THE INFLUENCE OF LiO LIGAND ON THE STRUCTURE OF THE PALLADIUM COBALT NANOALLOYS

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Abstract— The structural, electronic, and magnetic properties of small, neutral, bimetal with LiO structure was studied by using DFT method (with a GGA xc-functional). The lowest lying isomers are obtained. The effect of LiO molecule was examined. LiO molecule can adsorb topside or bridge side. In this study, LiO molecules do not prefer hollow side. Furthermore, when LiO molecule is adsorbed, the valence electrons are shared between cobalt and oxygen instead of oxygen and Palladium. Oxygen atoms have 3-fold or 4-fold bonding in this study.

Keywords—DFT,metal lnanocluster, nanoalloy,

I. Introduction

For Thanks to advance in new experimental techniques, scientists and engineers in the field of the material science or engineering can currently synthesize, characterize and design distinct materials with required size and arrangement and this encourages them to study specific structures. İmportantly, in the field of catalysis, this motivation has resulted in great advances in order to get better catalysts.

The mixed metal catalysis to obtain better catalysis than pure metals catalysis is used in different areas. For a direct methanol fuel cell, Serov at al [9] examined the efficiency of platinum-free palladium–cobalt catalysts in oxygen reduction. They found the dependence of catalytic activity on precursor nature for palladium chloride and palladium nitrate. Another study done by Jung and coworkers [5] is related to the Lithium air batteries. They studied metal-air batteries due to their high energy density but the critical challenges of these technologies involve slow kinetics of the oxygen reduction that is evolution reactions on a cathode. The slow rates of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) of metal-air batteries under development results in charge overpotentials that means large voltage gaps and low round-trip efficiency [2,3,8]. Hence, for both ORR and OER, lessening the overpotentials by electrocatalysts is of great significance for improving round-trip efficiency and cyclability. The catalysts that have been classically used for ORR and OER are made up of costly metals, such as Pt and Ir [7,11,12]. Their high cost restricts extensive usage in large-scale applications. There is a number of studies available for metal or mixed transition metal catalysis with LiO in the field of Li-air batteries.

However, to the best our knowledge, there has been no studies reported to date on the interaction of PdCo nanoparticles on LiO compounds Thus, it is worthy to investigate CoPdLiO nanoalloy complexes systematically in order to understand the mechanism and elucidate more details on the formation of small CoPdLiO nanoalloy complexes. This study may provide useful information for future experiments that concern the improvement of catalysis of Li-air batteries as well.

In this work, we have investigated the structural, electronic and magnetic properties of Co_nPd_mLiO ($2 \leq n+m \leq 4$) bimetallic clusters within the framework of the density functional theory. We present the obtained results and discuss the interaction complexes formed between CoPd bimetalic atoms and LiO in the following sections.

II. Computational Details

NWChem 6.0 package [10] has been used to achieve geometry optimizations, and to determine the total ground energies and the highest occupied and the lowest unoccupied molecular-orbital (HOMO–LUMO) gaps by DFT calculations. CRENBL [4] basis set and relativistic effective core potential (ECP) have been chosen for Pd and Co where the outer most electrons are treated as valence to reduce the number of electrons explicitly considered in the calculations. For Li and O atoms, the split valence 6-311++G** basis set has been employed. The reliability of the CRENBL basis set and ECP were determined by comparing atomic excitation energies with accurate all-electron calculations [4]. The default convergence criteria of the code have been employed during the calculations, which are 1×10^{-6} Hartree for energy and 5×10^{-4} Hartree/a_0 for energy gradient. The generalized gradient approximation (GGA) of Becke's exchange functional [1] and Lee-Yang-Parr correlational functional [6] is chosen in the present work. The geometry optimizations without any symmetry constraints in various electronic spin multiplicities were carried out.

III. Results and Discussion

The most stable structures of Pd_nCo_mLiO ($2 \leq n+m \leq 4$) bimetal lithium monoxide are presented in Figure 1 and the homo-lumo density plot is given in Figure 2. Besides, Table 1 indicates spin moment, binding energy, Fermi level and homo-lumo gap of the studied clusters. LiO is, see Figure 1, adsorbed on the PdCo nanoparticles in a molecular form with oxygen instead of lithium bonding to PdCo nanoparticles for each case studied in the present work. LiO molecule absorbed on PdCo surface on a top or bridge site and prefers to bind Co atom in these structures.

