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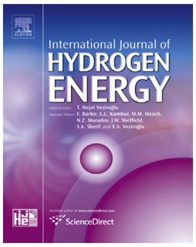

Theoretical investigation of adsorption and dissociation of H_2 on cluster Al_6Si

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A B S T R A C T

Using the density functional theory with the generalized gradient approximation, we have examined the adsorption and dissociation of H_2 on cluster Al_6Si. The stable geometrical structures of both the reactants and the products, the transition states, and the reaction paths for the dissociations are investigated. The results show that the adsorption energies of $H_2@Al_6Si$ are small, which implies they are not suitable for storing H_2 directly. However, the energy barrier for each reaction is found in the range of 0.437–1.154 eV, implicating that Al_6Si can store hydrogen with dissociating the H_2 into separate atoms.

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Introduction

Providing an abundant, clean, and secure renewable energy source is one of the key technological challenges for mankind [1–4]. The environment-friendly, safe, and cost-effective way to generate and store hydrogen has attracted much attention, due to it is no pollution and almost triples the gravimetric heat of combustion of gasoline. As an advanced way of H_2 production, the reaction of aluminum-based system with water has been extensively investigated [5,6]. In order to look insight into the microscopic mechanism of the $Al@H_2O$ reaction, some theoretical investigations have been performed [7,8]. For the reaction of pure aluminum cluster with water molecules, Khanna et al. [9] have demonstrated that the identical arrangements of multiple active sites in Al_{16}^-, Al_{17}^- and Al_{18}^- can result in the production of H_2 from water. Li et al. 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 fast H_2 generation rate observed experimentally [10]. They also suggested a mechanism to produce H_2 with Mg–Bi doped Al_{16} cluster and two reaction paths.

The adsorption and dissociation of hydrogen molecule on clusters are very important for hydrogen storage and hydrogenation reaction in heterogeneous catalysis, which have attracted wide interests [11–14]. Therefore, investigation of the adsorption mechanism for H_2 on clusters and understanding the dissociation reaction have been well performed. The H_2 adsorption and dissociation on a series of free small Pd clusters was reported [15–20]. Liu et al. [21–23] have studied the adsorption and dissociation of H_2 on Pd_n ($n = 4, 6, 13, 19, 55$) clusters using spin-polarized density functional theory (DFT) calculations. The dissociation of H_2 on $(ZrO_2)_n$ (n = 1–6)

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clusters was also theoretically investigated [24]. Pino et al. [25] calculated the transition states and reaction paths for the dissociation of a hydrogen molecule on small aluminum clusters Al_n ($n = 2–6$) using DFT.

Recently, Yang et al. calculated the transition states and reaction paths for the dissociation of a hydrogen molecule on Al_6C [26]. Their results show that the energy barrier for dissociation of H_2 is only 0.300 eV, which implies that Al_6C cluster is a potential candidate for storing Hydrogen. With this in mind, we investigate the adsorption and dissociation of H_2 molecule on Al_6Si cluster to explore more applications of the doped Al clusters. Based on hybrid DFT calculations, the geometrical structures of reactants, products and transition states for the dissociation of H_2 on Al_6Si cluster are calculated and analyzed. The reaction paths connected the reactant and product are optimized.

Computational methods

The calculations are carried out using the hybrid DFT method B3LYP [27] with the split basis sets with polarization functions 6-31G (d, p). Firstly, the isomers of Al_6Si are optimized. Then the adsorption sites are chosen and the H_2 molecule is placed to construct the adsorption systems. After the reactants and products are optimized and their energy stability has been confirmed by harmonic frequency analysis, the transition state (TS) is searched with QST2 method. The obtained transition state is confirmed with TS optimization and frequency calculation again. We then studied the dissociation process using the reaction path following algorithm intrinsic reaction coordinate (IRC) in order to clarify the connection between the reactants, the transition state and the products of the dissociation process. All the calculations are carried out using the GAUSSIAN 03 program [28].

