INTERACTION OF HYDROGEN WITH TRANSITION METALS — AN EHMO STUDY

C.S. SANKARAN NAMBOODIRI, R. VETRIVEL* and B. VISWANATHAN
Department of Chemistry, Indian Institute of Technology, Madras 600 036, India.
*Present address: Research Centre, Indian Petrochemicals Corporation Limited, Baroda 391 346, India.

ABSTRACT

The effective use of hydrogen as fuel depends on the possibility of efficient storage and transport. Recently, the storage of hydrogen as metal hydrides has been proved to be technologically viable and relatively a safer method. Different metal systems are being explored for this purpose. In the present investigation, an attempt is made to study the electronic interaction between hydrogen and various transition metals. The interstitial sites in metals are represented by suitable clusters and the hydrogen occupation is represented by placing the hydrogen atom at the centre of these clusters. Extended Huckel Molecular Orbital (EHMO) calculations have been performed on these clusters to know the site preference for hydrogen absorption and the relative strength of bonding of hydrogen to various transition metals. The observed behaviour is reasoned from the calculated energy band structure. To understand the enhanced activity of intermetallic compounds to absorb hydrogen, the interaction of hydrogen with various sites present in FeTi intermetallic compound is also studied.

INTRODUCTION

Fast depletion of fossil fuels warrants the use of alternative energy sources. The use of alternative energy sources such as solar, wind, geothermal, tidal, biomass etc. suffers from an inherent limitation that they are seasonal, intermittent and diffused forms of energy. Hence the effective use of these non-conventional energy sources requires a suitable media to store and transport energy. Hydrogen, a clean fuel which can be produced from these alternative energy resources has been proved as an ideal fuel for wide range of applications for e.g. from mobile appliances like internal combustion engines to stationary appliances like fuel cells. Hydrogen is conveniently stored and transported as metal hydrides with the advantages of safety and recycling ability.

Metal hydrides, in addition to having hydrogen storage capacity, have also proved themselves as good hydrogenation catalysts (1) and efficient heat pumps (2). In recent times, there are studies dealing with absorption-desorption characteristics of hydrogen on metals and intermetallic compounds, structure & stability of hydrides formed and the effect of pressure, temperature & composition on hydride formation, with a desire to have a fundamental understanding of the nature of interaction between hydrogen and transition metals.

In the present study, calculations have been performed to have a better understanding of the effect of electronic and structural factors in the interaction of hydrogen with transition metals like Sc, Ti, V, Fe, Co, Ni, Mo, Rh and Pd and an intermetallic compound, namely FeTi.

METHOD OF CALCULATION

Extended Huckel Molecular Orbital (EHMO) calculational method (3) has been adopted for the present study of molecular energy levels, binding energy, electron population etc. in metal clusters. Inspite of the approximations involved, useful information which corresponds with the experimental results are generated by this method. The computational time required for this calculation is also minimum. Unit cell dimensions of various metals needed for the calculation were taken from values reported by Galasso (4). The standard values of Valence Orbital Ionisation Energy (VOIE) and orbital exponent values were also collected from literature (5,6). All the parameters used for calculation are summarised in Table 1.

RESULTS AND DISCUSSION

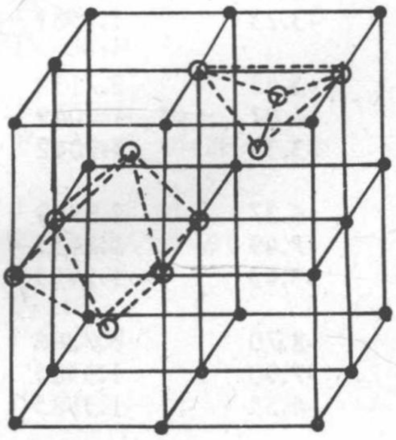
Cluster Models

All metals invariably exist in close-packed arrays - either cubic or hexagonal. Close-packed arrangement of atoms allows the metal to exist in anyone of the three structures namely body centred cubic (bcc), face centred cubic (fcc) and hexagonal close packed (hcp). These structures contain tetrahedral (td) and octahedral (oh) interstitial sites. Four and six metal atom clusters are chosen to model the td and oh sites, respectively. The interatomic distances are chosen from the unit cell dimensions of the metals involved. The td and oh sites of bcc and fcc lattice and td site of hcp lattice considered for investigation are shown in Figure 1. The metal hydrides are represented by placing a hydrogen atom at the centre of these sites. In addition, a 6-atom cluster representing two adjacent td sites and a 7-atom cluster representing two distant td sites in bcc and fcc lattice framework are also considered to study the simultaneous occupation of two sites by hydrogen atoms and the interaction among them.

