Generating H₂ from a H₂O molecule by catalysis using a small Al₆Cu cluster

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ABSTRACT

Only one H atom is extracted from a single H₂O molecule in a usual reaction for hydrogen generation. In this study, a three-step reaction has been identified for completely extracting H₂ from H₂O molecule with the catalysis of a small Al₆Cu cluster, based on the first principles calculations. All the reactants, products, and transition states are determined by optimization calculation and confirmed by frequency analysis. The intrinsic reaction coordinate is also calculated to validate the reaction process. Results show that the whole reaction is an endothermic reaction. The charge distribution is used to understand the novel reaction. It is found that Al₆Cu cluster can strongly capture H₂O molecule and extract the H₂ molecule completely, which may present a more efficient way to generate H₂ from a single H₂O molecule.

Keywords: H₂ generation, H₂O molecule, Al₆Si cluster, catalysis

1. Introduction

To build a renewable energy system is one of the most critical issues for the sustainable development of the mankind society and the natural environment. The practical new energy source requires a renewable fuel to replace the traditional energy carrier.

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Hydrogen is definitely an ideal fuel for this goal. Therefore, effective methods of hydrogen generation and storage have attracted considerable attention [1–3]. Hydrogen is considered as a clean alternative energy carrier because of its efficiency, abundance, and environmental friendliness [4]. Hydrogen also causes no pollution and produces almost threefold the gravimetric heat of combustion of gasoline [5–9]. Hydrogen generation has been extensively investigated by the reaction of aluminum-based system with water [10–28]. Russo *et al.* [13] studied the dynamics associated with the dissociation of water on an aluminum nanocluster using the ReaxFF reactive force field. Gai *et al.* [15] investigated hydrogen generation by the reaction of pure aluminum powder in water with the addition of $\text{Al}(\text{OH})_3$, $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$, or TiO_2 at mild temperatures. Wang *et al.* [16] investigated the production of hydrogen from aluminum and its alloy powder with aqueous alkaline solutions. Uehara *et al.* [17] found that hydrogen gas can be generated in the wet cutting of aluminum and its alloys during a chemical reaction between the fresh surface of aluminum and water. Fan *et al.* [23] presented an effective method for producing hydrogen via the hydrolysis of milled Al–Bi–hydride (or salts) in pure water at room temperature. Zhao *et al.* [26] have reported that the hydrogen can be generated by splitting water with Al–Ca alloy. Chai *et al.* [27] investigated hydrogen generation using the reaction between aluminum and water. They explored the effect of CoCl_2 and NiCl_2 on aluminum water reaction, and found that the formation of the amorphous Co catalyst with high specific surface area plays an important role in the aluminum water reaction. An experiment conducted by Liu *et al.* also shows that the hydrolysis of aluminum powder can be efficiently improved by milling with hydrides. [28]. Therefore, aluminum may be the most promising candidate for hydrogen

production.

The microscopic mechanism of the reaction between aluminum cluster and H₂O molecule has been explored in some theoretical studies [29–33]. The intrinsic reaction coordinate (IRC) is obtained for H₂O molecules, which dissociate into H₂ on aluminum clusters. For example, Khanna *et al.* [30] investigated the reaction of multiple active sites of Al₁₆[−], Al₁₇[−], and Al₁₈[−], which resulted in the production of H₂ from water, and found that the reactions of the metal clusters with small molecules often depend on cluster size. Li *et al.* [31] systematically examined the splitting pathway of one to two H₂O molecules in Al₁₆M (M = Al, Mg, and Bi) clusters to demonstrate the effect of metal doping (Mg and Bi) on aluminum hydrolysis in water. Reber *et al.* [32] examined the reactions of Al_n[−] + H₂O (where $n=7-18$), and showed how the complementary active sites may be best identified. Gas-phase reaction experiments on size-selected Al_n⁺ ($n = 3-19$) and H₂O have been reported [33], in which the products Al_nO⁺ and Al_n(H₂O)⁺ are detected. The production of Al_nO⁺ implies H₂ generation. The results of both experimental and theoretical studies show that H₂ can be generated using Al clusters comprising their cations and anions.

However, a few studies have focused on doped Al clusters. In particular, generating complete H₂ using only one water molecule is rarely reported. Only Arakawa *et al.* [33] reported the generation of H₂ with Al_n cations, but the mechanism is unclear. Therefore, we perform calculations to explore the mechanism for complete generation of the H₂ from a single H₂O molecule. Based on density functional theory (DFT) calculations, we have found that two H atoms can be extracted from one H₂O molecule in a three-step reaction by the catalysis of the Al₆Cu cluster. The reactant, product, and transition state (TS) are

optimized and the reaction mechanism is analyzed.

