



Stability and hydrogen storage properties of various metal-decorated benzene complexes

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ABSTRACT

Stability and hydrogen storage properties of various metal-decorated benzene complexes have been studied using a first-principles method. According to our results, most metals from the first to the third period of the periodic table can be strongly adsorbed on the benzene surfaces, except Be, Na, Mg, K, and Zn. Among the metals we studied Ca is the most promising adsorbate for hydrogen storage. Two Ca atoms prefer to be isolated on the benzene surfaces, one on each side, and each adsorbed Ca can adsorb up to four H₂ molecules, thus yielding a H₂ uptake of 9.2 wt%. The calculated binding energy is 0.45 eV/H₂, suitable for reversible hydrogen storage. The adsorbed Li and Sc can also adsorb a large number of H₂ molecules with suitable H₂ binding energies, but they are likely to dimerize on the benzene surfaces. Other metal adsorbates we studied are not suitable for hydrogen storage, because they will suffer from the large H₂ binding energy or the low hydrogen storage capacity.

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1. Introduction

The success of hydrogen economy critically depends on the discovery of hydrogen storage materials meeting the requirement of high gravimetric and volumetric density, fast kinetics, and favorable thermodynamics [1–4]. In recent years, light metal-decorated carbon-based materials [5,6] such as C₆₀ fullerene [7–12], graphene [13–15], small organic molecules [16–18], and metal-organic frameworks (MOFs) [19–24] have attracted much attention for potential applications in hydrogen storage. In these systems, the metal donates electrons to the host materials and occurs in a cationic form, and then it can adsorb a large number of H₂ molecules. Studies on these systems do provide promising results, and at the same time, they encounter various problems. For example, though light metal-decorated C₆₀ systems can adsorb a large number of H₂ molecules [7,9,12], they may suffer from the small hydrogen binding energy [7] or the strong clustering ability of the metal atoms [10,11].

We also find that when considering the hydrogen storage properties of materials such as C₆₀, MOFs and so on, the six-carbon ring often plays important roles. Metals are usually adsorbed above the six-carbon ring and then adsorb H₂ molecules, such as alkali

metals in C₆₀ [25], Ti atoms in C₆₀ [10], Li atoms in MOF-5 [19] and so on. From this point, we think that it will be interesting to investigate the hydrogen storage capability and capacity of one simple material containing the six-carbon ring, and to do this benzene is the simplest selection. Besides, we note that 3d-transition metal-benzene complexes have been successfully synthesized experimentally [26]. This makes it practically interesting to study the hydrogen storage properties of metal-decorated benzene complexes.

In this paper, we present theoretical studies on the stability and hydrogen storage properties of various metal-decorated benzene complexes. All the eighteen metals from the first to the third period of the periodic table are studied as adsorbates. We find that most metals are strongly adsorbed on the benzene surfaces, except Be, Na, Mg, K, and Zn. However, the adsorbed Al, Ga and transition metals from Ti to Cu are not suitable for hydrogen storage, because they cannot meet the H₂ binding energy or the H₂ gravimetric density requirements. The adsorbed Li and Sc can adsorb a large number of H₂ molecules per metal with a suitable H₂ binding energy, but they will dimerize on the benzene surfaces. Two Ca atoms prefer to be isolated on the benzene surfaces, one on each side, and each adsorbed Ca can then adsorb four H₂ molecules. The binding energy is always within a few tenths of an eV per H₂ molecule, suitable for reversible hydrogen storage. Further molecular dynamics (MD) simulations indicate that the Ca-decorated

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benzene complexes are stable at 300 °C. Based on these discussions, we suggest that Ca-decorated benzene complexes are the most promising media for hydrogen storage in this paper.

