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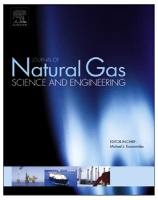

Effects of particle and pore sizes on the formation behaviors of methane hydrate in porous silica gels

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ABSTRACT

The formation behaviors of methane hydrate in porous media with different particle and pore sizes were studied in a closed system in the temperature range of 267.15–278.15 K. The silica gels were applied as the porous media for the experiments, in which the diameter ranges of the silica gel particles are 0.105–0.150 mm, 0.150–0.200 mm and 0.300–0.450 mm, respectively, and the mean pore diameters are 9.03 nm, 12.95 nm, 17.96 nm and 33.20 nm, respectively. The formation processes of methane hydrate show different behaviors in porous silica gels with different particle sizes. For the particle diameter range of 0.300–0.450 mm, three formation periods were observed for the experiments with the high driving force. For the particle diameter ranges of 0.105–0.150 mm and 0.150–0.200 mm, there is no remarkable discrete formation period, the hydrate durations of different experiments are basically same at the bath temperature above the freezing point and decrease with the increase of the temperature at the bath temperature below the freezing point. The formation rate of methane hydrate increases with the decrease of the particle size and the increase of the pore size. The final gas consumption increases with the increase of the mean pore diameter but is slightly affected by the particle size.

1. Introduction

Naturally gas hydrates have been known to be widely distributed in earth and attracted much attention as been recognized a potential energy resource (Makogon et al., 1971). The hydrate mainly exists in porous media, e.g., the sub-surface deposits in permafrost region and the offshore sediments in ocean (Kvenvolden, 1993, 1999; Milkov et al., 2004; Makogon et al., 2007). In addition, due to the large amounts of gas in small volumes (as much as 170 times the capacity of gas at standard temperature and pressure conditions), hydrate formation in the bulk and porous media also has been extensively studied for the application of the hydrate formation, such as gas storage and transport, sequestering carbon dioxide in the ocean, mixed gas separation, and seawater desalination, etc (Seo et al., 2005; Babu et al., 2013a, 2013b, 2014). The hydrate formation behaviors in porous media are the important for the reliable assessment of the feasibility of producing natural gas from the earth's gas hydrate reservoir and the application of the hydrate formation method. In order to understand formation morphologies and kinetics in porous media, many researchers have investigated hydrate formation behaviors in porous media. Distinct stages of formation for hydrate growth in porous media were observed (Katsuki et al., 2007; Fitzgerald et al., 2014; Zhang et al., 2014; Zhao et al., 2015).

A commercially viable application based on hydrate usually demands a rapid hydrate formation rate. Many porous materials have been proposed including dry water, hollow silica, nano silica powders and gels to enhance the hydrate formation rate and gas storage. Kono et al. (2002) studied the kinetics of methane hydrate formation within glass beads with different diameter and synthetic ceramic. They found that the sediment property will influence the reaction rate constant of hydrate formation. Liu et al. (2008) carried out the Raman spectroscopic observations of the formation and dissociation of methane hydrate in silica sands with different particle size. They considered that the particle size has no influence on hydrate composition. Linga et al. (2009a) studied the potential dependency of the kinetics of hydrate formation on the size of the silica sand bed. They concluded that the dependency of the results

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on the size of the bed should be taken in to account when modeling the rate of hydrate formation in a porous bed. Bagherzadeh et al. (2011) investigated the formation of methane hydrate in an unconsolidated bed of silica sand with different particle size and different initial water saturations using the magnetic resonance imaging technique. They observed that hydrate formation in such porous media is not uniform, and nucleation of hydrate crystals occurs at different times and different positions inside the bed. The formation was also found to be faster in a bed with lower water content and smaller particle size. Linga et al. (2012) found that the rate of hydrate formation in fixed bed column is significantly greater and thereby resulted in a higher percent of water conversion to hydrate in lesser reaction time. Kumar et al. (2015) reported the experimental data on the kinetics of methane hydrate formation in porous media with the different ratios of the silica sand and clay, and the different water saturations. They concluded that the presence of the clay reduces the hydrate formation kinetics significantly, and lower water saturation shows higher water to hydrate conversion rate in a pure sand bed as well as in a sand-clay mixture. Kang et al. (2009) studied the kinetics of methane and carbon dioxide hydrate formation in silica gel pores. They found that the rates of hydrate formation are closely related to the driving force. It was also noticed that the rate of hydrate formation is not dependent upon the pore size of the silica gel. Babu et al. (2013a) employed the hydrate based gas separation process with silica sand and silica gel to capture CO_2 from fuel gas mixture. They found that water conversion of up to 13% in silica gel bed is only achieved. Kumar et al. (2013) investigated the effect of silica gels of varying particle size and three different surfactants on CO_2 gas hydrate formation. They found that the presence of silica gel with higher surface area has positive effect on the rate of hydrate formation and water to hydrate conversion.

