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Cluster size effect on hydrogen desorption process from Li_nH_n–NH_3 hydrogen storage system

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ABSTRACT

$LiH + NH_3 \leftrightarrow LiNH_2 + H_2$ system is one of the most promising hydrogen storage systems. We perform *ab initio* calculations on Li_nH_n cluster and NH_3 molecule. We set Li_nH_n cluster ($n = 1$–4) as a model of disordered LiH surface. The H_2 desorption reaction process is strongly depend on the cluster size. Li_2H_2 cluster is favorable to react with NH_3 molecule.

1. Introduction

The hydrogen storage system based on LiH, an light ionic crystal, and NH_3, gas which is easily liquefied, desorbs and adsorbs hydrogen as follows:

$$LiH(solid) + NH_3(gas) \leftrightarrow LiNH_2(solid) + H_2(gas) \tag{1}$$

This system can store 8.1 mass% of hydrogen molecule and one of the promising candidate for on-board hydrogen storage [1]. The hydrogen desorption reaction of this system is exothermic and proceeds at room temperature, and the reverse reaction also proceeds at relatively low temperatures and low pressure [2]. The enthalpy and entropy changes of this system are experimentally estimated to be $\Delta H = 50 \pm 9$ kJ/mol and $\Delta S = 59 \pm 16$ J/mol K, respectively [3].

The natural process of hydrogen desorption from LiH and NH_3 is that $H^{\delta-}$ in LiH and $H^{\delta+}$ in NH_3 form H_2 molecule, and there are some studies on the reaction process of Li_1H_1 molecule and NH_3 molecule at 0 K [4,5]. We have also performed *ab initio* molecular-dynamics (MD) simulations on a model system consisting of Li_2H_2 cluster, a model of extremely disordered LiH surface, and NH_3 molecule, and have shown that the hydrogen desorption occurs by this process [6]. We have also shown that this reaction model can qualitatively reproduce experimental hydrogen desorption profiles by considering the reverse reaction [6]. However, the reaction mechanism between real LiH surface and NH_3 molecule is not clear.

The purpose of this paper is to get insights into the reaction between LiH surface and NH_3 molecule by performing simulations on the reaction with Li_nH_n cluster ($n = 1$–4), which corresponds to a model of disordered LiH surface, and an NH_3 molecule. We mainly discuss about the cluster size dependence of the activation energy of the H_2 desorption reaction.

2. Method

We have performed *ab initio* structure optimization calculation based on density functional theory (DFT) [7–13]. Exchange-correlation energy is treated by generalized gradient approximation (PBE–GGA) [14] and the interaction between ions and electrons is treated by projector augmented wave (PAW) method [15,16], where we consider 1*s*, 2*s*, and 2*s*2*p* electrons of H, Li, and N atom as valence electrons, respectively. The plane wave expansion is performed by Γ point. The cut-off energy of plane wave is 476 eV and that of pseudocharge density is 2040 eV. The structure optimization calculation is performed by projected velocity Verlet method [17] and we regard that the system becomes to be stable when the energy change is within calculation error during a few hundred steps. The time step for structure optimization is 1.94 fs.

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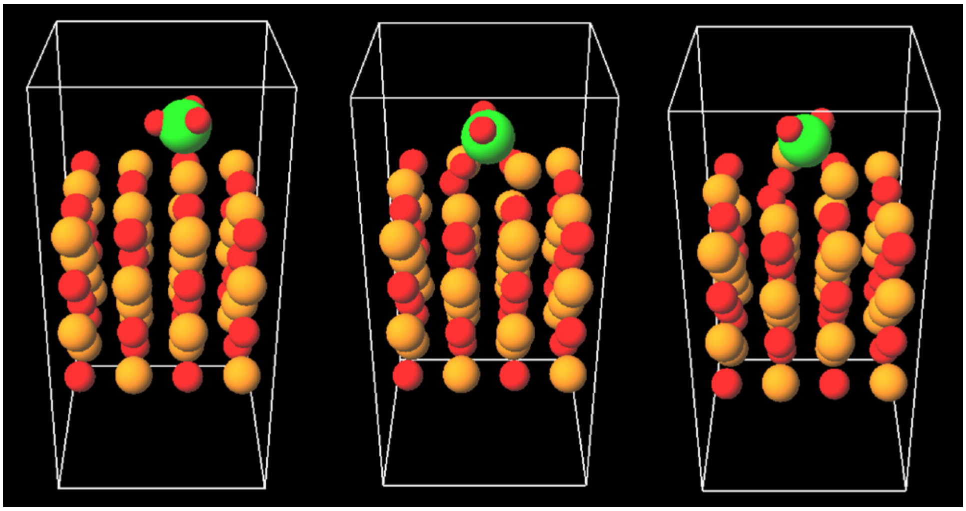

Fig. 1. Snapshots of the H_2 formation from $Li_{32}H_{32}$ slab and NH_3. The red balls show H atoms, the orange balls show Li atoms, and green balls show N atoms. The figures show, from left to right, the snapshots at the energy minimum before the reaction, at the transition state, and at the energy minimum after the reaction (For interpretation of references to color in this figure legend, the reader is referred to the web version of this article.).

