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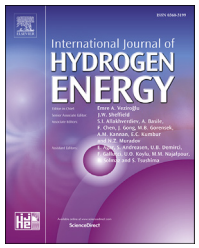

The reversible hydrogen storage abilities of metal Na (Li, K, Ca, Mg, Sc, Ti, Y) decorated all-boron cage B_{28}

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ABSTRACT

The density functional theory is used to study the hydrogen storage abilities of alkali metal Li (Na, K), alkaline-earth metal Mg (Ca), and transition metal Ti (Ti, Sc, Y) decorated B_{28}, which is the possible smallest all-boron cage and contains one hexagonal hole and two octagonal holes. The most stable structure of B_{28} explored by the calypso search is as same as that explored by Zhao et al. [Nanoscale 7(2015)15086]. It is calculated that the hollow sites outside of the cavities should be the most stable for all metals except for Ti. The average adsorption energy of H_2 molecules (E_{ad}) adsorbed by each Na (Ca, K, Mg, Sc, Y and Li) atom outside of the B_{28} cage are in the range from 0.2 to 0.6 eV, which is suitable for hydrogen storage under near-ambient conditions. However, the largest hydrogen gravimetric density (HGD) for the $B_{28}Sc_3$-$12H_2$ structure is smaller than the target of 5.5 wt% by the year 2017 specified by the US Department of Energy (DOE). Therefore, the metal Ti (Sc) decorated all-boron cage B_{28} should not be good candidates for hydrogen storage. The calculated desorption temperature and the molecular dynamic simulation indicate that the $B_{28}M_3$-nH_2 (M = Na, Li, Ca, K, Mg, Y) structures are easy to desorb the H_2 molecules at the room temperature (T = 300 k). Furthermore, the B_{28} cages bridged by the sp^2-terminated B_5 chain can hold Na (Li, Ca, K, Mg, Y) atoms to capture hydrogen molecules with moderate E_{ad} and HGD. These findings suggest a new route to design hydrogen storage materials under the near-ambient conditions.

Introduction

The growth of population and the limited supply of fossil fuels have forced the world to seek new kinds of alternative energy sources which are affluent, renewable, efficient, secure and pollution-free. In this regard, hydrogen is generally considered as a potential candidate. However, it is a great challenge to find hydrogen storage materials with large hydrogen gravimetric density (HGD) under ambient thermodynamic conditions [1,2]. The US Department of Energy (DOE) has presented the HGD target of 5.5 wt% by the year 2017 for hydrogen storage materials [3]. In order to make hydrogen storage medium can realize the reversible hydrogen storage under near-ambient conditions, the average adsorption energy per hydrogen (E_{ad}) should be intermediates between physisorbed and chemisorbed states (0.2–0.6eV) [4–6].

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Previous studies have explored that the pure nanomaterials cannot efficiently store hydrogen mainly due to the simple Van der Waals interaction between the hydrogen molecule and the surface [7–9]. For example, the hydrogen storage capacity of single-walled carbon nanotube is only 0.43 wt% [10]. On the experiment, the BN nanotube can store 2.6 wt% hydrogen under the 10 MPa pressure [11]. Therefore, many methods are attempted to improve the hydrogen storage capacities of pure B-, C-, N- based materials. The most effective way is to decorate the pure nanomaterials with transition metals [12–14], alkaline metals [15,16], and alkaline earth metals [17]. The reported HGD of Sc atoms coated porous fullerene B_{40}, Ca atoms dispersed B_{38} fullerene, Li atoms decorated graphyne,Y atoms dispersed C_{60} are 8.1 wt% [18], 6.5 wt% [19], 13.0 wt% [20], 6.3 wt% [21] respectively.

