

## Metallacarboranes: Toward Promising Hydrogen Storage Metal Organic Frameworks

Abhishek K. Singh,<sup>†,‡</sup> Arta Sadrzadeh,<sup>†</sup> and Boris I. Yakobson<sup>\*,†</sup>

Department of Mechanical Engineering and Materials Science, Department of Chemistry, and  
The Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University,  
Houston, Texas 77005, and Materials Research Centre, Indian Institute of Science,  
Bangalore 560012, India

Received May 25, 2010; E-mail: biy@rice.edu

**Abstract:** Using first principles calculations, we show the high hydrogen storage capacity of metallacarboranes, where the transition metal (TM) atoms can bind up to 5 H<sub>2</sub>-molecules. The average binding energy of ~0.3 eV/H favorably lies within the reversible adsorption range. Among the first row TM atoms, Sc and Ti are found to be the optimum in maximizing the H<sub>2</sub> storage (~8 wt %) on the metallacarborane cluster. Being an integral part of the cage, TMs do not suffer from the aggregation problem, which has been the biggest hurdle for the success of TM-decorated graphitic materials for hydrogen storage. Furthermore, the presence of carbon atom in the cages permits linking the metallacarboranes to form metal organic frameworks, which are thus able to adsorb hydrogen via Kubas interaction, in addition to van der Waals physisorption.

### Introduction

Hydrogen is considered as a promising renewable nonpolluting alternative to fossil fuels.<sup>1</sup> The success of hydrogen-based fuel cell depends upon materials that can store hydrogen efficiently and reversibly at ambient conditions. An extensive search for efficient hydrogen storage materials led to the finding of several promising candidates including metal hydrides,<sup>2–4</sup> graphitic sorption nanomaterials,<sup>5,6</sup> and metal organic frameworks (MOF).<sup>7,8</sup> Although promising, these individual storage materials suffer from one or the other form of practical difficulties; for example, too strong metal–H binding in metal hydrides often results in poor kinetics, whereas too weakly physisorbed H<sub>2</sub> in graphitic nanostructures and in MOFs requires storage at very low temperature. Between strong chemisorption and weak physisorption, there exists a Kubas<sup>9</sup> type of interaction, a “non-classical” form of binding of H<sub>2</sub> to metal with a binding energy of ~0.4 eV/H<sub>2</sub>, which is ideal for the reversible storage at ambient conditions. A single metal atom can bind multiple H<sub>2</sub> molecules<sup>9,10</sup> via the Kubas interaction, leading to high gravimetric and volumetric density.

The possibility of storing hydrogen via the Kubas interaction has been explored extensively for the case of transition metal (TM) decorated graphitic nanostructures<sup>11–16</sup> (nanotubes, fullerenes, and graphene). Depending upon the type of metal atom, such complexes<sup>13,15</sup> can store hydrogen up to 8 wt %. TM–ethylene complexes are once shown to store as much hydrogen<sup>14,17</sup> as 14 wt %. The idea has been extended to lighter metal decorated carbon materials<sup>18,19</sup> as well, where significant storage has been predicted. These materials are promising and, if experimentally realized, can easily meet the material-based DOE targets<sup>20</sup> for 2015. The biggest hurdle on the way to success of such materials is the tendency of metal atoms to aggregate.<sup>21,22</sup> It has been shown<sup>22</sup> that TM atoms cluster on the surface of graphitic nanostructures, which significantly reduces the storage wt %. To prevent the clustering of metal atoms, the doping of carbon nanostructures by boron has been proposed.<sup>13</sup> Because of stronger B–TM binding, boron acts as an anchor to the metal atom. The practical difficulty of doping

<sup>†</sup> Rice University.<sup>‡</sup> Indian Institute of Science.

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carbon nanostructures with boron remains a challenge for successful synthesis of such materials. So far, there are no experimental reports on well-separated transition metal atoms on the boron-doped carbon nanostructures.