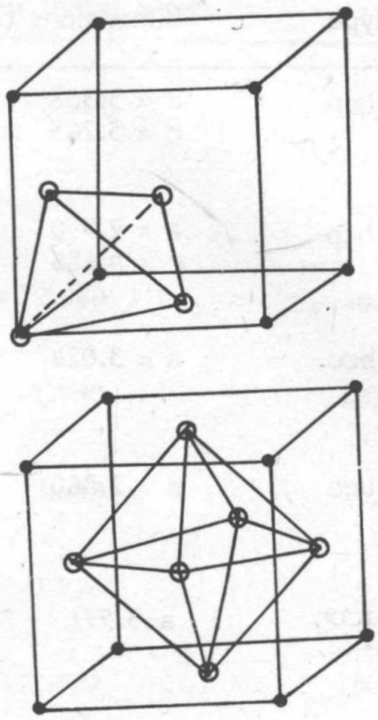
Studies on Fe, Co and Ni

Widely used intermetallics for storage of hydrogen as hydrides are Fe-Ti systems, R-Co (where R is a rare earth metal) systems and Mg-Ni systems due to some specific advantages (7). Hence, the interaction of hydrogen with the transition metal counter

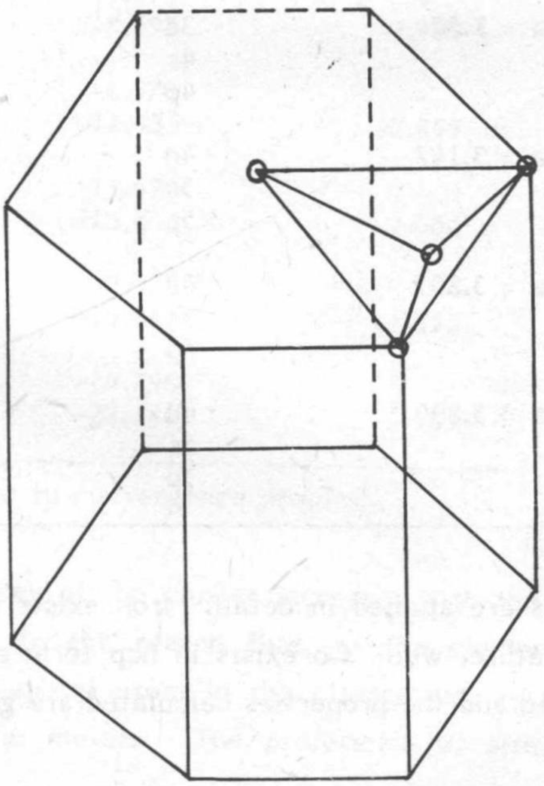
FIG. 1 VARIOUS SITES CONSIDERED IN TRANSITION METAL LATTICES



Td AND Oh SITES IN BCC LATTICE



Td AND Oh SITES IN FCC LATTICE



Td SITE IN HCP LATTICE

TABLE 1

Various parameters of transition metals used in the EHMO calculation

Metal	Crystal type	Unit cell dimensions (A°)	Valence orbitals considered	VOIEs (eV)	Orbital exponent
Sc	hcp	a = 3.308	3d	-4.65	2.3733
		c = 5.265	4s	-6.67	1.1581
			4p	-3.23	1.1581
Ti	hcp	a = 2.950	3d	-5.58	2.7138
		c = 4.686	4s	-6.07	1.2042
			4p	-3.35	1.2042
V	bcc	a = 3.024	3d	-6.37	2.9943
			4s	-7.49	1.2453
			4p	-3.43	1.2453
Fe	bcc	a = 2.860	3d	-8.70	3.7266
			4s	-7.90	1.3585
			4p	-4.55	1.3585
Fe	fcc	a=3.591	3d	-8.70	3.7266
			4s	-7.90	1.3585
			4p	-4.55	1.3585
Co	hcp	a = 2.507	3d	-7.18	3.9518
		c = 4.069	4s	-7.45	1.3941
			4p	-4.23	1.3941
Ni	fcc	a = 3.524	3d	-7.90	4.1765
			4s	-7.55	1.4277
			4p	-3.95	1.4277
Mo	bcc	a = 3.147	4d	-7.71	2.8481
			5s	-6.57	1.2212
			5p	-4.20	1.2212
Rh	fcc	a = 3.803	4d	-14.37	3.4937
			5s	-8.58	1.5286
			5p	-5.04	1.5286
Pd	fcc	a = 3.890	4d	-15.66	3.4040
			5s	-8.89	1.5680
			5p	-5.16	1.5680

