Lowest-energy structures of \((\text{MgO})_n\) \((n = 2–7)\) clusters from a topological method and first-principles calculations

Liang Hong\textsuperscript{a}, Haoliang Wang\textsuperscript{a}, Jingxin Cheng\textsuperscript{a}, Lingli Tang\textsuperscript{b,c}, Jijun Zhao\textsuperscript{a,b,*}

\textsuperscript{a} School of Physics and Optoelectronic Engineering, Dalian University of Technology, Dalian 116024, China
\textsuperscript{b} College of Advanced Science and Technology, Dalian University of Technology, Dalian 116024, China
\textsuperscript{c} School of Mathematical Sciences, Dalian University of Technology, Dalian 116024, China

Abstract

A topological method combined with first-principles calculations is used to generate isomer structures and to globally search on the potential energy surface of \((\text{MgO})_n\) clusters with \(n = 2–7\). In addition to the previously reported ground-state configurations, our approach has located many new metastable isomer structures. The growth pattern of MgO clusters can be classified into three motifs: the expansion of two-dimensional ring-like structures, the combination of basic units like quadrangle and hexagon, and the addition of atoms to smaller-sized clusters. The size-dependent stability and electronic properties of MgO clusters are analyzed. Hexagonal ring-like unit is found highly stable for \((\text{MgO})_n\) clusters, while the \((\text{MgO})_5\) cluster is not as stable as the clusters of other sizes.

1. Introduction

Magnesium oxide (MgO) is a prototype of simple metal oxides, which is widely used in technological applications. Its powder is considered as a kind of dopants to form high-temperature superconductor thick films [1,2] and also a very important metal oxide supporter of catalysis [3,4]. Bulk MgO is known as an inert material with a high melting point, as well as a typical wide gap insulator [5]. Recently, MgO nanostructures such as nanorods and nanotubes have been successfully fabricated and their physical properties have been investigated [6,7]. Thus, it is fundamentally interesting to elucidate the growth behavior of MgO clusters which can be considered as the embryo of MgO nanostructures.

In the past two decades, the atomic structures of small-sized MgO clusters have been investigated both experimentally and theoretically [8–25]. Saunders carried out experiments in a triple quadrupole mass spectrometer for MgO clusters and observed mass spectrum which indicated the stability of \((\text{MgO})_3\) subunits [8,9]. Ziemann and Castleman performed experimental measurements using laser-ionization time-of-flight mass spectrometry and found "magic clusters" for \((\text{MgO})_n\) clusters at \(n = 2, 4, 6, 9, 12, \text{and 15} [10]. Besides, they also performed rigid ion model calculations on these clusters, and found that the two-dimensional ring structures are energetically favorable when \(n = 2, 3, 4, 5\) and 7 [11]. Semi-empirical tight-binding calculations on \((\text{MgO})_n\) clusters \((n = 1–6)\), were performed by Moukouri and Noguera [12]. Regular shapes like square, regular hexagon, regular octagon and cube were predicted to be stable for small MgO clusters. However, Wilson showed that the perfect rectangle and hexagon are less stable after studied \((\text{MgO})_n (n < 30)\) clusters using a compressible-ion model. He found that nanotubes based on stacked hexagons are energetically favorable for small MgO clusters [13,14].

In addition to the empirical or semi-empirical simulations, more accurate \textit{ab initio} calculations on \((\text{MgO})_n\) clusters were carried out by Recio [15,16], Malliavin and Coudray [17], de la Puente et al. [18] and Jain et al. [19], respectively. Similar structures were reported for small-sized MgO clusters, e.g., the planar ring-like configurations for \((\text{MgO})_n (n = 2–5)\), the cubic structure as the global minimum of \((\text{MgO})_n\), the double hexagons structure and the double cubes structure for \((\text{MgO})_n\). However, the global minimal structures of \((\text{MgO})_5\) and \((\text{MgO})_6\) clusters were still under debate. For example, the structure of \((\text{MgO})_5\) predicted by Malliavin and Coudray has one more Mg–O bond than that reported by others. The ground state structure of \((\text{MgO})_7\) obtained by Puente with Coulomb–Hartree–Fock correlation correction is the bulk-like \((\text{MgO})_5\) piece with an additional MgO molecule, which has one less Mg–O bond than that presented by Recio; while Jain considered a cage-like structure as the global minimum for \((\text{MgO})_7\) cluster.

