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Density functional theory study on the structural and electronic properties of Ag-adsorbed $(MgO)_n$ clusters

GE GuiXian[1†], JING Qun[1] & LUO YouHua[2,3]

[1] Key Laboratory of Ecophysics and Department of Physics, Normal College, Shihezi University, Shihezi 832003, China;
[2] School of Science, East China University of Science and Technology, Shanghai 200237, China;
[3] Institute for Theoretical Physics, Henan University, Kaifeng 475004, China

Equilibrium geometries, charge distributions, stabilities and electronic properties of the Ag-adsorbed $(MgO)_n$ ($n=1-8$) clusters have been investigated by density functional theory (DFT) with generalized gradient approximation (GGA) for exchange-correlation functional. The results show that hollow site is energetically preferred for $n\geqslant 4$, and the incoming Ag atoms tend to cluster on the existing Ag cluster. The Mulliken populations indicate that the interaction between the Ag atom and Magnesia clusters is mainly induced by a weak atomic polarization. The adsorbed Ag atom only causes charge redistributions of the atoms near itself. The effect of the adsorbed Ag atom on the bonding natures and structural features of Magnesia clusters is minor. Furthermore, the investigations on the first energy difference, fragmentation energies and electron affinities show that the $Ag(MgO)_4$ and $Ag(MgO)_6$ are the most stable among studied clusters.

Ag $(MgO)_n$ clusters, geometries, electronic properties

Bulk MgO could be a very good substrate for growing thin films. Small clusters often present substantial deviations in their physical and chemical properties when compared to the molecule and the bulk phase. So it is instructive to investigate MgO clusters. In recent years, there are many studies in binary metal oxide clusters[1−25] including mass spectra and collision induced fragmentation (CIF) data, classical simulations, and *ab initio* calculations on MgO clusters. Although a lot of investigations focus on $(MgO)_n$ clusters, there are few investigations on the doped $(MgO)_n$ clusters. On the other hand, silver, one of the noble metals, has practical importance because of its role in photography, catalysis, and its potential use in new electronic materials[26−28]. In recent years, a series of experimental[29−32] and theoretical work[33−37] have been done to investigate electronic and thermodynamic properties, and microscopic mechanism for Ag atom deposition on regular and defective surfaces. Theoretically, Inntam et al.[34] studied the adsorption of Ag atoms on regular MgO(001) surface by means of cluster models, an upright mode was found to be the stable structure for Ag tetramers deposited on MgO(001) surface. In another *ab initio* study, the isolated Ag atom was adsorbed on regular surface and the Ag adsorption was associated mainly with a weak atomic polarization induced by the interaction between Ag atoms and MgO substrate[35,36]. Campbell et al.[29] and Larsen et al.[30] studied the adsorption energies for Ag atom deposited on MgO(001) by calorimetry methods. They found that the Ag-MgO interaction was weak from the measured heat of adsorption. When the Ag atoms are adsorbed on the $(MgO)_n$ clusters, such questions as how the adsorbed metal atoms aggregate and how the structural configurations of this system vary with increasing coverage are raised. What effect do the Ag atoms have on the electronic structure of magnesia clusters? It is instructive to investigate small Ag-adsorbed $(MgO)_n$ clusters to un-

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[†] Corresponding author (email: geguixian@126.com)

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derstand chemical bonding, optical property and if such a small cluster has the particular directional adsorption.

In this work, the total energy of system was carried out to determine the stable geometries of the adsorbed atom. The equilibrium geometries, electronic properties, gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have been systematically investigated. The bond nature between Ag and magnesia clusters was investigated in terms of electron density.

