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Semiclathrate-based CO_2 capture from fuel gas in the presence of tetra-n-butyl ammonium bromide and silica gel pore structure

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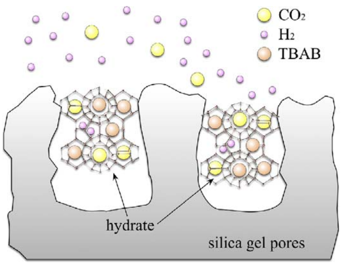
GRAPHICAL ABSTRACT



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ABSTRACT

Pre-combustion CO_2 capture technology was investigated via a hydrate-based gas separation process. Semiclathrate phase equilibria were measured for the simulated fuel gas from the integrated gasification combined cycle (IGCC) consisting of 40 mol% CO_2 and balanced H_2 in the presence of tetra-n-butyl ammonium bromide (TBAB) and porous silica gel particles containing water inside. The basic idea is an extension of our previous work [34], that is, using a porous silica gel structure made it possible to get rid of stirring the content inside the hydrate reactor and ensure the rapid hydrate formation with relatively short induction. TBAB was introduced to confined aqueous solution in silica gel pore structure, having nominal pore diameter of 100 nm, as a thermodynamic promoter and formed semiclathrate with the gas mixture under milder temperature and pressure conditions. Compositional analysis of semiclathrate and coexisting gas phases was also performed at various temperatures and TBAB concentrations. The highest CO_2 concentration obtained from the dissociated semiclathrate was 94 mol% formed at 277.15 K and 3.0 MPa, with 20 wt% TBAB solution in 100 nm silica gel. To demonstrate the highly-concentrated CO_2 outlet stream from the single-stage semiclathrate reactor, the kinetic study of CO2 distribution through fixed-bed type reactor charged with silica gel particles containing aqueous TBAB solution was also investigated. Utilization of porous silica gel makes it possible to capture higher concentration of CO2 in the semiclathrate phase, but it also reduced the total amount of gas consumed for semiclathrate conversion. However, the use of silica gel particles with TBAB enabled formation of semiclathrate hydrate under milder conditions and unstirred continuous method to a high extent and a high rate.

1. Introduction

Carbon dioxide (CO_2) generated by combustion of fossil fuels induces global warming, leading to various issues such as climate change and rise in sea level. A variety of strategies for carbon capture, utilization and storage (CCUS) has been investigated to prevent the

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catastrophe from rising greenhouse gas concentrations. CO_2 capture is the first and most important step among the mitigating activities needed (utilization and storage) for CO_2. Because a considerable amount of the global energy supply used for electricity still relies on thermal power plants burning fossil fuels, more efficient CO_2 capture technology is required. Pre-combustion CO_2 capture is the technology by which CO_2 is captured from fuel gas ($CO_2 + H_2$) used in an integrated gasification combined cycle (IGCC) [1–4]. Various methods, involving membrane [1], adsorption [2], and absorption [3,4], have been investigated and developed for pre-combustion CO_2 capture. Not only these methods but also hydrate-based gas separation (HBGS) has been considered as a possible strategy for CO_2 capture from fuel gas [5,6].

Clathrate hydrate consists of water host cages where gaseous, organic or ionic guests reside [7–9]. Gas hydrate is one of the types of clathrate hydrate in which gas molecules occupy the hydrate cavities. Gas separation, or capture of a particular gas species via hydrate formation, is realized by manipulating thermodynamic stability and degrees of hydrate cage occupation by gaseous guest molecules. However, even though gas hydrates are stable under high pressure and low temperature [7–9], HBGS could be made more energy efficient with the help of organic or ionic guests that improve the thermodynamic stability of the clathrate hydrate structure. Among the organic guests, tetrahydrofuran (THF) and cyclopentane (CP) are representative thermodynamic hydrate promoters. The melting temperatures of pure THF and CP hydrates are 277.55 K and 280.85 K, respectively, at atmospheric pressure [7]. In practice, these promoters have been utilized to induce hydrate-based CO_2 capture processes under relatively lower pressure and higher temperature [10–13]. However, the high vapor pressures of these organic guests induce rapid vaporization of the molecules, making it difficult to utilize them in practical CO_2 capture processes. Thus, another type of clathrate hydrate former without high vapor pressure should be considered.

