Density functional theory study of hydrogenated MAl$_{12}$ (M = Al,Li,Na,K) clusters

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Abstract. The structure and electronic properties of bare and hydrogenated metal (M= Al,Li,Na,K) embedded Al$_{12}$ cage clusters have been investigated systematically by density functional theory calculations. It has been found that the most stable Al$_{12}$H$_{12}$ and MAl$_{12}$H$_{12}$ clusters possess icosahedral symmetry. The stability analysis shows that hydrogenation of clusters enhances the stability of aluminum clusters, and LiAl$_{12}$H$_{12}$ is the most stable of all clusters considered. Mulliken population analysis indicates that significant charge transfer occurs between alkali atoms and Al atoms. The higher electron density on the H atoms in relation to the deformation electron density shows that electron is partially transferred from Al atoms to hydrogen upon adsorption.

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Key words: density functional theory, aluminum clusters, hydrogenated, stability

1   Introduction

For more than a decade, hydrogen as an alternative to traditional energy sources such as oil and natural gas has been the focus of research and development efforts in all technologically advanced countries of the world. It is strongly believed that hydrogen can help to address the growing demand for energy and slow down global warming. Therefore, the search for a cheap, light weight, low pressure hydrogen storage material is the focus of many ongoing researches. Small metal clusters, with atom-by-atom tunability of electronic structure and chemical activity, have great potentials in developing novel materials [1-8]. Materials composed of these magic clusters may be used as hydrogen storage and high energy-density materials [9-20]. Many efforts have been made to understand the

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adsorption behavior of hydrogen on aluminum clusters, and it has been found that stable aluminum hydride clusters can be formed via the adsorption [21-30]. The discovery of a diverse series of aluminum-hydride clusters, or alanes, by Li and colleagues [29,30] has given further credence to the existing idea that aluminum clusters might serve as hydrogen storage media with an outstanding capacity [28]. Moreover, alanes might also be applied as high-energy-density solid fuel of rockets [31], where both aluminum and hydrogen are burned as fuel.

Goldberg and Yarovsky [32] pointed out that stable $Al_{12}H_{12}$ caged system can be formed when H atom is absorbed on Al_{12} cluster. In the present research, we have studied hydrogenated embedded Al_{12} cage clusters using density functional theory (DFT) calculations. Also we have embedded alkali atoms into the cavity for the purpose of enhancing the stability of hydrogenated aluminum cluster.

2   Theoretical methods

All calculations are performed using DFT provided in the DMOL3 package [33,34]. In these calculations, the DFT method has been treated within the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof exchange-correlation potential (PBE) [35]. All the electron treatment and double numerical polarized (DNP) basis sets are employed. Self-consistent field (SCF) calculations are conducted with a convergence criterion for 10^{-6} hartee on total energy scale. For SCFmixing scheme is used for mixing the input densities and output densities from the current iteration to obtain the input density for the next iteration in the iterative solution. The density mixing criteria for charge and spin are 0.0025 and 0.0025, respectively.

To benchmark the modeling elements of the computational method employed in this study, calculations are done for Al_{13} at the first stage, due to the availability of their experimental and theoretical data for comparison. The average binding energy and HOMO-LUMO gap of Al_{13} are calculated to be 2.698 eV and 1.904 eV, respectively, agreeing well with the theoretical values [32].

