Effect of Co doping on catalytic activity of small Pt clusters

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Platinum is the most widely used catalyst in fuel cell electrodes. Designing improved catalysts with low or no platinum content is one of the grand challenges in fuel cell research. Here, we investigate electronic structures of Pt_4 and Pt_3Co clusters and report a comparative study of adsorption of H_2 , O_2 , and CO molecules on the two clusters using density functional theory. The adsorption studies show that H_2 undergoes dissociative chemisorption on the tetrahedral clusters in head on and side on approaches at Pt centers. O_2 dissociation occurs primarily in three and four center coordinations and CO prefers to adsorb on Pt or Co atop atoms. The adsorption energy of O_2 is found to be higher for the Co doped cluster. For CO, the Pt atop orientation is preferred for both Pt_4 and Pt_3Co tetrahedral clusters. Adsorption of CO molecule on tetrahedral Pt_3Co in side on approach leads to isomerization to planar rhombus geometry. An analysis of Hirshfeld charge distribution shows that the clusters become more polarized after adsorption of the molecules. © 2008 American Institute of *Physics*. [DOI: 10.1063/1.2839437]

I. INTRODUCTION

Platinum and platinum based alloy nanoparticles have received increasing attention due to their superior catalytic activities for a number of reactions. There have been several investigations carried out to improve the electrocatalytic activity of Pt and Pt-based alloys for hydrogen oxidation reaction and oxygen reduction reaction (ORR) in fuel cell electrodes.^{1,2} In particular, bimetallic Pt-Co alloy systems have often been employed. The oxygen reduction reaction catalyzed by Pt and Pt alloys is extensively investigated because of its importance in polymer electrolyte membrane (PEM) fuel cells.³ PEM fuel cells, currently the most widely studied low-temperature fuel cells, use a polymer membrane as an electrolyte facilitating proton transport from the anode, where a fuel such as H_2 is oxidized, to the cathode, where O_2 is reduced.^{4,5} The reduction reaction is limited by the slow kinetics even with pure Pt as catalyst. Designing improved cost effective catalysts with low or no Pt content is paramount to making fuel cells commercially viable. Therefore, studies related to the analysis of ORR catalyzed by Pt and Pt-based alloy systems continue to be a topic of active investigation. $^{6-11}$

The activity of a catalyst to a specific reaction is largely governed by the local electronic environment of the catalyst. Pure transition metal nanoparticles or clusters generate significant charge localization compared to their bulk crystal surfaces.¹² The active components of dispersed metal catalysts are small clusters and, therefore, the cluster properties rather than bulk properties are responsible for the observed characteristics.¹³ In general, doping modifies the local electronic properties of pure transition metal clusters. Indeed, Pt alloys of various compositions have been found to catalyze ORR at least as effective as pure Pt. The abundance and relatively low cost of nonprecious metals such as Co make Pt-Co alloy catalysts potentially cost effective alternatives to pure Pt catalysts.¹⁴⁻¹⁶ Electronic and structural properties of pure and doped transition metal clusters and their relationship with the observed macroscopic phenomena have become one of the most active areas of investigation in cluster science. Theoretical studies of transition metal clusters can provide detailed information on the electronic structure as well as on the adsorption and reaction properties. Small clusters effectively connect properties at the atomic scale to the macroscopic behavior of bulk crystals and provide an excellent platform from which one can study heterogeneous catalytic process on various substrates. The cluster model has been widely used for the study of chemisorption and reactions on transition metal surfaces because of the local character of the interaction between the adsorbate and the adsorbant. Hence, a detailed investigation of electronic structures of small clusters is important to elucidate the mechanisms of adsorption and reaction. The effect of cluster size and shape on reactivity is a key issue in nanostructured catalyst design.

Detailed understanding on the interactions of H_2 , O_2 , and CO on Pt and Pt-based alloy clusters is indispensable for controlling chemical reactions of PEM fuel cells since these adsorbates take part in the oxidation or reduction process of PEM fuel cells. Since pure Pt metal is known to suffer from

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CO poisoning in PEM fuel cells,¹⁷ it is advantageous to study the effect of doping for the prospect of observing promotion or poisoning effects.

Interactions of transition metal clusters with small molecules have recently been reviewed by Knickelbein.¹³ Physical properties of transition metal clusters have also been reviewed.¹⁸ Electronic structures of small Pt clusters have been the topic of a number of recent investigations. Dai and Balasubramanian¹⁹ reported electronic structures of Pt₄ clusters using complete active space multiconfiguration selfconsistent field (SCF) followed by multireference configuration interaction calculations employing relativistic effective core potentials for Pt atoms. Nakatsuji et al.²⁰ performed ab initio theoretical study of the interaction between H₂ molecule and small Pt clusters. Xiao and Wang²¹ investigated both planar and three dimensional Pt clusters and concluded that planar Pt clusters of up to nine atoms are as stable as their three-dimensional isomers. H_2 chemisorption on Pt_4 cluster was reported by Poulain *et al.*,^{22,23} while Nie *et al.*²⁴ carried out a systematic structural evolution of subnano-Pt clusters up to n=15 using density functional theory (DFT). Recently, Chen et al.²⁵ have performed DFT studies of sequential H₂ dissociative chemisorption on a Pt₆ cluster and Zhou et al.²⁶ on selected Pt_n (n=2-5, 7–9) clusters. DFT calculations of methane activation reaction on a Pt atom and a Pt₄ cluster have also been recently reported by Xiao and Wang.²⁷