2. Model and method

The whole work is based on first-principles spin-polarized calculations. We use the projector augmented wave (PAW) [27] method as implemented in the VASP codes [28], where the electronic exchange and correlation are approximated using the local density approximation (LDA) with Ceperly and Alder (CA) functional [29]. Single molecular complexes are treated in a $20 \times 20 \times 20 \text{ \AA}$ supercell with Γ k-point and an energy cutoff of 400 eV. By increasing the supercell size and the energy cutoff we find that the energy difference is less than 0.02 eV, indicating good convergence. During relaxations, all the ions are allowed to relax until the force acting on each ion is less than 0.01 eV \AA^{-1} . The calculated C–C distance in the benzene ring is 1.39 \AA , in good agreement with experimental reports [30]. Furthermore, we compare the LDA results with those of the generalized gradient approximation (GGA) with Perdew–Wang 91 (PW91) [31] and Perdew–Burke–Ernzerhof (PBE) [32] functionals. We find that LDA binding energies are slightly larger than those of GGA results. For example, in Ca-decorated benzene case the H_2 binding energy calculated within LDA is about 0.2 eV larger than that calculated within GGA. However, GGA calculations using PW91 and PBE give almost the same binding energies.

We examine various possible configurations of $\text{C}_6\text{H}_6\text{M}_n$ complexes and their corresponding H_2 binding properties. Here, M stands for any one of the eighteen metals from the first to the third period of the periodic table. We only consider complexes containing one ($n = 1$) or two ($n = 2$) M atoms because more metal atoms may lower the hydrogen storage capacity and thus should be avoided in the syntheses. Metal binding energy is calculated as $E_b(\text{M}) = [nE(\text{M}) + E(\text{C}_6\text{H}_6) - E(\text{C}_6\text{H}_6\text{M}_n)]/n$, where $E(\text{M})$, $E(\text{C}_6\text{H}_6)$ and $E(\text{C}_6\text{H}_6\text{M}_n)$ are the energies of the metal atom, the benzene molecule, and the $\text{C}_6\text{H}_6\text{M}_n$ complex, respectively. The H_2 binding energy is calculated as $E_b(\text{H}_2) = [E(\text{C}_6\text{H}_6\text{M}_n) + mE(\text{H}_2) - E(\text{C}_6\text{H}_6\text{M}_n + m\text{H}_2)]/m$. In this formula, $E(\text{H}_2)$ and $E(\text{C}_6\text{H}_6\text{M}_n + m\text{H}_2)$ are the energies of the H_2 molecule and the $\text{C}_6\text{H}_6\text{M}_n + m\text{H}_2$ configuration, respectively, and m is the number of the adsorbed H_2 molecules.

3. Results and discussions

3.1. Hydrogen storage in $\text{C}_6\text{H}_6\text{M}$ complexes

We start from $n = 1$ case. To study the hydrogen storage properties of various $\text{C}_6\text{H}_6\text{M}$ complexes, several points should be noted. First, different metals may have different adsorption sites on the benzene surfaces, and some metals may not be adsorbed on the surfaces completely. Second, even if some metals can be adsorbed on the surfaces, it does not mean they can further adsorb H_2 molecules. Third, even if some metals can satisfy the first and the second requirements, the metal adsorption sites may be different before and after H_2 adsorption. To make these questions clear, we first place various metals to different sites of the benzene surfaces and then completely relax the structures. The initial sites include the H-site (above the center of the carbon ring), the A-site (above one carbon atom), the S-site (above the C–C single bond), and the D-site (above the C=C double bond). Through the relaxed structures as well as comparisons of metal binding energies at different adsorption sites, we can judge which metals can be adsorbed on the benzene surfaces and where they will prefer to be adsorbed. To the stable $\text{C}_6\text{H}_6\text{M}$ complexes, H_2 molecules are added one by one

around the metals until they begin to escape. Through this process we can obtain the maximum number of adsorbed H_2 molecules $N_{\text{max}}(\text{H}_2)$ on various complexes and the atomic geometries. And finally, we can calculate the average H_2 binding energy and the H_2 gravimetric density for every case. Metal binding properties on benzene as well as their H_2 binding properties for $n = 1$ case are listed in Table 1, where only the configurations that can stably adsorb H_2 molecules have been shown.

