Na decorated B_6 cluster and its hydrogen storage properties*

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The structures and hydrogen storage properties of sodium atoms decorated B_6 clusters are investigated by the B3LYP method with a 6-311+G (d, p) basis set. For Na_mB_6 ($m = 1$–3) clusters, Na atoms are always inclined to separate far enough from each other and not cluster together on a B_6 cluster surface so that each Na atom has sufficient space to bind hydrogen molecules. The hydrogen storage gravimetric density of a two Na atoms decorated B_6 cluster is 17.91 wt% with an adsorption energy per H_2 molecule (AAE/H_2) of 0.6851 kcal·mol^{-1}. The appropriate AAE/H_2 and preferable gravimetric density of the two Na atoms decorated B_6 cluster complex indicate that it is feasible for hydrogen storage application in ambient conditions.

Keywords: Na_mB_6 ($m = 1$–3) clusters, density functional theory, adsorption energy, hydrogen storage capability

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1. Introduction

Hydrogen is widely viewed as the next generation of energy carrier to replace fossil fuels due to its abundance, high chemical energy and pollution-free burning. However, hydrogen storage is a "bottleneck" for the application of hydrogen as an energy carrier, for storage as gas under high pressure or as liquid at cryogenic temperatures has inherent problems associated with cost, safety and storage capacity. Solid-state materials provide an alternative choice for hydrogen storage, although there are no materials which can currently solve all the questions. For example, Zhang *et al.*[1] reported that alkali metal atom boride systems $LiBH_4$ and $NaBH_4$ can contain relatively high hydrogen concentrations of 18.5% and 10.7%, respectively. Unfortunately, in these metal boron hydrides, hydrogen atoms are held by strong covalent bonds in these systems and dissociating hydrogen requires high temperatures, which will hamper the hydrogen loading and unloading. For storage of hydrogen in molecular form, however, the adsorption energy of molecular hydrogen adsorbed on the material surface might be comparatively weak, which will favor the hydrogen loading and unloading. By this token, the storage of hydrogen in molecular form may be more beneficial than the storage of hydrogen in atomic form. So, the storage of hydrogen in molecular form has attracted much attention.

Early investigations showed that some of the materials, such as graphene, carbon nanotubes and fullerenes, can store hydrogen in molecular form, but later experiments proved otherwise. For instance, Shiraishi *et al.*[2] reported that the hydrogen storage gravimetric density of single-walled carbon nanotubes was only 0.3 wt%; Kajiura *et al.*,[3] reported that the highest storage capacity was 0.43 wt%. Theoretical study also confirmed that a high hydrogen content in pure carbon nanotubes cannot be achieved through weakly physical sorption with Van der Waals interaction.[4]

Recently, theoretical research[5–8] has shown that metal atoms, such as Sc, Ti and Ca, coated on carbon fullerenes and nanotubes substrates can bind hydrogen in molecular form with approximate binding energies of 0.3 eV/H_2 ∼ 0.5 eV/H_2, which are between the physisorption energy and the chemisorptions energy;[9] the gravimetric densities are 2.85 wt% ∼ 8.4 wt%. Hydrogen molecules are trapped around the dispersed doping metal atoms through electrostatic and polarization interactions.

Boron, nitrogen and carbon, neighbors in the periodic table, all possess very rich physical and chemical properties. Bhattacharya *et al.*[10] reported on replacing some carbon atoms with the light elements in carbon nanotubes to obtain a Ti-decorated BC_4N nanotube. Investigations indicate that this material exhibits a higher H-storage capacity (5.6 wt%) than the Ti-decorated carbon nanotube (5.3 wt%).[6] Theoretically, in order to obtain higher gravimetric density of H-storage, some investigators have extended the research from carbon nanotubes (fullerenes) to boron nanotubes (fullerenes) and evaluated the H-storage capability of metal atoms coated on boron fullerenes using theoretical methods. For example, Li *et al.*[11] designed a type of hydrogen storage medium, chained TiB_x. They found that the most stable TiB_5 chain can reach 7.3% hydrogen storage capacity with an average

