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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_4H_4 , C_5H_5 , and C_8H_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_{xy} 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]

I. INTRODUCTION

The rising population and standard of living around the world have made it necessary to look for alternate energy sources. The continued reliance on fossil fuels to supply 80% of the world's energy need is unwise not only because these sources are limited but also because of the adverse effect they have on the environment.¹⁻⁴ Thus, there is an urgent need to look for alternate energy sources that are abundant, renewable, clean, safe, and economical. Hydrogen is considered to be an ideal energy resource if the problems associated with its production and storage can be overcome. For application of hydrogen in the transportation sector of the economy, the key problem is its storage.

Materials capable of storing hydrogen with high gravimetric and volumetric density, operating under ambient thermodynamic conditions, and exhibiting fast hydrogen sorption kinetics are essential for practical applications. The storage of hydrogen as a compressed gas or in the liquid form are not practical because of cost, safety, energy content, and low density, although its kinetics are fast. Storage of hydrogen in solid state materials also has problems as the materials that store hydrogen with fast kinetics have low gravimetric and volumetric density, while those that have high gravimetric and volumetric density exhibit poor thermodynamics and kinetics.⁵⁻¹¹ The key to finding materials that are ideal for hydrogen storage is not only to understand, from a fundamental point of view, the interaction between hydrogen and the host material but also the manner in which it can be altered.

Hydrogen is commonly known to interact with metal surfaces in one of two ways: It is either physisorbed molecularly or chemisorbed atomically due to charge transfer from the metal surface to the antibonding orbital of the H_2 molecule. The binding energy of hydrogen in physisorbed state is of the order of a few meV's, while that in the chemisorbed

state is of the order of a few eV's. In the former case, desorption of hydrogen occurs at very low temperatures and is not ideal for storage under ambient thermodynamic conditions. In the latter case, the binding can be strong and desorption would require high temperatures. An ideal form of binding would be in between physisorption and chemisorption. Here the H_2 molecular bond would not break, but would slightly get elongated due to charge polarization and/or orbital overlap. This form of bonding was explored more than a decade ago by one of the authors of this paper, where it was shown that a metal cation can bind to multiple hydrogen atoms in molecular form.^{12,13} Here the ability of the metal cation to transfer electrons to the antibonding state of the H_2 molecule is diminished, and hence, the H_2 molecules are bound by the charge polarization mechanism. The binding energies of the hydrogen molecules are usually small (~ 0.2 eV) and the maximum number of H_2 molecules that can be stored by a single metal cation only depends on the steric condition. A second form of bonding, where the H_2 bonds do not break but only elongate, is when H_2 molecules interact with a transition metal atom with less than half-filled d shells.¹⁴ Here the orbital overlap between the H_2 molecules and the unfilled d orbitals of the transition metal atoms leads to stronger binding (~ 0.5 eV) than that in the former case.

In the current work, we take advantage of both of these forms of bonding by choosing a suitable substrate on which a transition metal atom such as Ti, through charge transfer, can remain in a positively charged state and hence bind a large number of hydrogen atoms. In addition, Ti being an early transition metal atom has nearly empty d orbitals. Thus, the interaction of H_2 molecules with its unfilled d orbitals can lead to binding energies intermediate between physisorption and chemisorption energies.

It has been reported¹⁵ earlier that the maximum number of hydrogen atoms a transition metal- C_5H_5 complex is capable of absorbing can be determined by using the 18-electron rule.^{16,17} In order to study the generality of this rule,

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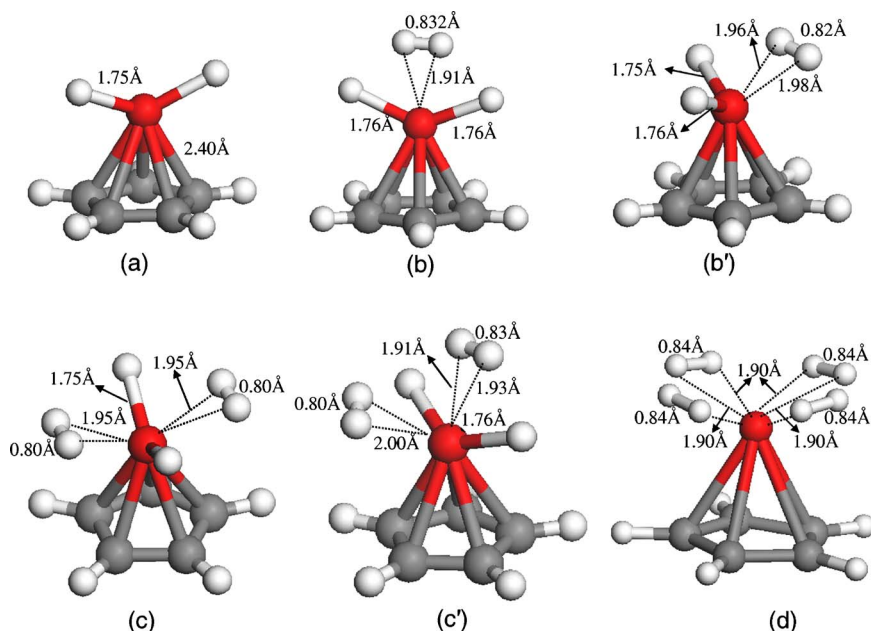


