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Hydrate-based pre-combustion capture of carbon dioxide in the presence of a thermodynamic promoter and porous silica gels

Sungwon Park[a], Seungmin Lee[b], Youngjun Lee[a], Yohan Lee[a], Yongwon Seo[a,*]

[a] School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology, Ulsan 689-798, Republic of Korea
[b] Green Technology Center, Korea Institute of Industrial Technology, Ulsan 681-802, Republic of Korea

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ABSTRACT

In this study, the feasibility of the hydrate-based pre-combustion capture of carbon dioxide in the presence of a thermodynamic promoter and porous silica gels was examined through stability condition measurements, gas uptake measurements, and microscopic analyses. When a fuel gas mixture of H_2 (60%) and CO_2 (40%) was used for gas hydrate formation, the addition of tetrahydrofuran (THF) yielded significantly enhanced hydrate stability conditions. Silica gels with a nominal diameter of 100.0 nm demonstrated increased gas consumption during gas hydrate formation, indicating higher conversion of water into gas hydrate. With only one step of hydrate formation, CO_2 concentrations of higher than 90% were achieved in the hydrate phase for all cases. It can be concluded that the hydrate phase composition is affected primarily by the cage occupancies of guest gases in the hydrate lattices whereas the vapor phase composition is strongly influenced by the conversion of water to gas hydrate and also partially by the cage occupancy of CO_2 in the hydrate phase. From powder X-ray diffraction (PXRD) patterns and Raman spectra, it was confirmed that the H_2 (60%) + CO_2 (40%) gas mixture forms structure I hydrate and the inclusion of THF induces the formation of structure II hydrate.

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1. Introduction

Gas hydrates are non-stoichiometric crystalline compounds formed when "guest" molecules of suitable size and shape are incorporated into the well-defined cages in the "host" lattice made up of hydrogen-bonded water molecules (Sloan and Koh, 2008). These compounds exist in three distinct structures, structure I (sI), structure II (sII) and structure H (sH), which contain differently sized and shaped cages (Sloan and Koh, 2008). Gas hydrates have been of great concern in the fields of energy and environment. In particular, recently, many examples of the use of gas hydrates as a means of separation and recovery of global warming gases, such carbon dioxide (CO_2) and sulfur hexafluoride (SF_6), have been reported (Kang and Lee, 2001; Seo et al., 2004, 2005; Linga et al., 2007; Kumar et al., 2009; Seo and Kang, 2010; Cha et al., 2010; Adeyemo et al., 2010; Lee et al., 2010a,b; Li et al., 2011; Eslamimanesh et al., 2012). Among various global warming gases, CO_2 emitted from the fossil-fueled power plants has been regarded as a major contributor to global warming. In response to this problem, integrated gasification combined cycles (IGCCs) have become attractive, as they are advanced power plants that emit less CO_2 and capture CO_2 efficiently (Hendriks et al., 1991; Josh and Lee, 1996). IGCC plants convert fossil fuels into a fuel gas mixture of H_2 and CO_2 via gasification and shift reaction (Hendriks et al., 1991; Josh and Lee, 1996). CO_2 can then be captured for sequestration and the resultant H_2 could be used in fuel cells or in gas turbines. CO_2 and H_2 are known to form gas hydrates, but under substantially different conditions. CO_2 forms sI hydrate at mild conditions, e.g., 1.2 MPa at 273 K, while H_2 forms sII hydrate at extremely high pressure, e.g., 200 MPa bar at 273 K (Sloan and Koh, 2008). Therefore, one of the most promising options to capture CO_2 from the fuel gas mixture is the hydrate-based method because CO_2, whose hydrate equilibrium condition is remarkably milder than H_2, is expected to be enriched in the hydrate phase, resulting in the high selectivity of CO_2 in the hydrate phase. Because CO_2 is removed before the fuel is burned, this type CO_2 capture is called pre-combustion capture.

The hydrate-based separation and recovery process is based on the selective partition of the target component between the hydrate and vapor phases. However, a main drawback of the hydrate-based process is that it requires high pressure for gas hydrate formation. However, the fuel gas mixture from the gasifier and shift reactor of IGCC plants is available at a pressure between 2.5 and 5.0 MPa (Hendriks et al., 1991; Josh and Lee, 1996), which indicates that additional pressurization might not be needed for gas hydrate formation especially at low temperature regions. Nonetheless, the stabilization of hydrate formation conditions should be achieved for the hydrate-based process to outperform conventional CO_2 capture methods. Extensive efforts have been made to

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* Corresponding author. Tel.: +82 52 217 2821; fax: +82 52 217 2819.
E-mail address: ywseo@unist.ac.kr (Y. Seo).

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stabilize hydrate formation conditions. Many researchers have reported that adding a small amount of water-soluble organic compounds called thermodynamic hydrate promoters, such as tetrahydrofuran (THF), acetone, and 1,4-dioxane, can significantly reduce the hydrate equilibrium pressures at a given temperature or raise the hydrate equilibrium temperatures at a given pressure (Jager et al., 1999; Seo et al., 2001; Kim et al., 2006; Hashimoto et al., 2006; Seo et al., 2008, 2009a,b). On the other hand, in order to substantially improve the gas/water contact and enhance the conversion of water to hydrate, water can be dispersed in the pores of silica gels with very high surface area per unit volume, and then, hydrates can be formed within the pores (Uchida et al., 2002; Anderson et al., 2003; Seo et al., 2005, 2009a,b; Adeyemo et al., 2010; Lee et al., 2010a,b; Lee and Seo, 2010). An additional benefit of using dispersed water in porous silica gels rather than bulk water for gas hydrate formation is that there is no need for power consumption caused by stirring the bulk water phase.

