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Research Article

Theoretical Investigation of the Hydrogenated Aluminum Cobalt Clusters

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Abstract

The chemisorptions of hydrogen on aluminum cobalt clusters are studied with density functional theory. The on-top site is identified to be the most favorable chemisorptions site for hydrogen, and the Al-top sites are the preferred one in the most cases for one hydrogen adsorption in Al_nCo except for Al_nCo (n=1, 4, 6, and 11) clusters. Top on the neighboring or opposition Al and Al atoms ground-state structures are found for two hydrogen adsorption on Al_nCo. The Al-Co, Al-H and Co-H bond lengths evolve very slowly with cluster size; and there is a slight increase in the mean Al-Co bond lengths after H adsorption on the AlCo clusters. In addition, the nearly constant value for Co-H and Al-H bond lengths on different clusters suggests their similar nature of bonding of H. In general, the binding energy of H and 2H are both found to decrease with a decrease in the cluster size. The large binding energies of the hydrogen and the large HOMO-LUMO gaps for Al_3CoH, $Al_{15}CoH$ and $Al_{14}CoH_2$ make these species behaving like magic clusters. Their stability is further suggesting by the fragmentation energies.

Keywords: Hydrogenated aluminum cobalt cluster; electronic properties; Density functional theory

Introduction

Bulk phase bimetallic systems provide a matter of increasing interest in pure and applied materials sciences and traditional fields of physics and chemistry (Lee et al. 2003; Singh et al. 2005; David and Sylvia 2006; Passacantando et al. 2006; Chen and

Johnson 2008; Quyuan et al. 2008). In catalytic chemistry and chemical engineering, real catalysts mainly consist of a heterometallic or bimetallic system, which can profoundly enhance reactivity and selectivity (Bond 1987). Thus, to get a deeper understanding of the microscopic behavior of these species, the study of bimetallic or so-called alloy clusters provides a suitable tool, since cluster science enables one to investigate chemical and physical properties starting from a single atom or molecule toward bulk phase as a function of size. Therefore, in the last decades a number of studies of bimetallic clusters and diatomic molecules have been performed (Tian et al. 2008; Laguna et al. 2010; Zanti and Peeters 2010; Lu et al. 2011; Zhao et al. 2011).

Among the candidate systems to have been considered, the bimetallic aluminum cobalt clusters

That has been the topic of some experimental and theoretical studies (Koel et al. 1985; Nonose et al. 1989; Menezes et al. 1991, 1993; Behm et al. 1994). Several years ago, Nonose and co-workers (1989) performed chemisorptions reactivity studies of neutral Al_nCo_m (n>m) and Co_nAl_m (n>m) clusters toward H_2 using a fast flow reactors. In that study, they found that the doping of Co_n clusters with only one Al atom reveals a remarkable increase of hydrogen chemisorptions rates compared to pure Co_n clusters. On the other hand, pure Al_n clusters do not adsorb hydrogen, which is comparable to Al bulk phase behavior (Koel et al. 1985). Knickelbein and coworkers (1991, 1993) succeeded in a comprehensive investigation of the size dependence of ionization energies of these clusters. These ionization energies studies show that the electronic shell structure of Al_nCo and Al_nCo_2 clusters remains similar to that of pure Al_n clusters. Morse and co-workers (1994) have performed resonant two-photon ionization spectroscopy on small diatomic AlCo aluminides. Pramann and co-workers (2001) have measured the photoelectron spectra of small mass-selected aluminum-rich Al_nCo^- (n=8-17), and cobalt-rich $Co_nAl_m^-$ clusters (n=6, 8, 10; m=1, 2) are measured at photon energies of 3.49 eV with the aid of a magnetic bottle photoelectron spectrometer.

