

PHASE EQUILIBRIA AND FORMATION KINETICS OF CARBON DIOXIDE, METHANE, AND NATURAL GAS IN SILICA GEL PORES

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ABSTRACT

Hydrate phase equilibria for the CO₂, CH₄ and natural gas in silica gel pores of nominal pore diameters 6, 30 and 100 nm were measured, and compared with the calculated results based on van der Waals and Platteeuw model. At a specific temperature, three-phase hydrate–water-rich liquid–vapor (HLV) equilibrium curves for pore hydrates were shifted to the higher pressure condition depending on pore sizes when compared with those of bulk hydrates. The activities of water in porous silica gels were modified to account for capillary effect, and the calculated results were in good agreement with the experimental data. To investigate the formation kinetics of each system, the isobaric method was applied. It was found that there were no difference in structure between hydrate in silica gel pore and that in bulk free state. Results showed that hydrate formation in the silica gel pores indicated significantly faster rates, intensively reduced induction times, increased gas consumption and conversion of water to hydrate as compared to hydrate formation in bulk free water or fine ice powder. Utilizing these superior characteristics, formation of hydrate in porous material is expected to present the process on gas separation or storage.

Keywords: gas hydrates, carbon dioxide, methane, natural gas, equilibrium, formation, kinetics

NOMENCLATURE

F	the shape factor of the hydrate-water interfacial curvature
r	the pore radius [m]
T_0	the nominal melting point of water [K]
$\Delta\mu_w^0$	the difference in the chemical potential between an empty hydrate and water [J/mol]
Δh_w^{fus}	the molar difference in enthalpy between ice and the liquid water [J/mol]
Δv_w^{fus}	the molar difference in volume between ice and the liquid water [m ³ /mol]
v_L	the molar volume of pure water [m ³ /mol]
θ	the wetting angle between the water and the hydrate phase [degree]
σ_{HW}	the interfacial tension between the hydrate and the water phase [J/m ²]

INTRODUCTION

Many researchers have taken interest in gas hydrates because of its promising characteristics, for example, self-preservation effect, capacity of gas storage in solid state, fluidity in slurry, spontaneous dissociation at suitable condition, large enthalpy change in phase transition, and so on [1]. Therefore, industrial applications using gas hydrates have been tried, and some of them are believed to success commercial process. Although potential applications are tried and examine, they still have some critical problems associated with hydrate formation, including slow formation rate, unreacted interstitial water as a large percentage of the hydrate mass, and the overall economics of process scale-up. Accordingly, a new and more efficient hydrate production method should be developed to overcome such problems, and a

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better understand of hydrate formation kinetics is required. Compared to thermodynamics of hydrate phase equilibria, study in hydrate formation kinetics is still in progress to understand. Although an increasing number of works on hydrate formation kinetics appeared, most of them are concerned with phenomenological and morphological aspects, focusing on modeling, simulation, and nucleation and growth of crystals. Relatively smaller amount of works than those of thermodynamic equilibrium have been dedicated to invent the enhanced method for hydrate formation rate and gas consumption amount.

One effective way for the increase of the hydrate formation rate and the reduction of power consumption in the hydrate formation process is to use additives. Surfactants such as SDS (sodium dodecyl sulphate) have been tested for methane and natural gas hydrate formation, and their accelerating effects have been reported in the literature [2]. In this report, the authors focus on employing gas hydrates in porous media as a gas storage method or reaction bed for gas separation. Porous materials such as silica gels have large internal volumes that enable them to bear water molecules inside, which can then be used for hydrate formation. Seo et al. [3] presented remarkable results for rapid CO₂ hydrate formation in porous silica gels. Their results showed that confined water does not hinder gas transfer into silica pores, which is a typical phenomenon in bulk hydrates; thus gas molecules can easily contact and diffuse into pores through a layer of bound water and assist the formation of hydrates in pores.

In this report, the three-phase HLV equilibria of CH₄, CO₂ and natural gas hydrates in porous silica gels were measured in order to identify the formation behaviors of the guest in porous media. In addition, the formation kinetics of CO₂ and CH₄ hydrates in silica gel pores were also investigated.