1 The computational method

To search the lowest-energy structures of $Ag(MgO)_n$ clusters, we have considered a considerable amount of possible structural isomers for each size. Full geometry optimizations were performed using the spin-polarized density functional theory (DFT) in a $DMol^3$ package[38]. In the electronic structure calculations, all electrons treatment and double numerical basis including *d*-polarization function (DNP)[38] were chosen. The exchange-correlation interaction was treated within the generalized gradient approximation (GGA) using PW91[39] functional. Self-consistent field calculations were done with a convergence criterion of 10^{-5} hartree (1 hartree = 110.5×10^{-21} J) on the total energy. The density mixing criteria for charge and spin are 0.2 and 0.5, respectively. In the geometry optimization, the converged thresholds are set to 0.004 hartree/Å for the forces, 0.005 hartree for the displacement and 10^{-5} hartree for the energy change. A 0.001 hartree of smearing is applied to the orbital occupation. Harmonic vibrational frequencies were computed at the same level in order to characterize the located structures, the vibrational frequencies for all clusters are real, confirming that the optimized structure indeed correspond to minima on the potential energy surface. The on-site charges are evaluated via Mulliken population analysis[40]. To test the accuracy of the functional, we have calculated the dimers for Ag_2, MgO, AgO and AgMg by using different functions. The calculated results and experimental values are presented in Table 1. As can be seen from Table 1, the calculated results using PW91 functional are in good agreement with the experimental values. It indicates that the employed PW91 scheme is reliable for Ag_2 and MgO. Consequently, the PW91 functional is reliable and accurate enough to be applied to describe the properties of the $Ag(MgO)_n$ clusters in this paper.

2 Results and discussion

2.1 Structures and population analysis

In Figure 1, the lowest-energy structures of silver adsorbed on $(MgO)_n$ and $(MgO)_n$ are depicted. Table 2 gives the Mg-O bond length, which is near Ag atom for the lowest energy structure of $Ag(MgO)_n$ and $(MgO)_n$ clusters. To determine the most likely adsorption site of single Ag atom on $(MgO)_n$ clusters, four different positions such as Mg-top, O-top, hollow, and the bridge sites have been considered, respectively. In order to illustrate the effect of adsorbed Ag atom on Magnesia clusters, geometry optimizations of $(MgO)_n$ (n = 1—8) clusters are also calculated by using identical functional and basis sets. This result is in good agreement with previous theoretical work[12,24].

The geometry of MgO is linear with Mg-O bond length of 1.767 Å, and the final optimized geometries of Ag(MgO) are shown in Figure 1. The ground state configuration (1a) is a planar structure (C_s) whose Mg-O bond length is 1.830 Å. In the ground state structure, the Ag is absorbed on O-top site. As a comparison, the pure $(MgO)_2$ cluster is also plotted in Figure 1($2a_0$), which is also a planar structure (D_{2h}). When the Ag atom is placed to Mg-top, O-top, hollow, and the bridge sites in $(MgO)_2$ cluster. Finally, the structure Ag adsorbed on the bridge with Ag atom deviating from Mg atom is the ground state structure (in Figure 1(2a)). The corresponding Mg-O bond length compared with that of $(MgO)_2$, which is near the Ag atom, is increased from 1.883 to 1.977 Å. The Ag-O bond length is 2.202 Å, the

Table 1 The calculated and experimental parameters of the ground state of MgO, AgO, AgMg and Ag_2

Methods	MgO			AgO			AgMg			Ag_2		
	E_b (eV)	R (Å)	ω (cm^{-1})	E_b (eV)	R (Å)	ω (cm^{-1})	E_b (eV)	R (Å)	ω (cm^{-1})	E_b (eV)	R (Å)	ω (cm^{-1})
PW91	3.2054	1.767	739.79	2.6169	2.064	447.60	0.8678	2.705	186.92	1.644	2.89	181.78
BLYP	4.3003	1.779	724.05	3.6844	2.088	428.66	0.7380	2.757	174.32	1.495	2.677	159.78
BP	3.0928	1.770	738.36	2.4707	2.069	442.48	0.7845	2.718	182.68	1.492	2.649	175.63
PBE	3.1970	1.778	696.10	2.6019	2.068	443.64	0.8702	2.719	183.27	1.637	2.649	175.86
Exp.	3.5124a)	1.749a)	785.0a)							1.660b)	2.89c)	192.4c)

a) From ref. [41]; b) from ref. [42]; c) from ref. [43].

