

Hydrogen Storage in Novel Organometallic Buckyballs

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Transition metal (TM) atoms bound to fullerenes are proposed as adsorbents for high density, room temperature, ambient pressure storage of hydrogen. C_{60} or $C_{48}B_{12}$ disperses TMs by charge transfer interactions to produce stable organometallic buckyballs (OBBs). A particular scandium OBB can bind as many as 11 hydrogen atoms per TM, ten of which are in the form of dihydrogen that can be adsorbed and desorbed reversibly. In this case, the calculated binding energy is about 0.3 eV/ H_2 , which is ideal for use on board vehicles. The theoretical maximum retrievable H_2 storage density is ~ 9 wt %.

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Hydrogen is viewed as a clean energy alternative that could one day replace fossil fuels. The U.S. Department of Energy has determined that a hydrogen storage density of 9 wt % will be required for fuel-cell powered vehicles to be able to replace petroleum-fueled vehicles on a large scale [1]. Very high pressure vessels are capable of storing hydrogen at 9 wt %, but the various practical considerations indicate that other solutions will be required. A few solid-state materials, such as Li_3N [2] and $Li_3Be_2H_7$ [3], can absorb up to 9 wt % hydrogen, but, at the present time, these systems are reversible only near 250 °C. Alanates such as $LiAl_4$ and $Ti(AlH_4)_4$ contain more than 9 wt % hydrogen, but these systems have not yet exhibited reversibility. The related $NaAlH_4$ material has shown 5 wt % reversibility at a temperature of 180 °C [4]. Compounds such as $NaBH_4$ contain a great deal of hydrogen that can be liberated upon reaction with water, but these materials must be regenerated by a chemical process off board [5].

In previous work, we measured the binding energies for nondissociative hydrogen adsorption on both carbon single-wall (~ 20 kJ/mol) [6] and multiwall nanotubes (~ 54 kJ/mol) [7] when nanosized transition metal (TM) species were present. These binding energies are significantly higher than what is expected for simple van der Waals (vdW) adsorption of H_2 on the carbon, and substantially lower than if atomic hydrogen were chemisorbed on the metal surfaces. The amount adsorbed and the first-order desorption process were inconsistent with dissociative hydrogen uptake by either surface chemisorption or bulk metal hydride formation. The observation that a trace amount of transition metal can lead to an enhanced capacity with a moderate binding energy caused us to explore the ways in which carbon and metals could be combined to construct new adsorbents capable of storing large amounts of hydrogen.

Here, we report an entirely new concept for storing hydrogen in its molecular form using rationally designed, novel organometallic molecules based on C_{60} . We show theoretically that the amount of H_2 that can be retrieved reversibly at room temperature (RT) and near ambient pressure can approach 9 wt %. The design is based on the

fact that both H_2 and cyclopentadiene rings ($Cp = C_5H_5$) can act as ligands for TMs. A TM atom interacts with a Cp ring through Dewar coordination [8] and with a dihydrogen ligand through a Kubas interaction [9]. Although each type of bonding is of historical importance in coordination chemistry [9,10], the combination of the two as a solution for hydrogen storage has never been seriously considered. Others have shown that isolated TM atoms can store up to six dihydrogen species [11,12], but the metal atoms are expected to coalesce and form bulk materials when hydrogen is removed. We show that a $Cp[ScH_2]$ complex can store 6.7 wt % of nondissociated H_2 , but these complexes may polymerize after hydrogen has been removed, making the process irreversible. However, when the complexes are arranged symmetrically on a buckyball, species such as $C_{60}[ScH_2]_{12}$ and $C_{48}B_{12}[ScH]_{12}$ are stable and can reversibly adsorb additional hydrogen, resulting in capacities of 7.0 and 8.77 wt %, respectively. Moreover, the reversible hydrogen is stored with a binding energy that is ideal for vehicular applications, 0.3–0.4 eV. Notice that stable TM-coated buckyballs [13] and nanotubes [14] have been recently synthesized.

We use a spin-polarized first-principles calculation as implanted in the Vienna Ab-initio Simulation Package (VASP) [15]. Ultrasoft pseudopotential with the Perdew-Wang 1991 [16] generalized gradient approximation yields practically the same results to an all-electron-like projector augmented-wave potential with the Perdew-Burke-Ernzerhof exchange-correlation functional [17]. An energy cutoff of 400 eV was used. Two cubic unit-cell sizes of dimensions 16 and 25 Å were used for complexes with Cp rings and C_{60} ligands, respectively, to maintain a similar vacuum region. As a benchmark, we calculated $CpMCp$ (the so-called metallocene molecule) from Sc to Ni. The M-C bond length of 2.05 Å for ferrocene is found to be nearly identical to the experimental value [18]. Also the calculated Sc cohesive energy of 4.08 eV is in reasonable agreement with the measured value of 3.9 eV [19].

