

# Molecular Dynamics Study of Replacement of CH<sub>4</sub> by CO<sub>2</sub> in Clathrate Hydrate with H<sub>2</sub>S

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Methane (CH<sub>4</sub>) is the major component of natural gas and exists as clathrate hydrate occurring in the deep seafloor sediment around Japanese Islands. The total amount of CH<sub>4</sub> hydrate around Japanese Islands is so abundant that it is considered to be a potential future energy resource. Carbon Dioxide (CO<sub>2</sub>) is considered to be responsible for global warming effect. The conception of replacement of CH<sub>4</sub> by CO<sub>2</sub> in clathrate hydrate has been conceived resulting in an innovative solution. Replacement of CH<sub>4</sub> by CO<sub>2</sub> from gas hydrate can recover CH<sub>4</sub> as a potential future energy resource meanwhile sequester CO<sub>2</sub>. Further, the formation of CO<sub>2</sub> hydrate leads to geological stabilization after decomposition of CH<sub>4</sub> hydrate. Recently, replacement of CH<sub>4</sub> by CO<sub>2</sub> has been studied both from experiments and simulations. However, the detailed mechanism of replacement process is still poorly known. Although the experiments using mixtures of CO<sub>2</sub> and various additives have been conducted, little work has been done with Hydrogen sulfide (H<sub>2</sub>S) on the replacement process. H<sub>2</sub>S as a concomitant of CO<sub>2</sub>, produced by developing oil or natural gas fields. Given H<sub>2</sub>S not negatively influence the replacement reaction, the mixture of CO<sub>2</sub> and H<sub>2</sub>S can be injected into clathrate hydrate with the advantage of lowering the overall cost and disposing of pollutants. Here, classical molecular dynamics (MD) simulations were performed to understand the effect of additive H<sub>2</sub>S imposed on the replacement process. MD simulations can investigate the physical interactions between different atoms and molecules on the basis of Newton's law and represent the relevant movements of the particles in the evolution, of which results can be visualized later on by using computational way. In this study, in order to investigate the microscopic mechanism of replacement process, we conducted simulations in three cases. 1) CH<sub>4</sub> hydrate + CO<sub>2</sub>, 2) CH<sub>4</sub> hydrate + H<sub>2</sub>S, 3) CH<sub>4</sub> hydrate + CO<sub>2</sub> + H<sub>2</sub>S, and investigated the influence of H<sub>2</sub>S on the replacement process of CH<sub>4</sub> by CO<sub>2</sub>. The temperature and pressure were set to 280 K and 6 MPa, respectively. Under this condition, CH<sub>4</sub> hydrate is decomposed and subsequently CO<sub>2</sub> and H<sub>2</sub>S hydrates are formed. Step interval was 1 femtosecond and the total simulation time was 200 ns in all cases. Within MD simulations, CO<sub>2</sub> molecules are trapped by water-forming cages. As for H<sub>2</sub>S, H<sub>2</sub>S molecules also replace with CH<sub>4</sub> and are trapped by cages as well. On the other hand, in all cases, replacement of CH<sub>4</sub> by CO<sub>2</sub> or H<sub>2</sub>S does not occur in the center of CH<sub>4</sub> hydrate crystals. This implies that it is difficult for CO<sub>2</sub> and H<sub>2</sub>S molecules to go deeper into bulk clathrate hydrate. In addition, the results show that H<sub>2</sub>S molecules decrease the total number of CO<sub>2</sub> molecules trapped by cages in comparison with injection of pure CO<sub>2</sub> phase. The replacement reaction of CH<sub>4</sub> and CO<sub>2</sub> occurs preferably in large cages, whereas, H<sub>2</sub>S molecules can replace CH<sub>4</sub> molecules in both small and large cages. Consequently, it is possibly ascribed to that CO<sub>2</sub> and H<sub>2</sub>S molecules compete with each other during the replacement progress of CH<sub>4</sub> hydrate. The formation rate of H<sub>2</sub>S hydrate was faster than that of CO<sub>2</sub> hydrate, which may due to stronger coulomb interaction between H<sub>2</sub>S and H<sub>2</sub>O molecules since they are polar molecules. Also owing to this, H<sub>2</sub>S becomes more competent over CO<sub>2</sub> during formation process of clathrate hydrate in the presence of mixture of H<sub>2</sub>S and CO<sub>2</sub>. From our results, the coulomb interaction between H<sub>2</sub>S and H<sub>2</sub>O may lead to stabilization of H<sub>2</sub>S hydrate and decrease the formation efficiency of CO<sub>2</sub> hydrate. The recovery rate of CH<sub>4</sub> is decelerated by H<sub>2</sub>S, which suggests the additive can impede the replacement progress of CH<sub>4</sub> hydrate.

All of the results suggest that the addition of H<sub>2</sub>S weaken the storage capability of CH<sub>4</sub> hydrate for CO<sub>2</sub>.

Keywords: Methane Hydrate, Carbon dioxide Capture and Storage , Replacement of CH<sub>4</sub> by CO<sub>2</sub>,  
Molecular Dynamics Simulation