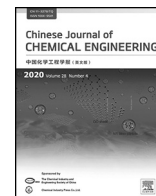




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Article

Accelerated methane storage in clathrate hydrates using surfactant-stabilized suspension with graphite nanoparticles

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ABSTRACT

In this study, enhanced kinetics of methane hydrate formation in the sodium dodecyl sulfate (SDS) solution with different concentrations of suspended graphite nanoparticles (GNPs) were investigated at 6.1–9.0 MPa and 274.15 K. The GNPs with rough surfaces and excellent thermal conductivity not only provided a considerable number of microsites for hydrate nucleation but also facilitated the fast hydrate heat transfer in the suspension system. At a relatively low pressure of 6.1 MPa, the suspension with 0.4 wt% of GNPs exhibited the minimum induction time of 22 min and maximum methane uptake of $126.1 \text{ cm}^3 \cdot \text{cm}^{-3}$. However, the methane storage performances of the suspensions with higher and lower concentrations of GNPs were not satisfactory. At the applied pressure, the temperature increase arising from the hydrate heat in the suspension system with the optimized concentration (0.4 wt%) of GNPs was more significant than that in the traditional SDS solution. Furthermore, compared with those of the system without GNPs, enhanced hydration rate and storage capacity were achieved in the suspensions with GNPs, and the storage capacities were increased by 3.9%–17.0%. The promotion effect of GNPs on gas hydrate formation at low pressure is much more obvious than that at high pressure.

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1. Introduction

Gas hydrates are nonstoichiometric crystalline compounds formed from water and gas (e.g., methane, ethane, and propane) under the conditions of low temperature and high pressure. The gas molecules (guests) are trapped in water cavities (host) that are composed of hydrogen-bonded water molecules [1,2]. One volume of hydrate can store 160–180 standard volumes of natural gas. As its excellent gas storage performance, the hydrate has been widely used in many fields, including fuel gas storage [3–5], carbon dioxide capture [6–8], mixture gas separation [9–11], and seawater desalination [12–14]. However, the slow formation rates as well as the relative low storage capacities are still major challenges in the large-scale practical application of this technology [2,4].

The process of hydrate formation is determined by the combination of the following three factors: i) sufficient gas–liquid contact (mass transfer) [15], ii) intrinsic hydrate nucleation and growth (reaction) [16], and iii) removal of hydrate heat during growth (heat transfer) [17,18]. Mechanical methods, such as water stirring [19–21], liquid spraying [22,23], and gas bubbling [24,25], have been employed to promote the hydrate formation by enhancing the mass and heat transfer of

hydration. However, these methods required energy consumption and complex operation. Therefore, kinetic promoters were added into the static water to accelerate the hydrate formation. Kalogerakis *et al.* [26] observed that the addition of surfactants in water could enhance the gas hydrate crystallization and growth, while the thermodynamics of the hydrate formation was almost unaffected. The presence of the surfactants enhanced the mass transfer of gas and liquid phases by reducing the interfacial tension at the gas–liquid interface [27–32]. Yosilism *et al.* [33] confirmed that the addition of surfactants could increase the gas–liquid contact by loosening the solid hydrate. In addition, porous media, such as activated carbon [34,35], silica gel [36], zeolite [37], and sand [38,39] saturated with water, were employed for increasing the gas–liquid contact area. However, the hydrate heat of these systems could not be removed quickly, and the accumulation of the heat could weaken the enhanced effect of the surfactant on the hydrate formation.

In view of this, an increasing number of studies have been carried out using innovative materials to enhance the thermal conductivity of the hydrate system. A porous aluminum foam with excellent thermal conductivity was used to accelerate the hydration by providing hydrate nucleation sites and enhancing the removal of hydrate heat [18,40]. However, the solid volume of metal foam occupied a considerable gas storage space in the fixed bed, and the formed hydrate tended to block the pores of the foam, leading to insufficient gas storage. Li *et al.* [41] reported that the formation rate of a refrigerant hydrate could be

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increased by the addition of low dose copper nanoparticles. Said *et al.* [42] also used nanofluids with different types of metal nanoparticles for promoting hydrate formation. However, the metal particles were easy to precipitate and agglomerate in the solution due to their large density, which could not realize the continuous heat remove for enhancement of the whole hydration process. Najibi *et al.* [43] observed that when a surfactant was added to the nanofluid, the particles could be uniformly and stably suspended in the solution. Mohammadi *et al.* [44] prepared a mixture system of zinc oxide nanoparticles and SDS for the hydrate formation, and the gas consumption and water conversion was found to be significantly promoted. Therefore, the addition of particles with low density, good thermal conductivity and large specific surface area in water, may be better for the stable enhancement of hydrate formation.

