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Mechanisms of H_2 generation for metal doped $Al_{16}M$ (M = Mg and Bi) clusters in water

Fen Li [a,c], *Lixian Sun* [a,b,*], *Jijun Zhao* [c,**], *Fen Xu* [b], *Huai-Ying Zhou* [b], *Qing-Ming Zhang* [d], *Feng-Lei Huang* [d]

[a] *Materials and Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Dalian 116023, China*
[b] *Faculty of Material Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, China*
[c] *College of Advanced Science and Technology, Dalian University of Technology, 116024, China*
[d] *State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China*

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ABSTRACT

We have systematically investigated the hydrolysis mechanism of metal doped $Al_{16}M$ (M = Al, Mg and Bi) clusters with H_2O molecules and proposed a reasonable elucidation for the experimentally observed fast H_2 generation rate and high H_2 yield in the Al–Bi based composite. Mg and Bi showed negative effect on the dissociation process of the first H_2O molecule, but accelerated further H_2 generation process. The investigation of persistent hydrolysis reactions demonstrated that the proton-transfer way makes the aluminum–water reaction a lasting process in the long-term H_2 generation in existence of Bi atom, which explains not only the previously observed fast H_2 generation rate but also high H_2 yields in the Bi added Al powder. Our experimental results of hydrogen generation form Al–Bi (Mg) mixture and water are in good agreement with the theory prediction. The facilitated hydrolysis reaction in $Al_{16}Bi$ cluster is attributed to the weakened hydroxide adsorption with the presence of Bi in the aluminum cluster, which is the key factor to accelerate the proton-transfer process.

1. Introduction

Hydrogen-based fuel cells have been wildly accepted as a promising system for future H_2-propelled vehicles, stationary and mobile applications in recent years [1]. The environment-friendly, safe, and cost-effective way to generate and store hydrogen has attracted much attention, due to the fossil fuel depletion and the undergoing air pollution. Firstly, the H_2 has to be manufactured for the development of hydrogen economy. As an advanced way of H_2 production, the reaction of metal with water has been extensively investigated [2–6]. Among those metals, aluminum was proposed to be the most promising candidate for hydrogen production [7]. However, the aluminum surface can be easily passivated by the thin coherent, adhering oxide coating, which leads to low reactivity as well as poor kinetic of the Al–H_2O system [8,9].

Recently, there are great deals of studies focusing on continuous facilitated hydrogen generation by the reaction of aluminum-based system with water [7,10–17]. It was found that ball milling the aluminum powder with the salts (especially NaCl and KCl) can induce localized pitting and rupture of the aluminum layer on the surface [10–15]. Apart from serving

* *Corresponding author*. Faculty of Material Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, China. Tel./fax: +86 411 84379213.
** *Corresponding author*. Tel.: +86 411 84709748; fax: +86 411 84706100.
E-mail addresses: lxsun@dicp.ac.cn (L. Sun), zhaojj@dlut.edu.cn (J. Zhao).
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as a nano-miller, salts also increased the solution temperature of Al powder during the fabrication and prevented the reoxidation of the fresh aluminum surface [10–15]. Nevertheless, the hydrolysis reaction with the additive of salt exhibits low hydrogen generation rate at the beginning and low hydrogen yield. Another widely adopted effective strategy is mechanical alloying with some elements (Zn, Ca, Ga, Bi, Mg, In, Sn and so on) by ball milling, which can create more defects on the alloy surface [7,16,17]. Fan et al. have found that the optimized alloy can react fast with water at the room temperature and obtained higher hydrogen production via the micro-galvanic cell of Al–Bi composite [16]. Furthermore, by milling with some salt compound, the alloy operated a high hydrogen generation rate and theoretic hydrogen yields.

On the other hand, in order to look insight into the microscopic mechanism of the Al–H_2O reaction, some theory investigations have been performed in silico [18–22]. For the reaction of pure aluminum cluster with water molecules, Khanna et al. have demonstrated that the identical arrangements of multiple active sites in Al_{16}^-, Al_{17}^-, and Al_{18}^- resulted in the production of H_2 from water, which explained the observed size selective reactivity of aluminum cluster anion with water [21]. Furthermore, they have elaborately investigated the favorable adsorption sites of water and the role of complementary active sites in breaking the O–H bond on Al_n ($n = 7$–18) cluster [22]. The mechanism of H_2 generation within aluminum cluster was recognized as the cooperation of two adjacent H atoms bound on the complementary active sites. On the other side, Shimojo et al. have predicted another mechanism with lower activation barrier, in which a pair of Lewis acid and base sites on the Al_n surface preferentially catalyzed hydrogen production by a so called chain of hydrogen-bond switching events [23].