The key to the success of hydrogen storage via Kubas interaction may lie in finding nanomaterials where the metal atoms are among the constituent elements (and thus cannot aggregate), yet retain their H-binding ability. One such class is metallacarboranes,<sup>23</sup> derived from the carboranes, one of the most studied classes of boron clusters. Carboranes are essentially borane clusters containing one or more carbon atoms. Replacing one or more BH units of carboranes by metal atoms leads to the formation of metallacarboranes. The advantage of having both metal and C in the same cage has been utilized in various applications, including even nanomotors.<sup>24</sup>

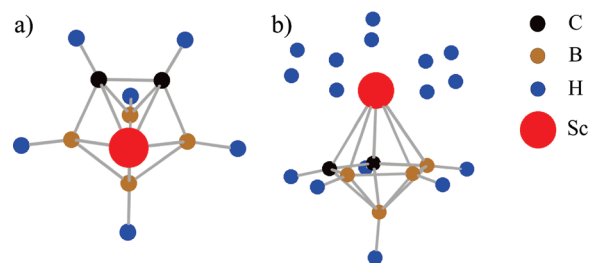
This sets the stage for investigation of hydrogen storage capacity of metallacarborane based MOF, further motivated by a recent Farha et al. demonstration that icosahedral carborane-based MOF can store up to 2 wt % of H<sub>2</sub> at 77 K via physisorption.<sup>25,26</sup> Here, we show that metal in metallacarboranes can bind multiple hydrogen molecules, while carbon can link the clusters to form three-dimensional frameworks. Replacing carboranes in MOF by metallacarboranes enhances the wt % due to adsorption of additional H<sub>2</sub> on metal atoms via Kubas interaction. This leads to storage of up to 8.8 wt % in metallacarboranes. Moving from a pure physisorption to Kubas type of H<sub>2</sub> binding increases the binding strength, which can ensure room temperature storage. The binding energies lie within the reversible adsorption range at ambient conditions. Sc and Ti are recognized as the most optimal metals in maximizing the storage capacity.

## Methods

The calculations are performed using the density-functional theory-based pseudopotential plane wave method as implemented in VASP.<sup>27,28</sup> The ion-electron interaction is treated with all-electron projector-augmented wave (PAW) pseudopotentials<sup>29,30</sup> using spin-polarized generalized gradient approximation of the Perdew–Burke–Ernzerhof (PBE)<sup>31</sup> for exchange and correlation. Gamma point is used for Brillouin zone sampling. Symmetry-unrestricted optimizations of both geometry and spin are performed using the conjugate gradient scheme until the forces on every atom are less than 0.005 eV/Å. Large vacuum spaces (~15 Å) are used in supercells to minimize any cell–cell spurious interactions. The binding energy of the adsorbed hydrogen is defined as  $E_b = (E(\text{H}_2) + E(\text{adsorbent-H}_{m-2}) - E(\text{adsorbent-H}_m))/2$ .

## Results and Discussion

The aim of our study is to assess the hydrogen storage capacity of metallacarboranes and also to find out the best metal atom, which can maximize the number of adsorbed H<sub>2</sub> mol-



**Figure 1.** The optimized structures of (a) C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>Sc (MCB1) and (b) fully hydrogen saturated C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>Sc-5H<sub>2</sub>.

**Table 1.** Average Magnetic Moment, Number of H<sub>2</sub>'s Adsorbed, wt %, Highest–Lowest Binding Energies of H<sub>2</sub>, and  $d_{\text{HH}}$  for Different Systems Studied