It is noticed that, graphite nanoparticles (GNPs) with a relatively small density and an excellent thermal conductivity have been used to enhance the heat transfer of phase change systems [45–47]. The process of hydrate formation is a special phase change process that occurs at high pressure. Inspired by this, we used a surfactant solution with suspended GNPs for methane enclathration in this study. The GNPs could provide numerous nucleation sites and act as heat transfer media during the hydration. Such uniform suspension prevented the aggregation of GNPs, which might be beneficial for a stable and efficient hydration.

2. Experimental

2.1. Materials

The graphite nanoparticles (GNPs) with a purity of 99.9% and an average particle size of 20 nm was purchased from Original Chemical Factory (China). A surfactant, sodium dodecyl sulfate (SDS) with a purity of

99.5%, was obtained from Shanghai Bio Science & Technology Co., Ltd. (China). Methane with the purity of 99.99% was purchased from Shanghai Weichuang Gas Co., Ltd. (China). The ultrapure deionized water was made in the laboratory.

2.2. Apparatus

Hydrate formation can be considered as a process of continuous pressure drop and temperature increase. In this study, the experiments of methane consumption based on pressure-volume-temperature measurements were conducted in a static system. The schematic diagram of the experimental apparatus is shown in Fig. 1. The hydrate reactor (Jiangsu Hai'an Petroleum Instrument Co., Ltd., China) is a stainless cylinder with an effective volume of 300 cm³ (50 mm in diameter, 153 mm in height), and its maximum allowable working pressure is 20 MPa. A thermostatic circulator bath (THD-3015, 243–373 K, Zhejiang Ningbo Tianheng Instrument Factory, China) with heating and cooling coils was used to control the temperature of the coolant (95 vol% alcohol solution). Two thermal resistances (Jiangsu Plaza Premium Electric Instrument Co., Ltd., China) with an accuracy of 0.01 K were installed into the reactor to measure the temperature of gas phase and liquid phase, respectively. A pressure transducer (DG1205, Guangzhou Senex Instrument Co., Ltd., China) with an accuracy of 0.01 MPa was used to measure the pressure of gas phase. The temperature, pressure, and time were collected at steps of ten seconds by a data logger (34970A, Agilent Technologies Co., Ltd., USA) connected to a computer.

2.3. Methane hydrate formation

To form methane hydrate, the storage material, that is, a suspension solution, needed to be prepared in advance. SDS was first dissolved into the deionized water to obtain surfactant solution, and then graphite

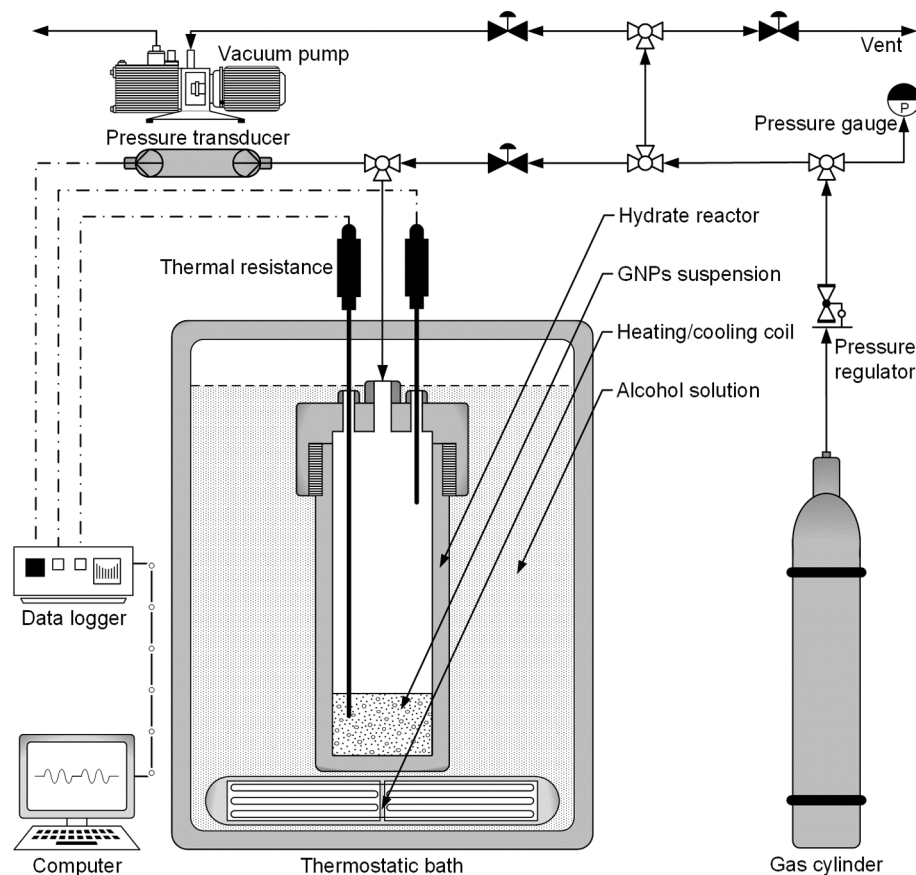


Fig. 1. Schematic diagram of the experimental apparatus.

