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Promoting and Inhibitory Effects of Hydrophilic/Hydrophobic Modified Aluminum Oxide Nanoparticles on Carbon Dioxide Hydrate Formation

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Abstract: Hydrate-based CO₂ capture from large emission sources is considered a promising process for greenhouse gas mitigation. The addition of nanoparticles may promote or inhibit the formation of hydrates. In this work, CO₂ hydrate formation experiments were performed in a dual-cell high-pressure reactor. Non-modified, hydrophilic modified and hydrophobic modified aluminum oxide (Al₂O₃) nanoparticles at different concentrations were added to assess their promoting or inhibitory effects on CO₂ hydrate formation. The equilibrium temperature and pressure, induction time, and total gas consumption during CO₂ hydrate formation were measured. The results show that the presence of Al₂O₃ nanoparticles exerts little effect on the phase equilibrium of CO₂ hydrates. Under the experimental conditions, the addition of all Al₂O₃ nanoparticles imposes an inhibitory effect on the final gas consumption except for the 0.01 wt% addition of hydrophilic modified Al₂O₃ nanoparticles. The induction time required for the nucleation of CO₂ hydrates mainly ranges from 70 to 90 min in the presence of Al₂O₃ nanoparticles. Compared to the absence of nanoparticles, the addition of non-modified and hydrophilic modified Al₂O₃ nanoparticle reduces the induction time. However, the hydrophobic modified Al₂O₃ nanoparticles extend the induction time.

Keywords: CO₂ hydrates; aluminum oxide nanoparticles; hydrophilic/hydrophobic modified particles; phase equilibrium; induction time; gas consumption rate

1. Introduction

Gas hydrates or clathrate hydrates, are non-stoichiometric compounds composed of water and gas molecules under specified pressures and low temperatures (generally above the freezing point of water). In the hydrate structure, water molecules form hydrate cages via hydrogen bonds in which gas molecules such as CH₄ and CO₂ are trapped [1–3]. One volume unit of CO₂ hydrates ideally contains 175 standard volume units of CO₂ gas and generates pure water upon disassociation [4]. Therefore, in recent years, researchers have studied CO₂ hydrates as a means of gas separation and seawater desalination [5].

CO₂ is a primary greenhouse gas generated by large fossil fuel end users, such as coal burning power plants, steel works, and chemical plants. CO₂ capture and storage (CCS) has attracted increasing attention [6–8]. Traditional CO₂ capture methods mainly include the chemical absorption method, adsorption method, and membrane separation method [9,10], but they experience the problems of a high energy consumption and small adsorption amount. The hydrate-based CO₂ capture process has

the advantages of environmental friendliness, a simple process, and low energy consumption, and is considered a CO₂ capture method with great application prospects [11,12].

In the process of CO₂ sequestration, hydrate formation will cause serious problems such as pipeline blockage [13,14]. The addition of inhibitors may effectively prevent hydrate formation [15]. There are three kinds of commonly used hydrate inhibitors: thermodynamic hydrate inhibitors (THIs), kinetic hydrate inhibitors (KHIs), and anti-agglomerant inhibitors (AAs). Among them, KHIs and AAs are low-dose hydrate inhibitors. THIs shift the hydrate phase equilibrium curve to higher pressures and lower temperatures [16–18]. Nanoparticles can be added to drilling fluids to maintain the wellbore stability. Nanoparticles have a dual function in terms of hydrate formation as a new additive, which mainly affects the kinetics of hydrate formation. The main influencing factors of nanoparticles are induction time, hydrate formation rate, gas consumption, storage capacity, and so on [19–21]. The suspensions of 0.1 wt%, 0.2 wt%, and 0.3 wt% of different nanoparticles (Al₂O₃, SiO₂, Cu, and Ag) were selected. During dissolution, the 0.3 wt% SiO₂ nanoparticles exhibit the most positive effect on gas consumption [20]. Three nanofluids of CuO, Al₂O₃, and SiO₂ with three concentrations show the promising effects on the reduction of the average induction time of CH₄ and CO₂ hydrate formation [21]. Moreover, certain nanoparticles have been found to impose a slight inhibitory effect on the thermodynamics of hydrates. Compared to deionized water at a given temperature, the formation pressure of CO₂ hydrate increases in suspensions of graphite nanoparticles. However, this inhibitory effect is independent of the concentration of graphite nanoparticles [22]. In addition, zinc oxide nanoparticles slightly inhibit the thermodynamics of CO₂ hydrate formation but increase gas consumption [23]. Different types of Al₂O₃ nanoparticles exhibit the dual effect of inhibiting and promoting the induction time of CO₂ hydrate formation, and may constrain gas consumption [24]. Therefore, the effects of nanoparticles on hydrate formation need to be considered from the aspects of thermodynamics and kinetics.