Several first principles ab initio calculations of the electronic structures of Pt-Co alloy systems have been reported.²⁸⁻³¹ Kootte et al.³¹ performed spin-polarized band structure calculations of $Co_x Pt_{1-x}$ alloys with x=0, 0.25, 0.5, 0.50.75, and 1, and reported density of states and magnetic moments of the clusters. Lee et al.³² investigated the electronic structure of bulk Pt-Co alloys using x-ray spectroscopy and DFT calculations. Using a combination of spectroscopic techniques including low energy electron diffraction and Auger electron spectroscopy, Lee et al.³³ studied the changes in surface stoichiometry of an ordered Pt₃Co(100) surface due to NO adsorption and observed significant surface reconstruction. Lu et al.³⁴ performed local spin density calculations of Pt_3X and Pd_3X (X=3d metals) compounds and found that spin polarization leads to ordering in Pt₃Co and Pd₃Cr. Roques et al.³⁵ carried out combined experimental and theoretical studies of the activity of Pt₃Co alloy surface toward O_2 reduction relative to the Pt catalyst. They found that the efficiency of ORR depends significantly on the surface composition and structure, and alloying Pt with transition metals, such as Co and Cr, leads to an enhancement of the reaction. Using DFT calculations, Shimodaira et al.³⁶ investigated reaction mechanisms at Pt alloy anode catalysts in PEM fuel cells. Extensive DFT calculations of adsorption and dissociation of OH, O2, H2O, and H2O2 on pure Pt and Pt clusters alloyed with Co, Cr, and Ni have been reported by Balbuena and co-workers.^{11,37-43} Stamenkovic *et al.*⁴⁴ reported trends in electrocatalytic activities of Pt₂M (M =Ni,Co,Fe,Ti,V) composite systems and found that Pt_3Co offered superior catalytic activity for ORR. Duong et al.⁴⁵ found that Pt₃Co alloy has slightly higher activity than Pt black in acidic medium toward the ORR and a reduced activity in alkaline medium. Carbon supported Pt–Co catalyst nanoparticles have been the topic of a number of recent experimental investigations^{46–48} and were found to possess improved catalytic properties in PEM fuel cells compared to pure Pt on carbon. However, the bonding, local electronic structures of Pt and Co atoms, and Pt-skin effect in these alloy system are still not fully understood.

While the interaction of H₂, O₂, and CO with pure Pt₄ clusters has been reported in the literature, such studies involving Pt-Co alloy systems are lacking. To gain physical insights into the catalytic properties of these systems, we have performed a systematic study of the electronic structures, bonding, and growth patterns of Pt₄ and Pt₃Co clusters using first principles DFT calculations. Although the size of the clusters considered in our study is rather small, we believe that the present calculations would provide mechanistic insights into the nature of bonding and reactivity of pure Pt and Co doped Pt toward the adsorption of H₂, O₂, and CO. Furthermore, catalytic reactions often occur at the sharp corners, edges, and defect sites of catalyst clusters or surfaces and these active sites are well characterized by small subnanoclusters. The main objective of this paper is to provide a comparative study of the electronic, geometric, and thermodynamic properties of H₂, O₂, and CO adsorption on Pt₄ and Pt₃Co clusters. The paper is organized as follows. The details of the computational methodology are given in Sec. II, followed by a presentation and discussion of the results in Sec. III. A summary of our findings and conclusions is given in Sec. IV.

II. COMPUTATIONAL DETAILS

Calculations reported here have all been performed using DFT within the generalized gradient approximation with the Perdew–Wang exchange-correlation functional⁴⁹ (PW91) as implemented in the DMOL³ package.⁵⁰ This method can perform accurate and efficient self-consistent calculations using a rapidly convergent three-dimensional numerical integration scheme. Double numerical basis sets augmented with polarization functions were utilized to describe the valence electrons and effective core potential was used for core electrons, which accounts for the relativistic effect important for Pt atom. A spin-polarized scheme was employed to deal with the electronically open-shell nature of Pt and Co atoms. The electronic charge on the cluster atoms was obtained by population analysis of Hirshfeld charge distribution.

All structures were fully optimized without imposing symmetry constraints. To obtain energetically the most stable structures, the conjugate gradient algorithm, with a SCF energy convergence tolerance of 10^{-6} hartree, was employed. For accurate calculations, we have chosen an octupole scheme for the multipolar expansion of the charge density and Coulomb potential. In the generation of the numerical basis sets, a global orbital cutoff of 4.5 Å was used. The maximum force and the maximum displacement were less than 0.002 hartree/Å and 0.005 Å, respectively. A thermal smearing of 0.004 hartree was applied to the orbital occupation for convergence.

The average binding energy of the Pt_mCo_n cluster (*m* = 3,4; *n*=0,1) is calculated using the expression

$$E_b = (mE_{\rm Pt} + nE_{\rm Co} - E_{\rm Pt_mCo_n})/(m+n), \qquad (1)$$

where $E_{Pt_mCo_n}$ and E_{Pt} and E_{Co} are the total energy of the bimetallic cluster, and the energies of an isolated Pt and Co atoms, respectively. E_b can be used to establish the relative stability of clusters with different structures.