When a metal atom is moved toward benzene, the large electronegativity of benzene facilitates the transfer of electrons from the metal atom to benzene, resulting in an electrostatic interaction between them and leaving the metal atom in a cationic form. It should be noted that the metal-benzene interaction may be related not only to the cationic charge state but also to the metal atom size, thus making the interaction or the binding energy complicated. The main group metal atoms such as Li and Ca trap H_2 molecules mainly by an electrostatic polarization mechanism, while the transition metal atoms do that mainly by the Kubas interaction [33]. The H_2 molecules transfer their σ electrons to the unoccupied transition metal d-orbitals, and then the transition metal back-donates its occupied d electrons to hydrogen σ^* antibonding orbitals. Therefore, H_2 binding energy and the maximum number of adsorbed H_2 molecules on the adsorbate should also be related to the properties of the metal d-orbitals, such as the d-energy and so on. From Table 1 we can see that the binding energies of Na and K are always negative, while those of Mg and Zn are always less than 0.2 eV/M, no matter where they are adsorbed. The negative or small binding energies indicate that these metals cannot form complexes with benzene molecules stably, so they are not suitable for hydrogen storage. Group IIIA elements Al and Ga are likely to occupy the A-sites, while other metals are likely to be adsorbed on the H-sites. It is obvious that all the metals except Zn are positively charged when forming complexes with benzene molecules. Besides, charge on the adsorbed transition metals from Sc to Zn decreases from $+1.06e$ to $-0.01e$, which is in agreement with the increased electronegativity from Sc to Zn.

We find that though group IIIA metals Al and Ga have considerable metal binding energies on the A-sites, they are not able to adsorb any H_2 molecules. Besides, when trying to place H_2 molecules around the adsorbed Fe atom, they will either escape or be dissociated. Therefore, Fe is also not a suitable adsorbate for hydrogen storage. The adsorbed Li, Ca, Sc and Ti can adsorb four H_2

Table 1
Metal and H_2 binding properties in $n = 1$ ($\text{C}_6\text{H}_6\text{M}$) case.

Metal	M-site ^a	$E_b(\text{M})$ (eV)	M-charge ^b	$N_{\text{max}}(\text{H}_2)$	$E_b(\text{H}_2)$ (eV)	H_2 weight (wt%) ^c
Li	H	0.54	+0.77e	4	0.22	8.6
Be	H	0.74	+1.24e	–	–	–
Na	–	–0.02	–	–	–	–
Mg	H	0.10	+0.05e	–	–	–
Al	A	1.15	+0.80e	–	–	–
K	–	–0.10	–	–	–	–
Ca	H	0.47	+1.02e	4	0.56	6.4
Sc	H	2.28	+1.06e	4	0.69	6.1
Ti	H	2.94	+1.22e	4	1.05	6.0
V	H	2.78	+0.96e	3	1.21	4.4
Cr	H	1.12	+0.81e	3	1.46	4.4
Mn	H	1.11	+0.67e	3	1.08	4.3
Fe	H	3.01	+0.55e	–	–	–
Co	H	3.12	+0.41e	2	1.26	2.8
Ni	D	3.10	+0.31e	2	0.92	2.8
Cu	S	0.77	+0.27e	2	0.60	2.8
Zn	H	0.17	–0.01e	–	–	–
Ga	A	0.82	+0.02e	–	–	–

^a The most stable site of various metal atoms.

^b Bader charge on various metal atoms.

^c H_2 gravimetric density.