Moreover, at a certain concentration and particle size range, hydrophilic SiO₂ nanoparticles inhibit CH₄ hydrate formation and growth. They increase the induction time required for hydrate formation and reduce gas consumption [25]. The dry water prepared from hydrophobic nanometer-sized silica exerts a thermodynamic promoting effect on hydrate formation, and relevant model results are in good agreement with experimental data [26]. Compared to water baselines, the addition of both hydrophobic and hydrophilic multiwall nanotubes (MWNTs) improves the growth rate of methane hydrates, and the growth rate varies with the change in MWNT concentration [27]. According to the above study [25–27], compared to non-modified nanoparticles, hydrophilic and hydrophobic modified nanoparticles have a significant effect on the formation of hydrate. The hydrophilic and hydrophobic properties of modified nanoparticles may be used to obtain the better hydrate promoters or hydrate inhibitors.

In this work, non-modified nanoparticles, hydrophilic modified nanoparticles, and hydrophobic modified nanoparticles of Al₂O₃ with an average diameter of 30 nm were applied to study their effect on CO₂ hydrate formation. The effects on the equilibrium of the hydrate phase, the induction time required for hydrate formation, and the final gas consumption were mainly measured and analyzed to evaluate the promoting or inhibitory effect of these Al₂O₃ nanoparticle additives. These Al₂O₃ nanoparticles could be applied to engineering practice according to their promoting or inhibitory effect.

2. Materials and Methods

2.1. Apparatus and Materials

Figure 1 shows a schematic diagram of the experimental setup adopted to study the effect of Al₂O₃ nanoparticle additives on CO₂ hydrate formation. The setup mainly consists of a high-pressure dual-cell reactor, a circulator bath and a data acquisition system. The custom-made reactor (Shandong ShiYi Science and Technology Co. Ltd., Dongying, China) has an effective volume of 240 cm³, and a high-pressure resistant glass window is installed on the front side of each cell of the reactor. The reactor is provisioned with a pressure sensor (UNIK5000, 0–25 MPa, ±0.2% FS BSL, GE, Connecticut, USA)

and a temperature sensor (PT100, -50 – 100 °C, $\pm(0.15 + 0.002 |t|)$, Tianjin Jinming Instrument Co. Ltd., Tianjin, China). The data acquisition system records the temperature and pressure in the reactor every 30 s and stores the data in a data processor (a personal computer). A cylindrical rotor is placed in each cell of the reactor and controlled by a magnetic stirrer (RCX-1100D, Tokyo Rikakikai Co., Ltd., Tokyo, Japan). A circulator bath (VIVO RT4, Julabo Technology Co., Ltd., Seelbach, Germany) is employed to control the reaction temperature.

Figure 1. Schematic of the experimental setup.

Carbon dioxide gas with a purity of 99.9% (Dalian Special Gases Co., Ltd., Dalian, China) was used for gas hydrate formation in this work. Al_2O_3 nanoparticles (Xuancheng Jingrui New Material Co., Ltd., Xuancheng, China) were employed as the additives. The characteristic parameters of the experimental materials are listed in Table 1. In addition, an ultrasonic homogenizer (Scientz-IIID, Ningbo Scientz Biotechnology Co., Ltd., Ningbo, China) was adopted to disperse the nanoparticles in water via ultrasonication. The preparation requires 10 min of ultrasonic dispersion for each nanofluid sample. Self-prepared deionized water was obtained with an ultrapure water polishing system (Aquapro2S, Aquapro International Company LLC, Delaware, USA), and the resistivity was measured to be $18.2 \text{ M}\Omega \text{ cm}^{-1}$.

