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Structural, Electronic and Magnetic Properties of ConO (n = 2∼10) Clusters: A Density Functional Study (Postprint)

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Abstract

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Full Text

Structural, Electronic and Magnetic Properties of ConO (n = 2∼10) Clusters: A Density Functional Study

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ABSTRACT

The structural, electronic, and magnetic properties of ConO (n = 2∼10) clusters have been systematically investigated within the framework of generalized gradient approximation density functional theory. The results indicate that the O atom occupies a surface-capped position in ConO (n = 2∼10) clusters. The stabilities of the host clusters are improved by adding one O atom, with maximum peaks in the second-order difference energy of ground-state ConO clusters found at n = 3, 6, and 8, indicating higher stability than their neighboring clusters. Compared with corresponding pure Con clusters, the O-doped cobalt clusters exhibit larger gaps between HOMO and LUMO energy levels, indicating enhanced chemical stability. In addition, O doping exerts different influences on cluster magnetism, which is further investigated through analysis of local magnetic moments, deformation charge density, and partial local density of states.

Keywords: density functional theory; cobalt-based clusters; geometries; electronic structures; magnetic properties

1. INTRODUCTION

Transition metal oxide clusters are widely used in high-temperature chemistry, materials science, microelectronics, and nanotechnology, and have attracted extensive theoretical and experimental attention over the past decade. For example, Clemmer et al. [**?**] reported experimental measurements of Sc-O bond energies and ionization potentials of ScO2 using guided ion beam reactions between ScO+ and NO2. Wang et al. [**?**] calculated the structural and magnetic properties of small transition metal oxide clusters TMnOm (TM = Sc, Ti, V, Cr, and Mn; n = 1, 2; m = 1∼6) using an ab initio density functional theory approach, revealing that cluster geometries are closely correlated with TM:O ratios and the number of valence electrons of the TM atoms. Yang et al. [**?**, **?**] studied the structural and electronic properties of LanO (n = 2∼12) clusters using density functional theory (DFT), finding that O doping prefers to stay outside the cluster and can greatly improve the stability of small Lan clusters. Additionally, the structures, electronic properties, and magnetic properties of transition metal (M = Cr, Mn, Fe, and Ni) oxide clusters and their anions and cations have been extensively studied [**?**]. Gutsev et al. [**?**] investigated the polarizability per atom of MO monomers (M = Fe, Co, and Ni), finding that doping resulted in a steep decrease in polarizability compared to atomic values. However, existing theoretical studies on ConO clusters remain insufficient, and the detailed structural and electronic properties of larger ConO (n 5) clusters are still unclear.

Therefore, it is desirable to extend ConO cluster studies to larger sizes to gain a comprehensive understanding of their exotic physical and chemical properties. We hope our work can provide powerful guidelines for corresponding experiments and promote the functional design of cluster-assembled materials. On the experimental side, mass-selected cobalt oxide cluster anions ConOm− (n = 5∼21, m = 0∼2) have been studied using photodetachment photoelectron spectroscopy (PES), indicating that O atoms cause only minor influences on electronic structures [?]. Jacobson and Freiser [?] performed Fourier transform mass spectrometry investigations on reactions of cationic Co dimers and trimers with O2, followed by kinetic studies of reactions between small Con+ clusters (n = 2∼9) and O2.

On the theoretical side, Kosuke et al. [?] reported structural results for cobalt oxide cluster cations ComOn+ using ion mobility spectrometry (IMS) combined with theoretical calculations to verify cluster structures, concluding that (CoO)3-5+ ions are monocyclic-ring structures while (CoO)6,7+ have compact tower structures. Therefore, a structural transition from ring to compact structures occurs at (CoO)6+. The ground states of CoOn (n = 1∼4) and their anions [CoOn]− were studied using density functional theory with the BLYP exchange-correlation functional [?]. However, research on single O-atom doped cobalt clusters remains scarce, except for Liu et al. [?] who studied the structure and magnetic properties of small ConO (n = 1∼5) clusters using density functional approaches.