molecules per metal at most, forming $C_6H_6M + 4H_2$ configurations. In Li, Ca and Sc cases, the H_2 gravimetric densities decrease gradually (see Table 1), but they are always higher than the gravimetric density (6 wt%) of the U. S. DOE target by 2010 [34]; the H_2 binding energies increase gradually, but they are always within a few tenths of an eV, suitable for reversible hydrogen storage. This is not the case for Ti adsorbate, which can also adsorb four H_2 molecules per metal, but the binding energy is 1.01 eV/ H_2 , too large to be reversible. We note that the binding energies in Ti-decorated C_{60} , graphene, and CNT cases are 0.55 [11], 0.35 [35], and 0.56 [35] eV/ H_2 , respectively, all smaller than the value in this work. However, the value in an isolated Ti^+ ion case is 1.07 eV/ H_2 [36], very close to that in this work. This is in good agreement with bader analysis that the adsorbed Ti carries a positive charge of 1.22e (see Table 1). $C_6H_6Li + 4H_2$ and $C_6H_6Ca + 4H_2$ are geometrically similar, so we only show the structure of the later one in Fig. 1(a) as an example. We can see from the figure that after H_2 adsorption, the adsorbate still occupies the H-site. The calculated C–Ca distance is 2.15 Å, much smaller than sum of the atomic radii of C and Ca (3.14 Å), indicating the formation of C–Ca chemical bonds. Besides, four H_2 molecules distribute symmetrically around the Ca atom, and the calculated H–H distance in the adsorbed H_2 molecules is 0.83 Å. This is slightly larger than the H–H distance (0.75 Å) in an isolated H_2 molecule, indicating a physisorption in a molecular manner. The atomic geometry of $C_6H_6Ti + 4H_2$ is shown in Fig. 1(b), and that of $C_6H_6Sc + 4H_2$ is also similar. The H–H distance is about 0.85 Å in Sc case and about 0.95 Å in Ti case. In order to judge whether the adsorbed H_2 molecules have dissociated, we show the charge distributions of $C_6H_6Ti + 4H_2$ in Fig. 1(c). From the figure, obvious charge distributions can be seen between the adsorbed hydrogen atoms composed of the H_2 molecules, indicating the hydrogen storage is in a molecular manner.

The adsorbed V, Cr and Mn can adsorb three H_2 molecules per metal as listed in Table 1, forming $C_6H_6M + 3H_2$ configurations. The three cases have similar atomic geometries, so we only show that of $C_6H_6Mn + 3H_2$ in Fig. 2(a) as an example. From the figure we can see that the three adsorbed H_2 molecules distribute symmetrically around the adsorbate. The calculated H–H distances in the adsorbed H_2 molecules are in the range of 0.88–0.95 Å in the three cases. Analysis of the charge distributions indicates that obvious chemical bonds are also formed between the adsorbed hydrogen atoms. Therefore, they are still adsorbed in a molecular manner. However, from Table 1 we can see that the average H_2 binding energy is always larger than 1.0 eV/ H_2 . This is too large to be reversible for hydrogen storage. Thus, V, Cr and Mn are not promising adsorbates for hydrogen storage.

The adsorbed Co, Ni, and Cu can adsorb two H_2 molecules per metal, and their configurations are shown in Fig. 2(b)–(d), respectively. We find from the figures that Co is still adsorbed on the H-site, while Ni and Cu change their adsorption sites after the

adsorption of H_2 molecules. Ni goes to the S-site and Cu goes to the D-site without any energy barrier. Through going to a new adsorption site, the charge carried by the adsorbate atom increases. For example, the charge carried by Cu adsorbed on the H-site is only +0.02e, while it increases to +0.27e after going to the D-site. The increased charge polarizes the H_2 molecules and decreases the total energy of the system. The calculated binding energies are 1.26 eV/ H_2 , 0.92 eV/ H_2 and 0.60 eV/ H_2 for Co, Ni and Cu cases, respectively. However, the gravimetric density is only 2.8 wt% in the three cases, too low for applications.