The adsorption energy is defined to measure the strength of H₂, O₂, and CO bonding to the Pt_mCo_n cluster (m=3,4; n=0,1), and it is calculated as

$$E_{\rm ad} = E_{\rm Pt_mCo_n} + E_{\rm X} - E_{\rm Pt_mCo_n-X},\tag{2}$$

where $E_{\text{Pt}_m\text{Co}_n-X}$ is the total energy of the complex and E_X is the energy of H₂, O₂, or CO molecule.

III. RESULTS AND DISCUSSION

A. Pt₄ and Pt₃Co clusters

For Pt₄ clusters, tetrahedral and planar rhombus geometric structures were optimized. A number of DFT calculations have shown that planar and tetrahedral Pt₄ clusters have comparable stability. The energy difference between the two structures is too small which can be considered as degenerate. Calculations by Xiao and Wang²¹ using the VASP program predicted the average binding energy per Pt atom in the tetrahedral structure to be 2.68 eV compared to 2.62 eV for the planar rhombus case. However, using the same code, Huda et al.⁵¹ showed that the average binding energy per Pt atom is nearly the same ($\sim 2.69 \text{ eV}$) for both geometries. Our recent calculations⁵² using the VASP code predicted nearly degenerate energies ($\sim 2.72 \text{ eV}$) for both geometries. Calculations by Nie *et al.*²⁴ using the DMOL³ code predicted that the tetrahedral geometry is slightly more stable than the planar one. They obtained an average binding energy per Pt atom for the tetrahedral geometry to be 2.55 eV. The present results computed using the DMOL³ code are in agreement with the results of Nie et al. We obtain an average binding energy of 2.52 eV for the tetrahedral structure compared to 2.47 eV for the planar rhombus isomer. The geometry optimized structures and the corresponding bond lengths are shown in Figs. 1(a) and 1(b). The Pt-Pt bond length in tetrahedral Pt₄ is found to be 2.68 Å compared to 2.59 Å for the terminal Pt-Pt bond and 2.67 Å for the central Pt-Pt bond in the rhombus structure. The energy gap E_{g} between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is 0.59 eV for the tetrahedron compared to 0.33 eV for the rhombus isomer.

The tetrahedral geometry of Pt_3Co cluster was obtained by replacing one Pt atom of the optimized tetrahedral Pt_4 cluster with a Co atom. Similarly, the planar geometry was obtained by replacing a central Pt atom of planar Pt_4 with a Co atom. The resulting geometries were optimized and the final structures are shown in Figs. 1(c) and 1(d). Pt is shown in blue and Co is shown in yellow. Similar to Pt_4 , the binding energies of tetrahedral and rhombus Pt_3Co clusters are found to be comparable. The three Pt–Pt bond lengths in tetrahedral Pt_3Co are 2.70, 2.70, and 2.75 Å, close to the value in Pt_4 . Pt–Co bonds are slightly shorter, 2.46, 2.47, and 2.49 Å.



FIG. 1. (Color online) Tetrahedral and planar rhombus structures of Pt_4 and Pt_3Co clusters. Pt is shown in blue and Co is shown in yellow.

Thus, average bond distance has decreased from 2.68 Å in Pt₄ to 2.59 Å in Pt₃Co. Interestingly, the HOMO-LUMO energy gaps in tetrahedron (0.28 eV) and rhombus (0.24 eV) structures of Pt₃Co are comparable. The smaller HOMO-LUMO gap for tetrahedral and rhombus Pt₃Co suggests that the reactivity of the two clusters are likely to be similar. The energetics of Pt₄ and Pt₃Co clusters are provided in Table I.

From now on, we will concentrate on tetrahedral clusters since in realistic catalytic systems the catalyst particles are essentially three dimentional. Figure 2 shows the top and side views of electrostatic potential superimposed on electron density of optimized Pt₄ and Pt₃Co clusters. In Pt₄ cluster (I), electron density is found to be high between any Pt-Pt bonds (shown in red) and low on the Pt atom (shown in blue). In Pt₃Co cluster (II), Co atom has depleted electron density (blue) while the three Pt atoms have enhanced electron density. The electrostatic potential of Pt_4 (I) indicates that electrons are fully delocalized while in Pt₃Co (II) electrostatic potential shows that electrons are more polarized toward the Pt atom. Thus, Co atom contributes electron density around the Pt atoms in Pt₃Co cluster due to its lower ionization potential (7.88 eV) compared to Pt (9.0 eV).⁵³ Also, with the electronic configuration of Pt and Co being $6s^2 5d^9$ and $4s^2 3d^7$, respectively, a charge transfer from Co to Pt leads to stability for the Pt₃Co cluster, as shown in the

TABLE I. Optimized structures, binding energies, and HOMO-LUMO energy gap (E_{o}) of tetrahedral and rhombus clusters of Pt₄ and Pt₃Co.

System	Average binding energy E_b (eV)	HOMO-LUMO energy gap E_g (eV)
Pt ₄ tetrahedral	2.52	0.59
Pt ₄ rhombus	2.47	0.33
Pt ₃ Co tetrahedral	2.68	0.28
Pt ₃ Co rhombus	2.72	0.24



FIG. 2. (Color online) Electrostatic potential superimposed on electron density maps of (I) Pt_4 and (II) Pt_3Co clusters.

calculated binding energy. As will be demonstrated below, this also leads to an enhanced adsorption of approaching molecules.

