Computational Materials Science 123 (2016) 106–110

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Replacement micro-mechanism of CH_4 hydrate by N_2/CO_2 mixture revealed by ab initio studies

Jinxiang Liu [a], Yujie Yan [b], Jiafang Xu [c], Shujuan Li [a], Gang Chen [a,*], Jun Zhang [d,*]

[a] School of Physics and Technology, University of Jinan, Jinan 250022, PR China
[b] Shandong Academy of Environmental Science, Jinan 250013, PR China
[c] School of Petroleum Engineering, China University of Petroleum, Qingdao 266580, PR China
[d] College of Science, China University of Petroleum, Qingdao 266580, PR China

ARTICLE INFO

Article history:
Received 20 February 2016
Received in revised form 17 June 2016
Accepted 21 June 2016
Available online 1 July 2016

Keywords:
Methane hydrate
Replacement mechanism
N_2/CO_2 mixture
Ab initio study

ABSTRACT

Ab initio calculations and molecular dynamics simulations were performed to investigate the thermodynamic and kinetic feasibility of the replacement of CH_4 from its hydrate by N_2/CO_2 mixture. Substitution of CH_4 in small and large cages with N_2 and CO_2 has negative Gibbs free energy, whereas the substitution by CO_2 in small cages is structurally unfavorable. The calculations show that the replacement process should be the substitution with CO_2 in large cages followed by N_2 in small cages, featuring with the produce of mixed N_2-CO_2 hydrate. Further, the simulations results indicate N_2 exhibits a faster diffusion motion than CO_2 in hydrate, implying the substitution by N_2 is more kinetically favorable to occur. Our results highlights that the replacement process should include the thermodynamically dominated CO_2 substitution simultaneous to the kinetically dominated N_2 substitution.

1. Introduction

Natural methane hydrates are non-stoichiometric crystalline solids in which methane molecules are encaged by hydrogen-bonded water cages. They typically form under high pressure (more than 0.6 MPa) and low temperatures (less than 300 K) [1,2], naturally occurring in marine and permafrost environments. Due to the huge reserves and high energy density [3–5], natural methane hydrates are potentially regarded as a strategic energy resource, which have attracted increasing interest worldwide [6–8]. To exploit CH_4 form the hydrates, several methods such as thermal treatment, depressurizing, and the addition of inhibitors into the hydrate layer, have been proposed [7,9,10]. However, these methods are based on the decomposition of the hydrates by external stimulations, which may lead to geological disasters such as earthquakes and submarine landslides [11–14]. Alternatively, the CO_2 replacement technique has been widely studied as an economically viable and environmentally friendly production method [15–18], which also provides a way to store CO_2 for a long term [19,20]. Although the replacement reaction will significantly depend on the experimental conditions [15,21], experimental studies have suggested that at least 60% of CH_4 can be recoverable through the direct injection of CO_2 into CH_4 hydrate layers [22–24].

Recently, nitrogen has been explored as a replacement promoter that can greatly improve the CH_4 recovery rate [25–28]. Park and coworkers [27] have experimentally estimated an 85% CH_4 recovery rate when exposing the methane hydrate to the N_2/CO_2 gas mixture. They suggested that CO_2 molecules preferably replace CH_4 molecules in large cages, while N_2 molecules attack CH_4 molecules in small cages and take these sites, thus increasing the recovery efficiency. In addition, the field test of CH_4 recovery using N_2-CO_2 gas mixture has been done in Alaska North Slope [29], which successfully demonstrates that this replacement technology is commercially viable. Although there are some experimental efforts on the investigation of the replacement mechanism, it is difficult to obtain the microscopic information of the replacement process by experiments.

In recent years, computer simulation techniques have offered some insights into the structural [30,31], thermodynamic [32,33] and dynamic characteristics [34,35] of the hydrate. Yezdimer [36] and Dornan [37] have calculated the change of Gibbs free energies for the mutation of CH_4 hydrate into CO_2 hydrate, and they demonstrated that CO_2 can spontaneously replaces CH_4 from the large cages, causing release of the CH_4. Stabilization energy calculations of Geng et al. [38] showed that CO_2 is less suitable for the small cage but is more suitable for the large cage, revealing that the CH_4-CO_2 binary hydrate is more stable than CH_4 hydrate or

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* Corresponding authors.
E-mail addresses: phdgchen@hotmail.com (G. Chen), sps_zhang@hotmail.com (J. Zhang).

http://dx.doi.org/10.1016/j.commatsci.2016.06.025
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CO_2 hydrate. Molecular dynamics simulations [39–41] suggested that the replacement process includes three steps: the cages are broken firstly, then CH_4 runs out of the cages and simultaneously CO_2 enters into the cages and occupy them. However, there are few studies about the replacement mechanism of CH_4 hydrate with the N_2/CO_2 gas mixture.