Results and discussion

The geometric structures of Al_6Si

Al_6Si has the same number of atoms and valence electrons as Al_6C. According to the three stable structures of Al_6C reported in the literature [26], we design initial structures of Al_6Si and perform optimization and frequency analysis. We have also obtained three optimized isomers, as is shown in Fig. 1. They are stable in energy because no imaginary frequency has been found for them. From the figure, one can find that the doped Si atom tends to locate on the surface of the cluster but not in the cage of the Al atoms.

The binding energy (BE) is the energy necessary to completely dissociate cluster into separate atoms. Therefore, we use BE to evaluate the stability of the cluster. The calculation formula of BE is:

$$E_b = E(Al_nSi) - nE(Al) - E(Si) \tag{1}$$

where the E (Al_nSi) is the total energies of the Al_nSi, E (Al) and E (Si) are the energy of single Al or Si atom. The BEs of the isomers of Al_6Si cluster are also shown in the Fig. 1. One can find that isomer “b” has the lowest BE among the three isomers, therefore, it is the most stable one. In addition, the lowest energy structure of Al_7 is a triangular prism with one more atom on its side face. It's BE is −12.420 eV at the theoretical level B3LYP/6-31G (d) [26]. However, the absolute value of BE for the lowest energy Al_6Si at the same theoretical level is about 2.000 eV larger than that of Al_7 cluster, which implies that the doped Si atom makes the Al_6Si cluster more stable than the pristine Al_7 cluster.

Adsorption of molecular hydrogen on cluster Al_6Si

For the case of the H_2 molecule adsorbed on Al_6Si, different sites of the cluster surface and different orientations of H_2 molecule are considered as the initial geometrical structures to find the various stable $H_2@Al_6Si$ structures. After optimization and frequency analysis, six stable structures are found and shown in Fig. 2. In the figure, the stable complex $H_2@Al_6Si$ structures from the isomer “a” of Al_6Si are represented with a1–a2, correspondingly, those from isomer “b” and “c” are represented with b1-b2 for, and c1-c2, respectively. One can also find that H_2 can be adsorbed on the top of both Al and Si atoms in the figure.

The adsorption energy is used to evaluate the adsorption strength. It is calculated as

$$E_a = E(H_2@Al_6Si) - E(Al_6Si) - E(H_2) \tag{2}$$

where E ($H_2@Al_6Si$) is the energy of the stabilized adsorption system, E (Al_6Si) is the energy of the Al_6Si cluster, and E (H_2) is the energy of the free H_2 molecule. The adsorption energies of the molecular adsorption configurations are presented in Table 1, which shows that the molecular adsorption of H_2 on Al_6Si is very weak. We can also find E_a of H_2 on Al_6Si is similar to that H_2 on Al_6C [26] but lower than the H_2 on $(ZrO_2)_n$ [24] and Pd_n ($n = 4, 6, 13, 19, 55$) [23].

Among these stabilized adsorption structures of the reactants, the distance between the H_2 and the cluster Al_6Si is about 4.7 Å, and the APT charge analysis shows that the two H atoms are negatively charged. Therefore, the interaction among the H atoms and the cluster Al_6Si in the reactants is not the hydrogen bond well-described by Zhao et al. [29].

Dissociation of molecular hydrogen on cluster Al_6Si

The small *Eas* of these complex structures of $H_2@Al_6Si$ implies that Al_6Si clusters cannot be used directly to store hydrogen. Therefore, we consider the dissociation process of the H_2 molecule on Al_6Si to explore the possibility of storing hydrogen with Al_6Si.

We firstly search the stable structures for the dissociated H_2 (i.e., the two H atoms separate “remotely”) adsorbed on Al_6Si. Using the obtained structures as products and the complex $H_2@Al_6Si$ structures above as reactants, we search the transition state connecting the reactant and product. In general, the most stable dissociation configuration is lower than the molecular adsorption states. Namely, the energy of the product is lower than reactant. Here, we firstly present the dissociation process started from configuration a1, a2 and b1.

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