nanoparticles were added into the solution. They were vibrated ultrasonically for two times with each run lasting 5 min at ambient temperature. The ultrasonic operation was carried out in two separate runs in order to minimize the accumulation of heat generated during ultrasonic vibration. It was noticed that the presence of SDS allowed GNPs to be stably dispersed in its solution for a long time. The concentration of SDS in each suspension was 0.045 wt%, and the concentrations of GNPs in suspensions ranged from 0.10 wt% to 1.00 wt%. After that, the prepared suspension (20.00 g) was placed in the hydrate reactor, and a vacuum pump (2XZ-2B, Shanghai Yulong Vacuum Pump Co., Ltd., China) was started to evacuate air from the reactor. Subsequently, the thermostatic bath was turned on to adjust the temperature alcohol solution. Once the designated temperature (274.15 K) was maintained constantly for five minutes, the reactor was pressurized with methane to attain the desired pressure (6.1–9.0) MPa. The intake pressure was monitored using a pressure gauge with the precision of 0.1 MPa. An exotherm was observed, as expected, because of the heat generated due to the hydrate formation. This was accompanied by a pressure drop in the system, as the methane was stored in the solid hydrate. The pressure drop of less than 0.05 MPa in 30 min was considered to be the completion of one hydration.

2.4. Calculation of gas uptake capacity

Gas uptake capacity (C_{up}) is defined as the standard volume of gas per unit volume of GNPs suspension. The capacity at time t , C_{up} , can be determined by the relation

$$C_{up} = \frac{22400\Delta n_{g,t}}{V_s} \quad (1)$$

Where V_s is the initial volume of GNPs suspension.

The molar amount of gas storage at time t during hydration, $\Delta n_{g,t}$, can be calculated using the relation

$$\Delta n_{g,t} = \frac{P_0 V_0}{Z_0 R T_0} - \frac{P_t V_t}{Z_t R T_t} \quad (2)$$

Where P , T , V and R are the pressure, temperature, volume of gas phase, and the universal gas constant ($8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), respectively. The gas compression factor Z during hydration is calculated by the Peng-Robinson Eq. [48]. The subscripts 0 and t appearing in the

equation denote the initial time and time t , respectively. The initial volume of gas phase, V_0 , is determined by the relation

$$V_0 = V_r - V_s \quad (3)$$

where V_r is the effective volume of the hydrate reactor.

Zhang *et al.* [49] reported that the volume of water would expand by 25% upon its conversion into the solid hydrate. In view of this, the volume of gas phase at time t , V_t , should be corrected using the relation

$$V_t = V_0 - 0.25\alpha_t V_w \quad (4)$$

where V_w is the volume of water in the GNPs suspension sample. α_t is the fraction of water converted into the solid hydrate at time t . The value of α_t is equal to the fraction of gas conversion, and it is determined by the relation

$$\alpha_t = \frac{\Delta n_{g,t}}{\Delta n_{g,e}} \quad (5)$$

where $\Delta n_{g,e}$ is the molar number of gas storage in hydrate phase at the equilibrium (final) time.

According to the idea unit cell formula of structure I, $2(5^{12}) \cdot 6(5^{12}6^2) \cdot 46\text{H}_2\text{O}$ [1], $\Delta n_{g,e}$ can be calculated using the relation

$$\Delta n_{g,e} = \frac{V_w}{18 \times 46} (2\theta_1 + 6\theta_2) \quad (6)$$

where θ_1 and θ_2 are the occupancy of gas molecules in small cavities and large cavities of hydrate, respectively, and they are calculated using Chen and Guo model [50].