When a diatomic molecule such as H_2 approaches the Pt₄ cluster, initially, it sees a symmetric electron density around the cluster. However, in the case of Pt₃Co, the diatom encounters an asymmetric electron density with electron rich Pt centers and an electron deficient Co center. At close proximity, the molecule can reorient in different configurations and interact with the atoms, edges, or the face of the cluster. The diatomic molecules considered in the present study, H₂, O_2 , and CO, could approach Pt atoms of Pt_4 at three different sites, namely, (i) Pt atop, (ii) Pt-Pt bridge, and (iii) Pt-Pt-Pt face as shown in Fig. 3(a). For Pt₃Co, we have considered five different adsorption sites, namely, (i) Co atop, (ii) Pt atop, (iii) Pt-Co bridge, (iv) Pt-Pt bridge, and (v) Pt-Co-Pt face, as shown in Fig. 3(b). Initially, the adsorbing molecules could approach head on and side on orientations resulting in six different adsorption configurations for Pt₄ and ten configurations for Pt₃Co clusters.

Before we discuss details of the adsorption of individual molecules we examine salient features of the frontier orbitals of the clusters and adsorbate molecules, that are involved in bond formation. An analysis of the molecular orbitals involved in bond formation can provide important insights into the stability and reactivity of different clusters with similar



FIG. 3. (Color online) Various adsorption sites considered for (a) Pt_4 and (b) Pt_3Co .



FIG. 4. (Color online) Analysis of HOMO and LUMO isosurfaces of Pt_4 and Pt_3Co clusters with H_2 , O_2 , and CO orbitals.



FIG. 5. (Color online) (a) Comparison of density of states (DOS) for *d* orbitals of Pt_4 and Pt_3Co . Contribution from one Pt atom to the *d*-orbital DOS of Pt_4 (b). A comparison of Pt vs Co atom contributions to the *d*-orbital DOS of Pt_3Co (c).





FIG. 6. (Color online) Final geometries of H_2 adsorption on optimized tetrahedral (a) Pt_4 and (b) Pt_3Co clusters with head on and side on orientations of the H_2 molecule. The H atom is shown in white.

geometries. Figure 4 shows the HOMO and LUMO of H_2 , O₂, CO, Pt₄, and Pt₃Co species along with the HOMO-1 and LUMO+1 of Pt₃Co. The low lying states of transition metal clusters can also participate in chemical reactions with gaseous species since the energy differences between HOMO and HOMO-1 and LUMO and LUMO+1 are, in general, very small. The shapes of H₂ molecular orbitals suggest that H-H activation preferentially takes place at the Pt atop site in both head on and side on modes of Pt₄ and Pt₃Co. Similarly, the shapes of O_2 HOMO and LUMO suggest that O_2 could bind to Pt₄ and Pt₃Co clusters in different orientations. The LUMO of O₂ could bind with the HOMO of Pt₄ in side on mode with two Pt atoms resulting in a four centered coordination. Likewise, the HOMO of O_2 can interact with the LUMO of Pt₄ in side on mode yielding a three centered coordination or in head on mode yielding a two centered coordination. Hence, one would expect that O2 would adsorb to the Pt₄ cluster in different modes with different binding energies. The shapes of CO orbitals indicate that it could bind to the clusters only through carbon center and only with one atom of the Pt₄ cluster (two centered coordination). In Pt_3Co , the energies of HOMO-1 (-4.01 eV) and HOMO (-3.93 eV) and LUMO (-3.65 eV) and LUMO+1 (-3.60 eV) are found to be very close. Hence, the LUMO of O_2 could bind either with the HOMO-1, resulting in bridged O_2 structure with two Pt atoms (four centered coordination) or with HOMO, resulting in O₂ bonded to one Pt atom of Pt₃Co (three centered coordination). Also, the HOMO of O₂ could bind with LUMO or LUMO+1 orbital of Pt₃Co, resulting in an oxygen coordinated to one Pt atom (two centered coordination). The shape of either HOMO or LUMO of CO indicates that it could bind LUMO or HOMO of Pt₃Co through carbon center and only with one atom (two centered coordination) of the Pt₃Co cluster.

Spin resolved partial density of states (DOS) of d orbitals near the Fermi level have been computed for optimized tetrahedral geometries of Pt₄ and Pt₃Co clusters and plotted as a function of energy in Fig. 5(a). As expected, the main feature of DOS spectrum near Fermi level for both the clusters are dominated by d orbitals. The result for the Pt₄ cluster is shown in green, while that for the Pt₃Co cluster is shown in red. Partial *d*-orbital DOS of one Pt atom of Pt_4 and *d* orbitals of Co and a Pt atom of Pt₃Co systems are shown in Figs. 5(b) and 5(c), respectively. It is seen that for the Pt_3Co cluster, the width of the DOS is broadened substantially with an energy shift of ~ 0.2 eV toward the Fermi level compared to pure Pt₄ cluster. The broadening and shifting of DOS peaks upon Co substitution is due to a partial d electron transfer from Co to Pt atoms resulting in an upshift of Co d orbitals above the Fermi levels. As discussed below, this leads to an enhanced reactivity for the Pt₃Co cluster toward the adsorption of H₂, O₂, and CO compared to the bare Pt₄ cluster. In the following subsections, we discuss details of the adsorption of H₂, O₂, and CO at various adsorption sites of Pt₄ and Pt₃Co.

B. Adsorption of H₂

Hydrogen molecule undergoes dissociative chemisorption at the Pt atom in both head on and side on approaches to

TABLE II. Initial and final conformations and adsorption energies (E_{ad}) of H₂ on tetrahedral Pt₄ and Pt₃Co clusters.