FIG. 1. (Color online) Optimized geometries of $\text{TiC}_5\text{H}_5(\text{H}_2)_n$ ($n=1-4$) along with important bond lengths (\AA). The energy difference (ΔE) between (b) and (b') is 0.12 eV, and between (c) and (c') is 0.02 eV with (b) and (c) being lower in energy than (b') and (c'), respectively.

we have carried out a systematic study of the hydrogen uptake by Ti deposited on three different molecular templates, namely, C_4H_4 , C_5H_5 , and C_8H_8 . 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 ($4n+2\pi$ 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 C_{60} 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 $10^{-6} e/\text{bohr}^3$ and 10^{-6} 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 allowed H_2 molecules to approach the Ti atom supported on the organic molecule from various directions and different orientations. 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 PW91PW91 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/ \AA 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 TiC_5H_5

We begin our discussion with the optimized geometries and energetics of $\text{TiC}_5\text{H}_5(\text{H}_2)_n$ as a function of n . The equilibrium geometries of the $\text{TiC}_5\text{H}_5(\text{H}_2)_n$ ($n=1-4$) complexes are shown in Fig. 1. The binding energy of the Ti atom to C_5H_5 was found to be 3.98 eV with the Ti atom lying 2.35 \AA from the carbon atoms. The first H_2 molecule ($n=1$) was found to dissociate on the TiC_5H_5 complex and bind atomically to Ti, with the distance between the two H atoms being 3.09 \AA [Fig. 1(a)]. Successive H_2 molecules, however, bind molecularly. The second H_2 molecule adsorbs onto the *on-top* site, at a distance of 1.91 \AA from the Ti atom [Fig. 1(b)].

B. Hydrogen adsorption on TiC_4H_4

We now discuss the various optimized geometries and energetics of $\text{TiC}_4\text{H}_4(\text{H}_2)_n$, where $n=1-5$. The optimized geometries of $\text{TiC}_4\text{H}_4(\text{H}_2)_n$ ($n=0-5$) corresponding to the ground state and low lying isomers are given in Fig. 2. Unlike the case of TiC_5H_5 , where the ground state corresponds to the Ti atom occupying the on-top site, the ground state of TiC_4H_4 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 C_4H_4 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 C_{60} , namely, 2.35 eV.²² Thus, the stability of the TiC_4H_4 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 C_4H_4 ($\Delta E = 4.39$ 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 H_2 molecules.

The first H_2 ($n=1$) 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 $\text{Ti}(\text{C}_4\text{H}_4)(\text{H}_2)_2$ 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 H_2 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 H_2 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 H_2 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 H_2 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 H_2 molecules (n) increases from 0 to 2.