Quaternary ammonium salts are representative ionic guests forming clathrate hydrate structures [8,9]. Because these materials are ionic, their vapor pressures are almost negligible. Among the ionic clathrate hydrates, tetra-*n*-butylammonium (TBA) cation-based hydrates exhibited higher thermal stability than THF and CP hydrates. The melting temperatures of the TBA salt hydrates are up to 300.15 K at atmospheric pressure, depending on the corresponding anion species [14]. Interestingly, a TBA cation occupies a combined set of four cage ($5^{12}6^2$ or $5^{12}6^3$ cages) across which each butyl group of a TBA cation stretches [15–17]. Due to the large size of the TBA cation, the combined cage includes some water molecules that are greatly distorted; so much that several hydrogen bonds between water molecules are broken [8,15–17]. This is the structural difference of TBA cation hydrates from genuine clathrate hydrates containing gaseous or organic guests [8,15–17]. Thus, TBA cation-based hydrates are called semiclathrate hydrates [9,15]. Because these ionic clathrate hydrates include empty cages (usually 5^{12} cages) [15,17], TBA salts can also be used as thermodynamic hydrate promoters, and they have been investigated for practical hydrate-based CO_2 capture processes [18–20]. Furthermore, a mixture consisting of organic (THF) and ionic (TBAB) hydrate promoters was also studied to improve the hydrate formation conditions for CO_2 capture [21]. Additionally, thermodynamic researches on the TBAB hydrate were performed for CO_2 capture process. Various thermodynamic models were developed to describe TBAB hydrate phase equilibria with the secondary guests, such as CH_4, CO_2, N_2, and their mixtures [22,23]. Another study predicted the dissociation conditions of binary TBAB + CO_2 hydrate and its crystal structure, depending on the CO_2 partial pressure [24], and moreover, the effect of a surfactant on the phase equilibria of TBAB + CO_2 hydrate was investigated [25].

Aqueous solutions have to be agitated to achieve an enhanced rate of hydrate formation, regardless of the thermodynamic hydrate promoters, and this requires significant amounts of energy consumption. Consequently, researchers have been searching for an efficient type of hydrate formation reactor that does not require stirring [12,26–31], and some of them utilized silica gels as porous media containing water in their pore structure, to form hydrates without stirring [32–35]. Silica gel can be obtained easily and cheaply, and provides a huge amount of pore volume, so we can use its pores as confined water storage sites for hydrate formation. Application of gas hydrate formation with porous silica gel to CO_2 capture from fuel gas was thus tried and it resulted in the feasibility of high CO_2 selectivity to hydrate phase, which was our first publication in this journal (2010) [32]. Then, we investigated the CO_2 selectivity depending on the various temperature and pressure conditions and the pore sizes of applied silica gel. In addition, the change in CO_2 concentration from once-through outlet flow reactor, loaded by silica gel particles containing water inside the pores, was investigated, which showed the remarkably shortened induction time and rapid gas consumption getting along with hydrate formation. That was our second publication in this journal (2013) [34]. However, there still remains an important point. The compression of the feed gas and stirring the content of hydrate reactor require a large amount of energy consumption. Although the porous silica gel leads to energy saving, the feed gas compression still remains as a drawback for gas hydrate process to capture CO_2. Thus, we tried to move even this compression problem by adding thermodynamic promoter like TBAB, and this is the present report.

In the present work, both a thermodynamic hydrate promoter and silica gel were used for hydrate-based pre-combustion CO_2 capture from fuel gas. Tetra-*n*-butylammonium bromide (TBAB) acted as an ionic promoter to improve the conditions for hydrate formation. Three phase (hydrate-liquid-vapor, HLV) equilibria were measured using TBAB solution in silica gel. In addition, compositional analysis was carried out before and after hydrate formation to evaluate the CO_2 capture performance of the HBGS process. Additional hydrate-based CO_2 capture was performed using the silica-gel-packed column reactor by allowing continuous feed gas flow.

2. Experimental section

2.1. Reagent

Tetra-*n*-butylammonium bromide (TBAB, ≥99.0%) was purchased from Sigma-Aldrich. The fuel gas composed of 60 mol% of hydrogen (H_2) and 40 mol% of carbon dioxide (CO_2) was supplied by Anjeon Gas (Korea). Deionized water was obtained using water purification equipment (Milli-Q RX45, Millipore). Spherical silica gel (SG, nominal pore size: 100 nm in diameter) was purchased from Silicycle (Canada). The textural properties of the silica gel are listed in Table 1. The reagents and materials were used without further treatment or purification.

2.2. Apparatus

The apparatus for hydrate phase equilibrium measurement and flow-type hydrate formation tests was depicted as shown in Fig. 1. The upper section of the apparatus diagram consists of the gas mixing compartment, boosting and buffer cell, and the high-pressure reactor which was used to determine the equilibrium dissociation curves for the CO_2-H_2 hydrates. Simulated fuel gas containing 40 mol% CO_2 and the balanced H_2 was prepared from the respective gas cylinder to buffer cell

Table 1
Textural properties of the silica gel*.

Mean particle diameter (μm)	40–75
Mean pore diameter (nm)	94.5
Specific pore volume (m^3/kg)	8.3×10^{-4}
Specific surface area (m^2/kg)	42.4×10^3

* Nominal pore size is 100 nm diameter.