Self-catalyzed hydrogenation and dihydrogen adsorption on titanium carbide nanoparticles

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Received 27 January 2006; in final form 28 April 2006
Available online 16 May 2006

Abstract

The adsorptions of H₂ on metallocarbohedrene Ti₈C₁₂, and nanocrystal Ti₁₄C₁₃ are studied using first-principles calculations. The Ti atoms serve as catalyst to mediate the dissociation of H₂ to form carbon hydrides, which otherwise would not form. Ti atoms on the surface of the nanocarbides are capable of coordinating with multiple dihydrogen ligands. High hydrogen capacities, 6.1 wt% for Ti₈C₁₂ and 7.7 wt% for Ti₁₄C₁₃, were obtained with more than 80% of the H bound in the energy range between 0.17 and 0.89 eV/H₂. Once the nanoparticles form a macroscopic material, the amount of chemisorbed hydrogen decreases, but additional hydrogen molecules is then up-taken through physisorption. Our study suggests that TiC nanoparticles have potential for H storage at near ambient conditions.

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Solid-state hydrogen storage has traditionally been studied in metal hydrides or on materials that adsorb hydrogen by physisorption. However, a new direction based on binding dihydrogen ligands [1] to nanoscale solid materials is now under exploration [2,3]. This approach promises to afford binding energies that are well suited for storage of hydrogen on-board vehicles (with a binding energy, $E_B = 0.2–0.6 \text{ eV/H}_2$). The reversibility of dihydrogen adsorption has been demonstrated for molecules [4], and the binding of multiple dihydrogen ligands to single transition metal (TM) atoms has been predicted [5,6]. The H:M ratio can be very high in this latter case, but it is unlikely that TMs will remain isolated upon H desorption. Very recently, density functional theory (DFT) studies showed that TM atoms supported on cyclopentadienyl (Cp) rings and buckyballs [2], and on carbon nanotubes (CNT) [3], have high reversible dihydrogen capacities. By demonstrating the feasibility of separating and stabilizing TMs on carbon networks, these studies provide a new direction toward high-capacity, room temperature, reversible hydrogen storage. However, it will be challenging to control the TM coordination with the buckyballs, as it is recently pointed out by Sun et al. [7] that clustering of TM atoms on the buckyball surface is energetically more favorable. Another issue is that the TMs may react with the carbon supports to form metal carbides.

Here we show that fully-relaxed nanoscale TM carbides, which have already been fabricated in laboratories, such as metallocarbohedrenes (MetCars) [8] and nanocrystals [9,10], can also bind dihydrogen ligands. Fig. 1 shows that a prototypical MetCar Ti₈C₁₂ can store a total 6.1 wt% of hydrogen, whereas a prototypical Ti₁₄C₁₃ nanocrystal can store a total 7.7 wt% of hydrogen with both dihydrogen and mono-hydrides. Noticeably, these nanostructures not only allow for dihydrogen binding energies (0.17–0.33 eV/H₂) to be significantly higher than physisorption but also allow for the carbon atoms to binding hydrides with significantly lower energies (0.64 and 1.31 eV/H₂, respectively) than a typical carbon hydride. Our study further reveals self-catalyzed hydrogenation of Ti and C atoms in these nanoparticles.

We use spin-polarized first-principles calculation as implanted in the Vienna Ab Initio Simulation Package (VASP) [11] and ultrasoft pseudopotential with PW91
generalized gradient approximation (GGA), which yields practically the same results to all-electron-like projector augmented-wave (PAW) potential with PBE exchange-correlation functional [13]. A cubic unit-cell of dimension 20 Å was used to maintain a vacuum region larger than 10 Å. An energy cutoff of 400 eV was used and the force criterion was set to 0.02 eV Å⁻¹ for structure optimization. To validate our methods for non-classical chemical interaction, we have calculated dihydrogen adsorption on the classic Cr(CO)₃(PH₃)₂ molecule and obtained a binding energy of 0.84 eV/H₂. This result compares favorably with the experimental value of 0.74 eV/H₂ [14].

The Ti₈C₁₂, shown in Fig. 2, is a prototypical MetCar of distorted T₈d symmetry [15,16], in which four Ti atoms form the corners of a tetrahedron (denoted as THN). The four remaining Ti are located on the face centers (denoted as thn), which form an inner tetrahedron. The 12 carbon atoms form six equivalent pairs (dicarbon) with a triple C≡C bond each, positioned along the edges of the tetrahedron. The structure is stable in part because it allows ‘Dewar coordination’ [17] between the dicarbons and the thn-Ti atoms. Although the Ti atoms are bonded to the carbon backbone, it has been experimentally demonstrated that they still coordinate with ligands such as C₆H₆, CH₃CN, and H₂O [18,19].

