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Kinetic behaviors of CO_2 hydrates in porous media and effect of kinetic promoter on the formation kinetics

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ABSTRACT

Formation behaviors of CO_2 hydrate in silica gels are investigated at various pressure and temperature conditions. In addition, a kinetic promoter of sodium dodecyl sulfate (SDS) is used in order to evaluate promotional effect on the formation behaviors in porous media. Formation rates and hydrate conversions are found to be large when higher pressure or lower temperature is used at a given temperature or at a given pressure, respectively. The formation rates are found to be affected more significantly when driving force larger than 1.0 MPa is applied. In addition, when the kinetic promoter is used, initial hydrate formation rates are found to increase so as to reach the final gas consumption more rapidly. Obtained results are expected to provide useful information for designing or evaluating a hydrate-based process using porous media.

1. Introduction

Crystal structures that are formed by enclathration of guest molecules into 3-dimensional lattice framework of host molecules are referred to as inclusion compounds (Atwood et al., 1984). Among a variety of inclusion compounds, in particular, ones in which water molecules act as the host are called gas hydrates. So far, various gas species as well as liquid organic substances have been reported to form gas hydrates (Sloan, 1998; Sloan and Koh, 2008). In the early stages, gas hydrates were regarded as hazardous materials because they could cause plugging problems in natural gas pipelines (Jamaluddin et al., 1991). Such hydrates are being investigated in order to use them for various applications such as energy storage or transportation because a large amount of gas can be stored in the form of a solid gas hydrate. Among various application areas, using methane and carbon dioxide as guest species is the most popular. For methane, since a huge amount of natural gas was known to occur naturally and exist in the form of the gas hydrate, many investigations have been made to utilize the natural gas hydrate as a future energy source (Lee and Holder, 2001). In addition to the natural gas hydrates, studies on synthesizing methane hydrate are being performed for the purpose of utilizing such hydrates as energy storage/transportation mediums. Since Gudmundsson reported the feasibility of the technique; a lot of research works have been performed by many researchers in order to compete the conventional techniques (Gudmundsson and Borrehaug, 1996; Khokhar et al., 1998). In case of carbon dioxide, growing attention is paid in order to use the synthesized gas hydrate for sequestrating greenhouse gas in deep oceans or under sea floors (Masutani et al., 1993; Spencer and North, 1997). Initially, stability region or physical properties of bulk CO_2 hydrates were major concerns (Song and Kobayashi, 1989; Udachin et al., 2001). In addition, in order to overcome economic disadvantages, a simultaneous process of CO_2 injection and CH_4 exploitation from the natural gas hydrate was suggested. Recently, Kang and Lee (2000) suggested that synthesized CO_2 hydrate can be also used to separate CO_2 from flue gas before sequestrating CO_2 in deep oceans.

However, formation kinetics in addition to phase equilibria are also critical in order to make any hydrate-based process more viable. In this respect, Seo et al. (2005) reported that formation rates of the gas hydrate can be faster in porous silica gels than the bulk phase. Other researchers published experimental results of three phase equilibria and modeling calculations of gas hydrates in porous media (Kang et al., 2008; Seo et al., 2002). As reported by Anderson et al. (2003), Kang et al. (2008), although gas hydrates can be formed faster in porous silica gels even without any mechanical agitation, hydrate formation in such porous media largely depends on contacts of gas molecules with water molecules in pores, which represents an inhibition effect of the phase equilibria in porous media (requiring more energy to form the hydrate phase). In addition, some researchers addressed the effect of surfactants (or kinetic promoters) on formation/dissociation rates and storage

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capacity of gas hydrates. Ganji et al. (2007a, 2007b) published research on the effect of some surfactants on the formation/dissociation behavior and storage capacity of gas hydrates at various surfactant concentrations. Zhang and Lee (2009a, 2009b) investigated formation kinetics using CO_2 hydrates under static conditions to identify kinetic promotion effect. Recently, Watanabe et al. reported that a critical factor affecting the hydrate-forming behavior is not the critical micelle concentration (CMC) of the surfactant, but the solubility. They provided experimental works supporting the argument by using sodium dodecyl sulfate (SDS) and HFC-32 (Okutani et al., 2007; Watanabe et al., 2005).

Although many studies on the phase equilibria and modeling of the gas hydrate in porous media have been performed, formation kinetics in porous media, even in porous media with kinetic surfactants, has not been sufficiently investigated so far. Therefore, in this report, formation kinetics of CO_2 hydrates in porous silica gels were investigated in a variety of temperature and pressure conditions. In addition, one of the kinetic promoters, SDS, was used in order to observe the effect of the promoter on the formation kinetics in the porous media. Obtained results can be used as helpful data in hydrate-based CO_2 sequestration or CO_2 separation processes. Furthermore, the results can provide useful information on kinetic behaviors and formation rate in porous media for establishing a CH_4/CO_2 replacement in natural porous media, such as clay minerals.

2. Experimental methods

CO_2 gas and SDS, supplied by Rigas (Korea) and Sigma-Aldrich Co., with stated minimum purity of 99.9 mol% and 99%, respectively, were used to form hydrate samples with deionized water, produced by a Millipore purifier, for this study. As the porous material, spherical silica gel of nominal pore diameter 100 nm was purchased from Silicycle. All the materials were used without further purification. The physical properties of silica gels were measured by mercury intrusion, with results found in our previous work (Kang et al., 2008).