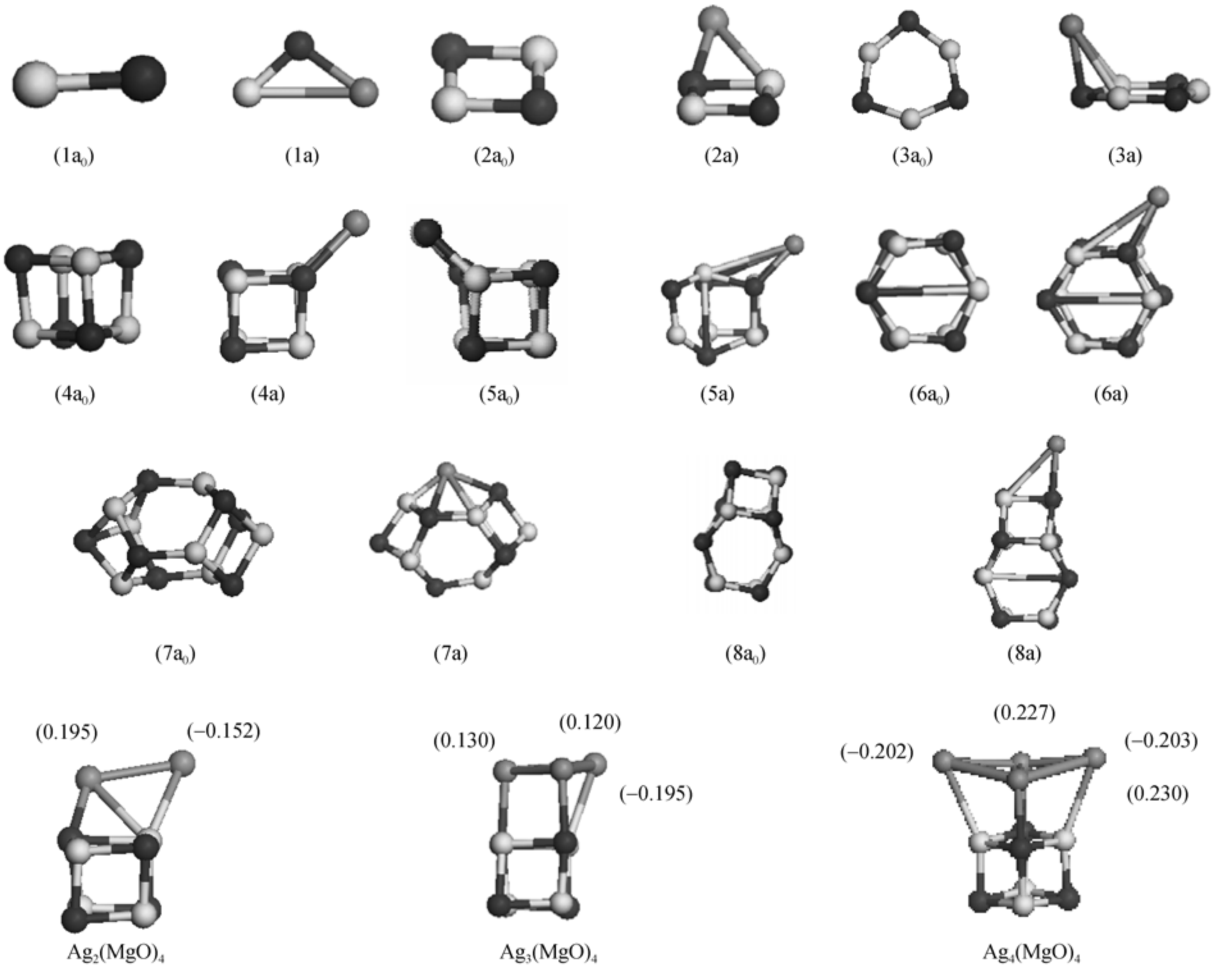


Figure 1 The lowest-energy structures for $Ag(MgO)_n$ and $(MgO)_n$ ($n = 1-8$) clusters. The white color balls represent Mg atom; the gray balls represent Ag atoms and the black balls represent O atom. Mulliken charges are given in parentheses.

Table 2 The Mg-O bond length r (Å) which is near Ag atom, atomic charge (e) on Ag, O atoms for the lowest energy structure of $Ag(MgO)_n$ and $(MgO)_n$ ($n = 1-8$) clusters

n	$(MgO)_n$		$Ag(MgO)_n$		
	O	$r_{\text{Mg-O}}$	Ag	O	$r_{\text{Mg-O}}$
1	–0.751	1.767	0.318	–0.804	1.830
2	–0.930	1.883	0.122	–0.876	1.977
3	–0.958	1.841	0.001	–0.868	1.892
4	–0.977	1.965	0.030	–0.916	2.115
5	–0.981	1.997	0.093	–0.915	2.012
6	–0.995	2.015	–0.008	–0.939	2.145
7	–1.002	1.965	0.014	–0.954	2.023
8	–0.998	1.916	–0.010	–0.941	1.964

