Theoretical thermodynamic study of CO and O_2 Adsorption on Au_{14} Nano Cluster

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ABSTRACT

The Density of State and the Natural Bond Orbital calculations were carried out to study the oxidation of CO on Au_{14} nano cluster through two different mechanisms and determining the best mechanism for the reaction. Chemisorption of O_2 and CO on the nano cluster led to change in energy, density of state and its thermodynamic properties. We calculated the energy band gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital and its role in the adsorption phenomenon.

Keywords: DOS; HOMO-LUMO gap; NBO; Au_{14} nano cluster; CO oxidation; thermodynamic properties

INTRODUCTION

In the recent years, gold has been attracting industrial and scientific interest for its catalytic activity in such reactions as propylene partial oxidation, odor decomposition, direct production of H_2O_2 from H_2 and O_2, and also CO oxidation at low temperatures [1-5]. Catalytic oxidation of carbon monoxide (CO) to form carbon dioxide (CO_2) has been profoundly investigated for its role in reducing air pollution: CO is one of the major pollutants emitted from automotive exhaust gases [6]. In addition, CO oxidation is key to the conventional hydrogen production processes for CO removal prior to the use of H_2 for fuel cell applications [7]. The coadsorption of O_2 and CO on gold catalysts is a notable topic. Experimentally, an enhancement of the activity for oxidation reactions such as preferential CO oxidation has been observed. This catalytic behavior has also been studied with theoretical calculations [8-12]. Sanches et al.,Lopez and Norskov studied the CO oxidation on unsupported small gold clusters using DFT method [10,13].

Despite all the investigations on Au catalysts, the reaction mechanism still remains uncertain. In order to grasp the catalytic mechanism, it would be useful to study the adsorption behavior of O_2 or CO on the Au clusters first, and there are already many works in this field [14]. The adsorption of molecules on small metal clusters in the gas phase is an active field of experimental and theoretical research. As early as 1991, Cox et al. performed a pioneer experimental work on the small molecules adsorbed on Au

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clusters [15]. The adsorbed oxygen is found as oxygen molecule- not as O or O_3 adsorption.

In the last few years, a great amount of theoretical and experimental works have been carried out regarding the reactivity of Au clusters, both free and supported ones, on surface toward different molecules like H_2, O_2, CO, and organic radicals [15-24]. Since the pioneering work of Haruta, it has been recognized that gold can exhibit surprisingly high catalytic reactivity when it is highly dispersed on reducible metal oxides (e.g., Tio_2) [1]. Many previous researches showed that the catalytic properties of clusters are dependent on the structure, leading to different adsorption energies and sites for different structures of clusters [25].

COMPUTATIONAL METHOD

First of all Au_{14} nano cluster is optimized by ESPRESSO package [26] Fig. 1. The energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO), Natural Bond Orbital (NBO) charge analysis and thermodynamic parameters were performed using Gaussian 03 [27].The functional used is B_3lyp and LANL2DZ basis set was used for Au atom and 6-311G(d,f) basis set was adapted for O_2 and CO molecules. DOS diagrams has been drawn using the software Gauss Sum 1.0.5 and all the structures have been drawn by the Gauss view 2.1.
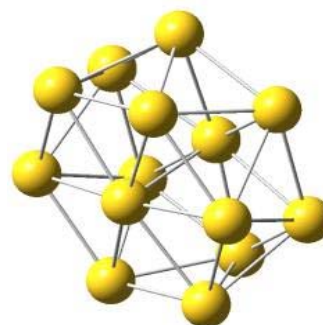

Fig. 1. Geometry of Au_{14} optimized by using ESPRESSO.

RESULTS AND DISCUSSION

All of calculations were carried out by the GAUSSIAN 03 program package that LANL2DZ and 6-311G(d,f) were employed at the B3LYP type of DFT procedure.