System		Head on approach			Side on approach		
	Initial orientation	E_{ad} (eV)	d _{H-H} (Å)	Final structure (Fig. 6)	E_{ad} (eV)	d _{H–H} (Å)	Final structure (Fig. 6)
Pt ₄ -H ₂	Pt atop	0.26	0.78	(i)	1.55		(iii)
Pt_4-H_2	Pt-Pt bridge	1.55	•••	(ii)	1.56	•••	(iii)
Pt_4-H_2	Pt-Pt-Pt face	1.56		(ii)	1.56		(iii)
Pt ₃ Co-H ₂	Co atop	0.52	0.85	(i)	0.51	0.85	(iii)
Pt ₃ Co-H ₂	Pt atop	1.78	•••	(ii)	1.64	•••	(iv)
Pt ₃ Co-H ₂	Pt-Co bridge	0.50	0.85	(i)	0.74	•••	(v)
Pt ₃ Co-H ₂	Pt-Pt bridge	1.78		(ii)	1.81		(iv)
Pt ₃ Co-H ₂	Pt-Co-Pt face	1.77		(ii)	1.77		(iv)



FIG. 7. (Color online) Calculated HOMOs and LUMOs of $Pt_4\text{--}H_2$ and $Pt_3\text{Co}\text{--}H_2$ systems.

a Pt₄ cluster. The resulting H–H and Pt–H separations are, respectively, d_{H-H} =1.93 Å and d_{Pt-H} =1.55 Å, as depicted in Fig. 6(a). The only exception is the head on approach of H₂ to a Pt atop site. In this case, H₂ remains in molecular form with the H–H bond length increased to 0.78 Å from the equilibrium value of 0.74 Å. Energetically, dissociative chemisorption of H₂ is more favorable than adsorption in molecular form. Chemisorption of H₂ leads to distortion of the tetrahedral structure with unequal Pt–Pt bond lengths. Interestingly, the final optimized structures for head on approach at Pt–Pt bridge site and Pt face are identical. Similarly, the final structures for side on approach at Pt atop, Pt–Pt bridge and Pt face are also equivalent. Thus, only the final optimized structure is presented in Fig. 6(a) for these cases.

For Pt₃Co, all orientations of H₂ approaching the cluster that are considered here lead to dissociative chemisorption at the Pt atom. In head on approaches to Co atop, Pt–Co bridge, and side on approach to Co atop, the H₂ molecule remains in molecular form at the Co site. The final geometries are given in Figs. 6(b) (i)–(v). For dissociative chemisorption, d_{H-H} =1.95 Å and d_{Pt-H} =1.56 Å. Similar to that of Pt₄, dissociative chemisorption of H₂ is found to be energetically more



favorable than adsorption in molecular form. As shown in Table II, the dissociative chemisorption energy of H_2 on Pt_3Co is about 0.25 eV higher than that of Pt_4 . Again, as in the case of Pt_4 , several initial adsorption configurations yield equivalent final structures and they are grouped together for both head on and side on approaches in Fig. 6(b). It is also interesting to note that dissociative chemisorption of H_2 at Pt-Co bridge site leads to isomerization to a rhombus structure. In Table II, initial and final geometries of Pt_4 and Pt_3Co clusters, corresponding adsorption energies, E_{ad} and bond lengths d_{H-H} for both Pt_4 and Pt_3Co , clusters are listed.

In order to understand the nature of the bonding between Pt_4 and Pt_3Co clusters and H_2 , the frontier orbitals of highest adsorption energy cases have been characterized. HOMOs and LUMOs of Pt_4 and Pt_3Co interacting with H_2 are shown in Figs. 7(a) and 7(b), respectively. The HOMO of Pt_4 and HOMO-1 of Pt_3Co have predominantly 5d character and match with the symmetry of the H_2 LUMO shown in Fig. 4. The favorable HOMO-LUMO overlap leads to the dissociation of the molecule.

Spin resolved DOS plots for *d* orbital of the Pt atom that is directly bonded to the H atom and H *s* orbital are shown, respectively, in Figs. 8(a) and 8(b) for Pt₄-H₂ interaction. Similar results for Pt, Co *d* orbitals, and H *s* orbital are shown, respectively, in Figs. 8(c) and 8(d) for Pt₃Co-H₂ interaction. Comparison of the DOS plots for the clustermolecular system and the bare clusters [Figs. 5(b) and 5(c)] indicates that DOS have broadened in both Pt₄ and Pt₃Co due to interaction with H₂. In particular, for Pt₃Co-H₂, the Pt *d* orbital has shifted more closer to the Fermi level. The DOS of H in Pt₃Co-H₂ is more pronounced than in Pt₄-H₂ near E_F indicating the strong interaction between Pt atom and H in Pt₃Co.

C. Interaction with O₂

Adsorption of O_2 on Pt_4 and Pt_3Co clusters is possible in three different modes: (i) both O atoms are bonded to the same substrate atom (superoxo, three center), (ii) O_2 is connected to a Pt or Co atom through a single bond (two center), and (iii) O_2 is adsorbed at the bridge site (peroxo, four cen-

FIG. 8. (Color online) DOS for Pt *d* and H *s* orbitals in Pt_4-H_2 [(a) and (b)], and Pt and Co *d* and H *s* orbitals for Pt_3Co-H_2 [(c) and (d)] systems, respectively. Only the *d*-orbital DOS of the Pt or Co atom directly bonded to the H atom is shown.