The lowest energy structure of Pd_2LiO has C_s point group symmetry in the triplet magnetic state. The Pd-Pd bond distance of Pd_2LiO is 2.44 A. The absorption of LiO results in the Pd-O bond distance as 1.90 A whereas the Li-O bond distance is 1.68 A The LiO molecule prefers to be adsorbed on PdCo on top site (see Figure 1b). The point group symmetry of the lowest structure of PdCoLiO is Cs with a B.E of 2.61 eV. The Pd-Co

bond distance is 2.27 A. The bond distance between Li and O in the PdCo nanoparticle is slightly different from that of the Pd_2LiO structure. The doping of a Co atom instead of a Pd atom leads to a very little stretch in the Co-O bond length where the Co-O bond distance become 1.75 A. The Co_2LiO (see Figure 1c) has 1.71 eV Fermi Energy in the Table 1. Furthermore, The B.E of Co_2LiO having 5 μ_B spin moment is 2.65 eV. This value is the highest value among at m+n=2, which shows if the ratio Co/Pd is increased, the B.E value is inclined to increase.

In the ground state structure of Pd_3LiO (see Figure 1d), LiO is adsorbed on the surface including triangular oriented Palladium atoms as a bridge site. When comparing with the structure of Pd_2LiO. The Li-O bond length is stretched by 0.14 A whereas the Pd-O bond length is elongated as 0.1 A. The average bond length of Pd-Pd is 2.73 A. The spin moment of the Pd_2LiO structure is 1 μB and the point group symmetry of this structure is C_s. The homo-lumo energy gap is calculated as 0.5 eV with direct gap and its Fermi energy is found as 3.78 eV. As coming to B.E, it is 2.36 eV (see Table 1). As one of the Pd atoms replaced with Cobalt atom, the lowest energy structure of Pd_2CoLiO becomes the structure possessing triangular bimetal unit including a Co atom is at apex and two Pd atoms at base.

The addition of a Co atom instead of a Pd atom is, see Figure 1e, very little effect on Li-O bond length (1.73 A) whereas the Li-O bond length is shrunk as much as 0.17 A after the removal of a Pd atom from this structure.

While distances between Pd and Co atoms are 2.40 and 2.41 A, the Pd-Pd bond distance is longer by 0.18 A than that of Pd_2LiO nanoparticle. LiO molecule prefers to be adsorbed on Co surface rather than Pd surface as a top site with a 1.71 A of Co-O bond length. Its binding energy is 2.64 eV in quartet magnetic state. The energy gap in this structure having Cs geometry is 0.73 eV with direct band gap.

As the Co ratio increases, the Pd_1Co_2LiO nanoparticle has also triangular unit with increasing B.E as 2.65 eV that is the highest value at m+n=3. LiO molecule prefers energetically to bind to two cobalt atoms, which is typically adsorption type in this study. The Co-O distances are 1.85 and c1.91 and the Co-Co distance is 2.36 A, which is longer as 0.25 A than that of the Co_2LiO while the Co-Pd bond distances are 2.43 A and 2.49 A, which are slightly longer than that of the CoPdLiO. Due to the doping of Co atom, the Li-O bond length seems to be less affected in this structure as well. The magnetic moment of Co_2PdLiO having C_1 symmetry is 5 μB. The HOMO-LUMO gap (HLG) is 0.83 eV with direct gap while the Fermi energy of this structure is 3.27 eV. The B.E of Co_3LiO nanoparticle is calculated as 2.53 eV. In this case, it can be noted that the evaporation of a Co atom to the cluster leads to increase in B.E importantly.

However, the HLG is 0.46 eV with indirect gap. The result is consistent with B.E value. As coming Fermi Energy Level, it has a value of 3.61 eV, which is shorter by 0.17 eV than that of Pd_3LiO nanoparticle. In the lowest structure of Co_3LiO in sextet magnetic state, The Li-O bond length upon removal of one Pd atom and addition one Co atom instead seems to be less affected since the bond length is 1.76 A but the Li-O bond length of free LiO is calculated as 2.434 A. That shows the bond length of Li-O is shrunk very much when LiO adsorbs on the nanoparticle surface.

