

# Hydrogen storage capacity of titanium met-cars

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## Abstract

The adsorption of hydrogen molecules on the titanium metallocarbohedryne (met-car) cluster has been investigated by using the first-principles plane wave method. We have found that, while a single Ti atom at the corner can bind up to three hydrogen molecules, a single Ti atom on the surface of the cluster can bind only one hydrogen molecule. Accordingly, a  $\text{Ti}_8\text{C}_{12}$  met-car can bind up to 16  $\text{H}_2$  molecules and hence can be considered as a high-capacity hydrogen storage medium. Strong interaction between two met-car clusters leading to the dimer formation can affect  $\text{H}_2$  storage capacity slightly. Increasing the storage capacity by directly inserting  $\text{H}_2$  into the met-car or by functionalizing it with an Na atom have been explored. It is found that the insertion of neither an  $\text{H}_2$  molecule nor an Na atom could further promote the  $\text{H}_2$  storage capacity of a  $\text{Ti}_8\text{C}_{12}$  cluster. We have also tested the stability of the  $\text{H}_2$ -adsorbed  $\text{Ti}_8\text{C}_{12}$  met-car with *ab initio* molecular dynamics calculations which have been carried out at room temperature.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Efficient use of the  $\text{H}_2$  molecule as an alternative and clean energy source relies on the discovery of a feasible and secure storage medium [1]. Significant efforts have been devoted to deducing nanostructures with a high surface/volume ratio which can make a high weight percentage (wt%) of  $\text{H}_2$  storage possible. Until now, various types of materials (carbon nanotubes, activated carbons, metal organic framework compounds, metal hydrides, clathrates, and carbide-derived carbons) have been examined [2]. In particular, carbon-based nanomaterials such as nanotubes [3] and metal hydrides such as alanates [4] have attracted attention. Single-wall carbon nanotubes (SWNTs), due to their high surface-to-volume ratio, have been the most studied materials. Recently, it has been shown that Ti decorated on several nanostructures, such as SWNT [5] and  $\text{C}_{60}$  [6, 7], have the potential to be a high-capacity hydrogen storage medium due to unique Ti– $\text{H}_2$  interactions [5]. However, owing to the open surfaces of SWNT and  $\text{C}_{60}$ ,

it is possible that decorated Ti atoms could in time form a cluster [8]. Hence, it is important to look at other structures where Ti is tightly bound in the system. It is known that Ti forms several high-symmetry clusters with carbons such as metallocarbohydrene,  $\text{Ti}_8\text{C}_{12}$ . It would be interesting to study the hydrogen adsorption properties of such Ti–C nanostructures. Here we followed this idea.

Guo *et al* [9] discovered a highly symmetric molecular cluster,  $\text{M}_8\text{C}_{12}$ , while investigating dehydrogenation reactions of hydrocarbons by titanium atoms, ions, and clusters in 1992. Metallocarbohydrenes (met-cars) forming a specific stoichiometry like  $\text{M}_8\text{C}_{12}$ , where M stands for a metal atom, were first observed for the early transition metals (Ti, V, Zr, and Hf), and later it was proved that this stoichiometry is also preferred for other transition metals (Fe, Cr, Mo) [10]. In addition to their stability and symmetry, they exhibit a relatively low ionization potential and exciting electronic and magnetic properties due to the presence of transition metal elements.

Although  $\text{Ti}_8\text{C}_{12}$  met-cars are one of the most studied clusters both theoretically and experimentally, the ground state and the geometry of  $\text{Ti}_8\text{C}_{12}$  have not been clarified. Guo *et al* [9] initially proposed a pentagonal dodecahedron geometry with  $T_h$  point-group symmetry. This structure can be visualized as a cube of Ti atoms with each face capped with a C dimer parallel to its two edges. Later, Dance [11] optimized a tetracapped tetrahedron structure of  $T_d$  symmetry using density functional formalism (DFT) and presented a transformation course from the  $T_h$  to the  $T_d$  form [12]. Dance's proposal has attracted considerable attention from both the theoretical and experimental points of views. All these studies have shown that the initially proposed  $T_h$  dodecahedron structure was energetically unstable and higher in energy by almost 15 eV.

