Gas Hydrate Process for Recovery of CO_2 from Fuel Gas

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Thermodynamic measurements were performed to show that it is possible to recover CO_2 from fuel gas (the mixture of CO_2 and H_2) by forming gas hydrates that removes CO_2 using water dispersed in the pores of silica gel particles. Hydrate phase equilibria for the ternary CO_2–H_2–water-in-pores were measured. In addition, the direct measurement of CO_2 content in hydrate phase shows that the obtained gas from the dissociation of hydrate contains more than 95 mol.% of CO_2. Compared with data obtained in case of bulk water hydrates, which shows just 70 mol.% of CO_2, the hydrate formation in porous silica gel enhances the feasibility of CO_2 separation process. Hydrate formation in porous solid particle makes it possible to use fixed bed or fluidized bed reactor, which can be advantageous due to the application of well-understood technologies in the industrial field.

1. Introduction

H_2 has attracted much attention as a clean energy source for future. Fuel cell is the representative example for the utilization of H_2. Ultimately H_2 should be obtained from the renewable energy source, for example solar or wind power and so on, because of its symbolic position of environmentally cleanness. It is general for producing H_2 from the conventional fossil fuel (coal gasification or methane reforming) up to now, and even expected until near future. Preparation of synthesis gas (mixture of CO, CO_2, and H_2) is the first step to H_2 production. The water-gas-shift (WGS) reaction is generally applied to the obtained synthesis gas for producing much amount of H_2 by supplying steam. The reaction brings out the mixture of CO_2 and H_2, which is generally called a fuel gas. The pressure swing adsorption (PSA) has been often used as one of the H_2 separation methods for fuel gas, however, further works are needed to improve efficiency and reduce operation cost of CO_2 capture process. CO_2 should be removed because of its global warming effect, and its capture and sequestrating cost decide the economical efficiency of the whole process emitting gas mixtures containing CO_2.

Gas hydrates are non-stoichiometric crystalline compounds formed when guest molecules of suitable size and shape are encaged into well defined host cages made up of hydrogen-bonded water molecules (Sloan and Koh, 2007). This compound exists in

three kinds of distinct structural families named as structure I, II and H. A huge amount of investigations covering phase equilibria and structure identification for pure and mixed hydrates have been accumulated in a variety of sources (Sloan and Koh, 2007; Carroll, 2003; Makogon, 1997). Based on phase equilibrium data showing distinctly divided concentration into coexisting phases, a novel gas separation method using gas hydrates has been suggested to capture CO_2 from flue gas consisting of CO_2 and N_2 (Kang and Lee, 2000; Seo *et al.*, 2005). Another novel CO_2 capture technology based on gas hydrates is the recovery of CO_2 from fuel gas, which contains about 40 mol.% of CO_2 and balanced H_2. Phase equilibria for CO_2–H_2–water system containing gas hydrates have been measured by some researchers (Sugahara *et al.*, 2005; Hashimoto *et al.*, 2006; Kumar *et al.*, 2006; Linga *et al.*, 2007a, b, c).

In the present study, phase equilibria for the ternary CO_2–H_2–water system in silica gel pores containing gas hydrates have been measured in a temperature range of 272–283 K and a pressure range up to 10 MPa. Gas hydrate formation in silica gel pores has been known that an inhibition effect is derived due to the capillary effect, but pores can supply a large amount of contact area between water and gas molecules in a short time, thus increases the rate of hydrate formation and enhances the conversion rate of water to hydrate compared with those of bulk water.

2. Experiment

Gas mixture composed of 40 mol.% CO_2 and 60 mol.% H_2 for the present study was supplied by Rigas Co. (Korea) and deionized water from a Millipore purifier was used. Spherical silica gel particles with nominal pore diameter of 100 nm were selected and purchased from Grace Davidson (USA) as the porous materials. All materials were used without further treatment. Properties of the silica gel particles were measured by mercury intrusion method with Autopore VI9500 (Micrometrics, USA), as listed in Table 1.

Table 1 Physical properties of silica gel sample

sample name	100 nm SG
Mean particle diameter (μm)	(40~75)
Mean pore diameter (nm)	94.5 (100)
Specific pore volume (m³/kg)	0.83×10^{-3} (0.8)
Specific surface area (m²/kg)	42.4×10^{3} (50)

Values in parentheses are data supplied by vendor.

Detailed description on an experimental setup and procedure can be found at the author's previous work (Kang *et al.*, 2008). Moreover, the composition of gas and hydrate phase was measured by gas chromatograph (Agilent 6890). Gas phase was directly sampled and analyzed, and the composition of the hydrate phase was measured by dissociating the existing sample in the reactor. A sudden depressurization to atmospheric pressure made dissociation of the hydrate, and then the measurement of the obtained gas in the cell provided the composition of the hydrate phase.

