Self-catalyzed hydrogenation and dihydrogen adsorption on titanium carbide nanoparticles

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Abstract

The adsorptions of H_2 on metallocarbohedrene Ti_8C_{12}, and nanocrystal $Ti_{14}C_{13}$ are studied using first-principles calculations. The Ti atoms serve as catalyst to mediate the dissociation of H_2 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 Ti_8C_{12} and 7.7 wt% for $Ti_{14}C_{13}$, were obtained with more than 80% of the H bound in the energy range between 0.17 and 0.89 eV/H_2. 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 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 stor-age. 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 proto-typical MetCar Ti_8C_{12} can store a total 6.1 wt% of hydrogen, whereas a prototypical $Ti_{14}C_{13}$ 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/H_2) to be sig-nificantly higher than physisorption but also allow for the car-bon atoms to binding hydrides with significantly lower energies (0.64 and 1.31 eV/H_2, respectively) than a typical car-bon hydride. Our study further reveals self-catalyzed hydro-genation 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

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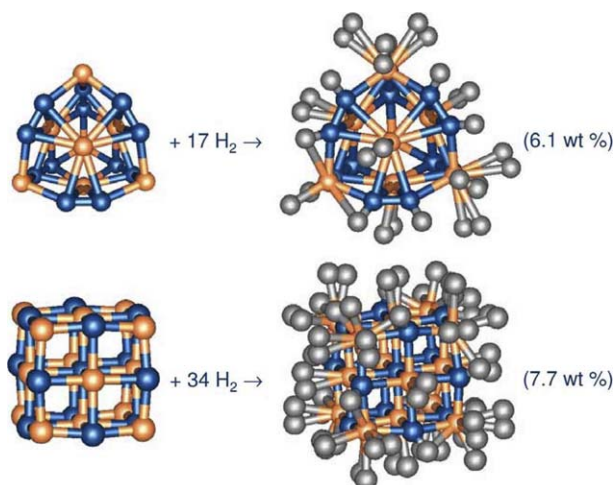E-mail address: yufeng_zhao@nrel.gov (Y. Zhao).

Fig. 1. Charging of the MetCar Ti_8C_{12} (upper panel) and nanocrystal $Ti_{14}C_{13}$ (lower panel) by hydrogen molecules. In the case of Ti_8C_{12}, 34 H atoms can be attached, corresponding to a total 6.1 wt%, whereas in the case of $Ti_{14}C_{13}$, 68 H atoms can be attached, corresponding to a total 7.7 wt%.

Fig. 2. (a) Electronic structure of Ti_8C_{12} (arrows indicate electron occupation). Labels give degeneracy under the T_d symmetry, but the actual symmetry is lower due to Jahn–Teller distortion [16,24]. (b, c) Hydrogen interaction with Ti_8C_{12} in a mixed ball-and-stick (front) and wireframe (back) representation. In (b), two H (dark grey) form hydrides at corner Ti (orange). In (c), 12 additional H bind as hydrides to C (blue). In addition, dihydrogen ligands (light grey) also form by coordinating with Ti: one on each γ site and three on each β site. There are two equivalent α and β sites, respectively, and four equivalent γ sites. For clarity, here only dihydrogens on one of the β and γ sites are shown. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

[12] 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 for structure optimization. To validate our methods for non-classical chemical interaction, we have calculated dihydrogen adsorption on the classic $Cr(CO)_3(PH_3)_2$ molecule and obtained a binding energy of 0.84 eV/H_2. This result compares favorably with the experimental value of 0.74 eV/H_2 [14].

The Ti_8C_{12}, shown in Fig. 2, is a prototypical MetCar of distorted T_d 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 η^2-'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 C_6H_6, CH_3CN, and H_2O [18,19].