2. Computational methods

First principles calculations are performed with the hybrid functional DFT (B3LYP) [34] implemented in the Gaussian 09 program [35]. B3LYP is a gradient-corrected hybrid DFT with exchange-correlation functional in Becke's three-parameter form, which includes a mixture of Hartree–Fock exchange with the VWN functional III for local correlation and LYP terms for non-local correlation. The mixed basis set of the 6–31G (d, p) is adopted. Geometry optimization and frequency calculation of all stationary points (reactants, products, and TS) for the reaction of H₂O molecule and Al₆Cu clusters are performed at the same theoretical level. Initially, the isomers of Al₆Cu are optimized. Then, the adsorption sites are chosen and the H₂O molecule is placed to construct the adsorption complex, which is the reactant of the first reaction step. One H₂ molecule and a separate O on Al₆Cu is the product of the last reaction step. After the reactant and product are optimized and their energy stability has been confirmed with harmonic frequency analysis, the TS is searched by using the QST2 method. The obtained TS is confirmed with TS optimization algorithm and another frequency calculation. All structures are fully optimized to local minima except for the TSs that are optimized with the constrained optimizations. Vibrational frequencies are used to confirm the minima geometries and the TS. Intrinsic reaction coordinate (IRC) calculations are performed at the same level to confirm the connection of the product and the reactant. Similarly, more TSs have been found, and the entire reaction path has been constructed. The activation energy ($E_{\text{activation}}$) or energy barrier for each reaction step is calculated according to the following formula:

$$E_{\text{activation}}=E(\text{TS})-E(\text{reactant}) \quad (1)$$

To determine the effect of the temperature on the $\text{H}_2\text{O}@\text{Al}_6\text{Cu}$ complex and the final product $\text{H}_2@\text{Al}_6\text{CuO}$, we performed molecular dynamics simulations using the atom centered density matrix propagation molecular dynamics model at 300 K, using the optimized structure as the initial structure. The time step is 0.1 fs and the total simulation time reaches 0.5 ps (5000 time steps). All calculations are convergent to the default criterion of Gaussian 09. The standard self-consistent energy convergence in the calculation is 1.0×10^{-6} Hartree.

3. Results and discussion

3.1. Al_6Cu Cluster

The stable isomers of Al_6Cu cluster are searched. The obtained structure is shown in Fig. 1(a). The figure displays that Cu atom is in the center of the planar hexagon formed by six Al atoms, which is obviously different from Al_6Si [36] and Al_6C [37] clusters where the obvious three-dimensional structure comprises all the atoms.

Binding energy (E_b) is the energy necessary to dissociate a cluster into separate atoms completely; E_b is an index of the energy stability of a cluster. Therefore, we use E_b to evaluate the stability of the Al_6Cu cluster. E_b is calculated using:

$$E_b=E(\text{Al}_6\text{Cu}) - 6E(\text{Al}) - E(\text{Cu}) \quad (2)$$

where $E(\text{Al}_6\text{Cu})$ is the total energy of the Al_6Cu ; $E(\text{Al})$ and $E(\text{Cu})$ are the energy of single Al and Cu atom, respectively. The absolute value of the calculated binding energy (E_b) of Al_6Cu cluster is -13.5704 eV, which is larger than that (-12.42 eV) of the pure cluster Al_7 [37] but smaller than that of Al_6Si (about -14.77 eV) [36] and Al_6C (about

−16.32 eV) [37]. Cu atom remarkably increases the stability of the pure cluster.

Experimentally, the Al_6Cu cluster could be generated by a magnetron-sputter cluster-ion source and thermalized through collisions with N_2 gas cooled by liquid nitrogen. According to the reaction $\text{Al}_6\text{Cu} + \text{H}_2\text{O} \rightarrow \text{O@Al}_6\text{Cu} + \text{H}_2$, $\text{O@Al}_6\text{Cu}$ and/or $\text{H}_2\text{O@Al}_6\text{Cu}$ could be observed as major reaction products to estimate the generation ratio of H_2 ; the details can be found elsewhere [33].

