

Clustering of Ti on a C₆₀ Surface and Its Effect on Hydrogen Storage

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Hydrogen storage materials suitable for applications in the mobile industry must meet some stringent requirements: The gravimetric and volumetric density should be high, the kinetics should be fast, and the thermodynamics should be such that the hydrogen absorption and desorption can take place at near-ambient conditions. Storage of hydrogen as a gas under high pressure or as a liquid at cryogenic temperatures has inherent problems associated with cost, safety, and storage capacity. Solid-state materials provide an alternative choice for hydrogen storage, although there are no materials that currently meet all the industry requirements. It is easy to see that to store hydrogen with high gravimetric density (10 wt %), the host materials must consist of light elements such as Li, Be, B, C, Na, Mg, and Al. The difficulty of using these light materials is that hydrogen is bonded either strongly via covalent or ionic interaction or weakly via van der Waals interaction. In the former it is difficult to desorb the stored hydrogen, while in the latter hydrogen desorbs easily at low temperatures.

Some of the early experiments showed that carbon nanotubes can be used as a hydrogen storage material, but later experiments proved otherwise. For example, Tibbetts and co-workers claimed that any reported capacity of higher than 1 wt % is due to experimental error.¹ This conclusion has been supported by Shiraishi and co-workers, who reported hydrogen gravimetric density of only 0.3 wt %, and by Kajiuura et al.,³ who reported the highest storage capacity to be 0.43 wt %. Theoretical study also confirms that high hydrogen content in the pure carbon nanotubes cannot be achieved through physical sorption.⁴ Recently, two theoretical groups^{5–8} have shown that metal atoms such as Sc and Ti coated on carbon fullerenes and nanotubes can bind hydrogen in molecular forms with a binding energy of the order of 0.5 eV/H₂ molecule and with gravimetric density of up to 8 wt %. The mechanism attributed to this large amount of hydrogen adsorption is similar to that shown by Niu et al.⁹ more than a decade ago. Using molecular orbital theory, these authors had shown that while a neutral Ni atom can bind only two hydrogen atoms in dissociated form, a Ni⁺ cation can bind up to six hydrogen molecules with a binding energy of about 0.4 eV/H₂ molecule. The bonding is governed by a polarization mechanism where the charge on the cation polarizes the H₂ molecule. In the case of a metal atom supported on the carbon fullerene, the large electronegativity of C₆₀ facilitates the transfer of electrons from the metal atom to C₆₀, thus leaving the metal atom in the cationic form. Hence, molecular hydrogen can be trapped by the metal ion through the charge polarization mechanism. However, in recent theoretical calculations the authors assumed that metal atoms coated on the C₆₀ remain in isolated form.^{5–7} These calculations pose some new questions: Would the metal atoms prefer to cluster on the fullerene surface? If so, how would the clustering of metal atoms affect the nature and amount of hydrogen that can be stored? Answers to these questions are important, as it

may limit the usefulness of carbon nanostructures as potential hydrogen storage materials. We have examined these issues by carrying out theoretical calculations of the interaction of Ti with C₆₀ and hydrogen. We show that Ti atoms prefer to cluster on the C₆₀ fullerene and that the nature of hydrogen bonding does depend on this clustering. We describe our theoretical procedure and results in the following.

Spin-polarized calculations of total energies and forces, and optimizations of geometry, were carried out using density functional theory and a plane-wave basis set with the projector augmented plane wave (PAW) method as implemented in the Vienna ab initio simulation package (VASP).¹⁰ The PW91 form was used for the generalized gradient approximation to exchange and correlation potential. The geometry of the metal-coated C₆₀ was optimized without symmetry constraint using a conjugate-gradient algorithm. We have used supercells with 15-Å vacuum spaces along *x*, *y*, and *z* directions for all the calculated structures. The Γ point is used to represent the Brillouin zone due to the large supercell. The energy cutoff was set to 400 eV, and the convergence in energy and force was 10⁻⁴ eV and 1 × 10⁻³ eV/Å, respectively. The accuracy of our numerical procedure was well tested for C₆₀ in our previous paper.¹¹ The calculated bond length and binding energy of H₂ are respectively 0.749 Å and 4.536 eV, which agree very well with experimental values of 0.741 Å and 4.533 eV. The calculated bond length (1.90 Å) of the Ti₂ dimer also agrees very well with the experimental value of 1.91 Å.