Ag-Mg bond length is 2.777 Å and the angle (∠OAgMg) is 44.976°. The ground state structure of $(MgO)_3$ cluster is a pentagonal structure [in Figure 1(3a$_0$)]. The structure obtained by adsorbing a Ag atom on the O-top site of the pentagon is the lowest energy structure of $Ag(MgO)_3$ cluster. The corresponding Mg-O bond length compared with that of $(MgO)_3$, which is near the Ag atom, is increased from 1.841 to 1.892 Å. When $n = 4$, the ground state structure of $(MgO)_4$ cluster is a cubic structure (in Figure 1(4a$_0$)), The ground state structure of $Ag(MgO)_4$ cluster is an octahedron which is obtained by adsorbing a Ag atom on the top of the lowest energy structure for $(MgO)_4$. In this structure, the Ag atom is adsorbed on the hollow site.

In order to investigate the distinction of growth behavior for $Ag_m(MgO)_n$, a number of different initial configurations of $Ag_2(MgO)_4$, $Ag_3(MgO)_4$ and $Ag_4(MgO)_4$ clusters have been optimized. The most stable structures are shown in Figure 1. When the second Ag atom is added, it binds to the first Ag atom. One Ag atom gets about 0.152 electrons, the other loses 0.195 electrons. The cluster gains an additional 2.27 eV energy as the second Ag atom is attached to $Ag(MgO)_4$. When the third Ag atom is added, it is also adsorbed on the frontal two Ag atoms and three Ag atoms form a triangular configuration. The cluster gains an additional 1.395 eV energy as the third Ag atom is attached to $Ag_2(MgO)_4$. When the fourth Ag atom is placed $Ag_3(MgO)_4$, the Ag atom automatically moves to the $(Ag)_3$ site and four Ag atoms form a cymbiform structure. According to above analysis, it indicates that the Ag atoms are easy to form Ag islands on the face of $(MgO)_n$ clusters.

The lowest energy structure of $Ag(MgO)_n$ ($n = 5$—8) is also formed by adsorbing a Ag atom on the ground state of $(MgO)_n$ clusters, where Ag atom is adsorbed on hollow site with Ag atom leaning to O atom. For $Ag(MgO)_8$ cluster, the corresponding Mg-O bond length near Ag atom compared with that of $(MgO)_8$ is increased from 1.916 to 1.964 Å. As can be seen from Table 2, in $Ag(MgO)_n$ clusters, the corresponding bond length of Mg-O compared with that of $(MgO)_n$ is increased. The increased value of Mg-O is less in $Ag(MgO)_3$ and $Ag(MgO)_8$ cluster than that of other clusters, which indicates the interaction is small between Ag and corresponding magnesia clusters.

For the lowest-energy structure of $Ag(MgO)_n$ clusters obtained in this work, the most structure of $Ag(MgO)_n$ ($n = 1$—8) is formed by adsorbing a Ag atom on the ground state of corresponding $(MgO)_n$ ($n = 1$—8) clusters. The frame of $(MgO)_n$ clusters is not disturbed by the Ag atom. The Ag is absorbed on different sites with cluster size increasing, which is different from that of the adsorption of the single Ag atom on the bulk magnesia[36].