To demonstrate the concept, we first consider the binding between a Cp ring and a single TM atom to form a CpM complex for the 3d series of metals, where $M = Sc$ to Ni.

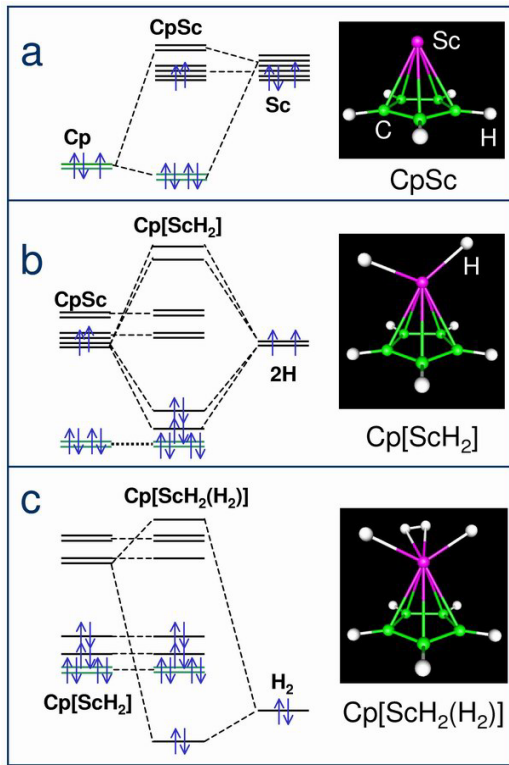


FIG. 1 (color online). Schematic energy diagram and structure model for hybridization of (a) Cp ring with Sc forming CpSc, (b) CpSc with 2H forming Cp[ScH₂], and (c) Cp[ScH₂] with molecular H₂ forming Cp[ScH₂(H₂)]. In (a), only the last two high-lying π states are shown for Cp. In (c), the two upper states of Cp[ScH₂] are neglected. Arrows indicate level occupation.

The calculated binding energies for the CpM systems are $E_b = 3.76, 3.87, 3.47, 2.30, 2.69, 2.97, 3.27,$ and 3.02 , respectively, for Sc, Ti, V, Cr, Mn, Fe, Co, and Ni. Other than Sc, the CpM binding energies trend in the order observed for the cohesive energy of the 3d TMs, except for a local swap between Mn and Cr, between Co and Ni, and between Ti and V [19]. For Sc, the cohesive energy is relatively small, whereas the binding energy to the Cp ring of 3.76 eV is the second largest. When a Sc atom and Cp ring interact, one electron is transferred from Sc to complete the last π bond of the Cp ring [Fig. 1(a)]. While such a one-electron transfer is universal for all TMs, giving rise to aromaticity in the Cp ring and the stability of the complexes, the large E_b for Sc is due to the separation between the Cp π bonding orbital and the metal d orbital being the largest of all the TMs studied here.

Taking CpSc as an example, next we consider the binding between the CpM complex and hydrogen. In naked CpSc, Sc has only two remaining valence electrons after transferring one to the Cp ring [Fig. 1(a)]. In general, the first added H₂ may bind to Sc as either a dihydride or a dihydrogen ligand. Here, the dihydride is much more strongly bound (1.31 eV/2H) than the dihydrogen ligand (about 0.3 eV/H₂) due to the strong M-H σ bonds [Fig. 1(b)]. The resulting Cp[ScH₂] has four empty d

TABLE I. Calculated consecutive binding energies of H₂ molecules (in eV/H₂). In the case of buckyballs, twelve H₂ were added per calculation. A similar trend with the Cp ring case in the table suggests that the procedure is justified.

	1st H ₂	2nd H ₂	3rd H ₂	4th H ₂	5th H ₂
Cp[ScH ₂]	0.29	0.28	0.46	0.23	
C ₆₀ [ScH ₂] ₁₂	0.30	0.35	0.42	0.26	
C ₄₈ B ₁₂ [ScH] ₁₂	0.31	0.35	0.30	0.33	0.24

orbitals [see Fig. 1(c)] that can bind four additional dihydrogen ligands with a relatively constant binding energy of about 0.3 eV per H₂ (see Table I). The H-H bonds are elongated by 4%–5% relative to the isolated molecule. There is no sign that the H₂ ligands weaken the TM-Cp ring bonds. Instead, the bond lengths between the TM and the Cp are shortened as the TM is saturated by H₂.