Rohmer *et al* [13] studied the structural and electronic properties of the ground and excited states of various met-cars composed of Ti, Zr, V, and Nb. They introduced seven different configurations as the local energy minima ( $T_d$ ,  $D_2$ ,  $D_{2d}$ ,  $C_{2v}$ , two types of  $D_{3d}$ , and  $C_s$ ) for  $\text{Ti}_8\text{C}_{12}$  met-car. From the geometry optimization,  $T_d$  was found to be the lowest-energy structure among the proposed seven conformations. More recently, asymmetric  $T_d^*$ , i.e. a distorted  $T_d$  structure in which only Ti atoms in the framework are rearranged, was reported [14] as the equilibrium structure of  $\text{Ti}_8\text{C}_{12}$ .

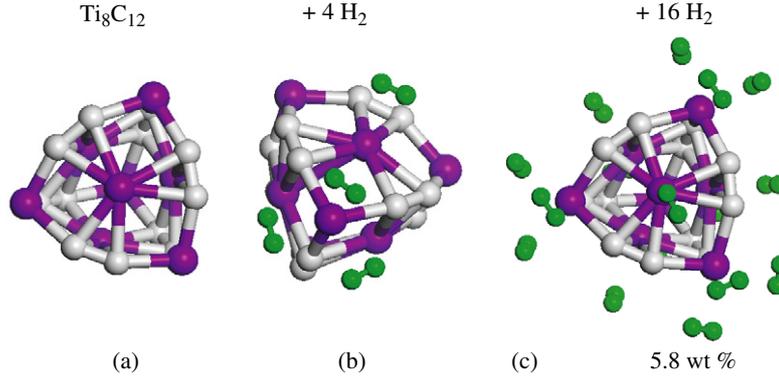
On the other hand, the calculated Raman spectrum of  $\text{Ti}_8\text{C}_{12}$ , together with the infrared absorption spectrum for  $D_{2d}$  and  $C_{3v}$  structures, has indicated that the  $C_{3v}$  symmetry is the one with the lowest-energy structure [15].

Later, Sobhy *et al* [16] obtained a geometry optimization for seven structures proposed by Rohmer *et al* [13] using spin-polarized DFT with a plane wave basis set.  $C_{3v}$  symmetry was found to be the most stable structure, and their electronic density of states (DOS) calculations showed that  $C_{3v}$ ,  $D_{3d}$ , and  $D_{3d}^*$  are spin-polarized structures. Besides, the vibrational spectra obtained from molecular dynamic (MD) simulations proves the stability of the  $C_{3v}$  and  $C_{2v}$  structures at finite temperature.

In the present work, we studied the adsorption of  $\text{H}_2$  molecules on the external and internal surfaces of  $\text{Ti}_8\text{C}_{12}$ . We have found that, while a single Ti atom at the corner can bind up to three  $\text{H}_2$  molecules, a single Ti atom on the surface of a cluster can bind only one  $\text{H}_2$  molecule. This shows that  $\text{Ti}_8\text{C}_{12}$  met-cars can bind up to approximately 5.8 wt%, approaching the minimum requirement of 6 wt% for practical applications.

## 2. Method

The binding geometry and the binding energy of hydrogen molecules adsorbed on Ti met-car have been calculated using first-principles pseudopotential plane wave methods [17, 18]



**Figure 1.** (a) Optimized bare  $\text{Ti}_8\text{C}_{12}$  structure with  $C_{3v}$  symmetry; (b) partial coverage of  $\text{H}_2$ :  $\text{Ti}_8\text{C}_{12} + 3\text{H}_2(\text{C}) + \text{H}_2(\text{S})$ , namely one  $\text{H}_2$  adsorbed onto surface Ti while three  $\text{H}_2$  are bound to the Ti atom at the corner; (c) full coverage of  $\text{H}_2$ :  $\text{Ti}_8\text{C}_{12} + 16\text{H}_2$ .

within DFT [19]. We have performed spin-polarized calculations with a generalized gradient approximation (GGA) [20, 21] and ultrasoft pseudopotential [18, 22]. All calculations have been carried out using the PW91 functional [20]. For the sake of comparison, some of the calculations have been repeated using the Perdew–Burke–Ernzerhof (PBE) functional [21]. The energy cutoff is taken to be 350 eV. By employing a periodically repeating cubic supercell with lattice constants  $a_{\text{sc}} = b_{\text{sc}} = c_{\text{sc}} = 20 \text{ \AA}$ , calculations have been performed in momentum space. All atomic positions before and after the  $\text{H}_2$  adsorption have been optimized by minimizing the total energy and total forces on the atoms. The convergence criteria adopted for the total energy and atomic forces are  $10^{-5}$  eV and  $0.05 \text{ eV \AA}^{-1}$ , respectively. We have also tested the stability of the  $\text{H}_2$ -adsorbed  $\text{Ti}_8\text{C}_{12}$  met-car with an *ab initio* MD method which is carried out at room temperature.