Using a hybrid \textit{ab initio} genetic algorithm method, Kwapien et al. [20] recently investigated the structural diversity and flexibility of MgO gas-phase clusters, to speed up the DFT calculations.
Their lowest-energy structures of \((\text{MgO})_n\) \((n = 2–7)\) clusters coincide with the predictions by Jain et al. [19]. Despite the aforementioned extensive studies, there is still controversy in the ground state structures of neutral MgO clusters even in small-sized ones. Since it is difficult to find a global minimum for a function with multiple global minima, the calculated structures can be easily entrapped in local minima. Moreover, merely limited number of initial structures was presumed in the previous studies, thus the reported structures cannot be guaranteed to be the global minimum. In this paper, a topological method is presented, which is capable of generating all the possible structures of MgO clusters under certain rules for the coordination number (CN) of each Mg and O atom. This new method was employed to search for the global minima of \((\text{MgO})_n\) \((n = 2–7)\) clusters. Besides the structures presented by the previous studies, some new low-energy structures were found.

2. Methods

2.1. Topological method

Due to the ionic character of the chemical bonding in MgO clusters, Mg and O atoms tend to arrange alternately. Thus, it is reasonable to rule out the Mg–Mg and O–O bonds and only consider Mg–O bonds in the MgO cluster structures. As proposed in our recent paper, the topological structure of a \((\text{MgO})_n\) cluster can be represented by a numerical sequence consisting of a series of integers that describe the connectivity of each Mg and O atom. As illustrated in Fig. 1, either the four Mg atoms or the four O atoms are numbered from 1 to 4 in the structure of \((\text{MgO})_4\), with their connectivity presented in the table on the right-hand side. Its topological sequence \((123124134234)\) is generated by combining all the integers in the structure of \((\text{MgO})_4\), with their connectivity presented in the table on the right-hand side. Its topological sequence \((123124134234)\) is generated by combining all the integers in the structure of \((\text{MgO})_4\), with their connectivity presented in Table 1. According to previously reported MgO cluster structures [8–25], here the possible CNs of both O and Mg atoms are considered to be one to six. The topological rule for Mg atoms is set to be the same as for O atoms. The maximal numbers of i-coordinated O atoms \((i = 1–6)\) in our structures are listed in Table 1. With regard to \((\text{MgO})_2\) and \((\text{MgO})_3\) clusters, we have performed an exhaustive search with all possible CNs.

Structures with one-coordinated atoms are not generated for \((\text{MgO})_n\) \((n = 4–7)\) clusters. Since the optimization results for \((\text{MgO})_n\) \((n = 2–6)\) clusters indicate that structures with many two-coordinated atoms are energetically unfavorable, thus for \((\text{MgO})_n\), the maximal numbers of two-coordinated Mg and O atoms are constrained to be two. Besides, relatively few O atoms of higher CN is considered in \((\text{MgO})_n\) \((n = 4–7)\) cluster, because the influence of the large and coordination-dependent polarizabilities of O atoms favors the formation of surface oxide sites, structures with high-coordinated O atom are not energetically competitive until large values of \(n\) are attained [27].

Structures that have two Mg (O) atoms bonding with the same three or more O (Mg) atoms are energetically unfavorable according to the optimization results of \((\text{MgO})_n\) \((n = 2–5)\) clusters, thus such structures were not generated for \((\text{MgO})_n\) and \((\text{MgO})_7\) clusters.