Since the pioneering work of Knight et al. (1984) exhibiting a direct relationship between the pronounced peaks in the mass ion intensities (commonly referred to as magic numbers) of Na clusters and electronic shell closure, considerable theoretical and experimental work has been carried out to search for new magic numbers in compounds as well as charged metal clusters (1997). The electronic shell closure derived from the Jellium model dictates that metal clusters with 2, 8, 20, 40 … electrons are particularly stable as they correspond to complete filling of 1s, 1s1p, 1s1p1d2s, 1s1p1d2s1f2p … groups of orbital, respectively. As Al, Co, and alkali metal atoms exhibit free-electron-like behavior in their respective bulk phases, one would expect the atomic and electronic structure as well as relative stabilities of cobalt-doped aluminum clusters to exhibit the same behavior as those of alkali atom-doped aluminum clusters (1994). Since both clusters contain the same number of valence electron; for example, if clusters are born neutral, $Al_{13}Co$ cluster should exhibit enhanced stability (and, hence, a peak in the mass spectra) over their neighbors, as it would contain 40 valence electrons.

Against this background, the sequential growth of small Al_nCo clusters with n=1-17 (Guo 2007, 2008) have been explored recently. And to obtain further insights on the nature of chemisorption of a single H_2 molecule on Al_nCo clusters, the extensive calculations of chemisorption of H_2 and sequential hydrogen loading on the above energetically stable clusters are studied. A detailed picture of chemisorption of H_2 on Al_nCo (n=1-15) nanoclusters based on an analysis of energies, HOMO-LUMO gap, Stability, fragmentation behavior, and Bonding nature are presented. So, the understanding of the adsorption of H_2 molecule on aluminum cobalt clusters could give useful insight on hydrogen interaction with other alloy clusters.

The paper is organized as follows: A brief account of the computational methodology is given in Sec. 2, followed by a detailed presentation and discussion of the first-principles calculations in Sec. 3 on small aluminum cobalt clusters with n=1-15 Al_nCo and up to two hydrogen atoms. These will provide an understanding of the nature of interaction of hydrogen with aluminum cobalt clusters and the magic behavior of these clusters. A summary of my findings and conclusions are given in Sec. 4.

Methodology

All calculations are performed using the density functional theory (DFT) provided by the Gaussian 03 suite of programs (Frisch 2004). The density functional is treated with the generalized gradient approximation (GGA) corrected-exchange potential of the B3LYP (Becke 1993), and its application has been shown to be effective (Guo 2007, 2008). The double-ξ basis set lanl2dz is employed (Hay 1985). Frequency analyses at the optimized structures are carried out at the same theoretical level to clarify if the optimized structures are true minima or transition states on the potential energy surfaces of specific clusters. All of the obtained, most stable clusters are characterized as energy minima without imaginary frequencies. The geometries are fully optimized. The structures of small Al_nCo (n=1-15) clusters are reported in my previous paper (Guo 2007, 2008).

Low energy structures may be missed if the starting configurations of the search are not set appropriately. In order to avoid this, ab initio simulations starting with several initial two-dimensional and three-dimensional structures are performed for each Al_nCo adsorbate cluster. For simulating the adsorption process, different orientations of the molecules with respect to the Al_nCo cluster are considered for optimization, and the H_2 molecules and the Al_nCo cluster are allowed to relax freely. To avoid computational bias, the cluster and H_2 chemisorptions geometries are fully optimized without imposing symmetry constraints until the maximum force is less than 4.5×10^{-4} eV/Å and the maximum displacement is less than 1.8×10^{-3} Å.

The Binding energies (BE) of Al_nCo and Al_nCoH_m are calculated based on eqs (1) and (2).

$$BE\ (Al_nCo)=E(Al_nCo)-nE(Al)-E(Co) \qquad (1)$$

$$BE\ (Al_nCoH_m)=E(Al_nCoH_m)-nE(Al)-E(Co)-mE(H) \qquad (2)$$

where m and n represent the size of the clusters, E(Al_nCo), E(Al_nCoH_m), E(Al), E(Co), and E(H) are energies of Al_nCo, Al_nCoH_m clusters, and Al, Co, H atoms, respectively.

Results and discussions

Hydrogen on Al_nCo(n=1-15)

The optimized geometries for the adsorption of one and two H atoms on small Al_nCo(n=1-15) clusters are shown in Fig.1. In Table 1 and 2, the values of the binding energy, the HOMO-LUMO energy gaps, and the mean nearest-neighbor bond lengths of Al_nCo(n=1-15) and Al_nCoH_m (n=1-15; m=1,2) clusters are displayed for all the isomers shown in Fig.1. For the chemisorptions of H_2 on the Al_nCo cluster, there are three possible adsorption sites: 1-fold on top, 2-fold edge, and 3-fold hollow site. The calculation result shows that the on-top adsorption configuration is energetically most stable.

