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Rapid and repeatable methane storage in clathrate hydrates using gel-supported surfactant dry solution

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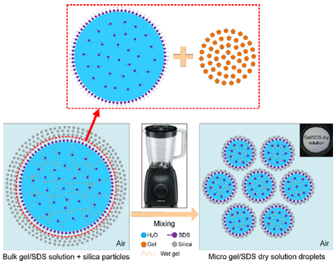
HIGHLIGHTS

- GDS has the merits of surfactant dry solution (DS) and gel-supported dry water (GDW).
- GDS can enhance formation rate and storage repeatability of methane hydrate.
- GDS droplets with greater storage capacity store methane faster than GDW droplets.
- GDS exhibits similar storage rate and better storage repeatability compared with DS.

GRAPHICAL ABSTRACT



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ABSTRACT

Gel-supported surfactant dry solution (GDS) was prepared by mixing gelling agent, sodium dodecyl sulfate (SDS) solution, hydrophobic silica nanoparticles and air in a high speed blender. GDS has the merits of surfactant dry solution (DS) and gel-supported dry water (GDW). The stack of micron-sized GDS droplets provides abundant gas transport channels and large surface area for gas–liquid contacting. Each droplet is a micro system with active surface and gelling structure. Methane storage in clathrate hydrates using GDS was investigated in a stainless steel vessel without stirring under the condition of 5.0 MPa and 273.15 K. The results demonstrated that the dispersed GDS droplets could significantly enhance formation kinetics, storage capacity and storage repeatability of methane hydrate. In addition, GDS exhibited faster storage rate (4.5221 $m^3\, m^{-3}\, min^{-1}$) and higher storage capacity (152.23 $m^3\, m^{-3}$) than GDW. Compared with SDS-DS, GDS has similar storage rate and better storage repeatability (by experiment of 9 cycles), but its storage repeatability slightly became poor and capacity decay occurred due to the agglomeration of droplets after these cycles of hydration/dissociation.

1. Introduction

Clathrate hydrates are crystalline compounds encaging noble gases or short chain hydrocarbons (guest) in hydrogen-bonded water cages (host). The presence of guest molecules can stabilize the host water lattice via weak van der Waals force under the high pressure and low temperature (Sloan and Koh, 2008). As an alternative energy source which is also an economical medium for natural gas storage and transportation, natural gas hydrates have attracted significant attention (Sloan, 2003; Koh and Sloan, 2007; Chong et al., 2016). It was reported that per unit volume hydrate could stably capture about 180 standard volumes natural gas (Sloan

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and Koh, 2008), which is close to the energy density of compressed natural gas (about 200 standard $m^3 m^{-3}$) under 20 MPa. In addition, excellent stability and high storage capacity of hydrates have promoted the development of gas separation (Fan et al., 2009; Liu et al., 2014; Babu et al., 2015), carbon dioxide capture (Linga et al., 2007; Gholinezhad et al. 2011; Babu et al., 2013a, 2013b; Zhong et al., 2015a, 2015b), seawater desalination (Park et al., 2011; Babu et al., 2014), solute purification (Yoon and Lee, 1997), juice concentration (Li et al., 2015) and hydrogen storage (Mao et al., 2002; Struzhkin et al., 2007) in the form of hydrate.

However, these technologies are critically challenged by the slow formation rate and low conversion ratio of gas to solid hydrates which lead to poor storage capacity. As is known, hydrate formation reaction is a physical interfacial phenomenon, and the main problems now are inadequate gas–water contacts and unreacted interstitial water trapped in the hydrate mass, and neither of them favors hydrate formation and growth. Therefore, increasing the area of gas–water phase interface is crucial for efficient hydration.

Mechanical enhancements, such as liquid stirring (Englezos et al., 1987; Hao et al., 2007; Zhong et al., 2015a, 2015b), liquid spaying (Fukumoto et al., 2001; Ohmura et al., 2002; Yamamura et al., 2011), gas bubbling (Maini and Bishnoi, 1981; Luo et al., 2007), were often applied in experimental processes to enhance hydrate formation kinetics. Nevertheless, mechanical perturbation with high energy consumption hindered industrialization of hydrate production. Researchers found that the addition of surfactants into water could achieve the enhancement of hydrate formation without mechanical perturbation (Karaaslan and Parlaktuna, 2000; Zhong and Rogers, 2000; Link et al., 2003; Zhang et al., 2007; Ando et al., 2012; Veluswamy et al., 2015). Indeed, the presence of surfactants increased gas–water contacts by changing the hydrate morphology (Yoslim et al., 2010), but the medium for gas storage remained continuous bulk liquid. Moreover, small grains of sand saturated with water, filled in a fixed bed reactor, was employed for enlarging the gas–water contact area (Linga et al., 2012). Hydrate formation rate and water conversion were both enhanced, but the solid sand occupied quite large space in the fixed bed column, resulting in serious storage capacity “penalty”. Grinding ice powder exposed in the gas provides substantial gas–ice contacts and increases hydrate formation rates (Staykova et al., 2003; Falenty et al., 2013), but the material must be prepared laboriously without melting.

