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Structure, reactivity, and electronic properties of V-doped Co clusters

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Structures and physicochemical properties of V-doped Co13 clusters have been studied in detail using density-functional-theory-based first-principles method. We have found anomalous variation in stability of the doped clusters with increasing V concentration, which has been nicely demonstrated in terms of energetics and electronic properties of the clusters. Our study explains the nonmonotonic variation in reactivity of Co13−mVm clusters toward H2 molecules as reported experimentally [Nonose et al., J. Phys. Chem. 94, 2744 (1990)]. Moreover, it provides useful insight into the cluster geometry and chemically active sites on the cluster surface, which can help to design better catalytic processes.

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I. INTRODUCTION

The interest in the studies of clusters is largely because of their possible technological applications which include the possibilities of developing novel cluster-based materials using the size dependence of their properties. Doping of clusters is an important possibility in this direction. In recent times, the fabrication of alloy clusters of different sizes with well defined, controlled properties by varying the composition and atomic ordering has caught considerable attention.1,2 Bimetallic alloy clusters have been known and exploited for last few years in various applications, especially in the catalytic reactions.3,4 Varying the ratio of the two constituents, one can alter the surface structures, compositions, and segregation properties.5,6 In this way, it is possible to tune the chemical reactivity at the surface of an alloyed cluster.7,8 Considering the huge possibility of using nanoclusters in catalysis, the study of cluster reactivity has become an interdisciplinary topic of present day research.9–12

About 2 decades ago, Nonose et al. measured the reactivity toward H2 of bimetallic CoV13 clusters using laser-vaporization technique and reported strong cluster size and composition dependence.13 Both V and Co are 3d transition metals. The substitution of Co by V atoms, one by one, should increase the reactivity of the alloy cluster toward H2 molecules as V, an early transition metal, has a high reactivity toward H2 in contrast to Co which has relatively low reactivity.14 Interestingly, it was found that the reactivity increased gradually, as expected, with the substitution of Co atom by V atom one by one in the Co13 clusters (n < 13), but for the Co13, there was a remarkable decrease in reactivity when a single Co atom was substituted by a V atom. However, the reactivity increased as the number of exchange V atoms increased further up to m = 3, while the fourth V-atom substitution did not increase the reactivity any more. In view of the high reactivity of elemental V, this sudden drop in reactivity of the Co13V cluster was rather surprising. The authors speculated a plausible icosahedral structure for the Co12V cluster with the active V atom at the cage center. Therefore, the V atom, being shielded geometrically from H2 by the 12 surface Co atoms, might have less chance to interact with H atoms. The chemisorption reactivity of cationic Co13−mVm+ clusters15 and anionic Co13−mV−m clusters16 also shows similar type of variation as that of neutral Co13−mVm clusters, which hints toward the dominant effect of geometric structure as compared to the electronic structure. For clusters, the ionization potential (IP) depends on the position of the highest occupied molecular-orbital (HOMO) level. For the pure metal clusters, Whetten et al. postulated that the reaction rate for cluster-H2 dissociative chemisorption is determined by the charge transfer from the HOMO to the lowest unoccupied molecular-orbital (LUMO) of the reactant gas H2 and an anticorrelation between IP and reaction coefficient could be observed.17 That means lower value of IP corresponds to higher reactivity and vice versa. However, the ionization energies of the Co13−mV−m clusters, measured by Hoshino et al. using photoionization spectroscopy show no such anticorrelation,18 again demonstrating the importance of geometrical structure. A rigorous first-principles study in terms of geometric and electronic effects is therefore very much needed to understand this anomalous nature of reactivity of Co13−mV−m (m = 0–4) clusters. In this paper, we have carried out an ab initio theoretical study on V-doped Co13 clusters. The whole study can be divided into three major parts. First part consists of an exhaustive search for the minimum-energy structures (MESs) for cluster of each composition, followed by stability analysis of these MESs in terms of various physical quantities in the second part, while the final part includes investigation of chemisorbed structures and understanding of cluster reactivity.