Two different LH- type mechanisms can be assumed for CO oxidation over $Au14$ cluster. Schematic illustrations of reaction pathways are shown in Fig. 2. (a) The first mechanism suggests that O2 can adsorb and interact with adsorbed CO forming a four- center surface complex. (b) the second mechanism suggests that O_2 adsorbs then directly dissociates and atomic O interacts with adsorbed CO.
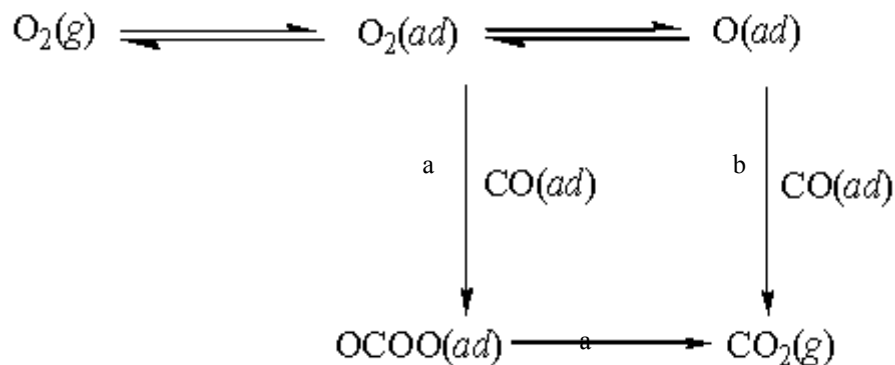

Fig. 2. General mechanism for CO oxidation on Au_{14}.

Density of state (Dos) in combination with molecular orbital (MO), especially frontier MO_s, give the overall electronic structure and reactivity of a system. The bond gap, E_g is defined as the difference in energies between the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbital. Many electronic and optical properties of clusters are directly related to the band gap, thus we have calculated these values.

The total Dos and frontier MO_s of the Au_{14} cluster are shown in Fig. 3. The left molecular orbital (HOMO) and the right molecular orbital (LUMO) reveal the Au_{14} composition.
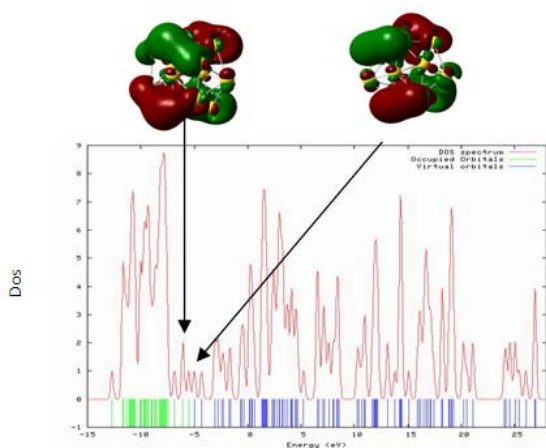
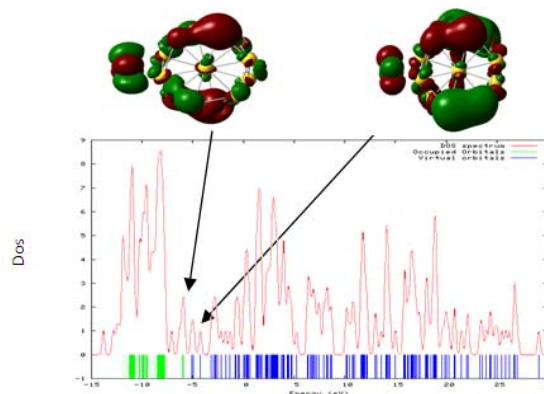The HOMO-LUMO charge density of Au_{14}-O_2 complex are plotted in Fig. 4.

Fig. 4. Density of state (DOS), HOMO (left) and LUMO (right) of Au_{14}-O_2.

The charge densities of Au_{14} and Au_{14}-O_2 complex show that the LUMO– HOMO gap has been increased from 0.517 to 0.736 eV and the band width has become more, moving to the negative values; i.e. the structure has been more stable following O adsorption.