parts of these compounds are studied in detail. Iron exists in both bcc and fcc form depending on the temperature, while Co exists in hcp form and Ni exists in fcc form. Various clusters considered and the properties calculated are given in Table 2.

TABLE 2

Calculated parameters for Fe, Co and Ni clusters

	Cluster	Binding energy (eV)	Binding Energy of hydrogen (eV) per metal atom	Charge on hydrogen atom
fcc:-	Fe-td	-11.942	-	-
	Fe-td+H	-14.857	-3.714	-0.3330
	Fe-oh	-16.762	-	-
	Fe-oh+H	-20.110	-3.352	-0.3976
	Fe-2 adj. td	-17.387	-	-
	Fe-2 adj. td+2H	-24.583	-2.049	-0.3483
	Fe-2 dis. td	-20.575	-	-
	Fe-2 dis. td+2H	-27.865	-1.990	-0.3543
bcc:-	Fe-td	-11.816	-	-
	Fe-td+H	-14.748	-3.687	-0.3406
	Fe-oh	-16.684	-	-
	Fe-oh+H	-20.497	-3.416	-0.4183
	Fe-2 adj. td	-17.647	-	-
	Fe-2 adj. td+2H	-24.918	-2.077	-0.3517
	Fe-2 dis. td	-20.406	-	-
	Fe-2 dis. td+2H	*	*	*
hcp:-	Co-td	-5.073	-	-
	Co-td+H	-8.798	-2.199	-0.5331
fcc:-	Ni-td	-8.570	-	-
	Ni-td+H	-11.435	-2.859	-0.3824
	Ni-oh	-11.420	-	-
	Ni-oh+H	-15.005	-2.500	-0.4324
	Ni-2 adj. td	-12.578	-	-
	Ni-2 adj. td+2H	-19.860	-1.655	-0.3994
	Ni-2 dis. td	-14.796	-	-
	Ni-2 dis. td+2H	-22.186	-1.585	-0.4076

* calculation not performed due to convergence problem.

Uniformly, the binding energy of the cluster increases with the size of the cluster. This observation may be due to the reason that, as the cluster size increases the co-ordination number of each metal atom in the cluster also increases, thus leading to stronger bonding among the metals. The preference of sites for absorption of hydrogen in these metals could be evaluated from the binding energy of hydrogen per metal atom. It is observed that the occupation of hydrogen in tetrahedral sites are preferred than in the octahedral sites. The void volume in tetrahedral sites are much less than that in octahedral sites and hydrogen prefers to occupy a compact volume by having strong interaction with the metal atoms.

There is a negative charge on the hydrogen atom indicating that there is transfer of metal electrons to the 1s orbital of hydrogen. The transfer of metal electrons to hydrogen is more facile when the hydrogen is in the tetrahedral hole because of proximity of the metals indicating a stronger interaction. The values of degree of bonding of hydrogen to metals are also in the same trend as their binding energy. However, it is also to be noted that though the binding energy of hydrogen in compact tetrahedral hole is more, the activation energy required by the hydrogen to enter this site (which is also an important factor that decides the amount of hydrogen uptake by metals) will be also relatively high. When two hydrogen atoms are simultaneously present in tetrahedral sites, adjacent positions are favoured rather than distant positions. This indicates that an optimum H-H internuclear distance must be maintained as proposed by Switendick (8), because the position of hydrogen energy levels critically depend on H-H distance. However, when two hydrogen atoms are occupied in adjacent tetrahedral positions, there is drastic decrease in the values of binding energy of hydrogen per metal atom, compared to single occupation. This trend is expected on the basis of experimental results also, since filling of two adjacent sites occur only at high pressures when the composition-pressure plots level off. Magnitude of charge on hydrogen is measure of electron transfer, but it does not signify the strength of bond. It is seen that the negative charge on hydrogen atoms increase when they are present simultaneously in two td sites, but there is decrease in binding energy indicating the electrostatic repulsion between the hydrogen atoms.

