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Improved hydrogen storage in Ca-decorated boron
heterofullerenes: a theoretical studySüleyman Er,^{†*a} Gilles A. de Wijs^b and Geert Brocks^c

We computationally investigate the hydrogen storage properties of calcium-decorated $C_{48}B_{12}$ boron-carbon heterofullerene molecules, and compare them to C_{60} (all-carbon) fullerene decorated with calcium. We employ density functional theory (DFT) on the lowest energy configurations of $C_{48}B_{12}$ molecules and find that these molecules have the following properties. (1) The most stable $C_{48}B_{12}$ isomers have an electron affinity that is 0.93–1.04 eV higher than their carbon only counterpart. (2) The binding of a Ca atom to $C_{48}B_{12}$ is ~ 2.2 eV stronger than its binding to C_{60} . (3) Unlike $C_{60}Ca_x$, $x = 1-6$, $C_{48}B_{12}Ca_x$ is stable with respect to decomposition into the fullerene molecules and Ca bulk metal. (4) $C_{48}B_{12}Ca_x$ binds up to six hydrogen molecules per metal center, leading to a gravimetric density of up to 7.1 weight percent (wt%). The hydrogen binding energies of up to ~ 0.24 eV open a prospect of hydrogen storage at ambient temperature.

Hydrogen is a clean energy carrier that shows promise in decreasing our dependence on fossil fuels. The US Department of Energy (DOE) suggests that by the year 2020, a successful onboard hydrogen storage system should have a hydrogen storage capacity of at least 5.5 wt% at moderate pressures, and should operate at delivery temperatures between -40 and 85°C .¹ The speed of (un)loading of hydrogen (from)to the storage material should be at least such that 5 kg of hydrogen should be loaded within 200 seconds.¹ Physisorption is preferred to chemisorption as no bonds need to be formed or broken during the process.

Physisorption materials with open or porous structures facilitate fast hydrogen kinetics, which facilitates loading of

hydrogen into the storage system. In physisorption materials, H_2 molecules are adsorbed onto substrates, typically *via* weak, van der Waals type interactions. Thus, binding hydrogen molecules to host materials requires very low temperatures and high hydrogen gas pressures. Such conditions are generally unsuitable for mobile applications, which require safe and practical means of storing hydrogen.

To improve the binding of hydrogen to physisorption materials, recent research has focused on dispersing metal atoms onto these materials. A stronger interaction with hydrogen molecules has important consequences for thermodynamics, and increases the operating temperatures of storage materials. To restrict the increase of the total system weight, resulting from the addition of metals, only a limited number of metal atoms can be used to decorate lightweight hosts. Atoms of simple, electropositive alkali or alkaline earth metals form very polar bonds with carbon-based (or boron-based) materials. Electrostatic interactions between (partially charged) metal atoms and the induced dipoles or multipoles on hydrogen molecules result in a binding energy that is 2–3 times higher than a typical van der Waals bond between hydrogen and a carbon-based material.^{2,3} Alkaline earth metals, such as Ca, have a larger effect on the binding energy than alkali metals, such as Li or Na. Recent studies have shown that functionalizing lightweight hosts with Ca atoms has important benefits.^{4–19}

Dispersing transition metal atoms, such as Sc or Ti, on carbon-based substrates, makes the adsorption energy of hydrogen molecules even larger.^{20–24} However, not all hydrogens are then bonded equally. Upon loading, the first hydrogen molecules are strongly chemisorbed in atomic form, and the subsequent ones are physisorbed in molecular form. This means that the full storage capacity cannot be addressed at a single operating temperature. Moreover, clustering of metal atoms will almost certainly occur, because of the relatively large cohesive energy of these transition metals (≥ 4 eV per atom). This, in turn, degrades the storage capacity even further.²⁵ Ca metal has a relatively small cohesive energy (≤ 2 eV per atom), so Ca atoms have a lower tendency to cluster on the host material

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once they are deposited. Ca atoms are expected to bind all hydrogen molecules reversibly *via* physisorption. Moreover, Ca is an abundant element, which is relatively low-cost when compared with transition metals such as Sc or Ti.