2.2. Ab initio methods

First, the initial structures generated by the above topological method were roughly relaxed with an empirical force field to achieve a reasonable three-dimensional geometry. These structures are then optimized using all-electron density functional theory (DFT) method as implemented in the DMol3 package [28,29]. Generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) function [30] was used for describing the exchange-correlation interaction. Double numerical basis set including d-polarization function (DND) were adopted [28,29]. Geometry optimization was performed without symmetry constraint using a convergence criterion of \(1.0 \times 10^{-5}\) Hartree on the maximum energy gradient and 0.005 Å on the maximum displacement for each atom. Self-consistent field (SCF) electronic structure calculations were carried out with a convergence criterion of \(10^{-6}\) Hartree on the total energy.

The present computational scheme is validated by comparing the DFT results and experimental data for the MgO monomer and bulk solid. The present PBE/DND methodology reproduces most experimental data quite well. For example, the Mg–O bond length, binding energy, vibrational frequency of MgO monomer from our calculations are 1.745 Å, 2.39 eV/atom, 808.6 cm\(^{-1}\) respectively, which agree reasonably with experimental values of 1.749 Å, 1.28 eV/atom, 785 cm\(^{-1}\) (except that the binding energy is overestimated by about 1 eV/atom) [31,32]. For MgO bulk, the theoretical lattice constant (4.23 Å) and cohesive energy (5.98 eV/atom) also coincide well with experimental data of 4.21 Å and 6.235 eV/atom [33,34]. Therefore, the DFT method employed here is suitable to describe the structures and energetics of the MgO clusters.

3. Results and discussion

The numbers of initial configurations and the locally stable structures after DFT relaxation for \((\text{MgO})_n\) \((n = 2–7)\) clusters are summarized in Table 2. Upon optimization, a large amount of structures that initially appeared to be discrepant were finally transformed into the same structures. As a result, the number of locally stable isomer structures reduces significantly, compared with that of the initial structures from topological method. Nevertheless, we still obtained

<table>
<thead>
<tr>
<th>O(i)</th>
<th>Bonded Mg(j)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 2 3</td>
</tr>
<tr>
<td>2</td>
<td>1 2 4</td>
</tr>
<tr>
<td>3</td>
<td>1 3 4</td>
</tr>
<tr>
<td>4</td>
<td>2 3 4</td>
</tr>
</tbody>
</table>

Topological sequence: 123 124 134 234

Fig. 1. Schematic graph of converting a three-dimensional \((\text{MgO})_4\) structure (left) into its topological sequence (right).
plenty of stable isomer structures whose number increases rapidly as the cluster size grows, e.g., from 1 isomers for (MgO)$_3$ to 130 isomers for (MgO)$_7$. Hence our method is capable of locating many locally stable structures on the PES that have not been reported in previous work.

The lowest-energy structures of (MgO)$_n$ clusters ($n = 2–7$) are shown in Fig. 2. Some metastable isomers are shown in Fig. 3, together with the relative energies of these isomers with respect to the lowest-energy structures. Vibrational analysis of all reported configurations was carried out to ensure that there are no imaginary frequencies corresponding to the saddle points on the potential energy surface. The global minimal structures obtained in this work agree excellently with the previous results by Jain et al. [19] and Kwapien et al. [20]. Planar ring-like configurations are found to be more favorable for (MgO)$_2$ and (MgO)$_3$ (see Fig. 2), in which each Mg (O) atom bonds with two O (Mg) atoms in an alternative way. The transition from two-dimensional (2D) to three-dimensional (3D) structures occurs at (MgO)$_4$, which owns a distorted cubic structure ($T_d$) as its global minimum. The most stable structure of (MgO)$_5$ ($C_s$ symmetry, 5a in Fig. 2) can be obtained by adding one MgO molecule to the edge of (MgO)$_4$ cube, which opens a Mg–O bond on the (MgO)$_4$. The lowest-energy $D_{3d}$ structure of (MgO)$_6$ is formed by two stagger hexagonal rings with Mg and O atoms distributed alternatively (6a in Fig. 2). The ground state of (MgO)$_7$ possesses a cage-like structure of $C_{3v}$ symmetry, again with Mg and O atoms located evenly on the vertices. Except for (MgO)$_5$ which contains a pair of two-coordinated O and Mg atoms, all the 3D structures of (MgO)$_n$ with $n = 4, 6, 7$ contain only the three-coordinated atoms.