Table 1. Characteristic parameters of the experimental materials.

Properties	VK-L30	VK-L30H	VK-L30G
modification treatment	non-modified	hydrophilic modified	hydrophobic modified
appearance		white powder	
average particle size (nm)		30	
packing density (g/cm^3)		0.25–0.35	
pH of aqueous solution		7–9.5	
specific surface area (m^2/g)		30–60	

2.2. Experimental Procedure

2.2.1. Characterization of the Al₂O₃ Nanoparticles

The micromorphology of the Al₂O₃ nanoparticles was observed by a scanning electron microscope (SU8220, Hitachi, Tokyo, Japan) and transmission electron microscope (HT7700 EXALENS, Hitachi, Tokyo, Japan). The contact angle of water on the Al₂O₃ nanoparticle powder surface and the surface tension between the nanoparticle suspension and air were measured with the DropMeter™ system (DropMeter A-100, MAIST Vision Inspection and Measurement Co. Ltd., Ningbo, China). The surface functional groups of the Al₂O₃ nanoparticles were characterized with an advanced Fourier transform infrared spectrometer (Nicolet 6700, Thermo Fisher Scientific, Waltham, MA, USA).

2.2.2. Phase Equilibrium Experiments

In this work, the phase equilibrium of the CO₂ hydrates was determined by the constant volume hydrate formation method. Before each test, the Al₂O₃ nanoparticle suspensions with a certain concentration were prepared with the ultrasonic homogenizer, and the reactor was cleaned with deionized water three times. Then, the high-pressure reactor was filled with 120 cm³ of the prepared suspension and vacuumed for 10 min with a vacuum pump to a negative pressure of 0.10 MPa.

Moreover, the circulator bath was set to 288.15 K, at which temperature hydrates could not be formed. Then, CO₂ was injected into the reactor to achieve the expected pressure. After the temperature and pressure had stabilized, the magnetic stirrer mixed the gas and suspension at a rotating speed of 400 rpm, and the circulator bath was set to 274.15 K and cooled the reactor at a cooling rate of approximately 0.20 K/min. The pressure and temperature were automatically recorded every 30 s. After the temperature and pressure in the reactor had stabilized, the circulator was stopped, and the temperature naturally rose. After reaching a certain temperature in the rising process, the hydrates began decomposing, and the observed hydrate decomposition caused a sharp rise in pressure. The starting point of CO₂ hydrate decomposition was considered as the equilibrium point of the CO₂ hydrate phase in this experiment. The collected temperature and pressure data were used to draw p–T curves.

2.2.3. Hydrate Formation Experiments

Different Al₂O₃ nanoparticle suspensions with concentrations of 0.005, 0.01, 0.05, 0.1, 0.3, and 0.5 wt% were selected as the additives. The methods of nanofluid addition and reactor vacuuming were the same as those in the phase equilibrium experiments. To maintain the same initial conditions after gas injection, the system temperature (292.26 K) was maintained above the hydrate formation temperature. Then, CO₂ was injected into the reactor to achieve a pressure of 4.50 MPa, and the magnetic stirrer was controlled then at a stirring rate of 400 rpm. Moreover, the temperature of the whole system was gradually reduced to 275.15 K at a cooling rate of 0.2 K/min. During the experiment, hydrate formation and its formation phenomenon could be observed through the visual window. The hydrate formation test lasted 6 h. Each group of experiments was repeated three times to obtain accurate results.

