

THE MECHANISM OF NANOPARTICLES PROMOTING THE FORMATION OF CO₂ HYDRATE: A REVIEW

Zucheng Cheng, Yu Liu, Weiguo Liu, Lanlan Jiang*, Yongchen Song

Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology,
Dalian 116024, China

(Corresponding Author) lanlan@dlut.edu.cn

ABSTRACT

The surge in atmospheric carbon dioxide has become a major contributor to the global warming effect. Using geology for CO₂ capture and storage (CCS) has been identified as a new and highly efficient mitigation measure. Hydrate-based CO₂ capture and storage is a promising technology for capturing CO₂ from the plants and storageing CO₂ as hydrate. The barriers for the new technology is the low formation rate and high energy cost. The purpose of this review is to summarize the influence of various nanoparticles on CO₂ hydrate, and to understand the influence mechanism of different nanoparticles on CO₂ hydrate, so as to provide a reasonable basis for future research.

Keywords: CCS, CO₂ Hydrate, nanoparticles, promote

1. INTRODUCTION

Global warming is caused by the rapid increase of greenhouse gases in the atmosphere, the main component of which is carbon dioxide[1]. Under severe conditions, more and more scholars are making efforts to reduce the concentration of carbon dioxide in the atmosphere. Among many measures to deal with the global warming effect, carbon dioxide capture and storage is considered the most important option for reducing CO₂ concentrations [2].

Currently, common carbon dioxide capture technologies mainly include physical adsorption and chemical adsorption. However, Li et al [3] had proposed the above methods has serious pollution, high cost, low efficiency and a series of problems. Accordingly, a method of converting carbon dioxide to hydrate is proposed [4]. One way is to use the ocean to replace the underground geological structure, and store the

dissolved CO₂ in the form of hydrates in the 1-3km ocean [5].

Natural gas hydrate is an ice-like crystalline substance formed by natural gas and water under high pressure and low temperature [6]. On the molecular scale, the formation of gas hydrates is due to the fact that water molecules in aqueous solutions combine to form cage cavities in the form of hydrogen bonds, and guest molecules (gas) stay in the cage under the action of van der Waals force to maintain the stability of the cage [7]. It is found that a volume of hydrate can contain 150-180 volumes of gas in theory [8]. How to improve the efficiency of CO₂ conversion into hydrate and shorten the conversion time becomes the focus of research.

Up to now, many different methods have been used to promote the formation of gas hydrate, such as stirring [9], water spraying [10], injecting gas as bubbles [11] and using ultrasonic wave [12]. The above approaches is easy to implement in the laboratory, but difficult to implement in CCS projects. Therefore, studies had been started on nanoparticles as a method to promote hydrate formation.

Li et al [13] proved that copper nanofluids can promote the formation of HFC134a hydrate. It is firstly proposed that nanoparticles promote the formation of hydrate. Then more and more nanoparticles and the mixed fluid of nanoparticles with surface additives have been found play a important role on promoting the hydrate, including shortening the stabilization time, inducing time and increasing gas consumption [14]–[20]. The specific statistical results are shown in Table 1.

In this review, the effects of different nanoparticles on CO₂ hydrate were summarized with to analysis the promoting mechanism from the perspective of heat and mass transfer.

Table 1. Effects of common nanoparticles on CO₂ hydrates. The values in the table are all obtained by comparing with the pure water under the same working condition.

| additive | working condition | Induction time | storage capacity | gas consumption |
|---|---------------------|----------------|------------------|--|
| SDBS Graphite [14] | 277.15 K 3.5 MPA | 85.1% | 35.8% | 86.4% |
| CuO [15] | 275.65 K 5.5MPA | 92.7% | 34% | |
| Zinc [16] | 2.2/2.6/3.2MPA | | | 16%/8%/6% |
| Graphene [17] | 277.15 K 6.9 MPA | 61.07% | 12.9% | |
| Al ₂ O ₃ /SiO ₂ / Ag/Cu [18] | 274.15 K 4 MPA | | | 77%(SiO ₂) 30%-65%(Cu Al ₂ O ₃) |
| Graphene oxide [19] | 279 K 3-5 MPA | 53-74.3% | | 5.1-15.9% |
| Graphite [20] | 277.15 K 3.5 MPA | 80.8% | | 12.8% |