Dry water (DW) droplets with higher specific surface and better stability than ice powder was used as gas storage medium under static situation innovatively (Wang et al., 2008; Carter et al., 2010; Shi et al., 2014). The problem that ice powder melts during preparation and transfer is almost non-existent in the dispersed system, and then the formation rate of gas hydrates is dramatically enhanced. DW can capture more volumes gas than surfactant solution, but the elevated rate of gas uptake is inferior to the rate enhanced by surfactant (Carter et al., 2010). Therefore, when DW was prepared, surfactant solution, instead of water, was used and its dry solution (DS) was produced for gas storage in our previous work (Fan et al., 2014). The surfactant-DS which has the advantages of good dispersion of DW and excellent activity of surfactant solution, exhibited about the same storage capacity as DW while the storage rate remains similar to surfactant solution. However, both DW droplets and surfactant-DS droplets aggregated to larger droplets or even form partial continuous solution after freezing hydration and warming dissociation. The destroyed droplets cannot recover to their original dispersion state. Carter's group utilized a gelling agent to form gel-supported dry water (GDW) to stabilize the DW droplet structure and improve its storage repeatability (Carter et al., 2010). However, the rate of hydrate formation in GDW remains the same as that in DW and less than that in surfactant-DS.

Considering the gas storage advantages of surfactant-DS and GDW, in this work, we attempt to prepare a new dry liquid (gel-supported surfactant dry solution, GDS) using gellan gum, sodium dodecyl sulfate (SDS) solution and hydrophobic silica nanoparticles. Kinetics and repeatability of methane hydrate formation in the GDS were investigated under given pressure and temperature. The work is a significant step towards study on kinetics and repeatable properties of gas hydrates formation in static dispersed systems.

2. Experimental

2.1. Gel-supported surfactant dry solution preparation

The preparation method of dry liquid has been reported (Binks and Murakami, 2006). Hydrophobic silica nanoparticles H18 with particle size range of 7–35 nm was supplied by Wacker Chemie AG. Sodium dodecyl sulfate (SDS) with certified purity of $>99\%$ and gellan gum with particle size range of 5–10 μm were both purchased from Shanghai Huyu Bio-technology Co., Ltd. To prepare GDS, SDS was dissolved in deionized water to form 0.03 wt% SDS solution. After that, poured the solution into a blender (Philips HR2105/90, 1.25 l), and then gellan gum together with silica H18 were also added into it in sequence. Mixed them at a speed of 18,000 rpm for three successive periods with each spanning 20 s under ambient conditions (not more than 313 K). The reason of dividing the total mixing time into three 20 s periods was that after long time mixing, the heat form mixer shaft would make the materials' temperature increase and GDS sample very probably became a paste without the dispersion. Thus, free flowing GDS droplets (or rather like solid particles) supported by gel were produced. Our previous work reported that SDS-DS with 7.5 wt% silica particles had uniform particle size, ample specific surface and the best storage properties (Fan et al., 2014). So we used the same silica content as our previous work in this study. The other components of GDS are SDS solution and gel, and four ratios of solution to gel were designed, as shown in Table 1.

2.2. Methane hydrate formation

In a closed gas–liquid system, information on the formation kinetics and the storage repeatability of gas hydrates can be obtained from the observed pressure-drop behavior during each hydration process. Gas consumption experiments based on pressure–volume–temperature (*P–V–T*) measurements reported in our previous paper (Yang et al., 2011) were conducted in this work. The experimental apparatus is shown schematically in Fig. 1. Before each test, a stainless steel high pressure vessel (50 mm in diameter, 153 mm in height and effective volume of 300 cm^3, Jiangsu Hai'an Petroleum Instrument Co., Ltd.) was washed with deionized water and loaded with 20.00 g GDS (or GDW/SDS-DS/bulk water). Afterwards a vacuum pump (2XZ-2B, Shanghai Yulong Vacuum pump Co., Ltd.) started to evacuate air from the apparatus, and then the vessel was flushed with methane (99.99% purity, Shanghai Weichuang Gas Co., Ltd.) three times to ensure the absence of air. Subsequently, a circulating coolant bath (THD-3015, Zhejiang Ningbo Tianheng Instrument Factory) with a heating/cooling coil was turned on to control the vessel temperature to 273.15 K. The coolant in the bath is 95 vol% alcohol solution. Two thermal resistance detectors (Pt100, ± 0.01 K, 253–473 K, Jiangsu Plaza Premium Electric

Table 1
Mixing ratios of 0.03 wt% SDS solution to silica and gel for preparing GDS.

SDS solution weight (g)	Silica weight (g)	Gel weight (g)	Gel contents (wt%)
43.75	3.75	2.50	5.0
41.25	3.75	5.00	10.0
38.75	3.75	7.50	15.0
36.25	3.75	10.00	20.0