We first determined the site a Ti atom would occupy on C₆₀. There are four different sites to be considered: the hexagonal sites on top of any of the 20 hexagons, the pentagonal site on top of any of the 12 pentagons, and the bridge sites corresponding to any of the 30 carbon double bonds or the 60 single bonds. The preferred position for Ti is found to be the hexagonal site, with a binding energy of 2.35 eV, which agrees with the result of Yildirim et al.⁷ We then studied the interaction of a hydrogen molecule with TiC₆₀ cluster. In the ground-state configuration, the hydrogen atoms are bound in nearly molecular form with a H–H bond length of 0.81 Å, with the Ti atom occupying the hexagonal site (Figure 1a). The binding energy of the H₂ molecule, defined as the energy difference between the TiC₆₀H₂ cluster and the TiC₆₀ and H₂ molecules, is found to be 0.55 eV. These results are also in agreement with the results of Yildirim et al.⁷ We should emphasize that when H₂ interacts with a single neutral Ti atom, it dissociates with a H–H distance of 3.12 Å, and the binding energy of TiH₂, defined with respect to the dissociated Ti and H₂ molecules, is 0.889 eV. However, the hydrogen atoms bind to a single Ti⁺ ion in a molecular form with a H–H bond length of 0.774 Å and a binding energy of 1.073 eV.¹² The molecular adsorption of H₂ on TiC₆₀ is due to the same mechanism as that on Ti⁺, namely that the Ti atom remains in a positively charged state due to transfer of an electron to the C₆₀ cage.

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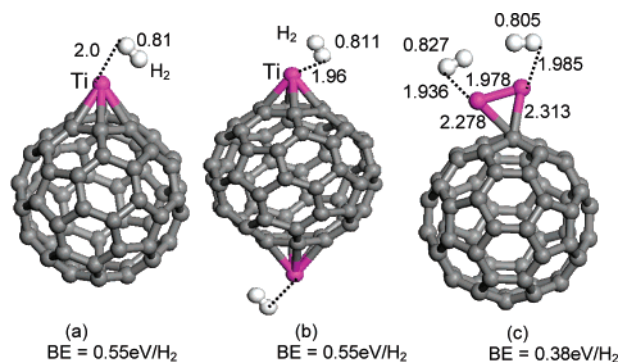


Figure 1. H_2 adsorbed on TiC_{60} and Ti_2C_{60} . The numbers represent bond lengths in Å. The red atoms are Ti and white atoms are H. BE is for the binding energy per H_2 .

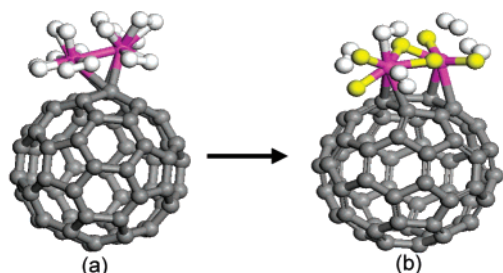


Figure 2. (a) Initial and (b) final configuration of eight H_2 molecules on Ti_2C_{60} . The atomic H atoms are shown in yellow.

We then studied if two Ti atoms supported on a C_{60} fullerene would like to remain isolated or form a cluster. We found that the structure where Ti atoms cluster (Figure 1c without H_2) is 1.29 eV lower in energy than when they remain isolated (Figure 1b without H_2). To see if this clustering of Ti atoms can alter the nature of hydrogen adsorption, we allowed two H_2 molecules to react with these structures. The resulting geometries are given in Figure 1b,c. We found that although hydrogen molecules still remain in molecular form in both cases, clustering reduced the interaction energy from 0.55 eV/ H_2 in Figure 1b to 0.38 eV/ H_2 in Figure 1c. The structure in Figure 1c is 0.92 eV lower in energy than that in Figure 1b.

