# 能量最低构型 $Ca_2B_4$ 团簇的储氢性能

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**摘要:**基于密度泛函理论,研究了 Ca<sub>2</sub>B<sub>4</sub>团簇的几何结构、电子特征和储氢性能。前 2 个与第 4 个能量最低构型 Ca<sub>2</sub>B<sub>4</sub> 01、Ca<sub>2</sub>B<sub>4</sub> 02和 Ca<sub>2</sub>B<sub>4</sub> 04有很高的热力学稳定性,分别最多可以吸附 12、12和 10 个氢分子,达到 16.3%、16.3%和 14.0%的储氢量,超过了 美国能源部提出的目标(5.5%)。Ca<sub>2</sub>B<sub>4</sub> 01(H<sub>2</sub>)<sub>12</sub>、Ca<sub>2</sub>B<sub>4</sub> 02(H<sub>2</sub>)<sub>12</sub>和 Ca<sub>2</sub>B<sub>4</sub> 04(H<sub>2</sub>)<sub>10</sub>的平均每个氢分子吸附能量分别为 0.58~4.21 eV、 0.54~3.69 eV和 0.10~0.12 eV。玻恩-奥本海默分子动力学模拟表明, Ca<sub>2</sub>B<sub>4</sub> 01和 Ca<sub>2</sub>B<sub>4</sub> 02 可作为潜在吸附氢气的候选目标,而 Ca<sub>2</sub>B<sub>4</sub> 04不行。吉布斯自由能校正的氢吸附能结果表明,在 101 325 Pa下, Ca<sub>2</sub>B<sub>4</sub> 01和 Ca<sub>2</sub>B<sub>4</sub> 02 吸附 12 个氢气分子有较大的可 调节的温度范围。

关键词:储氢;密度泛函理论;吸附;分子动力学;吉布斯自由能
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# Hydrogen Storage Capabilities of the Low-Lying Ca<sub>2</sub>B<sub>4</sub> Clusters

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**Abstract:** The structural feature and electronic property of  $Ca_2B_4$ , as well as its potential for hydrogen storage, have been studied using density functional theory. The first, second, and fourth low-lying isomers  $Ca_2B_4$  **01**,  $Ca_2B_4$  **02**, and  $Ca_2B_4$  **04** have high stabilities in thermodynamics and can adsorb 12, 12, and 10 H<sub>2</sub> molecules with respective H<sub>2</sub> gravimetric uptake capacity of 16.3%, 16.3%, and 14.0%, which far exceeds the target (5.5%) proposed by the US department of energy (DOE). The average absorption energies per H<sub>2</sub> molecule are in the range of 0.58-4.21 eV for  $Ca_2B_4$  **01**(H<sub>2</sub>)<sub>12</sub>, 0.54-3.69 eV for  $Ca_2B_4$  **02**(H<sub>2</sub>)<sub>12</sub>, and 0.10-0.12 eV for  $Ca_2B_4$  **04**(H<sub>2</sub>)<sub>10</sub>. Born-Oppenheimer molecular dynamic (BOMD) simulations indicate  $Ca_2B_4$  **01** and  $Ca_2B_4$  **02** are promising candidates for adsorbing hydrogen, but  $Ca_2B_4$  **04** is not. The results of hydrogen adsorption energies with Gibbs free energy correction indicate that 12 H<sub>2</sub> molecules on  $Ca_2B_4$  **01** and  $Ca_2B_4$  **02** are energetically favorable with a wide range of temperatures at 101 325 Pa.

Keywords: hydrogen storage; density functional theory; absorption; molecular dynamic; Gibbs free energy

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Hydrogen is considered to be a sustainable and eco-friendly energy carrier because of its abundance, easy synthesis, and high heat thermal capacity on the earth<sup>[1-2]</sup>. However, the wide-scale use of hydrogen fuel hinges on our ability to find safe and cost - effective hydrogen storage materials. The ideal hydrogen storage materials should meet the stringent requirements: high gravimetric and volumetric density, fast kinetics, and thermodynamics that allow reversible hydrogen adsorption and desorption in H<sub>2</sub> molecular form to take place under ambient conditions<sup>[3-6]</sup>. According to the guidelines set by the US Department of Energy (DOE), a minimum requirement for a system to be a potential hydrogen storage candidate is that it should possess a minimum H<sub>2</sub> gravimetric uptake capacity of 5.5% and delivery under 1 200 kPa pressure in the operating ambient temperature range of 233 to 333 K<sup>[7]</sup>.