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binding energy of 43.7 kJ·mol^{-1} per H_2. Li *et al.*[12] investigated the hydrogen adsorption and storage in Ca-coated boron fullerenes and nanotubes by means of density functional theory (DFT) computation. They obtained that B_{80} fullerenes coated with 12 Ca atoms can store up to 60 H_2 molecules with a binding energy in the range of 0.12 eV/H_2–0.40 eV/H_2, corresponding to a gravimetric density of 8.2 wt%, while the H-storage capacity in a Ca-coated boron nanotube is 7.6 wt% with a binding energy in the range of 0.10 eV/H_2–0.30 eV/H_2. Wu *et al.*[13] studied the hydrogen adsorption capacity of a metal-coated boron buckyball B_{80} with M = Li, Na, K, Be, Mg, Ca, Sc, Ti and V by DFT approach. They found that the hydrogen adsorption capacities reach up to 9.0 wt% and 7.9 wt% for $B_{80}Ca_{12}$ and $B_{80}Sc_{12}$, respectively.

In order to obtain a sufficiently high gravimetric density, not only the substrate material needs to be lightweight, but also the metal atoms need to be lightweight. More recently, Süleyman *et al.*[14] investigated the hydrogen adsorption properties of light alkali metal (Li, Na and K) doped planar boron sheets. They found that the Li-doped boron sheet is the best option for hydrogen storage, corresponding to a gravimetric density of 10.7 wt% with an average binding energy of about 0.15 eV/H_2.

The preferable gravimetric density and appropriate adsorption energy per H_2 molecule (AAE/H_2) indicate that alkali metal-doped boron-base materials are feasible for hydrogen storage application. Wu *et al.*[15] pointed out that B_6 was a core in $(BCO)_6$. Alexander and Ihsan[16] also proposed that B_6 was a basic unit for constructing larger boron clusters. Inspired by them, in this work, we take the B_6 cluster as a substrate and propose a Na atoms decorated B_6 cluster as one of the hydrogen storage materials. The stable structures of Na_mB_6 (m = 1–3), the interactions between the Na atoms and the B_6 substrate in Na_mB_6 (m = 1–3) and the interactions of H_2 with Na_mB_6 (m = 1–2) in $Na_mB_6 \cdot nH_2$ complex, as well as their hydrogen storage capacities, are discussed in detail.

2. Computational methods

This work is mainly performed by density functional theory (DFT), with Becke's three-parameter exchange and Lee–Yang–Parr correlation functional (B3LYP) on a triple zeta basis set 6-311+G (d, p) using a Gaussian 03 program package.[17] All geometries are fully optimized without any symmetry restriction and are characterized by harmonic vibrational frequency analysis at the same theoretical level after the optimization. The convergence criteria for the gradient, displacement and energy are set to be 0.00045 a.u., 0.0018 Å and 1×10^{-6} a.u. (a.u. is the abbreviation for atomic unit), respectively. The stability of the cluster configurations considered here is assessed by computing the vibrational frequencies under the harmonic approximation with analytical force constants. The AAE/Na and AAE/H_2 are defined as[18,19]

$$E_{\mathrm{AAE/Na}} = [E(B_6) + mE(\mathrm{Na}) - E(\mathrm{Na}_m B_6)]/m, \quad (1)$$

$$E_{\mathrm{AAE/H_2}} = [E(\mathrm{Na}_m B_6) + nE(H_2) - E(\mathrm{Na}_m B_6 \cdot n\mathrm{H_2})]/n, \quad (2)$$

where $E(B_6)$, $E(\mathrm{Na}_m B_6)$, $E(\mathrm{Na}_m B_6 \cdot n\mathrm{H_2})$, $E(\mathrm{Na})$ and $E(H_2)$ are the ground state electronic energies of B_6, $\mathrm{Na}_m B_6$, $\mathrm{Na}_m B_6 \cdot n\mathrm{H_2}$, Na atom and H_2 respectively. The subscripts m and n are the numbers of Na atoms and H_2 molecules, respectively.