3.2. Adsorption of a H_2O molecule on the isomers of Al_6Cu cluster

The adsorption of a H_2O molecule on Al_6Cu cluster is the first step to capture H_2O molecule. The stable structure of the $\text{H}_2\text{O@Al}_6\text{Cu}$ complex is optimized, as shown in Fig. 1(b). The energy stability has been confirmed with frequency analysis. The adsorption energy (E_a) can be used to evaluate the adsorption strength or the capture ability of the Al_6Cu cluster; E_a is defined as

$$E_a = E(\text{H}_2\text{O@Al}_6\text{Cu}) - E(\text{Al}_6\text{Cu}) - E(\text{H}_2\text{O}) \quad (3)$$

where $E(\text{H}_2\text{O@Al}_6\text{Cu})$ is the energy of the adsorption system, $E(\text{Al}_6\text{Cu})$ is the energy of the Al_6Cu cluster, and $E(\text{H}_2\text{O})$ is the energy of a free H_2O molecule. The present adsorption energy for H_2O molecule on Al_6Cu cluster is −0.4605 eV, which is smaller than that (−0.7098 eV) on Al_{17} cluster calculated by Li *et al* [31], implying that the reactant could not be significantly changed at room temperature. The calculated adsorption energy of $\text{H}_2\text{O@Al}_7^-$ is only −0.3429 eV. Thus, the adsorption energy of Al_6Cu cluster is much stronger than that of Al_7^- cluster; consequently, Cu-doped aluminum cluster has obviously larger adsorption energy. To determine the effect of temperature on the complex structure of Al_6Cu and H_2O , we performed molecular dynamics simulation at 300 K using the

obtained structures as the initial structure. The result ‘b’ in Fig. 2 shows that the distance (D_c) between the geometric centers of Al_6Cu cluster and that of H_2O molecule increases (from $4.30\text{\AA}$ to final $6.72\text{\AA}$) with time. We also perform another simulation with the initial structure of the H_2O molecule far away from Al_6Cu . The result ‘a’ in Fig. 2 shows that the far H_2O molecule is close to the Al_6Cu cluster, and the final D_c is also approximately $6.72\text{\AA}$. These results imply that Al_6Cu cluster can adsorb H_2O molecule and provide the first reactant structure at 300 K, although the equilibrium D_c becomes larger.

To understand the capture ability and favorable adsorption sites for the H_2O molecule, we analyzed the atomic polar tensors (APT) charge of Al_6Cu cluster, and that of the Al_7^- cluster as the counterpart. Careful examination of the charge on each atom indicates charge transfer between H_2O molecule and the clusters because the total charge on H_2O molecule is non-zero. The results in Fig. 3 show that for $\text{H}_2\text{O}@\text{Al}_7^-$, all the Al atoms have negative charge and one of H atom is charged with $+0.202e$ for an H_2O molecule that is close to the Al atom with $-0.110e$ of charge. For the Al_6Cu cluster, a $+0.111e$ charge is detected on one of the Al atoms because of the doped Cu atom, which adsorbs the O atom charged with $0.535e$ in the H_2O molecule. Therefore, the adsorption energy between H_2O molecule and Al_6Cu cluster is obviously stronger than that between H_2O molecule and Al_7^- . It also means that the coulomb interaction is responsible for the adsorption energy and the doped Cu atom significantly increases the ability of the cluster to capture H_2O molecule.

3.3. *H + OH product on the Al_6Cu cluster*

The whole reaction path for H_2 generation on the Al_6Cu cluster is presented in Fig. 4. First, the product $\text{H}+\text{OH}$ is considered as in the previous investigations [30, 31]. The

energy stable geometry of H+OH (“B” in Fig. 4) on the Al₆Cu cluster has been obtained (Fig. 4), and confirmed by frequency analysis. We also have obtained the TS using the QST2 algorithm. Then, both optimizations with TS algorithm and frequency calculation are carried out to confirm the TS (TS1 in Fig. 4). The barrier is 0.5517 eV and the imaginary frequency of TS1 reaches -1201.0 cm^{-1} . Starting from TS1, we optimize the reaction path with IRC algorithm.

3.4. *H₂ + O product on the Al₆Cu cluster*

Interestingly, another product O + H₂ (“D” in Fig. 4) on the Al₆Cu has been found. Its energy is 2.4821 eV higher than that of the structure “B”. However, the released energy of the first reaction reaches 2.4740 eV, which is slightly less than the energy barrier between “B” and TS3. The adsorption of the final product H₂@Al₆CuO is 0.1464 eV. Molecular dynamics simulation at 300 K is performed using the structure of the final product from the reaction path to determine the temperature effect on the product. The result in Fig. 5 demonstrates that the distance (D_c) between geometric center of H₂ and Al₆CuO cluster increases with the duration of simulation, implying that H₂ can be directly be released. To explore the relationship between the structure “D” and the reactant structure “B”, we searched the TS with the new reactant and product. A new TS (i.e., TS3 in Fig. 4), with different geometry and energy from those of TS1, is obtained. We performed IRC calculations after confirming the TS (i.e., TS3) by frequency analysis. Furthermore, another H+OH geometry (“C” in Fig. 4) on the Al₆Cu is found, with energy that is 0.3958 eV higher than that of B. Further calculations show that the structures “B” and “C” are connected by a lower TS (i.e., TS2 in Fig. 4). The barrier is only 0.6697 eV, implicating