Traditionally, the storage materials bind the hydrogen atoms primarily through three different processes<sup>[1,6]</sup>. In chemisorption, the H<sub>2</sub> molecules dissociate into individual atoms, migrate into the storage material, and are strongly bonded with the binding energy in the range of 2-4 eV like chemical hydrides<sup>[8-9]</sup>, in which the strong interaction makes it difficult to release H<sub>2</sub> during application. On the other hand, like the pure carbon-based nanostructures, the H<sub>2</sub> is bonded weakly via physisorption and remains in its molecular form with the binding energy in the range of few  $meV^{[10]}$ . However, the major drawbacks in physisorption are that the adsorption must be carried out at a very low temperature and high gas pressure. Recently, more attempts have been made to design and develop new hydrogen storage materials based on the third form of adsorption, which is intermediate between physisorption and chemisorption with the binding energy of 0.1-0.8 eV and considered to be essential for the faster adsorption and desorption kinetics for vehicular application. It includes metal-decorated nanomaterials<sup>[11-18]</sup>. transition metal - acetylene/ethylene<sup>[19-28]</sup>, and transition metal clusters<sup>[29-33]</sup>. For example, Sun et al.<sup>[14]</sup> predicted the hydrogen storage capacities of the Li<sub>12</sub>C<sub>60</sub> cluster in which each Li atom could adsorb a maximum of 5 H<sub>2</sub> molecules leading to a gravimetric density (w/w) of 13%. Durgun et al.<sup>[23]</sup> theoretically indicated  $Ti_2 - C_2H_4$  could adsorb a maximum of 10 H<sub>2</sub> molecules with the average binding energy of 0.45 eV. Du et al.<sup>[29]</sup> recently predicted that the carbon motif  $CTi_7^{2+}$  could bind 20 H<sub>2</sub> molecules at most, which resulted in a gravimetric density of 19%.

Compared with carbon - based materials, metal decorate boron clusters have also been considered a promising candidate for hydrogen storage<sup>[34-42]</sup>. For example, B<sub>6</sub>Li<sub>8</sub> was predicted to be an excellent hydrogen storage media with gravimetric density likely reaching up to a theoretical limit of 24%<sup>[35]</sup>. Du et al.<sup>[39]</sup> have investigated the hydrogen storage capacity of the Saturn - like charge - transfer complex  $Li_4B_{40}$ , in which each Li atom could bind 6 H2 molecules at most resulting in the gravimetric density of 10.4%. Just like the alkali metal decorated materials, boron clusters doped by transition metals have become a research hotspot<sup>[43-47]</sup>. Very recently, the highly stable  $Sc_2B_4^{2+}$  cluster was investigated as a promising candidate for hydrogen storage material, which corresponded to a hydrogen uptake of 17.49% and average binding energy of 0.42 eV<sup>[46]</sup>. As we know, the transition metal Sc is expensive and charge neutrality should be a consideration in the engineering of practical materials for hydrogen storage. On the other hand, we have called attention to the isoelectronic relationship of a Ca atom to a Sc<sup>+</sup> ion. Moreover, calcium has been suggested to functionalize the nanomaterials as hydrogen storage materials because of its relatively small cohesive energy and moderate interaction with H<sub>2</sub> molecules<sup>[15-16,40-41,48]</sup>. For example, the inverse sandwich Ca<sub>2</sub>B<sub>8</sub> was found to be a promising hydrogen storage material that showed moderate adsorption energy and high gravimetric density (10.6%) for H<sub>2</sub><sup>[48]</sup>.

Therefore, in the current work, we choose  $Ca_2B_4$  as the theoretical research model to investigate the corresponding geometrical configuration and electronic structures, and further probe into the hydrogen storage abilities of the low-lying isomers.

## **1** Computational methods

The 1 000 initial structures of Ca2B4 were generated

by a stochastic search method embedded in the Molclus program<sup>[49]</sup>, and the resulting structures were optimized in the singlet state and triplet state at the PBE0/6 - 311+G(d) level<sup>[50-53]</sup>, respectively. The PBE0 functional is an effective tool in studies of the metaldoped boron clusters<sup>[54-55]</sup>. The vibrational frequencies of all the local minima were confirmed at the same level to guarantee that the structures optimized are true minima on the potential energy surface. To obtain the reasonable adsorption energy of H<sub>2</sub> molecules on Ca<sub>2</sub>B<sub>4</sub> clusters, the molecular structures of the isolated and H2adsorbed Ca<sub>2</sub>B<sub>4</sub> were further fully optimized without any symmetry constraints using the  $\omega B97XD$  function $al^{[56]}$  in conjunctions with 6-311+G(d, p) basis set. The  $\omega$ B97XD functional with the long - range interactions has been proven to be an authentic method for predicting non - covalent interactions<sup>[29,39,42-43]</sup>. The basis set superposition errors (BSSE)<sup>[57]</sup> were corrected using the full counterpoise method for all the H2-adsorbed Ca2B4 structures. To evaluate the reversibility of storage of H<sub>2</sub> molecules, the successive adsorption energy  $(\Delta E_s)$  and the average absorption energy per H<sub>2</sub> molecule ( $\Delta E_a$ ) were calculated at  $\omega$ B97XD/6 - 311+G (d, p) level according to the following formulas:

$$\Delta E_{s} = E_{Ca_{2}B_{4}(H_{2})_{n-1}} + E_{H_{2}} - E_{Ca_{2}B_{4}(H_{2})_{n}}$$
(1)

$$\Delta E_{a} = (E_{Ca_{2}B_{4}} + nE_{H_{2}} - E_{Ca_{2}B_{4}(H_{2})_{n}})/n$$
<sup>(2)</sup>