II. COMPUTATIONAL DETAILS

The calculations have been performed using density-functional theory (DFT), within the pseudopotential plane-wave method as implemented in VASP code.19 We have used the projector augmented wave (PAW) pseudopotentials20,21 and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional22 for spin-polarized generalized gradient approximation (GGA). The 3d and 4s electrons were treated as the valence electrons for the transition-metal elements and the wave functions were expanded in the plane-wave basis
set with the kinetic-energy cutoff of 335 eV. The convergence of the cluster energies with respect to the cutoff value has been checked. Reciprocal space integrations were carried out at the Γ point. Symmetry unrestricted geometry and spin optimizations were performed using the conjugate gradient and the quasi-Newtonian methods until all the force components were less than a threshold value of 0.005 eV/Å. In order to ensure the structural trends found in the optimized structures, we have also carried out Bohn-Oppenheimer molecular dynamics\textsuperscript{23} within local-density approximation (LDA) for few specific clusters. Simple cubic supercells were used for cluster calculations with the periodic boundary conditions, where two neighboring clusters were kept separated by at least 12 Å vacuum space to make the interaction between the cluster images negligible. The cohesive energy (\(E_c\)) of a Co\(_n\)V\(_m\) alloy cluster is calculated with respect to the free atoms as

\[
E_c(\text{Co}_n\text{V}_m) = mE(\text{V}) + nE(\text{Co}) - E(\text{Co}_n\text{V}_m),
\]

where \(E(\text{Co}_n\text{V}_m)\), \(E(\text{Co})\), and \(E(\text{V})\) are the total energies of Co\(_n\)V\(_m\) cluster, an isolated Co atom, and an isolated V atom, respectively. One can also define the cohesive energy with respect to the Co and V bulk phases at equilibrium instead of isolated atoms. However, the cohesive energy variation with increasing V concentration follows the same trend irrespective of the way of cohesive energy definition. The second difference in energy for fixed size \((n+m=\text{constant})\) and variable composition is defined as

\[
\Delta^2E(\text{Co}_n\text{V}_m) = E(\text{Co}_{n+1}\text{V}_{m-1}) + E(\text{Co}_{n-1}\text{V}_{m+1}) - 2E(\text{Co}_n\text{V}_m).
\]

It gives the relative stability of alloy clusters having nearby compositions.

III. STRUCTURE

Since chemical reaction with clusters takes place on its surface, the atomic arrangement and the composition of cluster surface play an important role in chemical reactivity. Therefore, the first step toward the theoretical modeling of clusters is to determine their ground-state structure. In our earlier work,\textsuperscript{24} we studied the structure and magnetism of the pure Co clusters in detail. To obtain the MES having the optimized geometry as well as the optimized magnetic moment, we considered several probable starting geometries having closed packed atomic arrangement and allowed each of the geometries to relax for all possible collinear spin configurations of the atoms. We follow the same way of structural optimization here for the V-doped Co clusters (Co\(_{13-m}\)V\(_m\), \(m = 1–4\)). However, the situation for alloy clusters is quite cumbersome as one has to deal with a large number of starting geometries because of the presence of homotops (the term was first coined by Jellinek\textsuperscript{25,26}). The homotops have the same number of atoms, composition, and geometrical structure, but differ in the arrangement of the doped atoms. As for example, a single geometrical structure of an \(\text{Al}_p\text{B}_m\) alloy cluster with fixed number of atoms \((N = m+n)\) and composition \((m/n)\) ratio will give, in principle,
the Co12V cluster. First of all, the cohesive energy of the
with V atom doped at the center position, is the MES. Now
magnetic moment 23
H9262
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Co12V cluster and the presence of the singly doped V atom at
isomer in our calculation with total magnetic moment 25
H9262
Because of the icosahedral growth preference of the
optimal cuboctahedron, and two HCP geometries (from left to right) for
Co13 cluster. First of all, the cohesive energy of the
HCP cluster is less favorable and appears as the fifth
surface. For Co11V2 cluster, the second V atom can replace
any of the surface Co atoms, as all the surface sites of a
13-atom icosahedron are equivalent. After relaxation for all
possible spin configurations, we find that the MES has total
magnetic moment of 19
H9262 µB and total cohesive energy of
43.22 eV. The first and second isomers have magnetic
moments of 21
H9262 µB and 17
H9262 µB and they are 0.10 and 0.25 eV
above the minimum-energy state, respectively. In the MES,
the center V atom is again ferrimagnetically coupled with
the surface Co atoms and has much lower local magnetic
moment as it was in the case of the Co12V cluster, while the
surface V atom has the maximum local magnetic moment
and it is also ferrimagnetically coupled with the other surface
Co atoms.

