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Hydrogen storage and the 18-electron rule

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We show that the 18-electron rule can be used to design new organometallic systems that can store hydrogen with large gravimetric density. In particular, Ti containing organic molecules such as C_2H_6, C_3H_5, and C_4H_8 can store up to 9 wt% hydrogen, which meets the Department of Energy target for the year 2015. More importantly, hydrogen in these materials is stored in molecular form with an average binding energy of about 0.55 eV/H_2 molecule, which is ideal for fast kinetics. Using molecular orbitals we have analyzed the maximum number of H_2 molecules that can be adsorbed as well as the nature of their bonding and orientation. The charge transfer from the H_2 bonding orbital to the empty d_{x^2} and d_{x^2−y^2} orbitals of Ti has been found to be singularly responsible for the observed binding of the hydrogen molecule. It is argued that early transition metals are better suited for optimal adsorption/desorption of hydrogen. © 2006 American Institute of Physics. [DOI: 10.1063/1.2202320]
we have carried out a systematic study of the hydrogen uptake by Ti deposited on three different molecular templates, namely, C₂H₄, C₅H₅, and C₈H₈. Since these molecules have varying number of π-electron deficiencies, the metal atom deposited on these different templates is expected to have different hydrogen uptake capabilities. In addition, being π-electron deficient these systems will bind strongly to the metal atom. On the other hand, benzene being aromatic (4n + 2π electrons) does not bind strongly to Ti (the experimental binding energy is 0.96 eV) and the system may not be stable under H cycling. So, we have not included benzene in the current study. However, Yildirim et al.¹⁸ found that Ti deposited on the six-membered ring of C₆₀ will take only four hydrogen molecules. This is in accordance with the 18-electron rule, if one considers the six-membered ring as a six-electron system.

Thus, our work here not only verifies if the maximum hydrogen uptake by a transition metal deposited on different substrates is governed by the 18-electron rule, but is also expected to act as a guide in the selection of appropriate extended multidecker organometallic systems as potential hydrogen storage materials. Results obtained through self-consistent calculations based on the density functional theory (DFT) show that one can bind as much as 9 wt % hydrogen in these Ti based complexes. More importantly, the maximum hydrogen adsorption can indeed be predicted by using the 18-electron rule.¹⁶

The rest of the paper is organized as follows: The computational method employed in the work is presented in Sec. II, while the results are presented and discussed in Sec. III. Our conclusions along with the summary of the results are given in Sec. IV.

II. COMPUTATIONAL PROCEDURE

All the calculations were performed using the generalized gradient approximation (GGA) within the framework of the DFT. The gradient-corrected exchange and correlation functionals due to Perdew-Wang¹⁹ (PW91) were employed here. Double numeric basis sets (DNP), supplemented with polarization functions, were used for all the atoms. The computations were carried out using the DMO13 software.²⁰ In the self-consistent-field (SCF) calculations, the density and energy tolerances were set to 10⁻⁶ eV/bohr³ and 10⁻⁹ hartree, respectively. In the geometry optimization, all the structural parameters were fully optimized without any symmetry constraints, with an energy convergence of 10⁻⁵ hartree and a maximum gradient of 10⁻⁴ hartree/bohr. We have also permitted the breaking of the H–H bond. In order to confirm the accuracy of our DMO13 results, we have repeated these calculations using the GAUSSIAN 03 code.²¹

The PW91/PW91 functional form, along with the SDD basis set for Ti and the 6-31G** basis for C and H, as implemented in the GAUSSIAN 03 code, are used. In the GAUSSIAN 03 optimization, the convergence criteria for gradient and energy are set to 10⁻⁴ hartree/Å and 10⁻⁹ hartree, respectively. Unless otherwise stated, all the geometries and energetics discussed in the subsequent sections are based on DMO13 calculations.

III. RESULTS AND DISCUSSION

A. Hydrogen adsorption on TiC₅H₅

We begin our discussion with the optimized geometries and energetics of TiC₅H₅(H₂)n as a function of n. The equilibrium geometries of the TiC₅H₅(H₂)n (n=1–4) complexes are shown in Fig. 1. The binding energy of the Ti atom to C₅H₅ was found to be 3.98 eV with the Ti atom lying 2.35 Å from the carbon atoms. The first H₂ molecule (n=1) was found to dissociate on the TiC₅H₅ complex and bind atomically to Ti, with the distance between the two H atoms being 3.09 Å [Fig. 1(a)]. Successive H₂ molecules, however, bind molecularly. The second H₂ molecule adsorbs onto the on-top site, at a distance of 1.91 Å from the Ti atom [Fig. 1(b)].