The number of distinct initial geometries is important to the reliability of the ground-state structures obtained. In order to obtain the lowest-energy structures of $MAl_{12}H_{12}$ (M=Li,Na,K) clusters, different spin multiplicities and a considerable amount of possible initial structures are considered. We obtained the specific initial structures by several ways as follows: (1) The energetically most favorable geometries of other hydrogenation of aluminum clusters previously published in literatures are also taken as the guidance. (2) Using the same method, we firstly optimized the equilibrium geometries of $MAl_{12}H$ clusters. The lowest energy of $MAl_{12}H$ is calculated according to a single H atom attachment to an on-top, bridge, or hollow site. In these orientations, the hydrogen atom can bind with one, two, and three Al atoms, respectively. Results show that the on-top form, previously reported [21] as the most stable structure of $Al_{13}H$ cluster, is energetically favorable. (3) In general, clusters with higher symmetry and fewer surface atoms
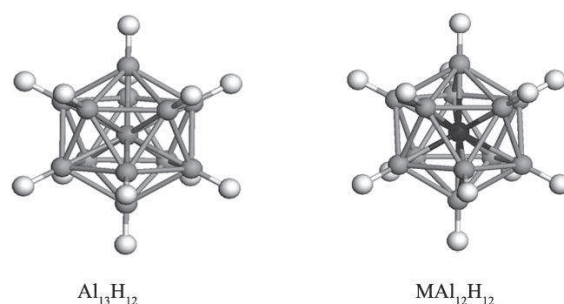
Figure 1: The calculated structures of $MAl_{12}H_{12}$ (M=Al, Li, Na, K) clusters.

are expected to be more stable. Therefore, according to a certain symmetry and the equilibrium geometries of $MAl_{12}H$ clusters, the initial geometry is constructed. Subsequently, it is found that each hydrogen atom is atop bonded to an Al ion, and all Al ions as well as hydrogen atoms are symmetrically equivalent in the cluster. For a given initial structure, spin-unrestricted calculations are performed for all allowable spin multiplicities. Starting with the spin singlet configuration of even-electron systems and the spin doublet configuration of odd-electron systems, the calculations are implemented until the minimum energy is reached. The harmonic vibration frequencies are also calculated so as to verify the nature of the stationary point on potential energy surfaces. If an imaginary vibrational mode is found, a relaxation along the coordinates of this mode is carried out until the true local minimum is actually obtained. Therefore, all isomers for each cluster are surely corresponding to the local minima.

3 Results and discussion

3.1 Structural features

The calculated lowest-energy structures of $Al_{13}H_{12}$ and $MAl_{12}H_{12}$ (M=Li,Na,K) clusters are shown in Fig. 1. For further analysis and discussion, geometry of bare and hydrogenated Al_{12} cluster is obtained in the same manner described in Section II. Fowler *et al.*[36] predicted that Al_{12} cluster had a D_{5d} symmetry at equilibrium using B3LYP/LanL2 DZ(d) basis set. However, we calculate the single point energy of Al_{12} cluster with our method and find it has an I_h symmetry whose energy is lower than that of D_{5d} structure by 0.12 eV. The different results are attributed to different computational details, but our result is consistent with that of Goldberg and Yarovsky [32]. In order to gain more insights into the structural features, main geometric parameters of bare and hydrogenated Al_{12}, Al_{13} and MAl_{12} (M=Al,Li,Na,K) clusters are summarized in Table 1.

Due to the symmetry, the nearest neighbor distance between Al atoms in Al_{12} is equivalent (2.725 Å) and is shorter than that in Al crystal where the shortest distance in the face-centered cubic lattice is 2.863 Å. It is also shorter than 2.812 Å, corresponding dis-

Table 1: Characteristic geometric features of bare and hydrogenated Al_{12} clusters.

Distance type	Al_{12}	Al_{13}	$Al_{12}H_{12}$	$Al_{13}H_{12}$	$LiAl_{12}H_{12}$	$NaAl_{12}H_{12}$	$KAl_{12}H_{12}$
Al1-Al2	2.725	2.812	2.732	2.787	2.772	2.829	2.918
Al-H			1.596	1.597	1.593	1.592	1.594
Al_t-CAl	1.438	1.478	1.436	1.465	1.457	1.487	1.534
CAl-CAl	2.212	2.396	2.329	2.373	2.358	2.406	2.482
H-H			4.410	4.468	4.446	4.503	4.593
COM-Al_s	2.569	2.675	2.599	2.651	2.636	2.690	2.775
Al_t-H			3.821	3.875	3.855	3.908	3.993
Al_t- Al_t	5.188	5.352	5.201	5.303	5.272	5.381	5.550
H_t - H_t			8.392	8.497	8.457	8.565	8.737