FIG. 9. (Color online) The same as in Fig. 6 but for the O_2 molecule, the O atom is shown in red.

ter) as shown in Fig. 9(a) (i)-(iv) for Pt_4 and Figs. 9(b) (i) (ix) for Pt_3Co . In both clusters, the highest adsorption energy was found for adsorption at the Pt or Co atop site (superoxo) followed by adsorption at the Pt or Co site through a single bond. The optimized O_2 bond lengths d_{O-O} were found to be 1.35 and 1.39 Å for superoxo mode, and 1.38 and 1.40 Å for the peroxo mode, 1.28 and 1.29 Å for single bond coordination, respectively, for Pt_4 and Pt_3Co . Our calculated chemisorbed O_2 bond lengths in both Pt_4 and Pt_3Co are consistent with the experimentally measured values⁵⁴ of O_2 bond length (1.37 ± 0.05 Å) in dissociative chemisorption of O_2 on Pt. Thus, only superoxo and peroxo modes lead to dissociation of the O_2 molecule. The energetics of O_2 adsorption in various initial orientations, final geometries, adsorption energies, E_{ad} , and bond lengths, d_{O-O} , are summarized in Table III for both pure Pt₄ and Pt₃Co clusters. The adsorption energies and bond lengths show that O_2 binds more strongly with Pt₃Co than Pt₄ in peroxo and superoxo modes. This is explained in terms of the enhanced electron density at the Pt site than the Co site in Pt₃Co. Microcalorimetric measurements of O_2 adsorption energies on different Pt surfaces^{55–57} reported energies in the range of 1.66–5.20 eV.

Frontier orbitals of Pt₄ interacting with O₂ orbitals resulting in three coordination and Pt₃Co interacting with O₂ orbitals resulting in four coordination are shown in Figs. 10(a) and 10(b), respectively. O₂ adsorption involves electron transfer from the 5*d* orbital of Pt to the antibonding π^* orbital of O₂ and subsequent back donation from the bonding orbital of O₂ to Pt resulting in a weakening of the O–O bond. Our findings are consistent with those of Li and Balbuena.³⁹

Spin resolved DOS plots for Pt *d* and O (s,p) orbitals are shown, respectively, in Figs. 11(a) and 11(b) for Pt₄–O₂ interaction. Similar results for Pt and Co *d* orbitals and O (s,p) orbitals, respectively, are given in Figs. 11(c) and 11(d) for Pt₃Co–O₂ interaction. The partial DOS shown corresponds to the Pt atom directly bonded to the adsorbate molecule. It is seen that Pt *d* orbital DOS is more broadened in Pt₃Co and closer to Fermi level than in Pt₄.

D. Interaction with CO

For the interaction of CO with the Pt_4 cluster, two modes of adsorption have been found: (i) CO bonded to Pt atop and (ii) CO adsorbed at a Pt–Pt bridge site. The adsorption energy was found to be higher for CO attached to Pt atop rather than the bridge site. Upon adsorption the CO bond elongates to 1.16–1.19 Å from the equilibrium value of 1.14 Å resulting in a Pt–C bond length of 1.84 Å for the Pt atop case. The final structures along with bond lengths are shown in Fig. 12(a) (i)-(iii).

As in Pt_4 cluster, adsorption of CO on tetrahedral Pt_3Co results in two modes of coordination for head on approaches. However, in side on approaches to all coordination sites except the Co atop site, the tetrahedral Pt_3Co isomerizes to a rhombus structure. The corresponding adsorption energies

TABLE III. Energetics (E_{ad}) and bond lengths of O₂ adsorption on tetrahedral Pt₄ and Pt₃Co clusters.

System		H	lead on app	oroach	Side on approach		
	Initial orientation	E _{ad} (eV)	d _{О-О} (Å)	Final structure (Fig. 9)	E _{ad} (eV)	d _{О-О} (Å)	Final structure (Fig. 9)
Pt ₄ -O ₂	Pt atop	1.29	1.28	(i)	1.53	1.35	(iii)
Pt_4-O_2	Pt-Pt bridge	1.54	1.35	(ii)	1.40	1.38	(iv)
$Pt_4 - O_2$	Pt-Pt-Pt face	1.54	1.35	(ii)	1.40	1.38	(iv)
Pt ₃ Co-O ₂	Co atop	1.51	1.29	(i)	2.10	1.39	(v)
Pt ₃ Co-O ₂	Pt atop	1.28	1.30	(ii)	1.68	1.36	(vi)
Pt ₃ Co-O ₂	Pt-Co bridge	2.13	1.39	(iii)	2.01	1.40	(vii)
Pt ₃ Co-O ₂	Pt-Pt bridge	1.33	1.29	(iv)	1.47	1.38	(viii)
Pt ₃ Co-O ₂	Pt-Co-Pt face	1.35	1.28	(ii)	1.32	1.29	(ix)



FIG. 10. (Color online) Calculated HOMOs and LUMOs of Pt_4-O_2 and Pt_3Co-O_2 systems.

are found to be the highest of all the approaches studied. The resulting structures and energetics are shown in Figs. 12(b) (i)–(vi) and Table IV, respectively. The adsorption energy of CO is found to be the highest of all the three adsorbing species considered and, in particular, interaction of CO with the Pt₃Co cluster is found to be even stronger than Pt₄ cluster. Experimental measurements of CO adsorption energy^{57–59} on various Pt surfaces yield values in the range of 1.2-2.1 eV compared to 2.40-2.70 eV in the present study. The relatively high adsorption energy values obtained in the present study indicate the high reactivity of small clusters due to exposed edges and corners compared to a regular surface.