3. Results and Discussion

Fig. 2 shows the history of pressure and temperature during the hydrate formation in the SDS solution with different concentrations of suspended GNPs (6.1 MPa). The hydration is a phase change process with exothermic effect at high pressure, and includes two stages of the random nucleation and the crystal growth [2]. An induction time of hydrate nucleation is defined as the time period from the moment when the phase equilibrium condition is met to the moment when the first hydrate crystal appears [51]. Once the nucleus is formed at the gas–liquid interface, the pressure decreases rapidly due to methane

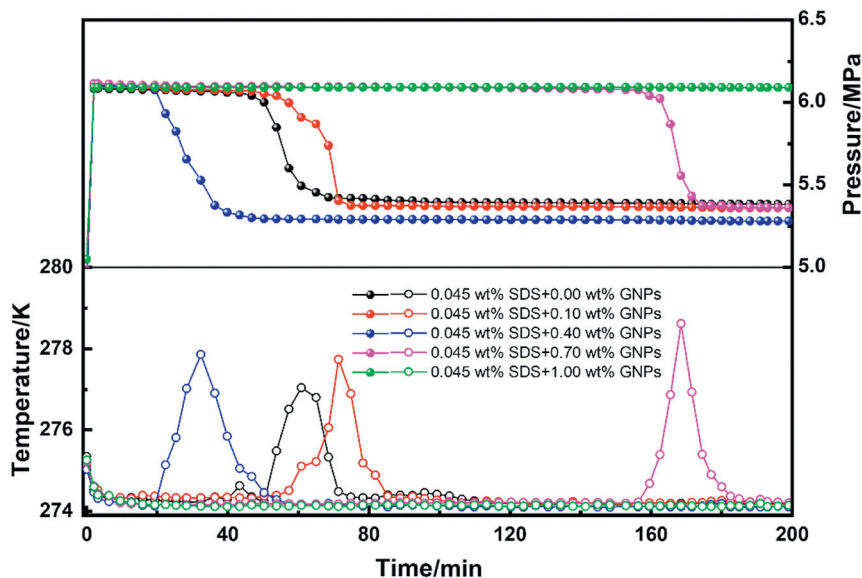


Fig. 2. The history of temperature and pressure during the hydrate formation in the suspensions with different concentration of GNPs ($P = 6.1 \text{ MPa}$, $T = 274.15 \text{ K}$).

Table 1

The induction time (t_{in}), maximum hydrate temperature (T_{hy}), maximum methane uptake capacity (C_{up}), and maximum uptake rate (R_{up}) for each hydration test at the experimental temperature of 274.15 K

Hydration system ^①	P_{exp}/MPa	t_{in}/min	Maximum T_{hy}/K	Maximum $C_{up}/\text{cm}^3 \cdot \text{cm}^{-3}$	Maximum R_{up} ^② / $\text{cm}^3 \cdot \text{cm}^{-3} \cdot \text{min}^{-1}$
0.045 wt% SDS	6.1	50	277.54	108.2	11.77
0.045 wt% SDS + 0.10 wt% GNPs	6.1	57	277.72	114.1	13.45
0.045 wt% SDS + 0.40 wt% GNPs	6.1	22	277.90	126.6	15.45
0.045 wt% SDS + 0.70 wt% GNPs	6.1	155	278.65	118.5	17.41
0.045 wt% SDS + 1.00 wt% GNPs	6.1	180	274.25	~6.0	~0
0.045 wt% SDS	7.0	19	279.10	138.9	22.27
0.045 wt% SDS + 0.40 wt% GNPs	7.0	16	280.61	147.9	24.14
0.045 wt% SDS	8.0	69	281.92	147.3	24.63
0.045 wt% SDS + 0.40 wt% GNPs	8.0	21	282.37	153.1	26.38
0.045 wt% SDS	9.0	25	282.03	151.2	31.54
0.045 wt% SDS + 0.40 wt% GNPs	9.0	16	282.81	162.8	37.11

^① The concentrations of SDS and GNPs are based on the mass of the suspension.

^② Methane uptake rate of each system was the derivation of the methane uptake over time, the maximum value of which indicated the fastest methane storage.

consumption. At the macroscopic level, the rapid pressure drop is usually accompanied by a fast temperature increase, owing to the heat generated from the growing hydrate crystal. The heat could be transferred to the probe of the thermal resistances quickly, indicating methane hydrate formation. As shown in Fig. 2, the sudden changes in temperature and pressure occurred in SDS solution and the suspensions with the GNPs concentrations of 0.10 wt%–0.70 wt%, but not occurred in the system with 1.00 wt% of GNPs. Moreover, the methane hydrate was formed earliest and the methane pressure decreased the most in the suspension with 0.40 wt% of GNPs, compared with other systems. This should be attributed to the appropriate particle concentration in the suspension, and the mass fraction (0.40 wt%) was perhaps the optimal concentration of GNPs. As methane and water molecules were gradually consumed during the hydrate formation, changes in temperature and pressure tended to flatten. The induction time, maximum hydrate temperature, maximum methane uptake capacity, and maximum uptake rate for each hydration test are listed in Table 1.