Despite the efforts mentioned above, the reaction mechanism of Al-based alloys and H_2O is insufficiently understood yet. Especially, how did the additive affect the hydrogen generation process in the real reaction? Among those metals, addition of Bi is highly interested in the present investigation since the previously reported fast H_2 generation rate and high H_2 yields in hydrolysis of Al alloy [16]. However, the proposed micro-galvanic mechanism can only account for the fast H_2 generation rate but not for the high H_2 production. There is no reasonable explanation for the explosion of passivated surface which is the key factor to inhibit further hydrolysis reaction. Therefore, in order to deeply elucidate the underlying hydrolysis mechanism and further design more efficient aluminum-based system for H_2 production, we performed first-principles calculation of the reaction mechanism between metal modified Al clusters and H_2O molecules by alloying Bi element with Al cluster. In addition, the reaction between Mg alloyed Al cluster and H_2O molecule has been taken into account for comparison.

2. Computational methods

First-principles calculations were performed using the density functional theory (DFT) implemented in the Gaussian 03 program [24]. We examined the energies and frequencies of Al_{17}, Al_{16}–Mg, Al_{16}–Bi clusters and all stationary points (reactants, products and the transition state) by performing the B3LYP hybrid functional [25]. All the structures were fully optimized to local minima except the transition states are found by constrained optimizations. The mixed basis set of the 6-31G (d, p) was adopted for Al, Mg, H, and O, and the LanL2DZ potential for Bi, respectively [26]. Vibrational frequencies and the intrinsic reaction coordinate (IRC) calculation were performed at the same level to verify the nature of the corresponding stationary point and to determine the zero-point energy (ZPE). The adsorption energy of water was calculated as followed:

$$E_{ads} = E(\text{products}) - E(Al_{16}M) - E(H_2O), \quad (1)$$

where the reactants are the $Al_{16}M$ (M = Al, Mg, and Bi) or otherwise specified. The binding energy of the hydroxide on the metal cluster was calculated as followed:

$$E_b = E(\text{products}) - E(Al_{16}M) - E(OH). \quad (2)$$

The activation energy was defined as:

$$E_a = E(TS) - E(\text{reactant}). \quad (3)$$

In addition, the natural bond orbital (NBO) [27] and the Hirshfeld charge [28] analysis have been carried out to understand the interaction mechanism between $Al_{16}M$ (M = Al, Mg and Bi) clusters and water. The highest energy occupied molecular orbital (HOMO) and the lowest energy unoccupied molecular orbital (LUMO) were adopted for predicting the adsorption and dissociation of H_2O.

3. Results and discussion

3.1. *Reactivity of the $Al_{16}M$ (M = Al, Mg, Bi) clusters with water*

Since the hydrolysis reaction of Al_{17} cluster in water has been profoundly investigated in the previous works, we have built the structural models of $Al_{16}M$ clusters by substituting one Al atom in Al_{17} cluster with other metal atom (M = Mg and Bi) to understand how did metal doping affect the hydrolysis reaction. The possible substitution sites for the M atoms on the clusters have been examined and the energetically favorable ones are displayed in Fig. 1. All these metal atoms occupied the most active site in Al_{17} cluster. One can see that Mg doped cluster preserved the pristine configuration of Al_{17} cluster. However, the configuration of $Al_{16}Bi$ cluster is dramatically distorted, implying that addition of Bi may create some defects and other active sites in the real Al–Bi alloy.

Next, we have calculated the binding energies of H_2O on these clusters, and summarized the results in Table 1. In general, substitution of Al atom with Mg has significantly enhanced the H_2O adsorption and the substitution with Bi has slightly decreased the H_2O adsorption. All of binding energies declined after the ZPE correction but that didn't affect the comparison among these clusters. Therefore, the ZPE correction isn't included in the further calculations. Besides, we have performed the NBO analysis to explore the interactions between the $Al_{16}M$ (M = Al, Mg and Bi) clusters and water molecule. In Fig. 2, the first column shows the LUMO orbital of the $Al_{16}M$ (M = Al, Mg and Bi) clusters. H_2O molecule binds