

Molecular Dynamics Study of Replacement of CH₄ by CO₂ in Clathrate Hydrate with H₂S

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Methane (CH₄) 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 CH₄ hydrate around Japanese Islands is so abundant that it is considered to be a potential future energy resource. Carbon Dioxide (CO₂) is considered to be responsible for global warming effect. The conception of replacement of CH₄ by CO₂ in clathrate hydrate has been conceived resulting in an innovative solution. Replacement of CH₄ by CO₂ from gas hydrate can recover CH₄ as a potential future energy resource meanwhile sequester CO₂. Further, the formation of CO₂ hydrate leads to geological stabilization after decomposition of CH₄ hydrate. Recently, replacement of CH₄ by CO₂ 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 CO₂ and various additives have been conducted, little work has been done with Hydrogen sulfide (H₂S) on the replacement process. H₂S as a concomitant of CO₂, produced by developing oil or natural gas fields. Given H₂S not negatively influence the replacement reaction, the mixture of CO₂ and H₂S 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 H₂S 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) CH₄ hydrate + CO₂, 2) CH₄ hydrate + H₂S, 3) CH₄ hydrate + CO₂ + H₂S, and investigated the influence of H₂S on the replacement process of CH₄ by CO₂. The temperature and pressure were set to 280 K and 6 MPa, respectively. Under this condition, CH₄ hydrate is decomposed and subsequently CO₂ and H₂S hydrates are formed. Step interval was 1 femtosecond and the total simulation time was 200 ns in all cases. Within MD simulations, CO₂ molecules are trapped by water-forming cages. As for H₂S, H₂S molecules also replace with CH₄ and are trapped by cages as well. On the other hand, in all cases, replacement of CH₄ by CO₂ or H₂S does not occur in the center of CH₄ hydrate crystals. This implies that it is difficult for CO₂ and H₂S molecules to go deeper into bulk clathrate hydrate. In addition, the results show that H₂S molecules decrease the total number of CO₂ molecules trapped by cages in comparison with injection of pure CO₂ phase. The replacement reaction of CH₄ and CO₂ occurs preferably in large cages, whereas, H₂S molecules can replace CH₄ molecules in both small and large cages. Consequently, it is possibly ascribed to that CO₂ and H₂S molecules compete with each other during the replacement progress of CH₄ hydrate. The formation rate of H₂S hydrate was faster than that of CO₂ hydrate, which may due to stronger coulomb interaction between H₂S and H₂O molecules since they are polar molecules. Also owing to this, H₂S becomes more competent over CO₂ during formation process of clathrate hydrate in the presence of

mixture of H_2S and CO_2 . From our results, the coulomb interaction between H_2S and H_2O may lead to stabilization of H_2S hydrate and decrease the formation efficiency of CO_2 hydrate. The recovery rate of CH_4 is decelerated by H_2S , which suggests the additive can impede the replacement progress of CH_4 hydrate. All of the results suggest that the addition of H_2S weaken the storage capability of CH_4 hydrate for CO_2 .

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