

IONIC RADIUS EFFECT ON RELATIVE STABILITIES OF ALKALINE EARTH OXIDE CLUSTERS

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ABSTRACT

We systematically investigate the structural and stabilities of alkaline earth oxide cluster isomers on the $(MO)_n$, 1–4,6,8,9,12 model clusters, M includes Mg and Ca, employing the B3LYP density functional theory. We have calculated the geometries, energetics (stability pattern) using molecular quantum mechanics, and results are presented

for cluster size effects on small MgO and CaO model clusters. We used four different basis sets, STO–3G, 6–311G, polarized 6–311G (d) and 6–311G (2d) basis sets for all calculations. Our calculations demonstrated a good correlation of ionic radius of cations and anions with stability of clusters. Two kinds of structural characterizing are found. Hexagonal ring based structures are found to be preferable in energy if ionic radius of cations and anions are different. If ionic radius are similar, rocksalt structures are the most stable. Our results suggest that the important contribution may arises from the Madelung potential of the ionic crystals and the packing due to the attraction and repulsion forces between ions.

KEYWORDS: MgO, CaO clusters, Stability, ionic radius, B3LYP calculations.

1. INTRODUCTION

In recent years, the cluster model approach has been widely employed to study the properties of solids. The structure and stability of alkaline earth oxide clusters could be entirely different in small clusters. In the case of magnesium oxide it has been shown that small clusters have in general mostly stable structure stability of $(MgO)_n$ based on hexagonal ring is slightly

preferred, while $(\text{CaO})_n$ based on rhombic structure is dominant for calcium oxide clusters. Consequently, there is a broad interest in the detailed convergence properties from cluster to bulk oxides with respect to size and shape. The effort has over the last few years, mainly focused on the structures and stabilities of MgO and CaO alkaline earth oxide, which both compounds are ionic crystal with NaCl structure. Studies of the electronic properties of MgO are motivated by its technological applications, such as in catalysis, microelectronics, and electrochemistry. In this context, many successful applications have been made.^[1-10] In addition, there are several applications on small clusters having peculiar features which have been used enormously for intensive understanding of the building blocks of materials. Theoretical work on ionic materials has been centered mostly in the family of alkali metal halides and studies of metal oxide clusters have been importance in many branches of surface physics, such as heterogeneous catalysis or corrosion. It does not come as a surprise that the route from the diatomic molecule to the FCC bulk structure is not a simple one. It is our aim to extract essential signatures of the growing simple metal oxide cluster. Support found for conception that a cluster is distinctly different from a bulk material both regard to structure and stability as long as the surface to bulk ratio is significantly greater than unity. It was also noted that the effective elongation of inter-ionic distances upon increasing the number of cluster atom is associated with the increasing the radius of the calcium and oxygen ions in the cluster field due to charge separation. This implies that the convergence of the effective cluster to the Madelung potential results from two contributions, first term is related to the number of ions (Coulomb interaction) contributing to the net attractive cluster field, and second which is repulsive interaction as it associated with the increased inter ionic distance with increased lattice field. The fact that MgO and CaO clusters are supposed to show similar properties, however differences can also possible as Ca atom has a larger size and polarizability and a lower ionization potential. This conjunction with the fact that the alkaline earth atoms lower in the periodic table carry more electrons than does magnesium. Moreover, from the theoretical point of view, Ca^{2+} is larger than Mg^{2+} and the polarizabilities of the oxide anions are also larger in CaO because the bonding is weaker than in MgO, so we can expect ionic size effects to play an important role in determining structural differences. In this context our observations appear to indicate that small clusters of $(\text{MgO})_n$ clusters present stability limit different from those of $(\text{CaO})_n$ clusters.^[4,5] Widespread application of CO_2 , NO_2 , SO_2 adsorptions are still limited because of a lack of suitable adsorbents. Moreover, carbon capture and storage is vital to facilitate the transition from our current fossil fuel dependency to a sustainable energy system. The concept of post combustion capture is based

