



Experimental and modeling study on controlling factor of methane hydrate formation in silica gels



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HIGHLIGHTS

- Formation experiments of methane hydrate in silica gels at constant pressure were performed.
- Kinetic models for hydrate formation under the reaction and gas diffusion controlled were built.
- The formation rate is gas diffusion limited in 129.5 Å and 179.6 Å silica gels.
- The formation rate is controlled by the reaction process in 332 Å silica gels.

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ABSTRACT

In order to study the mechanism of methane hydrate formation in porous media, the formation experiments of methane hydrate in porous media at the constant pressure were performed in the temperature range of 274.15–276.15 K and the pressure range of 5–8 MPa. The silica gels with the average pore diameters of 129.5, 179.6, and 332 Å were used as the porous media for the experiments. The experimental results indicate that the final gas consumption increases with the increase of the formation pressure and the decrease of the formation temperature. Based on the shrinking core model, the reaction-controlled kinetic model and the diffusion-controlled kinetic model for hydrate formation in silica gels were built, respectively. The reaction-controlled kinetic model well fits the kinetic data in 129.5 Å and 179.6 Å silica gels, and the diffusion-controlled model well fits the kinetic data in 332 Å silica gels with a relatively high regression coefficient ($R^2 > 0.99$). The formation rate of the methane hydrate is controlled by the gas diffusion process in 129.5 Å and 179.6 Å silica gels, and is controlled by the reaction process in 332 Å silica gels.

1. Introduction

Natural gas hydrate is expected to be a potential energy resource due to its enormous global volume distributed in sediment reservoirs. Natural gas hydrate has a great capacity of gas storage since there are as much as 170 m³ gas at standard temperature and pressure in 1 m³ hydrate [1–3]. In recent years, there is a renewed attractive interest in gas hydrate phenomenon for many industrial applications, such as natural gas storage and transportation, sequestering carbon dioxide, and mixed gas separation [4–7].

There are still many issues to be addressed for the application of the gas hydrate method. One of the main drawbacks is the low hydrate formation rate that would increase the production cost of this technology in an industrial scale [8,9]. One effective way to increase the

hydrate formation rate is to use additives, which have been tested widely and their accelerating effects have been reported in the literature [10–12]. In another proposed way, this limitation can be overcome through the incorporation of a solid surface. In the specific case of porous material containing cavities or holes, the hydrate forming gas and water molecules sorbed in porous media can well contact, thus speeding-up the growth kinetics. Experimentation with different types of porous media, such as activated carbon, carbon nanotubes, and silica gel, revealed that the hydrate formation in porous media is affected by the effect of the particle size [13,14], pore size, sediment surface, and water saturation, etc. [15–19].

Gas molecules can easily penetrate a bed of silica gel particles saturated with water compared to a bulk water phase, and the dispersed water presents a huge surface for contact between water and gas

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molecules in silica gel pores. Based on the experimental and theoretical investigations into the equilibrium conditions of gas hydrate in porous media, it has been found that the hydrates in porous media require the higher formation pressure and lower formation temperature than that in bulk due to the capillary effect of the porous media, which leads to the increase of energy cost during the hydrate formation [13,14,20,21]. However, higher gas consumption rate can be obtained for hydrate formation in porous media, which is an important advantage for the hydrate application technique because it does not need mechanical agitation. Seo et al. [22] presented remarkable results for rapid CO₂ hydrate formation in porous silica gels. Kang et al. [23] studied the precombustion capture of CO₂ from a simulated flue gas through CO₂ hydrate formation in silica gels. A higher formation rate of CO₂ hydrate was observed and silica gels are considered to be a promising material for CO₂ capture. Kang et al. [24] carried the kinetics studies on methane and CO₂ hydrate formation in silica gels. They found that the rates of hydrate formation are closely related to the driving force. It was also noticed that the hydrate formation rate is not dependent upon the pore size of the silica gels. Zhang et al. [25] experimentally investigated the hydrate formation behaviors in silica gels with different particle sizes and different pore sizes. The formation rate of methane hydrate increases with the decrease of the particle size and the increase of the pore size. These results show that the porous media can assist the hydrate formation. However, there are still many critical problems for the development of the commercial technology of the hydrate formation applications, including the low formation rate and water conversion, and the overall economics of process scale up [26].

