



Enhanced methane hydrate formation with cyclopentane hydrate seeds



Seungjun Baek^a, Yun-Ho Ahn^a, Junshe Zhang^b, Juwon Min^a, Huen Lee^a, Jae W. Lee^{a,*}

^aDepartment of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Daejeon 305-701, Republic of Korea

^bSchool of Chemical Engineering and Technology, Xi'an Jiatong University, Xi'an, Shaanxi 710049, PR China

HIGHLIGHTS

- CP hydrate seeds were introduced to promote CH₄ hydrate formation.
- sl CH₄ hydrate was massively formed from 0.0556 mol% CP and 500 ppm SDS solution.
- In a subcooling of 6.7 K, 160 v/v CH₄ was engaged in 50 min with no induction time.
- 2nd nucleation and growth of sl CH₄ hydrate on the CP hydrate seed were observed.

ARTICLE INFO

Article history:

Received 21 March 2017

Received in revised form 8 May 2017

Accepted 13 May 2017

Keywords:

Methane storage
Methane hydrates
Cyclopentane hydrates
Hydrate seed crystals
Enclathration kinetics

ABSTRACT

This work presents the kinetic promotion effect of slI cyclopentane (CP) hydrate seeds on sl CH₄ hydrate formation in sodium dodecyl sulfate (SDS) solutions. Gas hydrates are one of the promising materials for natural gas storage due to their high volumetric capacity and safety aspect. Generally, a crystal layer of gas hydrate is preferentially created on the surface of an aqueous phase which results in both low hydrate conversion and slow reaction without mechanical agitations. This study introduces CP hydrate seeds at very small quantities to accelerate the nucleation and growth of the CH₄ hydrate with SDS. To choose the appropriate amount of CP in the system for massive sl CH₄ hydrate formation, several hydrate slurries with various amounts of CP were characterized by powder X-ray diffraction and Raman spectroscopy. Additionally, from the visual observations of the hydrate growth behavior, the direction of hydrate crystallization significantly affected the hydrate growth and conversion rate. With the highest degree of subcooling, the volumetric storage efficiency reached 90% of the theoretical values in 50 min with no induction period, and this promotion effect was also confirmed in an expanded reactor system. Thus, slI CP hydrate seeds result in a dramatic improvement in the sl CH₄ hydrate formation rate and high volumetric storage capacity.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Natural gas has better fuel efficiency and emits smaller amounts of carbon dioxide during its combustion than that of other fossil fuels. Thus, the demand of natural gas has steadily grown as a primary energy resource, and it will account for 70–80% of the total fossil fuel consumption until 2040 [1]. At this stage, natural gas storage technologies have been developed to enhance the usability and transferability in various industrial fields. Two established approaches, compressed natural gas (CNG) and liquefied natural gas (LNG) have stringent requirements for the materials or design of storage tank, e.g., CNG storage vessels must withstand pressures up to 20 MPa while LNG requires special

insulated storage tanks in order to maintain a liquid temperature of 113.15 K [2–4].

Recently, many fundamental researches and technologies for natural gas production from the natural gas hydrate (NGH) reservoirs have been extensively investigated over the last two decades. They are usually based on the dissociation of hydrate structures or the replacement of guest species [5–9]. On the contrary, artificially synthesized clathrate hydrate has become a potential candidate as a natural gas storage medium because of its several advantages such as cost-effectiveness, non-explosiveness, and eco-friendliness (based on water) [10,11] and practical strategies have been also investigated to commercialize NGH as natural gas storage and transportation media [12,13]. Clathrate hydrates have three well-known crystal structures of structure I (sl, cubic $Pm-3n$, $6(5^{12}6^2) \cdot 2(5^{12}) \cdot 46H_2O$), structure II (slI, cubic $Fd-3m$, $8(5^{12}6^4) \cdot 16(5^{12}) \cdot 136H_2O$), and structure H (sH,

* Corresponding author.

E-mail address: jaewlee@kaist.ac.kr (J.W. Lee).

hexagonal $P6/mmm$, $1(5^{12}6^8) \cdot 2(4^35^66^3) \cdot 3(5^{12}) \cdot 34H_2O$ [14]. Natural gas can be enclathrated stably in the sII hydrate structure, and its theoretical storage capacity is up to 170 mL/mL [14,15].

However, practical limitations of hydrate-based natural gas storage technologies have been pointed out, especially for the difficult scale-up of the formation process due to slow growth and low conversion rate. The effective mass transfer of guest molecules is continuously reduced because the interface between the aqueous and gas phases is gradually covered by a low permeable hydrate film [15–17]. Thus, many studies have tried to improve the hydrate conversion by applying mechanical agitation (e.g., stirring speed) to maintain the contact of the gas and liquid [18,19]. Due to the Mpemba-like behavior of clathrate hydrate which is based on the cooperative relationship between the covalent bond and the hydrogen bond of host water-framework, starting hydrate formation at the higher initial temperature was also suggested as a new strategy for rapid hydrate formation [20]. However, they require significant energy during the formation of hydrates. Therefore, several chemical additives can be used as a hydrate formation promoter [10,14,16,18,21–24] to implement natural gas storage in the form of clathrate hydrates [24–28].