In CO adsorption to Pt_4/Pt_3Co , Pt–CO bond strength depends first on the σ donation from the bonding orbitals of CO (5 σ) to the LUMO of the Pt atom $[d_{\sigma^*}(z^2)]$ which leads to an overall increase in the electronic charge on Pt. Subsequent back donation from the filled 5*d* orbitals of Pt $[d_{\pi}(xz, yz)]$ to the empty antibonding $2\pi^*$ orbital of CO reinforces the resulting sigma bond. This synergic bonding^{60,61} is observed in the frontier orbitals of Pt₄–CO and





FIG. 12. (Color online) The same as in Fig. 6 but for the CO molecule, C and O atoms are shown in gray and red, respectively.

Pt₃Co–CO, as shown in Figs. 13(a) and 13(b), respectively. Upon CO adsorption on Pt₄, the electron density is depleted between Pt atoms leading to an overall increase in Pt–Pt bond lengths. Electron density between Pt–Pt and Pt–Co bonds in Pt₃Co is also lowered leading to increase in Pt–Pt and Pt–Co bond lengths in Pt₃Co. However, this increase is less than in the case of Pt₄. In CO adsorption, for instance, the bond length between Pt–C (1.84 Å) in Pt₄–CO is longer than Pt–C (1.78 Å) in Pt₃Co–CO confirming the presence of larger electron density at Pt sites in Pt₃Co.

FIG. 11. (Color online) DOS for Pt *d* and O (s,p) orbitals in Pt₄-O₂ [(a) and (b)], and Pt and Co *d* and O (s,p) orbitals for Pt₃Co-O₂ [(c) and (d)] systems, respectively. Only the *d*-orbital DOS of the Pt or Co atom directly bonded to the O atom is shown.

TABLE IV. Energetics (E_{ad}) and bond lengths of CO adsorption on tetrahedral Pt₄ and Pt₃Co clusters.

		Н	Head on approach			Side on approach		
System	Initial orientation	$E_{\rm ad}$ (eV)	d _{с-0} (Å)	Final structure (Fig. 12)	E _{ad} (eV)	d _{С-О} (Å)	Final structure (Fig. 12)	
Pt ₄ -CO	Pt atop	2.69	1.16	(i)	2.69	1.16	(iii)	
Pt ₄ –CO	Pt-Pt bridge	2.44	1.19	(ii)	2.69	1.16	(iii)	
Pt ₄ –CO	Pt-Pt-Pt face	2.44	1.19	(ii)	2.70	1.16	(iii)	
Pt ₃ Co-CO	Co atop	1.91	1.16	(i)	1.83	1.16	(v)	
Pt ₃ Co-CO	Pt atop	2.83	1.16	(ii)	2.78	1.16	(vi)	
Pt ₃ Co–CO	Pt-Co bridge	1.98	1.19	(iii)	2.81	1.16	(vi)	
Pt ₃ Co–CO	Pt-Pt bridge	2.40	1.19	(iii)	2.82	1.16	(vi)	
Pt ₃ Co–CO	Pt-Co Pt face	2.10	1.21	(iv)	2.82	1.16	(vi)	

To provide further insights into chemisorption of CO on both Pt_4 and Pt_3Co clusters, we examine the partial DOS of the frontier orbitals interacting with the clusters. The DOS plots for Pt *d* and C(s,p) orbitals in Pt_4 –CO are shown in Figs. 14(a) and 14(b), respectively. Similar results for Pt and Co *d* orbitals and C(s,p) orbitals in Pt_3Co –CO are shown in Figs. 14(c) and 14(d), respectively. The partial DOS shown corresponds to the Pt atom directly bonded to the adsorbate molecule. It is seen that there is a strong overlap between the *s* and *p* orbitals of C with the Pt *d* orbitals for both clusters. This is more favorable in the Pt_3Co–CO system because of the shift in the Pt *d* orbital toward the Fermi level relative to that of the Pt_4–CO system.

We have also performed similar adsorption studies on rhombus Pt_4 and Pt_3Co clusters since the binding energies of tetrahedral and rhombus isomers were found to be comparable (Table I). As in tetrahedral structure, H_2 preferentially undergoes dissociative chemisorption. Interestingly, O_2 adsorption on Pt_4 leads to an isomerization to tetrahedral geometry. The overall nature of CO adsorption is also similar to that of the tetrahedral clusters with the resulting geometries remaining largely in rhombus structure for both Pt_4 and



FIG. 13. (Color online) Calculated HOMOs and LUMOs of Pt_4 -CO and Pt_3Co -CO systems.

Pt₃Co. In all the three gaseous molecules studied, the nature of adsorption is predominantly chemisorption.