EXPERIMENT

The spherical silica gels (SG) with nominal pore diameters of 6, 30 and 100 nm were selected and purchased from Aldrich (6 nm) and Silicycle (30 and 100 nm) were used as the porous materials. All materials were used without further treatment. The properties of the silica gels with 6 and 30 nm pore diameters were measured by nitrogen adsorption/desorption experiments with ASAP 2400 (Micrometrics), and those with a 100 nm

pore diameter were measured by mercury intrusion, as listed in Table 1.

Sample Name	6 nm SG	30 nm SG	100 nm SG
mean particle diameter (μm)	150 to 250	40 to 75	40 to 75
mean pore diameter (nm)	5.51	30.1	94.5
specific pore volume (m ³ /kg)	8.4×10 ⁻⁴	8.4×10 ⁻⁴	8.3×10 ⁻⁴
specific surface area (m ² /kg)	586×10 ³	94.9×10 ³	42.4×10 ³

Table 1. Physical properties of silica gel samples

Composition	Ratios (%)
CH ₄	89.8562
C ₂ H ₆	6.400
C ₃ H ₈	2.710
<i>iso</i> -C ₄ H ₁₀	0.482
<i>n</i> -C ₄ H ₁₀	0.491
C ₅ H ₁₂	0.0205
N ₂	0.0403
Total	100.0

Table 2. Composition ratio of natural gas

The silica gels used in the experiment were first dried at 373 K for 24 hours before water sorption. Then, the pore saturated silica gels were prepared by placing the dried silica gels in a desiccator containing degassed water, evacuating the desiccator, and allowing more than three days to establish the solid-vapor equilibrium.

A schematic diagram of the experimental apparatus is shown in Figure 1. It consists of a semi-batch reactor with a temperature control system, a gas booster to supply hydrate forming gas to the reactor in an enough pressure, a mass flow controller to measure the flow rate of gas, and the accompanying data acquisition system. The hydrate formation reactor had an internal volume of about 475 cm³. After about 300 cm³ of silica gel containing pore water was charged, and the reactor was cooled down to the specified experimental temperature. When the temperature of the reactor was stabilized, vacuum pump connected to the reactor was used to remove the accompanying air inside. Then, the sufficiently pressurized hydrate forming gas in reservoir was charged to the reactor by a pressure 0.2 MPa lower than the equilibrium pressure. At this time the data

acquisition program started to read temperature, pressure, and gas flow rate at every second. Once the temperature and pressure in the reactor had stabilized, the pressure in the reactor was pressurized to a specified experimental pressure. As the gas in the reactor was consumed due to hydrate formation, the mass flow controller automatically opened to supply additional gas from the gas reservoir, and thus, maintain isobaric conditions. Dissolved amount of the hydrate forming gas by the solubility was measured by test runs, and was excluded from the accumulated amount of gas consumption.

When the mass flow controller was bypassed to ignore the isobaric measurement, the system could be adapted to measure the equilibrium conditions. Detailed measurement skill in distributed porous materials can be found in the literature [4].

To identify the crystalline structure of the gas hydrates formed in the silica gel pores and to compare them with those of the bulk state hydrate, a Bruker 400 MHz solid-state NMR spectrometer was used. In addition, the hydrate samples were characterized using a field emission scanning electron microscopy (FE-SEM, Hitach S-4700).

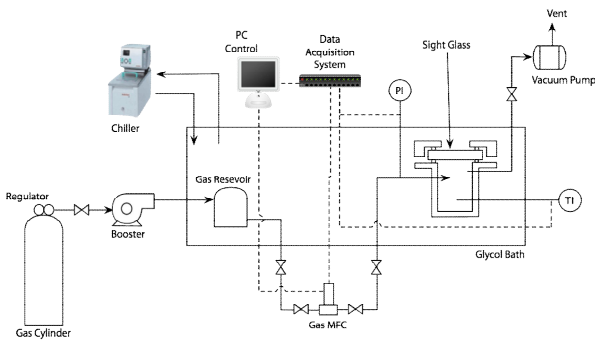


Figure 1. Schematic diagram of the experimental apparatus

RESULTS AND DISCUSSION

The phase equilibrium of hydrates in pores is clearly different from that in the bulk water to consider the pore size distribution, which requires more sophisticated method. In order to obtain accurate equilibrium points, the step heating method was used in this study. Anderson et al. [5] proved the superior accuracy and repeatability of the hydrate dissociation point determined by the step heating method when compared with continuous heating. For porous media with pore size distributions, the dissociation curve is typically obtained in a specific S shape, and the

slope inflection points at the mean diameter is taken for the equilibrium points corresponding to the nominal pore size, which is derived using the pore size distribution.