Where  $E_{\rm X}$  stands for the total energy of X (X=Ca<sub>2</sub>B<sub>4</sub>, H<sub>2</sub>, Ca<sub>2</sub>B<sub>4</sub>(H<sub>2</sub>)<sub>*n*-1</sub>, Ca<sub>2</sub>B<sub>4</sub>(H<sub>2</sub>)<sub>*n*</sub>). Notably, the spontaneous adsorption of H<sub>2</sub> can occur if the  $\Delta E_{\rm s}$  is positive, and the negative  $\Delta E_{\rm s}$  means the successive adsorption is difficult.

The  $H_2$  gravimetric density of  $Ca_2B_4$  was calculated using the following equation:

Gravimetric density= $M_{\rm H_2}/(M_{\rm H_2}+M_{\rm Ca_2B_4})\times100\%$  (3) Where  $M_{\rm H_2}$  represents the mass of the total number of H<sub>2</sub> molecules adsorbed and  $M_{\rm Ca_2B_4}$  represents the mass of the host Ca<sub>2</sub>B<sub>4</sub>.

Besides, Born - Oppenheimer molecular dynamics (BOMD) simulations at the temperatures of 77 and 300 K were performed for the relaxed structures of selected species  $Ca_2B_4$  **01**( $H_2$ )<sub>12</sub>,  $Ca_2B_4$  **02**( $H_2$ )<sub>12</sub>, and  $Ca_2B_4$  **04**( $H_2$ )<sub>10</sub> at the  $\omega$ B97XD/6-31+G(d, p) level.

All the geometry optimization and property calculation were performed using the Gaussian 09 package.

# 2 Result and discussion

# 2.1 Geometrical and electronic structure of Ca<sub>2</sub>B<sub>4</sub>

### 2.1.1 Geometrical structure of Ca<sub>2</sub>B<sub>4</sub>

A total of 16 low - lying isomers for  $Ca_2B_4$  were identified via extensive structural searches. To ensure the energetics, all optimized isomers were benchmarked using single-point CCSD(T) [58] calculations. Fig.1 represents the structures and relative energies of each isomer at the CCSD(T)/6-311+G(d)//PBE0/6-311+ G(d) level.  $Ca_2B_4$  **01** is the most stable structure, which is only 0.035, 0.078, and 0.089 eV less in energy than the top three competitors ( $Ca_2B_4$  02,  $Ca_2B_4$  03, and  $Ca_2B_4$  **04**), respectively. On the other hand, although  $Ca_2B_4$  02 and  $Ca_2B_4$  03 have the same geometries,  $Ca_2B_4$  02 with a singlet state is more stable than the triplet  $Ca_2B_4$  03. Therefore, the geometrical configurations, electronic properties, and the hydrogen storage abilities for the first, second, and fourth low-lying isomers Ca<sub>2</sub>B<sub>4</sub> **01**, Ca<sub>2</sub>B<sub>4</sub> **02**, and Ca<sub>2</sub>B<sub>4</sub> **04** were researched. The calculated key bond lengths of the bare and H<sub>2</sub> adsorbed compounds Ca<sub>2</sub>B<sub>4</sub> 01, Ca<sub>2</sub>B<sub>4</sub> 02, and Ca<sub>2</sub>B<sub>4</sub> 04 at  $\omega$ B97XD/6-311+G(d, p) level are listed in Table 1. Notably,  $Ca_2B_4$  **01**(H<sub>2</sub>)<sub>12</sub> and  $Ca_2B_4$  **02**(H<sub>2</sub>)<sub>12</sub> have the same geometries. Comparing the isolated Ca<sub>2</sub>B<sub>4</sub> isomers, the corresponding B-B and B-Ca bonds in  $Ca_2B_4$  **02**(H<sub>2</sub>)<sub>12</sub> and  $Ca_2B_4$  **04**(H<sub>2</sub>)<sub>10</sub> are not considerable change, which indicates the structures of Ca<sub>2</sub>B<sub>4</sub> are not distorted with adsorption of a maximum of H<sub>2</sub> molecules. Moreover, the smallest vibrational frequency (Table 1) of the bare isomers is predicted to be 98, 115, and 130 cm<sup>-1</sup>, which are sufficiently large to meet a stability criterion suggested by Hoffmann et al.<sup>[59]</sup> In addition, the energy gap  $(\Delta E_{\rm HI})$  between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) was also calculated to analyze the stabilities of  $Ca_2B_4$  **01**,  $Ca_2B_4$  **02**, and  $Ca_2B_4$  **04** due to a large  $\Delta E_{\rm HL}$  can reflect the high stabilities of compounds. The  $\Delta E_{\text{HL}}$  of Ca<sub>2</sub>B<sub>4</sub> **01**, Ca<sub>2</sub>B<sub>4</sub> **02**, and Ca<sub>2</sub>B<sub>4</sub> 04 are 4.02, 4.16, and 4.88 eV, respectively, indicating the three clusters have high stabilities. To further study