For Co10V3 cluster, depending on the different positions
of the two surface V atoms, there are three possible icosahedral
structures as shown in Fig. 3. However, the structure of
type A where the two surface V atoms are closest to each
other appears as the most favorable one. This type A icosahedral
structure with total magnetic moment of 21
H9262 µB is the
minimum-energy state with ferrimagnetic alignment of the
central V atom and ferromagnetic alignment of the surface V
atoms with the surface Co atoms. Both the central and the
surface V atoms have small values of local magnetic
moments in this case. There are several closely spaced isomers
of type-A icosahedral with magnetic moments of 19
H9262 µB,
13
H9262 µB, 23
H9262 µB, and 17
H9262 µB which are just 0.04, 0.08, 0.09, and
0.15 eV above the MES. We find that the optimal structures
of type B and type C are 0.20 and 0.31 eV above the MES,
respectively, and both of them have same total magnetic
moment of 13
H9262 µB.

For Co9V4, there are three V atoms on the surface. Con-
sidering two surface V atoms at closest to each other (fol-
lowing the ground-state configuration of Co10V3), different
positions of the third surface V atom can give rise to the four
icosahedral configurations as shown in Fig. 4. After optimi-
sation, it is found that the type A is the most favorable struc-
ture where all the three surface V atoms are closest to each
other and form an octahedron with the central V atom. The
optimal structure of type A icosahedron has total magnetic
moment of 15
H9262 µB and total cohesive energy of 42.35 eV. An-
other type-A icosahedrons with magnetic moments of 13
H9262 µB, 19
H9262 µB, 21
H9262 µB, and 17
H9262 µB are just 0.03, 0.07, 0.09, and
0.13 eV above the MES. The optimal type-B, type-C, and type-D
icosahedrons have total magnetic moments of 15
H9262 µB, 13
H9262 µB, and 15
H9262 µB respectively, and they are 0.15, 0.25, and 0.33 eV
above the MES.
The results of the structural optimizations, therefore, can be summarized as, unlike a HCP growth pattern of the pure Co cluster, the V-doped Co$_{13}$ clusters prefer to adopt an icosahedral packing. In such clusters, the most coordinated central site is occupied by a V atom, while the residual V atoms sit on the surface. The surface V atoms like to be closer to each other to form a group, thereby imparting more distortion to the structure and significantly alter the local surface charge density. The central V site in the MES of all compositions is always ferrimagnetically coupled and has lower magnetic moment. On the other hand, the surface V atoms can be ferrimagnetically or ferromagnetically coupled with the surface Co atoms and their local magnetic moments can be as low as the central V site or as high as the surface Co site, depending on the distribution of surface charge density in the clusters having different amount of V doping. Our prediction of icosahedral geometry for the minimum-energy states of V-doped Co clusters is in accordance with the speculation of a closed-shell geometry around the central site in Refs. 13 and 15.

To have more confidence about the structural trend as observed above, we have carried out few \emph{ab initio} molecular dynamics (MD) study for the Co$_{12}$V and Co$_{10}$V$_{3}$ clusters. To determine the lowest energy structures, we have heated up the clusters to 2000 K (which is close to the melting temperature 1768 K for bulk Co and 2183 K for bulk V). The clusters have then been maintained at this temperature for at least 6 ps and then allowed to cool again to 0 K. The cooling process has been done for 24 ps and maintained a very slow cooling rate of 1 K per one iteration throughout the process. The main results obtained from the MD run are: (a) it prefers to adopt the icosahedral pattern with same magnetic alignment of atoms as we predicted from zero-temperature relaxation; (b) for the Co$_{12}$V cluster, the V atom occupies the central position; (c) the surface V atoms for the Co$_{10}$V$_{3}$ cluster prefer to be closest to each other. These results provide reassurance and more confidence in our zero-temperature relaxation.