Analysis of the molecular energy levels of these clusters indicates that a single molecular orbital contributed mainly by 4s atomic orbital of metal is lying low, while the remaining levels almost form a band contributed by s, p and d orbitals. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) lie within the 'd' band. Occupation of hydrogen in these clusters introduces a new molecular orbital much below the existing levels and since there is only addition of one electron to the total occupancy, the HOMO and LUMO levels are little affected. This observed behaviour correlates with the experimental fact that the work function values of these metals are not affected by hydriding. Since there is no effective mixing of 1s orbital of hydrogen with valence orbitals of the metals, it can be concluded that there is no ionic interaction, but only van der Waal type of forces exist.

Studies on Sc, Ti and V

Though the promising candidates for hydrogen storage invariably contain transition metals, the main problem posed is that they increase the weight of the material. Hence there is some interest in the low atomic weight transition metals and hence studies on Sc, Ti and V are taken up. The calculated parameters for Sc(hcp), Ti(hcp) and V(bcc) clusters are given in Table 3.

TABLE 3

Calculated parameters for Sc, Ti and V clusters

Cluster	Binding energy (eV)	Binding energy of hydrogen per metal atom(eV)	Charge on hydrogen atom
hcp:- Sc-td	-0.019		-
Sc-td+H	-6.486	-1.622	-0.7634
hcp:- Ti-td	-3.397		-
Ti-td+H	-9.435	-2.359	-0.7327
bcc:- V-td	-1.202	-	-
V-td+H	-5.109	-1.277	-0.6630
V-oh	-3.591	-	-
V-oh+H	-7.984	-1.331	-0.6262
V-2 adj. td	-3.458	-	-
V-2 adj. td+2H	-11.056	-0.921	-0.6016

The binding energy of hydrogen in the tetrahedral sites of these metals are in the increasing order V$<$Sc$<$Ti. In the case of V, the occupation of oh site is preferred than the td site. The work function values calculated for Ti cluster using Koopman's theorem agree with the reported values of Liu and Companion (9), though it is twice the experimental value (10). The energy band diagram is similar to those observed for Fe, Co & Ni, and the HOMO and LUMO levels are insensitive to hydrogenation.

Studies on Mo, Rh and Pd

Some typical second row transition metals like Mo, Rh and Pd are also considered for calculation. These studies are aimed at understanding the interaction between

1s orbital of hydrogen and 4d orbitals of these transition metals. The binding energies of metal clusters and for hydrogen in td and oh holes of Mo(bcc), Rh(fcc) and Pd(fcc) are given in Table 4. In these metals also, the tetrahedral sites are the preferred sites of occupation. The energy band structure of Mo is similar to first row transition metals while those of Rh and Pd are different.

TABLE 4

Calculated parameters for Mo, Rh and Pd clusters

Cluster	Binding energy (eV)	Binding energy of hydrogen per metal atom (eV)	Charge on hydrogen atom
bcc:- Mo-td	-11.759	-	-
Mo-td+H	-16.885	-4.221	-0.5700
Mo-oh	-17.454	-	-
Mo-oh+H	-22.492	-3.749	-0.5200
fcc:- Rh-td	-23.967	-	-
Rh-td+H	-27.600	-6.900	+0.1483
Rh-oh	-36.160	-	-
Rh-oh+H	-39.826	-6.630	+0.1392
fcc:- Pd-td	-0.146	-	-
Pd-td+H	-3.316	- 0.829	+0.1222
Pd-oh	-0.323	-	-
Pd-oh+H	-3.241	-0.540	+0.2325

The charge on hydrogen, when it is incorporated to Rh and Pd clusters are positive contrary to the observation on all other metals. This is because the VOIEs of 4d orbitals is lower than the 1s orbital energy of hydrogen and hence flow of electrons is from hydrogen to metal and a positive charge is formed on hydrogen. The small magnitude of binding energy of hydrogen on Pd, deduced from the present calculations is at variance with the experimental heat of adsorption of hydrogen on Pd, which is very high. The analysis of energy levels of metal clusters shows that occupied molecular orbitals have contribution exclusively from metal d orbitals, while the unoccupied molecular orbitals have contribution from both s and d orbitals. In the case of clusters with hydrogen, the hydrogen 1s orbital contributes both to HOMO and LUMO. Hence a decrease in work function is predicted by the calculation, due to hydrogen absorption.