Relative energies ( $\Delta E$ ) are given in eV at CCSD(T)/6-311+G(d)//PBE0/6-311+G(d) level; Capital letters S and T in parenthesis denote the singlet state and the triplet state, respectively; Green spheres represent Ca atoms and the pink spheres represent B atoms

Fig.1 Optimized low-lying isomeric structures of Ca<sub>2</sub>B<sub>4</sub> at PBE0/6-311+G(d) level

Table 1B—B/Ca bond distances (nm) and the lowest vibrational frequency  $\omega_L$  (cm<sup>-1</sup>) of the isolated<br/>and multiple H<sub>2</sub> adsorbed compounds at  $\omega$ B97XD/6-311+G(d, p) level

Species	$d_{\rm B1-B2}$ / nm	$d_{\rm B1-B3}$ / nm	$d_{\rm B1-B4}/\rm nm$	$d_{\rm B2-B3}/\rm nm$	$d_{\mathrm{B2-Ca5}}$ / nm	$d_{\rm B3-Ca5}/\rm nm$	$\omega_{ m L}$ / cm <sup>-1</sup>
$Ca_2B_4$ <b>01</b>	0.165	0.172	0.153	0.165	0.244	0.274	98
$Ca_{2}B_{4}\ \boldsymbol{01}(H_{2})_{12}$	0.155	0.169	0.155	0.165	0.293	0.250	—
$Ca_2B_4$ <b>02</b>	0.158	0.170	0.158	0.173	0.234	0.248	115
$Ca_2B4 \ 02(H_2)_{12}$	0.155	0.169	0.155	0.165	0.293	0.250	—
Ca <sub>2</sub> B <sub>4</sub> <b>04</b>	0.158	0.154	0.154	0.154	0.268	0.248	130
$Ca_2B_4 \ 04(H_2)_{10}$	0.157	0.154	0.154	0.154	0.271	0.251	_

the thermodynamic stabilities, BOMD simulations were carried out for 5 ps at 300 K. As shown in Fig.2, the relative potential energies for  $Ca_2B_4$  **01**,  $Ca_2B_4$  **02**, and  $Ca_2B_4$  **04** in the simulated time show slight oscillations, suggesting their high stabilities at room temperature. To gain clear geometries, the extracted snapshots of  $Ca_2B_4$  **01**,  $Ca_2B_4$  **02**, and  $Ca_2B_4$  **04** at different simulation times (50, 2 500, and 5 000 fs) are also depicted in Fig.2.

2.1.2 Electronic structure of Ca<sub>2</sub>B<sub>4</sub>

To analyze the electronic structure and the effect of  $H_2$  molecules adsorbed, the Mulliken charge for Ca<sub>2</sub>B<sub>4</sub> isomer has been calculated at  $\omega$ B97XD/6-311G (d, p) level. As shown in Fig. 3, in Ca<sub>2</sub>B<sub>4</sub> **01**, the boron and calcium atoms carry about -0.183e, -0.651e, -0.181e, -0.092e, 0.554e, and 0.555e, respectively. For Ca<sub>2</sub>B<sub>4</sub> **02**, the four boron atoms (B1-B4) have -0.283e, -0.314e, -0.586e, and -0.314e, respectively. Two calcium atoms (Ca5-Ca6) have 0.749e and 0.749e, respectively. In Ca<sub>2</sub>B<sub>4</sub> **04**, the boron and calcium atoms carry about -0.234e, -0.234e, -0.646e, -0.646e, 0.880e, and 0.880e, respectively. The strong charges transfer from calcium atoms to boron atoms when these com-

pounds are formed. Therefore, partially charged Ca ion and B4 may produce a local electrostatic field that can polarize H<sub>2</sub> molecules and then bind them via the polarization mechanism. To further illustrate the above concept, the contour plots of the molecular electrostatic potential ( $E_{sp}$ ) of Ca<sub>2</sub>B<sub>4</sub> **01**, Ca<sub>2</sub>B<sub>4</sub> **02**, and Ca<sub>2</sub>B<sub>4</sub> **04** isomers were also obtained by Multiwfn<sup>[60]</sup>. As illustrated in Fig. 4, the calcium and boron atoms have a positive and negative potential, respectively. The map of  $E_{sp}$  diffusion accords with the Mulliken charge analysis, indicating the H<sub>2</sub> molecules should be preferentially ad-