3. Results and discussion

3.1. Structures of B_6 and Na_mB_6

Before investigating the hydrogen store capability of $\mathrm{Na}_m B_6$ clusters, we study all possible structures of B_6 clusters. Several of the isomers are shown in Fig. 1. Isomer 1 is the most stable configuration with a quasi-planar structure. Considering it as a basic unit, we first investigate hydrogen adsorption on the pure quasi-planar surface and find that the hydrogen adsorption on its surface exhibits either physical sorption with the weak van der Waals force or chemisorption through the strong covalent bond. This means that pure B_6 is not a good candidate for hydrogen storage directly.

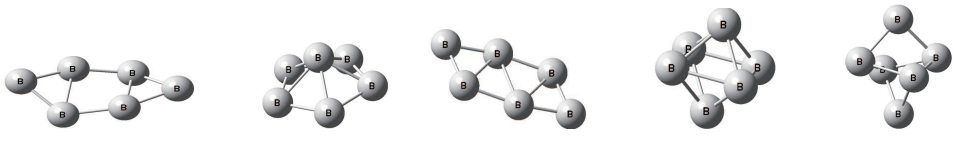


Fig. 1. Optimized structures of B_6 clusters.

Second, we consider that Na atoms are decorated onto the most stable B_6 surface with one, two and three Na atoms, separately. We change the position of Na atoms on the B_6 surface and relax all structures. Full geometry optimizations without symmetry restriction for all the possible patterns are carried out by the B3LYP/6-311+G (d, p) method. The most stable configurations of NaB_6, Na_2B_6 and Na_3B_6 are shown in Fig. 2. From Fig. 2, one can see that the Na atom is inclined to adsorb on one side of the quasi-planar B_6 cluster as a single Na atom on its surface. When two Na atoms are put on its surface, they are apt to be separated on different sides of the quasi-plane, but not symmetrically distributed. As three

Na atoms decorated the B_6 cluster, two Na atoms are loaded in the B_6 plane, the other Na is adsorbed on the side of the plane. The distribution of Na atoms shows that Na atoms always are inclined to separate far enough from each other and do not cluster on B_6 cluster surface so that each Na atom has sufficient space to bind hydrogen molecules. The calculated geometrical parameters of Na_mB_6 ($m = 1$, 2, and 3) clusters are listed in Table 1 along with the AAE/Na.

Table 1. Average distances of Na–B and B–B, adsorption energies of Na, charges on Na atom of Na_mB_6 clusters.

	D_{Na-B}/nm	D_{B-B}/nm	$E_{AAE/Na}$/kcal·mol^{-1}	charges on Na atom /a.u.
B_6	–	0.1631	–	–
NaB_6	0.2798	0.1628	57.3677	0.9356
Na_2B_6	0.2778	0.1620	51.0480	0.8956
Na_3B_6	0.2729	0.1618	42.5772	0.8237

Our calculations show that the Na–B and B–B average distances are 0.2798 nm and 0.1628 nm respectively with the AAE/Na 57.3677 kcal·mol^{-1} as a single Na atom is coated on the B_6 surface. When two Na atoms are decorated, the average distances are 0.2778 nm and 0.1620 nm respectively for Na–B and B–B, with the AAE/Na 51.0480 kcal·mol^{-1}. The average distances are 0.2729 nm and 0.1618 nm for the Na–B and B–B with the AAE/Na 42.5772 kcal·mol^{-1} when three Na atoms are decorated on the B_6 surface. The results indicate that the average bond distances and the AAE/Na decrease gradually with the increase of Na atomic number, but the AAE/Na for Na atom attaching to the substrate is large enough to prevent the Na atoms from clustering on the B_6 cluster surface. Such sufficient space and preferable binding strengths ensure that the Na-coated B_6 clusters can stably exist at room temperature.