To our knowledge, no systematic first-principles calculations have been performed on larger ConO (n = 2∼10) clusters. Our work aims to clarify how O atoms bind with Con (n = 2∼10) clusters through theoretical calculations using density functional theory, explore how stability changes after O doping, investigate how magnetic properties of host clusters are influenced by doping, and finally disclose the physical origin of magnetic behavior in ConO clusters. We hope this research provides theoretical guidance for practical applications of cobalt oxide cluster-assembled materials.

2. COMPUTATIONAL DETAILS

All calculations were performed at the DFT level using the DMol3 package in Materials Studio of Accelrys Inc [?]. The exchange-correlation interaction was treated within the GGA using the PW91 functional (GGA-PW91) [?]. The double numerical basis set augmented with d-polarization and p-polarization functions (DNP) was utilized. For numerical integration, a fine quality mesh size was used, and the real-space cutoff of the atomic orbital was set at 5.5 Å. The convergence criteria for structure optimization and energy calculations were set to fine, with tolerances for density convergence in SCF, energy, gradient, and displacement of 1 × 10 eV/Å, 1.0 × 10 a.u., 0.002 Hartree/Å, and 0.005 Å, respectively.

In geometry optimization procedures, we considered numerous initial structures including linear chains, planar, and three-dimensional structures to maximize our chances of finding ground-state configurations of the alloy clusters. We also examined other structures from LanO, ScnOm, YnO, MnnO, NbnO, ConRh, ConMn, ConV, and ConFe clusters [?, ?]. Additionally, due to spin polarization, all optimized geometries were re-optimized at various possible spin multiplicities. Consequently, the number of possible initial isomers increased rapidly with cluster size. Calculations were implemented until minimum energy was reached, and we confirmed the stability of lowest-energy structures as minima on the potential energy surface by verifying the absence of imaginary frequencies.

To validate our computational method, we first performed calculations on Co2 and CoO dimers using PW91, PBE, and BLYP functionals. As listed in Table 1 , we selected the PW91 method because its results are consistent with previous theoretical and experimental data, demonstrating that this method is effective and reliable for studying ConO (n = 2∼10) clusters.

3. RESULTS AND DISCUSSION

3.1 Geometrical Structures of ConO (n = 2∼10) Clusters

The low-lying geometries, symmetries, magnetic moments, and relative energies (ΔE) of ConO (n = 2∼10) clusters are shown in Figs. 1 and 2. The lowest-energy structures of pure Con clusters are included for comparison, and the lowest frequencies of Con and ConO clusters are listed in Table 2 .

For ConO clusters, numerous stable configurations were found for each cluster size, but only three are shown here. For the Co2O cluster, the lowest-energy structure is an isosceles triangle (C2v) with the O atom at the apex, having a total magnetic moment of 4 B, which is consistent with previous theoretical calculations [**?**]. A less stable structure with energy 0.106 eV higher features more relaxed Co-Co and Co-O bonds and a higher magnetic moment of 6 B.

The most stable Co3O cluster adopts a planar structure (C2v) with a total magnetic moment of 7 B. Its metastable structure (3 B) shares the same geometry but is energetically less favorable by only 0.022 eV, making them energetically degenerate and magnetically bistable states. The third stable isomer is a tetrahedron (Cs) with 5 B magnetic moment, differing completely from the ground and metastable states, and is 0.107 eV less stable than the lowest-energy structure.

For Co4O, the most stable structure is a triangular bipyramid (8 B) with the O atom at the apex and Cs symmetry, in good agreement with previous theoretical results [**?**]. The second lowest-energy structure has similar geometry with C3v symmetry, lying 0.021 eV higher in energy than the ground state. The next low-lying isomer (C2v), energetically less stable by 0.034 eV, exhibits double coordination of the O atom to the tetrahedron.

For Co5O, we considered many initial geometries including capped triangular bipyramids, octahedra, and pentagonal pyramids. The lowest-energy structure is a capped triangular bipyramid (Cs) with 11 B total magnetic moment, where the O atom occupies the capped position. The second stable isomer (9 B) shares the same geometry and symmetry, being only 0.003 eV higher in energy. Another stable isomer at higher energy (0.012 eV) differs in that the O atom prefers to bind at a bridge site of the Co5O cluster.