on the selective chemical absorption of carbon dioxide CO₂. To solve this problem, alkaline earth oxides have been developed, including MgO and CaO for better understanding of these properties may be of practical importance since these oxides are used as catalysts. Furthermore, high surface reactivity of MgO nanocrystals make these materials especially effective as adsorbents, which can be a promising strategy for the possible use of the development of oxide clusters with possible use as selective adsorbents or catalysts,^[11] and chemisorption properties of hexagonal MgO nanotubes.^[12] Also, the different reactivity of MgO *versus* CaO against CO₂ adsorption has been confirmed by previous study,^[13] mechanism of carbon dioxide capture by CaO.^[14] and adsorption of SO₂ at (MgO)₉ and (CaO)₉.^[15] In addition, the calculation of vibrational properties provided further insight into the stability of equilibrium structures. In this context our paper.^[16] has been calculated of (MgO)_n clusters as well as the mass spectra of (CaO)_nCa²⁺ cluster ions,^[17] in that IR spectra could give characteristic information about structures of the clusters.

In this work, We have performed a study on structures, stability of (MgO)_n and (CaO)_n ring clusters for n=1–4, 6, 8, 9, 12 employing a computational quantum method as density functional theory (DFT) approach. The ionic size and shapes effects of the cluster has been investigated. In addition, we will focus on differences between MgO and CaO cluster stabilities in terms of binding energy (BE). In particular, the bonding and ionic radius characteristics of the hexagonal and slab structure.

2. COMPUTATIONAL METHOD

The quantum calculations were employed with density functional theory (DFT) and B3LYP which Becke's three parameter with Hartree Fock exchange including the correlation term developed by Lee, Yang and Parr functional,^[18,19] and the outcomes of the DFT method are promising,^[20] and have been widely used. The equilibrium optimization for all structures (MO)_n 1–4, 6, 8, 9, 12 were calculated by applying B3LYP method. Four contracted Gaussian type orbital basis sets considered comprise STO-3G, 6-311G, 6-311G (d) and 6-311G (2d) are presented for comparison. In case of Mg and Ca, the 6-311G basis set was used throughout. For Ca, this acronym implies the inclusion one (d) polarization functions in order to test the energy stability. In the case of both oxides, each of the basis sets was employed throughout in order to learn whether the set requirements change with size of cluster. Analysis of basis effects on structures and stabilities were performed for Mg–O and

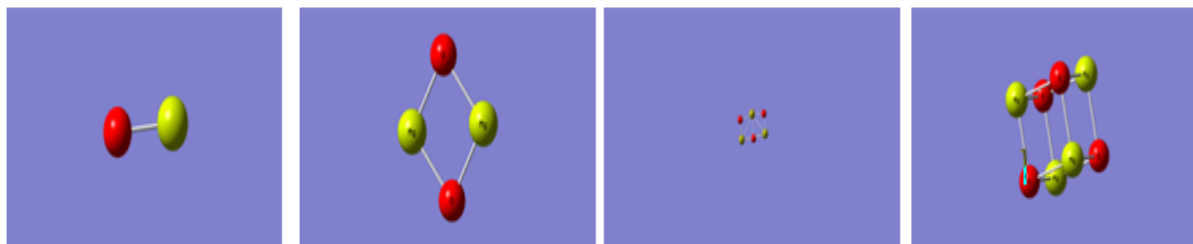
Ca–O clusters by optimizing the cluster structures. All calculations were performed with the Gaussian 09 program.^[21]