In addition to the above global minima, we also discuss the meta-stable isomers obtained from our global search method. For the (MgO)$_3$ cluster, we obtained only one finally stable structure although eleven initial structures were generated by our topological method. The structure of merged quadrangles is a popular motif in larger clusters (4c, 5c, 6b in Fig. 3). But in the case of the (MgO)$_3$ cluster, the isomer composed of two merged quadrangles is not stable and transformed to 3a after DFT optimization. The planar structures for (MgO)$_4$ (4b, 4c, 4d) and (MgO)$_5$ (5c, 5d, 5e) are 1–1.5 eV energetically less favorable than the lowest-energy structures. Planar structures for (MgO)$_6$ and (MgO)$_7$ were also obtained but not shown here owing to their instability (relative energy higher than 3 eV). Both the structures of 4b and 4c were reported in Ref. [16,18,25] but in a contrary order. The 5b structure ($C_{4h}$) is 0.76 eV less stable than the 5a structure and has not been reported previously. The structure 6b which has been reported in Ref. [17–19,24,25] can be considered as a fragment of MgO bulk solid and is only 0.33 eV less stable than the ground state 6a. Both 6a and 6b are significant in constructing large-sized clusters, noticing that 6a can be viewed as a section of hexagonal MgO nanotube. The structure 6c can be constructed by adding a (MgO)$_2$ subunit to 4a; 6d can be obtained by removing one Mg–O bond from 6c. However, both 6c and 6d have large relative energies (over 2 eV) with respect to 6a. The 7b and 7d isomers can be obtained by capping one MgO molecule to the most stable 6a structure for (MgO)$_6$. Similarly, the 7c, 7g, 7h structures can be constructed by adding one MgO molecule to 6b in different ways. Besides, 7g and 7h isomers with relative energy of about 1 eV have not been reported previously. Interestingly, 7g can be transformed into 7h by replacing each O (Mg) atom with Mg (O) atom; the same connection was found between 7e and 7i isomers. Considering that 7e (7g) is more stable than 7i (7h), it seems that the Mg-centered structures are energetically preferred to the O-centered ones.

### Table 1

<table>
<thead>
<tr>
<th>$\text{CN}_{\text{max}} - 1$</th>
<th>$\text{CN}_{\text{max}} - 2$</th>
<th>$\text{CN}_{\text{max}} - 3$</th>
<th>$\text{CN}_{\text{max}} - 4$</th>
<th>$\text{CN}_{\text{max}} - 5$</th>
<th>$\text{CN}_{\text{max}} - 6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MgO)$_2$</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(MgO)$_3$</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(MgO)$_4$</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>(MgO)$_5$</td>
<td>0</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>(MgO)$_6$</td>
<td>0</td>
<td>6</td>
<td>6</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>(MgO)$_7$</td>
<td>0</td>
<td>1</td>
<td>7</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

### Table 2

The numbers of initial configuration and locally stable final structures after relaxation of (MgO)$_n$ ($n = 2–7$) clusters.

