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Experimental Study on the Kinetics of the Natural Gas Hydration Process with a NiMnGa Micro-/Nanofluid in a Static Suspension System

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Abstract: Natural gas is a resource-rich clean energy source, and natural gas hydration technology is a promising method for natural gas storage and transportation at present. To realize the rapid generation of hydrates with a high gas storage capacity, in this paper NiMnGa micro-/nanoparticles (NMGs) with different mass fractions (0.1 wt%, 1 wt%, 2 wt%) were prepared with 0.05 wt% sodium dodecyl sulfate (SDS) and 1 wt% L-tryptophan to form static suspension solutions of gellan gum, and the methane hydration separation kinetics experiments were carried out under the condition of 6.2 MPa for the SDS-NMG-SNG (SNG) and L-tryptophan-NMG-LNG (LNG) systems. The results showed that the induction time of the systems with NMG micro-/nanoparticles was shortened to different degrees and the gas consumption rate was increased. The best effect was achieved in the SNG system with 1 wt% NMG, and the induction time was shortened by 73.6% compared with the SDS-gellan system (SG). The gas consumption rate of the system with L-tryptophan was better than that of the system with SDS, and the best effect was achieved in the system with 2 wt% NMG. The system with 2 wt% NMG had the best effect, and the problem of foam decomposition did not occur. The analysis concluded that NMG has strong mass transfer and phase-change heat absorption properties, which can significantly improve the kinetics of the natural gas hydrate generation process; L-tryptophan can weaken the diffusion resistance of methane molecules in the suspended static solution, further enhancing the mass transfer of the hydrate generation process. These findings will provide new perspectives regarding the application of phase-change micro-/nanoparticles in methane hydrate generation under static conditions.

Keywords: gas hydrate; phase-change nanoparticles; surfactants; static system; kinetic characteristics



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1. Introduction

Currently, with the increasing levels of population and the consequent increase in energy demand, our society faces a double challenge, namely the need to provide reliable and affordable energy for a growing population while also reducing environmental pollution [1]. The search for new alternative energy sources has become one of the most urgent scientific and technological research topics in the world today. Solidified natural gas technology is a promising solution, the main concept of which is to store natural gas in synthetic hydrate nuclei [2]. Natural gas hydrate, also known as combustible ice, is an

ice-like crystalline substance produced by natural gas and water under high-pressure and low-temperature conditions. It is a resource-rich clean fossil fuel type since it produces methane gas and small amounts of carbon dioxide and water after hydrate decomposition. As a resource it is equivalent to two times the total amount of all fossil energy sources, which can only meet human demand for another 1000 years [3,4]. However, natural gas hydration technology has problems such as a long induction time, slow gas consumption rate, low hydrate generation, and difficulty in removing the heat generated by hydrate. Thus, it is difficult to generate large quantities quickly in industrial applications.

Hydrate generation is an extremely complex process influenced by factors such as mass and heat transfer [5]. Dynamic or static intensification methods are mainly used in hydrate technology applications to improve the effects of mass and heat transfer and other factors in the hydrate generation process. Dynamic enhancement methods include stirring [6], spraying [7], and bubbling [8,9]. Dynamic intensification methods mainly enhance the generation of gas hydrate by increasing the gas–liquid contact area and rapidly dissipating heat from the hydration process [10]. However, the energy consumption required for dynamic intensification methods and the heat generated during their use are both large, which reduces the energy efficiency. Thus, the additional mechanical equipment and energy costs involved are obviously uneconomical. The static method promotes hydrate generation by adding surfactants, which are divided into thermodynamic and kinetic enhancers. Thermodynamic enhancers promote hydrate generation mainly by changing the phase equilibrium of hydrate generation, while kinetic enhancers promote hydrate generation mainly by reducing surface tension and mass transfer resistance [10]. The most commonly used thermodynamic promoters include tetrahydrofuran (THF) [11] and cyclopentane (CP) [12], while the most commonly used kinetic promoters include sodium dodecyl sulfate (SDS) [13], sulfonated lignin (SL) [14], and amino acids [15–17]. However, the rapid generation of hydrates in surfactant solutions releases a large amount of heat from the hydration reaction and the heat trapped in the reaction system will disturb the temperature stability of the hydration system which, in turn, will affect the hydrate generation process [18].

Numerous studies have shown that the hydrate generation process can be significantly accelerated by improving the mass and heat transfer conditions during the hydrate generation reaction [19]. Due to the large specific surface area and high thermal conductivity of nanoparticles themselves, they can enhance the heat and mass transfer conditions in the hydrate generation process. Therefore, scholars both at home and abroad have mostly used aqueous/solution systems with added nanoparticles for hydrate generation enhancement studies. Wu [2] et al. synthesized Fe_3O_4 nanoparticles and used sodium oleate (SO) and SDS bilayers for surface modification, leading to the significant improvement of the methane storage capacity and hydrate generation rate of the composite promoter. In addition, a magnetic field was successfully introduced in the reaction system, which further promoted hydrate generation due to the regular arrangement of $\text{SDS}\&\text{SO}@ \text{Fe}_3\text{O}_4$. Song [20] et al. prepared sulfonated carbon nanotubes (Scnts) by covalently grafting $-\text{SO}_3^-$ functional groups onto the surface of carbon nanotube (CNT) nanocarriers. Compared with pristine carbon nanotubes (PCNTs), Scnts nanofluids have a higher dispersion and stability. Yan Shuo [10] et al. compounded nanoparticulate graphene oxide (GO) with sodium dodecyl sulfate (SDS) to study the effects of compound promoters with different compound mass fractions on the hydrate generation properties of CO_2 gas. The results showed that GO with the addition of SDS can promote hydrate generation. The results also showed that the combination of GO and SDS could promote hydrate generation, greatly shorten the generation time, reduce the equilibrium pressure, increase the gas consumption, and accelerate the gas consumption rate. Gambelli [21] et al. studied the formation and decomposition of methane and CO_2 hydrates in pure quartz porous sediments containing Inconel 718 particles produced by gas atomization and showed that In particles have a dual function in this process: they act as promoters in the presence of CH_4 and as inhibitors in the presence of CO_2 . Nasir [22] et al. listed a literature review of nanoparticles studied in various

gas hydrate systems, including oxidized multi-walled carbon nanotubes (OMWCNTs), multi-walled carbon nanotubes (MWCNTs), multi-walled nanotubes (MWNTs), graphite nanoparticles, single walled carbon nanotubes, Ag, Cu, CuO, Al₂O₃, ZnO, and Al₂O₃. As with other promoters, factors affecting the nanoparticle promotion effect include induction time, formation rate, gas uptake/consumption, water-hydrate conversion rate and storage capacity, the addition of nanoparticles to the aqueous phase increases the heat and mass transfer rates, thus positively affecting the kinetics of gas hydrate formation.