To further understand the interaction between $(MgO)_n$ clusters and Ag atom, the Mulliken charge of clusters is performed. Table 2 lists the Mulliken charge for the ground state structures. In (MgO) cluster, the charge on Mg atom is 0.751*e*. When the Ag atom is attached on it, the number of electrons lost by Mg atom decreases to 0.486*e*. Consequently, the Ag atom loses 0.318 electrons, and O atom gets 0.804 electrons. In $(MgO)_2$ cluster, two Mg atoms both lose 0.930 electrons, and each of O atom gets 0.930 electrons. The adsorption of the Ag atom causes redistribution of charges throughout the cluster. The charge on O atom near Ag is decreased to –0.876*e* and the Ag atom loses 0.122 electrons. For $(MgO)_3$ cluster, each of O atoms gets 0.958 electrons. When the Ag atom is absorbed on it, the charge is not in average distribution. The number of electrons gets by O atom decrease to 0.868*e*, while the charge on Ag atom is 0.001*e*. From $n = 4$—8, there are few electrons transferred between Ag atoms and $(MgO)_n$ clusters. The small charge transfer on Ag atom suggests that the Ag adsorption is associated mainly with a weak atomic polarization induced by the interaction between the Ag atom and magnesia clusters, which is the reason that the Ag atoms don't disturb the frame of $(MgO)_n$ clusters. For $Ag(MgO)_4$ clusters, when another Ag atom is added, $(Ag)_2$ loses 0.053*e*; the third Ag atom is added, the charge on $(Ag)_3$ cluster is 0.055*e*. For $Ag_4(MgO)_4$, $(Ag)_4$ cluster loses 0.052 electrons. According to above analysis, it may be concluded that a few Ag atoms are added to $(MgO)_4$ clusters, the transferred charge between $(Ag)_n$ ($n = 2, 3, 4$) and $(MgO)_4$ is also small. It indicates there are similar interactions between Ag atoms and $(MgO)_4$ clusters to that of single Ag and $(MgO)_4$ clusters.

2.2 The relatives and electronic properties

It is known that the relative stability of the different sized clusters can be predicted by calculating the averaged binding energy. The averaged binding energy for $(MgO)_n$ and $Ag(MgO)_n$ clusters can be defined as the following formula:

$$E_{\mathrm{b}}[(\mathrm{MgO})_n] = \frac{-E[(\mathrm{MgO})_n] + nE[\mathrm{Mg}] + nE[\mathrm{O}]}{2n}, \qquad (1)$$

$$E'_{\mathrm{b}}[\mathrm{Ag(MgO)}_n] = (-E[\mathrm{Ag(MgO)}_n] + nE[\mathrm{Mg}] + nE[\mathrm{O}] + E[\mathrm{Ag}])/(2n+1), \qquad (2)$$

where $E[(\mathrm{MgO})_n]$, $E[\mathrm{Ag(MgO)}_n]$, $E[\mathrm{Ag}]$, $E[\mathrm{O}]$ and $E[\mathrm{Mg}]$ represent the total energies of the $(MgO)_n$, $Ag(MgO)_n$, Ag, O and Mg, respectively.

The calculated results on the averaged energies for $(MgO)_n$ and $Ag(MgO)_n$ clusters are plotted in Figure 2. As shown in Figure 2, the averaged binding energies increase dramatically with cluster size increasing. Thus, the clusters can continue to gain energy during the growth process. It is observed that the rate of the increase for the two species clusters is almost the same.

The relative stabilities of these clusters can be better

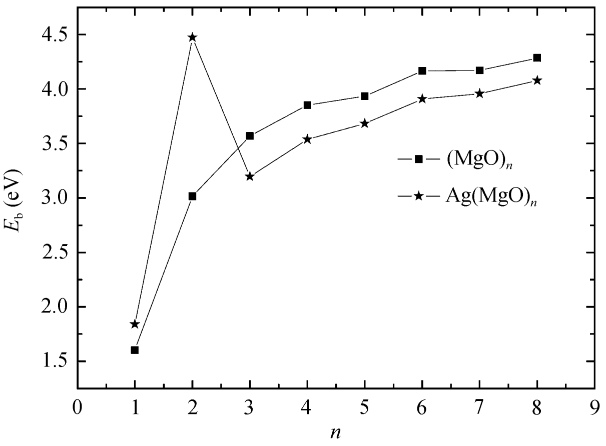


Figure 2 Binding energy versus cluster size for Ag(MgO)$_n$ and (MgO)$_n$ (n=1–8) clusters.

understood by calculating the incremental formation energies, i.e., the first order difference of cluster energies. We define the $\Delta E_b(n)$ as the following formula:

$$\Delta E_b(n) = E_b(n) - E_b(n-1), \qquad (3)$$

where $E_b(n)$ is the total binding energy of clusters. The first order difference of cluster energies for (MgO)$_n$ and Ag(MgO)$_n$ clusters are all presented in Figure 3. According to Figure 3, it shows apparently that the maximum values are 4, 6 among the investigated clusters, reflecting that the Ag(MgO)$_4$, Ag(MgO)$_6$ and (MgO)$_4$, (MgO)$_6$ clusters are the most stable geometry. It is noticed that the trend of the first order difference for (MgO)$_n$ and Ag(MgO)$_n$ clusters is almost the same, which indicates the small effect of Ag atom on the bonding natures of magnesia clusters.

