298.15 K was used. Styrene (St, A.R.), sodium p-styrene sulfonate (SS, A.R.) and acrylic acid (AA, A.R.) were purchased from www.aladdin-e.com. Potassium persulfate (KPS, A.R.) was provided by Shanghai Aibi Chemical Reagent Co., Ltd (Shanghai, China).

Preparation and characterization of the nano-promoters

The nano-promoters were prepared through soap-free emulsion polymerization with St as the hydrophobic monomer, while polymerizable monomers and KPS were applied as the hydrophilic monomers and initiators, respectively. Two polymerizable monomers with different hydrophilic groups ($-SO_3^-$ and $-COO^-$) were used to give rise to two kinds of nano-promoters, which were defined as $-SO_3^-$@PSNS and $-COO^-$@PSNS separately. A 250 mL flask equipped with an agitator was used to synthesize the nano-promoters in nitrogen environment, and a reflux condenser was employed. Firstly, the appropriate amount of deionized water, St and hydrophilic monomers were added into the flask in sequence, while the agitation was turned on at a speed of 300 rpm. Then, when the temperature was reached set value, the initiator solution was dropped into the flask at a rate of 1 drop per second, and subsequently the system was kept for 5 h until the end of polymerization. The recipe of the soap emulsion polymerization is given in Table S1, and the reaction temperature was set as 353.15 K, which was controlled by constant temperature oil-bath pans

The morphologies of the nano-promoters were observed by a transmission electron microscope (TEM, JEM-1200EX, Japan Electronics Co., Ltd., Japan), and it is clear from Figure 1 that both of the nano-promoters are uniform nanospheres. The hydrophilic group on the surface of the nano-promoters was determined with an infrared spectrometer (Nicolet iN 10, Thermo Fisher, USA), the adsorption peaks corresponding to the S=O and C=O confirm the existence of $-SO_3^-$and $-COO^-$ groups on the surface of $-SO_3^-$@PSNS and $-COO^-$@PSNS, respectively. The size distribution and zeta potential of the nano-promoters were determined by a Laser Particle Size Analyzer (Malvern Nano-s90, UK), and $-SO_3^-$@PSNS and $-COO^-$@PSNS produce the zeta potential of -31.8 mV and -20.36 mV separately. This confirms the existence of corresponding hydrophilic groups on the nano-promoters, and excellent stability is also anticipated through the electrostatic force between the nano-promoters.

Methane Hydrate Formation

A novel spiral-agitated reactor was used, the schematic diagram of which is presented in Figure S1, and more details can be found in our previous publications[24,35]. The high-pressure reactor is composed of a stainless-steel cylinder and a stirring rod, and the effective volume of the reactor is 581.71 mL. The stirring rod is equipped with screw blade, the pitch of which is 10 mm (see in Figure S2). Two windows are set up at the reactor to observe inner hydrate morphologies. The experimental temperature is acquired by a PT100 temperature transducer (± 0.1 K), while pressure is recorded by a BP801 pressure transducer (± 0.01 MPa). The reactor is supported by a bracket, so the inclined angle of the spiral-agitated reactor can be adjusted. All of the above devices are put in a thermostatic chamber. The consumed methane is measured by a flow totalizer with an uncertainty of 0.01 mL/min, and the flow, pressure and temperature data are logged by a data acquisition system every second.

Before hydrate formation experiments, the reactor was firstly adjusted to a set inclined angle, and hydrate formation under three inclined angles (25°, 35° or 45°) was evaluated in this work. Subsequently, the reactor was washed with deionized water three times, the stirring was turned on at a revolving speed of 60 rpm during cleaning, and then the reactor was flushed with methane three times. 120 mL solution was injected into the reactor, and the cooling system was turned on to precool the solution and methane. When the temperature inner the reactor reached the experimental temperature (275.15 K), methane was fed into the reactor to a desired pressure, and then the stirring was turned on. When the stirring rod was stuck by formed hydrates, the stirring was turned off, and hydrate formation continues in a static system. Three trails were performed at each experimental condition to ensure the repeatability. Methane storage capacity was defined as the STP volume of methane stored in per unit volume of hydrates, which can be calculated using Eq.