The aforementioned studies show that the uniform and stable dispersion of nanoparticles in the base fluid to generate well-dispersed, stable, durable, and low-agglomeration nanofluids is an important step in the study of nanofluid-enhanced mass transfer phenomena. By adding some surfactants, such as SDS and L-tryptophan, they have emulsification, dispersion, and wetting effects [23] and it can not only play the effect of uniform dispersion and stabilization of nanoparticles but also reduce the surface tension. Zhenzhen Liu [18] et al. used sodium dodecyl sulfate (SDS) solution containing suspended copper particles (CP) and stainless-steel fibers (SSF) to store natural gas in an inclusion complex at 4.0–7.0 MPa and 274.15 K. Yang [24] et al. mixed gelling agent, sodium dodecyl sulfate (SDS) solution, hydrophobic silica nanoparticles, and air in a high-speed stirrer. A gel-loaded surfactant dry solution (GDS) was prepared, and the results showed that the dispersed GDS droplets significantly improved the kinetics of the methane hydrate generation, the gas storage capacity, and the gas storage repeatability. Gellan gum, as a gelling agent, can form gel microdroplets under high-speed shear and act as a dispersion support [25,26]. The addition of surfactant and gellan gum can cause the nanoparticles to stably disperse at the gas–liquid reaction interface and effectively promote hydrate generation, but the high thermal conductivity and high specific surface area of nanoparticles alone are not sufficient to remove the heat generated by the hydrate generation, which affects any further hydrate generation. Relevant studies have shown that there are certain optimal concentrations of SDS and L-tryptophan, namely 0.05 wt% SDS and 1 wt% L-tryptophan [15,22,27–29]. Thus, this experiment was carried out under this concentration condition.

NiMnGa micro-/nanoparticles (NMGs), as a magnetic shape memory material with a thermoelastic martensitic phase transition, can induce a martensitic inverse phase transition. The temperature increase can induce martensitic inverse phase transition while absorbing surrounding heat [30,31]. If the external field effect is added to achieve the effect of suspension stabilization, energy consumption and economic problems will be encountered. Therefore, in this experiment, the junction cold gel was chosen as the suspension material added to the SG system and LG system to achieve the stable suspension dispersion of NMG micro/nanoparticles. Methane hydrate generation experiments were carried out under different concentrations of NMG at an initial pressure of 6.2 MPa to study the characteristics of methane hydrate generation in this static composite system. This work represents an important step in studying the kinetics and reproducibility of natural gas hydrate generation in a static dispersion system.

2. Materials and Methods

2.1. Experimental Materials

Metal Ni, Mn, and Ga were provided by Zhongnuo New Materials Technology Co., Ltd. (Beijing, China). High-purity nickel, electrolytic manganese and pure gallium metal were melted in a vacuum medium-frequency arc melting furnace (SR830, CSCI Co., Ltd, Beijing, China) in the ratio of Ni_{52.5}Mn_{22.5}Ga₂₅ to obtain button-shaped ingots; the alloy was subjected to homogenization solid solution treatment, ball milling and particle annealing in turn to finally obtain Ni_{52.5}Mn_{22.5}Ga₂₅ micro-nano particles. The specific preparation process is shown in the Supplementary Materials Experimental section. Sodium dodecyl sulfate (SDS) was supplied by Tianjin Guangfu Fine Chemical Research Institute (Tianjing, China), 99% pure L-tryptophan was supplied by Aladdin, and 99.9% pure gellan gum was supplied by Henan Kest Industrial Co. (Henan, China). Pure methane gas and high purity nitrogen gas were provided by Beijing Beixiang Special Gas Research Institute Co (Beijing,

China). The test water is Class II pure water treated by Thermo Fisher Scientific (Suzhou, China) water purifier.

2.2. Experimental Apparatus

The experimental system used for hydrate generation in a static system consisted of a high-pressure reaction system, temperature control system, pressure control system, and data acquisition system. The experimental device is shown in Figure 1 and mainly consisted of a visual high-pressure reactor, high- and low-temperature thermostats, a temperature sensor (PT100, Class B), a pressure sensor (DPI 701-E51GAP-F, Elbaissde), and a data collector. The effective volume of the visible high-pressure reactor is 110 mL, and the body is made of titanium alloy. The temperature sensor is customized by titanium alloy, the temperature measuring range is -50 – 100 °C, and the accuracy is 0.1%. The pressure sensor has a pressure measurement range of 0–20 MPa and an accuracy of 0.1%. The visual window was made of resin material and made it possible to observe the methane hydrate generation process and the hydrate status at any time. Electronic balance was supplied by Mettler Toledo, model MS105DU, with a precision of 0.01 mg.

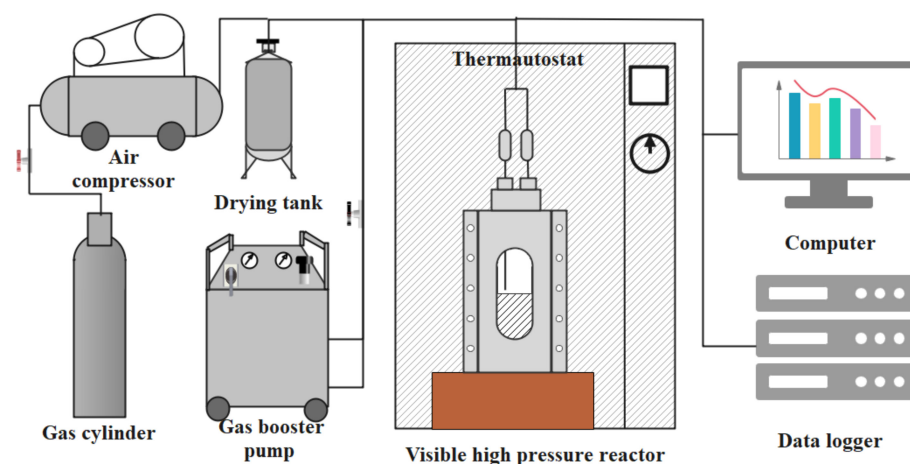


Figure 1. Schematic diagram of the hydrate formation experiment device in a static system.

2.3. Preparation and Characterization of Suspensions

First, 0.02 g of SDS (0.05 wt%), 0.40 g of L-tryptophan (1 wt%), 0.12 g of gellan gum (0.3 wt%) and different masses (0.04 g, 0.40 g and 0.80 g, respectively) of NMG powder were weighed on an electronic balance and measured in a beaker with 40 mL of pure water, and the weighed powder was poured into the beaker. Then, the stirrer (IKA T18, 3000–25,000 rpm) was turned on, the speed was set to 12,000 rpm, and the mixture was sheared and dispersed at high speed for 90 s. After the stirring was stopped, the suspension was transferred to the reaction kettle for experimental use. The size and homogeneity of the droplets were observed using an FEI Quanta 250 scanning electron microscope. The average diameter and particle size distribution of the NMG particles were determined using a Malvern Mastersizer 3000E laser particle size analyzer from Malvern Panalytical (Malvern, UK). Meanwhile, the NMG were tested for latent heat of phase change using a high-pressure differential scanning calorimeter (HP DSC) μ DSCVII from Mettler, Toledo (Straam, France).