The Co6O cluster (14 B) adopts an O-capped octahedron structure with C3v symmetry. In the metastable structure, the O atom coordinates with two connected Co atoms and is coplanar with four Co atoms of the octahedron. Another low-lying structure (Cs) with 0.029 eV higher energy shares the same configuration as the ground state but has a smaller total magnetic moment of 12 B, possibly resulting from decreased average bond length.

The ground-state structure of Co7O (15 B) is a bicapped octahedron with Cs symmetry, where the O atom occupies the capped position. The next two low-lying states have the same structure (C2v) with the O atom lying coplanar with the 5-membered ring of the hexagonal bipyramid. With total magnetic moments of 13 and 15 B, their energies are higher than the ground state by 0.044 and 0.051 eV, respectively.

The lowest-energy structure of Co8O can be viewed as a tricapped octahedron (Cs) with 18 B total magnetic moment, where the O atom caps the Co8 ground-state geometry. The metastable state is a bicapped pentagonal bipyramid (C2v) where the O atom lies in the middle plane opposite the bicapped position, with energy 0.021 eV higher than the lowest-energy structure. A side-capped tetrahedral prism isomer (Cs) with the O atom at the capped position, sharing similar total magnetism with the ground and metastable states, is the next stable structure at slightly higher energy (0.027 eV).

For Co9O, three low-lying structures are similar, all being bicapped tetragonal antiprisms, differing only in capping arrangement. The ground-state structure (19 B) with C4v symmetry has bi-capped atoms located opposite each other, while the metastable and third states are structurally identical (C3v) with the O impurity occupying an anterior capped position of pure Co9, showing notable instability (0.003 and 0.016 eV, respectively).

For Co10O, the structure differs from the Co10 cluster, which tends to form large layered structures. Three low-lying structures share the same configuration and symmetry. The metastable state (18 B) and third state (14 B) are higher in energy than the ground-state structure (20 B) by 0.027 and 0.0055 eV, respectively.

From this analysis, geometry optimizations reveal that O atoms tend to bind preferentially to bridge sites in Co2O and Co3O clusters. For ConO (n = 5, 6, 7, and 8) clusters, O prefers to bind to three coordination sites on the ground-state geometries of Con (n = 5, 6, 7, and 8), forming surface-capped structures. Although O also binds with three Co atoms in Co4O and Co10O, the binding mode differs, as these structures involve rearrangement of Co atoms rather than maintaining the original ground-state structure of pure cobalt clusters. For Co9O, O binds to a Co atom on the square edge in the most stable geometry. Overall, these results indicate that O atoms occupy surface-capped positions on Con (n = 2∼10) clusters, while numerous similar low-energy isomers exist as low-lying structures for ConO (n = 2∼10) clusters.

3.2 Stabilities and Electronic Properties

To investigate the influence of O doping on cluster stability, we computed and compared the average binding energies per atom of the lowest-energy ConO and Con clusters (Fig. 3 [Figure 3: see original paper]). The atomic average binding energy Eb(n) can be expressed by:

$$E_b(n) = \frac{nE(\text{Co}) + E(\text{O}) - E(\text{ConO})}{n+1}$$

where E is the total energy of the respective atom or cluster and n corresponds to the number of Co atoms. Fig. 3 shows that average binding energies of ConO clusters are larger than those of Con clusters, indicating that O doping improves host cluster stability. Moreover, average binding energies of ConO clusters increase with size, suggesting these clusters can continuously gain energy during growth. Specifically, Eb increases rapidly in the initial stage (n = 1∼ 7), while from n = 7 to 10, Eb exhibits an obvious convergence trend. The Eb trend for pure Co clusters matches previous theoretical results well [**?**, **?**, **?**].

