



DFT study of structural, electronic and vibrational properties of pure $(\text{Al}_2\text{O}_3)_n$ ($n = 9, 10, 12, 15$) and Ni-doped $(\text{Al}_2\text{O}_3)_n$ ($n = 9, 10$) clusters

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ABSTRACT

The geometrical, electronic and vibrational properties of pure $(\text{Al}_2\text{O}_3)_n$ ($n = 9, 10, 12, 15$) clusters and Ni-doped $(\text{Al}_2\text{O}_3)_{9-10}$ clusters are investigated by density functional theory. There are four different Ni-doped $(\text{Al}_2\text{O}_3)_9$ clusters and one Ni-doped $(\text{Al}_2\text{O}_3)_{10}$ cluster taken into account. Compared with the pure clusters, the Ni-doped $(\text{Al}_2\text{O}_3)_{9-10}$ clusters have narrower HOMO–LUMO energy gaps. The results indicate that the impurity of Ni atom is mainly responsible for the reduction of the HOMO–LUMO energy gap. One characteristic vibration band at about 1030 cm^{-1} is found in the vibrational frequencies of the Ni-doped $(\text{Al}_2\text{O}_3)_{9-10}$ clusters, which is caused by the asymmetric Al–O–Al stretching vibration. Another band at around 826 cm^{-1} involving the characteristic vibration of Ni–O bond is in good agreement with experimental results.

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1. Introduction

Alumina nanostructures play an important role in many fields, such as adsorbents [1–4], coatings [5–11], soft abrasives [12], and catalysts [13] or catalytic supports [14–17], as a result of their fine particle size, high surface area and catalytic activity. Chemical and physical properties are dependent on the size and shape of the nanostructures. Thus the novel alumina clusters have attracted more attention from theoretical and experimental studies. Experimentally, aluminum oxide clusters were synthesized in a molecular beam by laser vaporization from an aluminum rod in a pulsed nozzle source [18]. Onischuk et al. predicted the possible existence of the $(\text{Al}_2\text{O}_3)_{1-5}$ and $\text{Al}_{20}\text{O}_{30}$ fullerene-like structures in the experimental process of combustion of Al droplets in air at atmospheric pressure [19,20]. Theoretically, Linnolahti et al. proposed models for alumina clusters and tubes based on the platonic solids and Archimedean polyhedra which were explored by ab initio methods [21]. In addition, they found that linear, cyclic, and cage-like aluminosilicates and alumina nanostructures could be rationalized by a topological analogy with boron nitrides and hydrocarbons [22]. The initial geometries of the alumina clusters were taken from

fragments of the Al_2O_3 bulk crystalline structure by Song et al. [23]. Moreover, Martinez and Tenorio investigated electronic structure of Al_3O_n and Al_3O_n^- ($n = 1-3$) clusters with density functional, quadratic configuration interaction and electron propagator calculations, and the calculated results were consistent with the accurate assignment of anion photoelectron spectra [24]. Sun et al. studied the cage structures of small $(\text{Al}_2\text{O}_3)_n$ ($n = 1-5$) clusters, both cage and cage-dimer structures of the $(\text{Al}_2\text{O}_3)_n$ ($n = 6-10$) clusters and the onion structure of $(\text{Al}_2\text{O}_3)_{10}$ cluster [25]. They found that the onion structure of $(\text{Al}_2\text{O}_3)_{10}$ cluster was more favorable than cage and cage-dimer structures at this size.

Compared with the pure alumina nanostructures, Ni-doped alumina clusters have more wide applications. Nickel modified alumina [26–28] is also a well-known catalyst for reforming of methane, which is very useful in petrochemical industry. Nickel oxide is used in sensing devices and could serve as a transparent semiconductor [29]. It indicates that the insertion of Ni atom into alumina have potential application in the manufacturing of semiconductor devices. However, it is still lack of theoretical studies about the Ni-doped alumina clusters.

In the present work, we investigate the geometrical structures and stability of $(\text{Al}_2\text{O}_3)_n$ ($n = 9, 10, 12, 15$) clusters. Especially, we focus on the structural and electronic properties of four different Ni-doped $(\text{Al}_2\text{O}_3)_9$ clusters and the Ni-doped $(\text{Al}_2\text{O}_3)_{10}$ cluster. The electronic properties of the pure and Ni-doped $(\text{Al}_2\text{O}_3)_{9-10}$ clusters are discussed by means of the obtained frontier elec-

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Table 1

Symmetry, bond lengths (Å), bond angles (°) and binding energies per atom (E_b /eV) for $(\text{Al}_2\text{O}_3)_n$ ($n=9, 10, 12, 15$) clusters at BLYP level.