The fragmentation energies (*FE*) and the electron affinities (*VEA*) are another useful quantities for determining the stability of clusters. The fragmentation energy and the electron affinities (*VEA*) of Ag(MgO)$_n$ clusters can be defined by the following formula:

$$FE[n,n-1] = (E[\mathrm{Ag(MgO)}_{n-1}] + E[\mathrm{MgO}] - E[\mathrm{Ag(MgO)}_n]), \qquad (4)$$

$$VEA = E(n) - E(n)^-. \qquad (5)$$

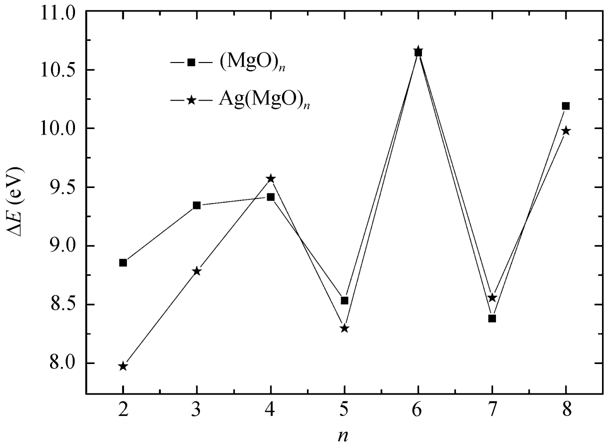


Figure 3 The first order difference of cluster energies versus cluster size for Ag(MgO)$_n$ and (MgO)$_n$ (n = 2—8) clusters.

The calculated fragmentation energies for these clusters are also shown in Figure 4. There are peaks at Ag(MgO)$_4$, Ag(MgO)$_6$, and subsequent dips suggest these clusters to be the most stable ones, which is in agreement with the result from first-order difference of energies.

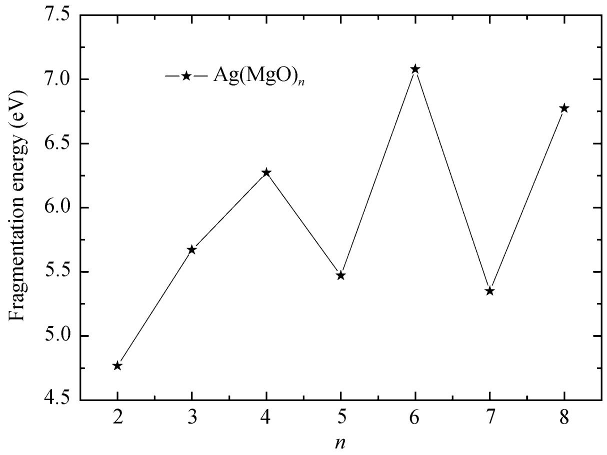


Figure 4 Fragmentation energy of the total energies for Ag(MgO)$_n$ (n = 1—8) clusters.

The electron affinities as a function of cluster size are shown in Figure 5. The *VEA* shows an odd-even alternation for the Ag(MgO)$_n$ clusters. The Ag(MgO)$_4$ and

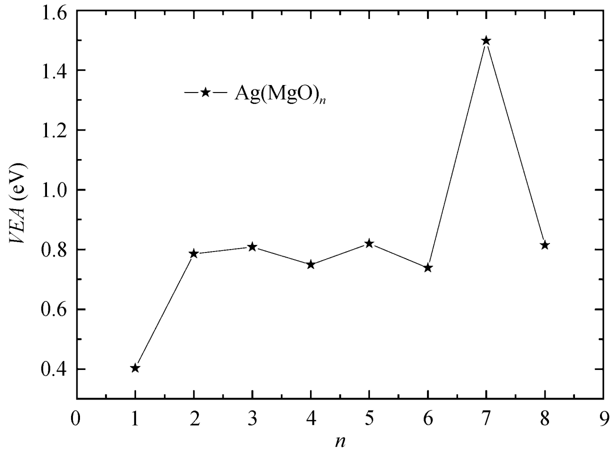


Figure 5 The electron affinities (*VEA*) of the total energies for Ag(MgO)$_n$ (n = 1—8) clusters.