2.4. Experimental Procedure

Methane hydrate was synthesized using the static system of SDS-NMG-gellan gum suspension and the static system of L-tryptophan-NMG-gellan gum suspension. The total gas consumption and gas consumption rate of the hydrate were obtained according to the changes in temperature and pressure during the synthesis process. The pressure-bearing capacity, gas tightness, temperature, and pressure sensor at zero points of the reactor were checked and calibrated before the experiment started, and the specific experimental steps

used were as follows. (1) Before the experiment, the reactor was cleaned three times with homemade pure water, dried, and treated. Then, 40 mL of suspension was poured into the reactor; the reactor lid was tightened; and the gas inlet line, temperature sensor, and pressure sensor were connected. Then, high-purity nitrogen gas was passed to check the gas tightness. (2) The thermostat was adjusted to the set temperature, the data collector was turned on, and the changes in temperature and pressure were recorded. When the temperature displayed by the data collector reached the set temperature, we opened the valves on the pipeline from the methane cylinder to the reactor in turn, combined the pressure readings from the pressure gauge and the data collector, purged the reactor with CH₄ at approximately 1 MPa, and closed the valves when the set pressure value was reached and the value remained stable after purging three times. (3) When the temperature started to rise and the pressure dropped, it was considered that the hydrate started to be generated, and when the temperature and pressure curves began to stabilize after a period of time, the hydrate was considered to be completely generated and the hydration reaction process was finished.

2.5. Data Processing Methods

The induction time of hydrate generation is an important parameter for characterizing the rapidity of hydrate generation. In this study, the induction time was defined as the time required from the time the pressure reached the initial pressure to the first significant temperature rise and pressure drop during the hydration reaction. The experimental system was a constant-volume system, and during hydrate generation the gas was dissolved in the liquid phase and the guest molecules of the gas phase entered the hydrate phase to generate hydrate, causing the amount of gas in the gas phase to decrease. The gas consumption during hydrate generation was used to calculate the amount of hydrate generated. The rate of hydrate gas consumption was expressed as the rate of methane gas consumption per unit time (i.e., the rate of gas consumption at a certain moment of the hydrate synthesis process). The calculation method used is described in the data processing methods section of the Supplementary Materials. During the hydration reaction, the molar amounts of gas consumed at any two moments are different. According to the gas equation of state, the cumulative consumption of methane gas at a moment n is calculated by combining the amount of gas substance n_t in the reactor at that moment with the amount of gas substance n_0 in the reactor at the initial moment, expressed as

$$\Delta n_H = n_0 - n_t = \frac{P_0 V_0}{Z_0 R T_0} - \frac{P_t V_t}{Z_t R T_t} \quad (1)$$

where P_0 and T_0 are the pressure and temperature values at the initial moment in the reactor; P_t and T_t are the pressure and temperature values at time t during the reaction; R is the gas constant; Z_0 and Z_t are the compression coefficients at the initial moment and time t , respectively, calculated by Pitzer's correlation equation. The gas consumption calculated from Equation (1) can be further divided by the number of moles of water used in the system to obtain the normalized gas consumption (moles of gas/moles of water). The normalized gas consumption is confirmed by Equation (2).

$$\Delta n = \frac{\Delta n_H}{n_w} = \frac{\frac{P_0 V_0}{Z_0 R T_0} - \frac{P_t V_t}{Z_t R T_t}}{n_w} \quad (2)$$

The rate of hydrate formation is characterized by the rate of methane gas consumption per unit time (i.e., the rate of gas consumption at a given moment in the hydrate synthesis process), denoted as

$$v = \left(\frac{d\Delta n}{dt} \right)_t \approx \frac{\Delta n}{\Delta t} \quad (3)$$

where v is the gas consumption rate and Δt is the time difference between a certain moment and the initial moment, taken as 10 s.

3. Results

3.1. Characterization Results

To test the particle size distribution of NMG micro/nanoparticles, the particle size of the NMG particles was measured using a Malvern Mastersizer 3000E laser particle size analyzer, the particle size distribution curve of which is shown in Figure 2. It can be seen that the median particle size D50 was 18.7 μm , indicating a cumulative distribution percentage of 50%, corresponding to a particle size of 18.7 μm . This parameter can express the overall particle size in a more comprehensive way.

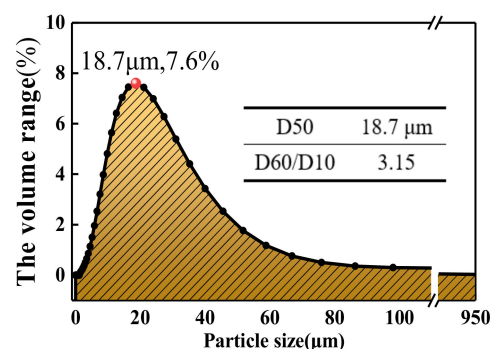


Figure 2. NMG particle size distribution curve.

The suspension times of the different systems are shown in Figure 3. In the LNG system, only a small amount of NMG was suspended in the upper layer of the suspended solution at 160 min, while the upper layer of the suspended solution was basically clarified at 320 min. In the SNG system, the NMG particles were uniformly suspended and dispersed in the solution from 0 to 320 min, and the NMG particles began to appear in the deposition state at 320 min. However, there was still NMG suspended in the solution, and when the suspension time was 640 min the upper layer of the suspended solution was nearly clarified. The test results showed that SDS, as a dispersant, played a good dispersing role and significantly promoted the suspension time. However, a suspension time of 320 min was still achieved by relying on the properties of the dispersion support of the junction cold gel.

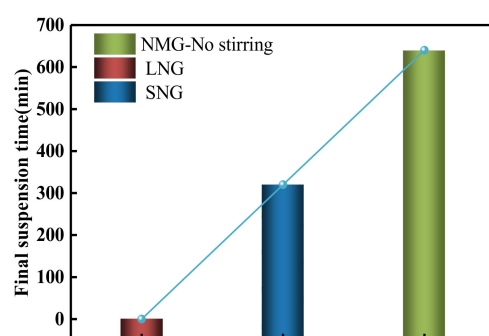


Figure 3. Final suspension time diagrams of different systems.