Inset: extracted snapshots at different simulation times (50, 2 500, and 5 000 fs); Green spheres represent Ca atoms and pink spheres represent B atoms

Fig.2 Variations of potential energy vs simulation time at 300 K for Ca<sub>2</sub>B<sub>4</sub> **01**, Ca<sub>2</sub>B<sub>4</sub> **02**, and Ca<sub>2</sub>B<sub>4</sub> **04** 



Fig.3 Mulliken charge of  $Ca_2B_4$  **01**,  $Ca_2B_4$  **02**, and  $Ca_2B_4$  **04** at the  $\omega$ B97XD/6-311G (*d*, *p*) level



Cyan spheres represent Ca atoms and the pink spheres represent B atoms

Fig.4  $E_{sp}$  maps of Ca<sub>2</sub>B<sub>4</sub> **01**, Ca<sub>2</sub>B<sub>4</sub> **02**, and Ca<sub>2</sub>B<sub>4</sub> **04** at the  $\omega$ B97XD/6-311G (*d*, *p*) level

sorbed on calcium atoms.

#### **2.2** $H_2$ adsorption behavior of Ca<sub>2</sub>B<sub>4</sub>

# 2.2.1 $H_2$ adsorption behavior of $Ca_2B_4$ **01**

We next studied the sequential hydrogenation of  $Ca_2B_4$  **01**. Based on the above analysis, the Ca atom is the most active atom in all sites during the process of  $H_2$  adsorption. Considering the symmetry of the isomers  $Ca_2B_4$  **01**, a number of  $H_2$  molecules were successively placed around every Ca atom, and the structures were optimized without any symmetry constraints at the  $\omega B97XD$  level of theory, respectively. The optimized structures of the isomer  $Ca_2B_4$  **01** with adsorbed multiple  $H_2$  molecules at the  $\omega B97XD$  level of theory are depicted in Fig. S1 (Supporting information). The selected relaxed configurations  $Ca_2B_4$  **01**( $H_2$ )<sub>12</sub> is depicted in Fig.5.

 $Ca_2B_4$  **01** can at most adsorb 12 H<sub>2</sub> molecules and the gravimetric density of stored hydrogen is 16.3%, which is about 3.3 times larger than the criteria of 5.5% proposed by DOE<sup>[7]</sup>. As listed in Table 2, the bond lengths of the adsorbed molecular form H<sub>2</sub> in  $Ca_2B_4$  **01**(H<sub>2</sub>)<sub>12</sub> are 0.075 nm, which is elongated compared to the bond length (0.074 nm) of isolated  $H_2$  at the same calculated level. Notably, the binding of the first molecule to  $Ca_2B_4$  **01** isomer has five different characteristics (Fig.S1). Among them, the H<sub>2</sub> molecule interacts dissociatively with two B atoms and the resulting borohydride structure is the ground - state (1a), which is 0.35, 0.37, 0.46, and 4.21 eV lower in energy than 1b, 1c, 1d, and 1e, respectively. It is for this reason that we have concentrated an adding successive H<sub>2</sub> molecules to the ground - state structure. Next, the adsorption of the second  $H_2$  molecule to  $Ca_2B_4$  **01** $(H_2)_1$ (1a) has two different characteristics. Here, hydrogen binds molecularly to one of the Ca atoms and the resulting isomer (Fig. S1, 2b) is 0.72 eV higher in energy

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Gray spheres represent H atoms

Fig.5 Optimized geometries of  $Ca_2B_4$  **01**( $H_2$ )<sub>12</sub>,  $Ca_2B_4$  **02**( $H_2$ )<sub>12</sub>, and  $Ca_2B_4$  **04**( $H_2$ )<sub>10</sub> at the  $\omega$ B97XD/6-311+G (d, p) level

Table 2Ca—H and corresponding H—H distances (nm) of  $Ca_2B_4 01(H_2)_{12}/Ca_2B_4 02(H_2)_{12}$  and<br/> $Ca_2B_4 04(H_2)_{10}$  at  $\omega B97XD/6-311+G(d, p)$  level

Bond	$Ca_2B_4 01(H_2)_{12}$	$/Ca_2B_4 02(H_2)_{12}$	$Ca_2B_4 \ 04(H_2)_{10}$		
	$d_{ m Ca-H}$ / nm	$d_{\mathrm{H-H}^{\mathrm{a}}}$ / nm	$d_{ m Ca-H}$ / nm	$d_{\mathrm{H-H}}$ / nm	
Са5—Н	0.259-0.281	0.075	0.236-0.268	0.076-0.077	
Са6—Н	0.260-0.281	0.075	0.235-0.267	0.076-0.077	

<sup>a</sup> Adsorbed H<sub>2</sub> in Ca<sub>2</sub>B<sub>4</sub> **01**(H<sub>2</sub>)<sub>12</sub> is in molecular form.

