EFFECT OF POROUS MEDIUM LOADING PROMOTOR AQUEOUS SOLUTION ON GAS HYDRATE FORMATION PROCESS

Xia Zhiming[1, 2, 3, 4], Yan Ran[1, 2, 3, 4], Chen Zhaoyang[1, 2, 3, 4], Li Xiaosen[1, 2, 3, 4,*], Zhang Yu[1, 2, 3, 4], Xu Chungang[1, 2, 3, 4], Cai Jing[1, 2, 3, 4]

[1] Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, P. R. China

[2] Key Laboratory of Gas Hydrate, Chinese Academy of Sciences, Guangzhou 510640, P. R China

[3] Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, P. R China

[4] Guangzhou Center for Gas Hydrate Research, Chinese Academy of Sciences, Guangzhou 510640, P. R China

ABSTRACT

Hydrate-based technologies have been regarded as one of the most promising options for reducing greenhouse effect and obtaining clean energy resource. However, there is an ongoing search for substances which could improve the gas-liquid mass transfer without mechanical consumption and in turn enhance process economics. In this work, nanoporous materials loading the solution of promoter was proposed to promote the formation process of gas hydrate by reducing the barrier of mass and heat transfer. The pressure drop curve and gas uptake for $CO_2/H_2/H_2O$ hydrate formation process were studied through 13X molecular sieve loading TBAB solution, the promotion effect was also compared with the other research. The results shown that 13X molecular sieve can significantly improve the pressure drop rate and gas uptake of $CO_2/H_2/H_2O/TBAB$ hydrate compared with the hydrate formed by agitation.

Keywords: Tetra-n-butylammonium bromide, hydrate, H_2, loading, 13X molecular sieve, separation

Corresponding author. Tel: +86 20 87057037. Fax: +86 20 87057037.
E-mail address: lixs@ms.giec.ac.cn.

1. INTRODUCTION

Over the past decades, several potential hydrate-based technological applications such as natural gas or hydrogen storage and transportation [1, 2], gas separation/capture [3]; carbon dioxide sequestration [4], sea water desalination [5] and cold storage have attracted increasing attention. Particularly, due to the safety elements, hydrate-based gas separation and storage technology has been regarded as one of the most promising options for purifying and storage hydrogen [6, 7].

However, the hydrate formation rate is one of the main obstacles for these potential hydrate-based applications [8]. Once hydrate nucleated successful, the heat and mass transfer for further hydrate growth will be prevent hold back by a thin hydrate film which forms on the water-gas interface [1]. Hence, the previous researchers proposed many methods to increase the contact area and to enhance the formation rate: (1) mechanical methods like stirring, spraying, and bubbling [9]; (2) materials such as fine ice powder [10], dry water [11], and other porous medias; (3) surfactants, such as linear alkyl benzenesulfonate (LABS), sodium dodecyl sulfate (SDS), and cetyltrimethylammonium bromide (CTAB). Apart from these efforts to increase the gas–liquid contact areas, some synergic additives were used as promoters to decrease the induction time and increase the gas hydrate formation rate. However, the promotion mechanisms for these promoters remain unclear [12].

Other than renew gas-liquid contact area, another approach to enhance the hydrate formation process is increasing the gas-liquid contact area. The different

materials employed by previous researchers to enhance the hydrate formation process were shown in Figure 3. Rahmati-Abkenar et al. experimental and theoretical evaluated ethane hydrate nucleation with the help of triangular silver nanoparticles [13]. The results demonstrated that silver nanoparticles declined the hydrate induction time up to 97.5% compared to pure water. The ethane hydrate/solution effective interfacial tension with the help of nanoparticles and hydrate/nanoparticle wetting angle were estimated based on heterogeneous nucleation. Celzard et al. comparatively studied for methane storage with dry and wet active carbons respectively [14, 15]. It was suspected from this study that more methane hydrate could be formed if more water was added. Siangsai et al. investigated the particle size effect of activated carbon on the formation and dissociation process for methane hydrate [16]. Nesterov, A.N. et al. studied the activity of powders of silicon, aluminium, zinc, titanium and magnesium oxides as promoters of natural gas hydrate formation [17]. They found that the gas hydrate nucleation depends on the properties of powder particle surface, in particular on functional groups that are present on the surface. And the particles surface with carbon-containing groups (in particular carbonate) is favor for hydrate formation. Consequently, the modification of the surface of oxide particles could be used to promote the gas hydrate formation process. Cuadrado-Collados et al. [18] found that activated carbons, as excellent host structures, could promote natural gas hydrate by 128% improvement compared to the dry carbon at 10 $^\circ$C and below6 MPa. Similar studies using ultrapure water give rise to a total methane adsorption capacity of 93 wt%, i.e. entropic effects exerted by salt play a significant role on the nucleation and growth process for methane hydrate. These findings open the gate towards the application of activated carbons with a highly developed nanoporous network as host structure for offshore methane storage in marine reservoirs.