[*] Al_t- Top Al atom, Al_s - Surface Al atom, H_t- Top H atom, COM - Cluster center of mass, CAl - Center of Al pentagon.

tance between Al atoms in Al_{13} cluster. The contraction of AlDAl distance in relation to Al_{13} cluster might be attributed to the lack of repulsive central ion in Al_{12} cluster. This is further demonstrated by the fact that the distance between the central and surface Al ions in Al_{13} cluster is 2.675 Å, while the distance between the center of mass (COM) and Al_s (surface Al atom), an ion on the surface of Al_{12} cluster, is only 2.569 Å. It should also be noted that the bonding is affected by the cluster geometry structure, since AlDAl distance in Al_2 molecule (2.653 Å) is much shorter than that between any Al pair of the clusters considered in this paper.

Hydrogenated $Al_{12}H_{12}$ and $MAl_{12}H_{12}$ (M=Al,Li,Na,K) clusters also possess icosahedral symmetry, where each hydrogen atom is atop bonded to an Al ion and all Al_s ions as well as hydrogen atoms are symmetrically equivalent. The measured distances between Al ions, pentagon planes and AlDH bonds in the optimized ground state structure are also given in Table 1. All characteristic distances, including the shortest AlDAl distance in the hydrogenated $Al_{13}H_{12}$ and $MAl_{12}H_{12}$ (M=Al,Li,Na,K) clusters are shorter than those in the bare clusters (not shown) except for $Al_{12}H_{12}$ cluster. As previously reported elsewhere, there is a slight reduction in the AlDAl distance of some Al_nH_m ($n=6-13, m=1,2$) clusters, due to H adsorption on the lowest energy sites. In the present research, we have also found that the AlDAl distance of $Al_{13}H_{12}$ cluster is indeed shorter (by 0.025 Å) than that of bare Al_{13} cluster. However, the AlDAl distance of $Al_{12}H_{12}$ cluster is slightly longer (by 0.007 Å) than that of bare Al_{12}. This, we suppose, might be attributed to the expansion of Al_{12} cluster upon adsorption of 12 hydrogen atoms in the absence of central Al atom.

Besides, the AlDH distance of $Al_{13}H_{12}$ cluster is the longest in all the hydrogenated clusters under investigation, but the AlDH bond length (1.597 Å) of $Al_{13}H_{12}$ cluster is much shorter than 1.685 Å, the AlDH bond length of AlH molecule (Table 1). The reason might lie in that Al atoms in clusters share electrons that participate in bonding with

Table 2: Binding energy per atom E_T^b (eV), the binding energy of H atom E_H^b (eV), HOMO-LUMO gap E_g (eV), charge of the atom in the central site of the Al_{12} cage Q (e), charges of the H atoms q (e) , and vertical ionization potential IP (eV) in the lowest-energy structures of bare and hydrogenated Al_{12} clusters.

Cluster	E_T^b	E_H^b	E_g	Q	q	IP
Al_{12}	2.556		0.986			
Al_{13}	2.698		1.904	-0.045		
$LiAl_{12}$	2.485		0.524	0.198		
$NaAl_{12}$	2.259		0.479	0.328		
KAl_{12}	1.899		0.217	0.697		
$Al_{12}H_{12}$	2.595	2.568	2.692		-0.118	7.539
$Al_{13}H_{12}$	2.550	2.382	1.847	-0.225	-0.148	6.947
$LiAl_{12}H_{12}$	2.757	2.769	2.708	0.078	-0.117	7.659
$NaAl_{12}H_{12}$	2.484	2.764	2.584	0.084	-0.120	7.513
$KAl_{12}H_{12}$	2.362	2.654	2.579	0.598	-0.119	7.410

H atom; or, as pointed out by Kawamura *et al.*[23], the 3*s* electrons on Al atoms are hybridized with the 3*p* state creating a shorter bond with H. Moreover, although the distance of the core AlDAl is different in various hydrogenated clusters, the AlDH bond length and the separation between the centers of Al and H pentagon rings are approximately the same. This indicates that the center atom almost has no influence on the AlDH bond length.