The experimental and theoretical studies done so far mainly explored pure carbon-based systems (fullerenes, nanotubes, graphene, graphyne and carbyne).^{7–19} In this work, we study the Ca decoration of carbon-boron heterofullerenes. The first heterofullerenes realized in experiments were boron-doped carbon fullerenes.^{26,27} Since then, a variety of heterofullerenes with different boron concentrations have been produced on a macroscopic scale.^{28–37} We show that incorporating boron stabilizes the Ca-decorated fullerene, and also increases the interaction of hydrogen molecules with this system. The optimal interaction strength can be obtained from the rationalization that follows.

The adsorption of molecules, such as H₂, under common conditions does not usually involve a first-order phase transition. This means that when operating at a fixed temperature T , the storing and unloading of hydrogen have to be done at two different gas pressures P_1 and P_2 , respectively. Assuming that physisorption of hydrogen can be described by the Langmuir adsorption model,³⁸ the fraction f of the total adsorption capacity that is reversibly loaded and unloaded at these pressures is maximally

$$f = \frac{\sqrt{P_1/P_2} - 1}{\sqrt{P_1/P_2} + 1}, \quad (1)$$

if the change in free energy ΔG_0 , which determines the adsorption reaction constant, is equal to

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 = \frac{RT}{2} \ln \left[\frac{P_1 P_2}{P_0^2} \right], \quad (2)$$

where $P_0 = 1$ bar is the standard pressure. Using Monte Carlo simulations, Bhatia and Myers³⁸ have argued that for hydrogen adsorption on a range of carbon substrates, the entropy change at standard pressure $\Delta S_0 \approx -8R$. It means that, *e.g.*, at room temperature for $P_1 = 30$ bar and $P_2 = 1.5$ bar, the optimum adsorption enthalpy is $\Delta H_0 \approx -0.15$ eV per H₂ molecule. As intrinsic properties, such as vibrations, of hydrogen molecules hardly change upon physisorption, one may approximate ΔH_0 by the $T = 0$ hydrogen binding energy, and neglect the contributions of zero-point motions. On substrates other than carbon based materials, a variation in the entropy change at standard pressure (ΔS_0) shifts the enthalpy change at standard pressure (ΔH_0). Recent experiments on porous solids with cationic metal centers, such as cation-exchanged zeolites and metal-organic frameworks with coordinatively unsaturated cationic metal atoms, suggest a positive and nonlinear correlation between ΔS_0 and ΔH_0 . These new studies estimate the ideal value of hydrogen binding energies ($-\Delta H_0$) to be between 0.23 and 0.26 eV per H₂.^{39,40} Accordingly, for the materials considered in the present work, we aim for molecular hydrogen binding energies that are between 0.15 and 0.26 eV per H₂.

We calculate such adsorption energies within density functional theory (DFT) calculations with the PW91 functional of the

generalized gradient approximation (GGA),⁴¹ using the Vienna *Ab initio* Simulation Package (VASP).^{42–44} Projector augmented waves (PAW)^{45,46} are employed, treating, for B and C, the electrons in the 1s shell as the frozen core, and for Ca all electrons up to and including the 3s shell. The PAW technique and the GGA-PW91 functional are sufficiently accurate for studying the interaction between molecular hydrogen and metals.^{2,3,6,47} To account for the dispersion (van der Waals) interactions we also carry out calculations using the DFT-D2 method of Grimme with its default force-field parameters as implemented in VASP.⁴⁸ Grimme's empirical correction scheme for common density functionals has been applied successfully to many chemical problems including molecular hydrogen.^{4,49–54} We find however that Ca loses part of its valence electrons. The resulting Ca ion is more difficult to polarize, hence its van der Waals interaction with molecular hydrogen is probably weakened. Thus, PW91 results can be taken as lower bounds for hydrogen binding energies whereas DFT-D2 results can be taken as upper bounds. The kinetic energy cutoff for the plane waves is set to 400 eV and the conjugate gradient (CG) algorithm is used for the geometry optimizations. All molecules are optimized using a periodic cubic box and Γ -point sampling. A sufficiently large cell parameter of 30 Å is used to avoid significant interactions between the periodic images. The optimizations are assumed to be complete when the total remaining forces on the atoms are lower than 0.01 eV Å⁻¹. In the following, we report the calculated numbers using the DFT-D2 method of Grimme. When discussing small binding energies, where van der Waals interactions could be significant, we report both DFT-D2 and PW91 results.