**IV. STABILITY ANALYSIS**

The observed atomic arrangement of the MES of the Co$_{13-m}$V$_{m}$ clusters as described in the previous section depends critically on the balance of several parameters like the relative strengths of various kinds of bonds present in a cluster structure, the relative atomic sizes, the amount of charge transfer between two different species of atoms, the energy gap between the HOMO and the LUMO, abundance of states near Fermi energy, etc. Below, we try to understand the structural stability of the clusters in terms of these parameters.

**A. Cohesive energy**

Figure 5 shows the plot of the cohesive energies of the MES of the Co$_{13-m}$V$_{m}$ clusters with increasing V concentration. The plot is with respect to the cohesive energy of the MES of Co$_{13}$ cluster. It is seen that the binding has increased considerably compared to that of the optimal Co$_{13}$ cluster with single V atom doping. However, the cohesive energies decrease sharply for the higher concentration of V atoms. For the double and triple V-atom doping, the cohesive energies are above the dashed line indicating their higher stability compared to the pure Co$_{13}$, while for the fourth V-atom doping, the cohesive energy is even lower than that of the pure Co$_{13}$. The relative stability among the clusters of nearby concentrations is more distinct when we plot the second difference in cohesive energies in the inset of Fig. 5. We use Eq. (2) to calculate the second difference. A sharp pick in the $\Delta_{2} E$ at $m=1$ points to the exceptional stability of the single V-doped cluster compared to the undoped or more than one V-doped clusters.

In order to understand the stability of the doped clusters, we have calculated the cohesive energies and the bond lengths of the Co-Co, Co-V, and V-V dimers as shown in Table I. It is seen that the V$_{2}$ dimer is the most stable and the bond length of the V$_{2}$ dimer is also about 14% shorter than that of the Co$_{2}$ dimer which has the least binding among the three. On the other hand, the cohesive energy and bond length of the Co-V dimer are intermediate of the Co$_{2}$ and the V$_{2}$ dimers. For the Co$_{12}$V cluster, we have seen that the center doping in icosahedral structure is the most favorable. Binary clusters are known to have the problem of segregation, where the doped atom can segregate at the surface or...
center. To a first approximation, if one of the homonuclear bonds is the strongest, then species tends to be at the center of the cluster.\(^1\) Our finding of central V doping is in accordance with this, as the V\(_2\) dimer has the strongest binding. The atomic radius of a Co atom and a V atom, being almost same, the substitution of the central Co atom in an icosahedral Co\(_{13}\) cluster by a V atom leaves the structure almost unperturbed. As for evidence, the center to vertex average distance and the average distance between two nearby vertices in the optimal icosahedral structure of the Co\(_{13}\) cluster are 2.334 and 2.450 Å. For the optimal Co\(_{12}\)V cluster, these values are almost same, 2.344 and 2.465 Å, respectively. Therefore, the large gain in cohesive energy of the Co\(_{12}\)V cluster over that of the Co\(_{13}\) cluster may be due to the enhanced cohesive energy of the CoV dimer over that of the Co\(_2\) dimer, though an atom in a dimer is quite different from an atom at the center of a 13-atom cluster. The V atom being at the central position, there are maximum number of CoV dimers in V-doped clusters.

For the clusters doped with more than one V atom, the favorable structure is again found to be of an icosahedral motif, in which the central site is always possessed by a V atom and the other V atoms lie on the surface. The number of the surface V atoms and the V-V bonds, therefore, increases with increasing V doping. It favors better binding. On the other hand, the presence of the V atoms on the cluster surface distorts the cluster geometry and increases the center to vertex average distance as well as the vertex-vertex average distance. Effectively, the cluster volume increases with the increasing V concentration, which destabilizes the structure. In Table II, we have listed the average distances between center to vertex as well as between two nearby vertices for the MES of Co\(_{13−m}\)V\(_m\) (\(m=0−4\)). We believe that the distortion in the structures is due to the charge-density variation induced by the presence of the V atoms on the cluster surface. The strained cluster structures resulted from distortion can be realized from some open bonds in Figs. 3 and 4. Therefore, though the number of the V-V bonds increases, which has better binding compared to the Co-Co or Co-V bonds, the overall cohesive energy decreases monotonically as we go from Co\(_{12}\)V to Co\(_9\)V\(_4\) by successive doping of V atoms. It is then obvious that the cluster geometry and the distribution of atoms on the cluster surface play an important role in deciding the cluster stability.