$Ag(MgO)_6$ are found to be particularly stable on the basis of electron affinity, with lower values of electron affinity than other clusters in the series.

The dissociation products of clusters are useful in vapor deposition or adatom adsorption on surfaces[44]. The most possible dissociation channels of $Ag(MgO)_n$ clusters considered as well as the corresponding dissociation are given in Table 3. The dissociation energies of the favorable dissociation channel, namely,

$$A_mB_n \rightarrow A_m + B_n \tag{6}$$

are defined by the following formula:

$$E = E[A_m] + E[B_n] - E[A_mB_n]. \tag{7}$$

Table 3 The most favorable dissociation channel and the dissociation energies (E_d (eV)) (the adsorption energies)

Clusters	Dissociation channel	E_d
$Ag(MgO)$	$Ag+MgO$	2.312
$Ag(MgO)_2$	$Ag+(MgO)_2$	1.429
$Ag(MgO)_3$	$Ag+(MgO)_3$	0.869
$Ag(MgO)_4$	$Ag+(MgO)_4$	1.023
$Ag(MgO)_5$	$Ag+(MgO)_5$	0.786
$Ag(MgO)_6$	$Ag+(MgO)_6$	0.803
$Ag(MgO)_7$	$Ag+(MgO)_7$	0.978
$Ag(MgO)_8$	$Ag+(MgO)_8$	0.768

The most favorable dissociation channel for the $Ag(MgO)_n$ clusters contains $(MgO)_n$ as a fragment, suggesting that the $(MgO)_n$ are more stable. The adsorption process is a converse process of the dissociation. The dissociation energies decrease with the cluster size increasing, suggesting that the energies absorbing one Ag atom are small as the cluster size increases. It indicates that the Ag atom is not easily adsorbed on the magnesia cluster as the size increases. When $n = 3$, 8, adsorption energies are smaller than that of others, which indicates Ag has small effect on $(MgO)_n$ and agrees with less increased of Mg-O bond length for $Ag(MgO)_3$ and $Ag(MgO)_8$ cluster.

The electronic properties of clusters are discussed by examining the energy gap between the HOMO and LUMO. The HOMO-LUMO gaps for $Ag(MgO)_n$ and $(MgO)_n$ clusters of the most stable structure are shown in Figure 6. As can be seen from Figure 6, the gaps of the pure $(MgO)_n$ clusters are from 0.7207 to 3.289 eV. When a single Ag atom is adsorbed, the gaps are from 1.963 to 0.000789 eV. When the second Ag atom is added to $Ag(MgO)_4$ cluster, the HOMO-LUMO gap of $Ag_2(MgO)_4$ is increased to 2.221 eV. When the

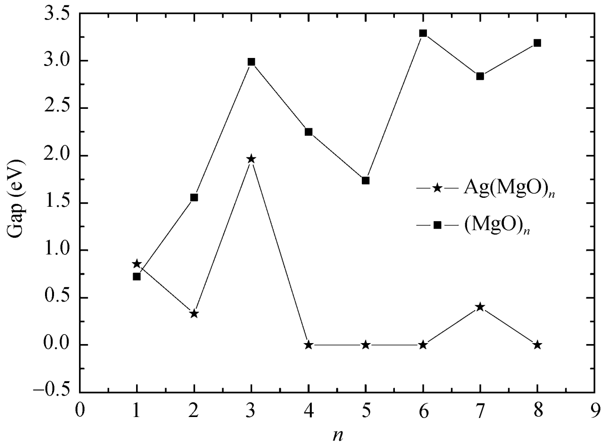
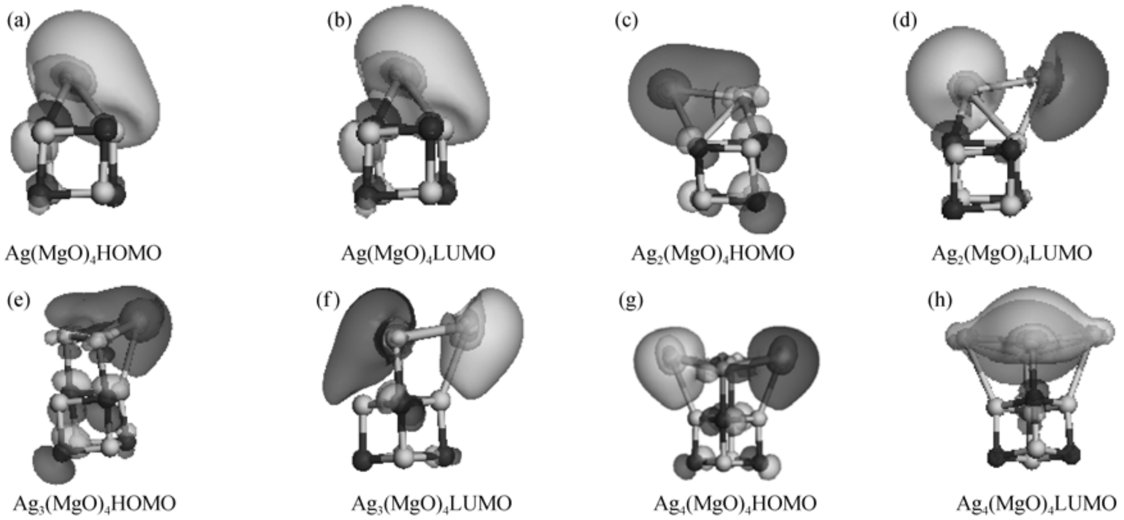