When the third H_2 molecule is added to this system, the first H_2 molecule, which dissociated in the beginning, now assumes a molecular form. In addition, all the three H_2 molecules are now almost parallel to the C_4H_4 [see Fig. 2(d)]. The configuration in which one H_2 is atomically bound and the remaining two H_2 are molecularly bound [Fig. 2(d')] is energetically degenerate ($\Delta E=0.05$ 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– H_2 bonding, the Ti atom prefers to occupy the on-top site of C_4H_4 . 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 H_2 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 H_2 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 C_4H_4 molecule [Fig. 2(f)]. The Ti–H distance for the fifth H_2 is 2.17 Å, while the H–H bond length marginally increased to 0.77 Å. This indicates that the fifth H_2 is weakly bound to the TiC_4H_4 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 H_2 and Ti. All attempts to bind the sixth H_2 molecule failed and the maximum number of hydrogen atoms that can be bound to $\text{TiC}_4\text{H}_4(\text{H}_2)_n$ is 5. This corresponds to 9.09 wt % hydrogen, which is the 2015 target of the Department of Energy. The energies gained, ΔE_n , in adding successive H_2 molecules to $\text{TiC}_4\text{H}_4(\text{H}_2)_n$ are shown in Table I. The average binding energy per H_2 molecule, ΔE_{av} , 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 H_2 molecules to the above Ti-organic complexes and the abrupt vanishing of the energy gain for $n=6$ in $\text{TiC}_4\text{H}_4(\text{H}_2)_n$ and for $n=5$ in $\text{TiC}_5\text{H}_5(\text{H}_2)_n$ are consequences of the 18-electron rule. Since Ti, C_4H_4 , and H_2 contribute respectively four, four, and two electrons to the valence pool of the $\text{TiC}_4\text{H}_4(\text{H}_2)_n$ complex, the total number of electrons for $n=5$ is $4+4+10=18$. Thus at most five hydrogen molecules can be attached to TiC_4H_4 . Similarly the total number of electrons in $\text{TiC}_5\text{H}_5(\text{H}_2)_4$ is $4+5+8=17$. Thus at most four H_2 molecules can be attached to TiC_5H_5 . 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 ΔE_n 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 TiC_8H_8

Based on the 18-electron rule one can predict that the maximum number of H_2 molecules that could be bound to the TiC_8H_8 complex should be 3, as this would correspond to the total number of electrons in $\text{TiC}_8\text{H}_8(\text{H}_2)_3$ to be $4+8+6=18$. To verify if this is indeed the case, we carried out similar calculations for $\text{TiC}_8\text{H}_8(\text{H}_2)_n$. The equilibrium geometries of the $\text{TiC}_8\text{H}_8(\text{H}_2)_n$ complex are given in Fig. 3. The binding energy of the Ti atom and its distance from the C_8H_8 molecule are 4.41 eV and 1.40 Å, respectively. We found once again that the first H_2 molecule binds to TiC_8H_8 dissociatively with the H–H and H–Ti distances of 1.86 and

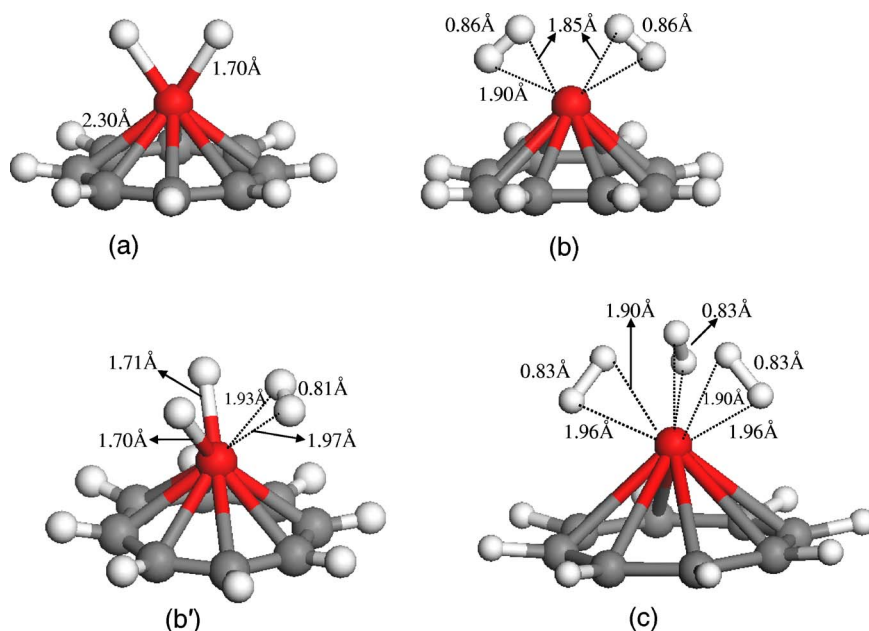


FIG. 3. (Color online) Optimized geometries of $\text{TiC}_8\text{H}_8(\text{H}_2)_n$ ($n=1-3$) along with important bond lengths (\AA). The energy difference (ΔE) between (b) and (b') is 0.02 eV with (b) being lower in energy than (b').