3. RESULTS AND DISCUSSION

3.1 MgO, Structure and Stabilities

MgO is a wide gap insulator with a band gap of 7.8 eV,^[22] in this context MgO (100) and MgO (111) nanosheets exhibit semi conductive properties with the band gaps varying from 4.23–4.38 eV.^[23] It is highly ionic crystal with NaCl structure for both MgO and CaO, a high melting temperature 3040 K and the formal charge of the Mg and O ions is very close to the nominal +2/-2 value.^[24] The MgO crystal has a rock-salt structure with a nearest M–O distance of 2.104 Å.^[25] The charge separation between cations and anions in MgO is the consequences of the Madelung potential which strongly contributes to a stabilization of the system. We present the calculated optimal structures for different size n . Various structures, including slab, hexagonal, octagonal rings and other types were investigated for magnesium oxide and calcium oxide clusters. For each cluster size, we obtain the most stable structures and some distortion structures. Figure 1 shows the most stable structure of $(\text{MgO})_n$ $n=1-4, 6, 8, 9, 12$. The B3LYP/ STO–3G, 6–311G, 6–311G (d) and 6–311G (2d) energies relative to the optimize energy structures and ionic charges are depicted in Tables 2,3,4,5. It can be seen that for $(\text{MgO})_n$ the hexagonal ring is the most stable structure for $n=3, 6, 9, 12$, while for $n=8$, the optimized structures are distorted. This result is also in agreement with our earlier calculations prediction.^[4,5] for $(\text{MgO})_{12}$ which optimized to stacked rings from basic hexagonal ring structure. In addition, it can be found that the clusters are basic of two subunits the rhombic ring of $(\text{MgO})_2$ and the hexagonal ring of $(\text{MgO})_3$. The binding energies are defined according to the reaction;

$$\Delta E = n^{-1}E(\text{MgO})_n - E(\text{Mg}) + E(\text{O}) \quad (1)$$



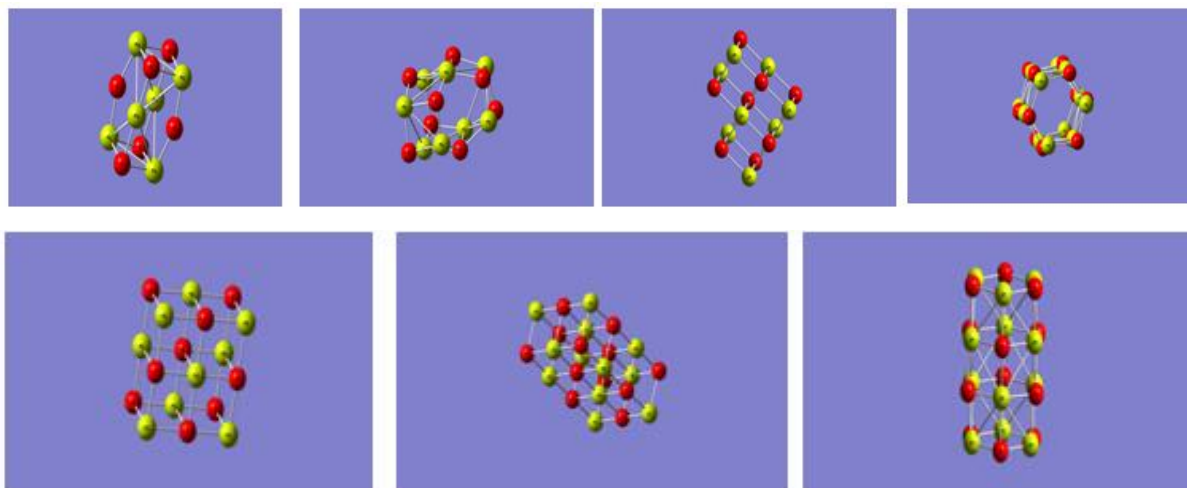


Figure 1: Structures of $(\text{MgO})_n$ ($n=1-4, 6, 8, 9, 12$) with the relative energies in eV with respect to the lowest-energy structures calculated by B3LYP/6-311G (2d). The dark (red) balls stand for O and the light (yellow) for Mg.