FIG.2 VARIATION OF BINDING ENERGY OF Oh CLUSTERS FOR VARIOUS METALS

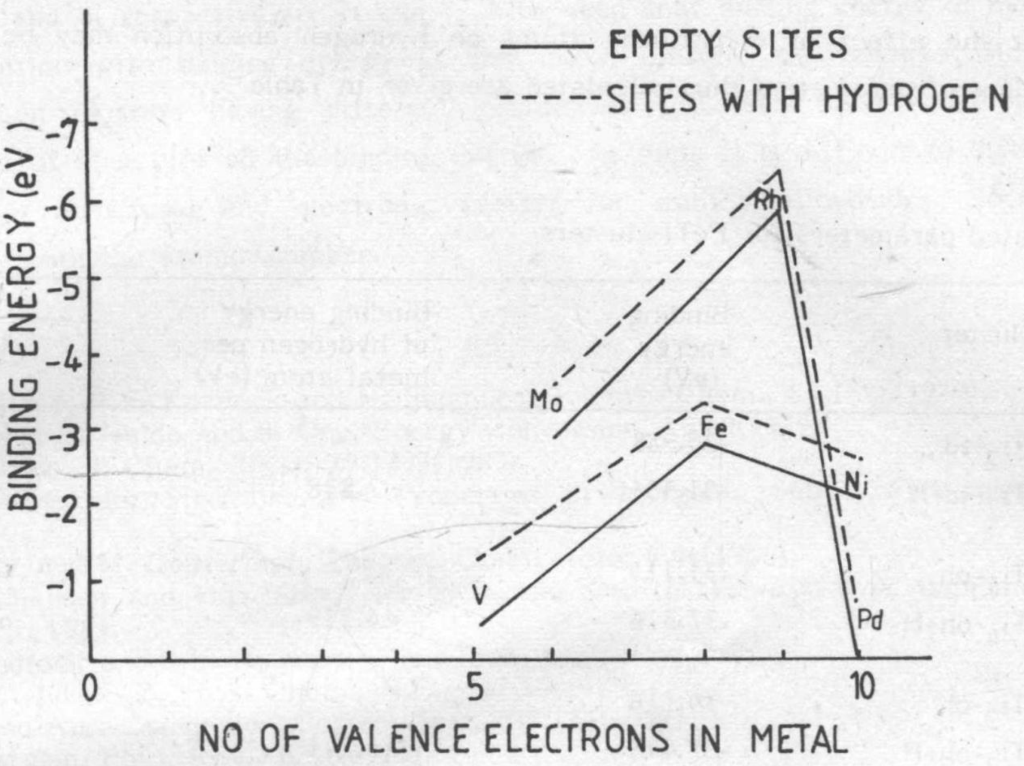
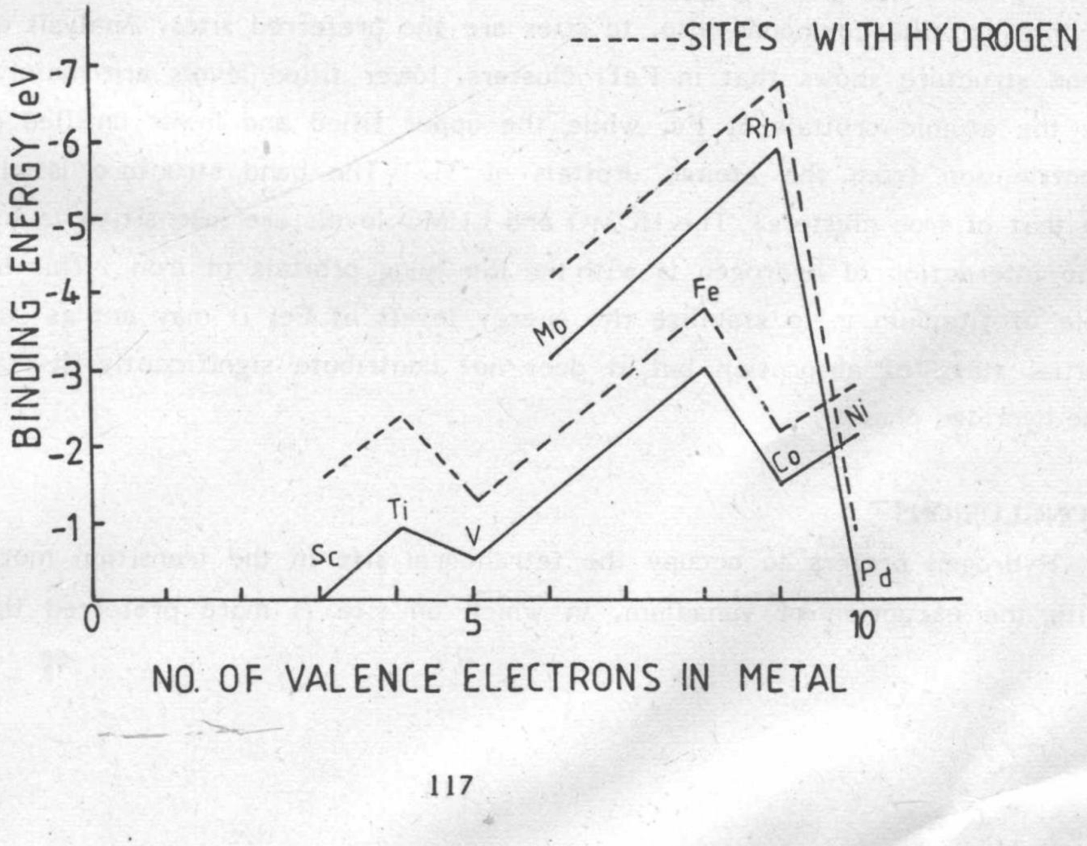