The methane uptakes and uptake rates in the suspension with different concentrations of GNPs at 6.1 MPa are shown in Fig. 3 and Table 1. Rapid methane hydrate formation occurred in all the suspensions except for that with 1.00 wt% of GNPs within 200 min. The large gas-liquid contact area and larger number of nucleation sites provided by the GNPs, might be the main origins of the enhanced gas storage

performances. In addition, the excellent thermal conductivity of the GNPs could accelerate the heat release of the hydrate crystal surface. Especially, the suspension with 0.40 wt% of GNPs had the smallest induction time (22 min) and the largest methane uptake of $126.1 \text{ cm}^3 \cdot \text{cm}^{-3}$. Compared with that of the SDS solution, the induction time was reduced by 28 min, and the uptake was increased by 17.0%. However, the methane storage performances of the suspensions with higher and lower concentrations of GNPs were not satisfactory. It indicated that the gas storage capacity of the suspension was not positively correlated with the concentration of GNPs, and the optimized concentration of GNPs in the suspension system for the efficient gas storage may be 0.4 wt%. The high concentration of GNPs in the suspension had a negative effect on the growth of hydrate, which could be attributed to the excessive aggregation of GNPs. The main factors affecting the stability of the nanofluid were the particle size, dispersion of the nanoparticles, and viscosity of the solution, which was reported by Kakati *et al.* [52].

In the solution system, with the addition of GNPs, the high specific surface area of the particles providing a greater attraction between the nanoparticles than repulsion, could easily lead to collision and agglutination of the nanoparticles. As suggested by Nashed *et al.* [53], the larger kinetic sizes of the aggregated particles led to decrease in the original specific surface area of the graphite particles. The mass transfer rate of the gas-liquid during the hydrate growth was also decreased. An

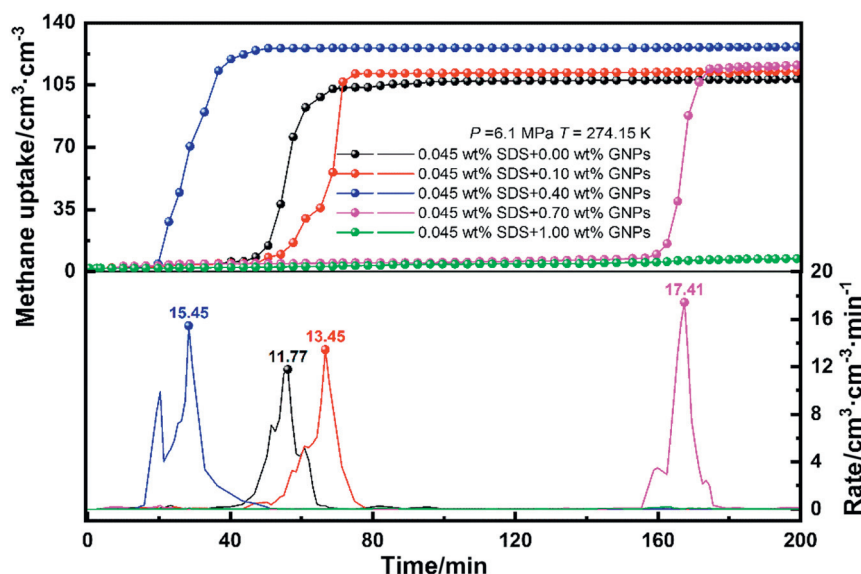


Fig. 3. The methane uptakes and uptake rates in the suspensions with different concentration of GNPs ($P = 6.1 \text{ MPa}$, $T = 274.15 \text{ K}$).

excessive particle agglutination could cause nanoparticle precipitation and influence the stability of the solution, thus decreasing the thermal conductivity of the solution. Although surfactants can, to some extent, disperse GNP stably and evenly, high concentrations of GNPs could have a negative effect on the stability of the dispersion system. The increase in the concentration of GNPs can increase the disorder of water molecules, leading to an increase in entropy [54]. In addition, the hydrate crystal growth required a large number of hydrogen bonds, which might lead to a change in the equilibrium conditions during the hydrate growth. However, the equilibrium condition of hydrate only determined the formation of hydrate, and has little effect on the growth of hydrate.

The methane uptake rate represents the hydrate formation rate controlled by the methane dissolution and hydrate growth, and it can be derived by methane uptake to the time. Its maximum value indicated the fastest methane storage. In the solution systems with 0 to 1.00 wt% of GNPs, the maximum methane storage rates were 11.77, 13.45, 15.45, 17.41, and $\sim 0 \text{ cm}^3 \cdot \text{cm}^{-3} \cdot \text{min}^{-1}$, respectively. In particular, the GNPs concentration of 0.70 wt% led to the largest gas uptake rate, but the induction time increased to 155 min, owing to the excessive addition of graphite. As shown in Fig. 3, two peaks of the gas uptake rate are observed for each experimental group. The first small spike of each curve corresponded to the rapid formation of hydrate at the gas–liquid interface. During this period, the formation of the thin hydrate shell at the gas–liquid interface led to a decrease in mass transfer. Subsequently, the pressure driving force could enable the methane to continue to contact the water through the pores of the hydrate shell and form a large amount of hydrate, which might lead to the appearance of a second peak. After rapid growth of the hydrate shell, its growth rate decreased gradually.