that the transition from the end of extracting one H atom to the start of extracting the second H atom is practicable. The barrier of TS3 is 2.8585 eV, which means that the extraction of the second H atom needs more energy than that of the first one. However, the energy of TS3 in Table 1 is 0.7803 eV higher than that of TS1. Considering the conservation of the system, the total energy to trigger the whole reaction is the first barrier plus the additional energy of the last barrier above the first barrier. By using Table 1, the calculated total energy is 1.3321 eV. We also noted that the last reaction releases energy of 0.7722 eV after overcoming the TS. The energy breaks the $\text{H}_2+\text{O}@\text{Al}_6\text{Cu}$ complex into H_2 and $\text{O}@\text{Al}_6\text{Cu}$ cluster, which means that the triggering energy of 1.3321 eV can extract a free H_2 from a H_2O molecule. Thus, the Al_6Cu cluster plays a remarkable role in the catalysis of the reaction for H_2 generation from water molecule.

We calculated the APT charges for “B” and “C” structures (Fig. 6). An interesting charge distribution is the negative charge of the separate H atom, which results in a +0.497e charge on the Al atom (labeled with 2 in the figure). The positive charged Al atom (labeled with 1) then adsorbs the negative O atom of OH radical. As a result, the OH radical approaches a Al (labeled with 1 in the figure) and form a new structure “C” with more positive charge on the Al atom (increase from +0.097 to +0.552e). Therefore, the change of the charge on atoms alters of the electrostatic interactions between Al atom and OH radical, which further induces the movement of OH. Finally, a new structure “C” formed as a reactant for the next reaction, which extracts the second H atom to form the H_2 molecule.

4. Conclusions

In conclusion, we identified the reaction paths for generation of an H₂ molecule from one H₂O molecule via catalysis with a small Al₆Cu cluster. The extraction of H₂ is completed with two reactions. The energy barrier of the first one is 0.5517 eV and that of the second one is 2.858 eV. The product of the first reaction can transit to the reactant of the second reaction by overcoming a 0.6697 eV barrier. The H₂ molecule is obtained with a three-step reaction. Considering the conservation of the system, the total energy to trigger the whole reaction and to release a free H₂ molecule is 1.3321 eV. The reactions show close relationship with the charge distribution of the Al₆Cu cluster. The dopant Cu atom is responsible for the increase of the ability of the Al₆Cu cluster to capture H₂O before reaction and the suitable charge distribution to support the two reactions. Molecular dynamics simulation for both the reactant and product shows that 300 K is a favorable temperature for the reaction, because the H₂O molecule can be caught and the H₂ molecule can be directly released at 300 K. The present findings provide a new insight into the release of H₂ from H₂O molecule via catalysis with Al₆Cu cluster, which is a promising way to produce hydrogen.

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Figure captions

Fig. 1. Stable structures of Al_6Cu and a H_2O molecule adsorbed on Al_6Cu cluster.

Fig. 2. Distance D_c (in Å) between the geometric center of Al_6Cu cluster and H_2O molecule vs. the simulation step.

Fig. 3. Atomic polar tensor charges of H_2O adsorbed on Al_6Cu and Al_7^- cluster.

Fig. 4. The reaction path for H_2 generation catalyzed by Al_6Cu cluster.

Fig. 5. Distance D_c (in Å) between the geometric center of Al_6CuO cluster and H_2 molecule vs. the simulation step.

Fig. 6. Atomic polar tensor charges for “B” and “C” structures.

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Fig. 3. Atomic polar tensor charges of H₂O adsorbed on Al₆Cu and Al₇⁻ cluster.

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Fig. 5. Distance D_c (in Å) between the geometric center of Al_6CuO cluster and H_2 molecule vs. the simulation step.

Fig. 6. Atomic polar tensor charges for “B” and “C” structures.

Table 1. Bond length and energy for the relative structures

Cluster	H–O (Å)	H–O (Å)	H–H (Å)	Energy (eV)
A	0.96949	0.96973	1.57197	0
TS1	1.19060	0.97356	1.80529	0.5518
B	2.71882	0.96672	2.88688	−1.9222
TS2	3.20628	0.96233	3.26875	−1.2525
C	4.73258	0.96155	4.61329	−1.5264
TS3	2.14931	1.14209	1.00815	1.3321
D	3.11878	2.37137	0.74746	0.5599