In this work, nanoporous materials loading solution was proposed to promote the formation process of gas hydrate by reducing the barrier of mass and heat transfer. The pressure drop curve and gas uptake for $CO_2/H_2/H_2O$ hydrate formation process were studied through 13X molecular sieve loading TBAB solution, the promotion effect was also compared with the other research.

2. EXPERIMENTAL SECTION

2.1 Materials

The CO_2/H_2 (40% /60% mol) gas mixture was purchased from Huate Gas Co., Ltd., Chaina. Tetra-n-butyl ammonium bromide (TBAB) with 99.99 % purity and the 13X molecular sieve were purchased from Aldrich Chemical Co. (The Asia headquarter and warehouse in Shanghai, China). The detail about the 13X molecular sieve was shown in Table 1. The chemicals were used without any further purification. The deionized water with the resistivity of 18.25 mΩ.cm-1 used in the work was produced by a ultra-pure water system supplied by Nanjing Ultrapure Water Technology Co., Ltd., China.

Table 1 The detail properties for the 13X molecular.

Property	Value
Size （mm）	3.0-5.0
specific surface area m^2/g	303.945

2.2 Apparatus

The main part of the experimental apparatus is a cylindrical crystallizer, which has 100 mL inner volume and is immersed in a temperature-controlled water both, it is made of high-pressure stainless steel and can endure the working pressure up to 20 MPa. The temperature is measured by PT100 with ±0.1 K uncertainty. The pressure is measured by MBS3000 with ±0.02 MPa uncertainty. The signals of both temperature and pressure are acquired by a data acquisition system (Keysight, 34970A). The residual gas phase composition is analysed by gas chromatography (GC2002). There is a scanning electron microscope (SEM) (Hitachi, S-4800) is used to take images for the hydrate samples. A schematic diagram of the experimental apparatus is shown in Fig. 1.
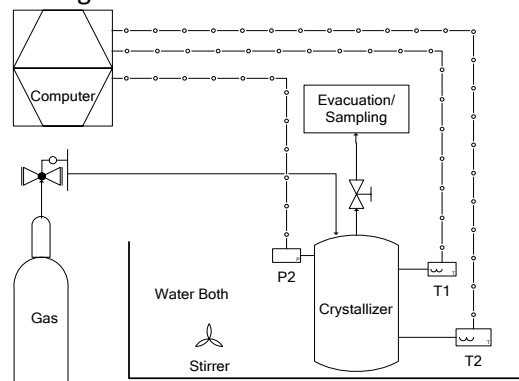

Fig. 1 Schematic diagram of the experimental apparatus.

2.3 Procedure

Briefly, the hydrate crystallizer with 13X molecular sieve loading TBAB solution was vacuumed and then filled with the experimental gas until the desired pressure at the specifically experimental temperature. Once the temperature was stabilized (typically within 1 min), turned on the stirrer in the crystallizer (set this time as the experimental starting time, t0), the experimental temperature and pressure in the system were recorded with time. After hydrate formed completely, the gas phase was sampled and analyzed with GC and the hydrate phase was sampled immediately to take SEM images.

3.   RESULTS AND DISCUSSION

To determine the influence of 13X molecular sieve on the hydrate formation process, the $CO_2/H_2/H_2O$ hydrate formation process with only TBAB solution and with 13X molecular sieve loading TBAB solution is studied respectively. As the pressure drop rate and the final drop shown in Fig. 2, compared with TBAB solution, 13X molecular sieve loading TBAB solution could obviously promote the $CO_2/H_2/H_2O$ hydrate formation process. Furthermore, the gas uptake for $CO_2/H_2/H_2O$ hydrate formation process with 13X molecular sieve loading TBAB solution is compared with that with only TBAB at different conditions. As Fig.3 shown, the gas uptake for $CO_2/H_2/H_2O$ hydrate formation process with 13X molecular sieve loading 0.29 mol% TBAB solution at 6MPa is 18.75 mmol/mol H_2O, but that is only 10.4 mmol/mol H_2O for 0.30 mol% TBAB solution at 6MPa and 5.8 mmol/mol H_2O for 0.29 mol% TBAB solution. It means that the 13X molecular sieve could obviously enhance the gas uptake for the $CO_2/H_2/H_2O$ hydrate formation process.

