Methane Hydrate Growth and its Recovery with Carbon Dioxide via Molecular Dynamic Simulations

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ABSTRACT

The three-phase molecular models consisting of gas, liquid water, and solid hydrate phase are used to study the coexisting condition, the growth mechanism of methane hydrate, and the replacement of methane in methane hydrate using carbon dioxide. The melting temperatures of methane hydrate at different pressures from such a model are found to be in good agreement with experiment. At temperatures below the melting point, the growth rate of methane hydrate is found to be dominated by (1) the solubility of methane in the liquid phase, (2) the diffusivity of methane in water, and (3) the absorption of methane by methane-filled incomplete water cages at the solid-liquid interface. The solubility, and hence the growth rate, increases with the partial pressure of methane in the vapor phase. The mass transport resistance from absorption and the diffusion of methane are two competing factors, with the absorption of methane at the interface found to be the rate limiting step. The presence of high concentration of incomplete clathrate hydrate cages presents strong affinity to dissolved methane at temperatures below the melting point. In addition to methane absorption, water molecules must be expelled to form the complete clathrate cages. Both processes lead to a methane concentration minimum at 5–9 Å in front of the growing interface. The methane concentration minimum provides the driving force for methane transport from the bulk to the interface. When liquid carbon dioxide is introduced to the system, spontaneous replacement of methane in the solid phase with carbon dioxide molecules can be observed. A large amount of carbon dioxide are found to penetrate into the cages and expel the existing methane, especially near the melting point of methane hydrate.

Keywords: gas hydrates, molecular dynamics simulation, growth

INTRODUCTION

Clathrate hydrates are the crystalline inclusion compounds consisting of cages formed by water molecules in which guest molecules are trapped[1]. Methane is one kind of guest molecules that stabilizes the water cages of clathrate hydrates structure. Methane clathrate hydrates naturally form and these are so abundant on the permafrost region and under the deep sea-floor sediments that these are considered as a new source of energy for at least 50 years. Recently, more attentions have been drawn by this new energy source and more researches are conducted by the group in the academia and industrial field for recovering the methane from methane clathrate hydrate.

Because exploring the reservoir of methane clathrate hydrates and recovering methane usually need huge budget, it is essential to reduce the cost of these procedures. In addition, during the procedure of recovering methane under the deep sea floor will cause the environmental and ecosystem damage. In order to reduce the cost of exploring the reservoir and recovering methane and avoid the environmental and ecosystem damages, the better understanding of methane hydrate formation and dissociation is important.

The molecular dynamics simulation is one of the most powerful tools to investigate the dissociation and formation phenomena and mechanism from the molecular scale. Many researches on structural and dynamical properties have been conducted and published at the last 10

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