FIG. 1. (Color online) Optimized geometries of TiC₅H₅(H₂)n (n=1–4) along with important bond lengths (Å). The energy difference (ΔE) between (b) and (b′) is 0.12 eV, and between (c) and (c′) is 0.02 eV with (b) and (c) being lower in energy than (b′) and (c′), respectively.
The H–H bond length of the second H₂ molecule is 0.83 Å, which is larger than the bond length of the free H₂ molecule, namely, 0.75 Å. Another configuration, in which the second H₂ is molecularly bound to the Ti, but not occupying the on-top site, is found to be 0.12 eV higher in energy [Fig. 2(b')]. The addition of a third H₂ resulted in two energetically degenerate (∆E=0.02 eV) configurations [Figs. 1(c) and 1(c')]. At n=4, all the H₂ molecules are molecularly bound, with their orientation being parallel to the C₅H₅ molecule [Fig. 1(d)]. Here the H–H distances are 0.84 Å and the H–Ti distances are 1.90 Å. In spite of having enough space available for another H₂ molecule to bind, attempts to attach the fifth H₂ failed. Thus, the maximum number of H₂ molecules that could be bound to the TiC₅H₅ complex is 4, which corresponds to a hydrogen wt % of 6.61. The energies gained in adding successive H₂ molecules, ∆Eₙ = E[TiC₅H₅(H₂)ₙ]−E[TiC₅H₅(H₂)ₙ₋₁]−E(H₂), are given in Table I. The average binding energy per H₂ molecule, ∆E avg = ∑∆Eₙ/n, in this system is 0.72 eV. These energies are in the ideal range for a material to possess the desired thermodynamic and kinetic properties.

Recently Zhao et al.¹⁵ have calculated these energies using the Vienna ab initio simulation package (VASP). Here the cluster is surrounded by a vacuum space and the calculations are performed using the plane wave basis and the supercell band structure technique. Their calculated ∆Eₙ values are 1.09, 0.101, 0.768, and 0.761 eV for n=1, 2, 3, and 4, respectively. While our results in Fig. 1 are in agreement with theirs in the sense that the first H₂ molecule binds dissociatively, and the rest bind molecularly, there are significant quantitative differences for n=2, 3, and 4: The second H₂ molecule in the study of Zhao et al. binds weakly, while the remaining two bind strongly. Our calculated ∆Eₙ values in Table I are 1.36, 0.51, 0.45, and 0.56 eV for n=1, 2, 3, and 4, respectively. In our study we see no qualitative difference in the binding energies of hydrogen molecules beyond n=1. It is difficult for us to understand the physical reason that will allow the second H₂ molecule to bind weakly, while the binding of the third and fourth H₂ molecules is almost a factor of 8 too strong as observed by Zhao et al.¹⁵ To ensure that our results are not influenced by the choice of the numerical basis sets in the DMOL3 code, we repeated the calculations using the GAUSSIAN 03 program suite. The corresponding GAUSSIAN results are compared with the DMOL3 results in Table I. Note that these results agree rather well.

**TABLE I. Energy gain ∆Eₙ (in eV) due to the successive addition of H₂ molecules to Ti(C₅H₅)ₙ complexes.**

<table>
<thead>
<tr>
<th>System</th>
<th>n</th>
<th>DMOL</th>
<th>GAUSSIAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC₅H₅(H₂)₁ₘ</td>
<td>1</td>
<td>1.36</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.51</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.45</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.56</td>
<td>0.56</td>
</tr>
<tr>
<td>TiC₅H₅(H₂)₂ₘ</td>
<td>1</td>
<td>1.03</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.26</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.47</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.75</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.22</td>
<td>0.35</td>
</tr>
<tr>
<td>TiC₅H₅(H₂)₃ₘ</td>
<td>1</td>
<td>1.07</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.28</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.36</td>
<td>0.20</td>
</tr>
</tbody>
</table>

¹⁵PW91/DNP.