Boron is in the fifth list of the periodic table. It has lighter weight and larger surface than carbon. The average binding energy (E_b) of Li atoms on the surface of the all-boron B_{36}, B_{40}, B_{38} are 2.45 eV [22], 3.08 eV [23], and 2.33 eV [19] respectively, however, they are larger than that of the Li atom on the pristine graphene (1.11 eV [24]). Also, the E_b of the Ca on the B_{38}(2.55 eV [19]) is also larger than that of Ca on the free-standing silicene (2.19 eV [25]). Therefore, the metal decorated B_n structures are more suitable for hydrogen storage than other atomic clusters. Consequently, the boron nanostructures such as B_{80} [26,27] and B_{38} [19] have been considered more appropriate for store hydrogen. Very recently, Zhao et al. [28] have searched out an all-boron cage B_{28} with the global minima energy, which should be the smallest all-boron cage and has one hexagonal hole and two octagonal holes. However, its hydrogen storage ability has not been reported until now, Therefore, in this paper, we choose B_{28} as the host material and search the most stable site for alkali atom (Li, Na and K), alkaline-earth atom (Mg and Ca) and transition atom (Ti, Sc and Y), then, we continue to explore their hydrogen storage abilities. Because B_{28} is much lighter than B_{38}, so the metal atoms decorated B_{28} structures are expected to show larger HGD. Section Computational details presents the computational details, section Results and Discussions shows our results and discussions, and the conclusion is given in section Conclusions.

Computational details

The calypso software [29–31] is used to search the most stable structure of the B_{28} structure. The numerical calculations use the density functional theory (DFT) [32] as implemented in the $DMol^3$ package [33]. The Perdew-Burke–Ernzerhof (PBE) [34] functional of the generalized gradient approximation (GGA) [35] is employed for the exchange-correlation potential [36]. The double numerical basis sets with polarization functional (DNP) basis sets is used. The approximate semi-classical dispersion correction scheme DFT-D proposed by Grimme (PBE+D2) is employed in all the calculations to consider the Van der Waals forces [37]. The importance of the PBE+D2 dispersion correction in performing DFT based simulations for many hydrogen storage systems [38–41] has been verified, such as Pd doped graphene [38], $C_{60}Ca_{32}$ [41] and so on. In addition, Kocman et al. [42] and Pykal et al. [43] have explored that the PBE+D2 method could provide fairly accurate results for hydrogen storage systems.

The electronic structure is obtained by solving the spin-polarized Kohn-Sham [44] equations self-consistently. In the electronic structure calculation, the DFT semi-core pseudo potential (DSPP) treatment method [45] for Sc, and all-electron treatment method for B and H are adopted. The spin polarization is considered for all the structures. In the course of optimization and molecular dynamics, all atoms are free to move. The self-consistent field procedure is done with a convergence criterion of 10^{-5} Hartree on the electron density. We use a convergence criterion of 0.002 Hartree/Å for force, 10^{-4}Å for displacement, and 10^{-5} Hartree for total energy in the geometry optimization. Since the localized natural atomic orbitals(NBO) can be used to describe the electron density, thus, the NBO charges are much more reliable and can obviously work very well for many structures [46]. The ground-state structures are determined by their minimal energies, which are further verified by no imaginary frequency in their harmonic frequency calculations [18]. The basis file is 3.5.

The accuracy of our computational method is tested by computing the H_2 and the porous boron fullerene B_{36}. The calculated bond length and binding energy (E_b) of H_2 are 0.75 Å and 4.55eV, which close to the experimental values of 0.74 Å and 4.52eV respectively [40]. For B_{36}, the calculated bond length of B–B is 1.66 Å, which near to the previous result of 1.67 Å [47]. We also use many other functionals to calculate the bond lengths and binding energies of H_2 and B_{36} as shown in Table 1. It can be found that the results under the Perdew-Burke-Ernzerhof (PBE) functional are in good agreement with the experimental result. Therefore, our computational scheme is suitable to study the boron nanostructures.

Results and discussions

Very recently, Zhao et al. [28] have explored a lowest-energy all-boron cage structure of B_{28}, which has one hexagonal hole and two octagonal holes. The asymmetric B_{28} cage is consisted of two B_{12} clusters linked by two B atoms and one B_2 dimer. We first to use the calypso software to search the lowest-energy structure of the B_{28} structure. All the low

Table 1 – The bond length of B–B(L_{B-B}) of B_{36}, as well as the bond length of H_2 (L_{H-H})and binding energy(E_b) of H_2 calculated by the PBE, PW91, VWN, BP, BLYP, BOP, HCTH functional.

		PBE	PW91	VWN	BP	BLYP	BOP	HCTH
B_{36}	L_{B-B}/Å	1.66	1.65	1.66	1.66	1.62	1.66	1.64
H_2	L_{H-H}/Å	0.75	0.75	0.74	0.75	0.74	0.74	0.74
	E_b	4.55	4.59	4.61	4.60	4.75	4.92	4.70