Electrostatic interactions are dominant in binding hydrogen molecules to metal atoms. Therefore, it is useful to make a charge analysis to determine the effective charges on the Na atoms. In general, it is impossible to distinguish atoms in a molecule in the quantum-mechanical sense; atomic charges are not observable. However, based on the natural bond orbital (NBO) analysis, the atomic charges can be obtained. Our calculations show that a large number of positive charges exist on each Na atom in the Na_mB_6 clusters ($m = 1$, 2, and 3), owing to the electron donation from B to the empty p orbital of Na and the back-donation from Na s orbital to B, a large number of neat electrons transfer from Na to the B_6 cluster. It indicates that the interaction between Na atoms and the B_6 cluster has a large ionic contribution. The positive charges on the Na atom decrease from 0.9356 a.u. to 0.8237 a.u. (Table 1) in the order of the Na atom number from one to three, which illustrates that the ionic interaction between Na atoms and the B_6 cluster weakens gradually with the increase of Na atom numbers.

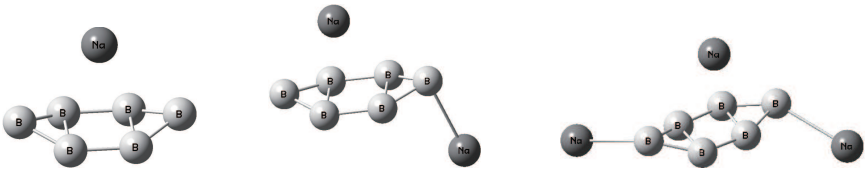


Fig. 2. Optimized structures of Na atoms decorated quasi-planar B_6 clusters.

3.2. Hydrogen molecules adsorption on NaB_6 and Na_2B_6

Constructing larger scale cluster materials with the Na_3B_6 complex may change the structures of boron nanotubes (fullerenes), we do not discuss the hydrogen storage of the Na_3B_6 cluster any more in this subsection. Therefore, we further investigate the hydrogen adsorption properties of NaB_6 and Na_2B_6 clusters, which is mentioned above.

The optimized structures $NaB_6 \cdot nH_2$ ($n = 1$–5) are shown in Fig. 3. When the fifth H_2 molecule is an adsorbed on Na atom, then one H_2 molecule is excluded from the NaB_6 cluster with a Na–H bond length of 0.4740 nm (see Figs. 3–5), which indicates that it can adsorb four hydrogen molecules at most for the single Na atom-decorated B_6 cluster.

The optimized structures of $Na_2B_6 \cdot (nH_2)_2$ ($n = 1$–7) are depicted in Fig. 4. When the seventh H_2 approaches each Na atom, then three hydrogen molecules are ejected from the Na_2B_6 cluster, in which the shortest Na–H bond length is about 0.4598 nm (see subfigs. 4–7 in Fig. 4). It indicates that the Na_2B_6 cluster can capture six pairs of H_2 at most for the double Na atoms-decorated B_6 cluster.

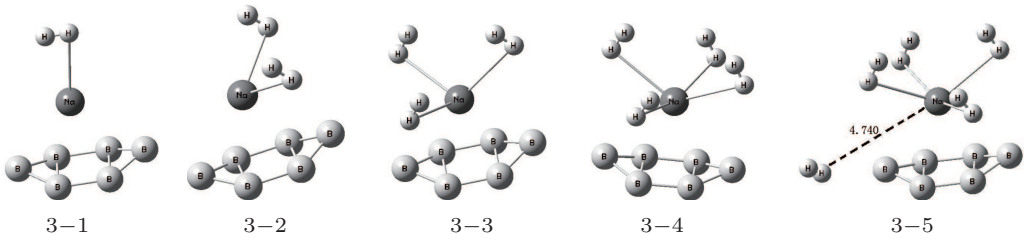


Fig. 3. Optimized adsorbing structures with hydrogen molecules on NaB_6 clusters.