Previous theoretical studies [20–24] revealed a singlet and a triplet molecular state of the Ti₈C₁₂ with similar energies. Although which state should be the true ground state is still in debate in the literature and spin state generally affects reactivity [25], we show that, in this particular case, it has little effect on the hydrogen adsorption because the energy difference between the singlet and triplet is very small relative to the reaction heat of hydrogenation. For the sake of discussion, we start with the triplet state shown in Fig. 2a. According to Ref. [22], the two unpaired electrons in the triplet should be localized on four THN-Ti atoms. We found that only two of the four THN-Ti atoms prefer to be hydrogenated, i.e., forming two Ti hydrides, with $E_B = 1.42$ eV/H₂. This differentiates the THN sites into the α and β sites in Fig. 2b. For convenience, we refer the thn-Ti atoms in Fig. 2b as the γ sites. Our calculation shows that further hydrogenation of the Ti atoms is energetically unfavorable. Next, we consider the singlet state. Intuitively, one might consider the singlet a good dihydrogen absorber. Indeed, one can place one by one the dihydrogen onto a Ti₈C₁₂ until all the Ti atoms are saturated with H₂ ligands: each THN-Ti takes three H₂ (average $E_B = 0.42$ eV/H₂) and each thn-Ti takes one ($E_B = 0.17$ eV/H₂). In total, 16 H₂ can be adsorbed onto one Ti₈C₁₂ molecule. However, it is energetically more favorable to first convert the singlet into a triplet and then form the two α-site hydrides in Fig. 2b, because the singlet-to-triplet promotion energy is at most a few tenth of eV [26], whereas the formation of the two hydrides lowers the total energy by almost 1.4 eV. In other words, even if the ground state of the H-free Ti₈C₁₂ is a singlet, it has little effect on the final result of hydrogenation.

An important question concerning Ti₈C₁₂ is whether hydrogenation of the carbon atoms will also take place. If it does, the process

$$\text{Ti}\equiv\text{C} + \text{H}_2 \rightarrow \text{Ti} = \text{CH} = \text{CH}$$

could be similar to acetylene hydrogenation that requires the conversion of a triple (carbon–carbon) bond to a dou-
The formation of the carbon hydrides depends critically on the reaction barrier. If an H$_2$ approaches the dicarbon from directly above, the calculated dissociation barrier is large (>2.5 eV), which is completely different from the spontaneous dissociation claimed by Liu et al. [28]. We believe this barrier should be high because in Ti$_8$C$_{12}$ the dicarbons are inert, similar to acetylene (H=C=C=H). However, we found a different reaction pathway, in which the Ti atoms serve as catalysts to reduce the barrier to <0.25 eV as detailed in the five frames in Fig. 3. This happens because, on a Ti the dihydrogen H--H bond length, 0.81 Å, is noticeably longer than that of a free H$_2$ molecule, 0.75 Å, thereby, easier to break. When two dihydrogen ligands on two of the THN-Ti atoms approach each other, the energy increase from frame 1 to frame 2 in Fig. 3 is small, because the interactions with the Ti atoms make the elongation of the dihydrogen bond much easier. The H--H ligands dissociate by transferring one H atom/each ligand to the middle dicarbon (in frame 3 and frame 4) eventually two carbon hydrides form as in frame 5. There is no additional barrier from frame 2 to frame 5. Such a catalytic effect is an inherent property of the MetCar molecule itself.

After the two α-site Ti atoms and the 12 C atoms are hydrogenated, the resulting Ti$_8$C$_{12}$H$_{14}$ can still take ten dihydrogen ligands: one on each γ-site Ti with $E_B=0.33$ eV/H$_2$, three on each β-site Ti with $E_B=0.17$ eV/H$_2$, but none on the α-site Ti (see Fig. 2c and Table 1). Of particular interest, hydrogenation of the dicarbons makes the γ-site Ti atoms (each resides in the center of three dicarbons) more reactive. As a direct result, the binding energy of the dihydrogen to the γ-site Ti (0.33 eV/H$_2$) is nearly doubled with respect to that without such hydrogenation (0.17 eV/H$_2$). The total H storage capacity, including both hydride and dihydrogen, is 6.1 wt%. The above discussion assumes that all the dicarbons are hydrogenated. In reality, however, depending on the actual hydrogenation conditions, there are other possibilities in which not all the dicarbons will be hydrogenated. Less hydrogenated dicarbons typically allows the MetCar molecules to bind more dihydrogen ligands with similar total storage capacities.