To observe the microstructure of the two systems, the two experimental systems were characterized using an FEI Quanta 250 SEM. Electron micrographs of the suspension and dispersion effect of NMG particles are shown in Figure 4 (4). The NMG micro/nanoparticles were polygonal irregular particles, and some of the surfaces showed a smooth and sawtooth appearance. The prepared gellan gum suspension showed a gel shape and could flow freely. The gellan gum solution was dispersed by high-speed shear to form a gellan gum suspension solution, forming independent water microdroplets that did not stick to each other. The suspensions of different systems are shown in Figure 4. An electron microscope image of the dispersion effect of the SNG suspension solution is shown in Figure 4 (5). NMG

particles are dispersed and distributed uniformly in the diagram. The dispersion effect of the LNG suspension is shown in Figure 4 (6). The distribution uniformity of NMG particles is poor, and some are agglomerated in the diagram. L-tryptophan, as a hydrophobic amino acid, can help the water form a large contact angle on the surface of the hydrophobic solution to form a water droplet. At the same time, the addition of L-tryptophan helped the formation of hydrophobic bonds between the microdroplets of gellan gum, which made the suspension solution of gellan gum more stable, and L-tryptophan did not form white foam during the high-speed shear dispersion.

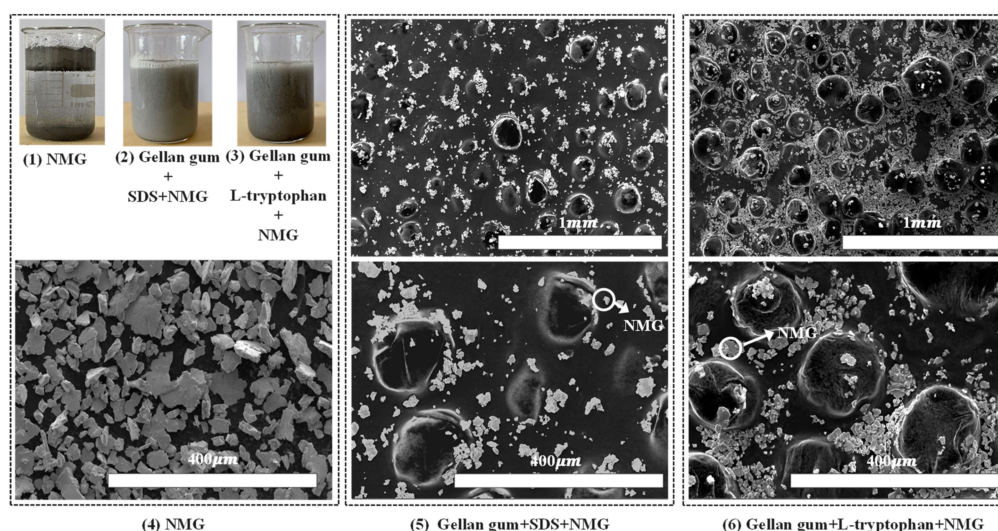


Figure 4. Electron microscopic map of the dispersion effect of NMG particles and suspension.

In order to grasp the degree of influence of different NMG and different pressure conditions on the phase change conditions, the parameters of phase change temperature, inverse phase change temperature and their latent heat were measured. Test results are available in the Support Information Test Results section.

3.2. Characteristics of the Natural Gas Hydrate Generation Process

Experimental studies on the kinetics of methane hydration processes in two different suspended static systems—the SDS system (system I) and the L-tryptophan system (system II)—were carried out under a static system for rapid hydrate generation. The experiments were carried out at an initial pressure of 6.2 MPa and an initial temperature of 2 °C. The methane hydration generation experiments were carried out at different concentrations of NMG using 0.1 wt% wt NMG, 1 wt% wt NMG, and 2 wt% wt NMG. The experimental conditions and average experimental results of methane hydrate in different systems are shown in Table 1, and all experimental results are shown in the Supplementary Materials in Table S1.

The temperature and pressure curves for each stage of hydrate generation for the two different systems are shown in the Supplementary Materials in Figure S1. Parameters such as induction time, total gas consumption, and gas consumption rate of hydrate generation for each group of experiments could be calculated from temperature and pressure. When a sudden drop in pressure along with a sudden rise in temperature occurred in the reactor immediately after the start of the experiment, this indicated that the induction time of hydrate generation was extremely short or even absent. Therefore, the induction time is defined in this experiment as the time taken from the entry of methane into the reactor to the initial formation of methane hydrate (i.e., the time required for the first temperature rise and pressure drop). The initial generation time of methane hydrate is determined by the sharp decrease in system pressure and the increase in system temperature caused by the exothermic nature of its generation. The change in pressure drop during hydrate production

is an important parameter for measuring the rate of hydrate gas consumption [32]. It can be seen from the pressure profile that the pressure drop in the SG system only occurred at approximately 0.2 MPa. When NMG was added, the pressure drop increased significantly, indicating that the addition of NMG elevated the gas consumption of the system.

Table 1. Experimental conditions and formation results of methane hydrate in different systems ($p = 6.2$).

Gas Sample	System	Gellan Gum /%	SDS /%	L-Tryptophan /%	NMG /%	No.	Induction Time /min	Gas Consumption/mmol of gas/mol of water	Gas Consumption rate/mmol of gas/mol of water/min	V _{15 min}	V _{avg}
99.99% CH ₄	I	0.3	0.05	0	0	1–3	5.94	3.51	0.18	0.09	
					0.1	4–6	2.06	34.19	0.63	0.14	
					1	7–9	1.57	37.42	0.89	0.2	
					2	10–12	1.50	34.57	0.68	0.18	
					0	1–3	3.22	38.48	0.82	0.15	
					0.1	4–6	2.78	41.74	1.14	0.19	
	II	0.3	0	1	1	7–9	3.11	41.3	1.15	0.19	
					2	10–12	2.94	42.99	1.12	0.21	

Figure 5a: Corresponding to the hydrate growth pattern of methane hydrate in system II-10 at different time points, a thin translucent hydrate layer was formed at the gas–liquid interface 1 min after the start of the experiment, followed by growth from the gas–liquid interface upward and downward along the reactor wall to form a translucent-like hydrate, while the liquid level surface in the center decreased, thus forming a crater-shaped hydrate growth pattern [16] and largely covering the entire reactor for 15 min. This hydrate growth pattern was usually favorable for hydrate generation kinetics since unconverted water can be attracted from the bulk liquid phase to the hydrate growth front through these well-connected channels by capillary effects, and the expansion of hydrate along the reactor walls significantly increased the gas/liquid/hydrate contact [16].

Figure 5b: A graph of the hydrate generation process for the example of system II-8. The hydrate generation process mainly consists of two stages, the nucleation stage and the growth stage; the nucleation stage refers to the generation of a stable nucleus in the gas solution up to the interfacial size (i.e., the green region in Figure 5b) and the time required is called the induction period [9]. The temperature–pressure curve shows that the temperature–pressure remains stable during this period, and it can be seen in Figure 5a that the hydrate film starts to appear on the liquid surface at 0–1 min, and then continues to grow. Therefore, in this experiment, there is no obvious nucleation process during hydrate generation (i.e., the induction period is short, so the induction period in this experiment is defined as the time period between the gas is pumped into the reactor and the first appearance of temperature rise and pressure drop). After nucleation, the process of rapid crystal growth into hydrate crystals on a macroscopic scale was called the growth phase. The yellow phase in Figure 5b shows the rapid hydrate growth phase, where the gas enters the hydrate cage during the growth process a sudden temperature rise and pressure drop occur. In the fast growth phase, a section of the concave curve appears, as hydrate growth requires the release of a large amount of heat, and the temperature rise induces martensitic inverse phase transformation in the NMG particles, which removes the heat generated during hydrate generation, resulting in a section of the concave temperature curve. This then enters the slow growth phase (i.e., the blue phase in Figure 5b) until the temperature–pressure curve no longer changes within 30 min, indicating complete hydrate generation (i.e., the stable phase of hydrate generation (pink phase in Figure 5b)).