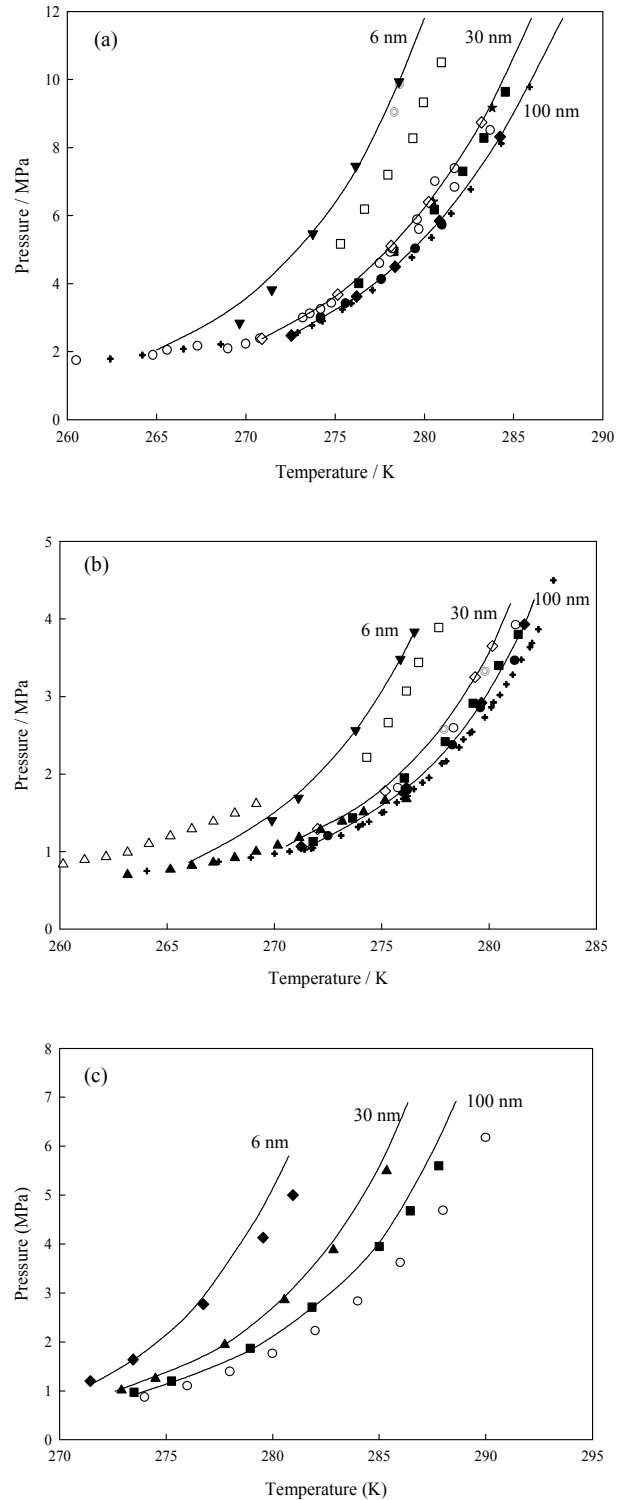


Figure 2. Hydrate phase equilibria in silica gel pores (a) CH₄, (b) CO₂, (c) natural gas

Figure 2 show the three-phase HLV equilibria of CH₄, CO₂, and natural gas in silica gel pores with nominal pore diameters of 6, 30, and 100 nm and the modeling prediction curves. As it can be clearly seen in the figure, the obtained results show good agreement with the values for silica gels with nominal diameters of 30 and 100 nm presented in other literature [6-10]. However, the phase equilibrium data moved into inhibited regions (where the thermodynamic stability is reduced to a lower temperature or a higher pressure at any given pressure or temperature, respectively) more often than those presented in the literature.