We calculate the binding energy E_b^{Ca} of a Ca atom to a (hetero)fullerene molecule from

$$E_b^{\text{Ca}} = \frac{1}{x} \left[E_{\text{C}_{48}\text{B}_{12}} + x E_{\text{Ca}(\text{bulk})} - E_{\text{C}_{48}\text{B}_{12}\text{Ca}_x} \right], \quad (3)$$

where $E_{\text{C}_{48}\text{B}_{12}}$ is the total energy of a (hetero)fullerene molecule, $E_{\text{Ca}(\text{bulk})}$ is the total energy per atom of calcium bulk metal, and $E_{\text{C}_{48}\text{B}_{12}\text{Ca}_x}$ is the total energy of a (hetero)fullerene molecule decorated with x Ca atoms. Note that a positive value of E_b^{Ca} means that the Ca-decorated (hetero)fullerene molecule is stable.

We first consider the interaction of a single Ca atom with a (hetero)fullerene molecule. We find that the Ca atom does not bind strongly to carbon-only fullerene. Using the total energy $E_{\text{Ca}(\text{atom})}$ of an isolated Ca atom instead of the bulk energy $E_{\text{Ca}(\text{bulk})}$ in eqn (3), we find a binding energy of 1.437 eV, in accordance with a previous study.¹⁹ However, if we use $E_{\text{Ca}(\text{bulk})}$ as a reference energy, as is more appropriate, then $E_b^{\text{Ca}} = -0.666$ eV. Such a negative value indicates that Ca-decorated C₆₀ molecules are thermodynamically not stable against decomposition into C₆₀ and Ca bulk. Therefore, there is an intrinsic driving force towards the clustering of Ca atoms, which severely impairs the potential use of C₆₀Ca as a hydrogen storage material.

The binding between Ca and C₆₀ is polar. If we perform a Bader charge analysis^{55,56} to estimate the effective charges on the atoms, we find that the Ca atom attains a charge of +1.38e. To increase the binding between Ca and fullerene, we consider

Fig. 1 Perspective views of DFT optimized $C_{48}B_{12}$ heterofullerenes: (a) the S_6 isomer, and (b) the C_i isomer. Carbon and boron atoms are shown as grey and purple spheres, respectively.

substitution of fullerene carbons with boron atoms in the latter. This creates an electron-deficient molecule and hence a better acceptor than C_{60} . Previous studies have shown that such substitutions are possible up to boron concentrations of 20 atom%, while retaining the fullerene structure.^{26,28–30,57–60} $C_{48}B_{12}$ has two low energy isomers of S_6 and C_i symmetry.^{57,58,60} We find that the S_6 isomer is 0.836 eV per molecule lower in energy than the C_i isomer, making the former thermodynamically much more stable. The increased acceptor character of these boron-substituted fullerenes is illustrated by their electron affinity. The calculated electron affinity of C_{60} is 2.77 eV, in good agreement with the earlier theoretical⁵⁷ (2.40 eV) and the experimental⁶¹ (2.69 eV) results. The calculated electron affinities for the S_6 and C_i isomers of $C_{48}B_{12}$ are 3.70 eV and 3.81 eV, respectively.

