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Density functional study on the bimetallic Ti_mZr_n $(n+m \leq 5)$ clusters and their interactions with H_2*

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Equilibrium geometries, stabilities, and electronic properties of small Ti_mZr_n $(n+m \leq 5)$ clusters were investigated using the density functional method. The ground states were determined, and it was found that the larger clusters and those consisting of more Zr atoms are more stable. The electronic properties of the clusters were discussed based on HOMO–LUMO gaps, vertical ionization potentials (VIP), and vertical electron affinities (VEA). Furthermore, we studied the interactions between those clusters and molecular hydrogen, and found that in all the cases dissociative chemisorptions occurred. According to the chemisorption energies, the pure Zr clusters are relatively more active towards H_2 when compared with the others except Ti_3Zr, which shows the highest activity. The magnetic moments of Ti_mZr_n and $Ti_mZr_nH_2$ were also compared, and the results show that the hydrogenated clusters have the same or decreased total magnetic moments with respect to the bare clusters except for Ti_3Zr_2.

Keywords: density functional theory, bimetallic cluster, hydrogen chemisorption

PACS: 36.40.–c, 36.40.Jn, 71.15.Mb **DOI:** 10.1088/1674-1056/27/9/093601

1. Introduction

In the past few decades, a great deal of attention has been paid to metallic clusters due to their unique physical and chemical properties, which can be drastically different from those of their bulk counterparts.[1–4] Investigations on clusters can also build a bridge for people to understand the evolution from atoms to bulk systems. With vast application prospects, studying the atom aggregation process and cluster stability is of great significance, about which theoretical methods can provide more details compared with experimental approaches.[5–7] While studying pure atomic clusters leads to fundamental understanding of the quantum size effects on the properties of the clusters, bimetallic clusters consisting of two different atoms have been found to have properties that differ from those of the pure constituent atom clusters.[8–12] Furthermore, by changing the cluster size and the atom number, some properties of a cluster may be adjusted for different applications.

As transition metal (TM) elements, zirconium and titanium have been extensively explored as structural and functional materials. Alloys consisting of Ti and Zr have huge potential in many fields such as biomedicine,[13] dentistry,[14] catalysts,[15] and storage systems.[16,17] Titanium and zirconium are 3d and 4d TM elements, which belong to the same family, with the outer electron configurations of $3d^24s^2$ and $4s^24p^64d^2$, respectively. Closeness and spatial overlap of d orbitals along with s and p orbitals usually make their interatomic reactions complicated.[18] Concerning their nanoclusters, many studies have been focused on them under the framework of the density functional theory (DFT). The evolutions of monoatomic Ti and Zr clusters have been extensively studied,[19–24] and their stable geometries, energetic, and electronic properties were the main topics. Those reports have reached the consensus that Ti_7, Ti_{13}, Ti_{15}, and Zr_7 are magic clusters. Moreover, it was found that many small clusters possess net spin magnetic moments, which is thought to be a common phenomenon for TM clusters. As a further step, some researchers have researched the doped and mixed Ti and Zr clusters using first-principle theories.[25–29] Besides, the investigations concerning the interactions of hydrogen molecules with the two kinds of bare clusters revealed that H_2 prefers a dissociative chemisorption on them.[30–33] Many similar theoretical studies on the adsorption or chemisorption of H_2 onto small clusters have been reported, which help people understand the catalytic mechanisms on surfaces and contribute to the development of clusters in hydrogen storage materials.[34–37]

However, studies of bimetallic Ti–Zr clusters have been rarely reported. To the best of our knowledge, only Wang *et al.*[38] carried out a fundamental investigation on $(TiZr)_n$ $(n = 1–7)$ clusters, and obtained their stable structures, bonding properties, infrared spectra, and so on. No study on Ti–Zr cluster systems with varied chemical compositions is available. Therefore, in this paper, we present a systematic study of the Ti_mZr_n $(n+m \leq 5)$ clusters. Furthermore, the chemisorption behaviors of H_2 on them are studied, which we hope can provide information for hydrogen storage applications.

This paper is organized as follows. In Section 2, we briefly describe the computational methods employed in this work. The results and discussion are presented in Section 3. Finally, we present the main conclusions in Section 4.

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2. Computational details

The geometry optimizations and vibrational frequency analyses of bare and hydrogenated Ti_mZr_n $(n+m \leq 5)$ clusters were performed by using the DFT method as implemented in the Gaussian program series. First, a variety of possible initial geometries of every cluster were established in GuassView 3.07. Then, those geometries were optimized in Gaussian 03, and the structures would change to the stable ones. The stable structures were obtained in the absence of imaginary frequency by computing the vibrational frequencies at the same theory level. Besides, all the geometries were optimized at different possible spin states. The lowest-energy structure of a certain cluster was defined as the ground state cluster.

