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REPLACEMENT BEHAVIOR OF CH_4 IN THE HYDRATE WITH CO_2 INJECTION BY MOLECULAR DYNAMICS SIMULATION

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ABSTRACT

Molecular dynamics simulations are used to study the replacement behavior of CH_4 in the hydrate with CO_2 injection. The molecular configurations and microstructure properties are analyzed with the systems containing the gas layer (CO_2 or CH_4) and the CH_4 hydrate layer. It is found that the H_2O molecules arrangement of hydrate surface is changed in the replacement process. These H_2O molecules of hydrate surface move and reform the solid cages, while H_2O molecules of the interfacial transition zone of the gas layer and the hydrate layer present the quasi-liquid structure. The simulation results indicate the H_2O molecules arrangement is affected by the gas molecules in replacement process.

Keywords: CH_4 hydrate, CH_4-CO_2 replacement, molecular dynamics simulation

1. INTRODUCTION

As a new clean energy source in the world, natural gas hydrate is distributed widely in the ocean sediments and permafrost areas. The CH_4 production from the natural gas hydrate reservoir by injecting CO_2 is a new exploitation method of the natural gas hydrates. It can not only store CO_2 to reduce the greenhouse gases emission but also produce CH_4 from the natural gas hydrate reservoirs. Experimental and theoretical researches have demonstrated the feasibility of the replacement of CH_4 in the hydrate with CO_2. On the thermodynamics researches, the equilibrium condition of the CO_2 hydrate was more moderate than that of the CH_4 hydrate [1]. On the kinetics researches, the Gibbs free energy (ΔG) of the CH_4-CO_2 replacement in natural gas hydrate was negative, which means the reaction of the CH_4-CO_2 replacement from natural gas hydrate was spontaneous [2]. Additionally, the micro analysis and component measurement in the process of the CH_4-CO_2 replacement from natural gas hydrate proposed that the CH_4–CO_2 replacement mainly occurred in the hydrate phase. [3]. However, it was difficult to understand the replacement mechanism of the hydrate by the experimental and numerical simulation method.

Molecular dynamics (MD) simulation has been proven to be a powerful tool to provide molecular level understanding of microscopic mechanisms. Recently, several simulation researchers investigated the mechanisms of the replacement of CH_4 in the hydrate with CO_2. Qi et al. reported the replacement process by MD. The simulation results confirmed that CH_4 was released from its hydrate and entered into the gas phase by the replacement with CO_2 [4]. Tung et al. used MD to investigate the conversion of the CH_4 hydrates to the CO_2 hydrate [5]. The results showed CO_2 swapped CH_4 or momentarily co-occupied with CH_4 in the cages of hydrate. Iwai et al. analyzed the phenomena of replacement of CH_4 hydrate with CO_2 by MD [6]. In the simulation, the hydrate partially melted and liquid water phase appeared. And CO_2 mainly occupied the large cage of the hydrate. As above researches, there has been concerned about the exchange of gas in the cages on the replacement process, while neglected the exchange of H_2O in these cages. In the work, we focus on the move process of H_2O in the CH_4 hydrate, when CH_4 produce from the CH_4 hydrate by CO_2. To eliminate

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the effect of liquid H_2O for the CH_4-CO_2 replacement process, we report the molecular configuration and microstructure properties with the systems containing the gas layer (CO_2 or CH_4) and the CH_4 hydrate layer.

2. COMPUTATIONAL DETAILS

The two-layer model consisting of a gas layer and a CH_4 hydrate layer is used in this work. The gas layer contains 100 CH_4 molecules or 100 CO_2 molecules and the CH_4 hydrate layer consists of a 2×2×4 unit cell of the structure I (sI) hydrate with all cages filled with CH_4 molecules. The systems containing CH_4 and CO_2 in the gas layer and the CH_4 hydrate layer are called System A and System B respectively, in this work.

The MD simulations are performed using the DL_POLY MD simulation package[7]. The interaction potentials of H_2O molecules are treated as the TIP4P/ice H_2O model[8], and CH_4 molecules are represented by the OPLS all atom (OPLS-AA) model[9]. A cutoff distance at half of the model cell length is used for the short-ranged interactions, while the long-range electrostatic interactions are calculated using the Ewald summation method. The Verlet Leapfrog algorithm is used to the equations of motion for translations and rotations with a timestep of 1 fs. Periodic boundary conditions are applied along all three directions of the systems.

The initially systems were energy minimized, and a short (100 ps) NVT simulation at 260 K was then performed to relax any extra stress at the two layer surface. The simulations of the CH_4-CO_2 replacement process runs are maintained at 277 K and 15 MPa by the isobaric-isothermal (NpT) ensemble with the time scale of 500 ns.