2. EFFECT OF NANOPARTICLES ON HEAT TRANSFER DURING HYDRATE FORMATION

2.1 Heat transfer during on hydrate formation

Temperature is a basic parameter affecting hydrate formation. Supercooling is necessary for crystallization. The higher the supercooling degree is, the greater the crystallization driving force of gas hydrate is, and the easier nucleation is needed. It was found that hydrate formation is an exothermic process and the amount of heat is proportional to the rate of hydrate formation in the system [21]. The accumulation of heat in the system affect the supercooling degree of hydrate formation and seriously hinder the further formation of hydrate. Effectively transferring the generated heat greatly promote the formation of hydrate.

2.2 Enhancement heat transfer with nanoparticles

The current heat transfer models consider that the heat transfer rate is directly proportional to the heat transfer coefficient, temperature difference, and interface area [22]. Compared with traditional solid particles, The production of nanofluids by suspending nanocrystalline particles in liquids can significantly improve the heat transfer performance of cooling fluids such as water or oil [23].

Nanoparticles have good thermal conductivity and play an important role in the formation of hydrate [24]. The thermal conductivity of several materials is shown in Table 2 [20].

Table 2. Heat-transfer coefficients of some nanoparticles

| material | wate r | grap hite | Al2 O3 | molecul ar sieve | glas s | SiO 2 |
|---|-----------|--------------|-----------|---------------------|-----------|----------|
| heat-transfer coefficient (Wm ⁻¹ K ⁻¹) | 0.61 | 129 | 40 | 0.1 | 0.7 | 7.6 |

Zhou [20] founded the induction time of CO₂ hydrate formed in the presence of graphite nanoparticles decreased by 80.8%, while the maximum CO₂ consumption increased by 12.8% in comparison to pure water.

In the presence of graphite, the heat transfer efficiency of the system is 20 times that of pure water in theory, the heat generated when the hydrate begins to form is transferred more quickly to the environment, thus accelerating the formation of the hydrate. In addition, graphite has the best thermal conductivity among common nanoparticles. Therefore, it can be predicted that it is also the most effective in promoting the heat transfer performance of hydrate

3. EFFECT OF NANOPARTICLES ON MASS TRANSFER DURING HYDRATE FORMATION

3.1 Mass transfer during hydrate formation

Mass transfer between gas and liquid affects the rate of hydrate formation and gas storage. When the hydrate is nucleated, the effect of mass transfer has the greatest influence on the hydrate formation rate. The amount of gas dissolved in the liquid phase is two orders of

magnitude greater than the amount of gas contained in hydrate.

3.2 Enhancement mass transfer with nanoparticles

3.2.1 Change the surface tension of the liquid

The initial formation of hydrate occurs mostly on the gas-liquid contact surface, and the gas-liquid contact area is limited. As the reaction progresses, the formation of hydrate hinder the mass transfer between the gas phase and the liquid phase.

Therefore, nano-solutions were used to change the mass transfer efficiency of the gas and liquid phases. Said[18] found that the solubility of CO₂ in 0.3%wt SiO₂ solution was 77% higher than that in pure water, and there was also an enhancement of 1%-15% in the solution of Cu and Al₂O₃. Besides, Dai et al [25] found that the induction time of CO₂ hydrate in the presence of graphene oxide nanoparticles was 77.14% shorter than that of pure water and the gas consumption was 15.89% higher. It was also found that the surface tension coefficient of the liquid would change significantly under different concentrations of nano-TiO₂, as shown in Figure 1[26]. These results showed the presence of nanoparticles can affect the surface tension of the liquid and enhance mass transfer.