The Pd_4LiO structure has, see Figure 1h, tetrahedral unit where the average Pd-Pd bond length is 2.72 A. The LiO is adsorbed on the Pd surface as bridge site where the Pd-O distances are 2.08 and 2.09 A that is very close to those of value of Pd_3LiO while the Li-O bond length is 1.79 A.

It can be concluded that the addition of a Pd atom to Pd_3LiO leads to expand the length of the triangular unit consisting of Pd atoms that is the base of Pd_4LiO structure. The total magnetic moment of this structure is 3 μ_B with C1 symmetry. The HLG is 0.03 eV with indirect band gap whereas the Fermi level is 2.11 eV. The addition of one Co atom with the removal of a Pd atom provides cobalt atom to bind the structure with 4-coordinated number and to preserve its tetrahedral unit with cobalt at apex. The Co-O bond length is similar as top site absorption is observed on the cobalt surface, where the bond length is 1.71 A.

The addition of a Pd atom to Pd_2CoLiO has little effect on the Li-O bond length. The B.E of Pd_3CoLiO is 2.64 eV in quartet magnetic state. The Fermi Level of this structure is 3.59 eV whereas the HLG is 0.50 eV with direct bandgap as well. The magnetic moment of the structure in Figure 1i is 5 μ_B with Fermi Energy of 3.36 eV.

The HLG is 0.49 eV with direct gap as well. The Co-Co bond distance upon LiO molecule is 2.30 A, which is slightly differ from that of Co_2PdLiO nanoparticle. The LiO molecule is adsorbed on cobalt surface as bridge site with bond length of 1.90 A whereas the Li-O bond length is 1.80 A.

Table 3 The Electronic Properties of Co_nPd_mLiO within the studied range in eV

STRUCTURE	SYM	MM (μ_B)	B.E (eV)	FL (eV)	EG (eV)	EGT
Co_2LiO	C_s	5	2.65	2.81	1.26	Direct
$CoPdLiO$	C_s	4	2.61	2.51	0.05	Direct
Pd_2LiO	C_s	3	2.07	2.05	0.42	Indirect
Co_3LiO	C_1	6	2.53	3.61	0.46	Indirect
Co_2PdLiO	C_1	5	2.65	3.27	0.83	Direct
$CoPd_2LiO$	C_s	4	2.64	3.65	0.73	Direct
Pd_3LiO	C_s	1	2.36	3.78	0.50	Direct
Co_4LiO	C_1	9	2.57	2.83	0.95	Indirect
Co_3PdLiO	C_s	8	2.61	3.87	0.61	Indirect
Co_2Pd_2LiO	C_s	5	2.68	3.36	0.49	Direct
Co_1Pd_3LiO	C_1	4	2.65	3.59	0.50	Direct
Pd_4LiO	C_1	3	2.33	2.11	0.03	Indirect

Furthermore, the B.E of Pd_2Co_2LiO nanoparticle is 2.68 eV with C_s point group symmetry. The addition of a Pd atom to Co_3LiO nanoparticle (see Figure 1k) leads to expand average Co-Co bond distance where the average bond distance is 2.375 A while the average Co-Pd distance is 2.52 A, which are shorter than that of $PdCo_2LiO$ structure. The LiO molecule prefers to bind Co surface instead of Pd surface with the Li-O bond length of 1.84 A. the HLG is 0.61 eV with indirect band gap while Fermi energy level is 3.87 eV. In this structure having C_s symmetry, the B.E value is 2.61 eV with total magnetic moment of 8 μ_B. The Co_4LiO nanoparticle has, see Table 1, 0.95 eV HLG

energy where bandgap type is found indirect while the Fermi Energy Level is 2.83 eV. The B.E of this structure having 9 μ_B is calculated as 2.57 A. The average bond length of Co-Co bond distance is 2.35 A. After the addition of a cobalt atom to the Co_3C_2H, the Co-O bond distances are found as 1.88 A and 1.89 A while Li-O bond length is 1.68 A.

