



Comparative study of the efficiency of Au, Ag, Pd and Pt based mono and bimetallic trimer clusters for the CO oxidation reaction

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Understanding synergistic effect by calculating electronic structure is essential to fine-tune the catalytic properties of bimetallic nanoalloy clusters which might be used for design of novel efficient catalysts. Density functional theory PBE0 calculations were performed to investigate the structure and energetics of various intermediates involved in the CO oxidation reaction catalyzed by Au_{3-x}Y_x (x = 0–3 and Y denotes Ag or, Pt or, Pd) trimeric clusters through two possible pathways: Eley-Rideal (ER) and Langmuir-Hinshelwood (LH). The results of this investigation show that the catalytic behavior of the nanocluster highly depends on its composition and the reaction site taken into consideration. The most active reaction centres of gold-silver, gold-palladium, gold-platinum clusters are gold, palladium and platinum atoms respectively. The gold-silver clusters and AuPt₂ prefer ER mechanism whereas, gold-palladium and Au₂Pt selectively favour LH mechanism in comparison to the other. Bimetallic clusters, in general, are more efficient in comparison to their pristine mono-metallic counterparts, in activating the O-O bond for the reaction and have relatively easy CO₂ dissociation. Overall results indicate that the alloyed clusters could potentially have a better catalytic activity as compared to pure gold clusters for CO oxidation at low temperatures.

Keywords: CO oxidation, heterogeneous catalysis, reaction mechanism, nanocluster composition, dopant, synergistic effects, Eley-Rideal (ER), Langmuir-Hinshelwood (LH).

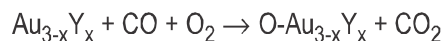
1. Introduction

Nanosized (< 5 nm) transition metal gold, although a noble metal, has been reported to be a good heterogeneous catalyst for a number of oxidation reactions at low temperatures (200–350 K)^{1–5}. Haruta *et al.* were the first to explore the latent qualities of supported nano gold clusters in catalyzing the carbon monoxide oxidation process at low temperatures¹. Later, many research studies have reported the catalytic properties of gold nanoclusters^{5–16}. Herzing *et al.*¹⁷ also gave an experimental evidence of catalysis by subnanometer species of ~10 Au atoms for carbon monoxide oxidation reaction. It was demonstrated in certain studies that anionic gold dimer is the smallest gold cluster that can catalyse CO oxidation reaction^{18,19}. Two different mechanisms for the reaction were proposed, one with a carbonate like intermediate and the other via peroxyformate like intermediate. There are studies of similar nanosize catalytic effects for silver^{20–24},

platinum²⁵ and palladium²⁶ clusters as well. So for almost three decades, metal clusters seem to be propitious models for new surface catalytic materials.

The principal facet in the catalysis of the carbon monoxide oxidation is the activation of O-O bond²⁷. Though CO is easily adsorbed on gold nanoparticles but, the oxygen molecules are neither strongly adsorbed nor activated^{28,29}. One way to solve this issue is to use the oxide support which usually plays a significant role in the activation of oxygen^{27–30}. The other way can be making an active catalyst by alloying gold nanoparticles with a metal of stronger reduction tendency^{31,32}. This will cause stronger electron transfer to oxygen as well as a good CO adsorption. Earlier, Wöste *et al.*³³ examined the CO oxidation catalysis by gold-palladium bimetallic nanoparticles supported on SiO₂, but did not observe synergistic effect compared to the performance of monometallic catalyst in their case which they explained by

the strong oxygen adsorption by palladium. Iizuka *et al.*³⁴ found that silver impurity in gold nanoparticles augments the reaction of CO oxidation and the degree of augmentation strongly correlates with the silver content on surface. The works of Liu *et al.*³¹ and Negreiros *et al.*³⁵ on supported gold-silver alloy systems both report that there is a strong synergistic effect in their high catalytic activity with silver playing a key role in the activation of oxygen. Wang *et al.*³⁶ also analysed the potential activity of gold-platinum tetramers for CO oxidation and suggested that Pt sites are the catalytically active centers in such alloys and reaction site is also very important for such systems. In addition to CO oxidation reaction, previous studies have shown that reaction rates can be accelerated by using nanoalloys as catalysts^{37–40}. In this paper, we consider a total of six unsupported bimetallic trimers along with four pristine clusters, with each atom of cluster having the same coordination number. One of the reasons to consider unsupported metal clusters in the gas phase for this paper is that we want to concentrate on the intrinsic metal effects, i.e. no incorporation of possible auxiliary effects of a support^{41–43}. Although such effects may be relevant, to first substantiate the presence of intrinsic metal effects^{44,45} is worthwhile, specifically when it has been discovered experimentally that nano gold structures with no support are also good catalysts^{46,47}. The other reason is that such exhaustive theoretical studies delineating the reaction mechanism involving metal cluster catalysts have rarely been conducted^{48–52}. The scope of this paper is confined to the analysis of the first part of CO oxidation reaction only where a nascent oxygen binds to the catalyst, that eventually gets released on the oxidation with the second molecule of CO. This reaction in presence of the catalysts considered in this paper can be formulated as follows:



We choose to analyse the above reaction by the two most plausible surface reaction mechanisms – one via formation of peroxy type TS (Eley-Rideal) and the other via formation of a superoxy type TS (Langmuir-Hinshelwood) given by ER pathways and LH pathways respectively in this paper. In LH mechanism^{53–59} two molecules adsorb on neighboring sites and the adsorbed molecules undergo a bimolecular reaction whereas, in ER mechanism only one of the molecules adsorbs and the other one reacts with it directly from the gas phase, without adsorbing^{18,60}. We have also used these mechanism definitions for our earlier work of benchmarking of DFT

functionals for the same CO oxidation reaction^{16,61}. The highlight of this thorough analysis is that we compare the catalytic activities of a variety of transition noble metals and their combinations as trimers with precise reaction mechanisms for CO oxidation.