Clusters	Symmetry	Al–O	O–Al–O	Al–O–Al	E_b
$(\text{Al}_2\text{O}_3)_9$	Cs	1.712–1.719	119.5	133.9	3.80
$(\text{Al}_2\text{O}_3)_{10}$	I_h	1.713–1.714	119.7	143.9	3.81
$(\text{Al}_2\text{O}_3)_{12}$	O_h	1.711–1.716	119.6	144.2	3.82
$(\text{Al}_2\text{O}_3)_{15}$	D_{5h}	1.709–1.714	119.9	144.9	3.83

tron density and density of states (DOS). Finally, the vibrational frequencies of the pure $(\text{Al}_2\text{O}_3)_n$ ($n=9, 10, 12, 15$) clusters and Ni-doped $(\text{Al}_2\text{O}_3)_{9-10}$ clusters are analyzed. A systematic study on the pure and metal-doped alumina clusters is expected, which will provide useful information for experimental and theoretical studies.

2. Computational method

Full geometry optimizations are carried out by DMol3 software based on the density functional theory (DFT) [30,31]. The ex-change-correlation interaction is treated within the generalized gradient approximation (GGA) [32] using the Becke's exchange [33] and Lee–Yang–Parr correlation [34] functional (BLYP). Full structural optimizations are obtained by using a convergence tolerance of energy of 1.0×10^{-5} Hartree, a maximum force is 0.002 Hartree/Å and a maximum displacement of 0.005 Å. In the electronic structure calculations, the double-numeric basis sets (DNP) is chosen. Self-consistent field (SCF) calculations are performed with a convergence criterion of 10^{-6} Hartree on the total energy. All the calculations employ a method based on Pulay's direct inversion of iterative subspace (DIIS) technique to accelerate SCF convergence. The density mixing criterion for charge and spin are set to 0.2 and 0.5, respectively. The orbital cutoff is set to be global with a value of 4.8 Å, and smearing is 0.005 Hartree. For the pure $(\text{Al}_2\text{O}_3)_n$ ($n=9, 10, 12, 15$) clusters, all electron treatment (all electron basis sets are used for light elements, such as hydrogen, carbon, and sulfur) is chosen [31]. For Ni-doped $(\text{Al}_2\text{O}_3)_{9-10}$ clusters, the DFT semi-local pseudo-potentials (DSPP) [35] are taken into account and spin-unrestricted calculations are performed. Vibrational frequencies are computed at the same level to characterize located structures. There are no imaginary frequencies in the process of geometry optimized, indicating that the optimized structures are indeed corresponded to the minima on the potential energy surface. In addition, vibrational frequencies for these clusters are obtained from a normal-mode analysis of the calculated Hessian matrix. Mayer bond order analysis gives valences that are close to the classical values, while Mulliken charges analysis and dipole moments analysis are all the oldest and still most frequently cited charge distributions. Total density of states (DOS) and partial density of states (PDOS) are calculated with taking into account a k-point of $(1 \times 1 \times 11)$.

3. Results and discussion

3.1. Pure and Ni-doped alumina clusters

In the case of pure $(\text{Al}_2\text{O}_3)_n$ ($n=9, 10, 12, 15$), we consider a series of possible initial configurations to obtain the stable ones. The optimized structures of pure clusters are shown in Fig. 1, and the corresponding geometrical parameters are listed in Table 1. In our study, the pure $(\text{Al}_2\text{O}_3)_n$ ($n=9, 10, 12, 15$) clusters are described as characterized by n -membered rings consisting of alternating Al and O atoms. The pure $(\text{Al}_2\text{O}_3)_9$ cluster displays a C_s symmetry with 8-, 10- and 12-membered rings, while the pure $(\text{Al}_2\text{O}_3)_{10}$ cluster shows twelve 10-membered rings with I_h symmetry. The pure $(\text{Al}_2\text{O}_3)_{12}$

Table 2

Bond lengths (Å), bond angles (°) and binding energies per atom, E_b (eV) for Ni-doped $(\text{Al}_2\text{O}_3)_{9-10}$ clusters at BLYP level.

Clusters	Ni–O	Al–O	O–Al–O	E_b
Ni1-doped $(\text{Al}_2\text{O}_3)_9$	1.805	1.725	119.3–120.2	3.70
Ni2-doped $(\text{Al}_2\text{O}_3)_9$	1.791	1.732	117.9–119.7	3.71
Ni3-doped $(\text{Al}_2\text{O}_3)_9$	1.793	1.734	117.9–121.1	3.71
Ni4-doped $(\text{Al}_2\text{O}_3)_9$	1.965	1.976	–	3.74
Ni-doped $(\text{Al}_2\text{O}_3)_{10}$	1.806	1.726	119.5–120.6	3.72

and $(\text{Al}_2\text{O}_3)_{15}$ clusters have the O_h and D_{5h} symmetry, respectively. In all clusters, the lengths of the Al–O bond are at a narrow range of 1.709–1.719 Å, which is very good agreement with the reported values [21,22,25]. The angles of O–Al–O for pure $(\text{Al}_2\text{O}_3)_n$ ($n=9, 10, 12, 15$) clusters are in the range of 119.5–119.9°. In addition, the angles of Al–O–Al increase from 133.9° to 144.9° along with increasing cluster size.

