

CO₂ Hydrate Conversion from Microscopic Ice Powder Under Low Pressure and Low Temperature

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The conversion rate of CO₂ hydrate from microscopic ice powder was analyzed through the use of a laboratory experiment and numerical models. In the experiment, fine ice powder, the mean diameter of which was 5.2 μm, was generated by means of an ultrasonic mist generator aimed at enhancing the formation rate under the constraint of the relatively low pressure and low temperature of 0.7 MPa and 253 K, respectively. The ice-to-hydrate conversion degree was obtained as a time variation through the measurement of the mass of the synthesized product of CO₂ hydrate and the remaining ice at different timings. In the numerical part, a fugacity-driven formation model incorporated with a shrinking-core model was applied to a single spherical ice particle. The coefficient of the CO₂ diffusion in the hydrate membrane was treated as an unknown parameter and was determined by the fitting of the model to the experimental results. The estimated diffusion coefficient was comparable with that proposed in the literature. It was also found that the conversion degree became no greater than about 60%. A possible explanation is the decrease of the CO₂ supply due to shrinking of the inter-particle pores. This inter-particle effect was modeled to represent the drastic reduction of the formation rate.

INTRODUCTION

Clathrate hydrates are crystalline water-based solids in which small molecules are trapped inside cages of hydrogen-bonded water molecules. Recently, the utilization of hydrate is getting more and more attention in many engineering fields. For example, the separation of CO₂ from mixed gas in the form of gas hydrate is expected to be an alternative method for capturing carbon at extensive emission sites such as thermal power plants. Since capturing is one of the most cost-consuming processes in carbon capture and sequestration (CCS), the development of an efficient capturing method is demanded. One of the most energy-consuming factors in forming CO₂ hydrate is the compression in a pressure-resistant tank (Linga, Kumar, and Englezos, 2007). To reduce the equilibrium pressure, the effect of additives such as tetrahydrofuran (THF) and cyclopentane (CP) is studied (Hashimoto et al., 2006; Linga, Adeyemo, and Englezos, 2007; Zhang et al., 2009). Tetra-n-butyl ammonium bromide (TBAB) or tetra-n-butyl ammonium fluoride (TBAF) hydrates are also considered to separate CO₂ at a lower pressure (Fan et al., 2009; Li et al., 2010).

Another method to realize CO₂ hydrate formation at a low pressure is to make it at a low temperature. For example, the required pressure for the equilibrium condition at the temperature of 253 K is reduced to as low as about 0.5 MPa (Yasuda and Ohmura, 2008). Usually this option is not taken because keeping the temperature low also requires energy and is costly. However, if we make use of the cold energy that is usually abundant in gas companies for liquefied natural gas, the cost associated with this method may become competitive with those of other conventional capturing methods such as chemical absorption by amine solution or physical absorption by porous media.

The rate of hydrate formation is also important in reducing the processing time and cost. It is anticipated that the formation rate becomes much smaller under the ice point. In fact, Yoon et al. (2004) observed the transformation process of methane hydrate into CO₂ hydrate by using Raman spectroscopy and found that the shielding effect of ice drastically reduced the formation rate of CO₂ hydrate. It is easily expected that the increase in the interface area at which hydrate formation occurs directly leads to the increase in the rate of hydrate formation. From this point of view, fine ice particles have often been used for increasing the rate of CO₂ hydrate formation. Takeya et al. (2000) measured the growth rates of CO₂ hydrate from small ice particles with average diameters of about 150 μm by performing X-ray diffraction experiments. They applied a two-stage model to interpret the formation mechanism and estimated the initial reaction rate and diffusion

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