2.3. Data Processing

CO₂ Consumption

The consumption of CO₂ during hydrate formation is calculated using the real gas law [23,28]:

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

where P and T are the pressure and the temperature of the reactor, respectively. R is the universal gas constant with a value of 8.314 J/(mol·K), and Z is the compressibility factor, which is obtained with

REFPROP (refrigerant physical property software). Subscripts 0 and t in Equation (1) refer to the initial conditions and the conditions at time t , respectively.

Equation (2) was applied for the evaluation of the volume of CO₂ inside the reactor at time t [29]:

$$V_t = V_{reactor} - V_{W_0} + V_{RW_t} - V_{H_t} \quad (2)$$

where $V_{reactor}$ and V_{w_0} are the reactor volume and initial volume of water, respectively. The V_{RW_t} and V_{H_t} values of the water reacted and hydrates formed at time t , respectively, can be obtained using the following equation [29]:

$$V_{RW_t} = M \times \Delta n_R \times v_w^L \quad (3)$$

$$V_{H_t} = M \times \Delta n_R \times v_w^{MT} \quad (4)$$

It is generally believed that CO₂ forms structure I hydrates, and the theoretical hydration number of CO₂ hydrates is $M = 5.75$ [30,31], while v_w^L is the molar volume of water, which is defined as follows [32]:

$$v_w^L = 18.015 \times \left[\begin{array}{l} 1 - 1.0001 \times 10^{-2} + \\ 1.33391 \times 10^{-4} (1.8(T - 273.15) + 32) \\ + 5.50654 \times 10^{-7} (1.8(T - 273.15) + 32)^2 \end{array} \right] \times 10^{-3} \quad (5)$$

v_w^{MT} is the volume of the empty hydrate lattice and it is defined as follows [33]:

$$v_w^{MT} = (17.13 + 2.249 \times 10^{-5}T + 2.013 \times 10^{-6}T^2)^3 \frac{10^{-30}N_A}{136} - 8.006 \times 10^{-9}P + 5.448 \times 10^{-12}P^2 \quad (6)$$

The gas consumption rate r (mol·min^{−1}) during hydrate formation is a very important for industrial applications and can be obtained using the following equation [34]:

$$r(t) = -\frac{n_i^{i-1} - n_i^{i+1}}{t_{i-1} - t_{i+1}} \quad (7)$$

where n_i^{i-1} and n_i^{i+1} are the mole numbers of gas in the gas phase at time intervals t_{i-1} and t_{i+1} , respectively.

3. Results and Discussion

3.1. Characterization Results of the Al₂O₃ Nanoparticles

The surface functional groups of the Al₂O₃ nanoparticles were characterized by Fourier transform infrared spectroscopy (FTIR). Figure 2 shows the FTIR spectra of the three kinds of Al₂O₃ nanoparticles.

The curves all reveal wide absorption bands in the wavenumber range from 400 to 1000 cm^{−1}, which is the characteristic absorption band of Al₂O₃. The peaks observed at 2850 and 2918 cm^{−1} are caused by the symmetric and asymmetric stretching, respectively, of the ethyl group (−CH₂−), and the absorption peak at 2971 cm^{−1} is caused by the methyl group (−CH₃) [35]. The embedding of such groups can be considered the successful modification of Al₂O₃ nanoparticles. The absorption peaks at 3443 and 1632 cm^{−1} correspond to the stretching and bending vibration absorption peaks of O−H, respectively. The absorption peaks of the hydrophilic modified Al₂O₃ nanoparticles are much higher at these two wavenumbers than those of the other two kinds of Al₂O₃ nanoparticles, indicating that the amount of hydroxyl groups on the surface is large [36]. In particular, the hydrophilic modified Al₂O₃ nanoparticles are much more hydrophilic than the other two kinds of Al₂O₃ nanoparticles.

Figure 2. Fourier transform infrared spectroscopy (FTIR) spectra of non-modified, hydrophilic modified and hydrophobic modified Al_2O_3 nanoparticles.

The micromorphology of the Al_2O_3 nanoparticles was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM) (please refer to Figure 3).