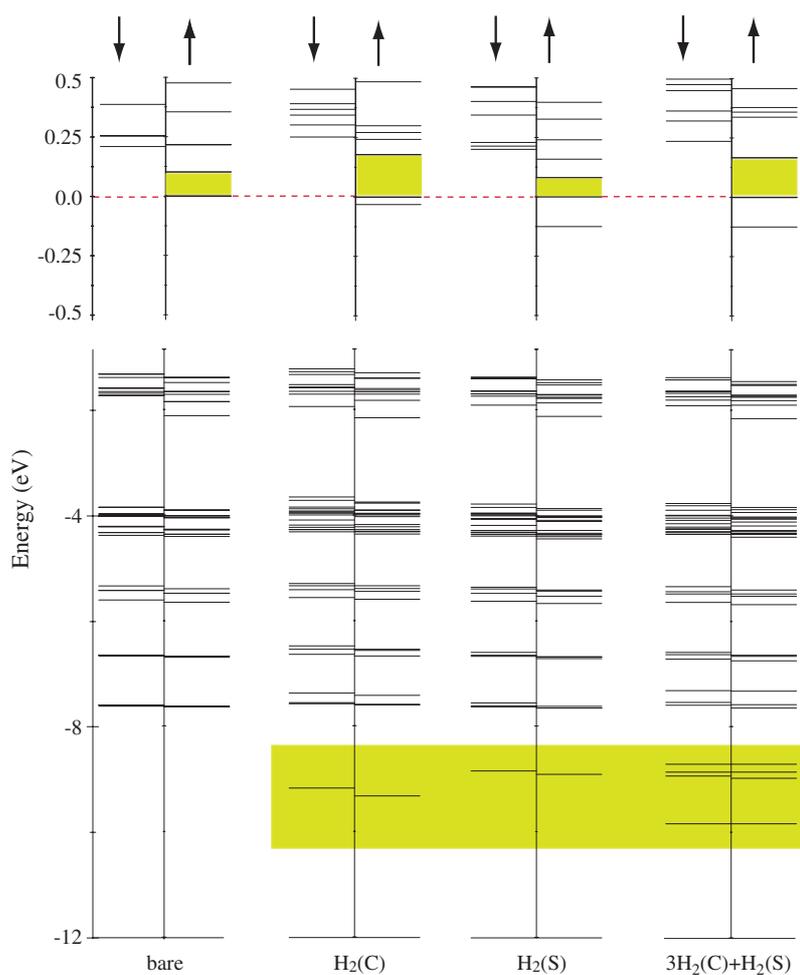
Average binding energies of  $n$   $\text{H}_2$  molecules adsorbed on  $\text{Ti}_8\text{C}_{12}$  are calculated from the spin-polarized total energy of  $\text{Ti}_8\text{C}_{12}$ ,  $E_{\text{T}}^{\text{sp}}(\text{Ti}_8\text{C}_{12})$ , the total energy of  $n$   $\text{H}_2$  molecules, and the spin-polarized total energy of  $n$   $\text{H}_2$  adsorbed  $\text{Ti}_8\text{C}_{12}$ , namely  $E_{\text{T}}^{\text{sp}}(\text{Ti}_8\text{C}_{12} + n \text{H}_2)$ :

$$\bar{E}_{\text{b}}(\text{H}_2) = [E_{\text{T}}^{\text{sp}}(\text{Ti}_8\text{C}_{12}) + E_{\text{T}}(n \text{H}_2) - E_{\text{T}}^{\text{sp}}(\text{Ti}_8\text{C}_{12} + n \text{H}_2)]/n, \quad (1)$$

where  $\bar{E}_{\text{b}} > 0$  shows that the system is stable. Actually,  $\text{H}_2$  molecules which are not bound have escaped from the met-car. We did not include the van der Waals contribution to the binding energy, since it is included partly by the DFT-GGA method used in the present study. However, based on our earlier analysis [23] we estimate the possible corrections to be  $E_{\text{b}}$  in the range of 20 meV.