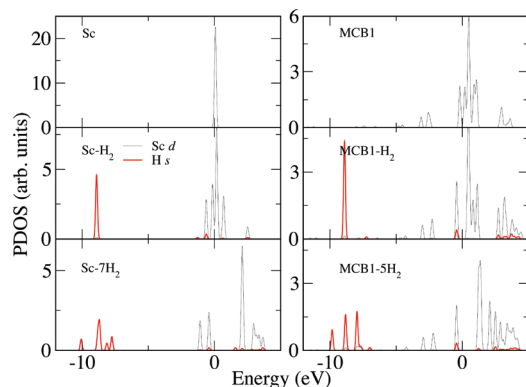
M (no. of d-electrons)	magnetic moment ( $\mu_B$ )	number of adsorbed H <sub>2</sub> 's	wt %	$E_b$ (eV/H)	$d_{\text{HH}}$ (Å)
Sc (1)	1	7	23.89	0.42–0.10	0.85–0.79
MCB1Sc (1)	1	5	7.85	0.26–0.10	0.84–0.78
MCB2Sc	1	5	5.38	0.26–0.01	0.79–0.77
MCB3Sc	2	10	8.81	0.21–0.01	0.79–0.77
MCB4Sc	0	8	6.38	0.17–0.08	0.81
Ti (2)	2	7	22.76	0.46–0.20	0.96–0.81
MCB1Ti (2)	2	5	7.68	0.38–0.13	0.85–0.77
MCB2Ti	2	5	5.29	0.34–0.12	0.84–0.77
MCB3Ti	4	8	6.93	0.32–0.16	0.78
MCB4Ti	2	6	4.75	0.25–0.03	0.80–0.78
MCB1 V (3)	3	4	6.09	0.30–0.24	0.89–0.80
MCB1Cr (5)	4	3	4.60	0.38–0.25	0.90–0.80
MCB1Mn (5)	5	3	4.50	0.37–0.23	0.92–0.79
MCB1Fe (6)	4	3	4.47	0.56–0.04	0.92–0.83
MCB1Co (7)	3	3	4.38	0.58–0.05	0.92–0.76
MCB1Ni (8)	2	2	2.96	0.58–0.31	0.94–0.79

ecules. Because of computational limitations, the smallest metallacarborane C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>M (where M = Sc, Ti, V, Cr, Mn, Fe, Co, and Ni) is chosen to carry out the search for the optimal metal atoms. The optimized structure of C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>M (MCB1) is shown in Figure 1a. The ground-state structures are spin polarized, and magnetic moments change with the type of metal atoms, as shown in Table 1. The transition metal atoms keep their atomic magnetic moments, due to strong exchange splitting in spin-up and -down states.

Hydrogen molecules are added subsequently to the MCB1, followed by unconstrained relaxation of the structure. As expected, the H<sub>2</sub> molecules bind to the metal via the Kubas interaction,<sup>9</sup> which is based on the Lewis concept of donation of electron pairs. In such complex, a  $\sigma$ -bonding electron pair (H:H) of H<sub>2</sub> molecule interacts with the d-orbital of a metal via electron donation, Figure 2. The uniqueness in the stabilization of M–H<sub>2</sub> complex is backdonation (BD), that is, the retrodonative donation of electrons from a filled metal d-orbital to the  $\sigma^*$  orbital of H–H bond. The BD is an important process in adding the H<sub>2</sub> to metal, in orienting the H<sub>2</sub> side-on to the metal, and in activating the dissociation of H–H bond. If the backdonation becomes too strong, it leads to overpopulation of  $\sigma^*$  orbital and results in the breaking of the H–H bond and eventually leads to a strong M–H bonding as in metal hydride. On the other hand, a balance of BD and  $\sigma$  donation stabilizes the Kubas complexes. Generally, the H–H bond length,  $d_{\text{HH}}$ , is stretched about 15–25% over its value in free H<sub>2</sub> (0.74 Å). The  $d_{\text{HH}}$  is controlled by the ability of metal to backdonate electrons and, therefore, varies with the change of metal atoms, Table 1.