Figure 3. SEM images of the (a) non-modified (b) hydrophilic modified and (c) hydrophobic modified Al_2O_3 nanoparticles and TEM images of the (d) non-modified (e) hydrophilic modified and (f) hydrophobic modified Al_2O_3 particles.

As shown in the figures, the agglomeration of the Al_2O_3 nanoparticles is obvious. Therefore, the shape of the Al_2O_3 nanoparticles cannot be accurately determined. The nanoparticles used in this work are prepared via the electrospray method and can be regarded as spherical particles.

Figure 4 shows images of water drops on the surfaces of the two modified Al_2O_3 nanoparticle powders. The average contact angles between the water drops and the hydrophilic and hydrophobic modified Al_2O_3 nanoparticle surfaces are 22.5° and 91.0° , respectively.

The hydrophilic modified Al_2O_3 nanoparticles exhibit a high hydrophilicity, while the hydrophobic modified Al_2O_3 nanoparticles exhibit a low hydrophobicity.

The interfacial tension between the modified Al_2O_3 nanoparticle suspensions and air was also measured with the pendent drop method. The interfacial tension between the hydrophilic and

hydrophobic modified Al_2O_3 suspensions and air is 73.91 and 72.57 mN/m, respectively. From the results, it can be inferred that the difference in interfacial tension between the various modified Al_2O_3 nanoparticles is small. The above characterization of the materials verifies the hydrophilic and hydrophobic properties of the Al_2O_3 nanoparticles and provides a basis for the interpretation of the experimental phenomena in the following sections.

Figure 4. Contact angle of pure water on the (a) hydrophilic modified and (b) hydrophobic modified Al_2O_3 nanoparticle powder surfaces.

3.2. Effect of the Al_2O_3 Nanoparticle Additives on the Hydrate Phase Equilibrium

No clear conclusion on the effect of nanofluids on the phase equilibrium curve of hydrate formation has been reported in the literature. Park et al. [37] found that there is a positive effect on the CO_2 hydrate phase equilibrium in the presence of multi-wall carbon nanotube (MWCNT) nanofluids. MWCNT nanofluids shift the equilibrium curve of CO_2 hydrates to lower pressures and higher temperatures. Yu et al. [22] indicated that graphite nanoparticles negatively affect the formation of CO_2 hydrates and that the concentration of graphite nanoparticles does not influence the phase equilibrium curve of CO_2 hydrate formation.

In this work, we evaluate the equilibrium pressure and temperature of the formation and dissociation of CO_2 hydrates in the presence of modified Al_2O_3 nanoparticles at a concentration of 0.1 wt%. Figure 5 shows the phase equilibrium pressures and temperatures of the CO_2 hydrates formed in deionized water, non-modified Al_2O_3 suspension, hydrophilic modified Al_2O_3 suspension, and hydrophobic modified Al_2O_3 suspension. We found that compared to deionized water, the Al_2O_3 nanoparticle additives impose little effect on the phase equilibrium pressure and temperature of the CO_2 hydrates. It can be inferred that the nanoparticle additives slightly impact the thermodynamics of hydrate formation. This effect is similar to that of surfactants on gas hydrate formation.

Figure 5. Phase equilibrium pressures and temperatures of the CO_2 hydrates in the presence of the Al_2O_3 nanoparticles.

3.3. Effect of the Non-Modified Al_2O_3 Nanoparticle Additives on the Kinetics of Hydrate Formation

Many kinds of nanofluids have been applied to hydrate formation in previous studies. However, the mechanism of how nanofluids affect hydrate formation remains unclear. In this work, different non-modified Al_2O_3 nanoparticle suspensions with concentrations of 0.005, 0.01, 0.05, 0.1, 0.3, and 0.5 wt% are selected as the additives. They are applied to test the inhibitory or promoting effect on CO_2 hydrate formation.

The induction time is an important index of the kinetics of hydrate formation [38]. From the induction time, it can be determined when hydrates begin to form and grow. However, there is no accurate definition of the meaning of the induction time, so in this work, the induction time is defined as the time from the beginning of the cooling process to the obvious rising point on the temperature curve (please refer to Figure 6) [39].