It is of great significance to choose a relatively accurate method to do computational calculations. In the present work, we adopted def2-TZVP,[39] a triple-zeta basis set, to treat all the atoms. To find an appropriate functional, we optimized Ti_2, Zr_2, and TiH dimers with a variety of exchange–correlation functionals, and compared the results with the values derived from experiments[40–43] as listed in Table 1. As we can see, the PBE method can present reasonable results for the concerned indicators, and thus it was chosen to calculate the concerned clusters.

Table 1. Calculated and experimental equilibrium distances (R), vibrational frequencies (ω), and dissociation energies (E_D) of the diatomic clusters.

Cluster	Ti_2			Zr_2			TiH	
	R/Å	ω/cm^{-1}	E_b/eV	R/Å	ω/cm^{-1}	E_D/eV	R/Å	E_D/eV
PW91PW91	1.891	480.0015	1.479	2.269	310.2521	3.781	1.764	2.381
B3PW91	1.860	533.6234	0.673	2.236	332.6855	2.859	1.737	2.155
PBE	1.896	470.8411	1.475	2.271	310.5388	3.777	1.767	2.359
PBE1PBE	1.856	543.0111	0.584	2.228	340.5031	2.870	1.740	2.134
BPBE	1.891	475.5173	1.284	2.270	304.8772	3.385	1.766	2.284
BP86	1.893	479.1850	1.512	2.273	309.8634	3.829	1.765	2.531
B3LYP	1.875	526.7591	0.849	2.254	332.2699	3.245	1.746	2.343
Exp.	1.946	409	1.540	2.241	305.7	3.052	1.785	2.12

3. Results and discussion

3.1. Structural properties

We first optimized the geometries of the bare Ti_mZr_n $(n+m \leq 5)$ clusters. The most stable structures together with their spin multiplicities and point groups are shown in Fig. 1. Table 2 shows some calculated results obtained from the ground state structures. The TiZr dimer has a bond length of 2.100 Å, which is between the bond lengths of Ti–Ti (1.896 Å) and Zr–Zr (2.271 Å) in the corresponding monoatomic dimers. For the trimers, Ti_3 and Zr_3 are both equicrural triangles and have the same symmetry of C_{2v}, while Ti_2Zr and Zr_2Ti are of the C_s symmetry, and the distances between the atoms of the two structures are different. When one Ti atom in the Ti_3 cluster is substituted by a Zr atom, the two bonds connecting it are elongated from 2.292 Å to 2.524 Å, and the Ti–Ti bond away from the changed atom is shortened from 2.407 Å to 2.163 Å. By contrast, the Zr_2T cluster has two shorter Ti–Zr bonds and a longer Zr–Zr bond after the Ti atom takes the place of the Zr atom in the Zr_3 cluster. All the tetramers are tetrahedrons. While the pure clusters are of higher symmetries (C_{2v} for Zr_4 and C_s for Ti_4), the mixed clusters possess the C_1 symmetry. As for the clusters with $n+m=5$, the geometries of the most stable structures are all trigonal bipyramids. We also present the structures with energies slightly higher than the minimum-energy ones for comparing. We can see that for the same chemical compositions, the differences of the two most stable structures lie in the atomic arrangements rather than the geometries. Another interesting phenomenon is that to lower the energies of the systems, the Zr atoms tend to occupy the apexes of these trigonal bipyramids, while the Ti atoms are more likely to be located at the middle planes.

From the above, the Ti_mZr_n $(n+m \leq 5)$ clusters can be seen as deriving from the Zr atoms taking the places of the original Ti atoms in the titanium clusters or vice versa. This may imply that the two metal elements are compatible and substitutable in some cases.

Now we discuss the structural stability, which can usually be described by the binding energy per atom (E_b). The E_b is calculated according to

$$E_b(Ti_mZr_n) = [mE(Ti) + nE(Zr) - E(Ti_mZr_n)]/(m+n), \quad (1)$$

where E(Ti), E(Zr), and E(Ti_mZr_n) are the total energies of the Ti atom, the Zr atom, and the Ti_mZr_n cluster, respectively. Figure 2 shows the results. It can be seen that for both pure clusters and mixed clusters, the binding energy per atom increases as the cluster size increases, indicating that these clusters become more stable during the growth process. For the clusters of the same size, it is notable that the binding energy increases monotonically with the increase of Zr atoms, and the changes are almost in a linear fashion. The reason is likely to be that the geometric structures of these same-sized clusters are highly similar, and the outer electron configurations of Ti and Zr are $3d^24s^2$ and $4d^25s^2$, respectively, which are also comparable. The lowest and highest values of E_b appear at the pure Ti clusters and Zr clusters, respectively. Thus, doping Zr atoms in Ti clusters may help to stabilize the clusters.