The subsequent hydrogenation of MCB1 corresponding to each metal atom is continued until the cluster stops binding any more H<sub>2</sub> molecules (Figure 1b). Different metal atoms adsorb

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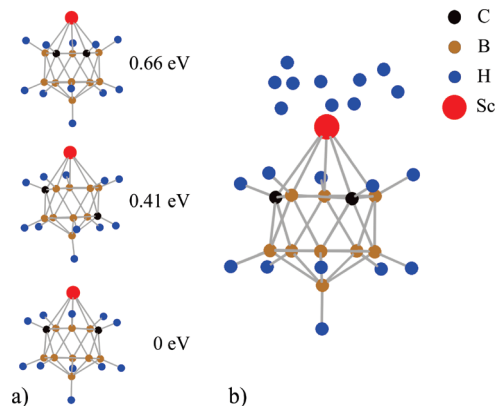


**Figure 2.** Orbital projected density of states (DOS) for different number of adsorbed hydrogen molecules on Sc (left column) and  $C_2B_4H_6Sc$  (MCB1, right column). The black and red lines correspond to d- and s-orbitals of Sc and H, respectively. For clarity, the H-s DOS is enhanced by a factor of 3. After the adsorption of the first hydrogen molecule, there remain empty d-orbitals (peaks right after the Fermi level), which do not interact with H s-orbital. However, for the fully saturated Sc atom or MCB1, there are no such peaks available.

a different number of hydrogen molecules. The  $H_2$  storage capacity of a transition metal atom decreases with increasing number of d-electrons, Table 1. As the number of d-electrons increases, the ability of the metal atom to accept the  $\sigma$  donated electrons from  $H_2$  decreases, which reduces the number of adsorbed  $H_2$  molecules. Among the first row transition metal atoms, Sc and Ti have the maximum number of available empty d-orbitals; therefore, they adsorb the largest number of  $H_2$  molecules as shown in Table 1.

To evaluate the effect of cluster-cage on the binding ability of a TM, we analyze the hydrogen binding to Sc and Ti when they are in atomic form,<sup>9</sup> as opposed to being part of metallacarborane. The hydrogen storage capacity of an isolated TM atom (Sc or Ti) is estimated. These TM atoms adsorb seven  $H_2$  molecules before the saturation, two more than in the MCB1 cluster. Both steric and electronic effects cause the reduction in the number of adsorbed  $H_2$  on MCB1. Geometrically, due to the presence of carborane, the  $H_2$  molecule cannot bind to one side of the metal atom. Furthermore, the TM atom interacts with the carborane via d-electrons following the donation–backdonation mechanism as shown in Figure 2 for the case of Sc. This essentially reduces the available number of d-orbitals, which leads to adsorption of a lesser number of hydrogen molecules on MCB1 as compared to the single metal atom. The overall binding behavior remains similar to the isolated atom. Figure 2 shows the difference between the hybridization of the  $H_2$  s- with the Sc d-orbitals upon the subsequent adsorption. In the case of Sc– $H_2$ , there are still empty d-orbitals available to bind more  $H_2$ 's, whereas after maximum adsorption every metal d peak has a corresponding peak from  $H_2$  s-orbitals. The same behavior can be seen for the Sc atom in the MCB1, Figure 2. Overall, metal keeps most of its ability to adsorb hydrogen even in the MCB1. We should also note that the adsorbed hydrogen molecules in both cases (Sc and Ti) stay in associated form, with bond elongation within the range for Kubas type of binding (Table 1).

In a series of TM, the range of binding energies is given in Table 1. The  $E_b$  values vary with the change of the metal atoms. Moving right in the periodic table, transition metal atoms' tendency to donate d-electrons to the  $\sigma^*$  orbital increases, which leads to increased H–H bond length and stronger average binding energies, Table 1. The lesser number of adsorbed



**Figure 3.** (a) The optimized structures of 1–2, 1–5, and 1–3- $C_2B_9H_{11}Sc$  (MCB2). The relative energies with respect to MCB2 are given. (b) The optimized structure of fully hydrogenated MCB2.