Figure 6. Pressure and temperature profiles of the hydrate formation experiment.

The results reveal that the non-modified Al_2O_3 nanoparticle additives at the different concentrations impose an inhibitory effect on the final gas consumption of CO_2 hydrate formation compared to that in deionized water (as shown in Figure 7a). The final gas consumption in deionized water is 0.194 mol. The final gas consumption is 0.105 mol in the 0.01 wt% non-modified Al_2O_3 nanoparticle suspension, which is 45.9% lower than that in deionized water. The final gas consumption is the lowest in the 0.3 wt% non-modified Al_2O_3 nanoparticle suspension, which is 51.6% lower than that in deionized water. In terms of the final gas consumption, the inhibitory effect of the Al_2O_3 nanoparticle additive concentration is obvious. These experimental observations agree well with previous studies on the promoting and inhibitory effects of oxide powder additives on gas hydrate formation. Nesterov et al. [24] found that the influence of Al_2O_3 powders on hydrate formation mainly depends on the surface functional groups and the particle size. The decrease of carbonate carbon, C-H carbon and total carbon on the nanoparticles surface inhibited the formation kinetics of hydrate. The size of the particle aggregates in deionized water is closely related to the concentration of carbonate (carbonyl and C-H carbon on the particle surface) [24]. Within a certain particle size range, larger particle size led to less gas consumption. The possible reason was that smaller nanoparticles provided higher surface free energy and were more conducive to gas-liquid contact [40]. We also speculate that the non-modified Al_2O_3 nanoparticle additives reduce the solubility of CO_2 in deionized water.

Figure 7. (a) The gas consumption, (b) the pressure drop, (c) the gas consumption rate and (d) the induction time during CO₂ hydrate formation in the various Al₂O₃ nanoparticle suspensions at the different concentrations.

Figure 7b shows the pressure drop during CO₂ hydrate formation in the non-modified Al₂O₃ nanoparticle suspensions at the different concentrations. Corresponding to the concentration increase from zero to 0.5 wt%, the pressure drop, sequentially, was 2.35, 1.27, 1.35, 1.28, 1.30, 1.24, and 1.33 MPa. These pressure drops are similar in different non-modified Al₂O₃ nanoparticle suspensions but lower than those in deionized water. The reduction in the pressure drop occurs because the formation of CO₂ hydrates in deionized water and the non-modified Al₂O₃ nanoparticle additives constrain formation.

Figure 7c shows the rate of gas consumption from the beginning to the end of the experiment (the duration of each formation experiment was 6 h in this work). The initial gas consumption rates are very high because of the high dissolution rate of CO₂ in water. The gas consumption rate in deionized water greatly increased at 134 min and reached a maximum value of 1.27×10^{-3} mol/min at approximately 153 min. A sudden pressure decrease accordingly occurred at the same time (please refer to Figure 7b). It is inferred that at this time, CO₂ hydrates quickly formed and consumed a large amount of CO₂. Based on the curves of the non-modified Al₂O₃ nanoparticle additives, the gas consumption rate was not related to the concentration of non-modified Al₂O₃ nanoparticles, and the gas consumption rate in the non-modified Al₂O₃ nanoparticle suspensions was lower than that in deionized water. At approximately 80 min, the gas consumption rate became very low.

In Figure 7d, from left to right, the induction time of CO₂ hydrate formation at the different concentrations is 82, 73, 78, 69, 73, 69, and 72 min, respectively. It is found that the non-modified Al₂O₃ nanoparticle suspensions with the different concentrations slightly reduce the induction time of CO₂ hydrate formation. This can be attributed to the additional nucleation sites provided by the nanoparticle additives. The lower the concentration of the non-modified Al₂O₃ nanoparticle suspension, the fewer hydrate nucleation sites there are. From the perspective of heat transfer, the hydrates generated much heat at the beginning of formation, and the nanoparticles increased the thermal conductivity of the

suspension so that the generated heat could be quickly released [41]. From the results, it is found that the addition of Al_2O_3 nanoparticles shortens the induction time and reduces the final gas consumption. Hence it can be inferred that the presence of Al_2O_3 nanoparticles exerts a strong inhibitory effect during the subsequent hydrate growth process.