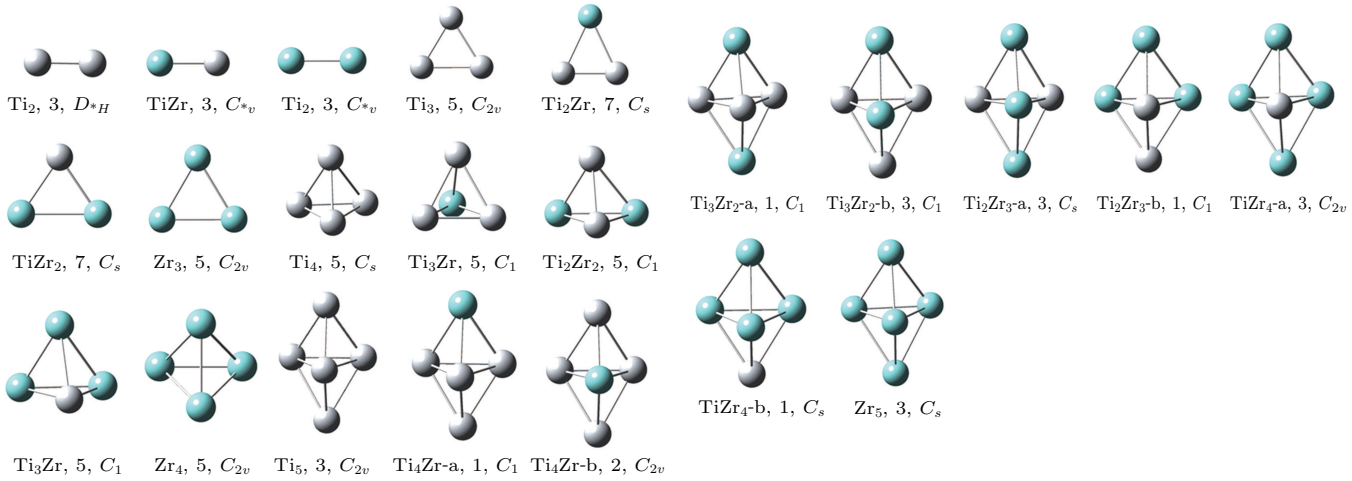


Fig. 1. (color online) Equilibrium structures, spin multiplicities, and point group symmetries of the Ti_mZr_n ($n+m \leq 5$) clusters. The gray balls and blue balls represent Ti and Zr atoms, respectively.

Table 2. Binding energies (E_b), HOMO, LUMO, HOMO–LUMO gaps (E_g), VIP, and VEA of the Ti_mZr_n ($n+m \leq 5$) clusters in units of eV.

Cluster	E_b	HOMO	LUMO	E_g	VIP	VEA	Cluster	E_b	HOMO	LUMO	E_g	VIP	VEA
Ti_2	1.475	–3.112	–2.399	0.713	6.212	0.548	Ti_2Zr_2	2.819	–3.033	–2.538	0.495	4.835	0.924
TiZr	1.672	–3.048	–2.621	0.427	5.985	0.704	$TiZr_3$	3.057	–3.038	–2.576	0.462	4.83	0.974
Zr_2	1.947	–2.994	–2.601	0.393	5.702	0.845	Zr_4	3.298	–3.047	–2.598	0.450	4.821	0.991
Ti_3	1.834	–2.925	–2.613	0.312	4.99	0.914	Ti_5	2.675	–3.233	–2.913	0.320	5.189	1.04
Ti_2Zr	2.140	–3.221	–2.674	0.547	5.24	0.819	Ti_4Zr	2.876	–3.267	–2.919	0.347	5.19	1.12
$TiZr_2$	2.379	–3.187	–2.707	0.480	5.171	0.959	Ti_3Zr_2	3.086	–3.269	–2.892	0.378	5.215	1.125
Zr_3	2.634	–3.055	–2.815	0.241	5.044	1.123	Ti_2Zr_3	3.291	–3.202	–2.936	0.266	5.167	1.124
Ti_4	2.354	–3.022	–2.491	0.532	4.854	0.785	$TiZr_4$	3.491	–3.200	–2.988	0.213	5.146	1.198
Ti_3Zr	2.584	–3.025	–2.552	0.473	4.842	0.877	Zr_5	3.690	–3.226	–3.015	0.211	5.077	1.245

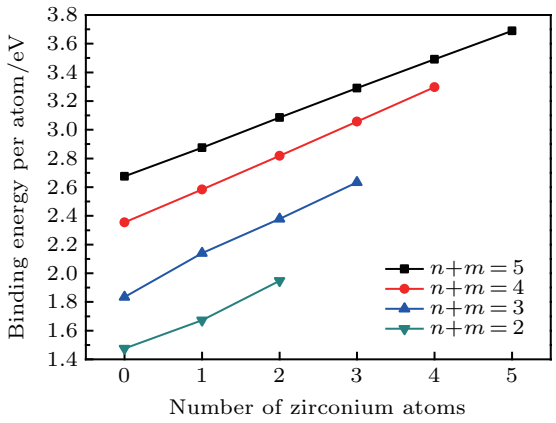


Fig. 2. (color online) Variations of binding energies as a function of the number of Zr atoms for the Ti_mZr_n ($n+m \leq 5$) clusters.