(S1), and the water-to-hydrate conversion was calculated using a hydration number of 6.1[36].

RESULTS

Enhanced Hydrate Formation

Hydrate nucleate kinetics can be greatly improved by spiral agitation, resulting in fast hydrate nucleation. It can be seen from Table S2 and S3 that hydrate nucleates rapidly within 5 min in pure water (5 MPa), and the longest induction period is only 7.3 min even under mild condition (3.8 MPa). The nucleation kinetics is further strengthened by nano-promoters, especially under mild conditions, and hydrate induction time is less than 5 min in both of the nano-promoter systems. In addition, hydrate growth kinetics is also enhanced due to the improvement of mass transfer induced by spiral agitation, giving rise to large gas storage capacity. Methane storage capacity in different systems is given in Figure 1, and it is clear that large methane uptake is accessible even in pure water, where hydrate growth kinetics strongly depends on driving force. The storage capacity is close to 70 V/V at 3.8 MPa, while it goes up to 139.54 V/V and 144.54 V/V at 5 MPa for the inclined angle of 35° and 45°, respectively, and water-to-hydrate conversion is more than 85%. Besides, it is worth noting that the convection [35] of liquid phase inner the spiral-agitated reactor intensifies with the increase in the inclined angle, so the mass transfer between gas and liquid is enhanced at large inclined angle, leading to the increase in conversion, but when the driving force was feeble, this effect was inconspicuous.

It is worth to note that the conversion increases by adding -COO^-@PSNS, but the effect also depends on the driving force and inclined angle. Apparently, the conversion increases with the increase in inclined angle at 3.8 MPa, and the maximum gas storage capacity of 141.33 V/V is obtained at 45°, but the promotion of COO^-@PSNS greatly degenerates at high pressure (5 MPa) at the same inclined angle, where the conversion is only 40.35 %. What is more noteworthy is that hydrate growth kinetics in -SO_3^-@PSNS systems is excellent even under mild condition (3.8 MPa), and the conversion is up to 97.29 % at 5 MPa and 35°, and large conversion (>85 %) can also be achieved for low pressure (3.8 MPa). In conclusion, the nucleation and growth kinetics of hydrates are enhanced by spiral agitation, making it possible to achieve admirable conversion (85%) in pure water, and this enhancement is further improved by nano-promoters, causing larger gas storage capacity. Additionally, compared with -COO^-@PSNS, -SO_3^-@PSNS performs better on the promotion, especially under mild conditions.

In order to clarify the promotion mechanisms of spiral agitation on hydrate growth kinetics in different systems, the rate of methane uptake was evaluated as shown in Figures 3 and 4, and it is clear that methane uptake rate is severely affected by driving force. The uptake rate in pure water is relatively stable during the stirring period at 5 MPa, which almost maintains a constant rate of 400 mmol/min, but it decreases rapidly after the agitation was turned off, demonstrating the excellent promotion of spiral agitation on hydrate growth kinetics. When nano-promoters are introduced, hydrate growth kinetics is significantly strengthened, and methane uptake rate increases up to 800 mmol/min. Moreover, the uptake rate decreases more slowly than that in pure water after turning off the agitation, this means that nano-promoters improve hydrate formation in static conditions.

In contrast, due to mass transfer limitation, hydrate growth kinetics is relatively feeble at low pressure (3.8 MPa), resulting in a lower uptake rate, as presented in Figure 4. The variation of methane uptake rate in the nano-promoter systems is similar to that in pure water at stirring stage, methane uptake keeps a constant rate of 100 mmol/min originally, and then it dramatically increases. Apparently, during the initial stage of hydrate formation, hydrate growth kinetics is controlled by spiral agitation, and the effect of nano-promoters is negligible. However, when the stirring was turned off, the scenario changes completely. As can be seen in Figure 4, methane uptake rate in pure water is very low during hydrate static formation stage, but it subsequently increases sharply at about 150 min in -SO_3^-@PSNS systems, and the rate peak even reaches 100 mmol/min. Moreover, this phenomenon lasts for nearly 300 min and is named as ”secondary uptake” stage, which should contribute to the large methane storage capacity in -SO_3^-@PSNS systems, and the occurrence of this phenomenon should be closely related to the characteristics of hydrates. Although there is no obvious phenomenon of “secondary uptake” in -COO^-@PSNS systems, methane uptake rate decreases more slowly than that in pure water at the inclined angle of 35° and 45°, and this prolongs the period of methane uptake, so large water-to-hydrate conversion is also obtained in -COO$^-$@PSNS systems.