3. RESULT AND DISSCUSSION

3.1 Replacement of Methane by Carbon Dioxide

Figure 1 shows the snapshots of configuration on System A and System B during the simulations. As seen in Figure 1, the initial configurations (0 ns) are composed of a gas layer (on the right) and a CH_4 hydrate layer (on the left). The CH_4 hydrate layer shows the integral structure of sI CH_4 hydrate along the z direction. In order to analyze the replacement process in more detail, we divide the CH_4 hydrate into eight sliced layers, A, B, C, D, E, F, G and H. Each layer is approximately 0.59 nm in thickness, and the thickness roughly corresponds to the distance of half a cell length in one unit CH_4 hydrate in the z direction. From Figure 1, we can see CH_4 molecules occupy all the cages in the CH_4 hydrate layer, while CH_4 molecules or CO_2 molecules uniformly distribute in the gas layer at 0 ns. On the surface of the CH_4 hydrate, some CH_4 locate in the half-open cages. It is caused by cutting the CH_4 hydrate model in the simulation systems. In the beginning of the simulation, CH_4 molecules located in the half-open cages dissolve into the gas layer. In the same time, the arrangement of H_2O molecules formed the half-open cages on the surface of the CH_4 hydrate are immediately distorted due to the diffusion CH_4 hydrate. Therefore, a quasi-liquid structure of H_2O molecules presents at the interface between the gas layer and the hydrate layer. Simultaneously, the balance of hydrogen bonds among H_2O molecules between this interface and the hydrate surface is destroyed. Then, the arrangement of H_2O molecules is disordered in the CH_4 hydrate surface. In Figure 1, we can see some cages of the CH_4 hydrate surface are broken at 100 ns. CH_4 molecules of the CH_4 hydrate depart from these broken cages and then diffuse into the gas layer. Consequential, CH_4 molecules or CO_2 molecules diffused from the gas layer to the CH_4 hydrate surface occupy these empty and distorted cages.

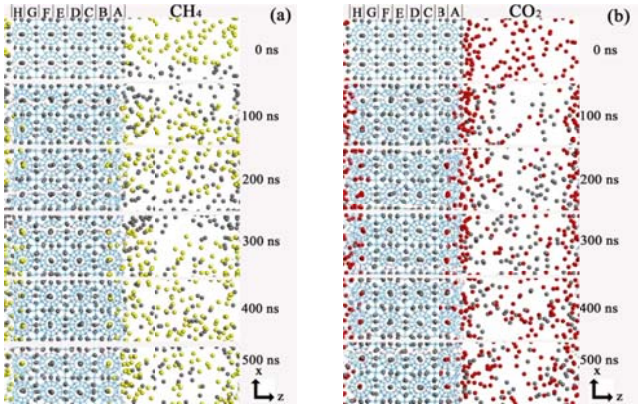

Fig 1 Snapshot of simulation configuration at *x-z* plane (a) System A, (b) System B. Yellow sphere indicates CH_4 molecules in initial gas layer; read sphere indicates CO_2 molecules in initial gas layer; grey sphere indicates CH_4 molecules in initial hydrate layer; red stick and white stick indicate H_2O molecules in the hydrate layer, respectively; the blue dashed line represents the hydrogen bonds

In System A, because the potential energy of CH_4 molecules (from the gas layer) in these cages is same that of CH_4 molecules (from the inner of the hydrate layer) in the hydrate cages, CH_4 molecules from the gas layer steadily occupy these cages. H_2O molecules around those CH_4 molecules (from the gas layer) rearrange to form the regular cages. As shown in Figure 1(a), the surface cages are broken at 0-200 ns, and these cages are regular again after 300 ns. There are a dynamics equilibrium on the CH_4 (the gas layer)-CH_4

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(the CH_4 hydrate layer) exchange. The result indicates the system with the CH_4 gas layer and the CH_4 hydrate layer is stable after 200 ns. In System B, the cages of the hydrate surface is not regular during the simulation, shown in Figure 1(b). It due to the potential energy of CO_2 molecules in the hydrate cages is higher than that of CH_4 molecules in the hydrate cages[10]. Therefore, CO_2 molecules tent to replace CH_4 molecules in the hydrate layer. The hydrate on System B is unstable, H_2O molecules of the hydrate surface frequently rearrange in the replacement process. In the same time, the amorphous CO_2 hydrate is formed in the hydrate surface. And it forms the mass transfer barrier during the replacement process. Therefore the replacing efficiency is decrease.

3.2 H_2O molecules arrangement of the replacement process

Figure 2 shows the snapshot of the surface configurations at *x-z* plane of System A and System B. The green sphere indicates H_2O molecules in initial layer A of the hydrate layer, the purple sphere indicates H_2O molecules in initial layer B of the hydrate layer and others molecules shown as Figure 1. It can be seen from Figure 2 that some H_2O molecules in the layer A move into the layer B, while some H_2O molecules in the layer B move into the layer A. the result indicates the cages of the hydrate surface is not only broken, but also the H_2O molecules arrangement of these cages is changed.

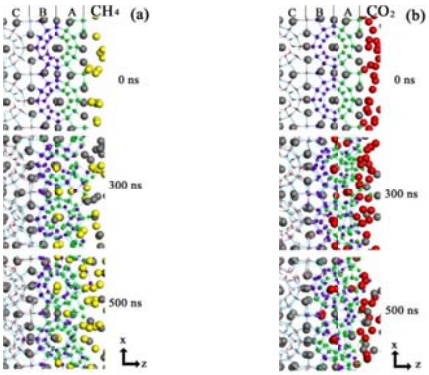

Fig 2 Snapshot of the surface configurations at *x-z* plane of (a) System A and (b) System B

Some cages configuration of the simulation systems at x-y plane are shown in Figure 3. It can be seen from Figure 3 some H_2O molecules in the layer A move into the layer B and arrange the polygon of the cages with some H_2O molecules in the layer B in the replacement process. Compared with the two simulation systems, the rearrangement cages are more regular in System A than those in System B.