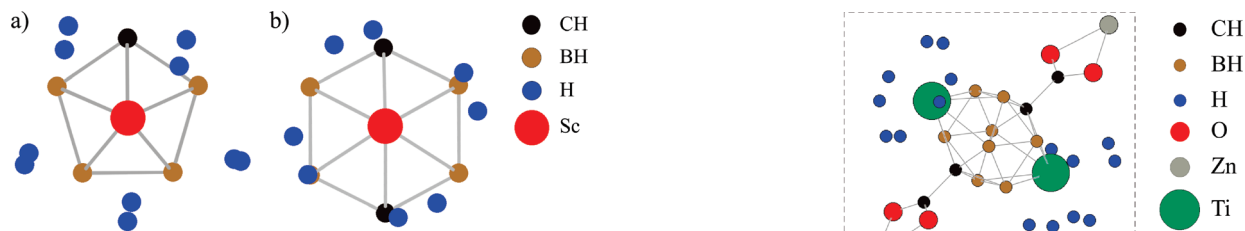
hydrogen, increased binding energy, and weight of the late TM atoms eventually make them less optimal for room temperature storage. Although Ti, V, and Cr have optimal binding energies, due to a smaller number of adsorbed  $H_2$  molecules on V and Cr, they will not be considered for further study. Sc- and Ti-based metallacarboranes store  $\sim 7.8$  wt %, which is maximum among the first row TM atoms and will be considered for the evaluation of hydrogen storage capacity of larger clusters.

Next, we estimated hydrogen storage capacities of more common metallacarborane clusters.<sup>23</sup> First, we consider  $C_2B_9H_{11}M$  ( $M = Ti$  and  $Sc$ ), derived from an icosahedral carborane. We calculated the binding energy of metal in three known isomers of  $C_2B_{10}H_{12}$ , by replacing one BH by a metal. Among the three nonequivalent positions of C atoms shown in Figure 3, 1–3- $C_2B_9H_{11}M$  (MCB2) has the lowest energy. The two carbon atoms do not choose to stay adjacent to each other and prefer to be on a pentagonal ring, which is connected to the metal atom.

Upon subsequent hydrogenation of MCB2, both Sc and Ti adsorb five  $H_2$  molecules via the Kubas interaction. The  $H_2$  wt % in this cluster is 5.38% and 5.30% for Sc and Ti, respectively. The  $d_{HH}$  and  $E_b$  reduce slightly from the pentagonal-MCB1 case. This is not surprising, as it has been shown<sup>9</sup> that, depending upon the ability to draw charge from the metal atoms, the carborane cage influences the  $H_2$  binding to the metal atom.

The storage capacity can be further enhanced if there is more than one metal atom in the metallacarborane cluster. In fact, most of the commonly observed metallacarboranes have two metal atoms. We study the  $C_2B_8H_{10}M_2$  ( $M = Sc$  and  $Ti$ ), where the metal atoms are at the two opposite apexes of the icosahedron. The positions of C atoms are optimized, and, among the nonequivalent structures of parent carborane, 1–5- $C_2B_8H_{10}M_2$  (MCB3) was found to be lowest in energy. In this configuration, each metal atom is bonded to four borons and one carbon. 1–3- and 1–2- $C_2B_8H_{10}M_2$  are 0.008 and 0.56 eV higher in energy, respectively. Upon hydrogenation, Sc (shown in Figure 4a) and Ti atoms totally adsorb 10 and 8  $H_2$ 's, respectively. The resulting wt % is 8.81 and 6.93 for Sc and Ti, respectively. The  $d_{HH}$  remains similar to the MCB2.

Finally, we studied a slightly larger symmetric metallacarborane hexagonal antiprism  $C_4B_8H_{12}M_2$  (MCB4,  $M = Sc$  and  $Ti$ ), having metal atoms at the two opposite apexes. Similar to the previous cases, the hydrogen binds to metal atom via Kubas interaction. The Sc and Ti atoms adsorb eight and six  $H_2$  molecules totally, resulting in 6.38 and 4.75 wt %, respectively,