3.2   Relative stabilities

It is well known that the relative stability of the aluminum-hydride clusters can be predicted by calculating the average binding energies $[E_b(n)]$, the vertical ionization potential (VIP), and HOMO-LUMO gaps. The average binding energies $[E_b(n)]$, the binding energy of the H atom, and VIP for Al_{12} and MAl_{12} (M=Al,Li,K,Na) clusters can be defined as

$$E_T^b = \frac{E_T(M) + nE_T(Al) + mE_T(H) - E_T(MAl_nH_m)}{n+m}$$
$$E_H^b = E_T(MAl_nH_m) - E_T(MAl_nH_{m-1}) - E_T(H)$$

where $E(\dots)$ is the single point energy based on corresponding optimized system.

The calculated average binding energies, the binding energy of the H atom, the VIP, and HOMO-LUMO gaps of Al_{12} and MAl_{12} (M=Al,Li,Na,K) clusters are shown in Table 2. Pure Al_{12} cluster has an average binding energy of 2.556 eV and a HOMO-LUMO gap of 0.986 eV, which are lower than those of icosahedral Al_{13} cluster (2.698 eV and 1.904 eV). This means that Al_{12} cluster is less stable than Al_{13}. MAl_{12} (M=Li,Na,K) clusters are least stable, having the biggest HOMO-LUMO gap of only 0.524 eV. However, hydrogen adsorption on the low energy sites of Al_{12}, Al_{13} and MAl_{12} (M=Li,Na,K) surfaces results
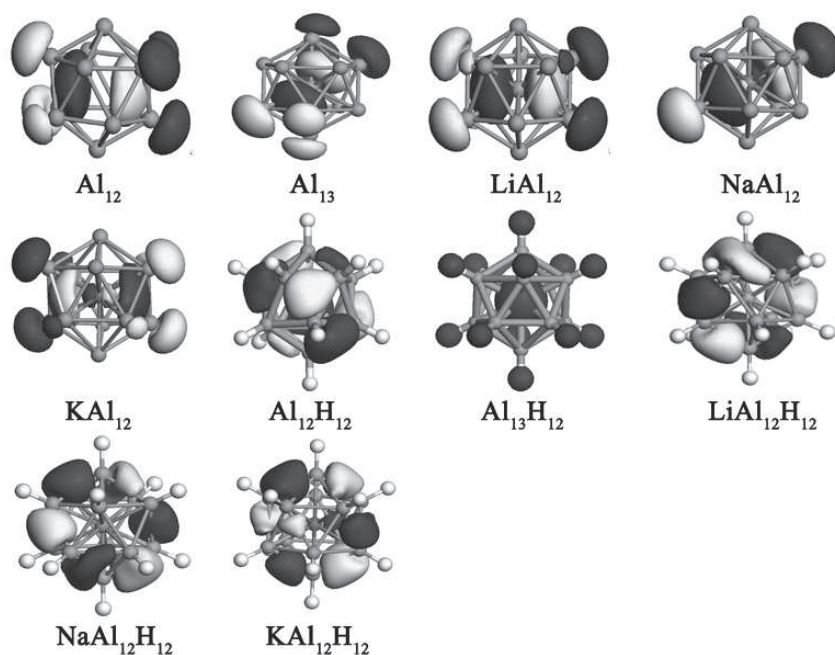
Figure 2: The HOMO charge density distribution of the corresponding clusters.