Please See Table 1 in the PDF Version

The predicted ground-state spin multiplicity for AlCo is found to be a triplet. The calculated equilibrium bond length is 2.50 Å. The associated Al-Co stretching frequency for the ground-state cluster is 267 cm^{-1}. It is seen that the BE of H on AlCoH (2.23 eV) is different to that of H on AlCo (5.58 eV). This shows that both AlCoH and $AlCoH_2$ have different stability.

The ground-state Al_2Co cluster is a spin doublet isosceles triangle with C_{2v} symmetry and a binding energy of 3.52 eV. The ground state corresponding to Al_2CoH cluster is a spin triplet with a Al-H bond length of 1.64 Å (Table 2) and an Al-H stretching frequency of 1751 cm^{-1}, and the H atom takes on-top adsorption with the Al atom, which is different from the structure of AlCoH with 2-fold edge model. The BE of H on Al_2Co is 6.22 eV. The C_{2v} isomer [Fig. 1(2c)] with two H atoms bridging in two Al atoms is found for the most stable geometry of Al_2CoH_2 cluster. Other optimized geometries are also considered for this cluster, for example, occupied different places of Al and Co atom (2d) or two H atoms are located on top Al atoms (2e). None of them are more stable than the ground state structure.

Please See Table 2 in the PDF Version

The ground-state Al_3Co cluster is a spin triplet tetrahedron [Fig. 1(3a)] with C_{3v} symmetry and a binding energy of 4.88 eV. Two optimized geometries are found for Al_3CoH cluster, both of the same multiplicity, doublets. Interaction of H 1-fold on top of Al_3Co [Fig. 1(3b)] with C_1 symmetry is favorable as compared to a 2-fold edge site of Al [Fig. 1(3c)] with C_s symmetry by 0.40 eV. The BE is big (3.40 eV) that it is difficult to make further interaction with hydrogen atom. In order to confirm this, I carried out calculation on Al_3CoH_2. Three configurations for H are studied: (i) where two H atoms are on the top sites of two neighboring Al atoms [Fig. 1(3d)], (ii) where two H atoms are on the top site of one Al atom **[**Fig. 1(3e)], (iii) where one H atom is bridging with two Al atoms and another one with Co and Al atoms [Fig. 1(3f)] making the C_s structure as shown in Figs. 1(3d)-1(3f). The energy difference of the first two of these is 0.82

eV (Table 2). Also the C_s structure 3f lies 0.94 eV higher in energy than the 3d structure. The BE for 2H is 6.36 eV (Table 2) and it shows that the interaction between two hydrogens on Al_3Co is not attractive. This energy is higher than the dissociation energy of H_2 (4.60 eV). Accordingly, hydrogen is likely to be dissociated on Al_3Co. The distance between two hydrogens on Al_3Co in the lowest-energy state is 5.32 Å as compared to the bond length of 0.75 Å in H_2. Therefore, two hydrogens are in a dissociated configuration. The dissociation can happen on a top site of Al_3Co. Since there are several such sites, the probability for such a dissociative process is also high.

The ground-state found for Al_4Co is a spin doublet pyramid (C_{4v}) structure [Fig. 1(4a)] with a binding energy of 7.24 eV. The spin multiplicity found for Al_4CoH is a spin singlet and its structure, different with small clusters above, prefers a top site of Co atom [Fig. 1(4b)] on it. In the case of two H on Al_4Co, two H atoms on the top site of Al atom [Fig. 1(4c)] is the ground state, and the spin multiplicity is quartet. The structure with two H atom taking 3-fold hollow site on two Al and one Co atoms [Fig. 1(4d)] is 0.16 eV higher in energy. Both 4c and 4d geometries are with C_{2v} symmetry.

