# 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.

## 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