Previous theoretical studies [20–24] revealed a singlet and a triplet molecular state of the Ti_8C_{12} 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
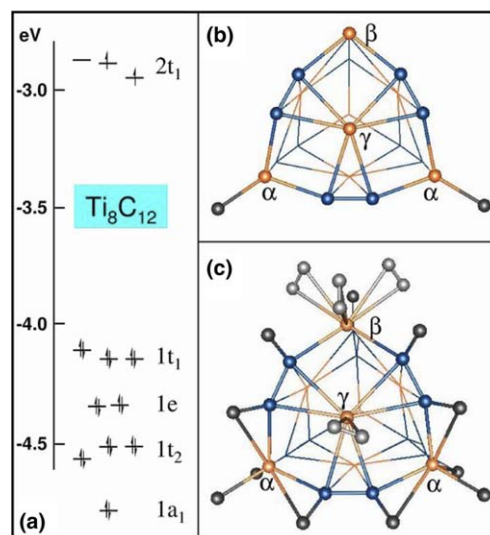
atoms. We found that only two of the four THN-Ti atoms prefer to be hydrogenated, i.e., forming two Ti hydrides, with $E_B = 1.42$ eV/H_2. This differentiates the THN sites into the α and β sites in Fig. 2b. For convenience, we refer the thn-Ti atoms in Fig. 2b as the γ sites. Our calculation shows that 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 Ti_8C_{12} until all the Ti atoms are saturated with H_2 ligands: each THN-Ti takes three H_2 (average $E_B = 0.42$ eV/H_2) and each thn-Ti takes one ($E_B = 0.17$ eV/H_2). In total, 16 H_2 can be adsorbed onto one Ti_8C_{12} 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 Ti_8C_{12} is a singlet, it has little effect on the final result of hydrogenation.

An important question concerning Ti_8C_{12} is whether hydrogenation of the carbon atoms will also take place. If it does, the process

$$Ti\text{—}C\equiv C\text{—}Ti + H_2 \rightarrow Ti\text{—}CH\text{=}CH\text{—}Ti \qquad (1)$$

could be similar to acetylene hydrogenation that requires the conversion of a triple (carbon–carbon) bond to a dou-

ble bond. Indeed, we found that reaction (1) elongates the carbon–carbon bonds from 1.33 to 1.40 Å. However, our reaction heat of 0.64 eV/H_2 is much smaller than that of conventional acetylene hydrogenation, 1.83 eV/H_2 [27]. The more than 60% reduction is due to the unique chemistry within MetCar molecules: the formation of two carbon hydrides breaks one π bond in a dicarbon, therefore, weakening Dewar coordination between dicarbon and γ-site Ti, as evidenced by the increase of the (γ-)Ti—C distance from 2.24 to 2.32 Å.

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_8C_{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.
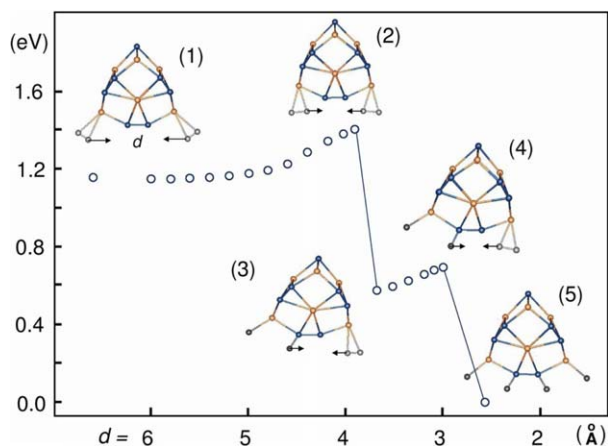

Fig. 3. A concerted low-barrier dissociation process of dihydrogen leading to the hydrogenation of Ti and C. The five insets, labeled (1)–(5), show the frames of the atomic structure along the pathway. Orange, blue, and grey balls are the Ti, C, and H atoms, respectively. Open circles in the main figure are the calculated energies, as a function of the decreasing distance *d* between the two H atoms marked in the frames by arrows. The dissociation of dihydrogens corresponds to sharp drops in the energy, as indicated by the solid lines. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

After the two α-site Ti atoms and the 12 C atoms are hydrogenated, the resulting $Ti_8C_{12}H_{14}$ 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_8C_{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_8C_{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_8C_{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_8C_{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, $Ti_8C_{12}H_{14}$ ($E_B = 0.64$ 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
Binding energy (E_B), hydrogen weight percent (wt%) and total number (*n*) of H adsorbed in Ti-based MetCar and nanocrystal