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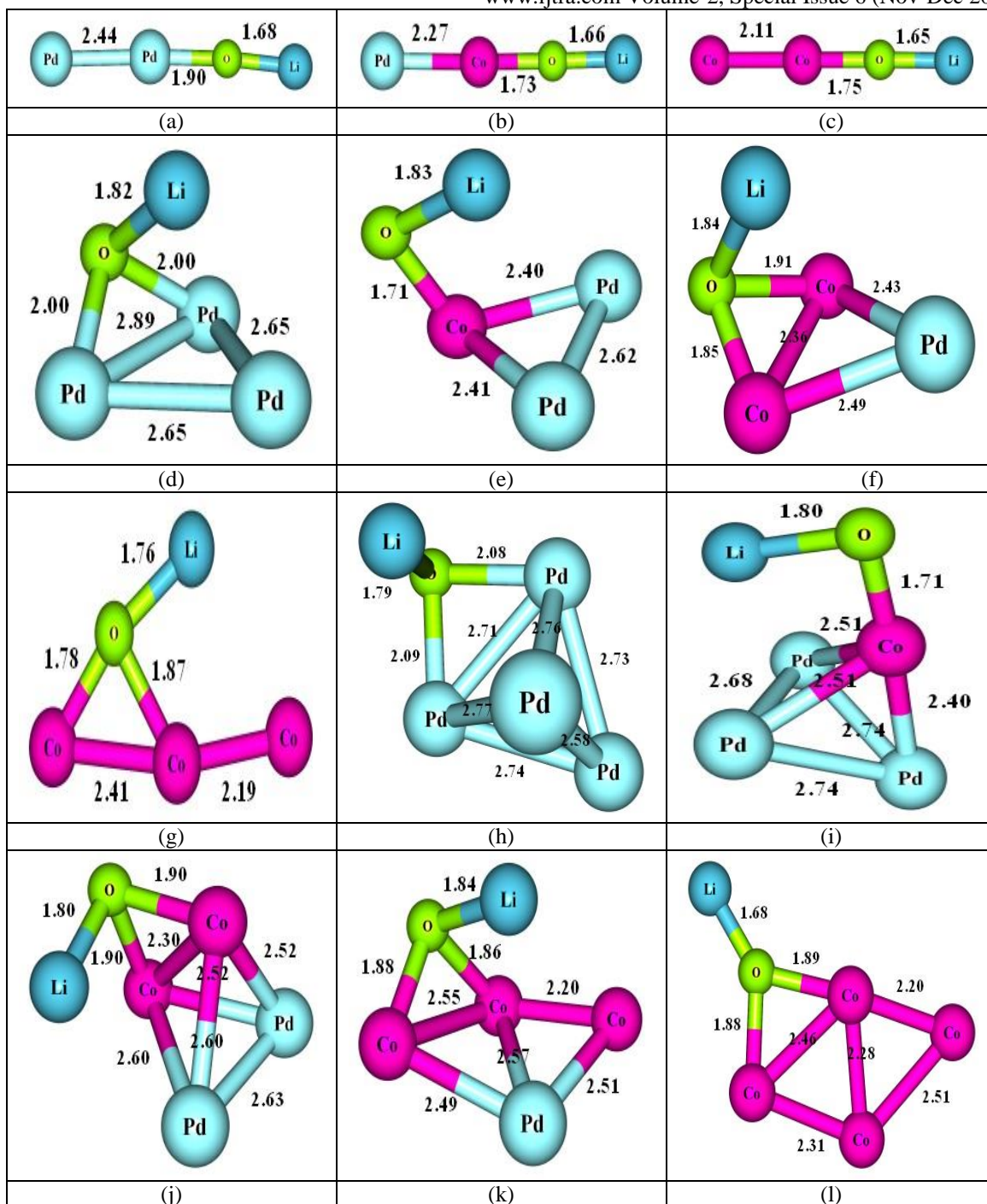
Figure 3.3.3 The optimized structure of Co$_m$Pt$_n$LiO (2≤ m +n≤3)