3.2. Hydrogen storage in $C_6H_6M_2$ complexes

In this section, we investigate the hydrogen storage in $C_6H_6M_2$ complexes, where two metal atoms are adsorbed on the benzene surfaces, one on each side. Binding properties of various metals and their hydrogen storage properties are listed in Table 2. From the table we can see metals such as Be, Na, Mg, K and Zn still cannot be adsorbed on the benzene surfaces, just as they do in $n = 1$ case. Of course, they cannot be used as adsorbates for hydrogen storage in this paper. $C_6H_6Al_2$ assumes an A–A configuration, where two Al atoms occupy two A-sites on each side of the benzene surfaces. However, when trying to add H_2 molecules to the complex, they always escape. Similar things happen to $C_6H_6Ga_2$. Therefore, Al and Ga are not suitable adsorbates for hydrogen storage too. The adsorbed Li and Ca will occupy the H-sites to form H–H configurations, and each of them can adsorb four H_2 molecules. Thus, $C_6H_6Li_2$ and $C_6H_6Ca_2$ can adsorb up to eight H_2 molecules, respectively. We note that each adsorbed Ca atom in graphene case can also adsorb four H_2 molecules [14]. However, each adsorbed Li atom can adsorb five and three H_2 molecules in C_{60} [7] and MOF-5 [19] cases, respectively. Atomic geometries are similar for $C_6H_6Li_2$ and $C_6H_6Ca_2$, so only the later one is shown as an example in Fig. 3(a). From the figure we can see that H_2 molecules distribute symmetrically around the adsorbate atoms, just as they do in $n = 1$ case. The $C_6H_6Li_2 + 8H_2$ configuration yields an extremely high H_2 gravimetric density of 14.8 wt%, much higher than requirement (9 wt%) of the U. S. DOE target by 2015 [34]. More importantly, the binding energy is 0.29 eV/ H_2 , suitable for reversible hydrogen storage. This is larger than that in the Li-decorated C_{60} [7] and MOF-5 [19] cases, which is about 0.08 and 0.12 eV/ H_2 , respectively. We think the different Li binding energies may be related with the differences of the electronegativity of the six-carbon rings in the three materials. The H_2 density in $C_6H_6Ca_2 + 8H_2$ is 9.2 wt% and the binding energy is 0.45 eV/ H_2 , also higher than the 2015 target and suitable for reversible hydrogen storage. Therefore, Li and Ca are very promising adsorbates for hydrogen storage when benzene molecules are used as adsorbents.

Two transition metal atoms can also adsorbed on the benzene surfaces to form double-decorated complexes and then adsorb H_2

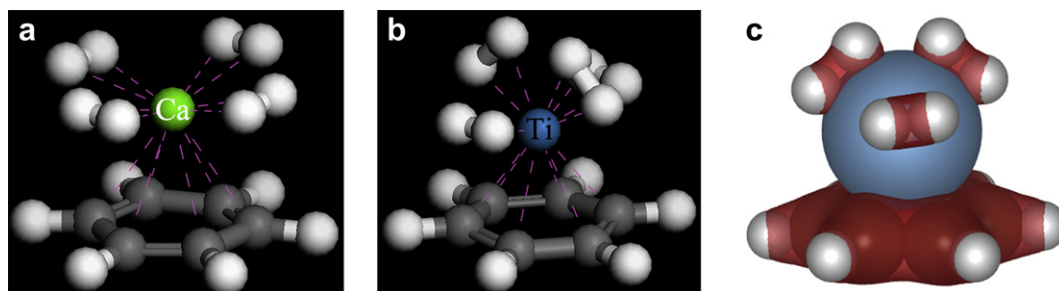


Fig. 1. Atomic geometries of (a) $C_6H_6Ca + 4H_2$, and (b) $C_6H_6Ti + 4H_2$ in a ball and stick style; (c) charge distributions of $C_6H_6Ti + 4H_2$ configuration in a space-filling style with an isosurface value of $0.08e/A^3$.

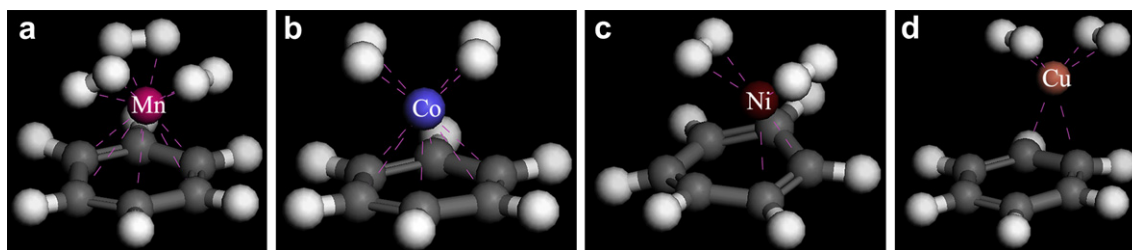


Fig. 2. Atomic geometries of (a) $C_6H_6Mn + 3H_2$, (b) $C_6H_6Co + 2H_2$, (c) $C_6H_6Ni + 4H_2$, and (d) $C_6H_6Cu + 2H_2$ configurations in a ball and stick style.