### 3. Results and discussions

In the present work, the  $C_{3v}$  structure is considered to be the most stable geometry of the  $\text{Ti}_8\text{C}_{12}$  met-car, as proposed in [16]. We reoptimized the  $\text{Ti}_8\text{C}_{12}$  with  $C_{3v}$  symmetry by employing both spin-polarized (sp) and spin-unpolarized (su) calculations. The calculated difference of spin-unpolarized and spin-polarized total energies, namely  $\Delta E_{\text{T}} = E_{\text{T}}^{\text{su}}(\text{Ti}_8\text{C}_{12}) - E_{\text{T}}^{\text{sp}}(\text{Ti}_8\text{C}_{12})$ , is found to be 176 meV, indicating that the ground state is magnetic with  $\mu = 2.1 \mu_{\text{B}}$ . Figure 1(a) shows the atomic structure of the  $\text{Ti}_8\text{C}_{12}$  cluster. The energy-level diagrams for the majority ( $\uparrow$ ) and minority ( $\downarrow$ ) spin states of the bare  $\text{Ti}_8\text{C}_{12}$  are presented in figure 2. While highest occupied molecular orbital (HOMO)  $\uparrow$  states are formed fully from Ti-3d orbitals, lowest



**Figure 2.** Energy-level diagrams of majority ( $\uparrow$ ) and minority ( $\downarrow$ ) spin states for  $\text{Ti}_8\text{C}_{12}$ ,  $\text{Ti}_8\text{C}_{12} + \text{H}_2(\text{C})$ ,  $\text{Ti}_8\text{C}_{12} + \text{H}_2(\text{S})$ , and  $\text{Ti}_8\text{C}_{12} + 3\text{H}_2(\text{C}) + \text{H}_2(\text{S})$ .  $\text{H}_2(\text{C})$  and  $\text{H}_2(\text{S})$  denote  $\text{H}_2$  molecule(s) adsorbed onto the Ti atoms located at the corner and centre of the surface of  $\text{Ti}_8\text{C}_{12}$ , respectively. The HOMO–LUMO gap region (top) and hydrogen levels (bottom) are highlighted. The zero energy is set at the HOMO  $\uparrow$  level.

unoccupied molecular orbital (LUMO)  $\uparrow$  states are derived from Ti-3d and C-2p orbitals. The HOMO–LUMO gap for majority  $E_g^\uparrow$  and minority  $E_g^\downarrow$  states is calculated to be 0.1 and 1.54 eV, respectively.

We inferred two different sites for the adsorption of  $\text{H}_2$ . These are Ti atoms at the centre of the surface and at the corners of  $\text{Ti}_8\text{C}_{12}$ . The binding energy of a single  $\text{H}_2$  molecule adsorbed to the Ti atom at the centre surface (signified as  $\text{Ti}_8\text{C}_{12} + \text{H}_2(\text{S})$ ) is calculated to be 0.22 eV. On the other hand, the Ti atom at the corners is capable of binding three  $\text{H}_2$  molecules with an average binding energy of 0.30 eV. The energy-level diagram in figure 2 indicates that, upon the adsorption of a single  $\text{H}_2$  molecule to the Ti atom at the corner, new states deriving from  $\text{H}_2$  molecular states and Ti-s, p, d orbitals appear at  $\sim -9$  eV, and  $E_g^\uparrow$  changes to 0.18 eV. A similar situation exists for  $\text{H}_2(\text{S})$  with a relatively weaker bond and  $E_g^\uparrow = 0.08$  eV. The energy-level diagram of  $\text{Ti}_8\text{C}_{12} + 3\text{H}_2(\text{C}) + \text{H}_2(\text{S})$  gives rise to several states at a range of energy of  $-8.5$