In the first mechanism the chemical adsorption of CO leads to a slight decrease of the HOMO- LUMO gap. As the Fig. 5 (a) and (b) unravel, the energy gap difference between the OC-Au_{14}-O_2 and $[Au_{14}$- O_2-CO$]^{TS}$ is extremely trivial.
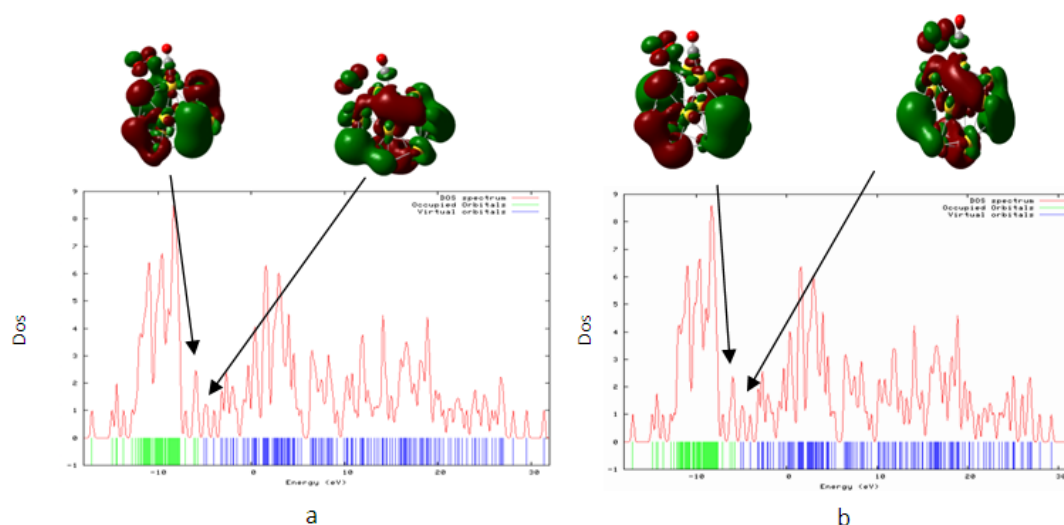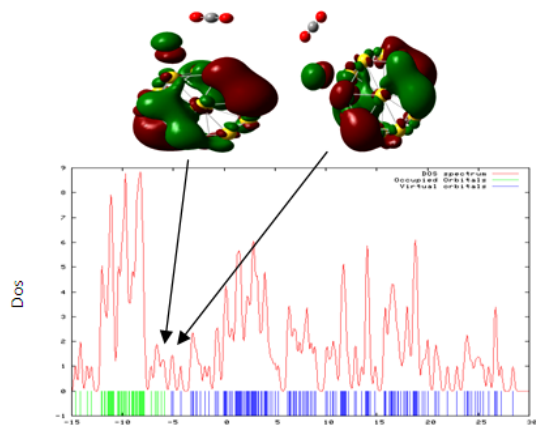

Fig. 3. Density of state (DOS), HOMO (left) and LUMO (right) of Au_{14}.

a

b

Fig. 5. (a) Density of state (DOS), HOMO and LUMO of OC-Au_{14}-O_2 and (b) $[Au_{14}$- O_2-CO$]^{TS}$.

The HOMO-LUMO charge density of Au_{14}- O+ CO_2 are plotted in Fig. 6.

Fig. 6. Density of state (DOS), HOMO and LUMO of Au_{14}- O+ CO_2.

Table 1. shows the HOMO- LUMO gap and total energy regarding every composition in the first mechanism. Given that the electron affinity decreases as gap increases, it can be concluded that since energy gap has increased due to O_2 adsorption, the cluster has lost electron. Electron transfer or hole contributes to change in density of state.

Similarly, the same data can be calculated for the second mechanism. The figures 7, 8 (a, b), and 9 are related to the O_2 *dissociation*, CO adsorption, transition and final states respectively.

Table 1. The HOMO- LUMO gap and total energy of Au_{14} nano-cluster and initial, transition and final states in the first mechanism

	species	E_n (eV)	E_g(eV)
1	Au_{14}	-12563.52	0.517
2	Au_{14}- O_2	-13428/23	0.736
3	OC-Au_{14}-O_2	-14016/92	0.735
4	[OC- Au_{14}- O_2]^{TS}	-14016/73	0.762
5	Au_{14}- O+ CO_2	-14017/38	0.685
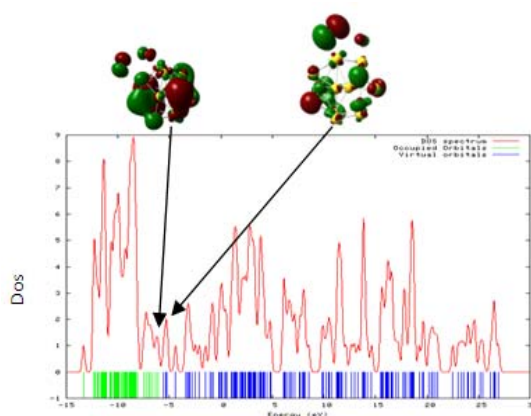
Fig. 7. Density of state (DOS), HOMO and LUMO of [Au_{14}- O]^{TS}.
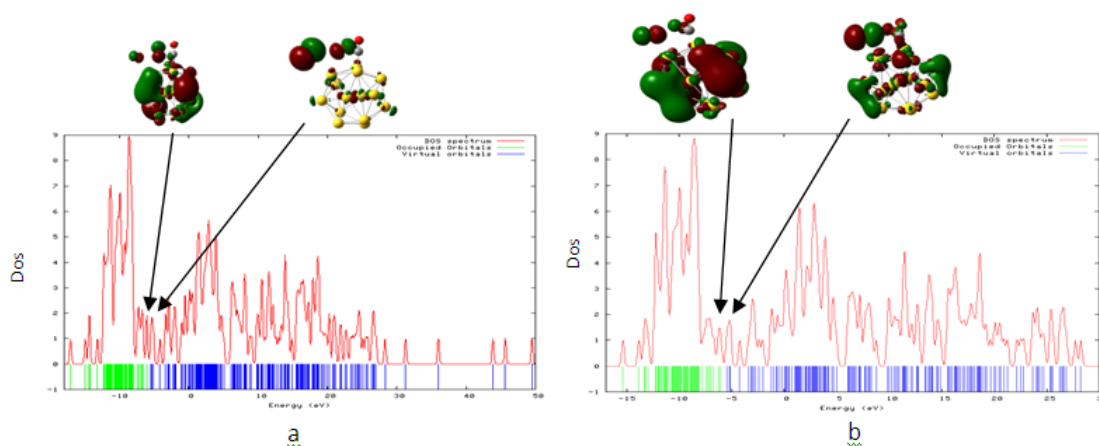
Fig. 8. (a) Density of state (DOS), HOMO and LUMO of OC-Au_{14}-O and (b) $[Au_{14}$- O-CO$]^{TS}$.