molecules. From Table 2 we can see the bader charge on the metals decreases from Sc to Zn. This is because the electronegativity increases in the same order. Due to the decrease of the charge, the metals polarize fewer and fewer H_2 molecules. Sc and Ti each can adsorb four H_2 molecules, and V to Fe each can adsorb three ones, while Co to Cu each can adsorb two ones only. Sc and Ti atoms are likely to be adsorbed on the H-sites to form $C_6H_6M_2$ complexes in H–H or sandwich-like configurations. After the adsorption of H_2 molecules, they still have similar atomic geometries, and we show the $C_6H_6Ti_2 + 8H_2$ configuration in Fig. 3(b) as an example. The H_2 density in Sc case is 8.7 wt%, very close to the U. S. DOE target by 2015 [34], and the binding energy (0.57 eV/ H_2) is also suitable for reversible hydrogen storage. Though H_2 density in Ti case is also high, the binding energy is somewhat high for reversible hydrogen storage. In V, Cr, Mn, and Fe cases, $C_6H_6M_2$ complexes also occur in H–H configurations and each complex can adsorb six H_2 molecules at most. After H_2 adsorption, the $C_6H_6M_2$ frameworks are almost unchanged. Once again, due to their similarities, we only show the atomic geometry of $C_6H_6Cr_2 + 6H_2$ in Fig. 3(c) as an example. The adsorption of the six H_2 molecules results in H_2 gravimetric densities from 6.3 wt% to 5.9 wt%. Particularly, the density in Mn case (see Table 2) just equals the requirement (6 wt%) of the U. S. DOE target by 2010 [34]. However, the binding energy in the four cases is always larger than 1.1 eV/ H_2 , too large to be reversible for hydrogen storage.

In Co, Ni, and Cu cases, each $C_6H_6M_2$ can adsorb four H_2 molecules, and the corresponding atomic geometries are shown in Fig. 3(d)–(f), respectively. The three metals are all stable at the H-sites before H_2 adsorption, but this is not the case after that. Now we examine them one by one. From Fig. 3(d) we can see after H_2 adsorption one Co atom relaxes to the upper site of the trapezoid (P_4 -site) composed of the four neighboring carbon atoms, while the

other one relaxes to the upper site of the triangular (P_3 -site) composed of the three neighboring carbon atoms. Finally, each adsorbed Co atom adsorbs two H_2 molecules, yielding a H_2 uptake of 3.9 wt%. However, the average H_2 binding energy is rather large (1.62 eV/ H_2), indicating the Co–benzene complex is not suitable for hydrogen storage. In Ni case, both Ni atoms relax to the D-sites after H_2 adsorption, one on each side of the benzene surfaces, and each metal adsorbs two H_2 molecules. Again, due to the large H_2 binding energy and the low gravimetric density, Ni-decorated benzene complex is also not suitable for hydrogen storage. Each Cu can also adsorb two H_2 molecules, and thus the $C_6H_6Cu_2$ complex can adsorb four H_2 molecules totally. However, after H_2 adsorption, one Cu goes to the S-site and the other goes to the D-site as shown in Fig. 3(f). The binding energy is 0.68 eV/ H_2 , suitable for reversible hydrogen storage, but the gravimetric density is 3.8 wt%, lower than the requirement of applications.

3.3. Dimerization of metals on the benzene surfaces

From above discussions, we find that at least Li, Ca and Sc are promising adsorbates when benzene molecules are used as adsorbents for hydrogen storage. However, there are still questions. Will these metals dimerize? If they do dimerize, what effects will they have on the hydrogen storage capability? To answer these questions, we will consider the dimerization of various metals on the benzene surfaces as well as their hydrogen storage properties in this section.

Dimerization studies are only focused on those metals that can be strongly adsorbed on the benzene surfaces as discussed in above sections. We first place two atoms of one metal on the same side of the benzene surfaces and then relax the structure. After full relaxations, we find that the distance between the two metal atoms is always small. For example, the equilibrium Li–Li distance on the benzene surface is 2.38 Å, much smaller than the calculated bond length of 2.76 Å of an isolated Li_2 dimer. It indicates that a Li_2 dimer is formed on the benzene surface. Similar thing happens to other metals, so they will form their corresponding dimers on the benzene surfaces too. However, to one metal which form is more stable? Is the dimer form or the isolated form? We calculate and compare the total energies of the two forms to every metal, finding that all the metals in this work except Ca have lower energy in the dimer form than in the isolated form. Therefore, Ca atoms will prefer to be isolated while other metals will prefer to dimerize on the benzene surfaces.

