Titanium-capped carbon chains as promising new hydrogen storage media

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Received 7th September 2010, Accepted 12th November 2010
DOI: 10.1039/c0cp01745k

The capacity of Ti-capped sp carbon atomic chains for use as hydrogen storage media is studied using first-principles density functional theory. The Ti atom is strongly attached at one end of the carbon chains via d-p hybridization, forming stable TiCₙ complexes. We demonstrate that the number of adsorbed H₂ molecules on Ti through Kubas interactions depends upon the chain types. For polyyne (n even) or cumulene (n odd) structures, each Ti atom can hold up to five or six H₂ molecules, respectively. Furthermore, the TiC₅ chain effectively terminated on a C₂₀ fullerene can store hydrogen with an optimal binding energy of 0.52 eV per H₂ molecule. Our results reveal a possible way to explore high-capacity hydrogen storage materials in truly one-dimensional carbon structures.

1. Introduction

To develop economical hydrogen energy, carbon nanostructures with sp²-like bonding functionalized by transition metal (TM),1–6 alkali metal (AM)7–9 and alkaline-earth metal (AEM) atoms10 have been expected to be promising storage materials due to their light weights and large surface areas. Recently, Iijima et al.10 transformed graphene to single sp²-hybridized carbon chains containing 16 carbon atoms. In addition, chains with metal atoms connected to the ends have been previously generated,11 and their magnetic, electronic, and transport properties have been studied extensively.12,13 These results inspired us to consider whether metal-capped carbon atomic chains are efficient hydrogen storage media. In this study, we conduct theoretical studies of high-capacity hydrogen storage media consisting of a Ti atom capped on two kinds of atomic carbon chains, cumulene (with double C–C bonds) or polyyne (with alternating singlet and triplet bonds). The number of adsorbed H₂ molecules was only determined by the type of chain. Each Ti atom in TiC₅ and TiC₈ can bind up to six and five H₂ molecules, respectively, corresponding to storage capacities of 10 wt% and 6.5 wt%. The average binding energy of H₂ molecules on TiC₅ and TiC₈ is 0.59 and 0.57 eV per H₂ molecule, respectively, which is between the physisorption and chemisorption energies.

2. Computational method

Numerical calculations were performed using spin-polarized density functional theory (DFT) with the Perdew–Wang (1991) exchange-correlation function,14 as implemented in the DMol³ package (Accelrys Inc.).15 A double numerical atomic orbital augmented by d-polarization functions (DNP) was employed as the basis set. In the self-consistent field calculations, the electronic-density convergence threshold was set to 1 × 10⁻⁶ electron Å⁻³. Geometric optimization was performed with convergence thresholds of 10⁻³ Ha for the energy, 2 × 10⁻⁵ Ha Å⁻¹ for the force, and 10⁻⁴ Å for the atomic displacements. We performed normal-mode analysis of the obtained structures to ensure that the structures optimized without any symmetry constraints were true minima of the potential-energy surface.

3. Results and discussion

We first consider the bonding energetics of a single Ti atom at one end of the Cₙ (n = 5–16) chains. The binding energies of Ti, shown in Fig. 1(a), are much larger than those of Ti on sp²-hybridized carbon materials,2–5 and the adsorption strengths are thus strong enough to maintain stable Ti-Cₙ structures at room temperature. Moreover, the Ti binding energies exhibit an interesting odd–even oscillatory behavior, consistent with the trend of Mulliken charge [see Fig. 1(a)]. This behavior suggests that the bonding between the Ti atom and the carbon chains has a significant ionic characteristic. In addition, the configurations of TiCₙ complexes exhibit significant differences for odd or even values of n. For instance, the C–C distances in TiC₅, depicted in Fig. 1(b), are rather uniform. In contrast, the bond lengths of TiC₈ alternate, consistent with σ–π bonding [Fig. 1(c)]. Contour plots of the total electronic charge density confirm these bonding patterns.

To elucidate the nature of the bonding, the projected density of states (DOS) shown in Fig. 1(d) and (e) illustrates the bonding orbitals of the C₅ (C₈) and Ti atom results from the
As mentioned above, the bonding orbitals of C5 hybridizes with two Ti-\(p_x\) and Ti-\(d\) orbitals. The C-\(p\) and Ti-\(d\) hybridization is evidently stronger in TiC8 than in TiC5, in accordance with the larger binding energy of TiC8. Since odd-numbered and even-numbered free chains have full and half-occupied HOMOs (highest occupied molecular orbitals), respectively, different states are responsible for the bonding of the Ti atoms to C5 or C8. From the examination of the geometry of the TiC5(H2)6 configuration in Fig. 3(a), we can understand the binding mechanism of the hydrogen molecule. The side molecules are more weakly bound, with a binding energy of 0.54 eV per H2 molecule and an elongated H–H bond distance of 0.810 Å, on average. All of these features are more energetically favorable than its isomer (not shown) by 0.20 eV. The image number considered is 16 to ensure that the obtained MEP is correct. In Fig. 2(a) and (b), the MEPs show that a single Ti atom is attached to the right end of C5 and C8 without any energy barrier. The other end is free and ready to be attached to any other structure with a high surface-to-volume ratio. The main Ti vibrational frequencies, 623 cm\(^{-1}\) in TiC8 and 359 cm\(^{-1}\) in TiC5, correspond to the stretching modes of C–Ti. These characteristic modes will provide a reference for the Raman/IR spectra of the synthesized materials. To this end, a monatomic carbon chain, realized by removing the carbon atoms from graphene through energetic electron irradiation inside a transmission electron microscope,\(^{10}\) can be used as the initial material in the fabrication process.