The fundamental understanding of the hydrate formation in silica gel pores is still in its infancy. The mechanism study would be of enormous help to understand the formation behavior of hydrate in pores of porous media and find the way to enhance the gas storage capacity in porous media using the hydrate method. To apply this principle, silica gels with three pore sizes, 129.5, 179.6, and 332 Å were chose to form methane hydrate within the pores. The particle sizes for different silica gels are 0.105–0.150 mm. The formation experiments of methane hydrate in silica gels were performed at the constant pressure. Based on the shrinking core model, the reaction-controlled kinetic model and the diffusion-controlled kinetic model of the hydrate formation in silica gels were built, respectively. The formation mechanism of the methane hydrate in silica gels with different pore sizes was analyzed and the controlling factors were determined.

2. Experimental section

2.1. Experimental apparatus

The core apparatus consists a high-pressure hydrate crystallizer (CR) and a supply vessel (SV) [27]. As shown in Fig. 1, the CR and SV are immersed in the water bath supplied by Xutemp Temptch Co., Ltd. The effective volume of the CR and SV is 416 cm³ and 1091 cm³, respectively. The pressure in the CR is regulated by a control valve supplied by Tescom with the uncertainty of ± 0.02 MPa. The pressure transmitters supplied by trafag Inc. with the span 0–25,000 KPa (± 0.1%) are used to measure the pressure inside the CR and SV. The temperature inside the CR and the water bath is measured using Pt1000 thermoprobes (JM6081) with the uncertainty of ± 0.05 K.

2.2. Materials

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. The average pore sizes of silica gels used in the experiments are 129.5, 179.6, and 332 Å, respectively. Fig. 2 gives the normalized pore size distributions of the silica gels, which was computed using the Barrett-Joyner-Halenda (BJH) method and applied to the desorption branch of the nitrogen isotherm. The

particle sizes for different silica gels were 0.105–0.150 mm. In the experiments, the same volume of water as the pore volume of the silica gels was mixed with the silica gels to obtain the water saturated samples. To ensure the same quantity of the water confined in the silica gels used in the experiments, the quantities of different kinds of silica gels were calculated by its pore volume. The quantities of the silica gels with the average pore diameters of 129.5, 179.6, and 332 Å used in the experiments are 138.3 g, 124.4 g and 112.1 g, respectively. The quantity of water confined in the silica gels is 148 g for different experiments.

2.3. Experimental procedure

The deionized water was added and mixed with the dried silica gels sufficiently to obtain water saturated samples. The prepared silica gel sample was then loaded into the CR. The apparatus was installed and purged with methane gas 4–5 times to remove the remaining air. Subsequently, the temperature of the water bath was set to the desired formation temperature of the experiment. When the temperature inside the CR was stabilized, methane gas was charged into the CR from the SV until the pressure reached the desired value. During the hydrate formation, the pressure in CR kept constant through the gas injection from SV. When the pressure in SV maintained constant more than 3 h, the hydrate formation was assumed to be completed and the hydrate was decomposed to begin a new experiment.

The amount of methane gas consumed at time t was calculated by:

$$n = \left(\frac{P_0}{Z_0} - \frac{P_t}{Z_t} \right) \times \frac{V}{RT} \quad (1)$$

where P_0 and P_t are the initial pressure and the pressure at time t in the supply vessel, respectively; T is the temperature in the supply vessel, which is constant and equal to the hydrate formation temperature during the experiments; the compressibility factors Z_0 and Z_t are calculated using the SRK equation [27]; V is the effective volume of the supply vessel.

3. Modeling of hydrate formation kinetics

Recently, the shrinking core model was used to study the kinetic of methane hydrate formed from ice particles [28], and the modeling results are in good agreement with the experimental data. In this work, the hydrate formation reaction is also considered as a shrinking-core process in porous media. The following assumptions are given:

- (1) During the hydrate formation, the hydrates are homogeneously distributed in the pores of the silica gels.
- (2) All the particles of the silica gels are spherical with the same diameter and are homogeneous. Thus, the characteristics of one single particle can represent all the particles of the silica gels.
- (3) The temperature in the CR is constant during the hydrate formation, and the temperature at different positions in the CR is same.

Fig. 3 gives the sketch of the shrinking-core model for the hydrate formation in one silica gel particle. It is assumed that the unreacted core gradually shrinks and the gas reacts with water at the unreacted core surface as the reaction (hydrate formation) progresses.

Based on above assumptions, when the hydrate formation is reaction-controlled, the hydrate formation rate in silica gels is formulated as:

$$r_e = \frac{dn}{dt} = S_{H,RC} k (f_s - f_E) \quad (2)$$

where r_e is the reaction rate of methane; n is the moles of methane formed; t is the reaction time, $S_{H,RC}$ is the area which the hydrate holds on the surface of the unreacted core, the radius of the unreacted core is R_C ; k is the formation constant, f_s is the fugacity of the methane gas at the formation pressure; f_E is the fugacity of the methane gas at the

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