Both the $C_{48}B_{12}$ isomers have pentagons containing a single B atom (Fig. 1). The S_6 isomer contains eight all-carbon and twelve C_4B_2 hexagons (Fig. 1a). Six of the latter contain B in *para* positions, whereas the others contain B in *meta* positions. The C_i isomer contains two all-carbon, twelve C_5B_1 , and six C_4B_2 hexagons (Fig. 1b). All six of the latter have B in *para* positions.

We find that the most favorable binding site of Ca is over the C_4B_2 hexagon centers, both in the S_6 and the C_i isomers, as shown in Fig. 2. The calculated binding energies of a single Ca atom, $x = 1$ in eqn (3), are 1.564 eV and 1.575 eV to the S_6 and C_i isomers, respectively. These values clearly demonstrate that binding of Ca to $C_{48}B_{12}$ is much stronger than to C_{60} . In contrast to $C_{60}Ca$, $C_{48}B_{12}Ca$ is stable with respect to clustering of Ca atoms, *i.e.* separation into Ca bulk and $C_{48}B_{12}$ molecules. Similar to $C_{60}Ca$, we perform a Bader charge analysis on $C_{48}B_{12}Ca$. The calculated Bader charges on Ca are +1.52e and to +1.51e for the S_6 and C_i isomers, respectively, indicating that the

bonding has a substantial ionic character, and that the two isomers behave very similarly regarding their bonding to Ca.

Next, we study the adsorption of H_2 molecules on $C_{48}B_{12}Ca$. We calculate the binding energy of hydrogen molecules to $C_{48}B_{12}Ca_x$ using eqn (4).

$$E_b^{H_2} = \frac{1}{y} [E_{C_{48}B_{12}Ca_x} + yE_{H_2} - E_{C_{48}B_{12}Ca_x(H_2)_y}], \quad (4)$$

where E_{H_2} and $E_{C_{48}B_{12}Ca_x(H_2)_y}$ are the total energies of the hydrogen molecule and the stepwise hydrogenated (hetero) fullerene–Ca system, respectively. A single Ca atom ($x = 1$) can bind up to six H_2 molecules, as illustrated in Fig. 2, with five H_2 in a ring around the protruding Ca atom, and the sixth H_2 molecule on top of the Ca atom. The first H_2 molecule is bonded with an energy of 0.265 eV per H_2 and 0.243 eV per H_2 , to the Ca-decorated S_6 and C_i isomers of $C_{48}B_{12}$, respectively. Additional H_2 molecules bind somewhat less strongly, see Table 1. At their fully hydrogenated states, the Ca-decorated S_6 and C_i isomers bind the hydrogen molecules with average binding energies of 0.245 eV per H_2 and 0.242 eV per H_2 , respectively. The calculations using the PW91 functional give similar results to the DFT-D2 method, but the average hydrogen binding energies are approximately 0.1 eV lower for both of the isomers (Table 1).

As $C_{48}B_{12}$ is isoelectronic with C_{60}^{12+} , and the bonding with Ca atoms has a substantial ionic character, one expects that $C_{48}B_{12}$ accommodates six Ca atoms with similar binding characteristics. This is achieved by putting a Ca atom over the centers of all C_4B_2 hexagons, both in the S_6 and the C_i isomers. Each of these Ca atoms is bonded strongly to $C_{48}B_{12}$ with average binding energies of 1.046 eV per atom and 1.082 eV per atom for the S_6 and C_i isomers, respectively (eqn. (3)). Note that, since these binding energies are calculated with respect to Ca bulk, we expect $C_{48}B_{12}Ca_6$ to be stable against the clustering of Ca atoms, which is again in contrast to Ca-decorated C_{60} .