B. Hydrogen adsorption on TiC₄H₄

We now discuss the various optimized geometries and energetics of TiC₄H₄(H₂)n, where n = 1–5. The optimized geometries of TiC₄H₄(H₂)n (n = 0–5) corresponding to the ground state and low lying isomers are given in Fig. 2. Unlike the case of TiC₅H₅, where the ground state corresponds to the Ti atom occupying the on-top site, the ground state of TiC₄H₄ in Fig. 2(a) is an inserted structure. Here the Ti atom inserts into the four-membered ring [Fig. 2(a)]. The low lying isomer with the Ti atom occupying the on-top site [Fig. 2(a')] is found to be 0.35 eV higher in energy than the configuration in Fig. 2(a). The binding energy of the Ti atom to C₄H₄ in the ground state configuration is calculated to be 4.74 eV. This is comparable to the cohesive energy of bulk Ti, namely, 4.85 eV, and significantly larger than the binding energy of Ti to C₆₀, namely, 2.35 eV. Thus, the stability of the TiC₄H₄ complex is assured. It is to be noted here that the Ti-capped isomer [Fig. 2(a')] corresponds to a local minima and is stable against dissociation into Ti and C₄H₄ (∆E = 4.39 eV). We show in the later part of this paper that the relative stability of the Ti-inserted structure over the Ti-capped structure continues to decrease with increasing addition of H₂ molecules.

The first H₂ (n = 1) molecule was found to dissociate and bind atomically to the Ti in both Ti-inserted and Ti-capped structures. The Ti-inserted structure [Fig. 2(b)] is again more stable than the Ti-capped isomer [Fig. 2(b')] by 0.29 eV. The binding energy of the dihydride to the Ti is calculated to be 1.03 eV. The Ti–H and H–H distances for the Ti-inserted (Ti-capped) configurations are 1.72 (1.73) and 2.84 (2.80) Å, respectively. In the Ti(C₄H₄)(H₂)₂ complex, two different structural configurations are found to be energetically nearly degenerate [Figs. 2(c) and 2(c')]. The Ti-inserted structure, with both the H₂ molecules bound to Ti in molecular fashion, is found to be the lowest energy structure [Fig. 2(c)]. In this configuration, the H–H bond length for both the H₂ molecules increased to 0.92 Å, while the Ti–H distance increased to 1.82 Å. The low lying Ti-capped structural isomer [Fig. 2(c')], with one H₂ bound atomically and the other molecularly, is only 0.07 eV higher in energy than the lowest energy structure [Fig. 2(c)]. In this Ti-capped isomer, though the second H₂ retains its molecular character, its bond length increased to 0.82 Å. It is noteworthy here that the energy difference between the Ti-inserted and Ti-capped structures decreases from 0.35 to 0.07 eV, as the number of H₂ molecules (n) increases from 0 to 2.

When the third H₂ molecule is added to this system, the first H₂ molecule, which dissociated in the beginning, now assumes a molecular form. In addition, all the three H₂ molecules are now almost parallel to the C₄H₄ [see Fig. 2(d)]. The configuration in which one H₂ is atomically bound and the remaining two H₂ are molecularly bound [Fig. 2(d')] is energetically degenerate (∆E = 0.05 eV) with the ground state geometry. It is interesting to note here that the Ti-inserted structure is 0.30 eV higher in energy than the lowest energy Ti-capped structure. Thus, in order to maximize the Ti–H₂ bonding, the Ti atom prefers to occupy the on-top site of C₄H₄. Addition of the fourth hydrogen molecule brings significant changes to the Ti-capped structure [Fig. 2(e)]. First, all the four hydrogen molecules bind molecularly with Ti. Second, there is an orientation change. The four H₂ molecules form a planar ring with Ti as the central atom. Repeated attempts to find a stationary point with different orientations of hydrogen molecules all collapsed to one isomer where all the hydrogen molecules remain planar. Here, the H–H bond lengths are elongated to 0.84 Å, which are larger than the bond length of a free H₂ molecule. The fifth hydrogen molecule directly occupies the on-top site over the Ti atom, with its bond axis parallel to the plane of the C₄H₄ molecule [Fig. 2(f)]. The Ti–H distance for the fifth H₂ is 2.17 Å, while the H–H bond length marginally increased to 0.77 Å. This indicates that the fifth H₂ is weakly bound to the TiC₄H₄ system. The molecular orbital (MO) analysis of this configuration, discussed in the later part of this paper, also clearly demonstrates the weak interaction between the fifth H₂ and Ti. All attempts to bind the sixth H₂ molecule failed and the maximum number of hydrogen atoms that can be bound to TiC₄H₄(H₂)n is 5. This corresponds to 9.09 wt% hydrogen, which is the 2015 target of the Department of Energy. The energies gained, ∆Eₙ, in adding successive H₂ molecules to TiC₄H₄(H₂)n, are shown in Table I. The average binding energy per H₂ molecule, ∆E₂ₙ, in this system is 0.55 eV. The above energies are in the ideal range for a material to operate with favorable thermodynamics and kinetics.