At this point, it is interesting to study the structure and energetics of the pure V\(_{13}\) cluster. Since experiment hints symmetric structure for the V\(_{13}\) cluster,\(^37\) we considered an icosahedral geometry and optimized it considering all possible spin configurations. Interestingly, the decreasing trend of cohesive energies for the Co\(_{13−m}\)V\(_m\) clusters with increasing V concentration continues also at \(m=13\), i.e., pure V\(_{13}\) cluster. The cohesive energy of the optimal V\(_{13}\) cluster is found to be lower than that of the pure Co\(_{13}\) cluster by about 3.73 eV. It indicates that V\(_{13}\) would be more reactive than any of the V-doped Co\(_{13}\) clusters. This tendency may be rationalized by considering the case of bulk V and Co, where the bulk V is more reactive than Co because of the lower d-band filling, relatively higher position of d-band center, and larger d-band width of V compared to Co. However, pure V does not have importance in catalysis because its high reaction tendency with absorbate tends to poison the surface without leaving any active site. The desorption energy is also high because of strong V-absorbate bond, which is again not favorable for catalysis.

### B. Spin gap

Analogous to HOMO-LUMO gap of a nonmagnetic cluster, one can define spin gaps for a magnetic cluster as,

\[
\delta_1 = - \left[ e_{\text{HOMO}}^\text{majority} - e_{\text{LUMO}}^\text{minority} \right],
\]

\[
\delta_2 = - \left[ e_{\text{HOMO}}^\text{minority} - e_{\text{LUMO}}^\text{majority} \right],
\]

and the system is said to be stable if both \(\delta_1\) and \(\delta_2\) are positive, i.e., the LUMO of the majority spin lies above the HOMO of the minority spin and vice versa. These represent the energy required to move an infinitesimal amount of charge from the HOMO of one spin channel to the LUMO of the other. So magnitude of spin gaps is a measure of chemical activeness of clusters. Higher gap means less reactive and vice versa. The positions of the HOMO and LUMO in both the spin channels and the values of \(\delta_1\) and \(\delta_2\) for the optimized structures of 13-atom V-doped Co clusters of all compositions considered here are given in Table III. It is seen that both the spin gaps \(\delta_1\) and \(\delta_2\) are positive for all the clusters. Also, Co\(_{12}\)V has the maximum value of \(\delta\)’s which

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**TABLE I.** Cohesive energies and bond lengths of Co\(_2\), Co-V, and V\(_2\) dimers in the present calculation. For comparison, we have also listed the experimental values for Co\(_2\) dimer (Ref. 35) and V\(_2\) dimer (Ref. 36).

<table>
<thead>
<tr>
<th>Dimer</th>
<th>Cohesive energy (eV/atom)</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(_2)</td>
<td>1.45</td>
<td>1.72</td>
</tr>
<tr>
<td>CoV</td>
<td>1.53</td>
<td>1.87</td>
</tr>
<tr>
<td>V(_2)</td>
<td>1.81</td>
<td>2.47</td>
</tr>
</tbody>
</table>

**TABLE II.** The average distances in Å between center to vertex and between two nearby vertices for the minimum-energy structures of all the studied clusters. For Co\(_{13}\), the values correspond to the optimal icosahedron.

<table>
<thead>
<tr>
<th>Bonds</th>
<th>Co(_{13})</th>
<th>Co(_{12})V</th>
<th>Co(_{11})V(_2)</th>
<th>Co(_{10})V(_3)</th>
<th>Co(_{9})V(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Center-vertex</td>
<td>2.334</td>
<td>2.344</td>
<td>2.354</td>
<td>2.375</td>
<td>2.398</td>
</tr>
<tr>
<td>Vertex-vertex</td>
<td>2.455</td>
<td>2.465</td>
<td>2.476</td>
<td>2.499</td>
<td>2.509</td>
</tr>
</tbody>
</table>
again indicates the highest stability of Co$_{12}$V cluster compared to the others. Because of this large spin gap, Co$_{12}$V has very low reaction tendency toward H$_2$ molecules. However, gap values decrease with increasing V concentration and therefore reactivity also increases as observed experimentally.