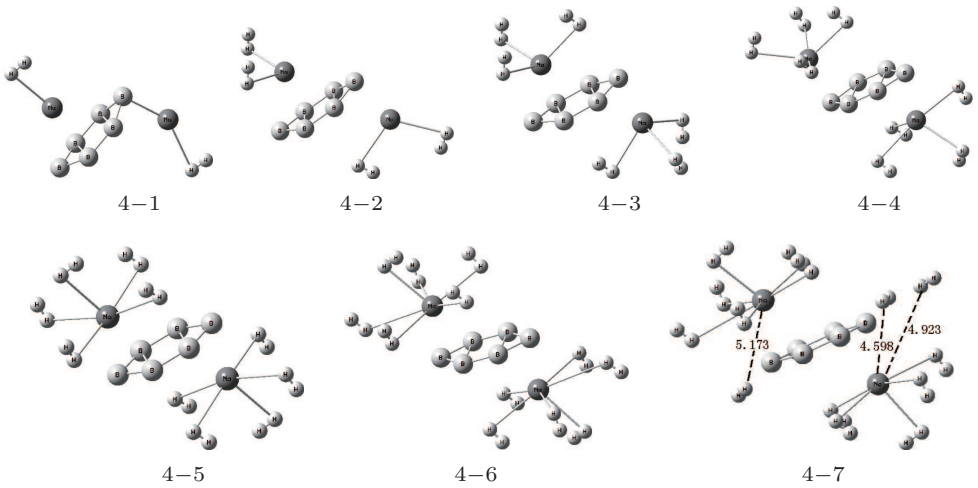


Fig. 4. Optimized adsorbing structures with hydrogen molecules on Na_2B_6 clusters.

The AAE/H_2, the average distances between H_2 and Na, the bond lengths of hydrogen molecules, the average charges on the Na atoms and H_2 molecules for both $NaB_6 \cdot nH_2$ and $Na_2B_6 \cdot nH_2$ are listed in Table 2. From Table 2, one can see that the AAE/H_2 and the average Na–H_2 distance change accordingly as more hydrogen molecules approach Na_mB_6 (m = 1–2), which indicates that the interaction between the Na atom and the H_2 molecules changes gradually with the increase of the H_2 number. The average H–H bond length in $Na_mB_6 \cdot nH_2$ (m = 1–2) is in the range from 0.0747 nm to 0.0748 nm, which is slightly longer than the bond length of an isolated hydrogen molecule (0.0744 nm optimized by B3LYP/6-311+G (d, p)); the average Na–H_2 bond length is in the range of 0.2505 nm–0.2916 nm. The gravimetric density of H_2 stored in Na_2B_6 can reach 17.91% with an AAE/H_2 of 0.6851 kcal·mol^{-1}, in agreement with experimental results of the binding energies between 0.4612 kcal·mol^{-1} and 2.3061 kcal·mol^{-1},[20,21] which allows both adsorption and desorption of hydrogen molecules in ambient conditions.

Table 2. Average distances of Na–H_2 and H–H, adsorption energies per H_2 and charges on Na and H_2 of $Na_mB_6 \cdot nH_2$.