**Table 1.** Calculated Ti–H and H–H bond distances,  $d$  (Ti–H) and  $d$  (H–H); total binding energy  $E_b$ ; average binding energy  $\bar{E}_b$  (i.e.  $E_b$  divided by  $n$  adsorbed  $H_2$ ) of adsorbed  $H_2$  molecules corresponding to partial ( $Ti_8C_{12} + 4H_2$ ) and full coverage ( $Ti_8C_{12} + 16H_2$ ).  $H_2(C)$  and  $H_2(S)$  indicate  $H_2$  molecules adsorbed onto the corner and surface Ti atoms, respectively.  $\mu$  is the magnetic moment of the relevant structure shown in figure 1.

|                       | $Ti_8C_{12}$ | $Ti_8C_{12} + 3H_2(C) + H_2(S)$ | $Ti_8C_{12} + 16H_2$ |
|-----------------------|--------------|---------------------------------|----------------------|
| $d$ (Ti–H) (Å)        |              | 2.1–2.2                         | 2.1–2.4              |
| $d$ (H–H) (Å)         |              | 0.78                            | 0.76–0.80            |
| $E_b(H_2)$ (eV)       |              | 1.20                            | 4.44                 |
| $\bar{E}_b(H_2)$ (eV) |              | 0.30                            | 0.28                 |
| $\mu$ ( $\mu_B$ )     | 2.11         | 2.06                            | 0                    |

**Table 2.** Binding energy  $E_b$  of  $H_2$  molecules added to the met-car one at a time.  $H_2(C_1)$ : first  $H_2$  at the  $C_1$  site;  $2H_2(C_1)$ : second  $H_2$  added to  $H_2(C_1)$ ;  $3H_2(C_1)$ : third  $H_2$  added to  $2H_2(C_1)$ ;  $3H_2(C_1) + H_2(C_2)$ : one  $H_2$  added to  $C_2$  corner, while  $3H_2$  attached to corner  $C_1$ ;  $H_2(S)$ : one  $H_2$  added to S;  $3H_2(C_1) + H_2(S)$ : one  $H_2$  added to S in the presence of  $3H_2$  at  $C_1$ . Results obtained using the PBE functional are shown for the same configurations.

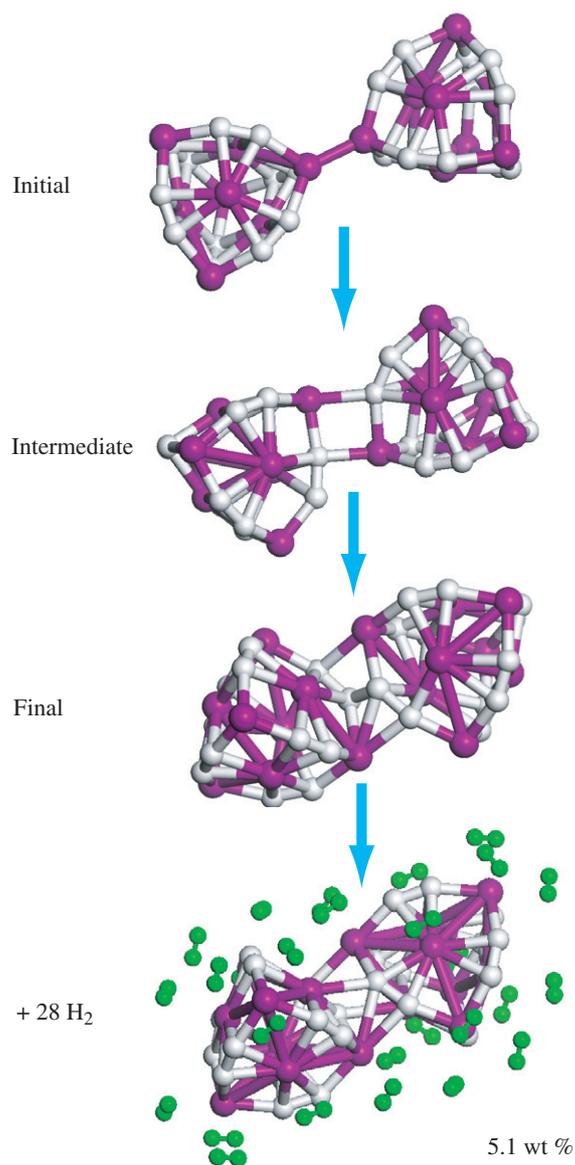
| Structure        | $H_2(C_1)$ | $2H_2(C_1)$ | $3H_2(C_1)$ | $4H_2(C_1)$ | $3H_2(C_1) + H_2(C_2)$ | $H_2(S)$ | $3H_2(C_1) + H_2(S)$ |
|------------------|------------|-------------|-------------|-------------|------------------------|----------|----------------------|
| $\bar{E}_b$ (eV) | 0.40       | 0.34        | 0.15        | Non         | 0.40                   | 0.22     | 0.22                 |
| PBE              | 0.39       | 0.32        | 0.13        |             |                        |          | 0.20                 |