In cluster physics, the second-order difference of cluster energies is another important quantity reflecting relative stability. The second-order difference energy Δ^2E(n) is calculated using:

$$\Delta^2 E(\text{Con}) = E(\text{Con+1}) + E(\text{Con-1}) - 2E(\text{Con})$$

$$\Delta^2 E(\text{ConO}) = E(\text{Con+1O}) + E(\text{Con-1O}) - 2E(\text{ConO})$$

As shown in Fig. 3, Δ^2E(n) exhibits obvious even-odd oscillatory behavior for Con clusters, indicating that Con clusters with even numbers of atoms are more stable than neighboring sizes. A similar trend is observed for ConO clusters except for Co3O. Local peaks appear at n = 3, 6, and 8, indicating these clusters are relatively more stable than their neighbors, while local minima appear at n = 5, 7, and 9. Overall, O doping does not influence the stability trend of clusters.

Additionally, the HOMO-LUMO gap is a characteristic quantity of electronic structure and stability, commonly used to measure cluster ability to undergo activated chemical reactions with small molecules. As shown in Table 2, HOMO-LUMO gaps of ConO are usually larger than those of Con clusters except for n = 8, suggesting high chemical inertness of doped ConO clusters. The larger Egap arises because O doping weakens Co-Co interactions in clusters, leading to larger Egap [**?**], consistent with binding energy trends. Notable Egap peaks appear at n = 3, 6, and 10, indicating these clusters are more stable than neighboring sizes, while stabilities for n = 5 and 8 are low.

To understand HOMO-LUMO gap differences between Con and ConO clusters, we plotted molecular orbital diagrams for n = 2, 4, 6, and 8 (Fig. 4 [Figure 4: see original paper]). This visualization clearly shows orbital types involved in bond formation. For Co2, HOMO consists of an anti-bonding orbital along the bond axis, while LUMO is also anti-bonding but from s orbitals. With O doping, an obvious bond formed by Co orbitals accounts for HOMO of Co2O, resulting in dramatic energy reduction. In Co2O LUMO, orbitals bond weakly with O p orbitals but remain anti-bonding. Compared with Co2, bonding in Co2O reduces HOMO energy substantially and LUMO energy slightly, responsible for the largest gap difference among all Con/ConO pairs.

Co4 HOMO shows strong bonding between para-Co atoms and s orbitals from the other two atoms, exhibiting distinct d-p hybridization characteristics, while LUMO lies 0.507 eV higher and consists of non-bonding from four d orbitals (d__yz and d__xz). When doped with one O atom, HOMO exhibits non-bonding overlap higher in energy than Co4, while Co4O LUMO shows both non-bonding and anti-bonding overlaps. As cluster size increases to n = 6, HOMO consists of six d__xy being non-bonding with bonds observed in LUMO, contributing to a small HOMO-LUMO gap. After O doping, large overlap is induced in HOMO and an in-plane bond in LUMO, while LUMO also has non-bonding perpendicular to the bond, resulting in much lower HOMO and higher LUMO. Both HOMO and LUMO of Co8 are mainly composed of non-bonding d orbital overlaps, with some obvious sideway overlaps between s, p, and d orbitals appearing in HOMO, forming d-s, d-p, and d-d delocalized bonds. Moreover, an obvious bond appears in Co8O LUMO, so bonding enhancement causes overall energy level reduction and a tiny gap decrease compared to Co8.

We also performed Mulliken population analysis for lowest-energy structures, with O atomic charges presented in Table 2. All O atoms are negatively charged, showing obvious charge transfer from Co to O, indicating O acts as a Mulliken charge acceptor. This charge transfer implies ionic bonding between Co and O in ConO clusters, an important reason for higher stability of doped ConO clusters [**?**].

To understand charge distribution between Co and O in doped clusters, we analyzed charge difference density for Co3O and Co6O clusters. Difference charge density is defined as the difference between total cluster charge density and superposition of atomic charge densities at the same spatial coordinates. As shown in Fig. 5 [Figure 5: see original paper], red indicates charge accumulation while blue represents depletion. Strong charge accumulation appears around O atoms in both Co3O and Co6O, while charge depletion occurs from vacuum to Co sites. The electron accumulation is highly localized, signifying ionic bond characteristics between O and neighboring Co atoms. Additionally, charge accumulation extent on O atoms is greater in Co6O than in Co3O.