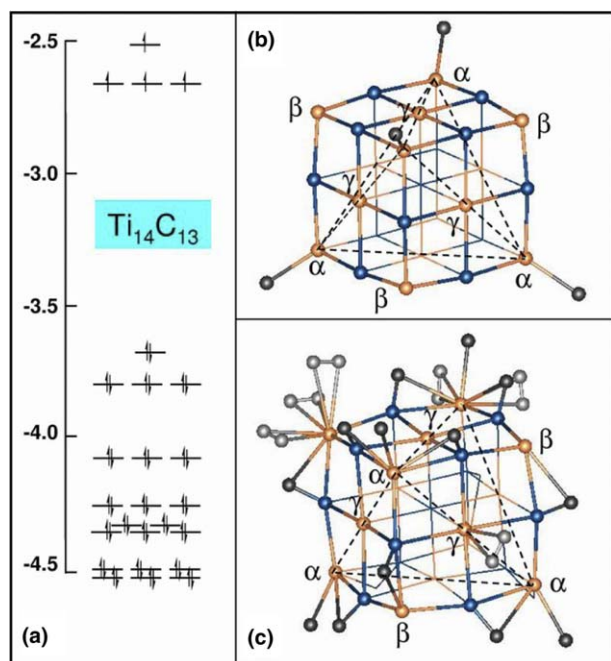|	E_B (eV/H_2)					wt% (*n*)
	α-Ti—H_2	β-Ti—H_2	γ-Ti—H_2	C—H	Ti—H	
Ti_8C_{12}	–	0.17	0.33	0.64	1.42	6.1 (34)
$Ti_{14}C_{13}$	0.19	0.20, 0.38	0.18	1.31	0.89	7.7 (68)

Fig. 4. (a) $Ti_{14}C_{13}$ electronic structure. (b) and (c) Its interaction with hydrogen. The $Ti_{14}C_{13}$ has a cubic structure with four equivalent α and β sites, respectively, and six equivalent γ sites. In (b), H atoms form hydrides with Ti on four of the eight corners of the cube. In (c), besides the spillover of 12 H to the carbon atoms, dihydrogen ligands form by coordinating with Ti: one at each γ site, three at each β site, and two at each α site. Similar to Fig. 2, only dihydrogens on one of the α, β, and γ sites are shown.

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 γ-site Ti with $E_B = 0.18 \, eV/H_2$, three on each β-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 α-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. Fig. 5a shows the fully relaxed MetCar dimer with a binding energy of 1.8 eV/molecule. The two MetCar molecules coordinate most strongly through the THN-site Ti atoms and the dicarbons aligned along the edges. Such coordination allows for formation of a diamond-like MetCar crystal as is shown in Fig. 5b projected to the (110) surface. In this predicted crystalline material, each Ti atom binds one dihydrogen and the two dicarbon in the uncoordinated edges bind four hydrogen atoms, resulting in a capacity of 10 H_2 per MetCar molecule (or 3.7 wt%) with binding energy of $0.2 \sim 0.6 \, eV/H_2$. Notice that the porous MetCar crystal (with pore size of 1.25 nm) should possess high potential of physisorption [32,33] in addition to the chemisorption. Due to the cubic symmetry, the nanocrystal $Ti_{14}C_{13}$ might form close-packed materials with less hydrogen capacity expected.
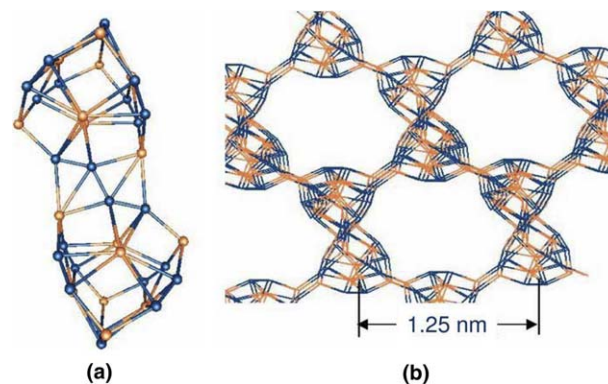

Fig. 5. (a) Two Ti_8C_{12} molecules attract most strongly through the edges to form a dimer. The binding is contributed by coordination between the THN-site Ti and the dicarbon. (b) Diamond-like structure projected to the (110) surface. In the calculation, both the atomic positions and the unit cell are allowed for relaxation. The crystal lattice is slightly deviated from the ideal diamond structure.

In summary, first-principles study reveals dihydrogen binding and self-catalyzed hydrogenation for both Met-Cars 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

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