The dissociation energy is another indicator to describe the stability of clusters, which is defined as follows:

$$\Delta E\left(\mathrm{Ti}_m\mathrm{Zr}_n\text{–Ti}\right) = E\left(\mathrm{Ti}_{m-1}\mathrm{Zr}_n\right) + E\left(\mathrm{Ti}\right) - E\left(\mathrm{Ti}_m\mathrm{Zr}_n\right), \quad (2)$$

$$\Delta E\left(\mathrm{Ti}_m\mathrm{Zr}_n\text{–Zr}\right) = E\left(\mathrm{Ti}_m\mathrm{Zr}_{n-1}\right) + E\left(\mathrm{Zr}\right) - E\left(\mathrm{Ti}_m\mathrm{Zr}_n\right). \quad (3)$$

The $\Delta E(\mathrm{Ti}_m\mathrm{Zr}_n\text{–Ti})$ and $\Delta E(\mathrm{Ti}_m\mathrm{Zr}_n\text{–Zr})$ are the energies needed to dissociate a titanium atom and a zirconium atom, respectively, from the Ti_mZr_n cluster. Figure 3 presents the variation of $\Delta E(\mathrm{Ti}_m\mathrm{Zr}_n\text{–Ti})$ with the change of the titanium atom number, and figure 4 presents the variation of $\Delta E(\mathrm{Ti}_m\mathrm{Zr}_n\text{–Zr})$ with the change of the zirconium atom number. Comparing the two graphs, we can see that for the same cluster, more energy is needed to separate a Zr atom than to separate a Ti atom, which means that Zr atoms take a more important role in the stability of the studied Ti_mZr_n clusters. Seeing Figs. 3 and 4 separately, it is found that as the number of Zr atoms increases, i.e., as the number of Ti atoms decreases, both $\Delta E(\mathrm{Ti}_m\mathrm{Zr}_n\text{–Ti})$ and $\Delta E(\mathrm{Ti}_m\mathrm{Zr}_n\text{–Zr})$ increase, indicating that the Ti_mZr_n cluster gets more stable when the Ti atoms are replaced by Zr atoms. The rule is exactly consistent with that of the averaged binding energies. For the clusters with different sizes, on the whole, the larger clusters ($n+m=4$ and 5) present the higher dissociation energies towards both a Ti atom and a Zr atom when compared with the smaller clusters ($n+m=2$ and 3), which indicates that the larger Ti_mZr_n clusters are characterized with the higher stability. In general, in larger clusters, interactions between atoms are stronger and more complicated, and thus the atoms bind with each other closely. As a result, the clusters are likely to possess higher stabilities.

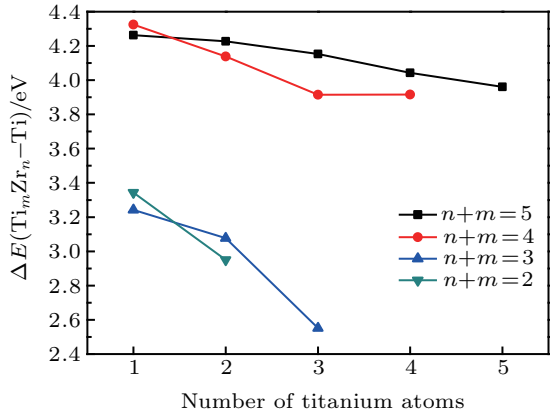


Fig. 3. (color online) Variations of dissociation energies towards a Ti atom as a function of the number of Ti atoms for the $\mathrm{Ti}_m\mathrm{Zr}_n$ ($n+m\leq 5$) clusters.

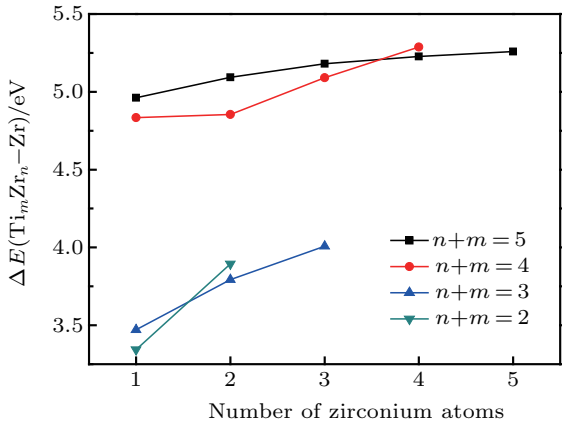


Fig. 4. (color online) Variations of dissociation energies towards a Zr atom as a function of the number of Zr atoms for the $\mathrm{Ti}_m\mathrm{Zr}_n$ ($n+m\leq 5$) clusters.