Now we turn our discussion to the interaction of hydrogen with Ti carbide nanocrystals. The Ti$_{14}$C$_{13}$ nanocrystal, shown in Fig. 4, has a cubic structure with Ti atoms on the corner (α- and β-) sites and face-center (γ-) sites and with C atoms on the edge-center and cube-center sites, respectively. Fig. 4a shows the electronic structure of Ti$_{14}$C$_{13}$. Similar to Ti$_8$C$_{12}$, the nanocrystal Ti$_{14}$C$_{13}$ also has an open-shell structure with four electrons in the highest occupied orbitals.

Here, hydrogen adsorption takes place in three distinct steps. First, four hydrides form on the four corners of the Ti tetrahedron [i.e., the four α sites in Fig. 4b] with $E_B=0.89$ eV/H$_2$, yielding Ti$_{14}$C$_{13}$H$_4$. Next, Ti on the α and β sites act as catalysts to dissociate up to six additional H$_2$ molecules, which are then transferred to the 12 edge-center carbon atoms as hydride species. Note that, the self-catalysis in Ti$_{14}$C$_{13}$ is qualitatively different from Ti$_8$C$_{12}$ as the H$_2$ dissociation here is spontaneous and barrierless. In Ti$_{14}$C$_{13}$, the carbons are single, instead of dicarbons as in the Ti$_8$C$_{12}$. Except for the central carbon, each carbon atom in Ti$_{14}$C$_{13}$ interacts with four Ti atoms, instead of six as in bulk TiC. Consequently, carbon atoms in Ti$_{14}$C$_{13}$ are chemically more reactive than those in Ti$_8$C$_{12}$. As a consequence, the strength of the C--H bonds in the resulting Ti$_{14}$C$_{13}$H$_{16}$ ($E_B=1.31$ eV/H$_2$) is more than twice as strong as that in H-loaded MetCar, Ti$_8$C$_{12}$H$_{14}$ ($E_B=0.64$ eV/H$_2$). In some sense, H transfer to carbons in Ti$_{14}$C$_{13}$H$_{16}$ resembles H ‘spillover’ to existing C dangling bonds in platinized carbon [29,30].

**Table 1**

<table>
<thead>
<tr>
<th>Binding (E$_B$)</th>
<th>Hydrogen weight percent (wt%)</th>
<th>Total number (n) of H</th>
<th>Adsorbed in Ti-based MetCar and nanocrystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Ti--H$_2$</td>
<td>0.89</td>
<td>6.1 (34)</td>
<td></td>
</tr>
<tr>
<td>β-Ti--H$_2$</td>
<td>0.33</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>γ-Ti--H$_2$</td>
<td>0.33</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>C--H</td>
<td>1.31</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Ti--H</td>
<td>0.89</td>
<td>0.89</td>
<td></td>
</tr>
</tbody>
</table>
which was also suggested as an important mechanism for H storage in carbon nanotubes [31]. Finally, Ti$_{14}$C$_{13}$H$_{16}$ binds another 26 dihydrogen ligands: one on each $\gamma$-site Ti with $E_B = 0.18$ eV/H$_2$, three on each $\beta$-site Ti (the first two with $E_B = 0.38$ eV/H$_2$ and the third with $E_B = 0.20$ eV/H$_2$), and two on each $\alpha$-site Ti with $E_B = 0.19$ eV/H$_2$ (see Fig. 4c and Table 1) to form Ti$_{14}$C$_{13}$H$_{68}$. The total H storage capacity in this case is 7.7 wt%.

So far all the discussions are focused on isolated nanoparticles. Practically, these nanoparticles have to be assembled into macroscopic materials with certain structures, which depend on the way of interaction between the nanoparticles. Similar to Fig. 2, only dihydrogens on one of the $\alpha$, $\beta$, and $\gamma$ sites are shown.

In summary, first-principles study reveals dihydrogen binding and self-catalyzed hydrogenation for both MetCars and TiC nanocrystals. These binding energies are suitable for operations at near-ambient temperature and pressure. Since both MetCars and TiC nanocrystals are experimentally available, this study should stimulate experimental testing and direct validation of the dihydrogen binding principle, which would be a vital step toward significant breakthroughs in hydrogen storage. Also, the unique catalytic functionality of the embedded Ti suggests that such nanomaterials may have other important applications beyond hydrogen storage, for instance, the development of alternative membranes for proton transport.

Acknowledgements

We acknowledge the support from the Office of Science, Basic Energy Sciences, Division of Materials Science and the Office of Energy Efficiency and Renewable Energy Hydrogen, Fuel Cell, and Infrastructure Technologies Program of the Department of Energy under Grant No. DE-AC36-99GO10337.

References


While Refs. [21] and [22] showed that the singlet state should be 0.1–0.13 eV lower than the triplet state; Ref. [23] predicted instead a triplet ground state. Recent configuration-interaction calculation with 80 active electrons [24] showed that the triplet state should be 0.12 eV above the singlet state. In our calculation, the triplet state is 0.02 eV lower than the singlet state.

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