	D_{H2-Na}/nm	D_{H-H}/nm	$E_{AAE/H2}$/kcal·mol^{-1}	charges on H_2/a.u.	charges on Na/a.u.
$NaB_6 \cdot H_2$	0.2505	0.0747	1.5530	0.0081	0.9191
$NaB_6 \cdot 2H_2$	0.2520	0.0748	1.3864	0.0059	0.9047
$NaB_6 \cdot 3H_2$	02565	0.0748	1.2453	0.0075	0.8921
$NaB_6 \cdot 4H_2$	0.2628	0.0747	1.0354	0.0373	0.5900
$Na_2B_6 \cdot 2H_2$	0.2570	0.0747	1.5730	0.0077	0.8922
$Na_2B_6 \cdot 4H_2$	0.2606	0.0748	1.0900	0.0219	0.7943
$Na_2B_6 \cdot 6H_2$	0.2624	0.0748	1.0172	0.0070	0.8841
$Na_2B_6 \cdot 8H_2$	0.2682	0.0747	0.8950	0.0072	0.8754
$Na_2B_6 \cdot 10H_2$	0.2718	0.0748	0.7844	0.0062	0.8766
$Na_2B_6 \cdot 12H_2$	0.2916	0.0747	0.6851	0.0056	0.8755

The interaction mechanism between H_2 and Na-decorated B_6 can be ascribed to the Kubas interaction, induced interaction and the electrostatic interaction.[18,19] The complex of NaB_6 or Na_2B_6 binds H_2 through hybridization between the hydrogen electron orbitals and the Na electron orbitals. When H_2 molecules approach a Na-coated B_6 complex, some electrons from the σ-bonds of H_2 molecules transfer to the empty orbitals of Na atoms. Meanwhile, some electrons from the bonding orbitals of Na atoms transfer to the empty σ^* antibonding orbital of H_2 molecules. The exchange of charge between Na atoms and H_2 molecules, consistent with induced interaction between the Na atoms and the H_2 molecules, causes the electron atmosphere density of the bonding orbital of H_2 molecules to decrease and the electron atmosphere density of the antibonding orbital of H_2 molecules to increase, which weakens the interaction between hydrogen atoms. Then the H–H bond length is elongated, but not broken. The resulting interaction between the H_2 molecules and the Na atoms lies between physisorption and chemisorption limits, which improves the H_2 adsorption on a Na-decorated B_6 cluster remarkably. In addition, each Na atom that possesses a large number of positive charges can capture as many H_2 molecules as possible by the polarization effect, as well as bind the B_6 substrate stably by ionic interaction between Na atoms and the B_6 cluster.

The average charges on Na atoms and H_2 among all the $Na_mB_6 \cdot nH_2$ clusters are listed in Table 2. One can see that a small quantity of charges transfer from H_2 to Na atoms. This is a polarization effect due to the electric field induced around the positively charged Na atom, which results in the fact that each Na atom can capture up to six H_2 molecules in a Na_2B_6 cluster.

4. Conclusions

In this work, the structures and hydrogen adsorption properties of NaB_6 and Na_2B_6 clusters are investigated with the DFT calculations. Due to the charge transfer from Na atoms to the B_6 cluster, the Na atoms strongly attach to the B_6 cluster. All Na atoms are always inclined to separate far enough from each other and not cluster together on the B_6 cluster surface so that each Na atom has sufficient space to bind hydrogen molecules. The electric field induced around the positively charged Na atoms polarizes the H_2 molecules, combined with the Kubas interaction and induced interaction, causes H_2 molecules to be able to bind the Na atoms-decorated B_6 clusters strongly. The hydrogen adsorption gravimetric density of a two Na atoms-decorated B_6 cluster is 17.91 wt% with an AAE/H_2 of 0.6851 kcal·mol^{-1}, which is between the physisorption energy and the chemisorptions energy. Indeed, the hydrogen storage capacity exceeds the target of the U.S. Department of Energy (9 wt% by the year 2015). Both the appropriate AAE/H_2 and the preferable hydrogen adsorption gravimetric density of the two Na atoms-decorated B_6 cluster complex indicate that it is feasible for hydrogen storage application in ambient conditions. Hence, our work would be useful for guiding the design of hydrogen storage materials, which are based on alkali metal–boron clusters.

As a part of this series of work, the investigations of the hydrogen storage capability of a three or more sodium atoms-decorated B_6 cluster are under way.

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