to  $-12$  eV, and  $E_g^\uparrow = 0.17$  eV. Figure 1(b) illustrates that the optimized binding geometry of one  $H_2$  is on top of a surface Ti atom and three  $H_2$  bound symmetrically to the Ti atom at the corner. The ground state of this  $Ti_8C_{12} + 4H_2$  structure is still spin-polarized with a magnetic moment  $\mu = 2.06 \mu_B$ , as expected.

Next, we discuss the geometry of the full coverage presented by figure 1(c). It is seen that the Ti met-car has the capacity to bind up to 16  $H_2$  molecules, corresponding to 5.8 wt%. This optimized configuration is shown in figure 1(c). The ground state of the  $Ti_8C_{12}$  at full hydrogen coverage (i.e.  $16H_2$ ) is non-magnetic; the excited magnetic state has  $\mu = 2 \mu_B$  and occurs 14 meV above the ground state. At full coverage we predict  $E_g^\uparrow = 0.39$  eV. The average binding energy  $\bar{E}_b$  is found to be 0.28 eV. None of the  $H_2$  molecules at full coverage dissociate, but some of the Ti(S)–H bond lengths elongate to 2.2 and 2.4 Å. The binding energy of partial and full-coverage cases,  $E_b$ , and the relevant structural parameters are given in table 1. The volumetric hydrogen density has been estimated to be 1.4% at full coverage.

While the average binding energy  $\bar{E}_b$  yields an overall picture of the storage capacity, we also carried out our analysis by calculating the binding energy of  $H_2$  to different sites where one molecule is added at a time. This analysis includes several possibilities, but we present only relevant cases in table 2. The binding energy  $E_b$  is computed as 0.40 eV when one  $H_2$  molecule adsorbed onto the  $C_1$  site. The binding energy of the second  $H_2$  molecule to the same site is found to be 0.34 eV. The binding energy of the third  $H_2$  molecule is found to be 0.15 eV. As clarified in table 2, the fourth  $H_2$  is non-binding to the  $C_1$  site. Another possibility is adding this molecule (the fourth one) to the site  $C_2$ , where  $C_2$  represents a different corner Ti atom. The  $H_2$  molecule binds to the  $C_2$  site with an energy of 0.40 eV. The S site can bind at most one  $H_2$  molecule with a binding energy of 0.22 eV. When one of the C sites is completely saturated with  $H_2$  molecules, the required energy for the addition of an  $H_2$  molecule to the S site is again 0.22 eV. The results obtained by using the PBE [21] functional are also shown in table 2. The binding energies calculated with PBE are slightly smaller than those obtained from PW91 [20].

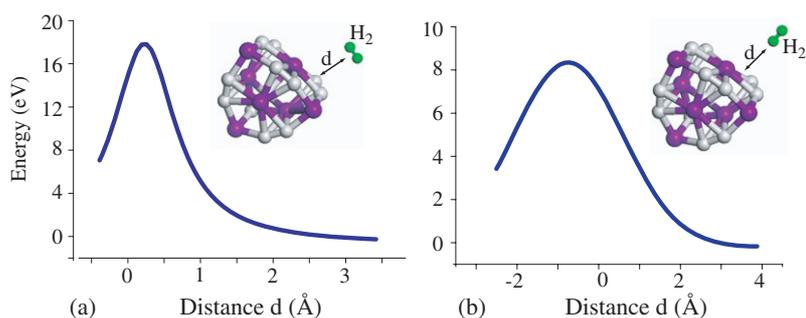
We also examined the possibility of dissociative adsorption of  $H_2$  by starting from the atomic adsorption of H. The initial H–H distance of 1.8 Å reduced upon relaxation, and



**Figure 3.** The linking of two Ti met-cars to form a ‘dimer’, which binds up to 28 H<sub>2</sub> molecules. Large and dark (smaller and white) balls indicate titanium (carbon) atoms, respectively. Hydrogen molecules are shown by small grey balls and stick.

eventually it reached the molecular bond distance. Both analyses performed at the S and C sites have excluded the dissociative adsorption of H<sub>2</sub>, unless the molecule is forced to be dissociated.