We first focus our attention on the metals that are more likely to dimerize. In general, dimerization of metals is less favorable for hydrogen storage. For example, dimerization of Li atoms on C_{60} surface reduces the weight percentage of hydrogen storage [11]. We have known from above discussions that Li and Sc are promising adsorbates, so we only consider their hydrogen storage capability after dimerization. Li_2 - and Sc_2 -dimer benzene complexes are geometrically similar, so we only shown the later structure in

Table 2
Metal and H_2 binding properties in $n = 2$ ($C_6H_6M_2$) case.

Metal	M-site	$E_b(M)$ (eV)	M-charge	$N_{max}(H_2)$	$E_b(H_2)$ (eV)	H_2 weight (wt%)
Li	H–H	0.62	+0.88e	8	0.29	14.8
Be	–	–0.20	–	–	–	–
Na	–	–0.06	–	–	–	–
Mg	H–H	0.09	+0.05e	–	–	–
Al	A–A	1.62	+0.34e	–	–	–
K	–	–0.09	–	–	–	–
Ca	H–H	1.04	+1.19e	8	0.45	9.2
Sc	H–H	3.11	+0.93e	8	0.57	8.7
Ti	H–H	3.41	+0.84e	8	0.90	8.4
V	H–H	2.48	+0.69e	6	1.24	6.3
Cr	H–H	1.20	+0.67e	6	1.20	6.2
Mn	H–H	1.51	+0.47e	6	1.12	6.0
Fe	H–H	2.23	+0.48e	6	1.18	5.9
Co	P_4 – P_3	2.77	+0.34e	4	1.62	3.9
Ni	D–D	2.83	+0.16e	4	1.40	3.9
Cu	S–D	1.06	+0.05e	4	0.68	3.8
Zn	H–H	0.16	–0.01e	–	–	–
Ga	A–A	1.34	+0.42e	–	–	–