3.2. Electronic properties

The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), i.e., the HOMO–LUMO gap, reflects the ability of an electron to be excited from an occupied orbital to an unoccupied orbital. Generally speaking, a larger HOMO–LUMO gap is related to enhanced chemical stability. The variation of the HOMO–LUMO gaps of the clusters versus the number of zirconium atoms is plotted in Fig. 5. The HOMO–LUMO gaps for the studied clusters range from 0.211 eV to 0.713 eV, indicating that these clusters have a semiconductive feature. The gap changes markedly with the cluster size, and the clusters with $n+m=5$ generally possess lower HOMO–LUMO gaps, which we consider results from their relatively low LUMO energies (see Table 2). In regard of the clusters of the same sizes, we can notice that the minima are always found at the pure zirconium cluster, and the clusters consisting of more Ti atoms are more likely to possess large gaps. Besides, for the bimetallic clusters, apart from Ti_2, the cluster of $\mathrm{Ti}_2\mathrm{Zr}$ possesses a significantly high HOMO–LUMO gap, indicating that it has better chemical stability.

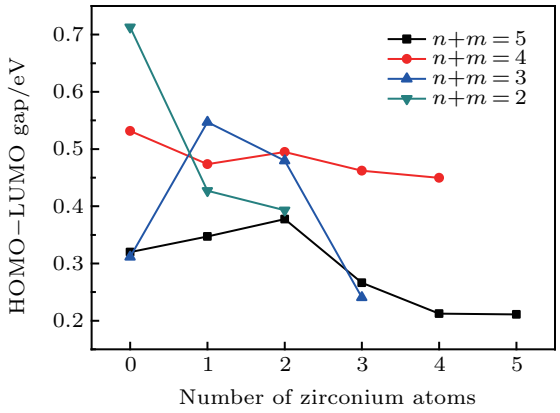


Fig. 5. (color online) HOMO–LUMO energy gaps as a function of the number of Zr atoms for the $\mathrm{Ti}_m\mathrm{Zr}_n$ ($n+m\leq 5$) clusters.

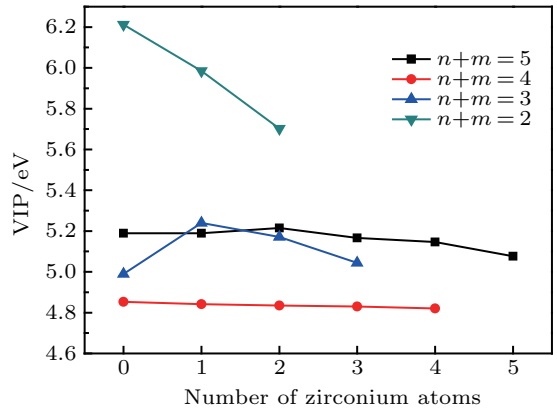


Fig. 6. (color online) Vertical ionization potentials as a function of the number of Zr atoms for the $\mathrm{Ti}_m\mathrm{Zr}_n$ ($n+m\leq 5$) clusters.

The ionization potential and electron affinity are another two significant parameters for the evaluation of chemical stability. In the present work, we have obtained the vertical ionization potentials (VIP) and the vertical electron affinities (VEA) of the $\mathrm{Ti}_m\mathrm{Zr}_n$ clusters, which are respectively calculated by

$$\mathrm{VIP}\left(\mathrm{Ti}_m\mathrm{Zr}_n\right)=E\left(\mathrm{Ti}_m\mathrm{Zr}_n^{+}\right)-E\left(\mathrm{Ti}_m\mathrm{Zr}_n\right), \quad (4)$$

$$\mathrm{VEA}\left(\mathrm{Ti}_m\mathrm{Zr}_n\right)=E\left(\mathrm{Ti}_m\mathrm{Zr}_n\right)-E\left(\mathrm{Ti}_m\mathrm{Zr}_n^{-}\right), \quad (5)$$

where $E(\mathrm{Ti}_m\mathrm{Zr}_n)$ represents the total energy of the neutral cluster, and $E(\mathrm{Ti}_m\mathrm{Zr}_n^{+})$ and $E(\mathrm{Ti}_m\mathrm{Zr}_n^{-})$ denote the total energies of the cationic and anionic species, respectively, with the same geometries of the corresponding neutral clusters. Generally speaking, when the VIP is larger, more energy should be required to remove an electron from the neutral structure without any structural relaxation, and a larger VEA value means that more energy is released when charging the neutral cluster with an extra electron. The VIP and VEA of the considered clusters are presented in Figs. 6 and 7, respectively. The dimers possess the markedly high VIP, while the tetramers are characterized with the lowest VIP. On the whole, when the numbers of atoms are the same, the clusters consisting of more Ti atoms tend to have the higher VIP. As for their behaviors of

VEA, the minima can be found at the dimers. The clusters with $n+m=5$ possess the largest VEA, implying that they are of lower chemical stability, which is consistent with the fact that their HOMO–LUMO gaps are small. In fact, it is believed that people can predict VEA from LUMO energy, and in this work, it can be verified from the low LUMO energies of these pentamers. The overall trend for each series is opposite to that of VIP, indicating that for the neutral Ti_mZr_n clusters, which are less likely to lose an electron (larger VIP), it is also more difficult to charge them with an electron (smaller VEA), thus being chemically stable. Apart from the dimers, one can see that Ti_2Zr is less active, which is consistent with the case of the HOMO–LUMO energy gap.

