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Hydrogen storage capacity of titanium met-cars

N Akman¹, E Durgun², T Yildirim³ and S Ciraci²

¹ Department of Physics, Mersin University, 33342 Mersin, Turkey

² Department of Physics, Bilkent University, 06800 Ankara, Turkey

³ NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

E-mail: ciraci@fen.bilkent.edu.tr

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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 Ti_8C_{12} met-car can bind up to 16 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 H_2 storage capacity slightly. Increasing the storage capacity by directly inserting 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 H_2 molecule nor an Na atom could further promote the H_2 storage capacity of a Ti_8C_{12} cluster. We have also tested the stability of the H_2 -adsorbed Ti_8C_{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 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 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 C_{60} [6, 7], have the potential to be a high-capacity hydrogen storage medium due to unique Ti– H_2 interactions [5]. However, owing to the open surfaces of SWNT and 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, Ti_8C_{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, M_8C_{12} , while investigating dehydrogenation reactions of hydrocarbons by titanium atoms, ions, and clusters in 1992. Metallocarbohydrenes (met-cars) forming a specific stoichiometry like M_8C_{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 Ti_8C_{12} met-cars are one of the most studied clusters both theoretically and experimentally, the ground state and the geometry of Ti_8C_{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 Ti_8C_{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 Ti_8C_{12} .

On the other hand, the calculated Raman spectrum of Ti_8C_{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 H_2 molecules on the external and internal surfaces of Ti_8C_{12} . We have found that, while a single Ti atom at the corner can bind up to three H_2 molecules, a single Ti atom on the surface of a cluster can bind only one H_2 molecule. This shows that Ti_8C_{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]

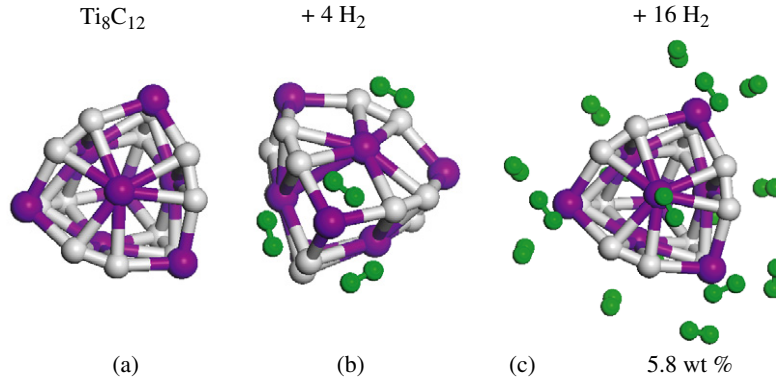


Figure 1. (a) Optimized bare Ti_8C_{12} structure with C_{3v} symmetry; (b) partial coverage of H_2 : $\text{Ti}_8\text{C}_{12} + 3\text{H}_2(\text{C}) + \text{H}_2(\text{S})$, namely one H_2 adsorbed onto surface Ti while three H_2 are bound to the Ti atom at the corner; (c) full coverage of H_2 : $\text{Ti}_8\text{C}_{12} + 16\text{H}_2$.

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 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 eV \AA^{-1} , respectively. We have also tested the stability of the H_2 -adsorbed Ti_8C_{12} met-car with an *ab initio* MD method which is carried out at room temperature.

Average binding energies of n H_2 molecules adsorbed on Ti_8C_{12} are calculated from the spin-polarized total energy of Ti_8C_{12} , $E_{\text{T}}^{\text{sp}}(\text{Ti}_8\text{C}_{12})$, the total energy of n H_2 molecules, and the spin-polarized total energy of n H_2 adsorbed Ti_8C_{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, 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_{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 Ti_8C_{12} met-car, as proposed in [16]. We reoptimized the Ti_8C_{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 Ti_8C_{12} cluster. The energy-level diagrams for the majority (\uparrow) and minority (\downarrow) spin states of the bare Ti_8C_{12} are presented in figure 2. While highest occupied molecular orbital (HOMO) \uparrow states are formed fully from Ti-3d orbitals, lowest