Synergistic promotion mechanisms

As mentioned above, hydrate growth kinetics is significantly enhanced by the synergistic effect of spiral agitation and nano-promoters under mild conditions. Since methane uptake rate corresponds to hydrate kinetics, its variation under different conditions was analyzed, and the schematic diagram of methane uptake rate for different scenarios were given in Figure 5(a). For high pressure (5 MPa), the rate curve is divided into two sections, a fast uptake stage with stirring (Stage I) and a slow uptake stage for hydrate static formation (Stage II). In comparison, it is clear from Figures 5(b) and 5(c) that the rate profiles can be divided into three stages at 3.8 MPa. An initial stage for hydrate stable growth (Stage I), following by a hydrate quick growth stage (Stage II), and finally a hydrate slow growth stage occurs under static condition (Stage III). In addition, compared with pure water and -COO$^-$@PSNS systems, an obvious "secondary uptake" stage appears in -SO$_3$$^-$@PSNS systems as seen in Figure 5(c).

High driving force

At higher pressure (5 MPa), when the stirring was turned on, spiral agitation can induce two-way convection, dual-agitation and continuous interfacial impact[35], and these effects cause methane to be dissolved into liquid phase quickly, and this excellent mass transfer leads to fast hydrate formation within minutes as seen in Figure 6(b). During stage I, hydrates were generated rapidly and massively, which were carried upwards from liquid phase at the bottom by spiral blades (Figure 6(b)-(c)), but lots of unconverted interstitial water is enclosed in hydrates. With the proceeds of hydrate formation, the liquid level is almost disappeared in about 30 min as presented in Figure 6(c), while methane uptake still remains a large rate at this time. Because the difference in hydrate morphologies and conversion would produce different hindrance to the spiral blades, the torque of the stirring rod was measured during hydrate formation, which was shown in Figure 7. Clearly, the torque is low and almost keeps constant at stage I, so it can be speculated that hydrates are relatively soft due to the existence of interstitial water. As hydrate growth goes on, the surface of hydrates is gradually hardened, and this hinders the continuous conversion of interstitial water. However, with the hardening of hydrate surface, large hydrate chunks are gradually crushed into small ones due to the effect of spiral agitation, and this further improves gas-liquid contact and mass transfer, causing a large methane uptake rate at this stage. It is clear from Figure 7 that the torque increases linearly with the increase in the conversion in the middle period of stage I, and this is obviously caused by the hardening of hydrate surfaces. In a word, large driving force causes fast hydrate growth kinetics, although surface hardening hinders inner mass transfer, it is improved by hydrate crush induced by spiral agitation, and this causes methane uptake keep a relatively high rate for a long period (50-60 min) in stage I, giving rise to a large conversion of ca. 50% in this period. Additionally, when nano-promoters were introduced, enhanced hydrate formation was observed as seen in Figure 3. It was reported that the nano-promoters could affect the morphology of hydrates by increasing their pore texture[25], and the improved porosity increases mass transfer of methane to the interior of hydrates, causing local methane uptake rate to be higher than that in pure water.

When the stirring was turned off in stage II, methane uptake rate in pure water decreases rapidly, and it maintains a relatively low value for a long time. The duration of each stage is summarized in Figure 8, and it can be seen that stage II lasts for nearly 10 h at the inclined angle of 35° and 45°. Although the conversion of interstitial water to hydrates is extremely slow due to the limitation of mass transfer, a large amount of methane is also stored in hydrates in this stage. In comparison, it only takes less than 5 h for the nano-promoter systems to get a similar effect, demonstrating the excellent promotion effect of nano-promoters. It is worth noting that there is no secondary uptake stage in -SO$_3$$^-$@PSNS, indicating that the conversion is relatively sufficient in stage I due to high driving force, and the t_{85} that corresponds to the time of 85% water-to-hydrate conversion is less than 172 min in -SO$_3$$^-$@PSNS systems (see in table S2).