And are taken per molecule. The lowest energy structures is the hexagonal ring structure for $n=3$, therefore the hexagonal ring is the most stable structures for $n = 6, 9, 12$. For $n=8$, two difference structures are obtained, spherical structure and the slab structure attached with $(\text{MgO})_2$ subunits (see Figure 1). For $n=9$, again two different structures are found. The three hexagonal stack and slab structures. In the case of $(\text{MgO})_{12}$, a four hexagonal ring stack made of $(\text{MgO})_3$ hexagonal ring possesses competing stability with the lowest energy slab structure 4-hexagonal ring stake . Moreover, it was suggested that the covalent interaction in small MgO clusters might be significant and responsible for the favor stability of the hexagonal ring and the stability increases with increasing cationic size (M^{2+}) as well. In this context, the large absolute differences in anion-cation radii preferable the hexagonal ring based structures, while similar ionic radii make the slab structures the preferred choice. Because of similar spheres of radii are best packed in the rock-salt type structures, in contrast, dissimilar ionic radii, preference for structures based on hexagonal rings. A four hexagonal ring stack made of four hexagonal ring possesses competing stability with the lowest energy slab structure. This means that $(\text{MgO})_n$ $n=3, 6, 9, 12$ prefer the hexagon to the rocksalt as a structural unit, and this has been confirmed by infrared spectra for $(\text{MgO})_{3n}$ ($n =2-5$).^[10] In addition, the repulsion is much greater between ions of like charges in the case of $\text{Mg}^{2+}\text{O}^{2-}$ clusters. This may causes the cluster structures to open out from cube shape at roughly $q= \pm 1$ to hexagonal ring at charges towards ± 2 . Moreover, table 3 shows the transfer charges between magnesium and oxygen 1.00e and 1.25e at $(\text{MgO})_{12}$, which means that strongly ionic bonds

in MgO clusters. In general, the Madelung potential is largest for MgO, and smallest for BaO. This is because the Madelung potential goes as $1/R$ (M–O). Also the electrostatic potential due to the ns electrons is largest for Mg^{2+} and smallest for Ba^{2+} . This is because of the different spatial extent of the Mg $3s$ compared to the Ba $6s$ orbital. On the other hand, the choice of the B3LYP functional was made in anticipation of future calculations on molecular adsorption to the clusters.^[26] Our previous work,^[4,5] has been investigated rings with different diameters and Baker *et al.*,^[27] for NaCl nanotubes. Table 1 shows the atomic and ionic radius for Mg, Ca, Sr, Ba and O.

Table 1: Some properties of the Mg, Ca, Sr, Ba and O (in pm).

Element	Electron Configuration	Atomic	Ionic (M^{2+}), (M^{2-})
Mg	[Ne] $3s^2$	160	72 pm
Ca	[Ar] $4s^2$	197	100 pm
Sr	[Kr] $5s^2$	215	118 pm
Ba	[Xe] $6s^2$	217	135 pm
O	$1s^2 2s^2 2p^4$	66	140 pm

Table 2: Formal charges, total energies (Ha) and binding energies (eV) in the hexagonal and slab structures of $(MgO)_n$ calculated by B3LYP/STO–3G basis set.

Cluster size	Structure	Ionic charge	Total energy	Binding energy
1	Monomer	± 0.47	–271.58555	5.60
2	Rhombic	± 0.56	–543.46603	9.61
3	Hexagonal ring	$\pm 0.54 < \Delta q < \pm 0.59$	–815.33486	10.8
4	Slab	± 0.599	–1087.35886	12.52
6	2-hexa ring stack	$\pm 0.57 < \Delta q < \pm 0.63$	–1632.21518	17.85
8	Slab	$\pm 0.58 < \Delta q < \pm 0.67$	–2448.60895	18.72
9	3-hexa ring stack	$\pm 0.57 < \Delta q < \pm 0.65$	–2448.60895	18.72
12	4-hexa ring stack	$\pm 0.59 < \Delta q < \pm 0.66$	–3265.01824	19.19

Table 3: Formal charges, total energies (Ha) and binding energies (eV) in the hexagonal and slab structures of $(MgO)_n$ calculated by B3LYP/6–311G basis set.