Al_5Co is a spin triplet structure [Fig. 1(5a)] with D_{3h} symmetry. Similar to Al_2Co and Al_3Co, one H is most favorable on a top site of Al atom [Fig. 1(5b)], and it is with a binding energy of 0.36 eV stronger than that of the bridging between Al and Co atom adsorption [Fig. 1(5c)]. The BE (2.98 eV) of H on Al_5Co is also one of the largest among all the clusters studied. Accordingly, Al_5CoH should have large abundance. Two H favor top sites of neighbor

Al and Al atoms [Fig. 1(5d)]. The BE of this isomer is 6.00 eV which is again quite large and slightly lower than the value for Al_3CoH_2. This should also make hydrogen dissociate on this cluster unless there is a barrier. Isomers with two H on different top sites of Al and Co atoms [Fig. 1(5e)] and the same Al atom have 0.30 and 0.42 eV higher energies, respectively.

For these small clusters the BE per H is high with n=1 and 5. And the addition of a second H increases nearly the same value of BE for n=2-5. On the other hand, for n=1, the addition of a second H increases the BE significantly. My calculations suggest that H_2 is likely to be combining at least on AlCo small cluster and these clusters could disintegrate, such as $AlCoH_2$, or combine with others to form energetically more favorable species.

The lowest-energy isomer of Al_6Co is a capped triangular prism structure [Fig. 1(6a)] with C_{2v} symmetry. Adsorption of single hydrogen on a top, edge or hollow site of Al atom or Co atom is considered. The BE (2.71 eV) of H on an edge site of two Al atoms of Al_6Co [Fig. 1(6b)] is the smallest among all the clusters. The fragmentation energy (see below) is also small and this gives further support for the instability of Al_6CoH. Accordingly, it may not have large abundances, and the structure (6c) with hydrogen on a top site lies 0.08 eV high in energy. For two hydrogen atoms on Al_6Co, several configurations are studied. These include two opposite top of Al and Al atoms in the different triangle [Fig. 1(6d)], two neighboring top of Al and Al atoms in the same triangle [Fig. 1(6e)] and different triangle [Fig. 1(6f)]. The calculated BE's given in Table 2. The most favorable adsorption sites are structure 6d. The two H have a similar configuration as in Al_4CoH_2. The BE for 2H is 5.32 eV and it shows that interaction between two hydrogen on Al_6Co is not more attractive than clusters discussed above. However, this energy is also higher than the dissociation energy of H_2 (4.6 0 eV). Accordingly, hydrogen is likely to be dissociated on Al_6Co. The distance between two hydrogens on Al_6Co in the lowest-energy state is very long as compared to the bond length of 0.75 Å in H_2. Therefore, two hydrogens are in a dissociated on Al_6Co. The dissociation can happen on a top site of Al_6Co. Since there are several such sites, the probability for such a dissociative process is also high.

For Al_7Co, the lowest-energy structure is a spin triplet with C_s symmetry [Fig. 1(7a)]. One hydrogen adsorption is favorable on the top of the headpiece Al atom [Fig. 1(7b)]. The BE (2.83 eV) of

H on Al_7Co is also one of the smallest among all the clusters studied. Isomers with H on the top site of capping Al atom [Fig. 1(7c)] and Co atom [Fig. 1(7d)] are 0.02 and 0.56 eV higher in energies, respectively. The small HOMO-LUMO gap is likely to make further interaction of hydrogen with this cluster energetically not so favorable. In order to confirm this, some calculations are carried out on Al_7CoH_2. Several initial configurations are considered for two hydrogens. These include H atoms on the top of two neighboring Al and Al atoms in the lower part of the Al_7Co cluster [Fig. 1(7e)]. This has the lowest energy. The HOMO-LUMO gap is lower (1.93 eV) and the addition of one more hydrogen to Al_7Co leads to a gain of 5.50 eV, an increase of more than 2.67 eV in the BE of H as compared to one hydrogen on Al_7Co. The other calculated positions for two hydrogens on Al_7Co are one on top of two distant Al atoms [Fig.