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than the ground-state structure (2a) in which the second H<sub>2</sub> molecule dissociates with two H atoms bridging between two Ca atoms. As listed in Table 3, the successive binding energies of the ground states of Ca<sub>2</sub>B<sub>4</sub> 01  $(H_2)_1$  and  $Ca_2B_4$  **01** $(H_2)_2$  are 4.21 and 1.67 eV respectively, indicating the binding of the first two molecules belongs to the chemisorption process. It is only when the third  $H_2$  molecule is added to **2a** that the binding becomes molecular, with successive energy of 0.11 eV. The H<sub>2</sub> molecules from the fourth to the twelfth also bind to the Ca atoms in nearly molecular form. The binding energies of each successive H<sub>2</sub> molecule are in the range of 0.11-0.12 eV as one proceeds from  $Ca_2B_4$  $01(H_2)_3$  to  $Ca_2B_4$   $01(H_2)_{12}$ . To confirm the adsorption of  $H_2$  molecules to  $Ca_2B_4$  **01** is reversible or not, the  $\Delta E_a$ of  $Ca_2B_4$  **01**(H<sub>2</sub>)<sub>n</sub> (n=1-12) are also illustrated in Table 3. Ca<sub>2</sub>B<sub>4</sub> **01** adsorbs 1-12 H<sub>2</sub> molecules with the  $\Delta E_{a}$  of 4.21 to 0.58 eV. It can be found that some  $\Delta E_{*}$  values are too large and exceed the energy criteria (0.1-0.8 eV) of the reversible hydrogen storage. Because the strong chemical bonds between the dissociation of the first two H<sub>2</sub> molecules and B/Ca atoms improve the  $\Delta E_a$ of compounds. However, more remarkably, the average adsorptions energy of  $Ca_2B_4$  **01**(H<sub>2</sub>)<sub>12</sub> is 0.58 eV, which is ideal for reversible hydrogen storage at near ambient conditions.

2.2.2  $H_2$  adsorption behavior of  $Ca_2B_4$  02

The optimized structures of H<sub>2</sub>-adsorbed Ca<sub>2</sub>B<sub>4</sub> 02

are depicted in Fig.S2. Notably, the binding of the first molecule to Ca<sub>2</sub>B<sub>4</sub> **01** isomer has three different characteristics (Fig. S2) and the ground - state structure of  $Ca_2B_4$  **02**(H<sub>2</sub>)<sub>1</sub> (**1a**') is exactly the same as  $Ca_2B_4$  **01**(H<sub>2</sub>)<sub>1</sub> (1a). As illustrated in Table 3, the successive binding energies of the ground state  $Ca_2B_4$  **01**(H<sub>2</sub>)<sub>1</sub> (**1a**') is 3.69 eV, indicating the binding of the first molecule belongs to the chemisorption process. It is when the second  $H_2$ molecule is added to 1a' that the  $H_2$  adsorbed structures  $Ca_2B_4$  **02** are exactly the same as the corresponding H<sub>2</sub> adsorbed structures Ca<sub>2</sub>B<sub>4</sub> **01**. The  $\Delta E_a$  of Ca<sub>2</sub>B<sub>4</sub>  $02(H_2)_n$  (n=1-12) are also listed in Table 3. Ca<sub>2</sub>B<sub>4</sub> 02 adsorbs 1-12 H<sub>2</sub> molecules with the  $\Delta E_a$  of 3.69 to 0.54 eV. The  $\Delta E_a$  of  $Ca_2B_4$  **02**(H<sub>2</sub>)<sub>12</sub> is 0.54 eV, which is ideal for reversible hydrogen storage at near ambient conditions.

2.2.3  $H_2$  adsorption behavior of  $Ca_2B_4$  04

The optimized structures of  $H_2$ -adsorbed  $Ca_2B_4$  **04** are depicted in Fig. S2.  $Ca_2B_4$  **04** can successively adsorb 10  $H_2$  molecules in total, from one to five  $H_2$ molecules on each Ca atom. The selected relaxed configuration  $Ca_2B_4$  **04** $(H_2)_{10}$  is depicted in Fig.5. The Ca— H distances and the corresponding H—H bond lengths are listed in Table 2. The Ca—H distances are in a range of 0.235-0.267 nm, and the corresponding H—H bond lengths are elongated to 0.076 - 0.077 nm. As shown in Table 3, the  $\Delta E_s$  values are in a range of 0.10-0.14 eV for  $H_2$ -adsorbed  $Ca_2B_4$  **04**. The positive energy