The dissociation equilibria obtained in this study show good agreement with the modeled prediction curve over a wide temperature range, as presented in the figures. The van der Waals-Platteeuw equation is used to model the phase equilibria of gas hydrates in bulk conditions, which is expressed as:

$$\frac{\Delta\mu_w^o}{RT_o} - \int_{T_o}^T \frac{\Delta h_w^{MT-I} + \Delta h_w^{fus}}{RT^2} dT + \int_0^P \frac{\Delta v_w^{MT-I} + \Delta v_w^{fus}}{RT} dP + \sum_m v_m \ln \left(1 - \sum_j \theta_{mj} \right) - \ln(\gamma_w x_w) = 0 \quad (1)$$

However, for the porous media, the high curvature of the solid-liquid interface contributes to the equilibrium pressure increase for the solid phase, which leads to the inhibition shift with respect to the bulk condition. Therefore, the last term in the van der Waals-Platteeuw equation can be modified as follows when considering the capillary effect attributed to the geometrical constraints within silica gel pres:

$$\ln a_w^{pore} = \ln(\gamma_w x_w) - \frac{F v_L \sigma_{HW}}{rRT} \cos \theta \quad (2)$$

Figure 3 shows the ¹³C NMR spectra of the CH₄ hydrates formed in the silica gel and the bulk condition at 200 K. As shown in the figure, the NMR spectra of CH₄ hydrates in silica gel show the same pattern as that of the CH₄ hydrate in the bulk state regardless of the pore size, which is the

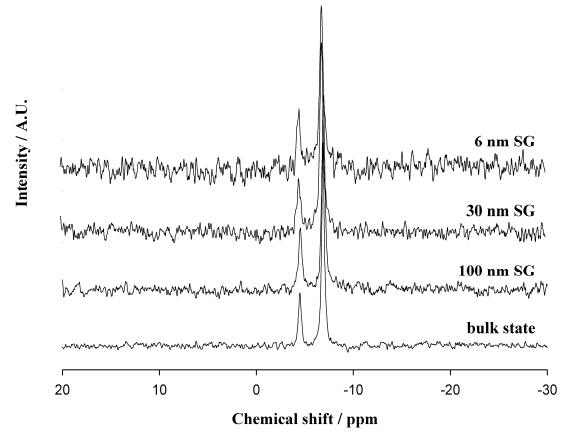


Figure 3. ¹³C NMR spectra of CH₄ hydrates in silica gel pores and bulk state at 200 K.

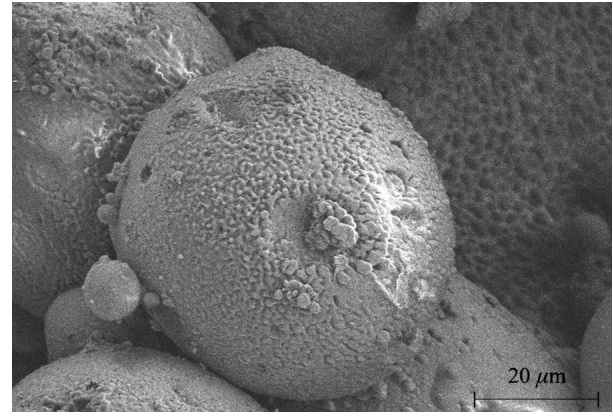


Figure 4. Low-temperature FE-SEM image for CH₄ hydrates formed in porous silica gels at 163 K.

clear evidence that the hydrate structure does not change even in pores, so that the prediction method and parameter values obtained from bulk water phase can be applied for pore hydrate system with suitable geometric modification.

Figure 4 shows the low-temperature SEM image for the CH₄ hydrate formed in the porous silica gels obtained at 163 K. It can be seen in this figure that the hydrate formation primarily occurs in silica gel pores and that the hydrates formed are protruded by volume expansion due to solidification. With this spectroscopic evidence, it can be concluded that hydrate formation occurs within the silica gel pores and that the structure formed is the same as that in the bulk state regardless of pore size.