Next, we address the question whether two met-cars can be bound when they become close to each other. The answer to this question is also relevant for the polymerization of met-cars. Individual (isolated) met-cars cannot be available for storage, even if they have relatively high capacity. Our analysis is summarized in figure 3. We first combined two met-cars interacting



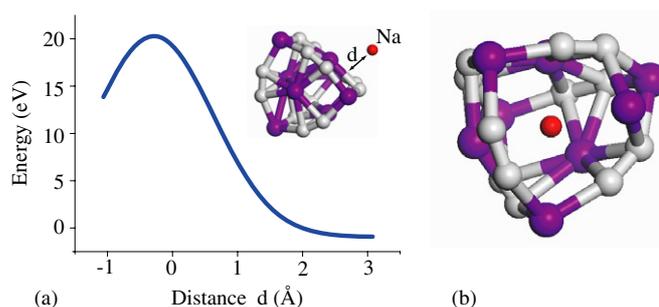
**Figure 4.** (a) Total energy versus the distance  $d$  of a single  $H_2$  approaching  $Ti_8C_{12}$  in a parallel way and (b) in a perpendicular way. The zero energy is taken as the sum of the total energies of  $Ti_8C_{12}$  and free  $H_2$  at infinite separation. Energy curves are fitted to a Lorentzian.

through two Ti atoms at the corner. Upon relaxation, two met-cars rotated to find a lower energy configuration, whereby the C–Ti bonds formed between different met-cars, as shown in figure 3(b), as an intermediate configuration<sup>4</sup>. Finally, the configuration in figure 3(c) is found to have even lower energy. The binding energy is calculated to be 2.3 eV. The storage capacity of this configuration is slightly reduced upon the dimerization of two met-cars. While a single met-car can hold up to 16  $H_2$  molecules, the dimer can bind up to 28  $H_2$  instead of 32  $H_2$ . The configuration in figure 3(c) suggests that various forms of polymerization can occur by adding met-cars consecutively to establish a framework for  $H_2$  storage. It is now reasonable to consider a polymer of met-cars, where all Ti atoms at the corners can take part in polymerization. Under these circumstances, the number of  $H_2$  molecules stored by each met-car reduces to a minimum value of 12, resulting in a gravimetric density of 4.4%.

Whether  $H_2$  molecules inserted into the  $Ti_8C_{12}$  cluster increase the wt% storage capacity is the next issue that we investigated. To this end, we examined the variation in the energy of  $H_2$  approaching the surface in different orientations. Figure 4 shows the variation in  $E_T^{SP}$  of  $H_2$  as a function of its distance  $d$  from the surface of  $Ti_8C_{12}$ . In figure 4(a), an  $H_2$  molecule approaches the met-car's surface in such a way that it is parallel to the surface. The energy almost does not change significantly until the distance 2.2 Å, at which the  $H_2$  molecule is attached to the  $Ti_8C_{12}$  system. Then it gradually increases up to the distance 1.7 Å, and afterwards a rapid increase can clearly be seen until the  $H_2$  molecule touches the surface. Due to the existence of a high energy barrier of 15.7 eV, we conclude that the  $H_2$  molecule cannot be inserted in the  $Ti_8C_{12}$  cluster. Figure 4(b) illustrates the variation in energy for an approach perpendicular to the surface of the met-car. Similarly to the previous case, it is again observed that the energy remains almost constant until  $d = 2.2$  Å and then it increases, first gradually and later very rapidly. This increase in energy, indicating an energy barrier of 6.9 eV in height, again prevents the  $H_2$  molecule from entering into the  $Ti_8C_{12}$  system. In fact, the atomic configuration of the met-car has changed and the total energy increased dramatically when the structure having one  $H_2$  inside is optimized.