Table 3	Calculated $\Delta E_s$ and $\Delta E_a$ with BSSE correction and without zero-point energy
	correction at $\omega$ B97XD/6-311+G (d, p) level

n	$Ca_2B_4$	$Ca_2B_4$ <b>01</b> $(H_2)_n$		$Ca_2B_4 02(H_2)_n$		$Ca_2B_4$ <b>04</b> $(H_2)_n$	
	$\Delta E_{ m s}$ / eV	$\Delta E_{\rm a}/{\rm eV}$	$\Delta E_{ m s}$ / eV	$\Delta E_{\rm a}$ / eV	$\Delta E_{ m s}$ / eV	$\Delta E_{\rm a}/{\rm eV}$	
1	4.21	4.21	3.69	3.69	0.12	0.12	
2	1.67	2.93	1.67	2.67	0.12	0.12	
3	0.11	1.99	0.11	1.82	0.11	0.12	
4	0.11	1.52	0.11	1.38	0.14	0.12	
5	0.12	1.23	0.12	1.13	0.10	0.12	
6	0.11	1.04	0.11	0.96	0.13	0.12	
7	0.11	0.91	0.11	0.84	0.12	0.12	
8	0.11	0.81	0.11	0.75	0.12	0.12	
9	0.11	0.74	0.11	0.68	0.13	0.11	
10	0.11	0.67	0.11	0.62	0.13	0.10	
11	0.12	0.62	0.12	0.58	—	—	
12	0.12	0.58	0.12	0.54	_	—	

values of  $\Delta E_s$  indicate that 10 H<sub>2</sub> molecules can be effectively adsorbed on Ca<sub>2</sub>B<sub>4</sub> **04**. Besides, the  $\Delta E_a$  of Ca<sub>2</sub>B<sub>4</sub> **04**(H<sub>2</sub>)<sub>n</sub> (n=1-10) are in a range of 0.10 to 0.12 eV which meets the criteria (0.1-0.8 eV) of reversible hydrogen storage. For Ca<sub>2</sub>B<sub>4</sub> **04**(H<sub>2</sub>)<sub>10</sub>, the gravimetric density of stored hydrogen is 14.0%. The result surpasses the target for hydrogen uptake capacity specified by DOE.

# 2.3 Reversibility of $H_2$ molecules on $Ca_2B_4$ 01, $Ca_2B_4$ 02, and $Ca_2B_4$ 04

To test the hydrogen release for  $Ca_2B_4$  **01**( $H_2$ )<sub>12</sub>,  $Ca_2B_4$  **02**( $H_2$ )<sub>12</sub>, and  $Ca_2B_4$  **04**( $H_2$ )<sub>10</sub> at ambient conditions, we performed the BOMD simulations at the  $\omega$ B97XD/6-31+G (*d*, *p*) level. The BOMD simulations were carried out with a time of scale of 800 fs with a trajectory step size of 0.5 fs at the temperatures of 77 and 298 K. Fig.6 shows the potential energies as functions of time, and the extracted snapshots at different simulation times (50, 100, 200, 300, 400, and 500 fs) are depicted in Fig.S3-S6. For  $Ca_2B_4$  **01**( $H_2$ )<sub>12</sub>/ $Ca_2B_4$  **02** ( $H_2$ )<sub>12</sub>, 10 H<sub>2</sub> molecules far from Ca sites have begun to run away from the host  $Ca_2B_4$  **01** cluster within 100 fs, and the H<sub>2</sub> molecules desorb faster at the higher temperatures. On the other hand, at the end of simulations of 77 and 298 K, only the first two H<sub>2</sub> molecules are still adsorbed in atom form, whereas the other ten H<sub>2</sub> in the molecular form completely escape from  $Ca_2B_4$  **01**, corresponding to a release ratio of 83.3%, which is excellent agreement with the discussed adsorption mechanism above. Interestingly,  $Ca_2B_4$  **01**(H<sub>2</sub>)<sub>2</sub> structure shows a high dynamic stability at 77 and 298 K, being in line with the values of  $\Delta E_{a}$  and  $\Delta E_{s}$ . Moreover, it can be found from the snapshots of Fig. S3 and S4 that the host clusters Ca<sub>2</sub>B<sub>4</sub> **01** and Ca<sub>2</sub>B<sub>4</sub> **02** are not significantly deformed during the dynamic simulation processes. Therefore, we can conclude that the clusters  $Ca_2B_4$  **01** and  $Ca_2B_4$  **02** are appropriate candidates for reversible hydrogen storage. For  $Ca_2B_4$  04(H<sub>2</sub>)<sub>10</sub>, at the processes of simulations of 77 and 298 K, although most of the H<sub>2</sub> adsorbed can also completely escape from Ca<sub>2</sub>B<sub>4</sub> 04, the host cluster Ca<sub>2</sub>B<sub>4</sub> 04 is significantly deformed. Thus, Ca<sub>2</sub>B<sub>4</sub> 04 is not an appropriate candidate for reversible hydrogen storage.