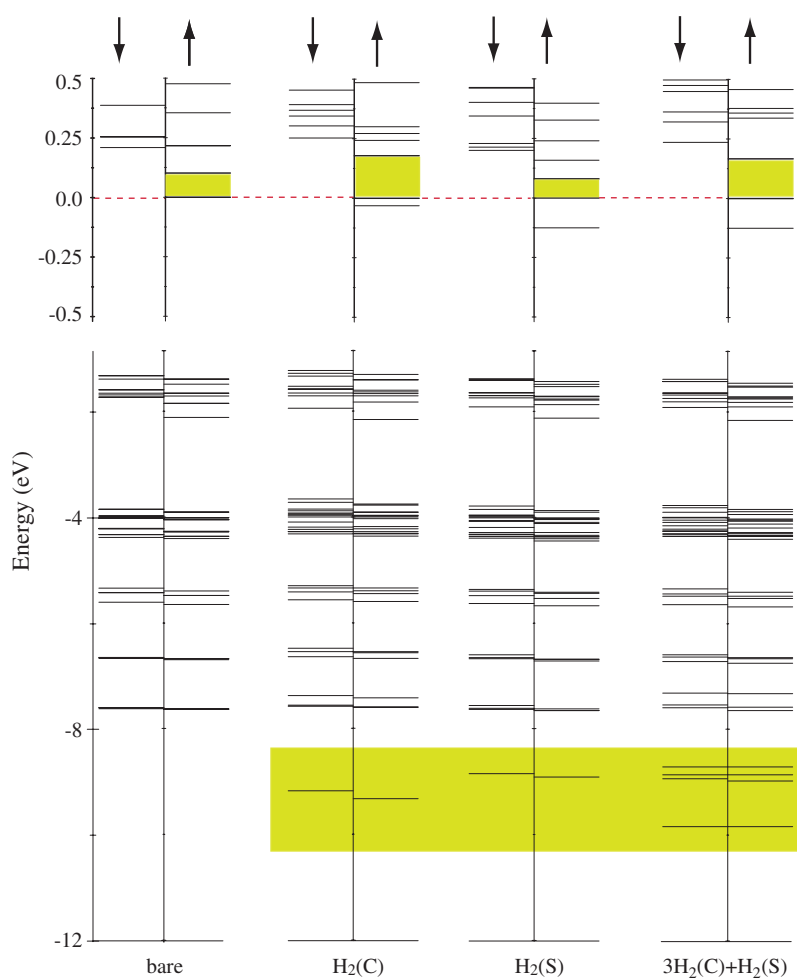


Figure 2. Energy-level diagrams of majority (\uparrow) and minority (\downarrow) spin states for Ti_8C_{12} , $\text{Ti}_8\text{C}_{12} + \text{H}_2(\text{C})$, $\text{Ti}_8\text{C}_{12} + \text{H}_2(\text{S})$, and $\text{Ti}_8\text{C}_{12} + 3\text{H}_2(\text{C}) + \text{H}_2(\text{S})$. $\text{H}_2(\text{C})$ and $\text{H}_2(\text{S})$ denote H_2 molecule(s) adsorbed onto the Ti atoms located at the corner and centre of the surface of Ti_8C_{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 H_2 . These are Ti atoms at the centre of the surface and at the corners of Ti_8C_{12} . The binding energy of a single 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 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 H_2 molecule to the Ti atom at the corner, new states deriving from H_2 molecular states and Ti-s, p, d orbitals appear at ~ -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. μ 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
μ (μ_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