3.4. Effect of the Hydrophilic/Hydrophobic Modified Al_2O_3 Nanoparticle Additives on the Final Gas Consumption

In this work, the effect of the modified Al_2O_3 nanoparticle additives on the final gas consumption is studied. The experimental results are shown in Figure 8.

Figure 8. Effects of the different concentrations and types of Al_2O_3 nanoparticles on the kinetics of CO_2 hydrate formation. The final gas consumption versus the dispersed solution concentration.

As shown in Figure 8, with increasing concentration of the hydrophilic modified Al_2O_3 suspension, the final gas consumption increases at first and then decreases. In the 0.01 wt% hydrophilic modified Al_2O_3 nanoparticle suspensions, the final gas consumption reaches a maximum value of 0.209 mol, which is 1.99 times that in the 0.01 wt% non-modified Al_2O_3 nanoparticle suspensions. Similarly, the addition of 0.05 wt% hydrophilic nanoparticles enhances the final gas consumption up to 86.5% over the level attained in the 0.05 wt% non-modified Al_2O_3 nanoparticle suspensions. As shown in Figures 3 and 5, the hydrophilic Al_2O_3 nanoparticles exhibit a high hydrophilicity, which enables these nanoparticles to be uniformly and stably dispersed in deionized water. This stability enhances the liquid phase mixing and improves the mass transfer between the unfilled water cages and gas molecules [42]. However, with increasing hydrophilic modified Al_2O_3 nanoparticle suspension concentration, the binding force between the hydroxyl groups on the nanoparticle surfaces and the water molecules is enhanced. The activity of water in the fluid weakens, and the final gas consumption decreases.

Compared to the non-modified Al_2O_3 nanoparticles, the hydrophobic modified Al_2O_3 nanoparticles also impose a promoting effect on the final gas consumption. The promoting effect reaches its peak when the hydrophobic modified Al_2O_3 nanoparticle suspension concentration is 0.05 wt%, and the final gas consumption is 1.49 times of that in the 0.05 wt% non-modified Al_2O_3 nanoparticle suspensions. The hydrophobicity of the hydrophobic modified Al_2O_3 nanoparticles alters the arrangement of the water molecules and redirects them to positions favorable for hydrate formation [43]. This can also be ascribed to the heterogeneous nucleation of gas bubbles occurring on the hydrophobic surfaces [44]. At low concentrations, the hydrophobic modified Al_2O_3 nanoparticle suspension concentration influences the final gas consumption little. However, when the concentration reaches 0.5 wt%, the agglomeration of

the hydrophobic Al_2O_3 nanoparticles is enhanced, and the promoting effect of their hydrophobicity on the final gas consumption is weakened.

In general, as the hydrophilic Al_2O_3 nanoparticles are readily dispersed in water, the effect of these hydrophilic Al_2O_3 nanoparticles on the final gas consumption is better than that of the hydrophobic Al_2O_3 nanoparticles. At a low concentration, the mass transfer of dissolved CO_2 is improved due to the greater mixing provided by Brownian motion [27]. However, at a high concentration, the Brownian nanoparticles face a greater opposition to their free motion in the presence of a large number of similar nanoparticles [45]. Due to the notable inhibitory effect of the non-modified Al_2O_3 nanoparticles, the final gas consumption in the presence of modified Al_2O_3 nanoparticles is lower than that in deionized water.

3.5. Effect of the Hydrophilic/Hydrophobic Modified Al_2O_3 Nanoparticle Additives on the Induction Time

The acquisition of the induction time has been explicitly explained in the previous section, and the experimental results are shown in Figure 9.

Figure 9. Effects of the different concentrations and types of Al_2O_3 nanoparticles on the kinetics of CO_2 hydrate formation. The induction time versus the dispersed solution concentration.