Therefore, in this work, we performed ab initio calculations and ab initio molecular dynamics simulations to investigate the replacement mechanism of CH_4 in the sI hydrate by N_2 and CO_2. The change of Gibbs free energy was calculated to establish the thermodynamic feasibility of N_2 and CO_2 to replace CH_4 in the cages. Energetic and structural characteristics of all possible mixed hydrates were analyzed to determine the preferential replacement pathway. Further, the diffusion of N_2 and CO_2 in hydrate is compared to understand the replacement priority of CO_2 and N_2.

2. Computational details

We firstly constructed one unit cell ($11.620 \times 11.620 \times 11.620$ Å^3) of *s*I hydrate, containing two dodecahedron (12 pentagonal faces; 5^{12}) and six tetradecahedron (12 pentagonal and 2 hexagonal faces; $5^{12}6^2$) cages, which was obtained from Lenz's data [42]. After adding guest molecules (CH_4 and/or CO_2 and/or N_2) in the center of the cages, the geometry optimization was carried out for the studied hydrates. Then, frequency calculations were performed to characterize the obtained stationary points as minima on the potential energy surface. Subsequently, we chose the optimized structure as the starting point and performed ab initio molecular dynamics simulations to investigate the motion of guest molecules. After an equilibration period of 3.0 ps in the canonical ensemble, we checked the fluctuations in energy and constraint forces to ensure that equilibration was achieved and that the statistical averages were stable.

All calculations and simulations were carried out by the DMol^3 program [43]. The Perdew-Burke-Ernzerhof (PBE) functionals [44] were used in the generalized gradient approximation for the exchange-correlation energy. Double numerical plus polarization (DNP) basis functions [45] were used to describe the atomic orbitals. The Van der Waals dispersion correction was introduced by the empirical Tkatchenko-Scheffler scheme [46]. The equations of motion were integrated with a 0.5 fs time step, and the system was coupled with a Nosé-Hoover chain thermostat [47] to a bath at 270 K to ensure solid behavior. The convergence criteria for the total energy, forces, displacement, and SCF interactions were set as 2.721×10^{-4} eV, 0.054 eV/Å, 0.005 Å, and 2.721×10^{-5} eV, respectively.

For the guest's mutation process (i.e. from CH_4 hydrate to CO_2 hydrate), the change of Gibbs free energy (ΔG) was calculated by:

$$\Delta G = \frac{\left(G_{hydrate}^{CO_2} + x \cdot G_{molecule}^{CH_4}\right) - \left(G_{hydrate}^{CH_4} + x \cdot G_{molecule}^{CO_2}\right)}{x} \tag{1}$$

where $G_{molecule}^{CH_4}$, $G_{molecule}^{CO_2}$, $G_{hydrate}^{CH_4}$ and $G_{hydrate}^{CO_2}$ denote the Gibbs free energies of CH_4 molecule, CO_2 molecule, CH_4 hydrate and CO_2 hydrate, respectively; x denotes the number of CH_4 molecules that were replaced by CO_2 molecules. The stability of the hydrate was evaluated by the cohesive energies (E_{coh}), taking CH_4 hydrate as an example, which can be expressed by the equation:

$$E_{coh} = \left[n \cdot E_{molecule}^{CH_4} + m \cdot E_{molecule}^{H_2O}\right] - E_{hydrate}^{CH_4} \tag{2}$$

where $E_{molecule}^{CH_4}$, $E_{molecule}^{H_2O}$ and $E_{hydrate}^{CH_4}$ represent the energy of CH_4 molecule, H_2O molecule and CH_4 hydrate, respectively; n and m denote the number of CH_4 and H_2O molecules in hydrate, respectively. The binding ability of the guest molecule in hydrate was compared through the interaction energy (E_{int}), which was defined as:

$$E_{int} = \left(E_{guest} + E_{residual}\right) - E_{hydrate} \tag{3}$$

where E_{guest} represents the energy of the guest molecule at its geometry in the hydrate, $E_{residual}$ and $E_{hydrate}$ represent the energy of the hydrate with and without one lost guest molecule, respectively.