E. Population analysis: Hirshfeld charge distribution

The total atomic charges from Hirshfeld population analysis for diatomic molecules and Pt₄ and Pt₃Co clusters before and after adsorption are given in Table V. The data correspond to orientations with the highest adsorption energies. The asterisk (*) indicates the coordinated atoms. In Pt₄, initially the charge is zero on each Pt atom. H₂ adsorption involves a charge transfer from Pt to H. In the case of O₂ adsorption on Pt₄, charge transfer occurs from Pt to the oxygen atom leading to a net positive charge on the Pt atom. In CO adsorption, electronic charge flows from Pt to the C atom leading to a net positive charge on the Pt atoms. The observed charge distribution for O₂ and CO adsorptions can be explained by an initial covalent bonding between the molecule and the metal, and subsequent metal-to-molecule π back bonding with the antibonding orbital of the molecule (LUMO).

In Pt₃Co cluster, due to charge transfer from Co to Pt, all the three Pt atoms have negative charges and the Co atom is positively charged. Upon H₂ adsorption on Pt atom in Pt₃Co, electronic charge around Pt is depleted due to charge transfer to H atoms. This induces further flow of electronic charge from Co to Pt with the net effect being that the Co atom becomes more positively charged in the chemisorbed cluster compared to the bare cluster. For O₂ adsorption, the Pt and Co atoms that are directly bonded to the O atoms become positive, while the other two Pt atoms remain largely unaffected. The lengthening of the O₂ bond due to adsorption could be due to the initial charge transfer from bonding orbital of Pt/Co to O_2 (dative covalent bond) and subsequent back donation from the bonding orbital of O2 to metal orbitals resulting in weak O-O bond. In all the three diatomic molecular adsorption, Co becomes more positive from its initial values. In general, the clusters become more polarized after adsorption of the molecules.

IV. SUMMARY AND CONCLUSIONS

Pt and Pt-based alloy nanoparticles have received increasing attention in recent years due to their electrocatalytic



FIG. 14. (Color online) DOS for Pt *d* orbitals and C (s,p) orbitals in Pt₄-CO [(a) and (b)], and Pt and Co *d* and C (s,p) orbitals for Pt₃Co-CO [(c) and (d)] systems, respectively. Only the *d*-orbital DOS of the Pt or Co atom directly bonded to the C atom is shown.

activities for the oxygen reduction reaction in fuel cell electrodes. In particular, Pt-Co bimetallic alloy has often been employed in polymeric electrolyte membrane fuel cells. Hence, to gain physical insight and to explore how the local environment of Pt atoms is changed due to the doping of Co atom, we have performed density functional theory calculations of Pt₄ and Pt₃Co clusters. The structural and physicochemical properties of pure and Co doped Pt clusters have been analyzed. On the optimized tetrahedral structures, chemisorption of H₂, O₂, and CO molecules in different orientations and at different adsorption sites has been investigated. It was found that chemisorption on the Co doped cluster is energetically more favorable for all three diatomic molecules studied. This is explained in terms of charge transfer from Co to Pt leading to an increased *d*-orbital density of states for the doped cluster near the Fermi level compared to the pure Pt₄ cluster.

An analysis of the frontier orbitals shows that in both O_2 and CO adsorptions, effective back bonding from the metal to adsorbed molecules occurs and that the overlap is more favorable in Pt₃Co. The adsorption studies show that while H_2 undergoes dissociative chemisorption on the tetrahedral clusters in both head on and side on approaches to Pt centers, O2 dissociation occurs in three and four center coordinations and CO prefers to adsorb on Pt or Co atop atoms. Interestingly, tetrahedral structure becomes distorted as a result of H_2 and O_2 adsorption and tetrahedral Pt_3Co transforms to a planar rhombus structure after CO adsorption. Also, H₂ and O2 adsorption at Co atop and Pt-Co bridge site lead to equivalent final geometries. Further analysis of Hirshfeld charges shows that the clusters become more polarized after adsorption of the molecules. The spin and orbital resolved DOS indicate that for the Pt₃Co cluster effective overlap between Pt and the adsorbates leads to higher chemisorption

TABLE V. Hirshfeld charge distribution for individual molecules and clusters before and after adsorption. The data given correspond to adsorption configurations with the highest adsorption energy. The asterisk (*) indicates the coordinated atoms.

Hirshfeld Charges								
	H ₂ O ₂		(СО				
H1	0	01	0	01	-0.109			
H2	0	02	0	C2	0.109			
	Pt ₄	Pt_4-H_2		Pt_4-O_2		Pt_4-CO		
Pt1	0	Pt1	-0.050	Pt1	0.053	Pt1	0.005	
Pt2	0	Pt2	0.084	Pt2	0.038	Pt2	0.046	
Pt3	0	Pt3	-0.007	Pt3	0.039	Pt3	0.022	
Pt4	0	*Pt4	0.035	*Pt4	0.096	*Pt4	0.000	
		*H1	-0.052	*O1	-0.117	01	-0.124	
		*H2	-0.054	*O2	-0.109	*C2	0.053	
	Pt ₃ Co	Pt ₃ Co-H ₂		Pt ₃ Co-O ₂		Pt ₃ Co-CO		
Pt1	-0.060	Pt1	-0.048	Pt1	-0.005	Pt1	-0.041	
Pt2	-0.050	Pt2	-0.053	*Pt2	0.116	*Pt2	-0.020	
Pt3	-0.058	*Pt3	-0.008	Pt3	-0.007	Pt3	-0.046	
Co4	0.168	Co4	0.211	*Co4	0.171	Co4	0.210	
		*H1	-0.063	*01	-0.115	01	-0.140	
		*H2	-0.056	*02	-0.160	*C2	0.036	

energy. We are currently exploring how the catalytic activity may be modified upon deposition of the clusters on different supporting materials.

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