1.70 \AA , respectively [Fig. 3(a)]. The first dissociated H_2 molecule took on the molecular form when the second H_2 molecule was bound to TiC_8H_8 [Fig. 3(b)]. The structural configuration in which one of the H_2 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 H_2 molecules could be bound to this complex and the geometry of the $\text{TiC}_8\text{H}_8(\text{H}_2)_3$ 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, ΔE_n , in adding successive H_2 molecules to TiC_8H_8 are given in Table I. The average binding energy per H_2 molecule, ΔE_{av} , 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 $\text{TiC}_4\text{H}_4(\text{H}_2)_5$, $\text{TiC}_5\text{H}_5(\text{H}_2)_4$, and $\text{TiC}_8\text{H}_8(\text{H}_2)_3$ in Figs. 1(d), 2(f), and 3(c), respectively, shows that there are two sets of H_2 molecules: In $\text{TiC}_4\text{H}_4(\text{H}_2)_5$ the one on the top site has a bond length of 0.77 \AA and is bound loosely (0.20 eV). The second set is the remaining four H_2 molecules which form a planar ring and have elongated H–H bonds (0.84 \AA). However, both $\text{TiC}_5\text{H}_5(\text{H}_2)_4$ and $\text{TiC}_8\text{H}_8(\text{H}_2)_3$ have only one kind of H_2 , where all the H–H bonds are around 0.84 \AA . An insight into the nature of the Ti– H_2 bonding and the orientation and the bond length variations of H_2 molecules can be understood from the MO analysis. The MOs responsible for Ti– H_2 interactions in $\text{C}_4\text{H}_4\text{Ti}(\text{H}_2)_5$ 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 C_4H_4 and C_5H_5 . The remaining two (d_{xy} and $d_{x^2-y^2}$), which are parallel to the carbon framework, interact with both bonding (d_{xy}) and antibonding ($d_{x^2-y^2}$) MOs of four H_2 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 C_8H_8 , owing to the extra two π electrons: the $d_{x^2-y^2}$ orbital is not available and only one orbital (d_{xy}) 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 $\text{TiC}_4\text{H}_4(\text{H}_2)_5$, due to the polarization of the relevant MO (d_{xz}) more towards the C_4H_4 rather than to H_2 [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 TiC_nH_n complexes charge is transferred from the metal atom to the organic molecule owing to the π -electron deficiency of the C_nH_n . As hydrogen molecules are added to the organometallic complex, the charge transfer from H_2 to the metal atom dominates, making Ti increasingly negative.

The consequence of the 18-electron rule is twofold; it

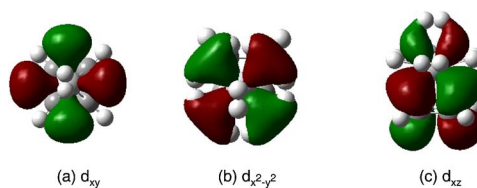


FIG. 4. (Color online) Three major molecular orbitals (MOs) responsible for H_2 and Ti interaction in $\text{TiC}_4\text{H}_4(\text{H}_2)_5$.

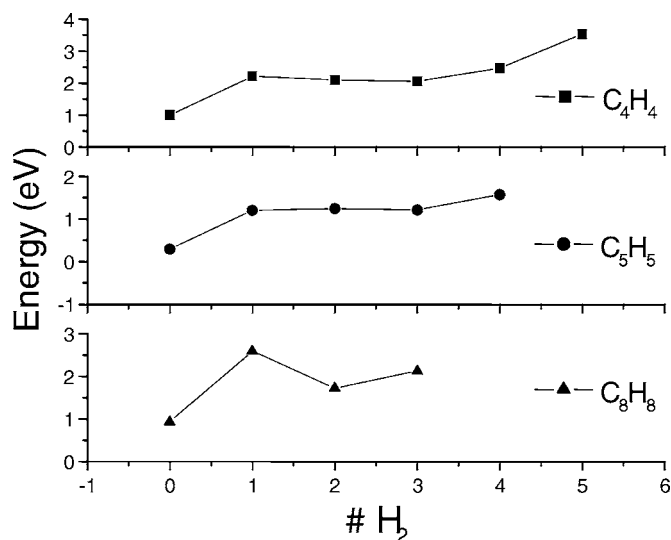


FIG. 5. The HOMO-LUMO gaps for TiC_4H_4 , TiC_5H_5 , and TiC_8H_8 complexes as H_2 molecules are added successively.

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} , which is known for its unusual stability. In particular, the HOMO-LUMO gap of the $\text{TiC}_4\text{H}_4(\text{H}_2)_5$ complex is the highest, namely, 3.53 eV, among the group and TiC_4H_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 π 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_4H_4 can store up to 9 wt % hydrogen, where 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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