3.3 Magnetic Properties

We now focus on magnetic properties of ConO (n = 2∼10) clusters. Total magnetic moments of ground-state ConO (n = 2∼10) clusters were calculated and presented in Figs. 1 and 2. For comparison, values for pure cobalt clusters are also plotted. Total magnetic moments of ConO clusters increase with size, showing a similar trend to Con clusters. For n = 2, 3, 6, 7, and 10, total magnetic moments remain constant after O doping, while those for Con (n = 4, 5) clusters decrease and values increase for n = 8 and 9. Interestingly, whether moments increase or decrease, the difference is consistently 2 B. The magnetic behavior of ConO (n = 1, 3, 5) clusters is similar to previous theoretical work [?].

To further explore magnetic origins, we selected ground-state ConO (n = 5, 7, 9) clusters as representatives to discuss O doping influence on local magnetic moments of host clusters (Fig. 6 [Figure 6: see original paper]). For comparison, local magnetic moments per atom of corresponding pure Con clusters are also shown. The magnetic moments of ConO clusters are chiefly derived from Co atoms, with very small O contributions. Magnetic moment reduction or enhancement upon doping stems from decreased or increased local magnetic moments on Co atoms. For instance, in Co5O, the local magnetic moment of Co atoms is reduced due to O doping, resulting in decreased total spin moment compared to pure Co5. For n = 9, enhanced local magnetic moments on Co in the doped cluster increase the total magnetic moment. For n = 7, O doping redistributes spin moments on Co atoms, decreasing local moments for Co atoms near O and increasing them for distant atoms, leaving total magnetic moments unchanged before and after O loading. A similar phenomenon appears in previous studies on atomic oxygen adsorbed Scn (n = 2∼14) clusters [?].

To further understand the magnetic mechanism of ConO (n = 1∼9) clusters, we provide partial (PDOS) and local (LDOS) contributions of different orbital components for Co5O, Co7O, and Co9O clusters as representatives. As evident from Fig. 7 [Figure 7: see original paper], magnetism in ConO mainly originates from Co atoms, whose electronic states below the Fermi level come primarily from d electron states with very small s and p contributions. For O atoms, below the Fermi level, the integrated area of spin-up p electrons nearly equals that of spin-down p electrons in LDOS, indicating O doping hardly affects cluster magnetism, consistent with local magnetic moment analysis. Additionally, between -4 and -6 eV relative to the Fermi level, clear hybridization occurs between O 2p and Co 3d, resulting in charge density rearrangement that influences cobalt cluster magnetic moments. Generally, relative shifts between spin-up and spin-down bands indicate the degree of spin exchange splitting, with greater splitting leading to larger spin polarization and magnetic moments [?]. As shown in Fig. 7, for Co5O, the spin-up d electron integrated area of Co5O/Co5 is evidently smaller than that of pure Co5. Meanwhile, the spin-down d electron peak of Co5O broadens around -5.5 eV below the Fermi level, further counteracting spin-up d electrons, indicating obvious spin exchange splitting reduction. Thus, total magnetic moment decreases after O doping of pure Co5. Compared with Co7, Co7O/Co7 shows little change in spin exchange splitting, and differences in integrated areas between spin-up and spin-down d electrons in pure Co7 and Co7O/Co7 are similar, so Co7O total spin moment remains unchanged. Additionally, Co9O/Co9 shows obvious spin exchange splitting, with the integrated area of spin-up d electrons evidently larger than spin-down below the Fermi level in LDOS, resulting in increased magnetism of O-doped cobalt clusters.

