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Abstract
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Transition-Metal-Ethylene Complexes as High-Capacity Hydrogen-Storage Media

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From first-principles calculations, we predict that a single ethylene molecule can form a stable complex with two transition metals (TM) such as Ti. The resulting TM-ethylene complex then absorbs up to ten hydrogen molecules, reaching to gravimetric storage capacity of ~14 wt %. Dimerization, polymerizations, and incorporation of the TM-ethylene complexes in nanoporous carbon materials are also discussed. Our results are quite remarkable and open a new approach to high-capacity hydrogen-storage materials discovery.

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Hydrogen is considered to be one of the best alternative and renewable fuels [1,2] because of its abundance, easy synthesis, and nonpolluting nature when used in fuel cells. However, the main concern is the safe storage and efficient transport of this highly flammable gas [3].

The main obstacles in hydrogen storage are slow kinetics, poor reversibility and high dehydrogenation temperatures for the chemical hydrides [4], and very low desorption temperatures or energies for the physisorption materials [metal-organic frameworks (MOF) [5], carbide-derived carbons [6], etc.]. Recently, a novel concept to overcome these obstacles has been suggested [7–14]. It was predicted that a single Ti atom affixed to carbon nanostructures, such as C60 or nanotubes, strongly adsorbs up to four hydrogen molecules [7,8,10]. The interaction between hydrogen molecules and transition metals is very unique, lying between chemi- and physisorption, with a binding energy of 0.4 eV compatible with room temperature desorption/absorption. The origin of this unusual “molecular chemisorption” is explained by well-known Dewar coordination and Kubas interaction [15]. The transition metals (TM) are chemically bonded onto different molecules or nanostructures through hybridization of lowest-unoccupied molecular orbital (LUMO) of nanostructure with TM d-orbitals (i.e., Dewar coordination). The resulting complex then binds multiple molecular hydrogens through hybridization between H2 − σ* antibonding and TM d orbitals (i.e., Kubas interactions).

Synthesizing the predicted structures of Ti decorated nanotubes/C60 was proven to be very difficult because of the lack of bulk quantities of small-diameter nanotubes and strong C60−Cn interactions in the solid phase. Moreover, Ti atoms uniformly coating the SWNT/C60 surface may be subject to clustering after several charging-discharging processes [16].

In searching for a more efficient and feasible high-capacity hydrogen-storage medium, we found that the C = C double bond of an ethylene molecule C2H4, mimics double bonds of C60 that strongly binds the TM atom (see Fig. 1) and therefore it is expected to support TM atoms strongly to provide a basis for high-capacity hydrogen storage via the Dewar-Kubas mechanism discussed above.

In this Letter, we explored this idea and indeed found that a single ethylene molecule can hold not only one but also two Ti atoms, i.e., C2H4Ti2, which then reversibly binds up to ten H2 molecules yielding an unexpectedly high storage capacity of ~14 wt %. These results suggest that ethylene, a well-known inexpensive molecule, can be an important basis in developing frameworks for efficient and safe hydrogen-storage media.

Our results are obtained from first-principles plane wave calculations within density functional theory using Vanderbilt-type ultrasoft pseudopotentials with Perdew-Zunger exchange correlation [17]. Single molecules have been treated in a supercell of 15 × 15 × 15 Å with Γ

FIG. 1 (color online). (a) One of the most stable structures of the Ti-C60 complex where the Ti atom (black) is bonded to a double bond with four hydrogen molecules attached (dark gray). (b) The local structure of the Ti-C60 double bond. (c) Replacing the end carbon atoms shown in (b) by H results in an ethylene molecule. This suggests that we may simply use the ethylene molecule to hold Ti atoms, which then binds multiple hydrogen molecules.
k-point and a cutoff energy of 408 eV. The structures are optimized until the maximum force allowed on each atom is less than 0.01 eV/Å for both spin-paired and spin-relaxed cases.