The significant binding energies of the H₂ molecules to the above Ti-organic complexes and the abrupt vanishing of the energy gain for n = 6 in TiC₄H₄(H₂)₆ and for n = 5 in TiC₅H₅(H₂)₅ are consequences of the 18-electron rule. Since Ti, C₄H₄, and H₂ contribute respectively four, four, and two electrons to the valence pool of the TiC₅H₅(H₂)₅ complex, the total number of electrons for n = 5 is 4 + 4 + 10 = 18. Thus at most five hydrogen molecules can be attached to TiC₅H₅. Similarly the total number of electrons in TiC₄H₄(H₂)₄ is 4 + 5 + 8 = 17. Thus at most four H₂ molecules can be attached to TiC₄H₄. These predictions based on the 18-electron rule are in exact agreement with the results obtained here from DFT calculations.

In Table I we compare the energies ∆Eₙ calculated using the DMOL3 code with those obtained from the GAUSSIAN 03 code. The small differences can be attributed to the numerical procedure and choice of basis sets and provide the level of confidence in the predicted energetics.

C. Hydrogen adsorption on TiC₆H₆

Based on the 18-electron rule one can predict that the maximum number of H₂ molecules that could be bound to the TiC₆H₆ complex should be 3, as this would correspond to the total number of electrons in TiC₆H₆(H₂)₃ to be 4 + 8 + 6 = 18. To verify if this is indeed the case, we carried out similar calculations for TiC₆H₆(H₂)₃. The equilibrium geometries of the TiC₆H₆(H₂)₃ complex are given in Fig. 3. The binding energy of the Ti atom and its distance from the C₆H₆ molecule are 4.41 eV and 1.40 Å, respectively. We found once again that the first H₂ molecule binds to TiC₆H₆ dissociatively with the H–H and H–Ti distances of 1.86 and
1.70 Å, respectively [Fig. 3(a)]. The first dissociated H₂ molecule took on the molecular form when the second H₂ molecule was bound to TiC₈H₈ [Fig. 3(b)]. The structural configuration in which one of the H₂ binds as a dihydride in Fig. 3(b) is 0.02 eV higher in energy than that when it binds as a molecule [Fig. 3(b)]. No more than three H₂ molecules could be bound to this complex and the geometry of the TiC₅H₅ complex is shown in Fig. 3(c). The H–H and H–Ti distances are again very similar to those in Figs. 1(d) and 2(f).

The energies gained, ΔEₐ, in adding successive H₂ molecules to TiC₅H₅ are given in Table I. The average binding energy per H₂ molecule, ΔE₂ₓ, in this system is 0.57 eV. The above energies are again in the ideal range for a material to operate with favorable thermodynamics and kinetics. These energies agree well with those obtained from the GAUSSIAN 03 code (see Table I). It is to be noted here that the binding energy of hydrogen in intermetallic hydrides is in the 1.0–1.5 eV range and it is well established that these hydrides satisfy the thermodynamic and kinetic requirements of ideal H storage materials. Therefore, the first hydrogen molecule in the present organometallic complexes though is bound more strongly than the subsequent hydrogen molecules; we have included it in calculating the hydrogen gravimetric density.