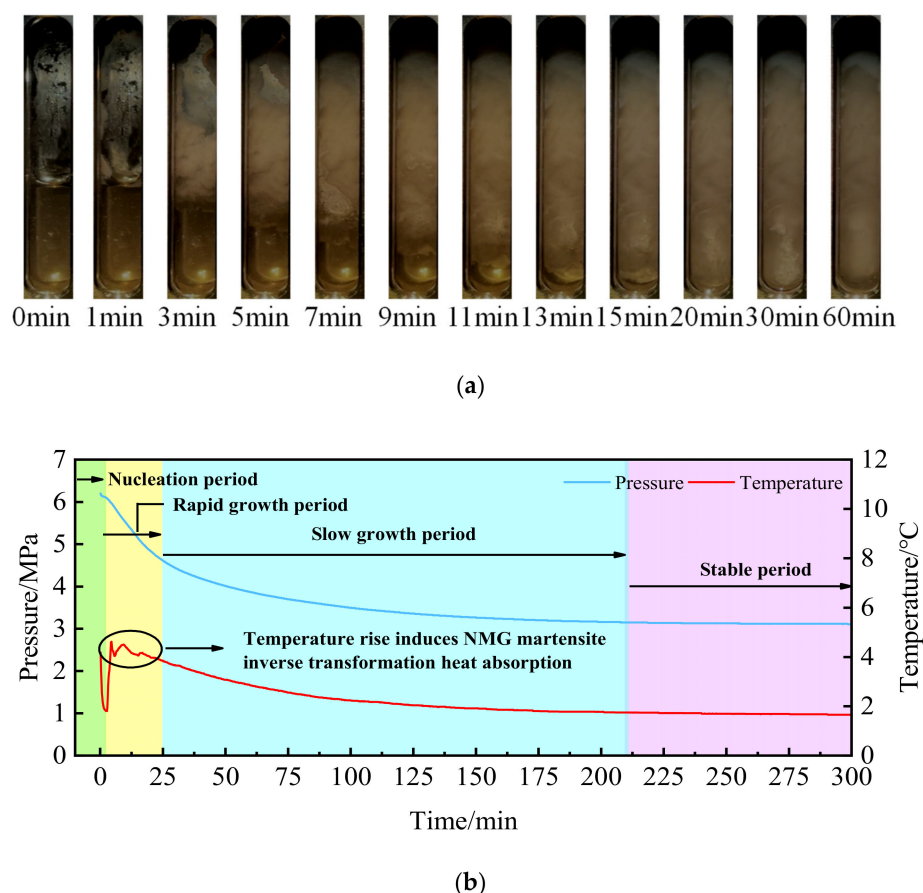


Figure 5. Hydrate formation process diagram of system II-10. (a) Morphology of hydrates at different points in time. (b) Hydrate generation process curves.

3.3. Induction Time

The induction time is one of the effective criteria for judging whether hydrates can be generated rapidly. Figure 6 shows the graphs of the induction times of the two systems, and the analysis of Figure 6 shows that both SNG and LNG can significantly shorten the induction time compared with the SG system. The experiments involving adding different mass fractions of NMG (0.1 wt%, 1 wt%, 2 wt%) to the SNG system led to a reduction in induction time by 62.5%, 73.6%, and 75.0%, respectively, and the induction time showed a gradual reduction with an increase in the NMG mass fraction, showing a trend of gradual shortening—i.e., the 2% NMG concentration was the best. In the LNG system, the addition of different mass fractions of NMG (0.1 wt%, 1 wt%, 2 wt%) led to a reduction in induction time by 13.7%, 3.4%, and 8.7%, respectively, while the mass fraction of NMG did not have a significant effect on the induction time.

SDS can reduce the surface tension of water, thus enhancing the mass transfer occurring between the gas and liquid phases [33]. At the same time, the addition of NMG enhances the thermal conductivity of the solution, which can enhance the heat transfer; in addition, the large surface area of NMG provides attachment points for the formation of nuclei, which further strengthens the mass transfer effect. On the other hand, the good thermal conductivity of NMG means that it can disperse the heat caused by the generation to make the hydration reaction finish quickly [20]. When using the SNG system, due to the presence of SDS a large amount of foam will inevitably be formed during hydrate decomposition, and the foam generated will lead to the loss of surfactant and even enter the pipeline system, creating some practical effects. In view of this, L-tryptophan was chosen to replace SDS in the methane hydrate generation experiment in this paper. The use of L-tryptophan as a surfactant can increase the contact area of the gas–liquid two-phase

and weaken the diffusion resistance of methane molecules in solution (i.e., the degree of dispersion of methane molecules present on the solution surface increases). The presence of L-tryptophan can shorten the induction time, while the hydrate does not produce a large amount of foam during decomposition, which improves the recyclability of NMG materials and the reproducibility of the experiment. As the concentration of NMG particles increases, the number of particles in the micro/nanofluid increases, the average free range between particles decreases, and the chance of mutual collision is greatly improved, which can shorten the induction time. However, in a static system, although supported by gellan gum, a small amount of agglomeration and partial sedimentation will still occur, thus preventing further gas–liquid contact and causing little change in the induction time.

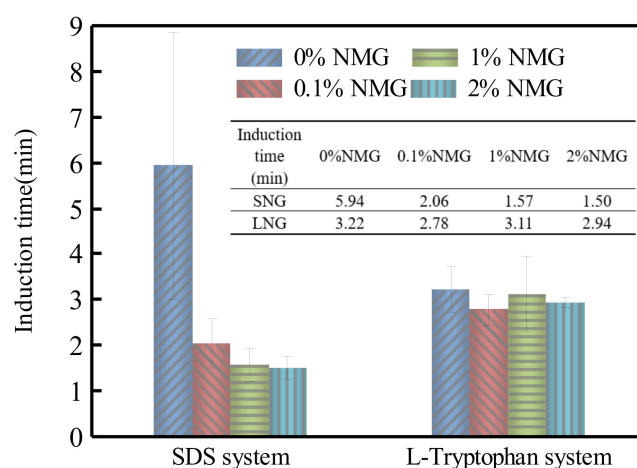


Figure 6. Induction time of different systems.