In this report, the hydrate formation behaviors in silica gels with different particle sizes and different pore sizes were experimentally investigated. The experiments were carried out in the bath temperature range of 267.15–278.15 K and the initial formation pressure range of 4.1–11.1 MPa. The objective of this work is to study the effects of pore size and particle size of the porous media on the formation kinetic behaviors of methane hydrate both above the freezing-point and below the freezing point.

2. Experimental section

Deionized water and methane gas with the purity of 99.9% from Fushan Hao Wen Gas Co. were used in the experiments. Silica gels were supplied by Qingdao Makall Group Inc. Table 1 gives the properties of all the silica gels. The normalized pore size distributions were computed using the Barrett-Joyner-Halenda (BJH) method and applied to the desorption branch of the nitrogen isotherm.

2.1. Apparatus

The details of the experimental apparatus have been reported in our previous work (Li and Zhang, 2011). The schematic drawing of the experimental apparatus is given in Fig. 1. The crystallizer has a maximum effective volume of 416 cm^3 and its cell is volume-variable with a movable piston. There is a Pt1000 thermoprobe (JM6081) with the uncertainty of ±0.05 K placed in the center of the crystallizer to monitor the sample temperature. The supply vessel is used to inject the gas into the crystallizer and has a volume of 1091 cm^3. The pressures in the crystallizer and the supply vessel are measured by the pressure transducers with a range of 0–25 MPa and the uncertainty of ±0.02 MPa. The crystallizer and the supply vessel are immersed in the water bath with a accuracy of ±0.1 K. A data acquisition system coupled with a computer is used to record the signals of the pressure and temperature.

2.2. Experimental procedure

The dried silica gels were mixed with the same amount of water to the pore volume of the gels. The gels was then spun at 3500 rpm for 5 min in a centrifuge to completely fill the pores with water (Adeyemo et al., 2010). In order to ensure the same gas-water ratio in the experiments with different silica gels, the water weight and the volume of the gas in the CR is same for different experiments by adjusting the effective volume through the piston in the CR. In the CR, the weight of water is 148 g and the gas volume is 208.4 ml for different experiments.

A known quantity of prepared silica gels was firstly loaded into the reactor cell. Then the cell was installed and purged with methane 4–5 times to remove the remaining air. The reactor was cooled to the desired value by adjusting the water bath. Once the temperature of the system was stabilized, methane gas was charged into the reactor cell to the given desired formation pressure. The pressure and temperature were recorded when the pressure reached the experimental value. The gas will be consumed and the pressure in the reactor will gradually decrease. When there is no significant change of the pressure in the reactor, the hydrate process was ended and the hydrate was decomposed by depressurization.

The moles of methane consumed in the experiments were calculated using the equation given by Li et al. (2008) from the measured pressure and temperature data. The water conversion was calculated by the gas consumption by assuming the hydration number to be 6.10 (Linga et al., 2009b).

3. Results and discussions

In this work, the silica gels with different particle size and pore size were applied as the porous media for the experiments. The experimental data are given in Table 2 and Figs. 2–8. In Table 2, P_0 is the initial pressure of the system, T_f is the bath temperature for the hydrate formation, and n_e is the total moles of the gas consumption at the end of the hydrate formation.

Table 1
Silica gel properties.

Silica gel type	Pore diameter/nm	Particle size distribution/mm	Pore volume/$ml^3\ g^{-1}$	Surface area/$m^2\ g^{-1}$
#1	9.03	0.105–0.150	0.86	496.5
#2	12.95	0.105–0.150 0.150–0.200 0.300–0.450	1.07	442.9
#3	17.96	0.105–0.150	1.19	359.8
#4	33.2	0.105–0.150	1.32	217.4

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