<table>
<thead>
<tr>
<th>(MgO)$_2$</th>
<th>(MgO)$_3$</th>
<th>(MgO)$_4$</th>
<th>(MgO)$_5$</th>
<th>(MgO)$_6$</th>
<th>(MgO)$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>2</td>
<td>11</td>
<td>36</td>
<td>999</td>
<td>3021</td>
</tr>
<tr>
<td>Final</td>
<td>2</td>
<td>1</td>
<td>7</td>
<td>15</td>
<td>64</td>
</tr>
</tbody>
</table>

**Fig. 2.** The lowest-energy structures of (MgO)$_n$ ($n = 2–7$) with their point group symmetry in the parenthesis.
Table 3 shows average length of the Mg–O bonds and the Mg–O–Mg and O–Mg–O bond angles for the lowest-energy structures of (MgO)_n clusters. The Mg–O bond lengths for smaller clusters (n = 2, 3) are shorter than others, which can be related to their 2D ring-like structure and lower coordination number of two. Meanwhile, the O–Mg–O bond angles are usually larger than the Mg–O–Mg angle owing to the larger ionic radius of O (about 1.24 Å) [35] with regard to Mg (about 0.71 Å) [35], which means stronger ion–ion repulsion and larger angles. This finding contradicts the regular shaped structures reported in previous studies [10,12,16], e.g., squares with all 90° bond angles and hexagons with all 120° bond angles. Note that both the Mg–O–Mg and

![Fig. 3. Metastable isomer structures of (MgO)_n (n = 4–7) clusters, with their relative energy in terms of the global minima and their point group symmetry in the parenthesis.](image-url)
O–Mg–O angles in bulk MgO solid are 90°. The deviation from 90° in the bond angles of present (MgO)\(_n\) clusters means bond distortion due to unsaturated coordination (two or three with respect to six in solid phase).

The growth pattern of MgO clusters can be classified into three motifs. The first type is the 2D ring-like structures consisting of two-coordinated atoms, such as 2a, 3a, 4b, 5e in Figs. 2 and 3. The second type is combination of basic units like quadrangle and hexagon. For instance, 4a is a stacking of two quadrangles, 4c is constructed by two paralleled quadrangles, and 6a is formed by two hexagons. As demonstrated by the growth from 4a to 5a to 6c, from 6a to 7b or 7d, and from 6b to 7c, 7g or 7h, the third motif is to add atoms to the smaller-sized clusters, which seems to be a general behavior in those clusters.

For the lowest-energy structures of (MgO)\(_n\) clusters, the binding energy, the HOMO–LUMO gaps and the second-order difference of total energy defined by $D^2E_n = E_{n+1} + E_{n-1} - 2E_n$ (where $E_n$ is the total energy of the (MgO)\(_n\) cluster) as function of cluster size $n$ are plotted in Fig. 4. The binding energy of MgO clusters increases rapidly from the monomer to the (MgO)\(_4\) cluster and becomes slower from (MgO)\(_5\) to (MgO)\(_7\) cluster. The HOMO–LUMO gaps of (MgO)\(_3\) and (MgO)\(_5\) are obviously larger than that of the others, which demonstrates the higher stability of the hexagonal ring-like units for MgO clusters. The $D^2E_n$ exhibits a pronounced minimum at (MgO)\(_5\). In other words, the (MgO)\(_5\) cluster is not as stable as the other clusters, due to its open structure with the two-coordinated Mg and O atoms.

4. Conclusion

A topological method is employed to generate the isomer structures of (MgO)\(_n\) clusters up to $n = 7$. The lowest-energy structures were then determined by geometry optimizations using DFT methods, which reproduce the previously reported ones well. In addition, we have located plenty of new isomers that have never been found before. The most stable structure transits from 2D ring-like configuration to 3D cage-like one, in which Mg and O atoms arrange alternatively. The structural growth pattern, the binding energies, HOMO–LUMO gap and second-order difference were discussed. Among these clusters, the (MgO)\(_5\) with an open structure is relatively less stable. The success of this topological method in small (MgO)\(_n\) clusters suggests its application in the large sized MgO clusters as well as the other compound clusters.

Acknowledgment

This work was supported by the Undergraduate Innovative Research Training Program (2010173) and the National Natural Science Foundation of China (No. 11174045, 11134005).

References