3.4. Gas Consumption

Gas consumption is an important index used to evaluate the effectiveness of gas hydrate storage as well as the gas content rate. Figure 7 shows the gas consumption curves of different systems with time, and Figure 8 shows the final gas consumption of different systems. Figure 8 shows that the gas consumption of the SNG system is higher than that of the SG system, and the final gas consumption of the system with a 1 wt% NMG mass fraction is 37.42 mmol of gas/mol of water, which is 10.7 times higher than that of SG (i.e., the addition of NMG under static conditions can significantly and significantly increase the gas consumption). NMG micro/nanoparticles can be uniformly dispersed and suspended in the solution under the action of the gellan gel, which provides a large number of stable contact channels between methane gas and water molecules and effectively promotes hydrate generation [34]. It was also found that the gas consumption of the L-tryptophan system was higher than that of the SDS system, and the 2 wt% NMG system had the largest gas consumption of 42.99 mmol of gas/mol of water. NMG micro/nanoparticles could promote the generation of methane hydrate from both the aspects of mass and heat transfer, while the addition of hydrophobic L-tryptophan could increase the gas–liquid contact area and weaken the methane molecules in the solution diffusion resistance (i.e., more methane molecules could enter the solution to participate in the reaction and increase the gas consumption).

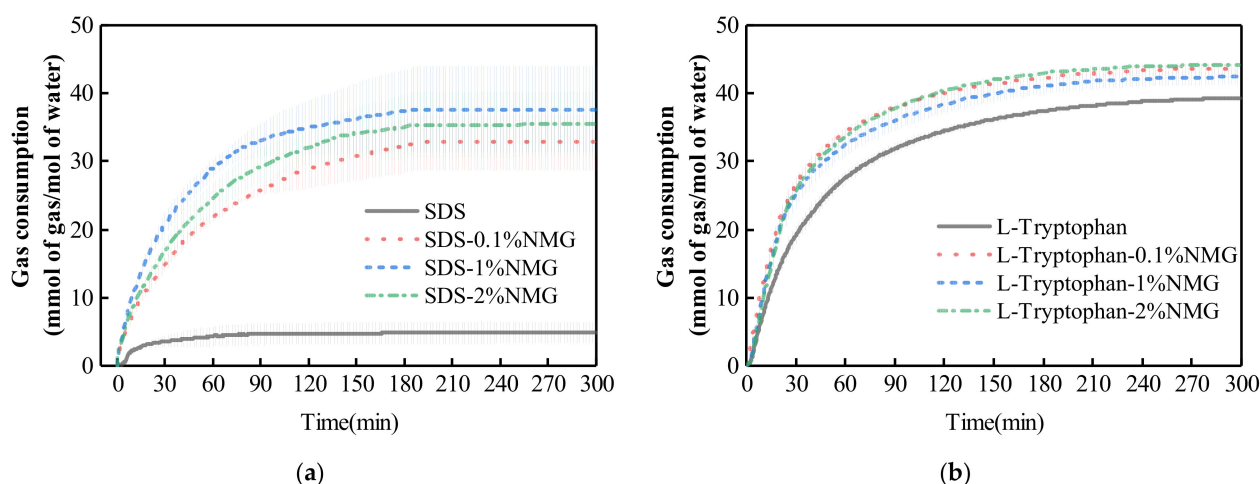


Figure 7. The curve of gas consumption with time in different systems. (a) SDS system. (b) L-tryptophan system.

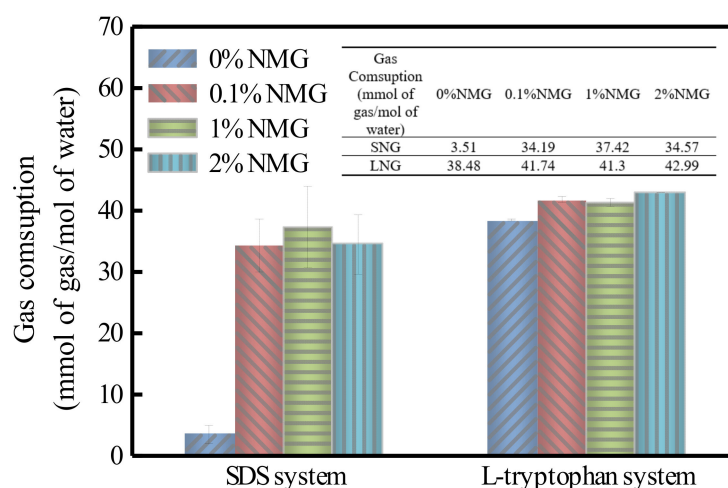


Figure 8. The curve of gas consumption with time in different systems.

3.5. Gas Consumption Rate

The gas consumption rate, as an important parameter of gas hydrate generation kinetics, is one of the criteria used to judge whether hydrates can be generated rapidly and in large quantities. Figure 9 shows the gas consumption rate curves with time for the two systems, and Figure 10 shows the 15 min gas consumption rate and the average gas consumption rate for different systems. From Figures 10 and 11, it can be seen that in the SDS system, the average gas consumption rates of the systems with NMG mass fractions of 0.1 wt%, 1 wt%, and 2 wt% were 0.14 mmol of gas/mol of water/min, 0.19 mmol of gas/mol of water/min, and 0.18 mmol of gas/mol of water/min, respectively (i.e., the gas consumption rates showed an increasing and then decreasing trend with an increasing NMG mass fraction). The analysis suggests that with the increase in the mass fraction, the number of NMG particles increases, which provides more nucleation sites for hydrate reaction. This means that the micro/nanoparticles will continuously come into contact and collide with each other in water due to Brownian motion, which plays the role of stirring and perturbing the liquid and accelerating the internal heat transfer. At the same time, due to the rapid generation of hydrate and the release of a large amount of heat, the NMG micro/nanoparticles undergo martensitic inverse phase transformation and absorb the surrounding hydrate generation heat. At the same time, due to the rapid hydrate generation heat release, NMG micro/nanoparticles undergo martensitic inverse phase transformation, absorbing the surrounding hydrate generation heat and controlling

the temperature rise in the system, thus accelerating the gas consumption rate. In the LNG system, the average gas consumption rate of the system was 0.19 mmol of gas/mol of water/min, 0.19 mmol of gas/mol of water/min, and 0.21 mmol of gas/mol of water/min when the mass fraction of NMG was 0.1%, 1%, and 2%, respectively, and the average gas consumption rate of NMG with different mass fractions showed a gradual increase with an increasing NMG mass fraction. The use of L-tryptophan instead of SDS led to a decrease in the dispersion of the solution, resulting in NMGs with different mass fractions showing similar results. In addition, agglomerative precipitation may occur with an increasing NMG mass fraction. However, the addition of L-tryptophan could effectively increase the contact area between methane and water, which led to an increase in the methane gas consumption rate in this system compared with the SNG system.