Fig. 4 shows the kinetic behavior of methane hydrate formation in the suspension with 0.4 wt% of GNPs at 7.0, 8.0, 9.0 MPa. At each pressure, when the GNPs was employed, an obvious promotion effect on the hydrate formation was observed, and methane was stored in the suspension much earlier, compared with the SDS solution. In the presence of GNPs, the maximum methane uptakes of SDS solution at the three pressures were increased to 147.9, 153.1, and $162.8 \text{ cm}^3 \cdot \text{cm}^{-3}$, respectively. The corresponding maximum rates were also significantly enhanced, reaching 24.14, 26.38, and $37.11 \text{ cm}^3 \cdot \text{cm}^{-3} \cdot \text{min}^{-1}$, respectively. This indicates that the addition of GNPs in the SDS solution could provide a rich nucleation interface, facilitating the interaction and combination between water and methane molecules. The highly dispersed GNPs not only provided numerous sites for hydrate nucleation and growth but also can be used as a good heat carrier to transfer the hydrate heat outward.

The temperature variations and methane uptakes during the hydrate formation in suspension with 0.4 wt% of GNPs at the applied pressures are shown in Fig. 5. In general, the hydrate nucleation is a stochastic behavior [55], but it is worth noticing that there is little difference in induction time of methane hydrate nucleation in the suspensions at these pressures. This may be due to the presence of GNPs with excellent thermal conductivity and rough surfaces, which reduced the randomness of hydrate nucleation in the suspensions. Moreover, a higher methane storage capacity was achieved at the higher initial pressure. As suggested by Natarajan *et al.* [51], the magnitude of the driving force can affect the degree of random behavior of nucleation, and hydrate induction times are far more reproducible at high pressures ($>3.5 \text{ MPa}$) than at lower pressures.

The maximum temperatures of the hydrate phase at different pressures are shown in Fig. 6. A moderate hydration process induced by a low pressure driving force leads to a small temperature increase, while a rapid hydration at relatively high pressure generates a significantly larger amount of heat leading to a higher temperature increase. Moreover, the temperature increase in the suspension system was greater than that in SDS solution at the same pressure. It shows that the addition of GNPs should accelerate hydrate nucleation and growth