The next and most important questions are the following: (1) What is the maximum number of H atoms that can be bound to the structure in Figure 1c? (2) Do all the H atoms bind molecularly? (3) What is the binding energy per H_2 molecule? To study the first question, we started by reacting 10 H_2 molecules (5 H_2 molecules on each Ti atom) with Ti_2C_{60} . The structure was found to be unstable, and one H_2 molecule was seen to fly away while two others dissociated and were bound to the C atoms. The maximum number of H_2 molecules that could bind to Ti_2C_{60} is eight. The corresponding geometry is shown in Figure 2b. Note that here only 10 of the 16 H atoms remain molecular, while the other 6 dissociated and bonded in atomic form. These structures are very different from those obtained by Yildirim et al.,⁷ where all the eight H_2 molecules remained nearly molecular. Although the average binding energy of 0.4 eV per two H atoms in Figure 2b is similar to the 0.49 eV/ H_2 calculated by Yildirim et al.⁷ when 12 Ti atoms were coated on the C_{60} fullerene, the atomic H atoms in Figure 2b bind more strongly than the H_2 molecules. This suggests that clustering of Ti alters not only the binding energy of H_2 molecules but also the nature of H bonding.

This study raises an important concern. What if 12 or 14 Ti atoms that Yildirim et al. have used in isolated form to store up to 7.5 wt

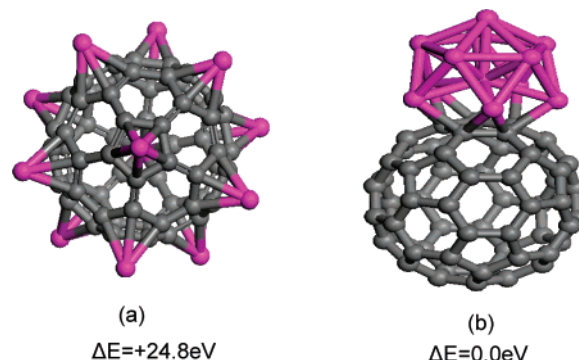


Figure 3. Two configurations of $\text{Ti}_{12}\text{C}_{60}$. The relative energy ΔE is evaluated referring to configuration (b).

% hydrogen did indeed cluster? This can affect the total H uptake. To address this concern we calculated the geometry of $\text{Ti}_{12}\text{C}_{60}$ cluster by first having the 12 Ti atoms occupy the 12 pentagonal sites (see Figure 3a) and then allowing them to form a cluster with a partial icosahedron frame (Figure 3b). The energy of the structure in Figure 3b is 24.8 eV lower than that of Figure 3a. This clearly shows that clustering of Ti atoms on a C_{60} surface is *energetically preferable*. It remains to be seen if the Ti_{12} cluster on a C_{60} surface can store up to $12 \times 4 \text{ H}_2$ molecules. We do not believe so for the following reasons: (1) The Ti atom residing inside the cluster cannot contribute to H_2 absorption. As the size of Ti clusters gets larger, more Ti atoms will remain inside the cluster and will not be able to trap H_2 . (2) Only the Ti atoms directly bonded to C_{60} are positively charged, while the charges on the other Ti atoms are negligible. Thus, the latter Ti atoms cannot trap H_2 molecules through the charge polarization mechanism. (3) The steric hindrance between H_2 molecules trapped on the Ti cluster will also limit the amount of storage. In fact, the available surface area for hydrogen molecules in Figure 3b is only 38% of that in Figure 3a. This gives the weight percentage of hydrogen stored to be 2.85 wt % ($0.38 \times 7.5 \text{ wt } \%$). In addition, the second reason mentioned above will reduce this number even further. Therefore, the clustering of Ti atoms on the carbon nanostructures not only significantly changes the nature of hydrogen bonding but also greatly reduces the weight percentage of hydrogen storage.

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