Cluster size	Structure	Ionic charge	Total energy	Binding energy
1	Monomer	± 0.62 (0.74 ^(a))	–275.24108	1.70
2	Rhombic	± 0.96	–550.63893	3.84
3	Hexagonal ring	± 1.06	–826.16197	4.86
4	Slab	± 1.03	–1101.64818	6.36
6	2-hexa ring stack	$\pm 0.95 < \Delta q < \pm 1.09$	–1652.54748	6.70
8	Slab	$\pm 1.04 < \Delta q < \pm 1.10$	–2203.41724	6.77
9	3-hexa ring stack	$\pm 0.91 < \Delta q < \pm 1.25$	–2479.08194	7.49
12	4-hexa ring stack	$\pm 1.00 < \Delta q < \pm 1.25$	–3305.46373	7.53

^(a) Reference 28.

Table 4: Formal charges, total energies (Ha) and binding energies (eV) in the hexagonal and slab structures of (MgO)_n calculated by B3LYP/6–311G (d) basis set.

Cluster size	Structure	Ionic charge	Total energy	Binding energy
1	Monomer	±0.55	–275.24198	4.01 (exp.3.56 ^(b))
2	Rhombic	±0.79	–550.66396	6.95
3	Hexagonal ring	±0.84	–826.04826	7.43
4	Slab	±0.85	–1101.70408	9.15
6	2-hexa ring stack	±0.86<Δq<±0.94	–1652.60469	9.74
8	Slab	±0.83<Δq<±0.98	–2203.62987	9.80
9	3-hexa ring stack	±0.86<Δq<±1.18	–2479.07808	10.25
12	4-hexa ring stack	±0.85<Δq<±1.25	–3305.46669	10.32

^(b) Reference.^[29]

Table 5: Formal charges, total energies (Ha) and binding energies (eV) in the hexagonal and slab structures of (MgO)_n calculated by B3LYP/6–311G (2d) basis set.

Cluster size	Structure	Ionic charge	Total energy	Binding energy
1	Monomer	±0.54	–275.27020	5.27
2	Rhombic	±0.81	–550.75645	8.21
3	Hexagonal ring	±0.84	–826.25979	9.35
4	Slab	±0.90	–1101.73586	9.73
6	2-hexa ring stack	±0.82<Δq<±1.20	–1652.76891	10.48
8	Slab	±0.79<Δq<±1.41	–2203.73772	10.63
9	3-hexa ring stack	±0.72<Δq<±1.71	–2479.23442	10.72
12	4-hexa ring stack	±0.73<Δq<±1.25	–3305.61125	10.85

3.2 CaO, Structure and Stabilities

Calcium oxide crystallizes in the rocksalt structure (face centered cubic), with mainly ionic bonding including some degree of covalency. It has a melting point of 2870 K. This prototype oxide possesses a wide band-gap of 7.1 eV,^[31] and high dielectric constant. Nanocrystalline CaO is also widely used as catalyst.^[13–15] and toxic waste remediation agent as well as for other fundamental applications.^[30] The equilibrium and structural parameters of (CaO)_n ring based clusters obtained using the B3LYP functional are depicted in Figure 2 and Tables 6, 7, 8, 9 show the most stable structure and some clusters for each size of (CaO)_n (*n*=1–4, 6, 8, 9, 12). The binding energy is calculated using the equation

$$\Delta E = n^{-1}E(\text{CaO})_n - E(\text{Ca}) + E(\text{O}) \quad (2)$$

Tables 6, 7, 8, 9 lists the calculated binding energies values and other properties of (CaO)_n clusters. The crucial importance of (d) polarization functions on Ca for describing the cluster binding CaO clusters was repeatedly emphasized. This effect has been shown for the charge