Fig. 9. Density of state (DOS), HOMO and LUMO of Au_{14}+ CO_2.

Table 2. The HOMO- LUMO gap and total energy of Au_{14} nano-cluster and initial, transition and final states in the second mechanism
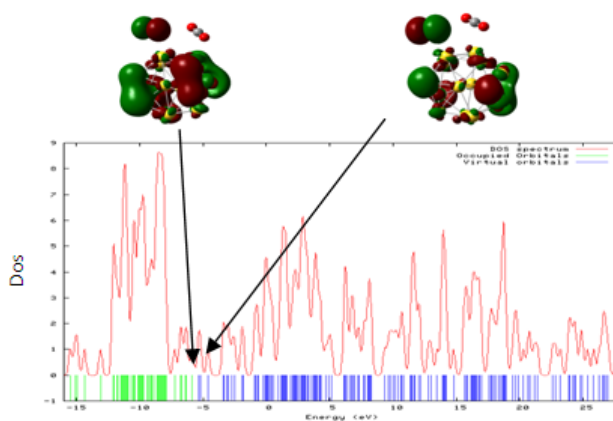
	species	E_n (eV)	E_g(eV)
1	Au_{14}	-12563.52	0.517
2	Au_{14}- O_2	-13428.23	0.736
3	$[Au_{14}$- O$]^{TS}$	-13422.94	0.544
4	O-Au_{14}- CO	-14011.59	0.572
5	$[Au_{14}$- O –CO$]^{TS}$	-14011.15	0.599
6	Au_{14}+CO_2	-14015/56	0.490

Table 2. shows the HOMO- LUMO gap and total energy regarding every composition in the second mechanism. Extreme energy gap reduction in the O_2 dissociation state is the main factor of the final product lack of stability for it causes the cluster not to take electron from the CO molecule.

Natural bond orbital (NBO) charge analysis was also carried out to understand the charge- transfer process occurring during the adsorption and reaction steps [29]. As for the CO oxidation mechanism, Natural bond orbital (NBO) on the atoms 11, 14, 15, and 16 was analyzed to find the effect of CO ligand increase on the $Au_{14}O_2$ cluster Fig. 10. In doing so, load transfer energy of Au 11 and 14 nuclei to the *antibonding molecular orbitals* of the two atoms of O 15 and 16 was investigated.
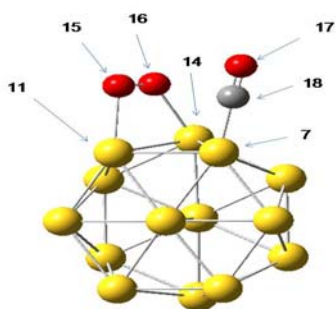
Fig. 10. Presentation of Au cluster and its adsorbed ligands.

Table 3. reveals that when CO adsorbs on $Au_{14}O_2$ charge transfer is aligned with the atoms 14 and 11 and the effect of the transfer was less evident on the O atoms not directly in contact with them.