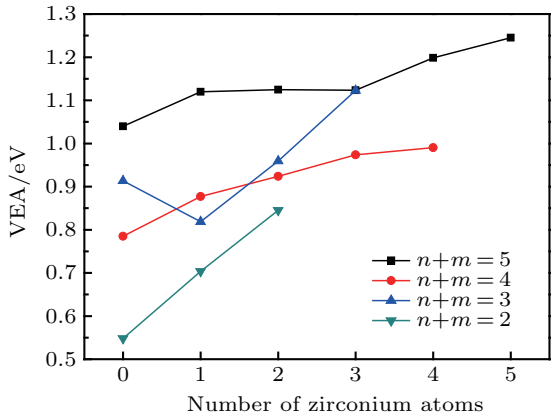


Fig. 7. (color online) Vertical electron affinities as a function of the number of Zr atoms for the Ti_mZr_n ($n+m\leq 5$) clusters.

3.3. Chemisorption of H_2 on the Ti_mZr_n ($n+m\leq 5$) clusters

One of the main motives of our current work is to investigate the chemical activity of the Ti_mZr_n ($n+m\leq 5$) clusters towards molecular hydrogen. We performed an exhaustive search in order to find the minimum-energy structures for the hydrogenated clusters. A hydrogen molecule was introduced to each cluster from various directions and distances, and the stable Ti_mZr_n structures in both the lowest and the second lowest energies were used in this step. The lowest-energy structures after hydrogenation as well as their spin states and point groups are displayed in Fig. 8. We also present the chemisorption energies, the H–H distances, and the net charges derived from the natural population analysis (NPA) in Table 3. We find that in some cases the ground states of $Ti_mZr_nH_2$ are obtained from the metastable structures of the bare Ti_mZr_n clusters. The H–H distances vary from 2.182 Å to 3.770 Å, which are far longer than the equilibrium bond length of H_2 (0.752 Å). Thus, the molecular hydrogen should be considered as dissociatively chemisorbed onto the considered clusters. Slight structural relaxations of the metallic clusters upon H_2 chemisorption were observed. For $n+m=2, 3, 4$, the dissociated H atoms prefer bridge sites of the Ti–Zr clusters, except for the Ti_4H_2 system, in which one H atom is located at the bridge site and the other is on the top of one face. Also, in each dimer-H_2 and trimer-H_2

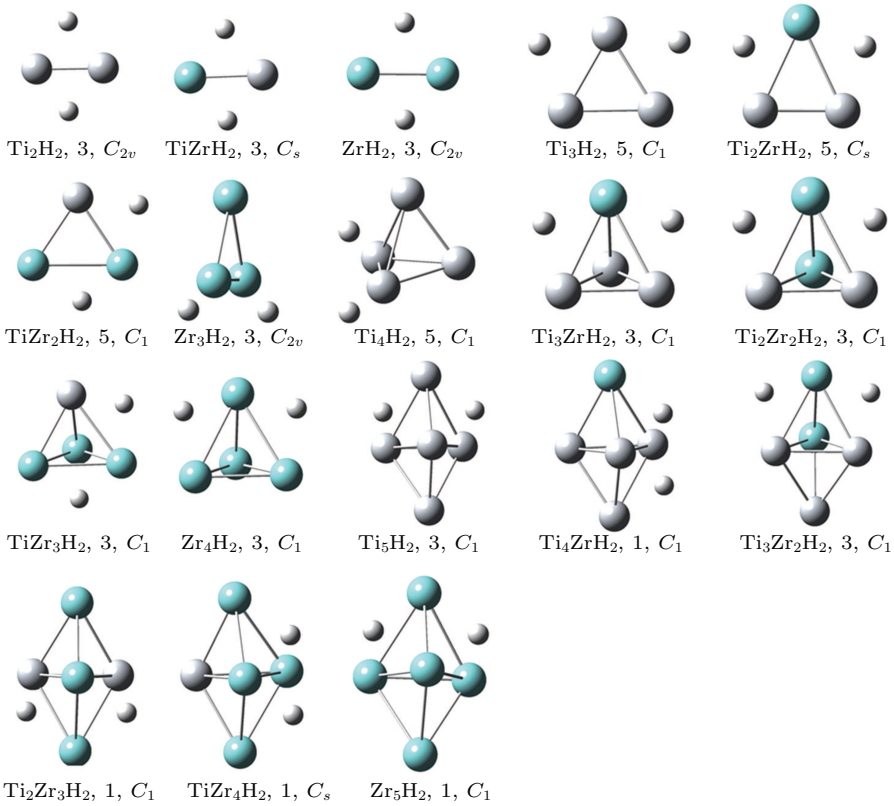


Fig. 8. (color online) Equilibrium structures, spin multiplicities, and point group symmetries of the hydrogenated Ti_mZr_n ($n+m\leq 5$) clusters. The big gray balls, big blue balls, and small gray balls represent Ti, Zr, and H atoms, respectively.