Figure 6 The energy gap between HOMO and LUMO versus the size of $Ag(MgO)_n$ and $(MgO)_n$ ($n = 1-8$) clusters.



$Ag(MgO)_4$HOMO $Ag(MgO)_4$LUMO $Ag_2(MgO)_4$HOMO $Ag_2(MgO)_4$LUMO

$Ag_3(MgO)_4$HOMO $Ag_3(MgO)_4$LUMO $Ag_4(MgO)_4$HOMO $Ag_4(MgO)_4$LUMO

Figure 7 HOMO and LUMO for $Ag(MgO)_4$, $Ag_2(MgO)_4$, $Ag_3(MgO)_4$ and $Ag_4(MgO)_4$ clusters.

third Ag atom is added to $Ag_2(MgO)_4$ cluster, the HOMO-LUMO gap of $Ag_3(MgO)_4$ is increased to 1.517 eV. When a Ag atom is adsorbed on the $Ag_3(MgO)_4$, the HOMO-LUMO gap of $Ag_4(MgO)_4$ is 1.920 eV. When a few Ag atoms are adsorbed $(MgO)_4$ cluster, the HOMO-LUMO gaps change a little , which indicates the gaps of $Ag_m(MgO)_4$ are relatively insensitive to the cluster size.

In order to further probe the adsorption of many Ag atoms on magnesia, the electronic structure of $Ag(MgO)_4$, $Ag_2(MgO)_4$, $Ag_3(MgO)_4$ and $Ag_4(MgO)_4$ clusters have been analyzed by studying the HOMO and LUMO. As shown in Figure 7, it can be seen that the electron density is almost populating on the Ag atoms and these neighboring atoms, which indicates that the main contribution to these frontier orbital comes from the Ag atom and these neighboring atoms. This suggests that the incoming Ag atom will preferably bind with an existing Ag atom in the next growth stage. The tendency to form Ag islands is dependent on the distribution of the HOMO and LUMO.

3 Conclusions

By using first-principle DFT-GGA calculations, the geometries, stabilities, and electronic properties of the Ag-adsorbed $(MgO)_n$ ($n = 1-8$) clusters have been systematically studied. The results are summarized as follows:

(1) Among various possible adsorption sites, O-top site is energetically preferred for $n \leqslant 3$, hollow site is energetically preferred for $n \geqslant 4$, and the incoming Ag atoms tend to cluster on the existing Ag clusters leading to the formation of Ag islands.

(2) Mulliken populations indicate that the adsorbed Ag atom only causes charge redistributions of the atoms near itself. The effect of the adsorbed Ag atom on the bonding natures and structural features of the magnesia clusters is minor. The interaction between the Ag atom and magnesia clusters is mainly induced by a weak atomic polarization.

(3) The energy gaps between the highest occupied and lowest unoccupied molecular orbit (HOMO-LUMO) remarkably decrease compared with the pure $(MgO)_n$ ($n = 1-8$) clusters. The investigations on the first energy difference, fragmentation energies and electron affinities show that the stabilities of the $Ag(MgO)_n$ ($n = 4$, 6) clusters have been enhanced.

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