Figure 2 shows the binding energy for consecutive adsorption of additional H₂ species to the CpM complexes for all 3d TM elements. For CpM complexes with lighter metal atoms, the first H₂ molecule prefers to dissociate to form two hydride species bound to the metal, whereas the subsequently adsorbed H₂ remain in the molecular dihydrogen form. The binding energy of the *dihydride* (i.e., the black open bars) decreases from left to right in Fig. 2. For the heavier Fe, Co, or Ni atoms, even the first H₂ is not dissociated. In general, the d level of the metal atoms decreases in energy with increasing atomic mass, giving rise to increased overlap with the low-lying σ state of the H₂ and a larger degree of hybridization. Indeed, the *dihydrogen* H₂ binding energies (the solid color bars) generally increase from left to right in Fig. 2. The maximum number of H atoms (N_{\max}) a TM atom can adsorb satisfies the 18-electron rule [20],

$$N_{\max} = 18 - n_v - 5 \quad (1)$$

where n_v is the number of valence electrons of the TM atom listed in Fig. 2, and 5 is the number of electrons

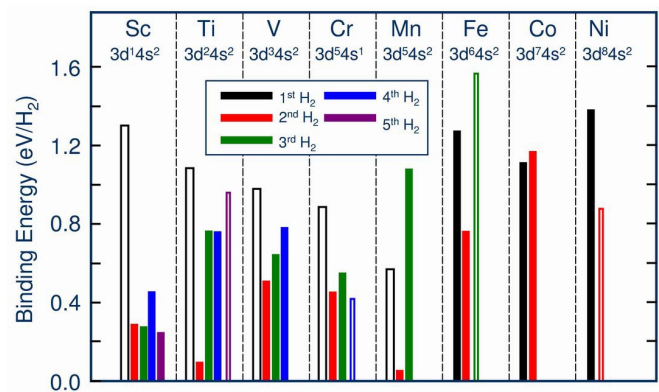


FIG. 2 (color online). Calculated consecutive binding energies per H₂ on CpM complexes where M is the 3d series, Sc to Ni. Open, solid, and half-width open bars indicate dihydride, dihydrogen molecule, and monohydride, respectively.

contributed by the Cp ring. Whenever the valence of the TM atom is not an odd number, one more H will be added as a *monohydride*, often with significant binding energy (half-width open bars in Fig. 2).

The CpM complexes can be considered as basic building blocks for larger organometallic molecules. For example, with the removal of 5 H from each Cp ring, we can envision 12 CpM units symmetrically arranged in a fullerene to form a 12-TM-coated $C_{60}M_{12}$. The distance between adjacent TM atoms is 6 Å, allowing enough space to accommodate H atoms and H_2 molecules. The binding between the TM and pentagonal rings of the C_{60} is, however, weaker than in isolated CpM molecules (e.g., 1.85 eV per Sc in $C_{60}Sc_{12}$ versus 3.76 eV per Sc in CpSc). This is because the aromaticity centered in the six-membered rings of C_{60} renders the molecule chemically more inert. When TM atoms coat the pentagons of the C_{60} , the molecule expands. Interestingly, the bonds of the pentagons expand by only 0.08%, whereas the hexagons connecting the pentagons expand by more than 3.3%. The net effect is electron localization and an aromaticity centered around the TM-coated pentagonal rings. Like the CpM species, $C_{60}M_{12}$ can be further stabilized by binding atomic H to form hydrides. For example, the Sc binding energy in $C_{60}[ScH_2]_{12}$ is 2.8 eV/Sc, which is 0.95 eV higher per Sc than without H. In further similarity to the isolated Cp[ScH₂], the $C_{60}[ScH_2]_{12}$ can bind four additional molecular H_2 per Sc to form $C_{60}[ScH_2(H_2)_4]_{12}$ [Fig. 3(a)]. The four dihydrogen ligands are reversibly available at RT, corresponding to a storage density of 7.0 wt%.

