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Ab initio study of the molecular hydrogen occupancy in pure H₂ and binary H₂-THF clathrate hydrates

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ABSTRACT

The hydrogen storage capacity in the clathrate hydrate was studied by ab initio calculations and ab initio molecular dynamics simulations. Thermodynamic and kinetic analysis shows that the cage occupancy in small and large cages is affected by each other, and THF has a stabilization effect on the hydrate structure. For pure H₂ hydrates, small cages can be occupied by single H₂ molecule or double H₂ molecules, while the corresponding occupancy in large cages is four or three H₂ molecules, resulting in a hydrogen storage capacity of ~3.8 wt% and ~4.4 wt%, respectively. For binary H₂-THF hydrates, small cages are likely to be singly occupied with H₂, but large cages can simultaneously accommodate one H₂ molecule and one THF molecule. The hydrogen storage capacity falls in between ~1.6 wt% and ~3.8 wt%. This study highlights the importance of the clathrate hydrates as a hydrogen storage material and also is helpful to understand the controversy about the hydrogen storage capacity in the clathrate structure.

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Introduction

Clathrate hydrates are non stoichiometric crystalline compounds in which guest molecules (e.g., noble gases, methane, nitrogen, carbon dioxide, oxygen) are physically incorporated into polyhedral cages formed by hydrogen-bonded water molecules [1–4]. Three crystalline structures, sI, sII, and sH, have been recognized in naturally occurring clathrate hydrates [5–7], which were determined by the size of guest

molecules. Recently, extensive studies [8–13] have focused on the incorporation of hydrogen within a clathrate structure, because hydrogen hydrates are potentially major constituents of icy satellites, and most notably, as a promising hydrogen storage material.

Historically, with a diameter of 2.72 Å, hydrogen was thought to be too small to support a clathrate structure. However, hydrogen has been now shown to form the sII structure by itself [9], the sI structure with a help gas [14,15],

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and the sII structure with organic promoters [16]. In the present work, we will focus on the sII structure (cubic, space group $Fd\bar{3}m$), composed of two types of clathrate cages: the small dodecahedron (12 pentagonal faces, 5^{12}) and the large hexakaidecahedron (12 pentagonal and 4 hexagonal faces, $5^{12}6^4$). Unfortunately, extremely high pressures (~ 220 MPa at 280 K) are required to stabilize pure hydrogen hydrates, which makes it impractical for technological applications (< 30 MPa) [17,18]. Therefore, great efforts are being made to bring down the synthesis pressure. For example, Florusse et al. [19] have reported that the synthesis pressures were greatly brought down (~ 5 MPa at 280 K) with adding tetrahydrofuran (THF), and Lu et al. [17] suggested that hydrogen hydrates can be formed at 15 MPa and 243 K by reacting H_2 gas with N_2 hydrates, but this occurs at the expense of reducing the hydrogen storage capacity because a considerable number of clathrate cages are occupied by the second guest component. To use as hydrogen storage materials, it is of great importance to determine the total storage capacity of the hydrate. Nevertheless, there are significant discrepancies about the hydrogen loading in clathrate cages of the sII structure.

Mao et al. [9] and Patchkovskii et al. [12] suggested that pure hydrogen hydrates can store ~ 5.0 wt% of H_2 with average occupations of two and four H_2 molecules per small and large cage, respectively. Lokshin et al. [20] and Inerbaev et al. [21] pointed out that the hydrogen occupancy in large cages was reversible between two and four molecules per cage by variation of pressure or temperature, while remaining single occupancy of small cages. Frankcombe and Kroes [22] found that H_2 molecules within large cages were highly mobile, giving cage occupations of up to six H_2 molecules per cage, with lifetimes measured in hundreds of picoseconds. Further, by tuning THF concentration, Lee et al. [10] and Sugahara et al. [23] reported that binary H_2 -THF hydrates can yield the hydrogen storage capacity of ~ 4.0 wt% and ~ 3.4 wt%, respectively, with large cages partially occupied by THF, which were also supported by Alavi's theoretical studies [24]. However, Hester et al. [25], Anderson et al. [26], Hashimoto et al. [27] and Strobel et al. [28] argued that the cage occupancies of binary H_2 -THF hydrates are independent of the THF concentration. They measured that large cages are completely occupied by THF and small cages are singly occupied by H_2 molecule, giving a maximum of ~ 1.0 wt% H_2 , in accordance with Papadimitriou's theoretical results [29]. More recent theoretical studies [30,31] showed that small and large cages can store up to two and four H_2 molecules, respectively, but Willow et al. [32] suggested that small cages can host three H_2 molecules. As the proposed H_2 storage target is currently 5.5 wt% by 2015, it is natural to wonder whether pure H_2 hydrates or binary H_2 -THF hydrates can achieve this goal.