Fig.6 Potential energy trajectories of (a)  $Ca_2B_4$  **01** $(H_2)_{12}/Ca_2B_4$  **02** $(H_2)_{12}$  and (b)  $Ca_2B_4$  **04** $(H_2)_{10}$  complexes at the temperatures of 77 and 298 K

# 2.4 Gibbs free energy corrected adsorption energies ( $\Delta E_{\rm G}$ )

To confirm the adsorptions of  $Ca_2B_4$  **01**(H<sub>2</sub>)<sub>12</sub> and  $Ca_2B_4$  **02**(H<sub>2</sub>)<sub>12</sub> are favorable or not at different temperatures, the  $\Delta E_G$  was calculated at different temperatures and 101 325 Pa. The formula is  $\Delta E_G = (E_{G,Ca_2B_4} + 12E_{G,H_2} - E_{G,Ca_2B_4(H_2)_{12}})/12$ , where  $E_{G,Ca_2B_4}$ ,  $E_{G,H_2}$ , and  $E_{G,Ca_2B_4(H_2)_{12}}$  are

the calculated Gibbs free energies of the bare cluster  $Ca_2B_4$ ,  $H_2$  molecule, and  $Ca_2B_4$  ( $H_2$ )<sub>12</sub>, respectively. The positive  $\Delta E_G$  value reflects that the adsorption of multiple  $H_2$  molecules on  $Ca_2B_4$  is energetically favorable at the corresponding condition. As shown in Fig. 7, the  $\Delta E_G$  of  $Ca_2B_4$  **01**( $H_2$ )<sub>12</sub> and  $Ca_2B_4$  **02**( $H_2$ )<sub>12</sub> are still positive at 400 K at 101 325 Pa. It indicates that both



Fig.7 Temperature dependence of  $\Delta E_{\rm G}$  values for Ca<sub>2</sub>B<sub>4</sub> **01**(H<sub>2</sub>)<sub>12</sub> and Ca<sub>2</sub>B<sub>4</sub> **02**(H<sub>2</sub>)<sub>12</sub> at  $\omega$ B97XD/6-311+G (*d*, *p*) level

 $Ca_2B_4$  **01**(H<sub>2</sub>)<sub>12</sub> and  $Ca_2B_4$  **02**(H<sub>2</sub>)<sub>12</sub> have fairly wide temperature ranges on which we can tune the thermodynamically favorable hydrogen adsorption just near room temperature at 101 325 Pa.

# **3** Conclusions

In this work, the structures, stabilities, and hydrogen storage behavior of Ca<sub>2</sub>B<sub>4</sub> have been researched using density functional theory. According to the calculations, the first, second, and fourth low-lying isomers  $Ca_2B_4$  01,  $Ca_2B_4$  02, and  $Ca_2B_4$  04 have high stabilities in thermodynamics at 300 K. For Ca2B4 01 and Ca2B4 **02**, the resulting  $H_2$  adsorbed structures are the same and up to 12 H<sub>2</sub> molecules can be bound. Ca<sub>2</sub>B<sub>4</sub> 04 can adsorb 10 H<sub>2</sub> molecules at most. The systems can have a maximum gravimetric density of 16.3% and 14.0% for  $Ca_2B_4$  **01** $(H_2)_{12}/Ca_2B_4$  **02** $(H_2)_{12}$  and  $Ca_2B_4$  **04** $(H_2)_{12}$ , respectively, which satisfy the target specified by US DOE. The  $\Delta E_a$  of 0.58-4.21 eV for Ca<sub>2</sub>B<sub>4</sub> **01**(H<sub>2</sub>)<sub>12</sub>, 0.54- $3.69~{\rm eV}$  for  ${\rm Ca_2B_4}~\textbf{02}({\rm H_2})_{12},$  and  $0.10\text{-}0.12~{\rm eV}$  for  ${\rm Ca_2B_4}$  $04(H_2)_{10}$  are in the range of the physisorption and chemisorption energy. The results of BOMD simulations indicate Ca<sub>2</sub>B<sub>4</sub> **01** and Ca<sub>2</sub>B<sub>4</sub> **02** can be promising candidates for adsorbing dihydrogen, but Ca<sub>2</sub>B<sub>4</sub> 04 is not. Moreover, the temperature-dependent Gibbs free energy corrected adsorption energies indicate Ca<sub>2</sub>B<sub>4</sub> 01 and  $Ca_2B_4$  **02** are suitable for storage H<sub>2</sub> with a wide range of temperatures at 101 325 Pa.

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