FIG.3 VARIATION OF BINDING ENERGY OF Td CLUSTERS FOR VARIOUS METALS



Studies on FeTi

FeTi is a stoichiometric intermetallic compound existing in CsCl structure with unit cell dimension of 2.976 Å (11). Different combinations of the number of constituent atoms are considered for forming the td and oh sites in the FeTi system, so that the effect of constituent atoms on hydrogen absorption may be understood. The values of parameters thus calculated are given in Table 5.

TABLE 5

Calculated parameters for FeTi clusters

Cluster	Binding energy (eV)	Binding energy of hydrogen per metal atom (eV)	Charge on hydrogen atom
Fe_2Ti_2-td	-25.988	-	-
Fe_2Ti_2-td+H	-31.351	- 7.838	-0.5327
Fe_2Ti_4-oh	-31.115	-	-
Fe_2Ti_4-oh+H	-37.316	- 6.219	-0.5480
Fe_4Ti_2-oh	-34.116	-	-
Fe_4Ti_2-oh+H	-37.446	- 6.241	-0.4318

It is seen that the binding energy of hydrogen on FeTi clusters is greater than either on Fe clusters or Ti clusters. The preference of sites in FeTi is in the increasing order.

$Fe_2Ti_4 < Fe_4Ti_2 < Fe_2Ti_2$

In intermetallic compound also, td sites are the preferred sites. Analysis of the energy band structure shows that in FeTi clusters, lower filled levels are mainly contributed by the atomic orbitals of Fe, while the upper filled and lower unfilled orbitals have contribution from the atomic orbitals of Ti. The band structure is almost similar to that of iron clusters. The HOMO and LUMO levels are insensitive to hydrogenation. The interaction of hydrogen is with the low lying orbitals of iron. This indicates that role of titanium is to stabilise the energy levels of Fe; it may act as catalyst in the initial stage of absorption but it does not contribute significantly in stabilisation of the hydrided phase.

CONCLUSIONS

Hydrogen prefers to occupy the tetrahedral site in the transition metals and FeTi with the exception of vanadium, in which oh site is more preferred than td site.

The change on hydrogen is positive, when absorbed in Rh and Pd clusters, while on all other cases, there is an increase in the electron charge density over hydrogen. The binding energies for tetrahedral and octahedral sites of various metals are plotted in figures 2 and 3, respectively. It can thus be seen that binding energy of hydrogen is in correlation with binding energy of the metal clusters themselves. However, calculations on clusters having different geometries will lead to an understanding of the effect of structure on the binding energy. As such, it is difficult to distinguish the effect of structural and electronic factors for stabilising hydrides, since both of them vary with the atomic number.

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