One can further reduce the weight of the fullerene and enhance the stability of the complex by substitutionally doping with boron. Boron-doped buckyballs have been experimentally observed [21] and, according to Ref. [22], one can substitute up to 12 boron atoms in C_{60} to form $C_{48}B_{12}$. The B dopants pull more charge from the TM to the buckyball and enhance the TM binding energy. For Sc-coated $C_{48}B_{12}Sc_{12}$, the binding energy is increased by 0.84 to 2.7 eV/Sc. This charge transfer leaves each Sc in the hydrogen-bare $C_{48}B_{12}Sc_{12}$ with only one valence electron. Hence, each Sc in $C_{48}B_{12}Sc_{12}$ can bind only a single monohydride to form $C_{48}B_{12}[ScH]_{12}$. The binding energy is further increased to 3.6 eV/Sc. Importantly, in addition to $C_{48}B_{12}[ScH]_{12}$ being more stable, the B-doped variant permits the binding of one additional molecular H_2 per Sc, giving rise to the formation of $C_{48}B_{12}[ScH(H_2)_5]_{12}$ [Fig. 3(b)]. In this case, the amount of H_2 retrievable at RT is 8.77 wt%. The binding energies of the five H_2 ligands remain similar to those for isolated Cp[ScH₂] species in Table I.

Next, we consider the process of H_2 storage and release. The energy per metal atom relative to its bulk is defined as

$$F(\text{per metal}) = (E_{\text{tot}} - \varepsilon - n_H \mu_H) / n_M - \varepsilon_M, \quad (2)$$

where E_{tot} is the total energy of a molecule, n_M and n_H are the number of metal and H atoms, respectively, ε is the

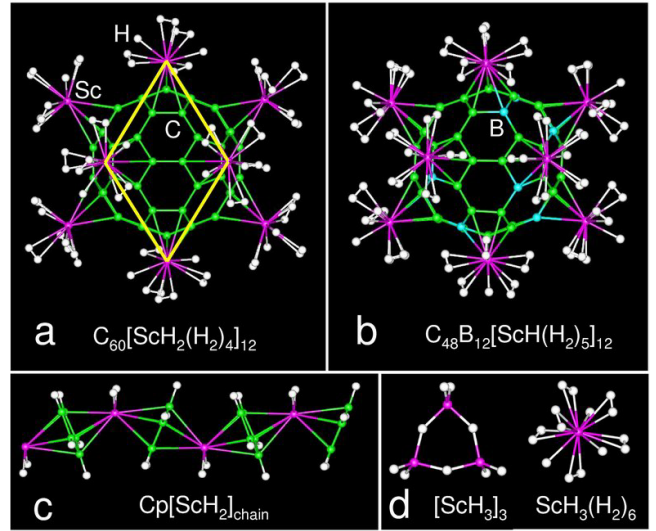


FIG. 3 (color online). Optimized atomic structures of (a) $C_{60}[ScH_2(H_2)_4]_{12}$, (b) $C_{48}B_{12}[ScH(H_2)_5]_{12}$, (c) Cp[ScH₂]_{chain}, and (d) [ScH₃]₃ (left) and ScH₃(H₂)₆ (right). For clarity, only part of the buckyballs is shown. A close-packed vdW solid formed from $C_{48}B_{12}[ScH(H_2)_5]_{12}$ would have a volumetric storage density of 43 kg H_2 /m³ even without consideration of the possibility of interlocking using the large open spaces indicated by the rhombus in (a).

energy of Cp, C_{60} , etc., and ε_M is the energy per metal atom in its bulk. The chemical potential of H, μ_H , is determined by [23]

$$\mu_H(T, p) = \mu_H(T, p^0) + \frac{1}{2} kT \ln\left(\frac{p}{p^0}\right), \quad (3)$$

where pressure $p^0 = 1$ atm, $T = 298.15$ K, and $\mu_H(T, p^0)$ was taken from Ref. [23].

Figure 4 suggests that the H-rich phases become more stable as the H_2 pressure increases. For example, Cp[ScH₂] spontaneously adsorbs molecular H_2 to form Cp[ScH₂(H₂)₄] at all pressures greater than ~ 1 atm. Unfortunately, due to the polarity of the Cp[ScH₂] unit, one-dimensional chains [depicted in Fig. 3(c)] are more stable than isolated Cp[ScH₂] by 1.37 eV/Sc. As a result, isolated Cp[ScH₂] species may polymerize and lose their ability to store hydrogen reversibly. The $C_{60}[ScH_2]_{12}$ and $C_{48}B_{12}[ScH]_{12}$ organometallic buckyballs (OBBs) show the same tendency to spontaneously adsorb dihydrogen at mild pressures, but with a higher H_2 content. As with the isolated Cp[ScH₂] species, the stored H_2 will be released when the pressure drops back below the crossover pressure, 0.53 atm for Cp[ScH₂(H₂)₄] and 1.40 atm for $C_{48}B_{12}[ScH(H_2)_5]_{12}$. In sharp contrast to isolated Cp[ScH₂], however, the Cp[ScH₂] units locked in the OBBs and are not free to polymerize. The local dipoles of the Cp[ScH₂] units are spherically oriented, leaving a net positive charge on the exterior. Thus, Coulomb forces will cause the molecules to repel one another, prohibit polymerization, and ensure reversibility. Thus, the OBBs