We first studied the bonding of a single Ti-atom to an ethylene molecule to form \( \text{C}_2\text{H}_4\text{Ti} \) [see Fig. 2(b)]. We found no energy barrier for this reaction. The binding energy is calculated by subtracting the equilibrium total energy \( E_T \) of \( \text{C}_2\text{H}_4\text{Ti} \) molecule from the sum of the total energies of free ethylene molecule and of Ti-atom:

\[
E_B(\text{Ti}) = E_T(\text{C}_2\text{H}_4) + E_T(\text{Ti}) - E_T(\text{C}_2\text{H}_4\text{Ti}).
\]

The Ti atom forms a symmetric bridge bond with the C = C bond of ethylene with \( E_B = 1.45 \) eV. Interestingly, it is also possible to attach a second Ti atom to the \( \text{C}_2\text{H}_4\text{Ti} \) to form \( \text{C}_2\text{H}_4\text{Ti}_2 \) [see Fig. 2(c)] without any potential barrier and about the same binding energy as the first Ti atom. In the optimized structure [Fig. 2(c)], each Ti atom is closer to one of the carbon atoms, leading to two different Ti-C bonds. Figure 2(d) shows that the bonding orbital for the one of the carbon atoms, leading to two different Ti-C bonds of ethylene with the optimized structure [Fig. 2(c)], each Ti atom is closer to and about the same binding energy as the first Ti atom. In the third Ti mode, Ti atoms vibrate parallel and perpendicular to the \( \text{C}_2\text{H}_4 \) plane with an energy of 0.4 eV and bond length of 0.82 Å. The resulting structure, \( \text{C}_2\text{H}_4(\text{TiH}_2-3\text{H}_2) \), is shown in Fig. 3(c). We note that these binding energies have the right order of magnitude for room temperature storage. Since the hydrogens are absorbed molecularly, we also expect fast absorption or desorption kinetics.

Finally, we also observed many other local stable configurations where all of the hydrogen molecules are bonded molecularly. One such configuration, denoted as \( \text{C}_2\text{H}_4(\text{TiH}_2-5\text{H}_2) \), is shown in Fig. 3(d). Here the H\(_2\) molecules stay intact and benefit equally from bonding with the Ti atom. The total ten hydrogen molecules absorbed by a...
single Ti-ethylene complex, C₂H₄(Ti-5H₂)₂, correspond to a ~14 wt% gravimetric density, which is more than twice of the criterion set for efficient hydrogen storage. By removing the top H₂ molecule, we find that C₂H₄(Ti-4H₂)₂ configuration is also a local minimum and has a slightly (0.08 eV/H₂) higher energy than the C₂H₄(TiH₂-3H₂)₂ configuration shown in Fig. 3(c). Our MD simulations indicate that the system oscillates between these two configurations. This is consistent with the observation that in Kubas compounds [15], the dihydrogen (i.e., 2H) and molecular (i.e., H₂) bonding are usually found to be in resonance [15].

The top hydrogen molecule in C₂H₄(Ti-5H₂)₂ has the weakest bonding in the system with Eᵣ = 0.29 eV, whereas the side H₂ molecules have the strongest bonding with Eᵣ = 0.49 eV/H₂ and significantly elongated H-H bond distance of 0.85 Å. This suggests the presence of two different H₂-C₂H₄Ti₂ bonding orbitals as shown in Figs. 3(e) and 3(f). The first one is the hybridization between the top-H₂ σ*-antibonding and the Ti-d orbital. The second one is the simultaneous hybridization of the side H₂ σ*-antibonding orbitals with the Ti-d orbital. Since the bonding orbitals are mainly between metal d- and hydrogen σ*-antibonding orbitals, the mechanism of this interesting interaction can be explained by the Kubas interaction [15].

We also calculated the normal modes of C₂H₄(Ti-5H₂)₂ and did not find any soft modes, indicating that the system indeed corresponds to a local minimum. Among many vibrational modes, we note that the H₂ stretching mode is around 2700–3000 cm⁻¹ for side H₂ and around 3300 cm⁻¹ for top H₂ molecules, significantly lower than the 4400 cm⁻¹ for free H₂ molecule. Such a shift in the mode frequency would be the key feature that can be probed by Raman/IR measurement to confirm a successful synthesis of the structures predicted here.