In order to design and operate the hydrate-based CO_2 capture process in the presence of thermodynamic promoters and porous silica gels, complex phase behavior and kinetic information as well as the structural characteristics of the gas hydrates formed from the fuel gas mixture (H_2 (60%) + CO_2 (40%)) should be thoroughly investigated. However, no systematic and comprehensive approaches on the feasibility of the hydrate-based CO_2 capture process from the fuel gas mixture using thermodynamic promoters and porous silica gels appear in the literature, even though several studies have separately covered equilibrium measurements, kinetic behavior, and structure identification (Hashimoto et al., 2006; Linga et al., 2007; Adeyemo et al., 2010; Seo and Kang, 2010; Kim et al., 2011; Li et al., 2011, 2012). In the present study, we examined the thermodynamic, kinetic, and microscopic aspects of the hydrate-based CO_2 capture process from the fuel gas mixture in the presence of THF and porous silica gels. First, the hydrate phase equilibria for the quaternary H_2 (60%) + CO_2 (40%) + THF + water mixtures at three different concentrations of THF (1.0, 5.6, and 10.0 mol%) and for the ternary H_2 (60%) + CO_2 (40%) + water mixtures in silica gel pores of nominal diameters of 6.0, 15.0, 30.0, and 100.0 nm were experimentally measured to determine the hydrate stability regions of the mixed gas hydrates at each condition. Second, the CO_2 concentrations of both the hydrate phase and vapor phase after hydrate formation were measured to examine the selective partition of the target gas. Third, the gas uptake and the vapor phase composition change during gas hydrate formation were also measured to confirm the amount of gas enclathrated, the formation pattern, and the time needed to complete the reaction. Furthermore, the structure transition of the mixed gas hydrates due to the inclusion of THF was confirmed via powder X-ray diffraction (PXRD) and Raman spectroscopy.

2. Experimental

2.1. Phase equilibrium measurements

The gas mixture of H_2 (60%) + CO_2 (40%) used for this study was supplied by PSG Gas Co. (Republic of Korea). THF with a purity of 99.9% was purchased from Sigma–Aldrich (USA). Silica gels of nominal pore diameters of 6.0 and 15.0 nm were purchased from Aldrich Co. (USA). Silica gels of nominal pore diameters of 30.0 and 100.0 nm were purchased from Silicycle Co. (Canada). Double distilled deionized water was used. All materials were used without further purification. To prepare the pore-saturated silica gels, which means that water exists only within pores, the silica gels were first dried at 393 K for 24 h before water sorption. Some amount of dried silica gel powder was placed in a bottle and an amount of water identical to the pore volume of silica gel was added to the powder. After mixing, the bottle was sealed off with a cap to prevent water evaporation. Then, the bottle was vibrated with an ultrasonic wave at 293.15 K for 24 h to completely fill the pores with water. The properties and pore size distributions of the porous silica gels used in this study were given in the previous papers (Seo et al., 2002, 2009a,b; Lee et al., 2010a,b; Lee and Seo, 2010).

The experimental apparatus for the hydrate phase equilibria was specifically designed to measure the hydrate dissociation pressures and temperatures accurately. The equilibrium cell was made of 316 stainless steel and had an internal volume of approximately 250 cm^3. Two sapphire windows at the front and back of the cell allowed visual observation of the phase transitions that occurred inside the equilibrium cell. The cell content was vigorously agitated using an impeller-type stirrer. The experimental

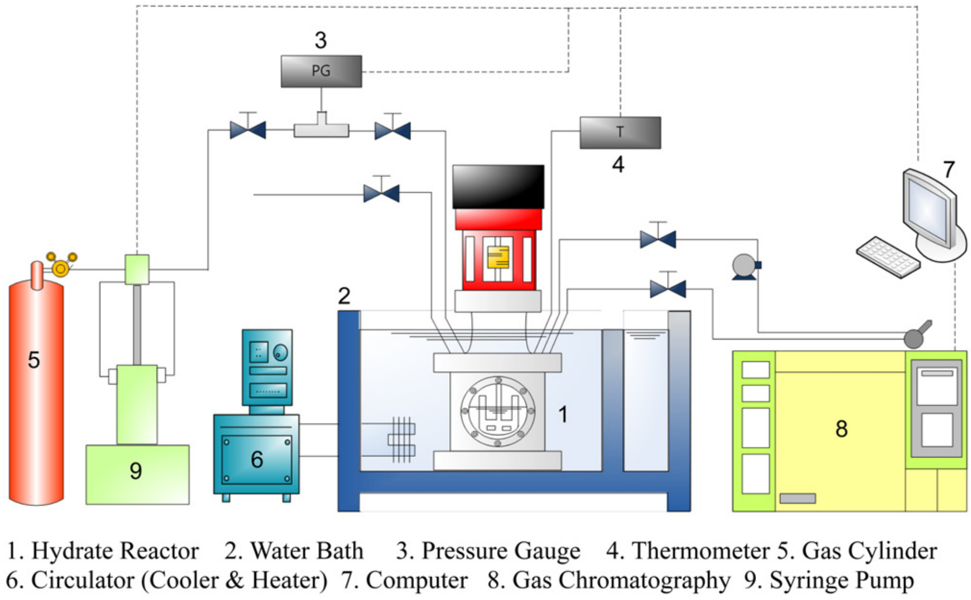

Fig. 1. The schematic diagram of experimental apparatus.

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