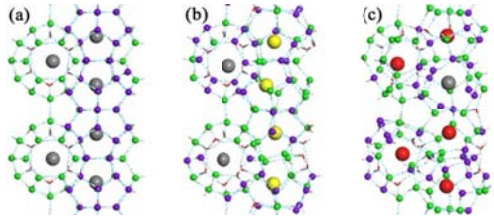

Fig 3 Cages configuration of the simulation systems at x-y plane (a) System A at 0 ns, (b) System A at 500 ns, (c) System B at 500 ns

To describe in detail the distribution of H_2O molecules in the hydrate surface, the radial distribution functions (RDFs) and the four-body order parameter ($F_{4\varphi}$OP) of the simulation systems are analyzed. In Figure 4, it can be seen that the first, second and third peaks for $g_{O\text{-}O}(r)$ in systems at 0 ns and 500 ns have the H_2O-H_2O distances of about 0.27 nm, 0.45 nm and 0.64 nm, respectively. The result agrees with that of $g_{O\text{-}O}(r)$ for the stable pure CH_4 hydrate [10], indicating the clathrate-like arrangement of H_2O molecules during the replacement process. From Figure 4, we can see the peak for $g_{O\text{-}O}(r)$ is lower and broader in the lay A than that in the lay D. It indicates that the regularity of the arrangement of H_2O molecules decreases in the hydrate surface, while the inner arrangement of H_2O molecules is not change. From Figure 4(a) and Figure 4(b), it is found that the distribution of H_2O molecules in the hydrate surface is more irregular in System B than that in System A. The same result is obtained by the analyzed $F_{4\phi}$Ops in Figure 5. The $F_{4\varphi}$OP profile along the z axis is computed as an average over 10 ps during simulation. From Figure 5, it can be seen the values of the $F_{4\varphi}$OP in the region of the layer C to the layer F of the hydrate at 490-500 ns are approximately closed to the value in the CH_4 hydrate structure (0.7)[11]. The result implies H_2O molecules of the simulation systems in this region present the solid structure in the replacement process. In the layer A, the layer B, the layer H and the layer G of the hydrate, the profile of the $F_{4\varphi}$OP falls suddenly at 490-500 ns. It reflects the clathrate arrangement is broken in the hydrate surface. Comparing the *z*-profile for the $F_{4\varphi}$OPs of two simulation systems, we can find the $F_{4\varphi}$OP of the hydrate surface in the System A is higher than that in System B. It implies that the cages of System A are more regular than those cages of System B in the hydrate surface.

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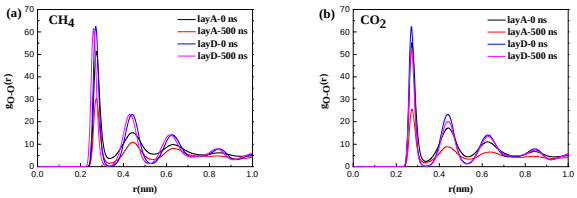

Fig 4 RDFs of the simulation systems (a) in System A, (b) in System B

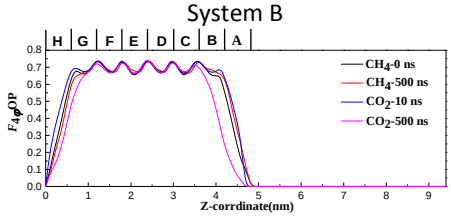

Fig 5 *Z*-profiles for the $F_{4\varphi}$OP of H_2O molecules

4. CONCLUSIONS

In this work, the molecular-scale replacement process of CH_4 in the hydrate with CO_2 is investigated by MD simulation. The change of the H_2O molecules arrangements shows the different hydrate structure of the simulation systems in the replacement process. In the beginning of the simulation, the arrangement of H_2O molecules formed the half-open cages on the surface of the CH_4 hydrate are distorted due to the diffusion CH_4 hydrate. A quasi-liquid structure of H_2O molecules presents at the interface between the gas layer and the hydrate layer. Consequentially, H_2O molecules of one cage of hydrate surface move to another cage and arrange the polygon of the cage with some H_2O molecules in another cage in the replacement process. In System A, H_2O molecules of the hydrate surface rearrange to form the regular cages. In System B, H_2O molecules of the hydrate surface frequently rearrange and the structure of System B is unstable. In the same time, by analyzing the RDFs and the $F_{4\varphi}$OP in the simulation systems, we found that the arrangement of H_2O molecules in the hydrate surface is more regular in System A than that in System B. The results indicate the H_2O molecules arrangement is revealed to exert the different structures on the replacement process. The simulations provide the helpful information to the investigation of the behavior of the CH_4-CO_2 replacement.

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