Now we investigate the interaction between these complexes and hydrogen molecules. The first H2 molecule is found to dissociate on both TiC5 and TiC8 complexes and bind atomically to Ti, with interatomic H distances of 3.003 Å [Fig. 3(a)] and 2.748 Å [Fig. 3(b)], respectively. Such a dissociation is observed in most TM–hydrogen binding [ref. 2] due to excessive charge transfer from the TM to the antibonding \(\sigma^*\) state of H2. Additional H2 molecules, however, bind molecularly around the Ti atom, since the charge transfer per H2 molecule is not enough to destabilize the dihydrogen state when more hydrogen molecules are added to the system.

For TiC5, several initial configurations of the second H2 molecule were considered in the search for the lowest energy structure. The structure in which one of the H2 molecules binds as a dihydride is 0.09 eV higher in energy than the structure in which both H2 molecules bind in a molecular form [Fig. 3(a)]. We continue to introduce successive hydrogen molecules near the Ti atom. Surprisingly, it is energetically favorable for the TiC5 complex to adsorb 6 H2 molecules, corresponding to a ~10 wt% gravimetric density. A close examination of the geometry of the TiC5(H2)6 configuration shows that the adsorbed hydrogen molecules are divided into two sets [Fig. 3(a)]. First, the molecule on the top binding site, which is vertical to the carbon chain axis, has a bond length of 0.808 Å and the largest bonding energy, 0.82 eV. Second, the H–H bonds of the side H2 molecules lie almost parallel to the chain axis, with the lower H atoms of each H2 molecule tending to tilt toward the chain. The bond lengths between the Ti and the lower (upper) H atoms are 1.910 Å (1.970 Å). The side molecules are more weakly bound, with a binding energy of 0.54 eV per H2 molecule and an elongated H–H bond distance of 0.810 Å, on average. All of these features suggest different bonding mechanisms (to be discussed below) for the two sets of H2 molecules on TiC5.

On the other hand, when the second H2 molecule is bound to TiC8, the structural configuration shown in Fig. 3(b) is more energetically favorable than its isomer (not shown) by...
Insight into the nature of Ti-H₂ bonding and the orientation of H₂ molecules can be gained from the DOS and molecular orbital (MO) analyses. The metal-dihydrogen binding of TiC₅(H₂)₆, shown in Fig. 3(c), stems primarily from the Kubas interaction. In the energy range from −10 to −6 eV (region I), the d orbitals of Ti are hybridized with the σ orbitals of the hydrogen molecules, resulting in charge transfer from the hydrogen to the metal. Region II of Fig. 3(c) highlights that the hybridization of the Ti-d orbitals with the H₂ σ*-antibonding orbitals is responsible for keeping the side H₂ molecules parallel and the top H₂ molecule perpendicular to the TiC₅ chain. The isosurface plots of these states, as shown in Fig. 3(d), clearly confirm that the bonding is dominated by the overlap between the Ti-d and H₂σ states. To better understand the orientation of the side H₂ molecules, we also plotted the deformation charge in Fig. 3(a). The charge distribution around the lower H sites, marked in yellow, indicates that these H atoms lose a greater amount of charge. With the help of Mulliken charge population analysis, we identified that the upper H atom has a charge of 0.04 e, while the lower one carries 0.12 e due to charge transfer from H to the C atom. Thus, the distances between the Ti and the upper or lower H depend on the strength of the Coulomb interactions between the H and the C atoms. The Kubas interaction is likewise found in TiC₈(H₂)₅. Fig. 3(e) shows that the Ti-d orbitals interact with the σ orbitals of the H₂ molecules. The hybridization between the Ti-d orbitals and the side H₂ molecules’ σ*-antibonding orbitals plays a role in keeping them planar [Fig. 3(f)], in contrast to the situation in TiC₅(H₂)₆. The top hydrogen in TiC₈(H₂)₅ interacts with Ti rather weakly compared to the rest of the hydrogen molecules, as the relevant MO is more heavily polarized toward the C₈ rather than toward the H₂ [see Fig. 3(g)]. The Kubas interaction mentioned above leads to variations in the effective charge of the Ti atom. The Mulliken charge of the Ti atom varies from positive to negative as the number of hydrogen molecules increases. When the fifth (sixth) H₂ is adsorbed onto TiC₅ (TiC₈), the Ti atom carries −0.13 (−0.49) electrons.