C. Density of states

Figure 6 shows the spin-polarized total density of states (DOS), Co-projected DOS, V-projected DOS, and total $d$-orbital-projected DOS for the MES of Co$_{12}$V, Co$_{11}$V$_2$, Co$_{10}$V$_3$, and Co$_9$V$_4$ clusters. It is seen that the total DOS and the total $d$-projected DOS are almost overlapping each other. This indicates that the cluster properties are mostly dominated by the $d$-electrons which is generally expected for transition-metal clusters. The trend in structural stability and reactivity of the clusters as discussed in the previous sections is also obvious from the nature of the total DOS. The majority-spin channel of each cluster has a gap. This gap is maximum for the Co$_{12}$V cluster and it decreases as the number of surface V atoms increases. In the minority-spin channel, there is finite amount of states at the Fermi energy and these are contributed solely by the exterior surface atoms, as the central atom does not have any contribution at the Fermi energy (cf. Fig. 7). It is also seen that the states are more localized in case of the Co$_{12}$V cluster, while they are gradually spreading out and therefore the DOS height, especially in the majority-spin channel, decreases with the increasing V concentration. At this point, it is relevant to mention a com-

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Majority channel</th>
<th>Minor channel</th>
<th>Spin gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HOMO</td>
<td>LUMO</td>
<td>HOMO</td>
</tr>
<tr>
<td>Co$_{13}$</td>
<td>-3.60</td>
<td>-3.35</td>
<td>-3.48</td>
</tr>
<tr>
<td>Co$_{12}$V</td>
<td>-3.93</td>
<td>-2.61</td>
<td>-3.39</td>
</tr>
<tr>
<td>Co$_{11}$V$_2$</td>
<td>-3.71</td>
<td>-2.83</td>
<td>-3.43</td>
</tr>
<tr>
<td>Co$_{10}$V$_3$</td>
<td>-3.41</td>
<td>-2.98</td>
<td>-3.34</td>
</tr>
<tr>
<td>Co$_9$V$_4$</td>
<td>-3.46</td>
<td>-3.02</td>
<td>-3.33</td>
</tr>
</tbody>
</table>

Figure 6. (Color online) Total DOS per atom, Co projected DOS per atom, V-projected DOS per atom, and total $d$-projected DOS per atom for the optimal structures of Co$_{12}$V, Co$_{11}$V$_2$, Co$_{10}$V$_3$, and Co$_9$V$_4$. The smearing width is fixed at 0.1 eV. Vertical line through zero is the Fermi energy ($E_F$).
FIG. 7. (Color online) Total DOS of the central V atom in the optimal structures of Co12V, Co11V2, Co10V3, and Co9V4. The Fermi energy \(E_F\) is fixed at zero.

common feature observed in case of extended surface. The gas-

gaseous molecules absorb well on clean surface of an early tran-

tion metal as well as on the surface with a multilayer of late

transition metal, but not on the surface with a monolayer of

late transition metal. For example, the photoemission exper-

iments by El-Batanouny et al.38 showed that a H atom ad-

sors well both on the clean Nb(110) surface as well as on

the surface with a multilayer of Pd, but does not adsorb on

Nb(110) surface with a monolayer of Pd and this is due to

the decrease of density of states of \(d\) electrons of Pd near the

Fermi level. Similar behavior had been observed also in case

of a monolayer of Pd on W(110) surface in the experiment of

CO adsorption.39 Although, a cluster of 13 atoms is substan-

tially different in its property from that of the surface or bulk,

one may resemble the stability of the \(\text{CO}_{12}\) cluster toward H

adsorption with that of extended surface, where the central V

atom of \(\text{CO}_{12}\) corresponds to an early transition-metal sub-

strate and the exterior 12 Co atoms correspond to a late

transition-metal monolayer.

In order to see the chemical activity of the central V atom,

we have plotted in Fig. 7 the projected total DOS of the

central V atom for each of the \(\text{Co}_{13-m}\text{V}_m\) clusters. First of all,

it is seen that there is no finite states at the Fermi energy,

meaning that the central V atom is not chemically active.