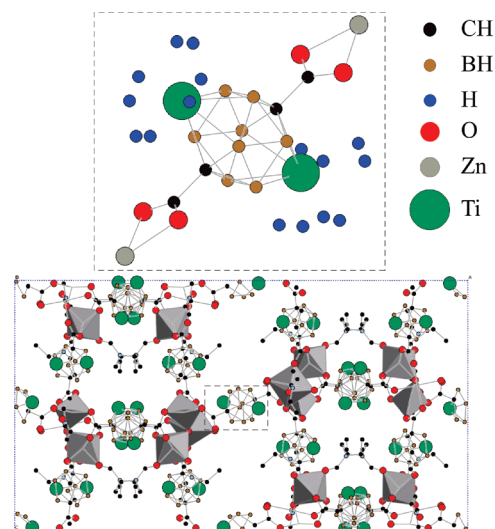
**Figure 4.** (a) A view along the Sc---Sc axis of the optimized fully hydrogenated structures of (a) pentagonal antiprism  $1-5-C_2B_8H_{10}Sc_2(MCB3)-10H_2$  and (b) hexagonal antiprism  $C_4B_8H_{12}Sc_2(MCB4)-8H_2$ .

as shown in Figure 4b. The average binding energies and magnetic moments show similar trends as observed in previous cases. Therefore, MCB4 can also store hydrogen in significant wt %. However, due to an increase in the number of atoms and volume of the cage, the gravimetric as well as volumetric capacities will be reduced.

The importance of the presence of carbon atoms in the metallacarboranes is that they can bind to linkers such as metal–carboxylate, which will connect these clusters in a three-dimensional framework as demonstrated for the carborane-based MOF.<sup>25</sup> Therefore, it is important to estimate how carboxylate affects the overall storage capacity of the metallacarboranes. We tested this by adding  $COOZn$  to the carbon atom and hydrogenating the cluster. The number of adsorbed  $H_2$  molecules remains the same as in the original metallacarborane. Each carboxylate group can attach up to four metallacarborane clusters. In the case of  $1-5-C_2B_8H_{10}Ti_2$ , the wt % (calculated only considering the Kubas type of  $H_2$ ) reduces from 6.93% to 5.65%, which is still larger than the DOE 2015 target.<sup>20</sup> Taking these into account, we show a model structure of metallacarborane-based MOF in Figure 5. The structure is derived from the experimentally synthesized carborane MOF<sup>25</sup> by replacing two BH units by metal atoms. Such MOFs have larger pore size and could physisorb an additional  $H_2$  molecule, Figure 5. This will further enhance the  $H_2$  storage in the metallacarborane-based MOFs. Therefore, metallacarborane-based MOFs are indeed promising materials for efficient  $H_2$  storage.

## Conclusions

In summary, we show the viability of metallacarboranes as natural hydrogen storage materials. The metallacarboranes bind hydrogen via the Kubas interaction, with the binding energies lying in the reversible storage range. The Sc and Ti are found



**Figure 5.** Optimized structure of corresponding  $1-5-C_2B_8H_{10}Ti_2$  (MCB3) with the Zn-carboxylate groups attached. Shown is the likely structure of a MOF with MCB3 linkers, analogous to that experimentally reported<sup>25</sup> (here, two BH units are replaced by Ti atoms in every carborane cage).

to be the optimum metal atoms maximizing the number of stored  $H_2$  molecules. Being an integral part of the metallacarboranes, Sc and Ti atoms do not cluster and remain isolated. Depending upon the structure, metallacarboranes can adsorb up to 8 wt % of hydrogen, which exceeds the DOE goal for 2015.<sup>20</sup> Furthermore, carboxylate-based connectors have no effect on the number of adsorbed  $H_2$  molecules. Therefore, in addition to adsorbing  $H_2$  via the Kubas interaction, metallacarborane-based MOFs will also physisorb  $H_2$  in the pores. Given the recent progress made in the carborane-based MOFs, and abundance of metallacarboranes, such materials can soon become experimental reality.

**Acknowledgment.** The Robert Welch Foundation (C-1590) and the Department of Energy (BES Grant DE-FG02-09ER46598) are gratefully acknowledged for support.

**Supporting Information Available:** Energies and Cartesian coordinates of all the optimized geometries discussed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA10454S