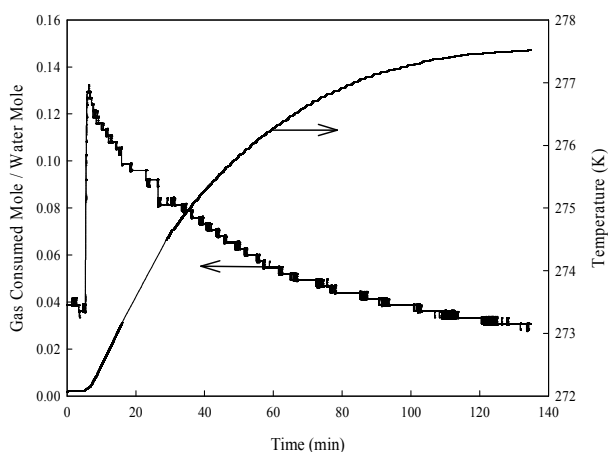


Figure 5. Rate of CH₄ consumption for hydrate formation in the 100 nm silica gels at 273.15 K and 6.0 MPa.

Figure 5 shows the typical pattern graph of the gas uptake curve during hydrate formation, as well as the temperature profile. As the system pressure is set to the specified experiment pressure, molecules of hydrate forming gas are consumed to form hydrate, thus mass flow controller is open to maintain the pressure as the set value. Consumption of the gas molecules are continued until a degree of conversion yield is obtained, and then the rate of gas consumption is nearly close to zero so that the accumulated curve vs. time becomes flat at a constant value. In particular, Figure 5 shows an explicit induction time where nucleation or turbidity point is named, however according to repeated experiments in many cases of temperature and pressure, the induction time does not appear. At the nucleation point, a temperature increase is noticed. This change is due to the exothermal process for gas hydrate formation, which is released in the crystallization process. Conventional mechanical stirring type reactor not only renews the interface between water and gas phase, but also disperse the released heat to draw through the jacket of the reactor. Gas hydrate formation in porous silica gel bed is originally impossible to make particles mixed, because there is no mixing effect on the bed as its property, so that an improvement to achieve the released heat removal should be invented. Fluidized bed type reactor can be considered as a candidate for heat removal with solid particles.

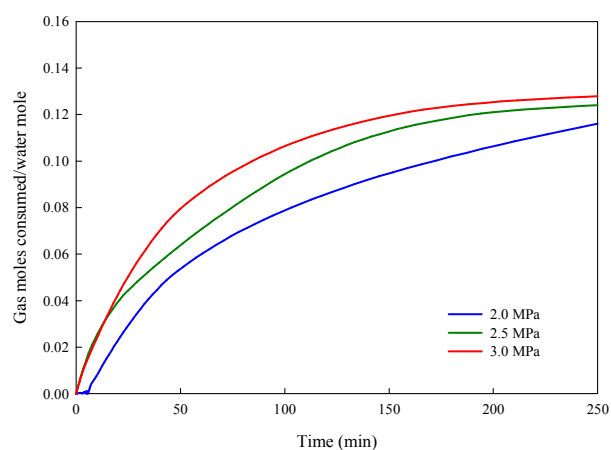


Figure 6. Formation kinetic curves of CO₂ hydrate at pressures of 2.0, 2.5, and 3.0 MPa and at temperature 274.15 K in the 30 nm silica gels.

The formation kinetic experimental results of CO₂ hydrates in the silica gel pores are presented in Figure 6. All the experimental curves in Figure 6 represent that the hydrate formation begins as the gas molecules are supplied at the set pressure, that is, there are no induction time. Of course some induction time within 15 minutes appeared during over 50 times of experiments with CO₂, CH₄, and natural gas. As the pressure increases, the hydrate formation rate also increases as expected, because of the increase of the driving force for hydrate formation. Recent reports on the kinetics of hydrate formation from fine ice powders, similar to this solid particle system, showed 50~70% conversion of ice to hydrate normally in 15~20 hours [11]. In the present work, we produced hydrate in 80~90% yield within 3 hours for CO₂, and within 1 hour for CH₄ and natural gas. This rapid formation kinetics of pore hydrates can be affirmatively applied to the hydrate process requiring high speed of hydrate formation.

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