Finally, the stability of C₂H₄(Ti-5H₂)₂ structure has been further studied by carrying out ab initio molecular dynamic calculations performed at 300 and 800 K. While all ten H₂ molecules have remained bound to the C₂H₄Ti₂ molecule at 300 K, they start to desorb above 300 K and all of them are desorbed already at 800 K, leaving behind a stable C₂H₄Ti₂ molecule. This prediction suggests that all the stored hydrogen molecules can be discharged easily through heating.

We next discuss the possibility of the dimerization and polymerization in the course of recycling and its effect on the hydrogen storage capacity. We found that two molecules can form a dimer through a Ti-Ti bond as shown in Fig. 4(a). The dimer formation is exothermic with an energy gain of ΔEₐ = 2.28 eV, and leads to a stable structure. The ground state is ferromagnetic with μ = 6μₘ. While each Ti atom at both ends of the dimer can bind 5 H₂ molecules, two linking Ti-atom can absorb only 4 H₂ totaling to 14 H₂ per dimer. As a result, the gravimetric density obtained by the dimer is lowered to ~10 wt%. The total energy can be further lowered by adding more C₂H₄Ti₂ molecules to the dimer, and eventually by forming a paramagnetic polymer as shown in Fig. 4(c). The polymerization energy per molecule is calculated to be 2EP = 2.69 eV and the H₂ storage capacity is further lowered to 6.1 wt%. Polymerization did not change the binding energy of the H₂ on Ti-atom significantly, and therefore should not affect the desorption temperature.

In order to prevent C₂H₄Ti₂ molecules from forming a possible polymer phase during recycling, one can imagine
incorporating these TM-ethylene complexes in a nanoporous material such as MOF [5] and carbide-derived carbons [6]. As an example, we consider a C2H4Ti2 adsorbed above and below the center of a hexagon of a graphene layer. Here the graphene is taken as a prototype system which represents the internal structure of a carbon-based nanoporous material. We find that TM-ethylene complexes can form a stable structure with the graphene surface. As shown in Figs. 4(e) and 4(f), single and double C2H4Ti2 molecules assembled on a 3 × 3 graphene layer can hold 7 and 14 H2 with an average binding energy of 0.43 and 0.41 eV/H2, respectively. The binding energy of the C2H4Ti2 molecule is found to be −2 eV. The actual binding energy in nanoporous materials could be even higher because of curvature effects [18]. The maximum gravimetric density achieved in this present framework is 6.1 wt %.

It is important to know if the results reported above for M = Ti hold for other metals. Therefore we are currently studying a large number of metals and the details will be published elsewhere [19]. Our initial results are summarized in Table I, which clearly indicates that most of the light TM atoms can be bound to ethylene and each of them can absorb up to five H2 molecules. Scandium is the ideal case but for practical reasons Ti is the best choice of elements. Cr binds very weakly while Zn does not bind at all to the C2H4 molecule. Interestingly, Zr forms a stronger bonding with C2H4 than Ti and can absorb up to ten H2 molecule with an average binding energy of 0.6 eV. Heavier metals such as Pd and Pt can also form complexes with C2H4 but bind fewer hydrogen molecules with significantly stronger binding energy than Ti. Table I also gives the binding energies with respect to bulk metal energies. The negative value for Eb indicates endothermic reaction. Because of the very low vapor pressure of many metals, it is probably better to use some metal precursor to synthesize the structures predicted here.

In conclusion, we showed that an individual ethylene molecule functionalized by two light transition metals can bind up to ten hydrogen molecules via Dewar-Kubas interaction, reaching a gravimetric density as high as ~14 wt %. We propose to incorporate the TM-ethylene complex into carbon-based nanoporous materials to avoid dimerization/polymerization during recycling. Our results open a new approach to the high-capacity hydrogen-storage materials discovery by functionalizing small organic molecules with light transition metals.

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