Here, we try to track these questions by performing ab initio calculations and ab initio molecular dynamics simulations to determine the number of H_2 molecules in clathrate cages of the sII structure. The thermodynamic and dynamic stability of pure H_2 and binary H_2 -THF hydrates was evaluated as the function of the cage occupancy. Besides, molecular and electronic structural analyses were carried out to investigate the stabilization effects of THF on the hydrates. This study would be helpful to understand the hydrogen density within sII hydrogen clathrates.

Computational details

To reduce the computational cost, the primitive cell with 34 H_2O was used to represent the crystallographic host lattice for the sII structure, which was taken from Lenz's data [33]. After filling small and large cages with the hydrogen clusters of $(H_2)_{i=1-2}$ and $(H_2)_{j=1-4}$, respectively, the geometry optimization was carried out for pure H_2 hydrates. All structures are global minimum on the potential energy surface since there is no imaginary frequency in the vibrational analysis. Subsequently, the optimized structures were selected as the starting points of ab initio molecular dynamics simulations and were allowed to relax for 5.0 ps in the canonical (NVT) ensemble. For binary H_2 -THF hydrates, the small and large cages was filled by $(H_2)_{i=1-2}$ and $(H_2)_{j=0-2}$ plus one THF, respectively, and the similar calculation procedures were performed for regarding the effects of THF on the cage occupancy. All calculations and simulations were conducted by means of the Becke-Lee-Yang-Parr [34,35] (BLYP) exchange-correlation functional and the double numerical plus polarization (DNP) basis set [36] as implemented in the DMol³ program [37]. The semiempirical Tkatchenko-Scheffler approach [38] was applied to describe the dispersion interactions, which can improve non-bonding interactions in the standard DFT description. Because the quenched pure H_2 hydrates can be stable up to 145 K at ambient pressure [9], the simulation temperature was set to 140 K, controlled by Nosé-Hoover chain thermostat [39]. The time step of 1.0 fs was used for the integration algorithm in the simulations. 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.

The thermodynamic stability of the hydrates was evaluated by the cohesive energy, E_{coh} (with zero-point energy corrections), which was obtained by the equation:

$$E_{coh} = [x E_{hydrogen} + y E_{water} + z E_{THF}] - E_{hydrate} \quad (1)$$

where $E_{hydrogen}$, E_{water} , E_{THF} , and $E_{hydrate}$ represent the energy of the H_2 molecule, the H_2O molecule, the THF molecule, and the hydrate, respectively; x , y , and z denote the number of H_2 , H_2O , and THF molecules, respectively. The interaction energy (E_{int}) between the H_2 molecule and the hydrate was calculated by:

$$E_{int} = (E_{hydrogen} + E_{residual}) - E_{hydrate} \quad (2)$$

where $E_{residual}$ represents the energy of the hydrate with one lost H_2 molecule. The deformation energy (E_{def}) of the host lattice to accommodate hydrogen clusters was calculated, as

$$E_{def} = E_{cage} - E'_{cage} \quad (3)$$

where E_{cage} and E'_{cage} represent the energy of the host lattice with and without hydrogen clusters, respectively. The diffusion motion of molecules was characterized by the mean square displacement (MSD), as

$$MSD = \langle (\vec{r}_i(t) - \vec{r}_i(0))^2 \rangle \quad (4)$$

where $\vec{r}_i(t) - \vec{r}_i(0)$ is the distance traveled by molecules over some time interval of length t , and the angular brackets denote an ensemble average.

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