The optimized structures of the fully hydrogenated $C_{48}B_{12}Ca_6$ molecules are shown in Fig. 3. As for $C_{48}B_{12}Ca$, we find that a maximum of six H_2 molecules are adsorbed per Ca atom. Consequently, the fully hydrogenated molecules have the chemical formula $C_{48}B_{12}Ca_6(H_2)_{36}$. Each heterofullerene molecule then contains 7.1 wt% H_2 with average binding energies of 0.249 eV per H_2 (0.152 eV per H_2 with PW91) and 0.244 eV per H_2 (0.148 eV per H_2 with PW91), for the S_6 and C_i isomers, respectively.

For physisorbed molecules, one may expect that these energies also determine the kinetics, and that no additional

Fig. 2 Optimized structures of $C_{48}B_{12}Ca(H_2)_y$, $y = 1–6$ of the S_6 isomer. Carbon, boron, calcium and hydrogen atoms are shown as grey, purple, yellow and turquoise spheres, respectively.

Table 1 Calculated binding energies of Ca atoms to $C_{48}B_{12}$ isomers with respect to bulk Ca metal (E_b^{Ca}), Bader charges on the Ca atoms (Q), average binding energies ($E_b^{H_2}$) of H_2 molecules to $C_{48}B_{12}Ca$ (see Fig. 2)

Isomer	E_b^{Ca} (eV)	Q (e)	$E_b^{H_2}$ (eV)					
			1 H_2	2 H_2	3 H_2	4 H_2	5 H_2	6 H_2
S_6	1.616	+1.47	0.175	0.163	0.164	0.156	0.151	0.152
S_6 (DFT-D2)	1.564	+1.52	0.265	0.255	0.255	0.249	0.246	0.245
C_i	1.626	+1.46	0.161	0.161	0.154	0.156	0.149	0.149
C_i (DFT-D2)	1.575	+1.51	0.243	0.243	0.239	0.246	0.243	0.242

kinetic energy barriers are involved in the adsorption process. To illustrate this, we carried out *ab initio* molecular dynamics (AIMD) simulations on the $C_{48}B_{12}Ca(H_2)_6$ molecule in the micro-canonical ensemble.⁶² Due to the presence of lightweight elements, we used a short time step of 1.0 fs in the AIMD simulations. Using the average kinetic energy of the atoms as a measure of the temperature, the latter is stepwise increased from 50 K to 300 K in 50 K steps, where at each temperature the simulations are performed for 15 ps. Fig. 4 shows the radial distribution function for Ca–H pairs and the structures at the end of each equilibration step. In the simulation run, five hydrogen molecules stay adsorbed at temperatures ≤ 150 K, and all are desorbed at temperatures ≥ 300 K. This behavior is consistent with the absence of any kinetic barrier for desorption.

Fig. 3 Perspective views of the fully optimized Ca-decorated heterofullerenes in their fully hydrogenated states, $C_{48}B_{12}Ca_6(H_2)_{36}$. (a) and (b) correspond to the S_6 and C_i isomers, respectively.

Fig. 4 The radial distribution functions (RDFs) of Ca–H at the end of 15 ps AIMD equilibration runs using the DFT-D2 method at 50, 100, 150, 200, 250 and 300 K for the S_6 isomer based $C_{48}B_{12}Ca(H_2)_6$ molecule. The boxes shown at the right show the structures at the end of each run.

In summary, we studied the functionalization of boron heterofullerenes with Ca atoms for high density hydrogen storage. We find that six Ca atoms interact strongly with $C_{48}B_{12}$, and the dispersed Ca atoms are thermodynamically stable against metal clustering, unlike Ca atoms dispersed on C_{60} . The bonding between Ca and $C_{48}B_{12}$ has a substantial ionic character, and the well-exposed, (partially) charged Ca atoms bind up to six H_2 molecules per Ca with an average binding energy of ~ 0.24 eV per H_2 (DFT-D2) and ~ 0.15 eV per H_2 (PW91). These energies are in the range needed for onboard hydrogen storage, yielding 7.1 wt% H_2 . Furthermore, the predicted hydrogen binding energies are only weakly dependent on H_2 loading.

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