4. CONCLUSION

Using first-principles DFT-GGA calculations, we systematically studied the geometries, stabilities, and magnetic properties of O-doped Con clusters, with results summarized as follows:

1. In the most stable ConO cluster structures, O atoms prefer to occupy surface-capped positions on Con (n = 2∼10) clusters. Geometry optimizations reveal O atoms tend to bind at bridge sites in Co2O and Co3O clusters; O atoms are capped by three coordination sites in ConO (n = 5, 6, 7, and 8) clusters; for Co9O, O atoms are capped by four coordination sites, with corresponding Con maintaining the original ground-state structure of pure cobalt clusters. Additionally, analyzing the most stable geometries of Co4O and Co10O clusters shows O atoms prefer three-coordinate binding with Co atoms, but Co atoms undergo obvious rearrangement, and the Co10O cluster exhibits a layered structure model.
2. Analysis of second-order energy differences reveals that ConO clusters at n = 3, 6, and 8 possess relatively higher stabilities than their neighbors, meaning O doping improves stability of Co3O, Co6O, and Co8O clusters.
3. By analyzing HOMO and LUMO of Con and ConO (n = 2, 4, 6, 8) clusters, we conclude that the gap is mainly determined by bonding strength between atomic orbitals.
4. Compared to pure cobalt clusters, magnetism calculations show total magnetic moments for ConO clusters exhibit different changing trends. Due to hybridization between Co 3d states and doping-O 2p states, local magnetic moments of Co atoms change. However, O atom contributions to total moments in ConO clusters are negligible. Thus, magnetic moment reduction or enhancement by doping can be attributed to decreases and increases in local magnetic moments of Co atoms.

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Table 1. Calculated bond lengths and binding energy per atom of Co and CoO clusters using different density functional theory methods

Method	R (Å)	Eb (eV/atom)	R (Å)	Eb (eV/atom)
PW91	2.123	2.74	1.595	3.94±0.14
PBE	2.130	2.31	1.631	1.72
BLYP	-	-	-	-
Theoretical	2.123/2.130[28,29]	-	1.595[17]	-
Experimental	2.31[30]	-	1.631[31]	-

Fig. 1 [Figure 1: see original paper]. Ground-state geometries of the corresponding bare Co clusters and the lowest-energy structures and low-lying isomers of ConO (n = 2∼6) clusters. Distances are given in Å.

Fig. 2 [Figure 2: see original paper]. The same as those in Fig. 1 but for n = 7, 8, 9 and 10. Distances are given in Å.

Table 2. Frequencies (cm ^{1}), HOMO-LUMO gaps (eV) and total spin magnetic moments (B) of Con/ConO clusters. The charges (e) on O atoms of ConO clusters are also presented

Cluster size (n)	Frequency	HOMO-LUMO gap	Total spin moment (B)	Charge (e)
2	327.9/224.6	0.263/0.886	4/4	-0.82
3	257.7/43.9	0.632/0.946	7/7	-0.91
4	71.6/119.3	0.507/0.756	10/8	-0.88
5	86.5/42.5	0.353/0.590	11/11	-0.85
6	140.4/121.2	0.233/0.658	14/14	-0.87
7	69.8/76.6	0.353/0.642	15/15	-0.89
8	79.1/81.5	0.423/0.370	16/18	-0.86
9	85.4/42.7	0.198/0.389	17/19	-0.84
10	70.6/30.9	0.257/0.431	18/20	-0.83

Fig. 3 [Figure 3: see original paper]. Average binding energies per atom and the second-order difference energies of the most stable structures of Con and ConO clusters as a function of cluster size

Fig. 4 [Figure 4: see original paper]. 3D isosurface HOMO and LUMO diagrams of Con and ConO clusters (n = 2, 4, 6, 8)

Fig. 5 [Figure 5: see original paper]. Calculated deformed charge density plots for Co3O (left) and Co6O (right)

Fig. 6 [Figure 6: see original paper]. Local atomic magnetic moments on each atom of the lowest-energy structures of ConO (n = 5, 7, 9)

Fig. 7 [Figure 7: see original paper]. Partial (PDOS) and local (LDOS) density of states of Con and ConO (n = 5, 7, 9) clusters. The broadening width parameter is chosen as 0.1 eV

Note: Figure translations are in progress. See original paper for figures.

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