3. Results and Discussion

Although the shifted syngas (fuel gas) contains small amount of CH_4, O_2, H_2S and other trace gases, the fuel gas can be treated as a binary mixture of 40 mol.% CO_2 and 60 mol.% H_2. It is well known that CO_2 forms gas hydrates as a single guest, but H_2 is encaged into the lattice of gas hydrates under extremely high pressure condition. Kim and Lee (2005) reported that H_2 can be incorporated into cages of the gas hydrates with CO_2 by ^{13}CP and H^1 NAS NMR experiment. Based on that fact, the three-phase (hydrate–water-rich liquid–vapor, HLV) equilibria for ternary CO_2–H_2–water mixtures in silica gel pores of 100 nm diameter were measured to provide the hydrate formation and dissociation conditions, which can be used as the operating conditions for CO_2 separation process through gas hydrate formation. The results showed and suggested that the existence in pore raises the equilibrium pressure at a specific temperature because of the capillary effect in pores. Figure 1 shows the results of HLV equilibrium conditions along the variable CO_2 concentrations, and the increase of CO_2 concentration in the fuel gas decreases the corresponding equilibrium pressure at a specific temperature. It is worthy of bearing in mind that the degree of inhibition by pores should be as small as possible, because larger degree of inhibition requires lower temperature and higher pressure conditions to utilize gas hydrate formation for gas separation process. Even silica gels having small pore diameters supply higher surface areas and pore volumes in general, those of larger pore diameters show adjacent HLV equilibrium data to those of bulk water hydrate.
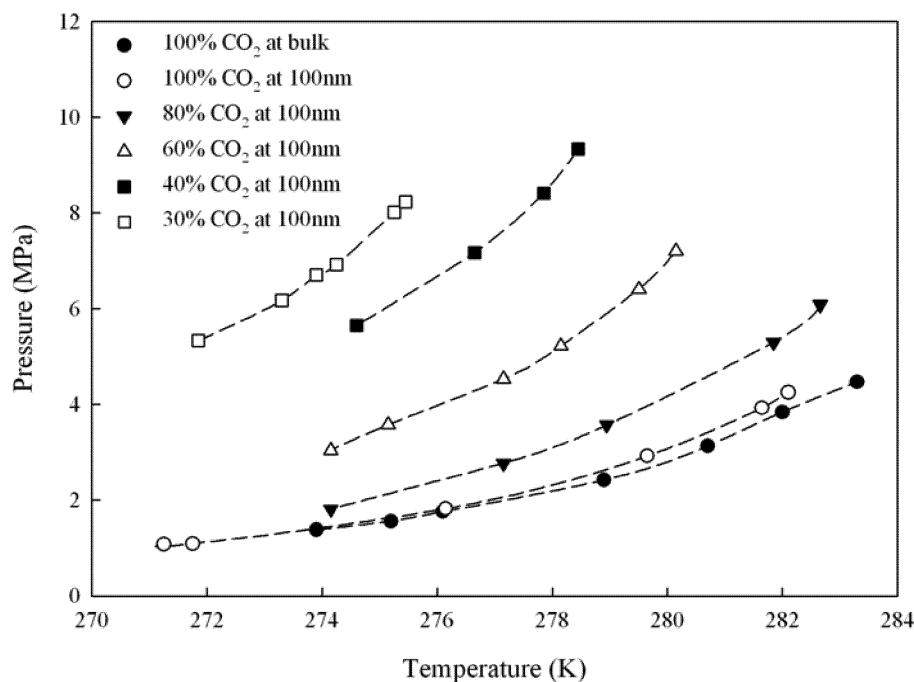

Figure 1. Hydrate phase equilibria for ternary CO_2–H_2–water mixtures with different CO_2 concentration in 100 nm silica gel pores.
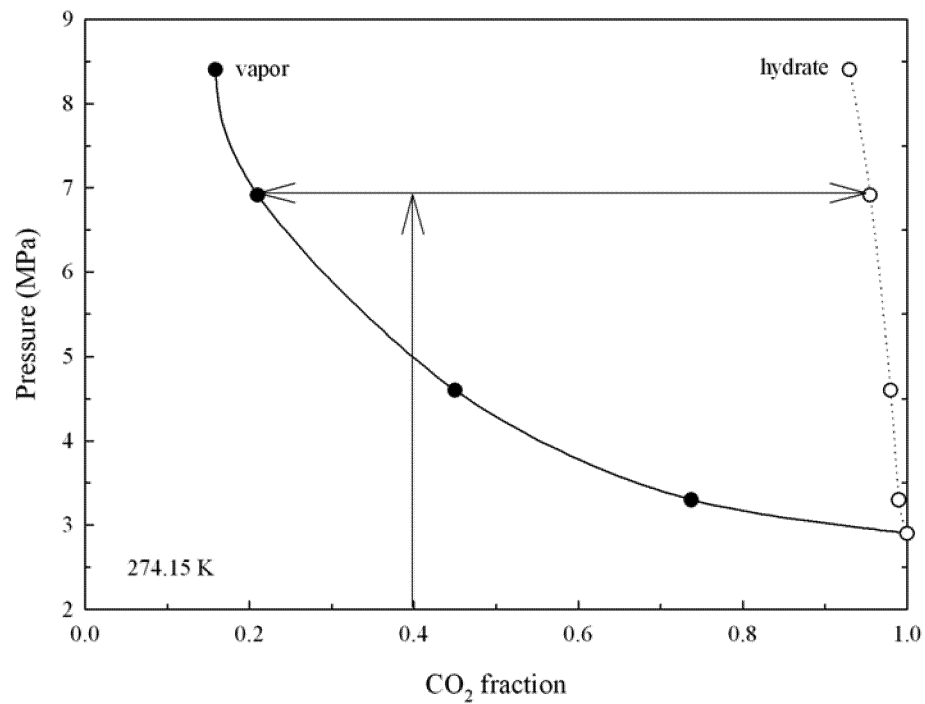
Figure 2. Pressure-concentration diagram of the ternary CO_2–H_2–water system measured at 274.15 K and 6.85 MPa. Arrows indicates how the feed gas is distributed.