distribution in bulk CaO. The lowest energy $\text{Ca}^{2+} \text{O}^{2-}$ clusters can be seen compact cage-like structures with rhombic based on the NaCl structure.^[3] The bond length of a charged ions forces all ions closer together which increases the repulsion between like ions, this causes the cluster structures to rocksalt structures. Using B3LYP/6–311G (d) basis set, one can note that the Milliken charge (Ca–O) increases from ± 0.73 to ± 0.77 at 6–311G (2d). It can clearly be seen from table 8 and 9 that the STO–3G basis set exaggerate the Ca–O charge separation ± 0.20 , ± 1.26 compared with ± 0.90 , ± 0.122 for 6–311G basis set. Furthermore, it is interesting to note how this basis set produces too long ionic charges and too small binding energies in both MgO and CaO systems.

The alkaline earth metal atoms have the largest sizes. With increase in atomic number, the atom becomes larger. The ionic radius M^{2+} , $\text{M}=\text{Mg}, \text{Ca}$ are smaller than the parent atom, however, the size of Mg^{2+} is smaller than Ca^{2+} due to this, Mg^{2+} has more covalent character than Ca^{2+} that causes a decrease in polarity. It is interesting to note that the atomic and ionic radii of alkaline earth metals increase on moving down the group IIA, they increase in size while going from Mg to Ba. The calculated Milliken charges on the metal and ion charges are $+0.53 < q < +1.11$ and $-1.12 < q < -0.86$ for 3–hexagonal ring stack. In a view of the fact the metal and ions and oxygen charges close to +1 and –1 respectively. The values of the partial charges indicate the slightly higher ionic character of CaO molecule and $(\text{CaO})_2$ compared to the MgO molecule and $(\text{MgO})_2$ clusters. Furthermore, it is observed that on the metal ion increases with increasing atomic number of the metal ion (± 1.06 , $\pm 0.95 < q < \pm 1.09$, $\pm 0.91 < q < \pm 1.25$ for $(\text{MgO})_3$, $(\text{MgO})_6$, $(\text{MgO})_9$ and, $\pm 1.20 < q < \pm 1.38$, $\pm 1.13 < q < \pm 1.35$, $(+0.85 < q < +1.43)$ ($-1.33 < q < -1.25$) for $(\text{CaO})_3$, $(\text{CaO})_6$, $(\text{CaO})_9$ respectively, indicating the increasing involvement of metal ion size.

It can be seen that the rhombic ring is most stable structure for $n = 2, 4, 6, 9, 12$, while the hexagonal structure is the most stable structure for $n = 3$. The stability pattern has been ordered as slab structure followed by 2–hexagonal ring stack, which is supported by.^[3]

Furthermore, the value of BE increases with the increase in cluster size, which is in accordance to their increment in the ionic charges which leads to larger Ca–O increments.