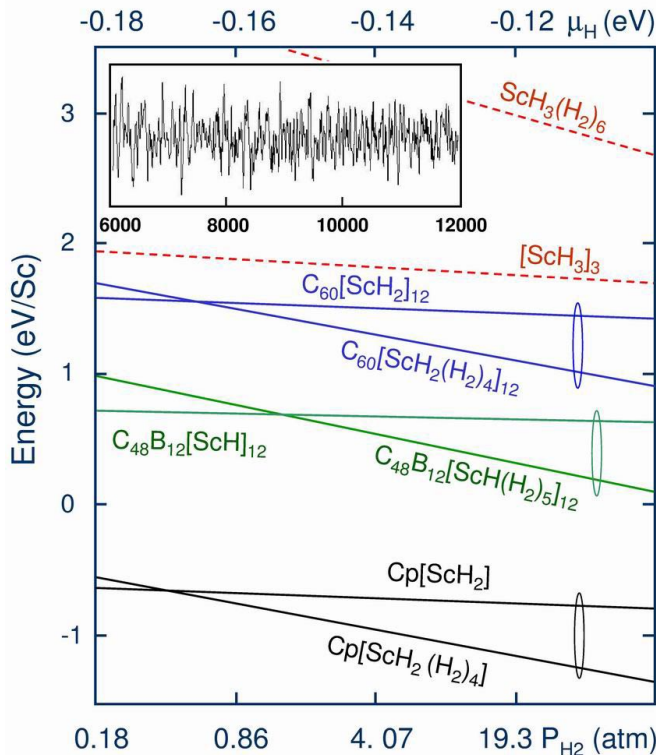


FIG. 4 (color online). Energy per Sc defined by Eq. (2) versus H_2 pressure (lower axis) and H chemical potential (upper axis) for the various organometallic molecules. Inset shows molecular dynamic simulation of $C_{48}B_{12}[ScH]_{12}$ at $T = 1000$ K. Horizontal axis is the time step.

should offer a better way to organize and stabilize the CpM species in space.

Another important issue is the stability of the OBBs disintegration into various small Sc-hydrogen clusters plus C_{60} or $C_{48}B_{12}$ fullerene. First-principles calculations show that a $[ScH_3]_3$ trimer [see Fig. 3(d), left] and a $ScH_3(H_2)_6$ cluster [Fig. 3(d), right] are among the lowest energy H-poor and H-rich Sc hydride clusters, respectively, but these species are less stable than the OBBs (Fig. 4). The energies of Sc_2 and Sc_4 are 3.5 and 2.5 eV/Sc, respectively, so the dissociation of OBBs via Sc cluster formation is also unlikely. Molecular dynamic (MD) simulations provide further evidence that the OBBs are stable. We studied $C_{48}B_{12}[ScH]_{12}$ using 0.4 fs time steps. First, we preheated the system to 1000 K using a linear scaling scheme for 6000 steps. Then, we continue the MD at 1000 K for another 6000 steps using the Nose algorithm. Figure 4 (inset) shows the simulated energy fluctuation, which is consistent with the observation that our OBB structure is intact throughout the simulation. Hence, we expect that the proposed storage materials are sufficiently stable at their intended operation temperatures about 300 K.

In conclusion, we have developed a rational approach to designing hydrogen storage adsorbents with very high capacity that should operate within a relatively small pres-

sure range near ambient at RT. Hydrogen storage densities approaching 9 wt % are possible when the $C_{48}B_{12}[ScH]_{12}$ OBB is fully charged. On the basis of Dewar coordination to bind transition metals to carbon rings and a Kubas interaction to bind dihydrogen species, we believe a new class of nanoscale organometallic materials even beyond the buckyballs could be synthesized that may charge and discharge hydrogen reversibly without degradation of the host.

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