in change of stability of the clusters. Besides, hydrogenated clusters, except for $Al_{13}H_{12}$, are more stable than corresponding bare clusters. Moreover, $Al_{12}H_{12}$ cluster has a higher average binding energy (2.595 eV) and HOMO-LUMO gap (2.692 eV) than $Al_{13}H_{12}$ clusters (2.550 eV and 1.847 eV), indicating that $Al_{12}H_{12}$ cluster is more stable. This agrees well with that reported in Ref. [32]. Particularly, $LiAl_{12}H_{12}$ is the most stable of all clusters considered in this study, and it has a relatively large HOMO-LUMO gap of 2.708 eV and VIP of 7.659 eV. The reason might lie in that lithium ion has a relatively short radius, making it feasible for Li atom to form a closer group with Al core.

To further compare the relative stability of the hydrogenated clusters, we have calculated the binding energy of H atom in clusters $Al_{12}H_{12}$ and $MAl_{12}H_{12}$ (M = Al,Li,Na,K). The binding energy of H atom in $LiAl_{12}H_{12}$ is the highest (2.769 eV), and that of H atom in $Al_{13}H_{12}$ is the lowest (2.382 eV). In combination with the calculated binding energy of an isolated H_2 molecule (4.556 eV) and relevant experimental value (4.750 eV), we can see that the binding energy of H atom is much higher than half of the dissociation energy of H_2. This implies that H_2 can be dissociated on Al_{12}, Al_{13} and MAl_{12} (M=Li,Na,K).

3.3 HOMO-LUMO gap and charge transfer

As listed in Table 1, the hydrogenated clusters have larger HOMO-LUMO energy gaps than the bare clusters. This means that the hydrogenated clusters are relatively more chemically stable than the bare clusters. The reason might lie in that the dangling bonds
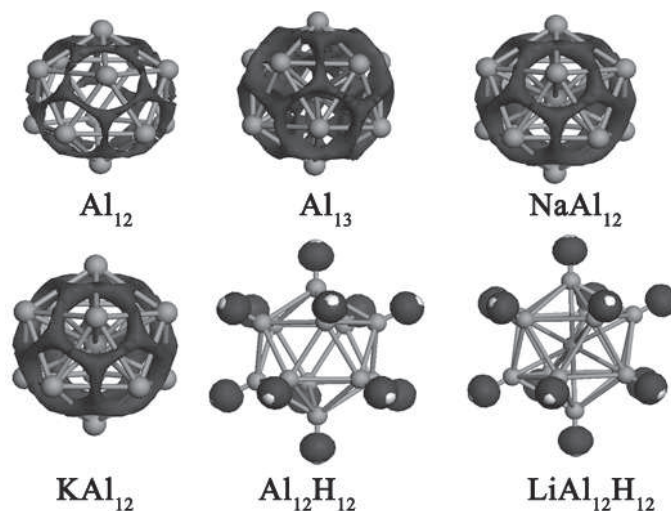
Figure 3: Deformation electron density of the corresponding clusters.

of the outer layer aluminum atom are eliminated after adsorbing a hydrogen atom. Considering that the regions with a highly localized charge have strong activity, we can naturally observe in Fig. 2 that most of the charge of additional electron is localized at the on-top sites of the surfaces of Al_{12} and MAl_{12} (M = Al,Li,Na,K) moieties. This well corresponds to the preference of Al_{12} and MAl_{12} (M = Al,Li,K,Na) moieties towards hydrogen absorption.

The charges of $Al_{12}H_{12}$ and $MAl_{12}H_{12}$(M=Al,Li,Na,K) clusters are mainly localized between two Al atoms, which indicates that the bridge sites should provide many opportunities to absorb more hydrogen atoms. Study in this respect is being underway.