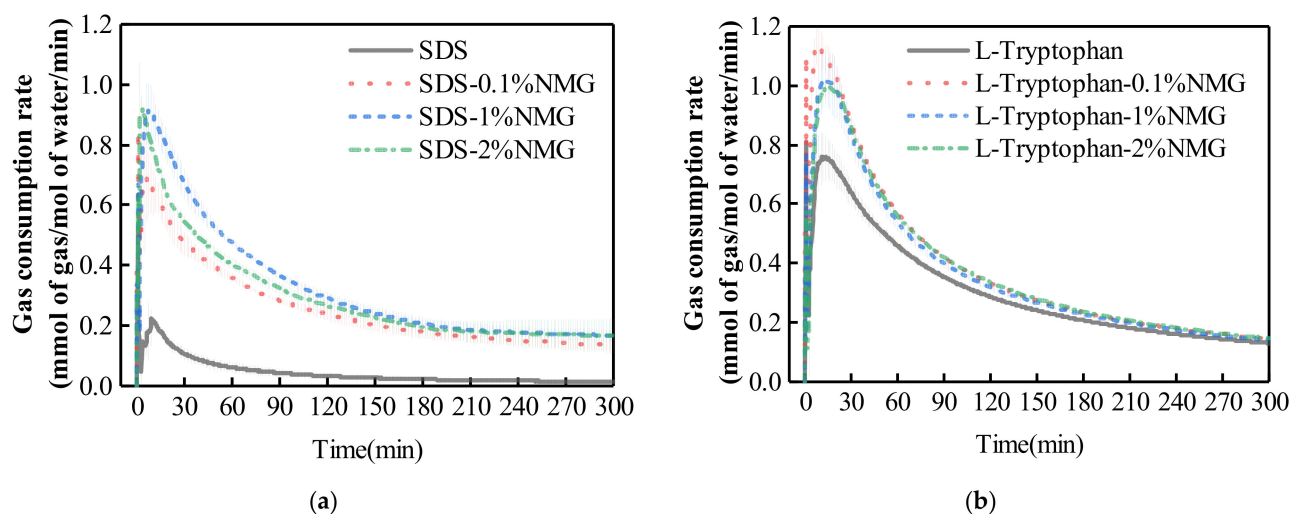


Figure 9. Curve of the gas consumption rate with time in different systems. (a) SDS system. (b) L-tryptophan system.

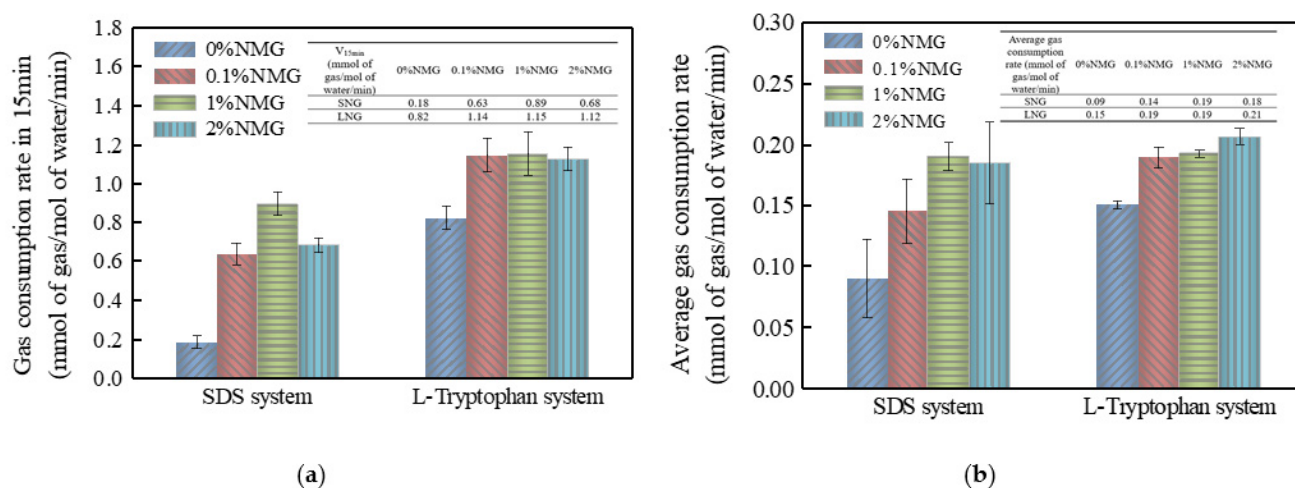


Figure 10. Gas consumption rate at 15 min and average gas consumption rate of different systems. (a) Gas consumption rate at 15 min. (b) Average gas consumption rate.

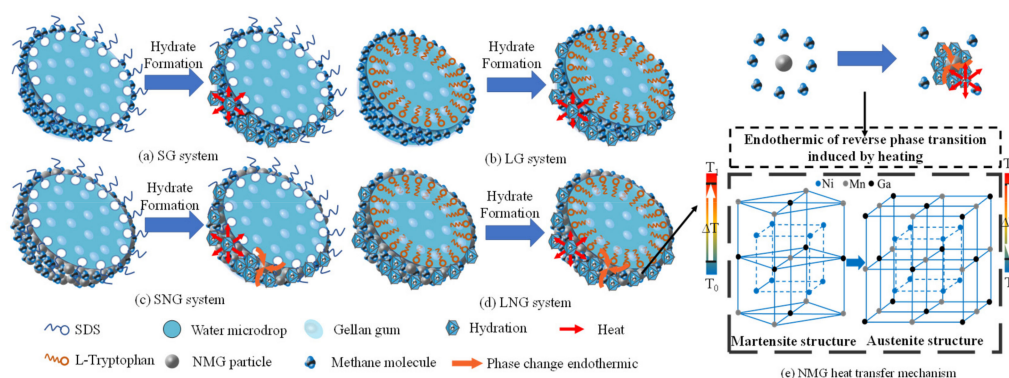


Figure 11. Diagram of the enhancement mechanism of the formation of hydrate. (a) SG system, (b) LG system, (c) SNG System, (d) LNG system and (e) NMG heat transfer mechanism?