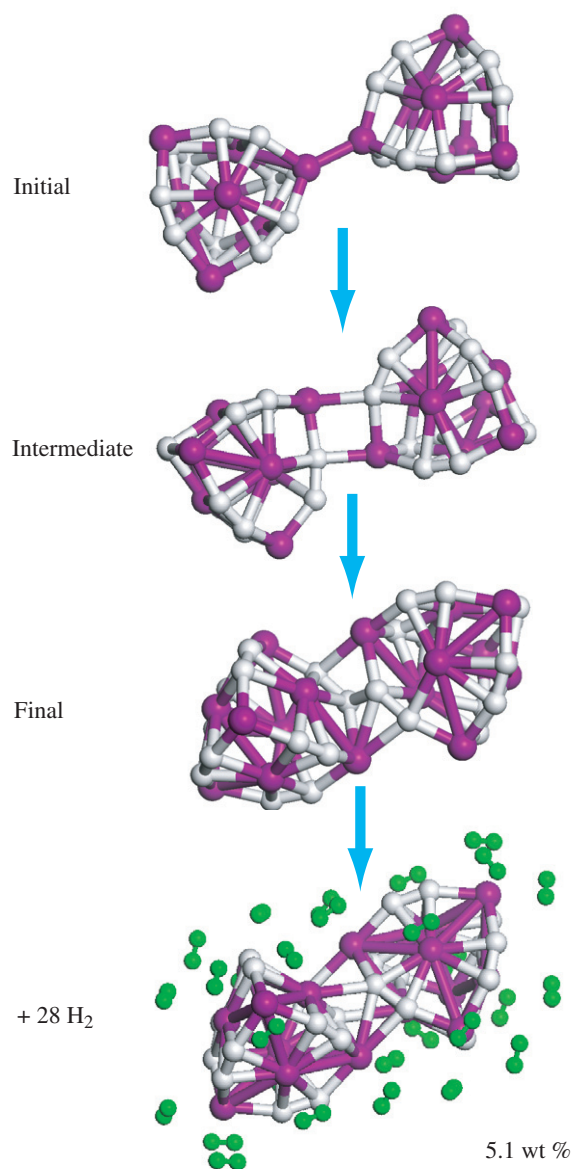


Figure 3. The linking of two Ti met-cars to form a ‘dimer’, which binds up to 28 H₂ molecules. Large and dark (smaller and white) balls indicate titanium (carbon) atoms, respectively. Hydrogen molecules are shown by small grey balls and stick.

eventually it reached the molecular bond distance. Both analyses performed at the S and C sites have excluded the dissociative adsorption of H₂, 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

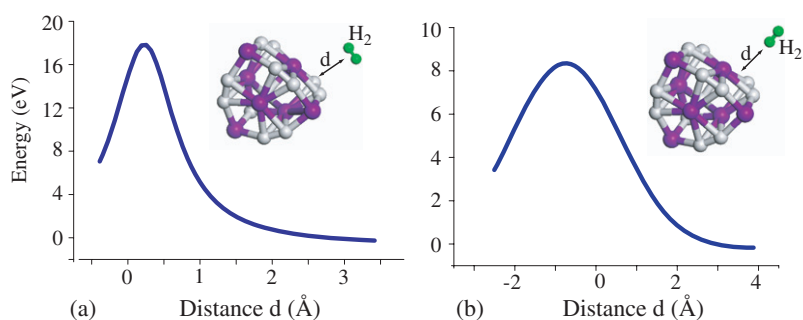


Figure 4. (a) Total energy versus the distance d of a single H_2 approaching Ti_8C_{12} in a parallel way and (b) in a perpendicular way. The zero energy is taken as the sum of the total energies of Ti_8C_{12} and free H_2 at infinite separation. Energy curves are fitted to a Lorentzian.

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 configuration⁴. 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

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

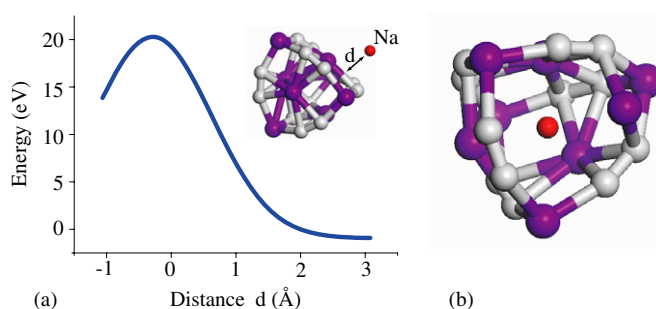


Figure 5. (a) Variation in energy as a single Na atom approaches Ti_8C_{12} , as shown by the inset. The zero energy is taken to be the sum of the total energies of Ti_8C_{12} and the free Na. (b) Relaxed geometry after Na is implemented in Ti_8C_{12} .

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 Ti_8C_{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 impossible⁵. 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 H_2 molecules onto a Ti_8C_{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 2×10^{-15} s. After 0.2 ps has been completed, we have observed that H_2 molecules are desorbed from the cluster upon heating to 300 K, but Ti_8C_{12} itself remained intact. These results suggest that some of the 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 Ti_8C_{12} molecule can attach three H_2 molecules, each Ti atom at the surface can attach only one 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 Ti_8C_{12} has prevented 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 H_2 uptake on the Ti_8C_{12} cluster, we also considered the insertion of an alkali atom in Ti_8C_{12} . Na atom having only one valence electron would donate this electron to the LUMO. However, similarly to the H_2 , Na has been prevented from entering into Ti_8C_{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 Ti_8C_{12} is a cage-like structure, it can only take up a H_2 molecule from the outside.

⁵ 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 Ti_8C_{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 Ti_8C_{12} cluster exhibits interesting features for H_2 adsorption. The investigation of these features when the cluster is placed on a surface is in progress.

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