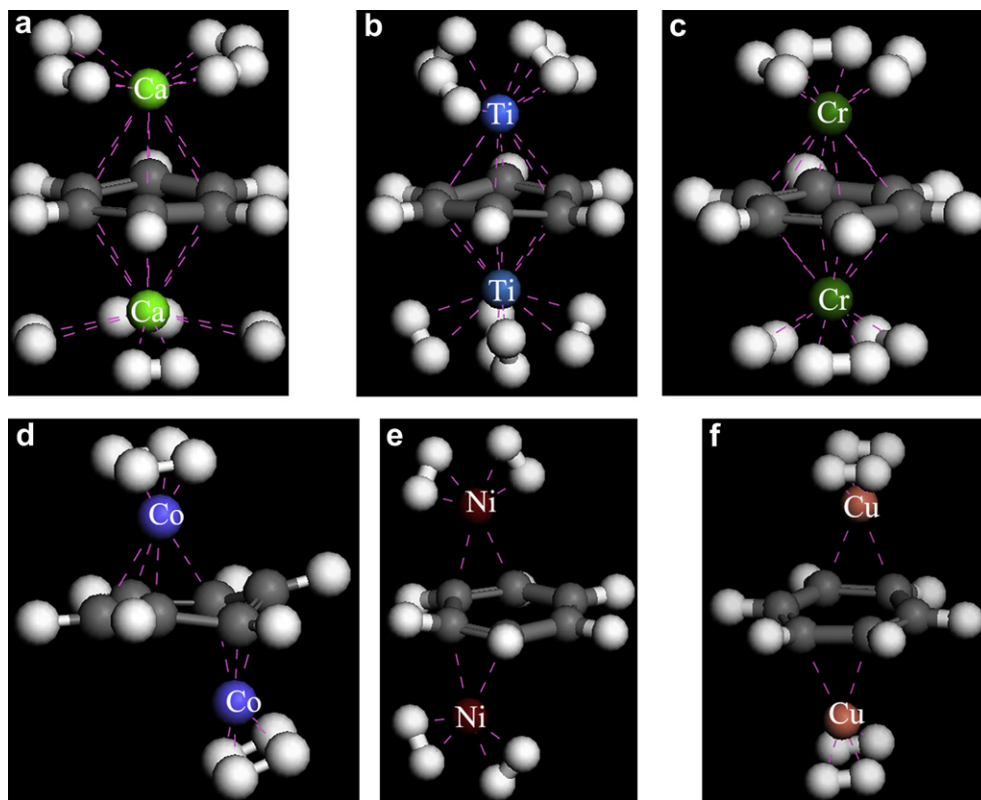


Fig. 3. Atomic geometries of (a) $C_6H_6Ca_2 + 8H_2$, (b) $C_6H_6Ti_2 + 8H_2$, (c) $C_6H_6Cr_2 + 6H_2$, (d) $C_6H_6Co_2 + 4H_2$, (e) $C_6H_6Ni_2 + 4H_2$, and (f) $C_6H_6Cu_2 + 4H_2$ configurations in a ball and stick style.

Fig. 4(a). From the figure we can see that the formation of the metal dimer slightly distorts the benzene geometry. By adding H_2 molecules one by one to the adsorbed and dimerized metals, we find that Li_2 and Sc_2 can finally adsorb four H_2 molecules per dimer at most. The geometry after H_2 adsorption in the Sc_2 -dimer case is shown in Fig. 4(b) as an example again. Here the H_2 densities are 8.0 wt% and 4.6 wt% for Li_2 - and Sc_2 -dimer benzene complexes, respectively, remaining high or moderate. The calculated binding energies are 0.25 eV/ H_2 and 0.48 eV/ H_2 , respectively, still suitable for reversible hydrogen storage. Therefore, Li and Sc are promising adsorbates for hydrogen storage compared with other metals, though they will dimerize on the benzene surfaces.

Finally, we would like to do further discussions on Ca metal. As just discussed, two Ca atoms will prefer to be isolated on the benzene surfaces, one on each side, forming an H–H or a sandwich-like configuration as discussed in Section 3.2. According to our calculations, this configuration is about 0.54 eV lower than the

dimer one. In order to test the stability of the $C_6H_6Ca_n$ complexes further, first-principles molecular dynamics simulations are performed on $C_6H_6Ca + 4H_2$ and $C_6H_6Ca_2 + 8H_2$ systems. The simulations are performed at 300 °C with a time step of 1fs for 10ps. Results indicate that though some H_2 molecules escape from the metals, the complex frameworks are always stable. Combined with the high H_2 densities and the suitable H_2 binding energies, we can judge that Ca is the most promising adsorbate for reversible hydrogen storage.

4. Conclusions

In summary, we have performed first-principles studies on the stability and hydrogen storage properties of various metal-benzene complexes. We find Ca is the most promising metal when forming complexes with benzene for hydrogen storage. Besides, Li- and Sc-decorated benzene complexes can also store a large number of H_2 molecules with suitable H_2 binding energies, so they are also promising for reversible hydrogen storage. Other metals we studied are not suitable for reversible hydrogen storage. We think that this work will be interesting for the studies on hydrogen storage in materials containing six-carbon rings such as C_{60} , CNTs, MOFs and so on, especially for the selection of metal adsorbates. Finally we hope this study could motivate further experimental and theoretical studies on hydrogen storage in metal-benzene complexes and benzene ring contained materials.

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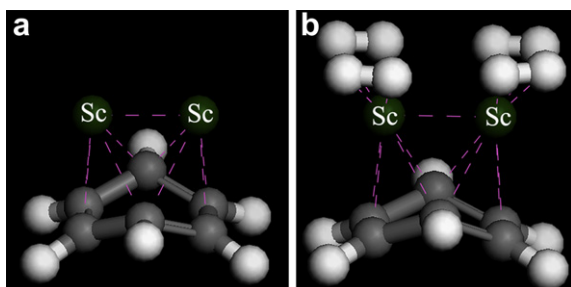


Fig. 4. Atomic geometries of Sc_2 -dimer benzene complex in a ball and stick style (a) before and (b) after H_2 adsorption.

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