Thermodynamic parameters such as enthalpy change (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS) have been calculated for the reaction Au_{14} + $O_2 \rightarrow Au_{14}O + CO_2$ at 298.15K by Eqs 1-4 and are listed in table 5.

$$\Delta_r H^\circ(298K) = \sum_{Products} \Delta_f H^\circ_{Prod}(298K) - \sum_{Reactants} \Delta_f H^\circ_{React}(298K) \quad (1)$$

$$\Delta_r H^\circ(298K) = \sum (\varepsilon_\circ + H_{Corr})_{Products} - \sum (\varepsilon_\circ + H_{Corr})_{Reactants} \quad (2)$$

$$\Delta_r G^\circ(298K) = \sum_{Products} \Delta_f G^\circ_{Prod}(298K) - \sum_{Reactants} \Delta_f G^\circ_{React}(298K) \quad (3)$$

$$\Delta_r G^\circ(298K) = \Delta_r H^\circ(298K) - T\Delta_r S^\circ(298K) \quad (4)$$

It is seen that in this temperature both the enthalpy change ($\Delta_r H^\circ$) and the Gibbs free energy change ($\Delta_r G^\circ$) are negative, i. e., it is a exothermic and spontaneous reaction. The entropy change ($\Delta_r S^\circ$) is positive, i. e., it is of the entropy increase type. Considering the changes in thermodynamic functions, the reaction is favorable because of the negative enthalpy change ($\Delta_r H^\circ$) and the positive entropy change ($\Delta_r S^\circ$).

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Table 3. Charge transfer energy for Au_{14}- O_2 and Au_{14}-O_2-CO in 6-311G (d,f) and LANL2DZ/B3LYP

Structure	charge transfer energy(kcal/mol)			
	CR $Au_{11}\rightarrow Ry^*\ O_{15}$	CR $Au_{14}\rightarrow Ry^*\ O_{16}$	CR $Au_{11}\rightarrow Ry^*\ O_{16}$	CR $Au_{14}\rightarrow Ry^*\ O_{15}$
Au_{14}- O_2	46.25	25.83	40.21	15.67
OC-Au_{14}-O_2	53.2	32.59	39.07	15.23

Table 4. Calculated thermochemistry values from GAUSSIAN for the reaction $Au_{14} + O_2 \rightarrow Au_{14}O + CO_2$. All values are in Hartrees

	Au_{14}	O_2	CO	$Au_{14}O$	CO_2
ε_0	-1896.96064	-150.252295	-113.277857	-1972.08095	-188.540119
E_{ZPE}	0.005349	0.003258	0.004622	0.006741	0.010895
E_{tot}	0.035314	0.005625	0.006983	0.038397	0.013572
H_{corr}	0.036258	0.006569	0.007927	0.039341	0.014517
G_{corr}	-0.080180	-0.01577	-0.014563	-0.078487	-0.009875
$\varepsilon_0 + E_{ZPE}$	-1896.955291	-150.249037	-113.273235	-1972.074209	-188.529224
$\varepsilon_0 + E_{tot}$	-1896.925326	-150.246670	-113.270874	-1972.042553	-188.526547
$\varepsilon_0 + H_{corr}$	-1896.924382	-150.245726	-113.269929	-1972.041609	-188.525603
$\varepsilon_0 + G_{corr}$	-1897.040819	-150.268064	-113.292420	-1972.159437	-188.549994

Table 5. Thermodynamic parameters ($\Delta_r H^\circ$, $\Delta_r G^\circ$, $\Delta_r S^\circ$) for the reaction $Au_{14} + O_2 \rightarrow Au_{14}O + CO_2$ at 298.15K.

$\Delta_r H^\circ$kcal	$\Delta_r G^\circ$kcal	$T\Delta_r S^\circ$kcal
-65.69	-67.85	2.16

CONCLUSION

In this work a theoretical study of the O_2 and CO adsorption properties on Au_{14} nano cluster was studied. In examining the features of Au_{14} nanocluster and given the tables and figures, it may be concluded that the cluster becomes more stable by CO and O_2 adsorption and its energy gap increases. The energy gap represents conductivity of the clusters. The more energy gap, the less conductivity due to the difficulty of electron transfer. from two proposed LH mechanisms as possible ways for oxidation of CO on Au_{14} nano cluster we found that the main reaction pathway is CO + O_2 → OOCO → CO_2 +O.

Through electron density transfer to the cluster,CO increases the charge flow toward the atoms 11 and 14 and hence to the O atoms having direct contact with Au atoms.

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