Earlier calculations have shown that alkali metals adsorbed on a single-wall carbon nanotube increases the binding energy if  $H_2$  is adsorbed directly onto the alkali atoms [23]. We examined such a possibility that Na atom insertion in  $Ti_8C_{12}$  may increase the  $H_2$  uptake by donating electrons to the LUMO state. The energy variation when a single Na atom approaches a  $Ti_8C_{12}$  cluster is shown in figure 5(a). As is seen, the energy is negative and almost does

<sup>4</sup> This intermediate configuration can be a local minimum in the Born–Oppenheimer surface.



**Figure 5.** (a) Variation in energy as a single Na atom approaches  $\text{Ti}_8\text{C}_{12}$ , as shown by the inset. The zero energy is taken to be the sum of the total energies of  $\text{Ti}_8\text{C}_{12}$  and the free Na. (b) Relaxed geometry after Na is implemented in  $\text{Ti}_8\text{C}_{12}$ .

not change until the distance 2.2 Å. Then it increases very rapidly until the Na atom touches the surface of the Ti met-car. Because of a large energy barrier of 19.8 eV in height, an Na atom cannot be inserted into a  $\text{Ti}_8\text{C}_{12}$  cluster. Even when it is inserted in it, it destroys the structure very quickly. The result, shown in figure 5(b), again proves that Na atom insertion in this molecule is seen to be impossible<sup>5</sup>. The binding energy of Na on the outer surface of the Ti met-car is found to be very weak, and hence its affect on the storage capacity is irrelevant.

Having discussed the adsorption of  $\text{H}_2$  molecules onto a  $\text{Ti}_8\text{C}_{12}$  molecule, we next present our *ab initio* MD simulation on  $\text{Ti}_8\text{C}_{12}-16\text{H}_2$  in order to test whether the system under study is stable. We have accomplished MD simulation at room temperature for 100 time steps, each step taking  $2 \times 10^{-15}$  s. After 0.2 ps has been completed, we have observed that  $\text{H}_2$  molecules are desorbed from the cluster upon heating to 300 K, but  $\text{Ti}_8\text{C}_{12}$  itself remained intact. These results suggest that some of the  $\text{H}_2$  molecules adsorbed on the met-car can desorb even below room temperature, but the met-car itself is stable at room temperature.

#### 4. Conclusion

By using first-principles total energy calculations, we have shown that, while each Ti atom at the corner of a  $\text{Ti}_8\text{C}_{12}$  molecule can attach three  $\text{H}_2$  molecules, each Ti atom at the surface can attach only one  $\text{H}_2$  molecule on top of itself. This way, one can achieve 5.8 wt% H storage. Molecularly adsorbed hydrogens can be released when the system is heated up sufficiently. The attractive interaction between two met-cars gives rise to the dimerization. Dimerization is the first step towards polymerization, whereby the storage capacity (wt%) is reduced slightly. Since the met-car considered in this paper is a cage-like structure, we have also investigated the H storage capacity of its interior region. We found that a high energy barrier at the surface of  $\text{Ti}_8\text{C}_{12}$  has prevented  $\text{H}_2$  from entering into the cage. Even when it was inserted into the met-car, it is dissociated into two H atoms with a negative binding energy. To promote  $\text{H}_2$  uptake on the  $\text{Ti}_8\text{C}_{12}$  cluster, we also considered the insertion of an alkali atom in  $\text{Ti}_8\text{C}_{12}$ . Na atom having only one valence electron would donate this electron to the LUMO. However, similarly to the  $\text{H}_2$ , Na has been prevented from entering into  $\text{Ti}_8\text{C}_{12}$  by a high energy barrier at its surface. Even when the Na atom enters inside the met-car, it destroys the structure very quickly. The results presented in this work revealed that, although  $\text{Ti}_8\text{C}_{12}$  is a cage-like structure, it can only take up a  $\text{H}_2$  molecule from the outside.

<sup>5</sup> In the calculation of the energy barrier, the atomic structures have not been optimized.

The quantum MD simulation, carried out at room temperature, shows that the  $\text{Ti}_8\text{C}_{12}$  molecule is quite stable and that it is possible to desorp (or unload) most of the stored hydrogen molecules by heating the system without breaking any bonds in the met-car. In summary, the  $\text{Ti}_8\text{C}_{12}$  cluster exhibits interesting features for  $\text{H}_2$  adsorption. The investigation of these features when the cluster is placed on a surface is in progress.

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