As one of chemical additives, some sII hydrate self-forming agents can be considered as a kinetic hydrate promoter because of its thermodynamic promotion effect [29–31], and they have been investigated in a non-stirred system [32,33]. One finding suggested that the binary (THF + CH₄) hydrate formation had porous and dendritic crystal growth along the reactor wall. This specific growth behavior avoid the production of hydrate layer at the interface between gas and aqueous phases, thereby it can allow continuous contact of guest and water molecules. For this reason, the morphological change of the hydrate growth induces rapid hydrate formation [24]. Moreover, iodomethane, which is a water-immiscible sII hydrate former and has a higher density than water [23], showed a unique growth behavior of vertical hydrate growth with methane.

Despite sII hydrate formers inducing rapid hydrate formation, the gas storage capacity is also reduced by the occupation of the hydrate promoters in the large cage of the sII hydrate structure. Actually, the theoretical methane storage capacity is 172 v/v in the sI hydrate structure with both small and large cages occupied; however, it is only 115 v/v in the sII hydrate structure with only the small cages occupied [34,35]. To achieve a rapid formation rate without sacrificing the methane storage capacity, it is necessary to dose sII hydrate formers as small as possible.

This work introduces a novel concept of hydrate seeds as a kinetic hydrate promoter; the rapid formation of pure sI CH₄ hydrates induced by tiny amounts of sII cyclopentane (CP) hydrates in the presence of sodium dodecyl sulfate (SDS) in an unstirred reactor. Since the dissociation temperature of the CP hydrate is around 280.15 K at ambient pressure [36–38], CP hydrate seeds can be easily prepared without any pressurization. To optimize the amount of the CP hydrate seeds for the maximum formation of sI CH₄ hydrates, the conversion of sI CH₄ hydrates and sII binary (CP + CH₄) hydrates with different CP amounts was characterized with powder X-ray diffraction (PXRD) and Raman spectroscopy. The hydrate morphology and growth behavior were also investigated at various initial pressures or driving forces, then the hydrate formation kinetics was simultaneously measured. It was demonstrated that a small driving force is enough to achieve instantaneous nucleation and 159 v/v methane storage capacity. CP hydrate-induced rapid methane enclathration provides fundamental insights into hydrate crystallization in terms of “hydrate formation on the top of the seed hydrates” and a high natural gas storage density with NGH techniques.

2. Material and methods

2.1. Materials

Methane (CH₄, with a purity of 99.95%) was supplied by Samo Gas (Republic of Korea). Deionized water was made by Millipore Direct-Q purification system with a resistivity of 18.2 MΩ cm⁻¹. Cyclopentane (CP, with a purity of 98%) and sodium dodecyl sulfate (SDS, with a purity of ≥99%) were purchased from Sigma-Aldrich. Ethanol (CH₃CH₂OH, with a purity of 99.5%) was purchased from Samchun pure chemicals (Republic of Korea).

2.2. Experimental apparatus

Fig. 1 shows a schematic diagram of the experimental set-ups for hydrate crystallization in visualization and expanded volume reactors. A high-pressure reactor equipped with two windows was used for the visual observation (Fig. 1(A)). The total volume was around 44.75 cm³. To obtain the clear images, we confined the hydrate growth region to a 10 cm³ vial and set the focal length of the optical stereoscope adopted with a Nikon DS-Fi1 HD color camera at the surface of the SDS solution in the vial. The reactor was immersed into a transparent acryl bath filled with ethanol, and the temperature of the bath was controlled by a low-temperature bath circulator (RW3-1025, JEIO Tech co., Ltd., Republic of Korea). The temperature was maintained to 274.65 K during the hydrate formation, and the temperature of the reactor was monitored with a digital thermometer (DAIHAN Scientific Co., Ltd., Republic of Korea, ±0.05% accuracy). The amount of SDS solution was quite small (2.5 cm³), and thus, the temperature did not significantly fluctuate by the exothermic hydrate growth. A digital pressure gauge (Additel 681, Additel Corporation, USA, ±0.2% full-scale accuracy) was connected to the top of the visualization reactor, and it measured the pressure every 5 s. The expanded volume experiments used two high-pressure vessels: one was the hydrate formation reactor, and the other was a reservoir with pre-cooling methane gas (Fig. 1(B)). The reason for injecting precooled methane gas was to minimize the temperature fluctuation at the initial stage of hydrate crystallization. Because the volume of the expanded reactor (270 cm³) was larger than that of the visualization experiment reactor, the temperature of the gas phase in the reactor cannot stabilize within a few minutes. The two high-pressure reactors were immersed into a bath, and the temperature of the bath was maintained at 274.65 K. The temperature and pressure of the reactors were simultaneously recorded with an acquisition interval of 5 s using a four-wire Pt-100 Ω probe (±0.05% full-scale accuracy) and a pressure transducer (PMP5073, Druck, United Kingdom, ±0.02% accuracy) during the hydrate formation.

2.3. Experimental procedures

The experiments had two parts: one part was the spectroscopic analyses of the mixed sI CH₄ hydrates and sII binary (CP + CH₄) hydrates with various sII CP hydrate contents in the system, and the other part was the kinetics of the hydrate formation with different driving forces at a specific temperature.

2.3.1. Spectroscopic analyses of mixed hydrates

The experiments in this work were conducted using CP with different concentrations of 0.0556, 0.556, and 2.78 mol%, which are 1%, 10%, and 50% of sII hydrate's stoichiometric amount (5.56 mol %), to prepare mixed hydrate samples from 500 ppm SDS solution. After injecting the CP + SDS solution (20 cm³) to the high-pressure reactor (30 cm³), the reactor was flushed with methane gas in sev-

Download English Version:

<https://daneshyari.com/en/article/4915932>

Download Persian Version:

<https://daneshyari.com/article/4915932>

[Daneshyari.com](https://daneshyari.com)