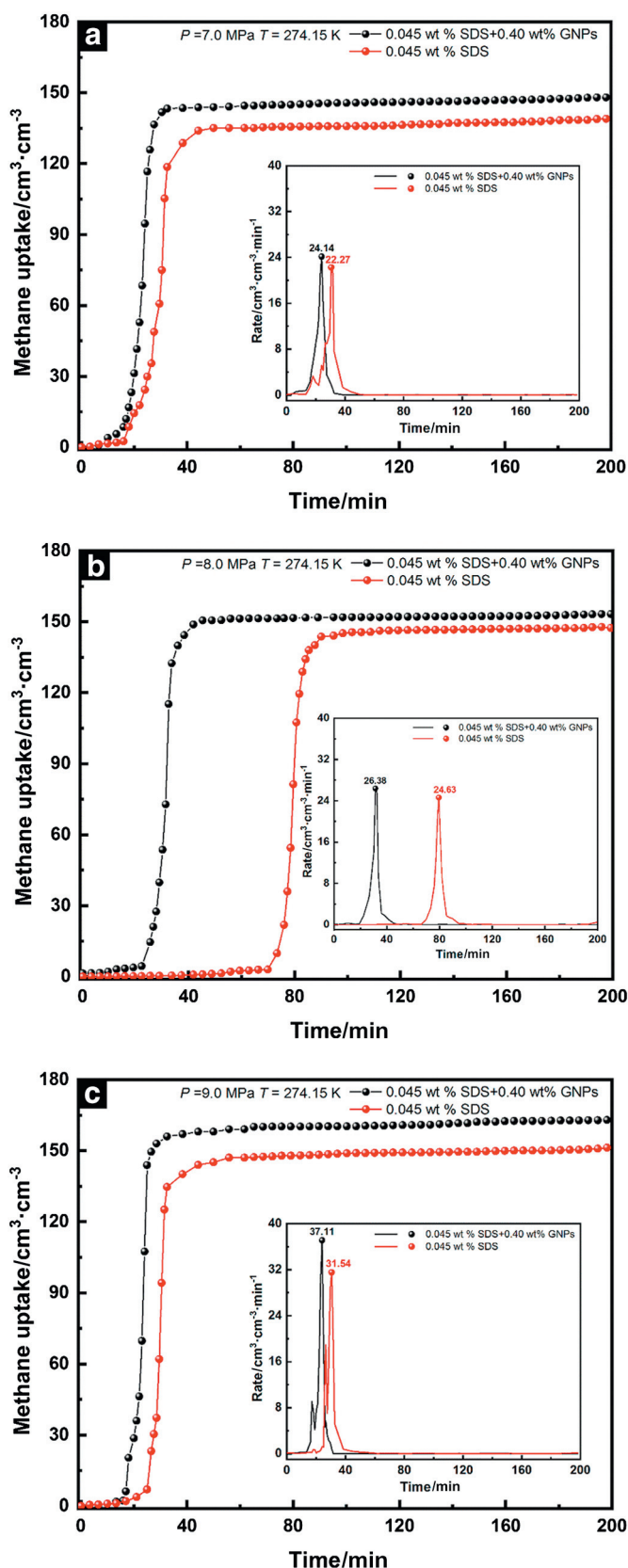


Fig. 4. Kinetic behavior of methane hydrate formation in suspensions at the different pressures (0.40 wt% GNPs, $P = 7.0\text{--}9.0 \text{ MPa}$, $T = 274.15 \text{ K}$).

with a large number hydrate heat released, and the heat could be transferred to the front end of the thermal resistance, indicating a higher temperature. The maximum values of methane uptakes increased by

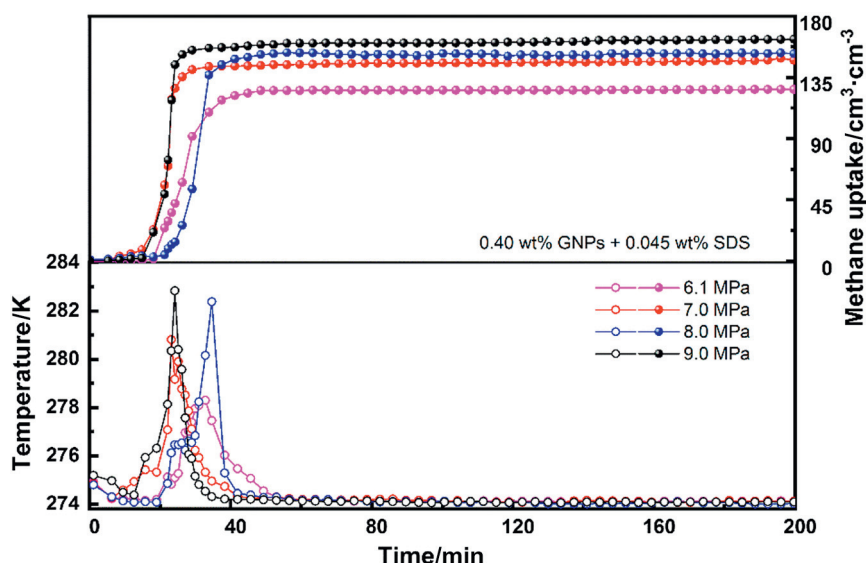


Fig. 5. The temperature variations and methane uptakes in the suspensions with 0.4 wt% of GNPs at the applied pressures.

17.0%, 6.5%, 3.9%, and 7.7% at the pressures of 6.1–9.0 MPa are shown in Fig. 7. The enhancement of maximum gas uptake at low pressure (6.1 MPa) is obviously better than that at relatively high pressures (7.0–9.0 MPa). This implies that the presence of GNPs may play a primary role in the enhanced hydrate formation at the low pressure, and the promotion effect of the particles is less evident at the high pressure.

Fig. 8 illustrates the process of the methane hydrate formation in the solution with suspended GNPs. In the suspension, nanoparticles with rough surfaces and good thermal conductivity were evenly dispersed. There are a great amount of nucleation sites on the rough surface of particles covered. Once the hydration conditions were met, the hydrate nuclei were rapidly formed on the surface of the particles, and a few nuclei appeared in the liquid phase (stage i). As the hydrate nuclei gradually grew, a thin solid hydrate shell formed (stage ii), accompanied by a large amount of heat generated. The released hydrate heat could be quickly transferred outward through the route of hydrate-particle-hydrate. Without the inhibition of heat accumulation, the thin hydrate layer thickened rapidly (stage iii). Therefore, the presence of GNPs could promote more methane and water converted into solid hydrate

by enhancing the heat and mass transfer of hydration, compared with the SDS solution.