Based on the measurement of the equilibrium conditions, we tried to investigate the component fraction to coexisting phases by preparing distribution diagram. At a specific temperature, pressure difference from equilibrium condition is recognized as a driving force. As the driving force increases, the density of correspond hydrate also increases. It means that the conversion ratio from water to hydrate also increases. The HV region is then chosen to be the investigation area.

Concentration of each phase was measured by direct gas sampling of remaining gas through gas chromatograph. After that, the remaining gas hydrates were dissociated by pressure lowering so that whole of the encaged gas were made to evolve from hydrates. Thus, one more gas analysis gave us the gas composition of hydrate phase. As seen in Figure 2, the considerable enrichment of CO_2 in the hydrate phase was obtainable. The 40 mol.% of CO_2 mixture formed gas hydrate in silica gel pores and the obtained gas hydrate was determined to be more than 95 mol.% of CO_2 while the remaining gas phase contained 21 mol.% of CO_2 at 274.15 K, 6.85 MPa and 100 nm SG. This result suggests that a conceptual CO_2 recovery process using gas hydrate formation can be constructed. The pressure difference from the equilibrium pressure at 274.15 K was about 1.4 MPa according to Figure 2. As close to equilibrium pressure, the obtainable CO_2 concentration in hydrate phase increases and is expected to be more than 98 mol.%. However, it seems that very low gas consumption rate (that is, hydrate formation rate) is anticipated. Higher operation pressure also needs larger investment cost. Therefore, we

should make a compromise among operational condition parameters. Studies on hydrate formation kinetics are also required to decide and optimize operating condition. An alternative kinetic measurement for hydrate formation in silica gel pore would be studied in a soon, using a continuous fixed-bed type reactor. Most of previous studies on the hydrate formation kinetics have been performed by using a batch type reactor (Sloan and Koh, 2007). Gas consumption rate is investigated in an isochoric reactor in usual batch type reactor, but the result is strongly dependent upon geometry of the reactor so that measurement in a flow-type reactor is preferred in recent days (Okano *et al.*, 2005). This kind of formation kinetics is particularly important in case of gas mixtures to be separated, because the continuous gas separation reactor where hydrate formation occurs is simulated at such a reactor after all.

Compared to the similar trial of Linga *et al.*'s (2007b), the suggested process in this work becomes simpler than theirs, because only one reactor for hydrate formation is needed in this work while their work requires two stages with bulk water. According to their study, 40 mol.% CO_2 and 60 mol.% H_2 mixture forms gas hydrate slurry, that means close operating condition to equilibrium point, at the first reactor. The obtained hydrate is then dissociated in a separation drum and released to be 80 mol.% CO_2 mixture. Second reactor forms hydrate slurry once again and repeat dissociation to obtain the purified CO_2-rich (98~99 mol.%) gaseous stream. To reduce stages for hydrate formation and dissociation is a big merit for simpler process and reducing investment and operating cost. Furthermore, most of previously reported hydrate formation methods are to use hydrate slurry that is the mixture containing hydrates and unreacted water. For making hydrate slurry, the operating condition should be close to equilibrium condition because water and slurry coexists. As mentioned above, it is difficult to obtain the rapid and high conversion rate as the operation condition is close to equilibrium condition. Hydrate slurry contains less gas concentration and thus larger amount of slurry would be needed to treat a specific mass of feed gas comparing to the case of HV operation.

Of course the formation rate of the corresponding gas mixtures should be considered for the development of CO_2 recovery process. However, the larger contact area between water and gas molecules in silica gel pores than bulk water must have enhanced the formation rate. In the future work the authors will investigate the rate of hydrate formation in silica gel pores and the optimized operation conditions.

4. Conclusions

A new type of hydrate formation in silica gel pore was suggested for CO_2 and H_2 gaseous mixture to apply CO_2 separation process. Primary results of equilibrium dissociation conditions for 40 mol.% CO_2 and 60 mol.% H_2, which simulated for fuel gas, were measured. According to the result, one stage hydrate formation and dissociation gave a CO_2 rich gaseous stream, more than 98 mol.% of CO_2. Compared to previously reported similar conceptual method, using porous silica gel particle provided an enhanced result for CO_2 separation through gas hydrate formation. The hydrate formation kinetics would be investigated and measured in a continuous fixed bed

reactor in near future work. Gas separation process like a PSA process is expected to separate CO_2 from fuel gas.

Acknowledgement

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