The above results demonstrate that the interaction between one Ti atom and the carbon chain is very strong, and the binding energy of H₂ on TiC₅ is optimal for room temperature application. Now the question arises: can the storage performance of TiC₅ be influenced by introducing another Ti? We first discuss the second Ti atom saturating the free end of TiC₅ (n = 5, 8). The binding energy for Ti to the TiC₅ (TiC₈) is 4.31 eV (4.39 eV), which is obviously much large than that of Ti on the sp² carbon nanostructures. However, further functionalization through Ti atoms bridging other C–C bonds makes the chain unstable, due to the fact that the small separation between Ti atoms leads to stronger Ti–Ti coupling. At the end, the linear chains are transformed to the clusters composed of C and Ti atoms, which is also confirmed by other theoretical studies. Therefore only consider two Ti atoms each capping one end of the C₅.

Next, we studied the H₂ storage capacity of the TiC₅Ti complex. TiC₅Ti and TiC₇Ti can adsorb 12 and 10 H₂ molecules, respectively, with average binding energies of 0.53 and 0.55 eV per H₂ molecule. As shown in Fig. 4(a) and (b), the gravimetric densities of stored H₂ molecules for TiC₅Ti...
becomes 13.3 and 9.4 wt% when \( n = 5 \) and \( n = 8 \), respectively. Analysis of the electronic structures of the TiC\(_n\)Ti-(H\(_2\))\(_{12}\) and TiC\(_n\)Ti-(H\(_2\))\(_{10}\) shows that the Kubas interaction between H\(_2\) and TiC\(_n\) mentioned above also applies to the TiC\(_n\)Ti complex. Note that the introduction of the second Ti atom to TiC\(_n\) not only keeps the number of adsorbed H\(_2\) per Ti on odd- or even-numbered chains, but also the binding energies of the H\(_2\) with metal atoms.

Because controlling the number of atoms per chain in the synthesis of carbon chains may be difficult with today’s technology, it is important to know whether the results reported above for TiC\(_5\) and TiC\(_8\) are applicable to other Ti-capped carbon chains and how they vary with chain length. To this end, we have also studied the potential of TiC\(_{15}\) and TiC\(_{16}\) complexes as storage media, and we found that the number of adsorbed H\(_2\) molecules is six and five, respectively.

The corresponding bond lengths of H\(_2\) and Ti-H\(_2\), as depicted in Figs. 5(a) and (b), are very similar to those in TiC\(_5\)(H\(_2\))\(_6\) and TiC\(_8\)(H\(_2\))\(_5\). Furthermore, the average binding energies of H\(_2\) molecules to TiC\(_{15}\) and TiC\(_{16}\) are, respectively, 0.54 and 0.59 eV per H\(_2\) molecule, which are very close to the values found in the case of TiC\(_5\)(H\(_2\))\(_6\) and TiC\(_8\)(H\(_2\))\(_5\). The bonding mechanisms between Ti and H\(_2\) presented above also holds for these chains. This suggests that the length of the chains does not affect the hydrogen adsorption performance. In summary, the finding that a single Ti atom-capped, odd-numbered (even-numbered) carbon chain can bind up to six (five) hydrogen molecules is very general.

While the above results are promising for isolated TiC\(_n\) systems, one can imagine terminating the other end of these complexes with suitable graphitic nano-objects. These new structures not only represent the typical interface in realistic nanostructures produced by cluster beam deposition. Here we choose C\(_{20}\) fullerene as the end-capping candidate, as it is the most frequently experimentally synthesized curved \( sp^2 \) system. An increasing amount of experimental evidence shows that these hybrid \( sp + sp^2 \) carbon-based systems (with linear chains connecting \( sp^2 \)-type fragments) exhibit unusual electronic and optical properties. Fig. 5(c) illustrates that a TiC\(_5\) chain can be effectively stabilized by termination on C\(_{20}\). The calculated binding energy (with respect to the isolated TiC\(_5\) plus the fully relaxed C\(_{20}\)) is 2.79 eV. As shown in Fig. 5(d), the TiC\(_{5}\) assembled on the C\(_{20}\) structure can hold 6 H\(_2\) molecules, with an average binding energy of 0.52 eV per H\(_2\) molecule.

4. Conclusion

In conclusion, using all-electron DFT calculations, we have shown that each Ti atom adsorbed on even or odd-numbered carbon atomic chains can bind up to five or six hydrogen molecules, respectively. Note that the number of adsorbed H\(_2\) molecules depends only on the type of chain. We propose that the TiC\(_3\) chain terminated effectively on a C\(_{20}\) fullerene can also store 6 H\(_2\) molecules with an average binding energy of 0.52 eV per H\(_2\) molecule. Recent experiments have produced junctions between a single carbon chain and two fullerenes, which have provided a way to synthesis the \( sp + sp^2 \) system we proposed here. We hope that the theoretical results presented here will provide a useful reference for the design of high-capacity hydrogen storage materials in the laboratory.

Acknowledgements

This work was supported by the National Science Foundation of China under Grant No. 10774148, the special funds for the Major State Basic Research Project of China (973) under Grant No. 2007CB925004, and the Knowledge Innovation Program of the Chinese Academy of Sciences under Grant Nos KJCX2-YW-W07 and KJCX2-YW-N35. Part of the calculations were performed at the Center for Computational Science of CASIIPS.
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