4. Conclusions

In this study, a suspension system with graphite nanoparticles (GNPs) was prepared for the promotion of methane hydrate formation. The addition of a surfactant (SDS) into water was used to stabilize the particles in the solution, and prevented the particles accumulation. The experimental results showed that the highly dispersed GNPs with abundant nucleation sites and good thermal conductivity had a crucial role for the fast methane hydrate formation. In the suspension with an optimized concentration of GNPs (0.4 wt%), the methane uptakes were increased by 3.9%–17.0% at the applied pressures, compared with that in the SDS solution. The relatively high concentration of GNPs might lead to a negative effect on the rapid formation of hydrates owing to the agglomeration of the particles. The beneficial effect of GNPs on gas hydrate formation at low pressure is much more remarkable than that at high pressure. This research results are expected to

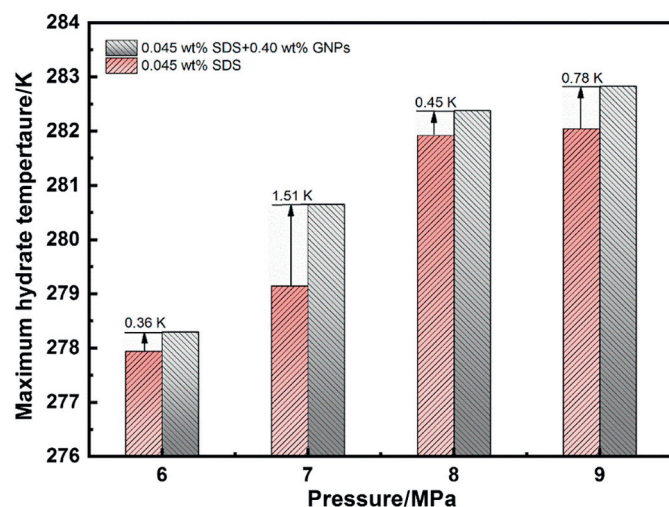


Fig. 6. The effect of GNPs on the maximum hydrate temperature at different pressures ($T = 274.15$ K).

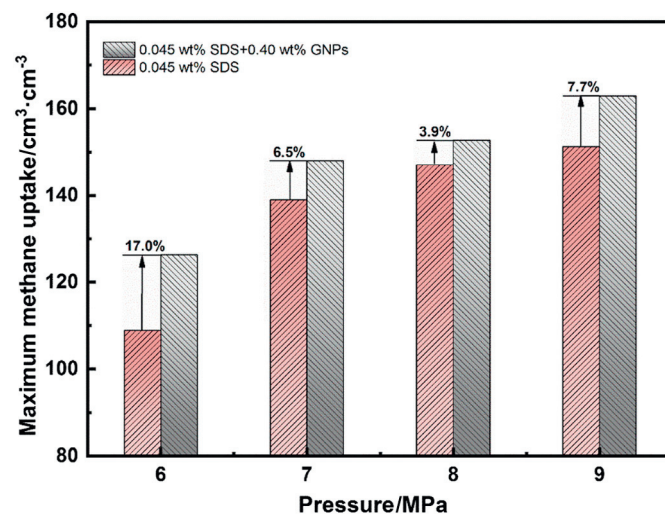


Fig. 7. The maximum methane uptakes at the different pressures ($T = 274.15$ K).

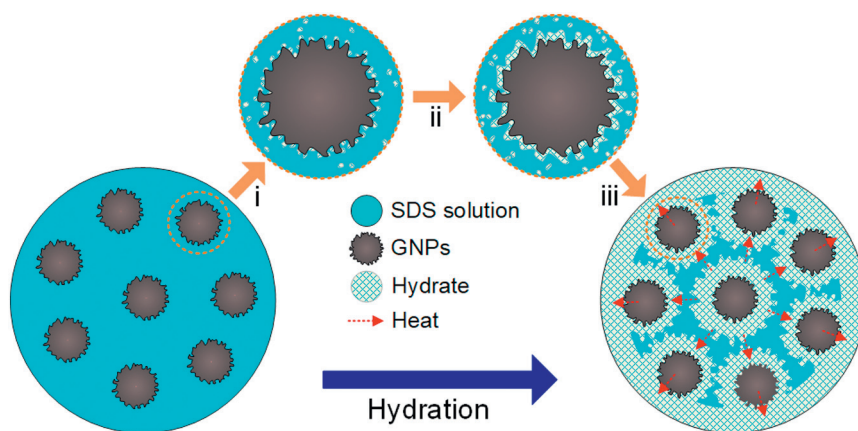


Fig. 8. Schematic microscopic interpretation of the hydrate formation in GNPs suspension.

provide useful information for the rapid large-scale natural gas storage using clathrate hydrate in the static system.

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