Extensive researches have been conducted to determine the charge distribution in icosahedral Al_nH_m clusters. As previously suggested, electron transfer must occur in Al_nH_m clusters so that they exhibit magic behavior within the jellium model. Then the question arises whether electron transfer occurs from Al_n cluster to hydrogen or hydrogen atom donates its electron to Al_n framework upon adsorption onto the cluster surface. Khanna and Jena[37], Burkart *et al.*[38] suggested that the electron transfer occurs towards the Al_{13} framework in $Al_{13}H$ cluster so as to fill the open electronic shell of this cluster. Jung and Han [28,39] and Kawamura *et al.*[23] argued that the charge transfer from H to Al_{13} is unlikely, since the VIP of H (13.6 eV) is much higher than that of Al_{13} (6.49 eV), which might facilitate a charge transfer to hydrogen. They suggested that in contrast to the electron transfer in $NaAl_{13}$ or $LiAl_{13}$ whose alkali metal donates its electron to hydrogen-like Al_{13} "superatom", the electron transfer occurs from the Al_{13} superatom to hydrogen in $Al_{13}H$ cluster. The stability of $Al_{13}H$ cluster is attributed to a strong interaction between Al_{13} and H, as confirmed by the analysis of the charge density. Besides, our calculations show that Al_{12} cluster has a lower VIP of 5.92 eV. This implies that, as suggested in Refs. 23, 28, and 40, the charge transfer in this case is most likely to occur

from Al_{12} cluster to hydrogen atoms.

Mulliken population analysis indicates that significant charge transfer occurs in the aluminum hydride clusters under investigation, which is different from the case of neutral Al_{13} cluster whose Al atom at the central site is weakly anionic (see Table 2). This is primarily related to the different Pauling's electronegativity of the atoms. Namely, the electronegativity of various metallic atoms is ranked as $Al > Li > Na > K$. Due to the difference of electronegativity between K and Al atoms, there is a large amount of charge transformation in KAl_{12}. The Al atoms on the surfaces of MAl_{12} (M=Li,Na,K) clusters are all negatively charged, which results in increase of the Al-Al distance owing to columbic repulsion. Therefore, MAl_{12} (M=Li,Na,K) clusters have reduced stability than Al_{13}. Moreover, as seen in Table 2, the magnitude of the charges of Li, Na, and K atoms decreases after adsorption of hydrogen, and a large amount of charge transfer occurs from MAl_{12} (M=Li, Na, K) moiety to negatively charged hydrogen atoms. The variation of charge of MAl_{12} (M=Li,Na,K) clusters can also be identified by taking into account the spatially deformed charge distribution in the clusters. As shown in Fig. 3, the charge of MAl_{12} (M=Li,Na,K) clusters with a contour value of $0.025e/Å^3$ are mainly distributed between the two Al atoms before hydrogen adsorption, and a large amount of extra charge accumulates on the hydrogen atoms after hydrogen adsorption.

4   Conclusions

In summary, we have studied the structure and electronic properties of hydrogenated MAl_{12} (M=Al,Li,Na,K) clusters by using DFT with generalized gradient approximation. The analysis of stability in association with calculation of average binding energy, vertical ionization potential and HOMO-LUMO gap shows that the hydrogenated clusters have better stability than the aluminum clusters; and in particular, $LiAl_{12}H_{12}$ cluster has extremely high stability. The analysis of deformation electron density shows that H atoms in the hydrogenated MAl_{12} clusters have a higher electron density, which indicates that partial electron transfer from Al atoms to hydrogen atoms occurs upon hydrogen adsorption. Hydrogenated MAl_{12} (M=Al,Li, Na,K) clusters with increased stability could be used as promising candidates for synthesizing new assembled cluster materials. Nevertheless, some problems need to be solved before enabling hydrogen economy of the hydrogenated MAl_{12} (M= Al,Li,Na,K) clusters. Namely, the hydrogen capacity of the Al cluster hydrides is not high enough; the binding energy of hydrogen atoms in the clusters is small; and further investigation is needed to pursue hydrogenated aluminum clusters with a higher concentration of hydrogen atoms.

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