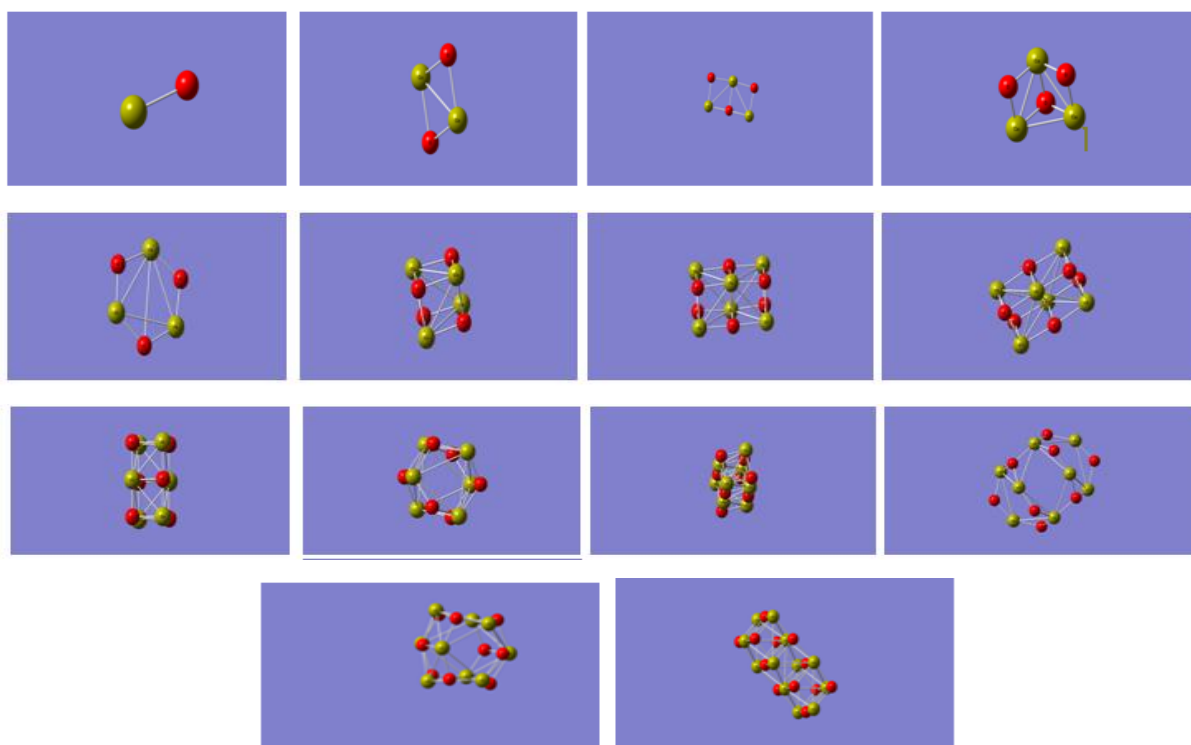


Figure 2: Structures of $(\text{CaO})_n$ ($n=1-4, 6,8,9,12$) with the relative energies with respect to the lowest-energy structures calculated by B3LYP/6-311G (2d). The dark (red) balls stand for O and the light (yellow) for Ca.

Table 6: Formal charges, total energies (Ha) and binding energies (eV) in the hexagonal and slab structures of $(\text{CaO})_n$ calculated by B3LYP/STO-3G basis set.

Cluster size	Structure	Ionic charge	Total energy	Binding energy
1	Monomer	± 0.20	-744.727857	2.37
2	Rhombic	± 1.26	-1489.65478	5.08
3	Hexagonal ring	$\pm 0.22 < \Delta q < \pm 0.31$	-2234.605292	6.20
4	Slab	± 0.32	-2979.654109	7.42
6	2-hexa ring stack	$+0.30 < \Delta q < +0.34$ $-0.34 < \Delta q < -0.32$	-4469.660548	8.24
8	Slab	$+0.33 < \Delta q < +0.34$ $-0.34 < \Delta q < -0.32$	-5959.665950	8.64
9	3-hexa ring stack	$+0.30 < \Delta q < +0.36$ $-0.36 < \Delta q < -0.34$	-6704.718627	8.93
12	4-hexa ring stack	$+0.32 < \Delta q < +0.35$ $-0.37 < \Delta q < -0.32$	-8939.77609	9.27

Table 7: Formal charges, total energies (Ha) and binding energies (eV) in the hexagonal and slab structures of (CaO)_n calculated by B3LYP/6–311G basis set.