In the case of Ni-doped pure $(\text{Al}_2\text{O}_3)_9$ cluster, we take into account all of possible positions where a nickel atom can replace an aluminum atom. When a nickel atom replaces Al1, Al2 and Al3, Al4 in the pure $(\text{Al}_2\text{O}_3)_9$ cluster (Fig. 1), we can obtain the corresponding stable Ni1-, Ni2-, Ni3-, and Ni4-doped $(\text{Al}_2\text{O}_3)_9$ clusters, respectively. It is noticed that there is only one possible position for Ni doped in the pure $(\text{Al}_2\text{O}_3)_{10}$ cluster, and the Ni-doped $(\text{Al}_2\text{O}_3)_{10}$ cluster is also stable. The optimized structures are shown in Fig. 2, and the corresponding geometrical parameters are presented in Table 2. The structures of Ni1-, Ni2-, and Ni3-doped $(\text{Al}_2\text{O}_3)_9$ clusters have small changes with each other, but the structure of Ni4-doped $(\text{Al}_2\text{O}_3)_9$ cluster where there are four new Al–O bonds formation presents dramatic change among the stable Ni-doped $(\text{Al}_2\text{O}_3)_9$ clusters. In addition, there are no remarkable changes for the geometric structures between the pure and Ni-doped $(\text{Al}_2\text{O}_3)_{10}$ cluster.

In the structures of Ni1-, Ni2-, Ni3- and Ni4-doped $(\text{Al}_2\text{O}_3)_9$ clusters, Ni atom is threefold coordinated with three nearest-neighbor O atoms. The average lengths of Ni–O bond in the Ni1-, Ni2- and Ni3-doped $(\text{Al}_2\text{O}_3)_9$ clusters are 1.805, 1.791 and 1.793 Å, respectively. Moreover, the three O atoms are all twofold coordinated with the three corresponding nearest-neighbor Al atoms in the Ni1-, Ni2- and Ni3-doped $(\text{Al}_2\text{O}_3)_9$ clusters. The average lengths of the Al–O bond near Ni atom in the Ni1-, Ni2-, and Ni3-doped $(\text{Al}_2\text{O}_3)_9$ clusters are 1.725, 1.732 and 1.734 Å, respectively. In comparison with the lengths of Al–O bond in the pure $(\text{Al}_2\text{O}_3)_9$ cluster, the average lengths of the Al–O bond near Ni atom in the Ni1-, Ni2- and Ni3-doped $(\text{Al}_2\text{O}_3)_9$ cluster are all increased by 0.006–0.022 Å. In the Ni4-doped $(\text{Al}_2\text{O}_3)_9$ cluster, Ni atom is also threefold coordinated with three nearest-neighbor O atoms. The distance is 1.965 Å between Ni atom and its nearest-neighbor O atom with three-fold coordination. Obviously, it is reasonably that the O atom is bonding with near Al atom, namely, the new Al–O bond is formed. The length of new Al–O bond is 1.976 Å which is far larger than the lengths of other three Al–O bonds (1.727, 1.771, 1.785 Å). Moreover, the angles of O–Al–O for Ni1-, Ni2-, and Ni3-doped $(\text{Al}_2\text{O}_3)_9$ clusters are in the range of 117.9–121.1°, while the angles of O–Al–O present dramatic change for Ni-doped $(\text{Al}_2\text{O}_3)_9$ cluster. In one word, these structural parameters indicate that the geometric structures are in dependence on different doping sites. The average lengths of Ni–O and Al–O bonds for Ni-doped $(\text{Al}_2\text{O}_3)_{10}$ cluster are 1.806 and 1.726 Å, respectively. In addition, the angles of O–Al–O for Ni-doped $(\text{Al}_2\text{O}_3)_{10}$ cluster are in the range of 119.5–120.6°. It is noteworthy that the bond lengths and bond angles of the Ni-doped $(\text{Al}_2\text{O}_3)_{10}$ cluster are close to those of Ni1-doped $(\text{Al}_2\text{O}_3)_9$ cluster.

To analyze the stability of the pure clusters and the Ni-doped $(\text{Al}_2\text{O}_3)_{9-10}$ clusters, we calculate the binding energies per atom,

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