Moreover, the influence of TBAB concentration on the synergic effect of 13X molecular sieve loading TBAB solution was also studied. The gas uptakes for $CO_2/H_2/H_2O$ hydrate with 13X molecular sieve loading different TBAB solution are compared in Fig. 4. As Fig. 4 shown, the synergic effect of 13X molecular sieve loading TBAB solution on the gas uptake increase with the TBAB concentration below 1.00 mol%; then that decrease with increasing of the TBAB concentration.

It is very interesting that the 13X molecular sieve loading TBAB solution has the exciting effect on the hydrate formation process. It may be profit from that the 13X molecular could promote the mass and heat transformation process. However, the detail mass transfer mechanism for the CO_2/H_2 hydrate formation

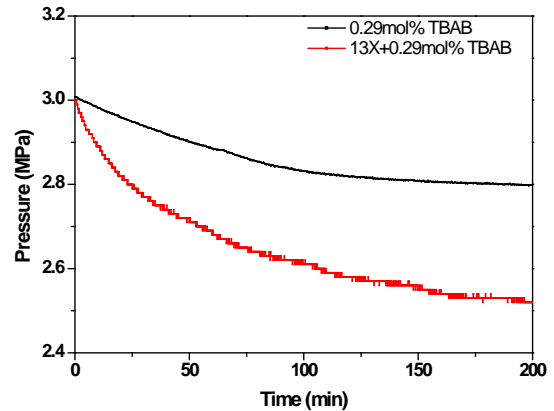process with 13X molecular sieve loading TBAB solution should be insighted with the help of SEM, CTtechnology.

Fig. 2 The pressure drop curves for $CO_2/H_2/H_2O$ hydrate formation process with TBAB solution and 13X molecular sieve loading TBAB solution.
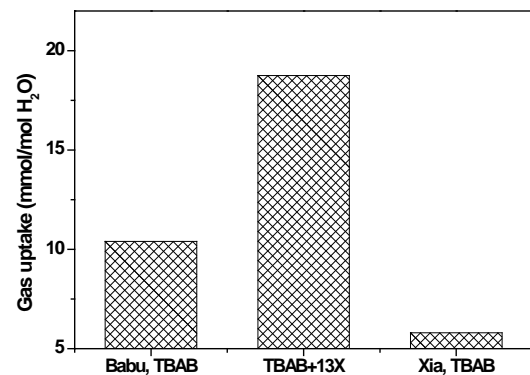

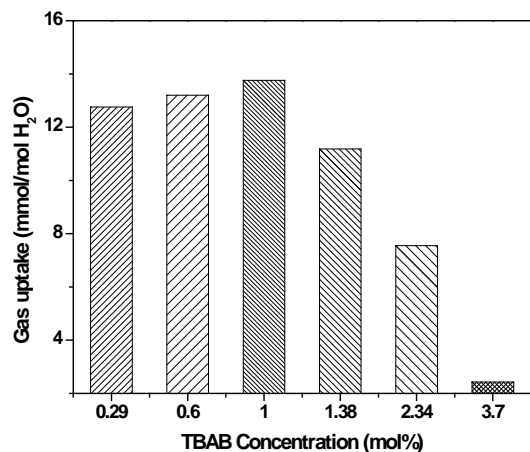**Fig. 3** Comparison of gas uptake for $CO_2/H_2/H_2O$/TBAB hydrate formation process with and without 13X molecular sieve.

Fig. 4 Comparison of the gas uptake for $CO_2/H_2/H_2O$ hydrate with 13X molecular sieve loading different TBAB solution.

4.   CONCLUSIONS

In this work, nanoporous materials loading solution was proposed to promote gas hydrate formation process by reducing the barrier of mass and heat

transfer. The pressure drop curve and gas uptake for $CO_2/H_2/H_2O$ hydrate formation process were studied through 13X molecular sieve loading TBAB solution, the promotion effect was also compared with the other research. The results shown that 13X molecular sieve can significantly improve the pressure drop rate and gas uptake of $CO_2/H_2/H_2O$/TBAB hydrate compared with the hydrate formed by agitation, which means that the nanoporous materials would decrease the energy penalty for the hydrate formation process. Furthermore, TBAB concentration has influence on the synergic effect of 13X molecular sieve loading TBAB solution for the $CO_2/H_2/H_2O$ hydrate formation process.

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