Low driving force

Compared with high pressure, hydrate growth is more complicated under lower pressure (3.8 MPa), which is divided into three stages. Regardless of pure water or two nano-promoter systems, methane uptake is stable at a rate of about 100 mmol/min for about 1 h after the stirring was turned on, demonstrating that hydrate growth kinetics is governed by spiral agitation in stage I. In this stage, hydrate growth kinetics is sluggish due to low driving force, thus a large amount of interstitial water is enclosed by hydrates, which cannot be shaped up, causing the effect of nano-promoters doesn't work, and the conversion is only about 20%. As the proceeds of hydrate growth, its surface is gradually hardened, and then it can be broken into smaller pieces on account of continuous stirring, and then the gas-liquid contact and mass transfer are greatly improved, so the uptake rate drastically increases in stage II. Interestingly, the conversion is close to 50% at the end of stage II, which is approximately equivalent to that in stage I at 5 MPa. Obviously, stage I at high pressure is divided into two stages when pressure is low due to slow hydrate growth kinetics. In contrast, hydrate growth kinetics is fast at high pressure, so the hardening and crush of hydrates is fast, causing only one stage occur during stirring. Subsequently, the interstitial water is suffered severely by mass transfer limitation, causing the declination of conversion efficiency, and then the promotion effect induced by spiral agitation disappears, so methane uptake rate almost unchanged after turning off agitation. In stage III, inner interstitial water is difficult to permeate outward due to the limitation of hydrate shells, so hydrates mainly grow inward with the diffusion of methane inward, and this leads to lots of interstitial water remains unconverted in pure water due to low driving force, causing low final conversion (<50%).

Comparably, the scenarios in nano-promoter systems are significantly improved, especially for -SO$_3^-$@PSNS systems, and the unique "secondary uptake" phenomenon increases the final conversion to a large extent. The excellent ductility and porosity of hydrates formed in -SO$_3^-$@PSNS systems are very similar to that in amino acid system[9,37]. The increased ductility of hydrates reduced their hardness, making large hydrate chunks to be easily broken into small ones, thus alleviating the restrictions of mass transfer. Additionally, the rich porous properties improve the permeability of hydrates, this is beneficial to the conversion of inner interstitial water, and with the inward growth of hydrates, micro cracks would occur due to space constraint, which further increases mass transfer and the conversion of interstitial water. However, no obvious "secondary uptake" phenomenon was observed in -COO$^-$@PSNS systems. Considering that methane uptake remains a relatively large rate after turning off agitation in -COO$^-$@PSNS systems, it can be speculated that the porosity of hydrates formed in -COO$^-$@PSNS systems is also excellent, while the ductility should be poor. Moreover, the conversion of interstitial water in -COO$^-$@PSNS systems strongly depends on the effect of previous agitation, causing it to be more sensitive to the inclined angle. In addition, it is worth to note that the reaction time of stage III in pure water is short at 3.8 MPa, while it is greatly prolonged in the presence of nano-promoters as presented in Figure 8, and it is precisely the extension of stage III that causes the final conversion to be satisfied. In a word, the effect of nano-promoters under low driving force only works after the formation of hydrates, and the presence of nano-promoters made up the low conversion under the conditions.