1(7f)] or two opposite Al atoms [Fig. 1(7g)]. The energy, the HOMO-LUMO gap, and other structural information are given in Table 2. The energies of the isomers [Fig. 1(7f, 7g)] are close to that of Fig. 1(7e), and their energy differences with 7e are 0.08 and 0.31 eV, respectively.

Al_8Co has Cs symmetry [Fig. 1(8a)]. This structure can be very roughly decomposed into two interacting entities: structure Al_4Co and Al_4 are bridged with two Al-Co and Al-Al bonds. Similar to Al_4Co, this cluster would be anticipated not to favor to react with one hydrogen; indeed, the BE of H is 2.57 eV similar to Al_4Co of 2.24 eV. One H is favorable on a top site of Al atom in the top part of Al_8Co [Fig. 1(8b)], and from now on, all the clusters later have the same geometry. Structure Fig. 1(8c) with H atom on a top site of another Al atom is only 0.06 eV less stable. Therefore, the interaction depends very sensitively on the electronic and atomic structures of clusters. Adsorption of two hydrogen are studied on a few selected sites which included two neighboring faces with H atoms on the different Al atoms [Fig. 1(8d)], the two H atoms on the top sites of neighboring Al and Al atoms in the upper part of Al_8Co [Fig. 1(8e)], and two opposite top sites of neighboring Al atoms in the upper part of Al_8Co [Fig. 1(8f)]. The 8d isomer has the lowest energy (Table 2). The BE of this isomer is 5.57 eV, which is larger than Al_nCo (n=2, 4, 6 and 7) and similar to AlCo and slightly slower than the value for Al_3Co and Al_5Co.

The lowest energy structures for Al_9Co, $Al_{10}Co$ and $Al_{11}Co$ clusters are spin triplet structure with C_1 symmetry, spin doublet structure with C_2 symmetry, and spin triplet structure with C_1 symmetry, respectively. And the binding energies are 16.87, 18.39 and 20.86 eV. The Al_9Co may be viewed as an Al atom attached to the most stable form of Al_8Co. H adsorption on Al atom [Fig. 1(9b)], a doublet, is the most stable with a binding energy of 2.64eV. The ground state corresponding to Al_9CoH_2 cluster is a spin singlet with an average Al-As bond length of 2.378 Å, which is the same as Al_9CoH. Two H favor top sites of neighbor Al and Al atoms [Fig. 1(9c)]. Just like the Al_3Co and Al_5Co, Al_7Co clusters discussed above. Two H adsorption on distant Al and Al atom [Fig. 1(9d)], a spin singlet is a substable structure with a binding energy of only 0.09 eV less than the ground state.

Both of $Al_{10}Co$ and $Al_{11}Co$ clusters adsorb H on Al atom [Fig. 1(10b) and 1(11b)], and the lowest energy structures for both $Al_{10}CoH_2$ and $Al_{11}CoH_2$ clusters are also two H prefer on the top sites of neighbor Al and Al atoms [Fig. 1(10c) and (11c)].

For $Al_{12}Co$, the C_s symmetrical $Al_{12}Co$ cluster [Fig. 1(12a)] has been computed to be the most stable using B3LYP/lanl2dz method. Adsorption of single hydrogen on the top site of Al atom [Fig. 1(12b)] is considered. The BE (2.88eV) of H on $Al_{12}Co$ is one of the largest among all the clusters studied. However, the HOMO-LUMO gap is small (1.39 eV). The small HOMO-LUMO gap is likely to make further interaction of hydrogen with this cluster energetically so favorable. In order to confirm this, calculations on $Al_{12}CoH_2$ are carried out. Several initial configurations are considered for two hydrogens. These include two H atoms on the top sites of neighboring and opposite Al and Al (Co) atoms in the same hexagon and two H atoms on the top sites of Al and Al (Co) atoms in the neighboring faces. The 1(12d) isomer is 0.62 eV less stable as compared to the 1(12c) isomer that is the most favorable. In order to further check the results obtained from the

B3LYP method, BE's for H on the top sites of $Al_{12}Co$ is calculated using the PW91 method. It is found that the BE's of hydrogen is 2.69 eV. This result is quite close to the value (2.88 eV) obtained from the B3LYP method.