Table 3. Chemisorption energies towards H_2 (ΔE_{CE}), H–H distances (R_{H-H}), and charges of the Ti–Zr host clusters and H atoms for the $Ti_mZr_nH_2$ ($n+m \leq 5$) clusters.

Cluster	ΔE_{CE}/eV	R_{H-H} /Å	Charge			Cluster	ΔE_{CE}/eV	R_{H-H}/Å	Charge		
			host	H-1	H-2				host	H-1	H-2
Ti_2H_2	1.289	2.745	0.4881	–0.2618	–0.2263	$Ti_2Zr_2H_2$	2.041	3.343	0.7145	–0.2618	–0.4527
$TiZrH_2$	1.483	2.768	0.5245	–0.2729	–0.2516	$TiZr_3H_2$	2.102	3.362	0.7426	–0.2729	–0.4697
Zr_2H_2	1.586	2.887	0.5327	–0.2872	–0.2455	Zr_4H_2	2.174	3.373	0.7782	–0.2872	–0.4910
Ti_3H_2	1.951	3.770	0.4116	–0.3047	–0.1069	Ti_5H_2	1.710	2.882	0.5181	–0.3040	–0.2141
Ti_2ZrH_2	1.734	3.270	0.3412	–0.2766	–0.0646	Ti_4ZrH_2	1.666	2.192	0.4266	–0.2766	–0.1500
$TiZr_2H_2$	1.876	3.456	0.5328	–0.2926	–0.2402	$Ti_3Zr_2H_2$	1.771	3.367	0.7644	–0.2842	–0.4802
Zr_3H_2	2.240	2.337	0.3577	–0.2349	–0.1228	$Ti_2Zr_3H_2$	1.808	3.007	0.4805	–0.2349	–0.2456
Ti_4H_2	1.688	2.377	0.2645	–0.1174	–0.1471	$TiZr_4H_2$	1.778	2.346	0.5153	–0.2211	–0.2942
Ti_3ZrH_2	2.947	3.340	0.3839	–0.2341	–0.1498	Zr_5H_2	1.936	2.976	0.5334	–0.2338	–0.2996

system, the atoms are not located in the same plane. When it comes to $n+m=5$, the H atoms are on the tops of the faces, except for Ti_3Zr_2, in which the H atoms are located at the bridge sites. The top sites are not practical in all the studied clusters as the hydrogen molecule is always pushed away from the clusters and there exist imaginary frequencies in the optimized systems. Thus, at least two metallic atoms in each cluster are involved in the interaction with H atoms.

The activity of H_2 on these clusters can be investigated by calculating the chemisorption energies for the systems according to

$$\Delta E_{CE}(Ti_mZr_n) = E(Ti_mZr_n) + E(H_2) - E(Ti_mZr_nH_2), \quad (6)$$

where $E(H_2)$ and $E(Ti_mZr_nH_2)$ denote the total energies of H_2 and the hydrogenated Ti_mZr_n cluster, respectively. The chemisorption energies range from 1.289 eV to 2.947 eV, and the variation is clearly shown in Fig. 9. We notice that the pure Zr clusters are more active towards H_2 when compared with the Ti counterparts, characterized by the higher chemisorption energies. Most of the clusters possess chemisorption energies between those of the same-sized pure titanium and zirconium clusters. The dissociative chemisorption of H_2 on a cluster is always accompanied with a charge transfer process. From Table 3, it is clear that the H atoms attract electrons from the host clusters, resulting in the formation of metal hydride. It is found that when the H atoms are located at the bridge sites of the host clusters, more electrons transfer to the two H atoms. For example, for $n+m=5$, Ti_3Zr_2 has transfered more charges to the H atoms when compared with the other clusters. As the host clusters become positively charged after hydrogenations, we can compare the chemisorption energies with the vertical ionization potentials of the clusters. In general, except for Ti_3Zr, the trends for ΔE_{CE} and VIP are opposite; this is because it is harder for the clusters with larger VIP to loose electrons, so they are less likely to transfer electrons to the H atoms, thus showing lower activity towards H_2. This results in the lower chemisorption energies of the clusters with higher VIP.

In Fig. 9, another noteworthy phenomenon is that the maximum of ΔE_{CE} is found at the Ti_3Zr cluster. To better understand it, we present the HOMO and LUMO distributions of the $Ti_mZr_nH_2$ clusters with $n+m=4$ in Fig. 10. For these clusters, the delocalization for the frontier orbitals is obvious. The s-d hybridization can be observed between H atom and Ti or Zr atom as well as between the TM atoms in the host clusters. For both orbitals, the states between two H atoms and between each H atom and the host cluster are most dense and delocalized for Ti_3ZrH_2, that is, the interaction is strongest within the Ti_3ZrH_2 cluster, which we consider is likely to be the reason behind the markedly large chemisorption energy for Ti_3Zr towards H_2. This also indicates that Ti_3Zr shows high activity with respect to hydrogen, thus promising to be applied as a catalyst in some hydrogenation and dehydrogenation processes.