Also, each of the majority- and minority-spin channels has

two large peaks: one is deep below the Fermi energy and

another is above the Fermi energy. However, the peak

heights gradually decrease; the states are broadened out and

shifted toward higher energy with increasing V concentrations.

It is therefore indicating that the presence of surface V

atoms induces some sort of chemical activeness to the central

atom.

V. CHEMISORPTION WITH \(\text{H}_2\) MOLECULES

In order to gain some understanding about the cluster

chemical reactivity, we have investigated the chemisorbed

structures of the \(\text{Co}_{13-m}\text{V}_m\) clusters upon \(\text{H}_2\) adsorption. To

check the robustness of our chemisorption calculations in-

volving H atoms, we have first calculated the cohesive en-

ergy, bond length, and vibrational frequency of \(\text{H}_2\) dimer.

TABLE IV. Theoretical values of cohesive energy, bond length, and vibrational frequency for \(\text{H}_2\) dimer in the present calculation. Experimental values in Ref. 41 are also given for comparison.

<table>
<thead>
<tr>
<th></th>
<th>Cohesive energy</th>
<th>Bond length</th>
<th>Vibrational frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory</td>
<td>4.520</td>
<td>0.752</td>
<td>4339</td>
</tr>
<tr>
<td>Experiment</td>
<td>4.750</td>
<td>0.741</td>
<td>4395</td>
</tr>
</tbody>
</table>

Our calculated values have been listed in Table IV. These

values are typical for gradient-corrected calculations of \(\text{H}_2\),

which have been done before40 and they agreed reasonably

well with experiment.41

We have then performed an exhaustive search for the

MES, taking \(\text{H}_2\) at different possible places on the MES of

the corresponding bare cluster for each composition. Figure

8 shows our calculated lowest-energy chemisorption struc-

tures after \(\text{H}_2\) absorption for clusters of all compositions.

First thing to notice is that \(\text{H}_2\) molecule chemisorbs disso-

catively in each case, i.e., the distance between the two H at-

omolecules in the chemisorption structures is much larger than

the \(\text{H}-\text{H}\) bond length of an isolated \(\text{H}_2\) molecule.

The chemisorp-

tion gives rise to moderate perturbation to the structures and

makes them more symmetric (i.e., surface bonds are now less

dispersive) compared to the parent structure without hydro-

gen. There are three possible ways for the H atoms to be

adsorbed on each cluster: on top of an atom (one fold), at a

bridge position between two atoms (twofold), and at the hol-

low site of a triangular plane on the cluster (threefold).

Again, as the surface contains two species of atoms for

\(\text{Co}_{11}\text{V}_2,\text{Co}_{10}\text{V}_3,\text{and Co}_{9}\text{V}_4,\) then the onefold position can be

on top of a surface V atom or on top of a surface Co atom.

Twofold position can be the top of a V-V bond, Co-V bond,
or a Co-Co bond which can be nearer to or away from the V

site. Similarly, in triangular plane, there are several possibili-

ties: (i) all three atoms can be V atoms (only possible for

\(\text{Co}_{9}\text{V}_4),\) (ii) one Co atom and two V atoms, (iii) two Co

atoms and one V atom, and (iv) all three are Co atoms. We

have considered all these possible combinations during opti-

mization. It is, however, seen that in each of the optimized

structures, H atoms absorb at the hollow site on the surface

and for \(m=2,\) they prefer the association of the local V

atom. For example, in the \(\text{Co}_{9}\text{V}_4\text{H}_2\) cluster, one H atom ab-

sorbs at the hollow site of V-V-V triangular plane and the

other H atom on top of a V-V-Co triangular plane. For

\(\text{Co}_{11}\text{V}_2\text{H}_2,\) the H atoms appear to absorb at the bridge posi-

FIG. 8. (Color online) The calculated minimum-energy chemi-

sorption structures with \(\text{H}_2\) on the minimum-energy structures of

\(\text{Co}_{13-m}\text{V}_m\) \((m=0–4).\) It is clearly seen that hollow site on the

surface is preferred by chemisorbed hydrogen. Color convention is

the same as in Fig. 2 with small pink colored dots representing H atom.
tions, but they are inclined with an angle such that the absorption tends toward a threefold configuration. The preference of more coordinated hollow site is likely due to geometric arrangements. It allows the H atom to interact more with the V or Co atoms. On the other hand, the V-site preference of H atom is due to the formation of stronger s-d bond with V atom compared to that with Co atom.

