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Generating H_2 from a H_2O molecule by catalysis using a small Al_6Cu cluster

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ABSTRACT

Only one H atom is extracted from a single H_2O molecule in a usual reaction for hydrogen generation. In this study, a three-step reaction has been identified for completely extracting H_2 from H_2O molecule with the catalysis of a small Al_6Cu 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 Al_6Cu cluster can strongly capture H_2O molecule and extract the H_2 molecule completely, which may present a more efficient way to generate H_2 from a single H_2O molecule.

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. 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 $Al(OH)_3$, γ-Al_2O_3, α-Al_2O_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 H_2O molecule has been explored in some theoretical studies [29–33]. The intrinsic reaction coordinate (IRC) is obtained for H_2O molecules, which dissociate into H_2 on aluminum clusters. For example, Khanna et al. [30] investigated the reaction of multiple active sites of Al_{16}^-, Al_{17}^-, and Al_{18}^-, which resulted in the production of H_2 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 H_2O molecules in $Al_{16}M$ (M = Al, Mg, and Bi) clusters to demonstrate the

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effect of metal doping (Mg and Bi) on aluminum hydrolysis in water. Reber et al. [32] examined the reactions of $Al_n^- + H_2O$ (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 H_2O have been reported [33], in which the products Al_nO^+ and $Al_n(H_2O)^+$ are detected. The production of Al_nO^+ implies H_2 generation. The results of both experimental and theoretical studies show that H_2 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 H_2 using only one water molecule is rarely reported. Only Arakawa et al. [33] reported the generation of H_2 with Al_n cations, but the mechanism is unclear. Therefore, we perform calculations to explore the mechanism for complete generation of the H_2 from a single H_2O molecule. Based on density functional theory (DFT) calculations, we have found that two H atoms can be extracted from one H_2O molecule in a three-step reaction by the catalysis of the Al_6Cu 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 Vosko, Wilk and Nusair (VWN) functional III for local correlation and the correlation functional of Lee, Yang, and Parr (LYP) 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 H_2O molecule and Al_6Cu cluster are performed at the same theoretical level. Initially, the isomers of Al_6Cu are optimized. Then, the adsorption sites are chosen and the H_2O molecule is placed to construct the adsorption complex, which is the reactant of the first reaction step. One H_2 molecule and a separate O on Al_6Cu 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 quadratic synchronous transit (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 ($E_{activation}$) or energy barrier for each reaction step is calculated according to the following formula:

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

To determine the effect of the temperature on the $H_2O@Al_6Cu$ complex and the final product $H_2@Al_6CuO$, 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:

$$E_b = E(Al_6Cu) - 6E(Al) - E(Cu) \quad (2)$$

where $E(Al_6Cu)$ is the total energy of the Al_6Cu; $E(Al)$ and $E(Cu)$ 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 $Al_6Cu + H_2O \rightarrow O@Al_6Cu + H_2$, $O@Al_6Cu$ and/or $H_2O@Al_6Cu$ 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 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 $H_2O@Al_6Cu$ 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

$$E_a = E(H_2O@Al_6Cu) - E(Al_6Cu) - E(H_2O) \quad (3)$$

where $E(H_2O@Al_6Cu)$ is the energy of the adsorption system, $E(Al_6Cu)$ is the energy of the Al_6Cu cluster, and $E(H_2O)$ is the energy of a free H_2O molecule. The present adsorption energy for H_2O

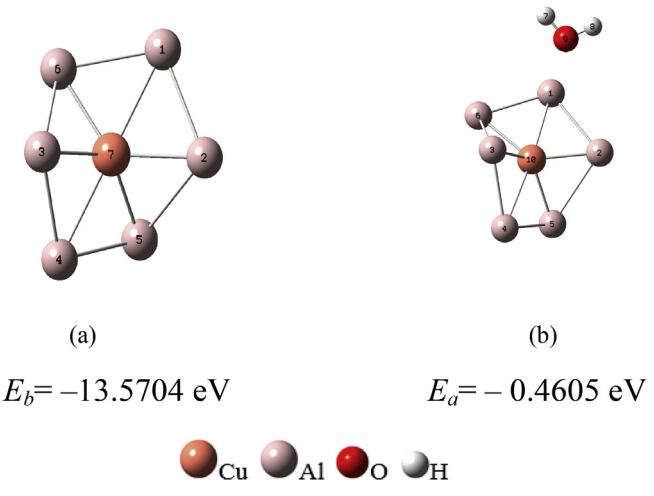

Fig. 1. Stable structures of Al_6Cu and a H_2O molecule adsorbed on Al_6Cu cluster.