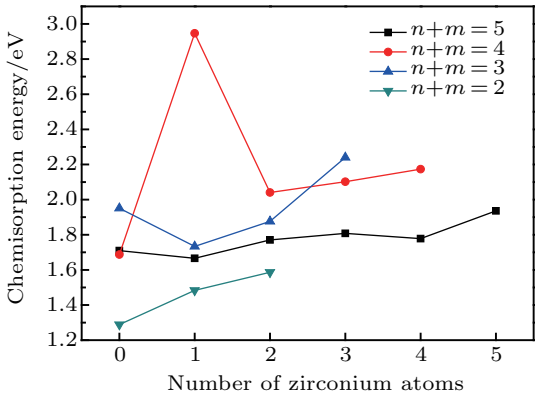


Fig. 9. (color online) Variations of H_2 chemisorption energies as a function of the number of Zr atoms for the $Ti_mZr_nH_2$ ($n+m \leq 5$) systems.

We finally discuss the magnetic properties of the $Ti_mZr_nH_2$ clusters. To compare the hydrogenated clusters with the bare clusters, their spin magnetic moments are listed together in Table 4. In most cases, the total magnetic moments of these clusters have decreased after chemisorbing H_2, and

there are four $Ti_mZr_nH_2$ clusters of which the magnetic moments have quenched, implying their electrons are all paired. It is interesting to find that for the pure titanium clusters, the magnetic moments remain the same after hydrogenation. This may be because H_2 has a weak influence on the pure Ti clusters, which can possibly be reflected by their relatively small ΔE_{CE} values.

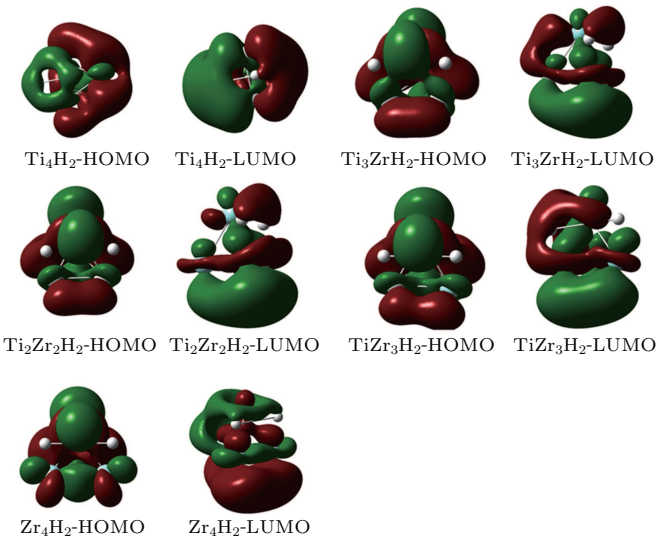


Fig. 10. (color online) HOMO and LUMO distributions of the $Ti_mZr_nH_2$ $(n+m=4)$ clusters.

Table 4. Magnetic moments of the bare (μ_0) and hydrogenated (μ) Ti_mZr_n $(n+m\leq 5)$ clusters.

Cluster	μ_0	μ	Cluster	μ_0	μ
Ti_2	2	2	Ti_2Zr_2	4	2
TiZr	2	2	$TiZr_3$	4	2
Zr_2	2	2	Zr_4	4	2
Ti_3	4	4	Ti_5	2	2
Ti_2Zr	6	4	Ti_4Zr	0	0
$TiZr_2$	6	4	Ti_3Zr_2	0	2
Zr_3	4	2	Ti_2Zr_3	2	0
Ti_4	4	4	$TiZr_4$	2	0
Ti_3Zr	4	2	Zr_5	2	0

4. Conclusion

The equilibrium geometries, stabilities, and electronic properties of small Ti_mZr_n $(n+m\leq 5)$ clusters were investigated by using density functional calculations combining the PBE functional with the def2-TZVP basis set. The ground state structures of the clusters of the same size are similar to each other. According to the averaged binding energies, the clusters become more stable as the cluster size gets larger and as the number of Zr atoms increases. The clusters consisting of more Ti atoms are usually characterized by larger HOMO–LUMO gaps and VIP as well as smaller VEA, implying their electronic structures are of higher stability. Moreover, the interactions between molecular hydrogen and the stable Ti_mZr_n clusters were investigated. Our results show that H_2 prefers dissociative chemisorptions onto the bridge or face sites of the considered clusters. We calculated the chemisorption energies of these systems and found the pure Zr clusters are more active towards H_2 when compared with the Ti counterparts. The maximum of ΔE_{CE} appears at the Ti_3ZrH_2 cluster, which may be understood by analyzing their HOMO and LUMO states, when strong interactions among the H atoms and the host cluster can be observed. Besides, the total spin magnetic moments of these clusters have decreased or remained the same after hydrogenation except for Ti_3Zr_2.

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