The calculation cell is an cubic cell with the edge length of 10 Å. We put one Li_nH_n cluster ($n = 1$–4) and one NH_3 molecule in the cell. To obtain the structures and energies during the reaction, we made the distance of a H atom in Li_nH_n and a H atom in NH_3, which form the H_2 molecule in our previous study [6], closer step by step, and performed the structure optimization at each H–H distance. We also performed the same calculation on LiH (1 0 0) surface and NH_3, where we make the (1 0 0) surface by setting $Li_{32}H_{32}$ slab, with the unit cell of $(x, y, z) = (8.308$ Å, 8.308 Å, 16.616 Å).

3. Results and discussion

In Fig. 1 we show the snapshots of the H_2 formation from $Li_{32}H_{32}$ slab and NH_3 at the energy minimum before the reaction, at the transition state, and at the energy minimum after the reaction. From Fig. 1 we can see that, though H_2 dimer is formed from LiH (1 0 0) surface and NH_3 as metastable state, the H_2 dimer is buried in the surface and is not desorbed from the surface. The H_2 dimer is not desorbed from the surface even if we perform MD simulations at finite temperatures after the H_2 dimer formation.

In Fig. 2 we show the snapshots of the H_2 desorption from Li_nH_n cluster and NH_3 at the energy minimum before the reaction, at the transition state, and at the energy minimum after the reaction. The H_2 molecule is easily formed from Li_nH_n cluster and NH_3 molecule for $n = 1$–4. At the energy minimum before the reaction, for $n = 1$–4, the NH_3 molecule stays on a Li atom directing its N atom to the Li atom. At the transition state, we can also see that two H atoms which make the dimer and N atom are lined up linearly. The H–H–N angles are 155.7°, 174.6°, 178.4° and 174.8° for $n = 1$, 2, 3 and 4, respectively. At the energy minimum after the reaction, for $n = 1$–4, the system becomes a system consisting of a $Li_nH_{n-1}NH_2$ cluster and an H_2 molecule. The NH_2 stays at the position of the H atom, which forms the H_2 molecule, in Li_nH_n before the reaction. The H_2 molecule stays near the $Li_nH_{n-1}NH_2$ cluster, i.e., weakly adsorbs to the cluster.

From these results, we can say that the geometrical reaction processes for $n = 1$–4 are similar to each other, though the N–H–H angle takes a bit smaller value for $n = 1$.

In Fig. 3 we show the potential energy change during the reaction. The x-axis shows, from left to right, the sum of the energies of isolated Li_nH_n cluster and isolated NH_3 molecule ($Li_nH_n + NH_3$), the energy minimum of Li_nH_n and NH_3 where NH_3 stays on Li_nH_n (Li_nH_n–NH_3), The energy maximum during the H_2 formation (transition state), the energy minimum of $Li_nH_{n-1}NH_2$ and H_2 where H_2 stays on $Li_nH_{n-1}NH_2$ ($Li_nH_{n-1}NH_2$–H_2), and the sum of the energies of isolated $Li_nH_{n-1}NH_2$ cluster and isolated H_2 molecule ($Li_nH_{n-1}NH_2 + H_2$), respectively. The broken line shows the energy of LiH (1 0 0) surface and NH_3 before the reaction. We take the energies of $Li_nH_2 + NH_3$ as the origin of the energy.

We can see that the changes of the total energy of the reaction are $\Delta E = 0.44$–0.72 eV. These energies are similar to the change of enthalpy estimated by the experiment [3], $\Delta H \simeq 50$ kJ/mol (corresponding to about 0.5 eV). The adsorption energies of NH_3 on Li_nH_n (Li_nH_n–NH_3) are deeper (~0.65–0.94 eV) than that of NH_3 on LiH surface (~0.34 eV) and the depth of the energies become deeper with decreasing n. The adsorption energies of H_2 on $Li_nH_{n-1}NH_2$ (difference between $Li_nH_{n-1}NH_2$–H_2 and $Li_nH_{n-1}NH_2 + H_2$) are small (~ 0.06–0.13 eV). It means that the H_2 molecule can easily desorbed from the $Li_nH_{n-1}NH_2$ cluster after the formation of the H_2 molecule.