A closer examination of the geometries of TiC₄H₄(H₂)₅, TiC₅H₅(H₂)₄, and TiC₆H₆(H₂)₃ in Figs. 1(d), 2(f), and 3(c), respectively, shows that there are two sets of H₂ molecules: In TiC₆H₆(H₂)₃ the one on the top site has a bond length of 0.77 Å and is bound loosely (0.20 eV). The second set is the reaming four H₂ molecules which form a planar ring and have elongated H–H bonds (0.84 Å). However, both TiC₅H₅(H₂)₄ and TiC₆H₆(H₂)₃ have only one kind of H₂, where all the H–H bonds are around 0.84 Å. An insight into the nature of the Ti–H₂ bonding and the orientation and the bond length variations of H₂ molecules can be understood from the MO analysis. The MOs responsible for Ti–H₂ interactions in C₄H₄Ti(H₂)₅ are given in Fig. 4. Among the five d orbitals of Ti, only three orbitals have the right symmetry to interact with the π orbitals of C₄H₄ and C₅H₅. The remaining two (dₓz and dᵧz), which are parallel to the carbon framework, interact with both bonding (dₓz) and antibonding (dᵧz) MOs of four H₂ molecules [Figs. 4(a) and 4(b)]. While the first interaction results in the charge transfer from hydrogen to the metal and subsequent elongation of the H–H bond, the second interaction is responsible to keep the hydrogen molecules planar. However, Ti interacts differently with C₅H₅, owing to the extra two π electrons: the dₓz orbital is not available and only one orbital (dᵧz) is vacant to interact with the hydrogen molecules. Consequently, H–H bonds are elongated, but the hydrogen molecules can adopt a nonplanar configuration since they are free to rotate. The fifth hydrogen in TiC₆H₆(H₂)₅, due to the polarization of the relevant MO (dᵧz) more towards the C₅H₅ rather than to H₂ [see Fig. 4(c)], interacts with Ti rather weakly than the rest of the hydrogen molecules. The consequences of the orbital interactions were also reflected in the charge variations of the Ti. The effective charge of the metal atom, irrespective of the organic template, varies from positive to negative depending on the number of hydrogen atoms bound to it. In TiC₆H₆, complexes charge is transferred from the metal atom to the organic molecule owing to the π-electron deficiency of the C₆H₆. As hydrogen molecules are added to the organometallic complex, the charge transfer from H₂ to the metal atom dominates, making Ti increasingly negative.

The consequence of the 18-electron rule is twofold; it
not only limits the number of hydrogen atoms that a given substrate-metal combination can take, but also makes the system more stable as we approach the 18-electron limit. It is well known that the kinetic stability of a system is governed by the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap,23 the larger the gap, the more stable is the system. We have plotted the HOMO-LUMO gaps of the above hydrogen decorated metal-organic systems as a function of the number of hydrogen molecules in Fig. 5. We note that the energy gaps sharply rise after the addition of the second hydrogen molecule and remain relatively constant as subsequent hydrogen molecules are attached, and then increase again once the 18-electron rule is satisfied. These energy gaps are comparable to that of C_{60}^\text{\textsuperscript{-}}, which is known for its unusual stability. In particular, the HOMO-LUMO gap of the TiC_{4}H_{4}(H_{2})_{2} complex is the highest, namely, 3.53 eV, among the group and TiC_{4}H_{4} stores the largest wt % of hydrogen among the systems studied.

IV. SUMMARY AND CONCLUSIONS

In conclusion, we have shown that one can determine the maximum number of hydrogen atoms that can be stored in a metal-organic complex using the 18-electron rule. To maximize hydrogen storage, the transition metal atom should have nearly empty d shells and the organic frame should have fewer \pi electrons. The latter choice makes the bonding between the organic frame and the transition metal strong, while the former allows electrons from the bonding orbitals of the H_{2} molecules to hybridize with the empty d orbitals of the transition metal atom. Consequently, the H_{2} bonds weaken and get slightly elongated, but do not break. The resulting binding energies of the hydrogen molecules to the supported transition metal atom are intermediate between physisorption and chemisorption energies. In particular, we have shown that TiC_{4}H_{4} can store up to 9 wt % hydrogen, while the average binding energy of the H_{2} molecule is 0.55 eV. This not only meets the gravimetric density target set by the Department of Energy for the year 2015, but the binding energy is ideal for the system to operate under ambient thermodynamic conditions. The success of this simple rule for one metal-organic system can also be extended to multidecker systems with more than one metal atom and ligand. Furthermore, it provides a robust mechanism for searching for hydrogen storage materials with high gravimetric density and favorable thermodynamic and kinetic properties.

ACKNOWLEDGMENTS

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