A high-pressure reactor, made of 316 stainless steel with a sight glass for visual observation, was used for measuring formation kinetics of the CO_2 hydrates. Internal volume of the high-pressure reactor was 350 cm^3. Before the sorption of aqueous SDS solution and charging of the reactor, about 250 cm^3 of silica gels were allowed to be dried at 373.0 K for 24 h. Then, the dried silica gels were inserted into a bottle and mixed with 200 cm^3 of SDS solution. During this procedure, the mixing bottle was sonicated to promote sorption of aqueous solution into silica gel pores. The total amount of sorbed solution in the silica gel pores was compared with measured mass of silica gels before and after saturation and was found to be almost identical with the nominal pore volume (volume ratio=0.83) of silica gels. After charging the high-pressure reactor with the SDS-saturated silica gels, the reactor was cooled to desired experimental temperatures and time was allowed to pass for the temperature to be stabilized. The internal temperature of the reactor was measured by K-type thermocouple with an accuracy of ±0.1 K. Next, the sufficiently pressurized CO_2 gas in the reservoir was introduced to the reactor up to desired experimental conditions. During the hydrate formation, an external circulator and an ISCO pump were used, respectively, in order to keep the temperature constant and compensate for the pressure drop due to hydrate formation. The data acquisition system was used to record the temperature (by K-type digital thermometer), pressure (by a digital pressure transducer whose span and resolution were 0–10.0 MPa and ±0.1% of the full scale), and gas flow rate (by digital thermal mass flow controller, 5850E, Brooks Instrument LLC), which can produce an output signal linear to the mass flow rate, ranging from 0 to 200 l/min with an accuracy of ±1% of the full scale along with time throughout the experiments at an interval of 10 min.

3. Results and discussion

For the purpose of applying CO_2 hydrates to separation and sequestration, many researchers have reported fundamental phase equilibria for CO_2 hydrates at various conditions. As reported in some of the literature, the three-phase equilibria of CO_2 hydrates in bulk state are moved to the inhibited region (requiring higher pressure at a given temperature or lower temperature at a given pressure in order to stabilize the CO_2 hydrate phase) when porous media are used to form CO_2 hydrates. Moreover, the inhibition effect is found to be more significant as average pore size of the porous media decreases. Such inhibition can be explained by the decreased activity of water in the saturated pores. Therefore, when porous media are used for hydrate-based processes, it can be expected that higher cost and energy will be required to keep the whole process than would be necessary using a bulk hydrate-phase. If faster formation of CO_2 hydrate can be achieved by using porous media, it may provide great advantages for whole practical hydrate-based process, even though there exists the disadvantage of T–P condition for formation.

Fig. 1 and Table 1 show formation kinetics of CO_2 hydrates in 100 nm porous silica gels at various pressures for a given

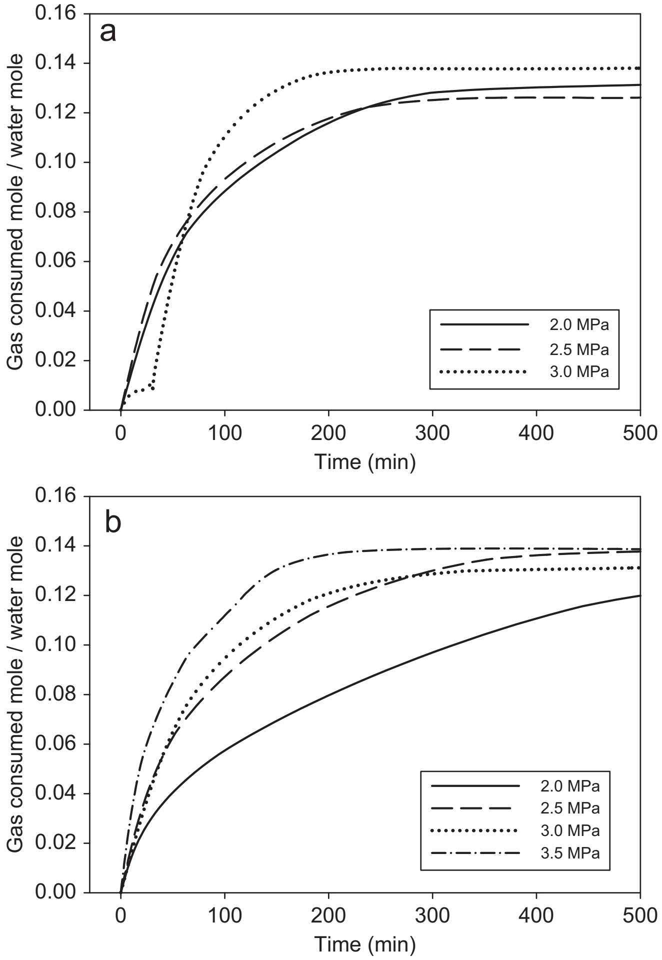

Fig. 1. Formation kinetics of the binary CO_2+water mixtures in silica gels at various pressure conditions: (a) formation temperature of 273.2 K; (b) formation temperature of 275.2 K.