4. Discussion

Micro/nanoparticles easily agglomerate and condense, which leads to settling and makes them difficult to disperse in the base solution, affecting the stability of the nanofluid [35]. Therefore, in this paper, the addition of the junctional cold gum to the solution, after high-speed shearing, formed the structure of micro/nanoparticles encapsulated in water, which could disperse micro/nanoparticles and enhance the stability of micro/nanofluids. Figure 11 shows the enhanced mechanism of hydrate generation. SDS can reduce the surface tension at the interface of the liquid phase, which can cause methane gas to enter the solution and enhance the solubility of gas, Figure 11a. Hydrophobic L-tryptophan, which can increase the contact area of the gas–liquid phase and increase the dispersion of methane molecules on the surface of the solution so that more methane molecules can enter the solution to participate in the reaction, Figure 11b. Second, in the experimental system containing NMG, due to the large specific surface area and surface activity of NMG micro-/nanoparticles, the irregular and serrated metal surface could provide more nucleation sites for hydrate, which can promote hydrate nucleation [36] and shorten the induction time. A larger specific surface area can also increase the gas–liquid contact area, meaning that more methane molecules can enter the liquid phase and participate in the reaction [35]. At the same time, the high thermal conductivity of NMG as a metal particle can enhance the thermal conductivity of the liquid, which, in turn, improves the thermal conductivity [17] and accelerates the removal of the heat generated during hydrate generation. Importantly, NMG particles are a magnetic shape memory material with thermoelastic martensitic transformation. Based on the results of the phase transformation experiments and the changes of the experimental temperature curve, it can be assumed that the heat released by the hydrate formation may induce the reverse martensitic transformation of the NMG particles, and absorb the surrounding heat at the same time, the rapid formation of hydrate generates heat to induce martensitic inverse phase transition of NMG (Figure 11c,d), i.e., the occurrence of the transformation from martensite structure to austenite structure (Figure 11e), which requires a certain amount of heat absorption, and thus the absorption of surrounding heat reduces the system temperature, providing a lower temperature environment for the subsequent rapid hydrate formation.

In the SDS-NMG complex system, the long alkyl chains of SDS molecules are adsorbed to the outer wall of NMG under hydrophobic and van der Waals forces [37], forming a transparent bubble film wrapped around the outer layer of aqueous microdroplets. This further has the effect of uniformly dispersing NMG, allowing NMG to be uniformly and stably dispersed in the suspension, thus providing a larger specific surface area and more nucleation sites for methane molecules. At the same time, due to the adsorption effect, the surfactant aggregates at the solid–liquid interface, leading to the formation of nucleation at the vessel wall and micro/nanoparticles. The large number of hydrate particles can be viewed as a porous media-like structure, providing a capillary force that continuously adsorbs the solution to the reactor wall, preventing the hydrate from being

generated at the gas–liquid interface and then preventing the gas from continuing to dissolve, further promoting the kinetic process of the hydration reaction (Figure 11c). In the L-tryptophan-NMG complex system, L-tryptophan can weaken the diffusion resistance of methane molecules in the liquid phase, and more methane molecules can attach to the surface of NMG, leading to gas hydrate formation. Meanwhile, the presence of gellan gum can provide a skeleton for the uniform dispersion of NMG. Additionally, the hydrates formed in the presence of L-tryptophan are porous and flexible in nature, and the increased porosity of hydrates contributes to increased capillarity. Water molecules tend to form local structures near hydrophobic surfaces, which helps to encapsulate the gas components in the hydrate phase, resulting in a higher gas uptake and ensuring the faster occupancy of hydrate-forming gases (mainly CH_4), leading to a higher rate of hydrate growth [15,38]. Related studies have also shown that the hydrophobicity of amino acids and the presence of aromatic side chains in the chemical structure are likely to lead to enhanced superior kinetics of methane hydrate generation [16,29]. Additionally, the methane hydrate formed using SDS solution in the SDS complex system generates a large amount of foam when dissociation is performed, while L-tryptophan, as a green surfactant, does not generate foam during the decomposition of hydrate generation. Thus, it does not affect the subsequent experiments and does not bring out the NMG particles from it when repeated experiments are performed, allowing it effective reproducibility. The L-tryptophan system is superior to the SDS system in terms of recycling and environmental effects.

In summary, in the synergistic process with SDS or L-tryptophan, the characteristics of NMG micro-nano particles (large specific surface area and surface activity, etc.) accelerate the hydration mass transfer process, and its high thermal conductivity and phase change heat absorption characteristics promote the hydration heat transfer process. The above combined effects significantly shortened the induction time of hydrate generation, and enhanced the gas consumption as well as the gas consumption rate of the hydrate generation process.

5. Conclusions

NMG phase-change-type micro/nanoparticles and L-tryptophan or SDS were added to a gellan gum solution, and suspension solutions of SNG and LNG were prepared after high-speed shearing. Methane hydrate generation experiments were carried out under static suspension conditions using this solution system. The effects of the two systems on the methane hydrate generation kinetic process were investigated using kinetic parameters such as induction time, total gas consumption, and gas consumption rate.

Compared with the SG and LG systems, both the SNG and LNG systems could shorten the induction time of methane hydrate generation and increase the gas consumption rate. Among the SDS systems, the SNG system showed the most significant reduction in induction time, with the shortest induction time of 1.50 min achieved for the 2 wt% NMG mass fraction system. This is 75.0% shorter than that for the SG system and 53.4% shorter than that for the LG system. Meanwhile, with the increase in the NMG mass fraction, the total gas consumption and consumption rate showed a trend of increasing first and then decreasing (i.e., there was an optimal NMG mass fraction). In the L-tryptophan system compared with the LG system, the LNG system shortened the induction time to a small extent but was able to maintain a higher gas consumption and faster gas consumption rate, while the total gas consumption and gas consumption rate were higher at an increased NMG mass fraction. The total gas consumption and gas consumption rate gradually increased as the NMG mass fraction increased. The total gas consumption and consumption rate of 2 wt% NMG were 42.99 mmol of gas/mol of water and 0.21 mmol of gas/mol of water/min, respectively, and it was also found that when the SNG system was used for the warming decomposition of methane hydrate, a large amount of foam was generated, which led to the partial loss of NMG micro/nanoparticles and solution and increased the loss of material and environmental pollution, while the LNG system was used for the warming decomposition of methane hydrate. The system only generated a small amount of foam

during the warming and decomposition of methane hydrate, which did not cause a loss of particles and solution. Additionally, the system had a good material recyclability and good experimental reproducibility.

The results of this study will provide a reference for the rapid generation of methane hydrate using a static system.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w14050745/s1>. Figure S1: Temperature and pressure curves of the gas hydration process under different systems; Table S1: Experimental conditions and results of methane hydrate in different systems ($p = 6.2$ MPa, $T = 2$ °C); Experimental section.

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Abbreviations

NMG	NiMnGa micro-/nanoparticles
SDS	sodium dodecyl sulfat
SNG	SDS-NMG-gellan gum system
LNG	L-tryptophan-NMG-gellan gum system
SG	SDS -gellan gum system
LG	L-tryptophan-gellan gum system
THF	tetrahydrofuran
CP	cyclopentane
SL	sulfonated lignin
SO	sodium oleate
Scent	sulfonated carbon nanotubes
CNT	surface of carbon nanotube
GO	graphene oxide
n_0	the amount of gas substance in the reactor at the initial moment
n_t	the amount of gas substance in the reactor
P_0	the pressure values at the initial moment
T_0	the temperature values at the initial moment
P_t	the pressure values at time t
T_t	the temperature values at time t
R	the gas constant
Z_0	the compression coefficients at the initial momen
Z_t	the compression coefficients at the time t
v	the gas consumption rate
Δt	the time difference between a certain moment and the initial moment

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