Al_nCo (n=13-15) take the C_1, C_1 and C_s structures as their ground states, respectively. For Al_nCoH (n=13-15), the ground states reveal top H bonding to the Al atoms [Fig. 1(13b), 1(14b) and 1(15b)]. The spin multiplicity found for them are all doublet. Top on the neighboring Al and Co atoms ground-state structures are found for Al_nCo (n=13-15) [Fig. 1(13c), 1(14c) and 1(15c)].

Stability and fragmentation behavior

In order to check the stability of the lowest-energy isomers vibrational frequencies for selected clusters have been calculated using the B3LYP/lanl2dz level of theory. It is found that the lowest-energy isomers of all kinds of clusters discussed above have all real frequencies and are, therefore, stable. Figure 2 shows the plot of the BE of one and two H atoms on Al_nCo clusters. As discussed in the previous section, the BE is large for H with n=3, 5, 7, 10, 12, and 15 of Al_nCoH atoms. And, for 2H, clusters with n=3, 5, 10, 12, and 14 have higher BE's. The stability of these complexes is further studied from the fragmentation energies (Table 3). Channels with $Al_{n-1}CoH_m$, $Al_{n-2}CoH_m$, or $Al_{n-1}CoH_{m-1}$ molecule being one of the fragments have been studied. It is noted that in all these processes, the fragmentation energy is the largest for $Al_{15}CoH_2$ and therefore, it is expected to be among the most stable species. Also the fragmentation energies for

Al_3CoH, Al_8CoH_2, $Al_{14}CoH$, $Al_{14}CoH_2$, and $Al_{15}CoH$ are next largest for all these channels, suggesting them to be other stable clusters. On the other hand the fragmentation energy for $Al_{13}CoH_2$ is 0.74 eV for $Al_{n-1}CoH_m$ +Al channel and it is close to the lowest values. The small clusters of Al_4CoH also have lower values.

Please See Table 3 in the PDF Version

Bonding nature

In order to understand the bonding nature of hydrogen on aluminum cobalt clusters, the bond lengths in both hydrogenated clusters and pure aluminum cobalt clusters are discussed. From Table 1 and 2, one finds that the Al-Co bond lengths increase generally as the size of the cluster increases. The Al-Co, Al-H and

Co-H bond lengths for the top adsorption on Al_nCo clusters are in the range of 2.256-2.622, 1.599-2.052 Å and 1.505-1.740 Å, respectively. Thus, one can conclude that these bond lengths evolve very slowly with cluster size. In addition, the nearly constant value for Co-H and Al-H bond lengths on different clusters at specific adsorption sites suggests the similar nature of bonding of H in different clusters. From Table 2 and Fig. 1, one can also see that hydrogen would like to be onefold with the Al_nCo clusters.

Summary

The result on hydrogen interaction with aluminum cobalt clusters has been presented. Hydrogen undergoes chemisorptions and interacts strongly with aluminum cobalt clusters. The Al-on top sites are the most stable chemisorptions site for one hydrogen adsorption in most Al_nCo clusters except for Al_nCo (n=1, 4, 6, and 11) cluster. Top on the neighboring Al and Al atoms ground-state structures of Al_nCo (n=2, 3, 5, 7, 9, 10, 12, 13, 14, 15) and top on the opposite Al and Al atoms ground-state structures of Al_nCo (n=4, 6, 8, 11) are found for two hydrogen adsorption on Al_nCo cluster. And there is a slight increase in the mean Al-Co bond lengths after H adsorption on the lowest-energy sites of the most AlCo clusters. In addition, the nearly constant value for Co-H and Al-H bond lengths on different clusters at specific adsorption sites suggests the similar nature of bonding of H in different clusters. In general, the binding energy of H and 2H are both found to decrease with a decrease in the cluster size. And the result shows that large binding energies of the hydrogen atoms and large highest occupied and lowest unoccupied molecular-orbital gaps for Al_3CoH, $Al_{15}CoH$ and $Al_{14}CoH_2$ make these species behaving like magic clusters. The stability of these complexes is further suggesting being the stable clusters from the fragmentation energies.

Please See Figure 1 in the PDF Version

Please See Figure 2 in the PDF Version

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