Cluster size	Structure	Ionic charge	Total energy	Binding energy
1	Monomer	±0.90	-752.70241	1.12
2	Rhombic	±1.22	-1505.64680	4.41
3	Hexagonal ring	±1.20<Δq<±1.38	-2258.57669	5.37
4	Slab	±1.27	-3011.589273	6.42
6	2-hexa ring stack	±1.13<Δq<±1.35	-4517.51747	7.03
8	Slab	+1.20<Δq<+1.36 -1.36<Δq<-1.25	-6023.44911	7.34
9	3-hexa ring stack	+0.85<Δq<+1.43 -1.33<Δq<-1.25	-6776.44084	7.52
12	4-hexa ring stack	+0.90<Δq<+1.43 -1.34<Δq<-1.23	-9035.36899	7.78

Table 8: Formal charges, total energies (Ha) and binding energies (eV) in the hexagonal and slab structures of (CaO)_n calculated by B3LYP/6–311G (d) basis set.

Cluster size	Structure	Ionic charge	Total energy	Binding energy
1	Monomer	±0.73	-752.79951	3.76
2	Rhombic	±0.89	-1505.79641	6.44
3	Hexagonal ring	±0.89<Δq<±0.98	-2258.76322	7.07
4	Slab	±0.95	-3011.80850	7.91
6	2-hexa ring stack	+0.93<Δq<+0.99 -1.01<Δq<-0.95	-4517.82706	8.43
8	Slab	+0.96<Δq<+1.02 -1.02<Δq<-0.94	-6023.84766	8.70
9	3-hexa ring stack	+0.84<Δq<+1.05 -1.05<Δq<-0.95	-6776.86834	8.82
12	4-hexa ring stack	+0.90<Δq<+1.05 -1.01<Δq<-0.94	-9035.907947	9.01

Table 9: Formal charges, total energies (Ha) and binding energies (eV) in the hexagonal and slab structures of (CaO)_n calculated by B3LYP/6–311G (2d) basis set.

Cluster size	Structure	Ionic charge	Total energy	Binding energy
1	Monomer	±0.77	-752.81043	4.76 (exp 4.16 ^(c))
2	Rhombic	±0.91	-1505.82482	6.83
3	Hexagonal ring	±0.91<Δq<±0.97	-2258.80009	7.40
4	Slab	±0.96	-3011.86622	8.30
6	2-hexa ring stack	+0.97<Δq<+1.00 -1.01<Δq<-0.95	-4517.88195	8.67
8	Slab	+0.88<Δq<+1.00 -1.01<Δq<-0.96	-6023.90144	8.79
9	3-hexa ring stack	+0.53<Δq<+1.11 -1.12<Δq<-0.86	-6776.92452	8.98
12	4-hexa ring stack	+0.97<Δq<+1.02 -1.00<Δq<-0.96	-9035.9770	9.16

^(c) Reference. ^[29]

3. CONCLUSIONS

The stabilities of small alkaline earth oxide clusters of $(MO)_n$ $n=1-4, 6, 8, 9, 12$, $M=Mg$ and Ca have been determined by means of density functional theory studies using B3LYP method calculations. We have mainly found two candidate structures, the hexagonal ring and slab shape structures. An explanation based on the formal charges of ionic charges and binding energies has been suggested. Basis sets effects on the cluster stabilities have been determined.

The main results are summarized as follows

- a. Oxide materials offer a wide range of interesting of physical and chemical properties.
- b. The rocksalt and hexagonal ring structures are two dominant low-energy structural for small $(MgO)_n$ and $(CaO)_n$ clusters and it results in magic sizes $n=3, 6, 9, 12$.
- c. When the cluster size is small, the hexagonal $(MgO)_3$ ring is found to be favored. In contrast, the slab structures are preferred for the $(CaO)_n$ clusters.
- d. The order of Madelung potential is $MgO > CaO$, while the order of polarity is $CaO > MgO$.
- e. According to the results, the geometries optimized with 6-311G, 6-311G (d) and 6-311G (2d) sets are nearly closed except for some differences in magnitude of charges. However, for a better alternative a polarization functions (d) and (2d) are added to give additional larger basis sets. On the other hand, the STO-3G is of no use either for structure or for binding energy estimates.
- f. Mixed covalent and ionic bonding property always exist in MgO and CaO nanoclusters.

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