By comparing the energy during the reaction with $n = 1$ in the present result and that by Kar et al. [4] we can see that the overall form of the energy is similar to each other, though there are some difference between the values of the energies (about 0.1–0.2 eV). We can regard that these quantitative differences in energies come from the different basis set.

The energies of transition state is lower than that of $Li_nH_n + NH_3$ when $n \leq 3$ and higher when $n = 4$. However, it does not mean that the system immediately goes over the transition state by the adsorption energy of NH_3 on Li_nH_n, since, in this calculation, the energy of transition state is related to only a degree of freedom, i.e., H–H distance, while there are many degrees of freedom in the systems and the contribution of the adsorption energy to a degree of freedom is small.

In Fig. 4 we show the relation between potential energy and H–H distance (the interatomic distance between two H atoms which form H_2 dimer) during the reaction. In this figure the origin of the energy is that of Li_nH_n–NH_3. (Note that the origin of the energy is that of $Li_nH_n + NH_3$ in Fig. 3.) The left side of the figure corresponds to Li_nH_{n-1}–H_2 before the reaction in Fig. 3 and the right side (out of the figure) corresponds to Li_nH_n–NH_3 after the reaction in Fig. 3. The points where energy takes maximum value corresponds to transition state and the energy of this point corresponds to the activation energy.

From Fig. 4, we can see that the activation energy takes smallest value when $n = 2$ (~ 0.35 eV), and takes larger value when n is larger

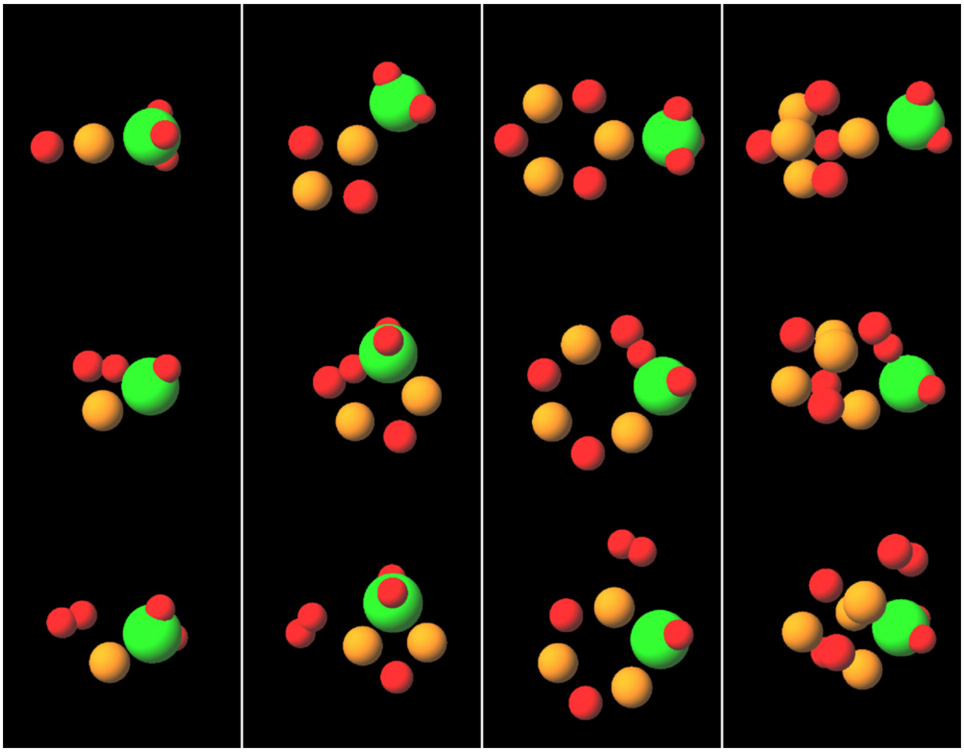

Fig. 2. Snapshots of the H_2 desorption from Li_nH_n cluster and NH_3. The red balls show H atoms, the orange balls show Li atoms, and green balls show N atoms. The figures show, from left to right, $n = 1, 2, 3, 4$. The top figures show the snapshots at the energy minimum before the reaction (Li_nH_n–NH_3), the middle figures show these at the transition state, and the bottom figures show these at the energy minimum after the reaction (Li_nH_{n-1}–NH_3) (For interpretation of references to color in this figure legend, the reader is referred to the web version of this article.).