3. Results and discussion

3.1. Thermodynamic analysis

In earlier preliminary studies [48], we have explored the thermodynamic stability of CH_4 and CO_2 hydrates and its relation to the replacement reaction. According to the change of Gibbs free energy as shown in Fig. 1(a), we found that CO_2 can fully replace CH_4 in all cages of the *s*I hydrate. However, we note that the replacement reaction occurring in the small cages can induce the deformation of the cages and thus this process is less favorable on the basis of the hydrate structure. In contrast, CO_2 is more likely to replace CH_4 in the large cages. Here, we further explored the change of Gibbs free energy for the replacement of CH_4 in hydrates by N_2, as shown in Fig. 1(b), where the species in brackets is guest molecule, *S* and *L* represents the small (5^{12}) and large ($5^{12}6^2$) cages, respectively. The optimized structures of several hydrates are shown in Fig. 2. Although N_2 can also fully substitute CH_4 in small and large cages, the free energy shows that N_2 preferentially substitute the CH_4 in small cages, featuring with a more negative value (-0.204 eV per cage substitution). This is due to that the molecular radius of N_2 almost coincides with the small cage. From Table 1, we can confirm that N_2 has a larger interaction energy in the small cage than that in the large cage (0.427 eV vs. 0.391 eV), and that $(N_2)_S(CH_4)_L$ hydrate has a higher stability than $(CH_4)_S(N_2)_L$ hydrate (43.825 eV vs. 43.309 eV). Besides, Table 1 shows that both $(N_2)_S(CH_4)_L$ and $(CH_4)_S(N_2)_L$ hydrates have the same hydrogen bond length and cage radius as the CH_4 hydrate, which indicates that the replacement of CH_4 with N_2 does not change the hydrate structure. Therefore, the replacement of CH_4 using the N_2/CO_2 mixture could be regarded as two independent processes: one is N_2 replacement within small cages and the other is CO_2 replacement within large cages. Since the replacement of CH_4 with CO_2 in large cages has a strong tendency (-0.255 eV per cage substitution), this replacement process is more likely to occur and will not interfered by N_2, agreeing well with Dornan's results [37]. Through above analysis, one can conclude that the replacement process should be $(CH_4)_{S,L} \rightarrow (CH_4)_S(CO_2)_L \rightarrow (N_2)_S(CO_2)_L$.

In addition, Fig. 1(b) shows that $(N_2)_S(CH_4)_L$ hydrate can spontaneously mutate into N_2 hydrate ($\Delta G = -0.054$ eV); whereas the mutation of $(CH_4)_S(N_2)_L$ hydrate into N_2 hydrate is thermodynamically unfavorable ($\Delta G = 0.075$ eV). This suggests that only N_2 hydrate forms through the pathway: $(CH_4)_{S,L} \rightarrow (N_2)_S(CH_4)_L \rightarrow (N_2)_{S,L}$. As for N_2 hydrate, the substitution of N_2 with CO_2 in either small cages or large cages has negative change of free energy, which indicates that it can subsequently transfer into CO_2 hydrate. The change of free energy per CO_2 substitution in small cage is more negative than that in large cage (-0.246 eV vs. -0.182 eV), seemingly that CO_2 has a more thermodynamically feasibility to residue in small cages. Actually, Table 1 shows that small cages are enlarged and large cages are compressed when N_2 in small cages are replaced by CO_2, whereas the host lattice can maintain the same structure for the substitution in large cages. As a result, $(N_2)_S(CO_2)_L$ hydrate is more stable than $(CO_2)_S(N_2)_L$ (43.558 eV vs. 42.820 eV). This result indicates that CO_2 is likely to replace N_2 in large cages rather than in small cages. Therefore, the second scenario for the substitution process is $(CH_4)_{S,L} \rightarrow (N_2)_S(CH_4)_L \rightarrow (N_2)_{S,L} \rightarrow (N_2)_S(CO_2)_L$.

Compared with CO_2 substitution, the substitution with N_2/CO_2 mixture can significantly improve the replacement efficiency by