Ultimately, hydrate growth depends on mass transfer and reaction kinetics. A schematic diagram of hydrate growth in different systems is given in Figure 9. The reaction kinetics is strong under high driving force, thus hydrate growth is mainly limited by mass transfer in this situation. In the initial stage (stage I) of hydrate formation, the mass transfer that enhanced by the spiral agitation accelerates hydrate growth, resulting in quickly hardening of hydrate surface, and this causes large hydrate chunks to be easily crushed into small ones by spiral agitation and further increases the mass transfer. When the stirring is turned off (stage II), hydrates continue to grow inward, but part of interstitial water remains unconverted due to the limitation of mass transfer. However, this scenario is improved by the addition of nano-promoters, which increase the porosity of hydrates, giving rise to enhanced mass transfer and large conversion. In comparison, although mass transfer is enhanced by spiral agitation, hydrate growth kinetics is poor under low driving force, so hydrate growth is mainly limited by reaction kinetics in this situation, and this causes low conversion in the initial stage (stage I), where hydrates are difficult to be harden and crushed. With further reaction, hydrate chunks gradually harden and then are broken into small ones by spiral stirring. At this time, the gas-liquid contact and mass transfer are both greatly intensified, resulting in larger methane uptake rate in stage II. After the stirring is turned off (stage III), interstitial water is continuously converted at an extremely slow rate, and this is improved by nano-promoters, which can increase hydrate porosity. Moreover, hydrates ductility is also improved in -SO_3^-@PSNS systems, this induces micro cracks, which further enhances mass transfer and gives rise to the "secondary uptake" phenomenon, ensuring excellent methane storage capacity under mild conditions.

DISCUSSION

In our recent work, the synergistic effect of amino acids and spiral agitation on promoting hydrate growth kinetics was evaluated[24]. Excitingly, the composite system performs well under mild conditions, and a storage capacity of 146 V/V was obtained in 0.3 mmol/L L-methionine solution under 3.8 MPa and 60 rpm. However, when the revolving speed was reduced to 30 rpm, the promoting effect became poor, and the maximum methane storage capacity of 128 V/V was only achieved in the system of 2 mmol/L L-methionine. In comparison, the synergistic effect of nano-promoters and spiral agitation performs better on promoting the growth kinetics of hydrates, and the excellent promotion was also observed under milder conditions. It is clear from Figure 10 that methane storage capacities in -COO^-@PSNS and -SO_3^-@PSNS systems are 141.33 V/V and 147.28 V/V separately for 30 rpm, which increase by 10.4% and 15.1% compared with L-methionine under the same conditions, and methane uptake rate in -COO^-@PSNS systems is faster than that in amino acid systems. Moreover, it is worth noting that the concentration of nano-promoters is only 1 mmol/L, which is also easy to synthesize and store. Therefore, in view of the excellent promoting of nano-promoters under mild conditions, its synergistic effect with spiral agitation provides a new insight for the industrial production of SNG technologies.

CONCLUSIONS

In order to promote hydrate formation kinetics under mild conditions, two nano-promoters of -SO_3^-@PSNS and -COO^-@PSNS were prepared, and hydrate formation in a spiral-agitated reactor was carried out, while the synergistic effect of spiral agitation and nano-promoters on hydrate formation kinetics was evaluated. Hydrate nucleation is significantly enhanced by spiral agitation, causing the induction time to be less than 10 min in pure water even at low pressure (3.8 MPa), and this promotion is further improved by nano-promoters. Hydrate growth kinetic is controlled by mass transfer and driving force, although hydrate initial growth kinetics is enhanced by spiral agitation, hydrate later growth is sluggish due to the limitation of mass transfer, especially in pure water under low driving force, giving rise to low methane storage capacity of 79.58 V/V at the inclined angle of 45°. However, this scenario is greatly improved by nano-promoters, and large methane storage capacities of 147.28 V/V and 141.33 V/V are obtained in the systems of -SO_3^-@PSNS and -COO^-@PSNS, respectively, which increase by 85.07% and 77.59%. Ultimately, spiral agitation and nano-promoters contribute to initial and later hydrate formation separately, and their synergistic effect gives rise to enhanced hydrate formation kinetics under mild conditions. Compared with amino acids reported in our previous work, the presented nano-promoters performs better under milder conditions, and considering that the nano-promoters are easy to synthesize and store, their synergistic effect with spiral agitation provides a new insight for the industrial production of SNG technologies.

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DECLARATION OF COMPETING INTEREST

The authors declared that there is no conflict of interest.

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