or smaller than 2 (∼ 0.52, 0.60 and 0.96 eV for $n = 1, 3$ and 4, respectively). The energy change of the system with $n = 4$ is similar to that of the system with LiH surface. The energies of Li_nH_{n-1}–H_2 after the reaction are larger than that of Li_nH_n–NH_3 before the reaction when $n = 1$, 4, and smaller when $n = 2$, 3. It means that the cluster size with $n = 2$, 3 is favorable to react. The potential barrier of the reverse reaction is considerably small when $n = 1$ while it takes relatively higher value when $n \geq 2$. The position (H–H distance) of transition state also depends on n. The position of transition state takes the longest value when $n = 2$, and takes shorter value when n is apart from 2.

The ball-milled LiH, which has high reactivity with NH_3 [18], may have many disordered structures corresponding to Li_2H_2 cluster on its surface. Impurities may also make disordered structures on LiH surface. An impurity that makes a disordered structure similar to Li_2H_2 cluster on LiH surface should increase the reactivity of LiH with NH_3.

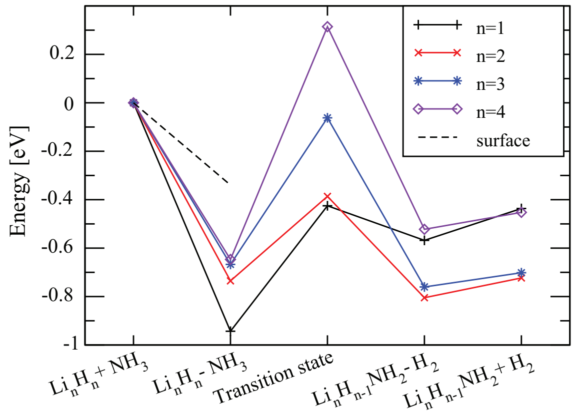

Fig. 3. The energy change during the reaction. The *x*-axis shows, from left to right, the sum of the energies of isolated Li_nH_n cluster and isolated NH_3 molecule ($Li_nH_n + NH_3$), the energy minimum of Li_nH_n and NH_3 where NH_3 stays on Li_nH_n (Li_nH_n–NH_3), The energy maximum during the H_2 formation (transition state), the energy minimum of $Li_nH_{n-1}NH_2$ and H_2 where H_2 stays on $Li_nH_{n-1}NH_2$ ($Li_nH_{n-1}NH_2$–H_2), and the sum of the energies of isolated $Li_nH_{n-1}NH_2$ cluster and isolated H_2 molecule ($Li_nH_{n-1}NH_2 + H_2$), respectively. The broken line shows the energy of LiH (1 0 0) surface and NH_3 before the reaction. We take the energies of $Li_nH_2 + NH_3$ as the origin of the energy.

4. Summary

We have performed *ab initio* calculations on the H_2 desorption from Li_nH_n cluster ($n = 1$–4) and NH_3. Though the geometrical reac-

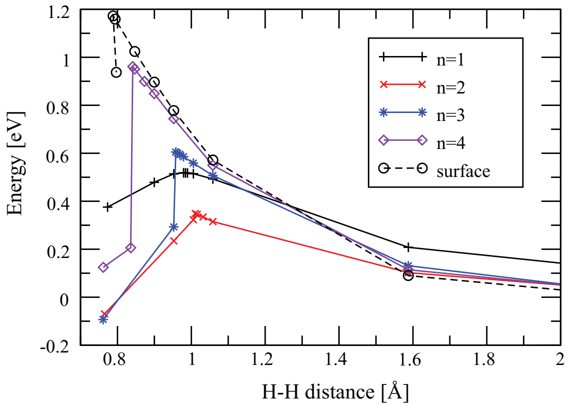

Fig. 4. The H–H distance dependence of the potential energy. The left side of the figure corresponds to Li_nH_{n-1}–H_2 before the reaction in Fig. 3 and the right side (out of the figure) corresponds to Li_nH_n–NH_3 after the reaction in Fig. 3. The origin of the energy is that of Li_nH_n–NH_3. (Note that the origin of the energy is $Li_nH_n + NH_3$ in Fig. 3.)

tion processes are similar to each other, the energy changes during the H_2 desorption reaction process are strongly depend on the cluster size. Since the activation energy of H_2 desorption takes smallest value when $n=2$, we can regard that one of the possible reaction processes is that a disordered structure on LiH surface similar to Li_2H_2 cluster reacts with an NH_3 molecule.

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