The higher reactivity of the Co$_{13}$ cluster compared to the Co$_{12}$V cluster, while both of them have the same 12 Co atoms on the surface, can be understood from charge-transfer analysis. We have computed the charge enclosed within a sphere around each surface atom of the optimal structures of Co$_{12}$H$_2$ and Co$_{12}$VH$_2$ clusters. It is seen that the amount of charge on the surface Co atoms in the Co$_{13}$H$_2$ cluster is larger by about 0.2 (in unit of electronic charge) than that of Co$_{12}$VH$_2$ and it is mainly contributed by the $d$ electrons of surface Co atoms. Therefore, stronger 3$d$-1$s$ interaction between surface Co atoms and chemisorbed H atoms in case of Co$_{13}$H$_2$ increases its reactivity. This result is in accordance with that of Fujima and Yamaguchi$^{42}$ who also predicted the stronger interaction between 1$s$ of H atom and the 3$d$ orbital of the surface Co atom in the Co$_{13}$H$_2$ cluster compared to that in the Co$_{12}$VH$_2$ cluster using density of state analysis. They showed that the antibonding orbital component between the H 1$s$ electron and the 3$d$ electron of the surface Co atoms shifts further away above the HOMO in case of Co$_{13}$H$_2$ compared to that of Co$_{12}$VH$_2$, while the bonding orbital components for both the clusters stay almost at the same energy position below the HOMO. Extending the charge-transfer analysis for the Co$_{13}$−$m$V$_{m}$H$_2$ clusters with $m=2$, 3, and 4, we find that the average charge per surface V atom is gradually increasing with the increase of V concentration which indicates the formation of stronger V-H bonds at the surface with increasing V doping. Average charge per surface Co atom for these three clusters, however, remains almost the same.

Figure 9 shows the plot of chemisorption energy with increasing V concentration, where the chemisorption energy is defined as

$$D_f(E) = E(\text{Co}_{13-m}\text{V}_m) + E(\text{H}_2) - E(\text{Co}_{13-m}\text{V}_m\text{H}_2).$$

(4)

It is a positive quantity and gives a measure of binding strength of H$_2$ molecule with the cluster. The plot shows a minimum for Co$_{12}$VH$_2$, again indicating the lowest binding efficiency of Co$_{12}$V with H. However, chemisorption energy increases with increasing V concentration. The source of this chemisorption energy is the cluster rearrangement energy (i.e., the energy change due to the geometrical rearrangement of the cluster upon chemisorption) and the efficient cluster-absorbate bonding in presence of V due to more efficient s-d hybridization.

VI. SUMMARY AND CONCLUSIONS

To summarize, we have studied the geometric and electronic structures of V-doped Co$_{13}$ clusters and their chemisorption toward hydrogen molecules using first-principles density-functional calculation. The lowest-energy structures of all compositions prefer to have icosahedral geometry, unlike hexagonal symmetry preference of the pure Co clusters. For the Co$_{12}$V cluster, the single V atom prefers to sit at the central site, thereby guarded by all the surface Co atoms and cannot participate directly in the chemisorption reaction. Consequently reactivity of Co$_{12}$V becomes very less. On the other hand, for more than one V atom doping, the additional V atoms reside on the surface and come in direct contact with chemisorbed H atoms and reactivity increases. Our calculated spin gaps, density of states, and charge-transfer analysis explain nicely the stability of clusters and their tendency toward chemisorption. In the chemisorbed structures, H atoms adsorb dissociatively at the more coordinated hollow sites and they prefer V site association due to stronger 3$d$-1$s$ hybridization. To have better insight into the chemisorption reaction, one needs to study the transition states for the optimal cluster of each composition and we believe that calculation of activation barriers will also lead to same conclusion as we have predicted here.

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