The induction time after the addition of the above non-modified and hydrophilic modified Al_2O_3 nanoparticle additives is shorter than that without nanoparticle addition. However, the hydrophobic modified Al_2O_3 nanoparticles extend the induction time. The hydrophilic Al_2O_3 nanoparticles exhibit a better nucleation promoting effect than do the hydrophobic Al_2O_3 nanoparticles. In the six different hydrophilic Al_2O_3 nanoparticle suspensions, the induction times for hydrate formation are similar at nanoparticle concentrations of 0.01 and 0.05 wt%. The induction time for CO_2 hydrate formation is 82 min in deionized water. Due to the increasing hydrate nucleation sites provided by the nanoparticles, the hydrophilic and non-modified Al_2O_3 nanoparticles promote the induction period of hydrate formation. When the amount added of the hydrophobic Al_2O_3 nanoparticles ranges from 0.005 to 0.1 wt%, the induction time gradually increases, and the inhibitory effect on hydrate nucleation gradually increases to a peak at 0.1 wt%, but the maximum induction time is 6 min longer than the minimum value. It could be considered that the hydrophobic Al_2O_3 nanoparticle suspension concentration exerts little effect on the induction time. Because the agglomeration of nanoparticles on the dispersed liquid surface is not conducive to the gas-liquid contact, the effect of the hydrophobic Al_2O_3 nanoparticles on the induction time is inhibited.

In summary, all the experimental results reveal an inhibitory effect on the final gas consumption except for the 0.01 wt% addition of hydrophilic modified Al_2O_3 nanoparticles. Moreover, the 0.01 wt% addition of hydrophilic modified Al_2O_3 nanoparticles exhibits a promising effect on the reduction

of induction time. Due to Brownian motion, the mass transfer of the hydrophilic modified Al_2O_3 nanoparticles is enhanced at low concentration. Moreover, the hydrophilic groups on the surface of the nanoparticles make nanoparticles easy to disperse, and nanoparticles provide more sites for hydrate nucleation. In addition, the promoting or inhibitory effect of Al_2O_3 nanoparticles is related to the experimental conditions and has a high degree of randomness. Further work is needed to reveal the microscopic mechanism of the effect of hydrophilic and hydrophobic nanoparticles on hydrate formation.

4. Conclusions

In this study, non-modified nanoparticles, hydrophilic modified nanoparticles, and hydrophobic modified nanoparticles of Al_2O_3 with an average diameter of 30 nm are employed to study their effects on the formation of CO_2 hydrates. The results demonstrate that the presence of Al_2O_3 nanoparticles imposes little effect on the phase equilibrium of CO_2 hydrates. Under the experimental conditions, all the experimental results reveal an inhibitory effect on the final gas consumption except for the 0.01 wt% addition of hydrophilic modified Al_2O_3 nanoparticles. The promoting or inhibitory effect depends on the particle size and surface functional groups of the Al_2O_3 nanoparticles. When considering the influence of the hydrophilicity and hydrophobicity on the final gas consumption, we find that both exert promoting effects. The reasons are that hydrophilicity enables the Al_2O_3 nanoparticles to be more easily dispersed in deionized water and hydrophobicity alters the arrangement of water molecules on the hydrophobic surface. In terms of the induction time for CO_2 hydrate formation, the hydrophilic and non-modified Al_2O_3 nanoparticles reduce the induction time over the hydrophobic Al_2O_3 nanoparticles.

Based on this study, non-modified Al_2O_3 nanoparticles could be applied to CO_2 geological sequestration to prevent hydrate formation in pipes. These experimental data also indicate that nanoparticle surface modification could be applied to efficiently promote hydrate formation. Nanoparticle surface modification provides a theoretical basis for hydrate-based CO_2 capture. However, the influence of nanoparticles on hydrate formation is very complicated and requires the comprehensive consideration of a variety of influencing factors. This study only considers macro-level processes, while the micro-mechanism remains unclear, which requires follow-up efforts.

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