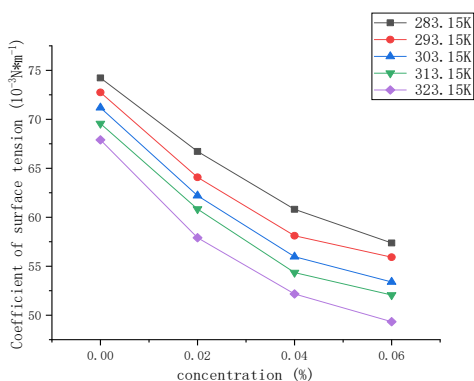


Fig 1. The surface tension coefficient of TiO₂ solution with different concentration at different temperature[26]

3.2.2 The wettability of the gas-water interface

At present, most of the analysis on the enhanced mass transfer of nanofluids focus on the surface tension of the liquid, but it is still rare about the wettability of nanomaterials is still rare. As hydrate growth, water mainly moves under the action of capillary force [27]. Continuous hydrate formation requires a continuous flow of gas in contact with water. Hydrate formed on the gas-water contact surface can inhibit the contact between gas and water in further. Changing the

wettability of gas-water contact surface can enhance the capillary force and promote the formation of hydrate.

Besides, heterogeneous nucleation is common in the process of hydrate formation. Compared with homogeneous nucleation, heterogeneous nucleation has a higher surface utilization rate, and the smaller the contact angle of gas-liquid contact surface, the greater the possibility of heterogeneous nucleation [28].

Esmail [29] measured the contact Angle of 20uL water on the surface of glass(27°), sapphire(49°) and PVC(79°). It was found that the halo propagated 50% faster on the glass plate than sapphire, but hardly on PVC. The experimental results are shown in Figure 2. The results show that the higher the wettability, the faster the propagation of the surface halo and the easier the formation of hydrate.

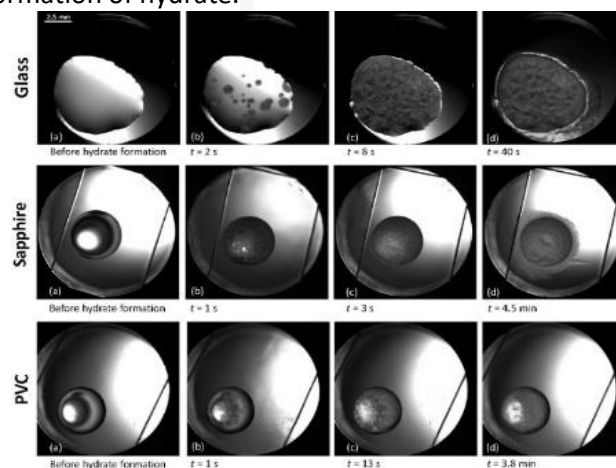


Fig 2. The growth state of hydrate at the interface of glass, sapphire and PVC[29]

3.3 Discussion

It was found that SiO₂ and GO are hydrophilic and the surface tension of the nano-solution formed by them is significantly lower than that of pure water solution. The lower the surface tension, the better the wettability of the liquid, and the more obvious the mass transfer between gas and liquid. Therefore, the existence of nanoparticles promote mass transfer, accelerate the nucleation of hydrate, and promote the formation of hydrate.

At present, the research method of nanoparticles to promote hydrate formation is mainly to mix nanoparticles with water and then react with gas molecules. The calculation and expression of induction time, gas consumption and conversion rate show its promoting effect, which does not accord with the actual geological conditions of carbon dioxide geological

sequestration. There are few reports on the microscopic analysis of nanoparticles promoting hydrate formation at the core scale. Future research priorities need to be focus on the influence of nanoparticles on heat and mass transfer in the hydrate formation process from the microscopic scale which combining with MRI, microfocused X-ray CT and other equipment.

4. CONCLUSIONS

Nanoparticles can effectively promote the formation of CO₂ hydrate, by reducing induction time, increasing gas consumption and improving the conversion rate. Nanoparticles have high heat transfer efficiency, which can effectively transfer the heat generated during the formation of hydrate. The higher specific surface area of nanoparticles reduce the surface tension of the solution, promote the dissolution of gas and enhance mass transfer. The wettability of gas-water contact surface is changed, the capillary force is enhanced, and the probability of heterogeneous nucleation is increased. Future research priorities need to be focus on the influence of nanoparticles on heat and mass transfer in the hydrate formation process from the microscopic scale to apply the technology.

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