To the best of our knowledge, no such detailed systematic study of carbon monoxide oxidation reaction on such bimetallic trimers is available yet. A comprehensive theoretical inspection of the potential energy surface for CO oxidation reaction on unsupported bimetallic and monometallic trimers has been performed and the relative studies are presented in this paper to give a deep insight into the intrinsic metal effects on the reaction mechanism.

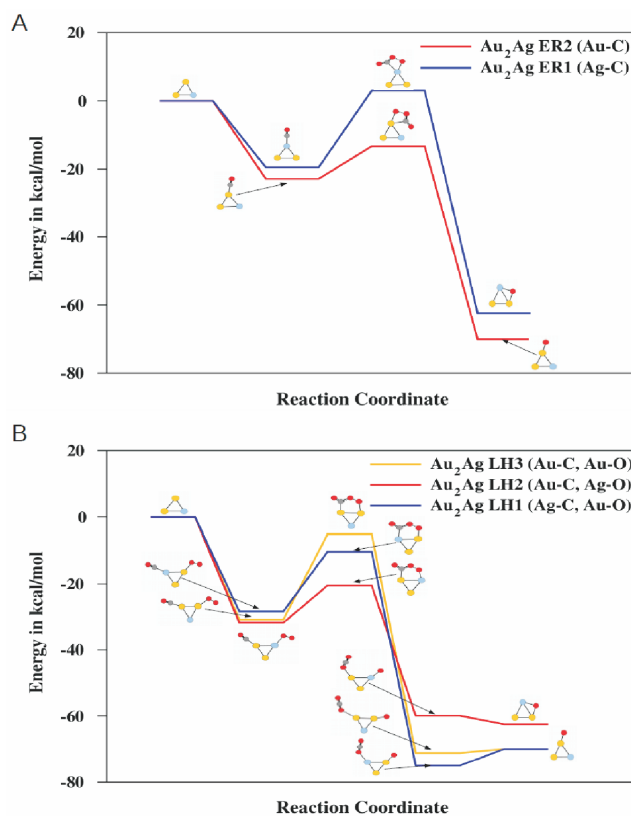


Fig. 1. Potential energy surfaces for CO oxidation catalyzed by Au_2Ag cluster. The corresponding intermediates and transition states related to pathways are also presented. The sum of energies of free Au_2Ag , CO and O_2 is set to zero as a reference. All energies are in kcal/mol. (A) The two possible ER mechanisms: The blue line represents the PES for mechanism via CO adsorption at Ag (blue) atom while the red one represents the mechanism in which CO is adsorbed at Au (yellow) atom. (B) The three possible LH mechanisms with different CO and O_2 adsorption sites. Each different combinations of adsorption sites are labeled as (Ag-C, Au-O), (Au-C, Ag-O), (Au-C, Au-O) and marked by different colors.

2. Methods

Previous benchmarking evaluations have shown that the exchange-correlation DFT functional of Perdew, Burke and Ernzerhof (PBE0)^{4,61–63} was sufficiently accurate for describing noble-metal systems^{11,64–67}. PBE0 was also shown to be adequate for CO oxidation on Au₃ cluster. All the calculations reported here were performed using the PBE0 functional using the Gaussian 09 suite of programs⁶⁸. Stuttgart-Dresden (SDD) double- ζ basis set was used to model the valence electrons explicitly and the corresponding SDD relativistic effective core potential^{69–72} was used to model the core electrons for the metals⁷³. The introduction of effective core potential also reduces the basis set superposition error (BSSE)^{74–76} in the calculations. The keyword “5d” is also used in conjunction with the basis set keywords to use five pure d functions in the calculations. We used the 6-31+G(d) split-valence Pople basis set for the carbon and oxygen atoms, which includes single polarization and diffuse functions.

No symmetry constraints were used in the geometry optimization calculations. The vibrational frequency calculations were done to verify the nature of different stationary points found on the potential energy surfaces. These stationary points were identified as either minima with no imaginary frequency or TS with one imaginary frequency. Then, to identify the minima connected through the transition state we use Gonzalez-Schlegel method for intrinsic reaction coordinate (IRC) calculations⁵⁸. Lowest spin states were considered for all the clusters.

3. Results and discussion

The d-d and s-d interaction between dopants and gold atoms can modify the electronic properties of clusters which may alter their interaction with the incoming O₂, CO and CO₂ molecules^{77–79}. Thus, the intent is to elucidate composition and reaction site dependency of cluster reactivity for CO oxidation reaction and to compare the catalytic behaviour of gold-based clusters with monometallic gold trimer Au₃. Fig. 1 shows all the possible potential energy surfaces for CO oxidation reaction catalyzed by Au₂Ag cluster through (A) ER mechanisms and (B) LH mechanisms. The potential energy surface for this reaction catalyzed by other clusters considered in the paper are given in the Supplementary material.

3.1. Analysis of different reaction sites of bimetallic clusters

There are two possible pathways to study reaction catalyzed by pure clusters – one ER pathway and one LH pathway. But for bimetallic clusters, we have two ER pathways – one with CO adsorption at Au site and the other with CO adsorption at Y site and three LH pathways – one with Au-Y site with CO adsorbed at Au (labeled as Au-C, Y-O), the other with Au-Y site with CO adsorbed at Y (labeled as Y-C, Au-O) and, the third with Au-Au (labeled as Au-C, Au-O) site for singly doped whereas Y-Y site for doubly doped clusters (labeled as Y-C, Y-O) as shown in Fig. 2. CO adsorption at A

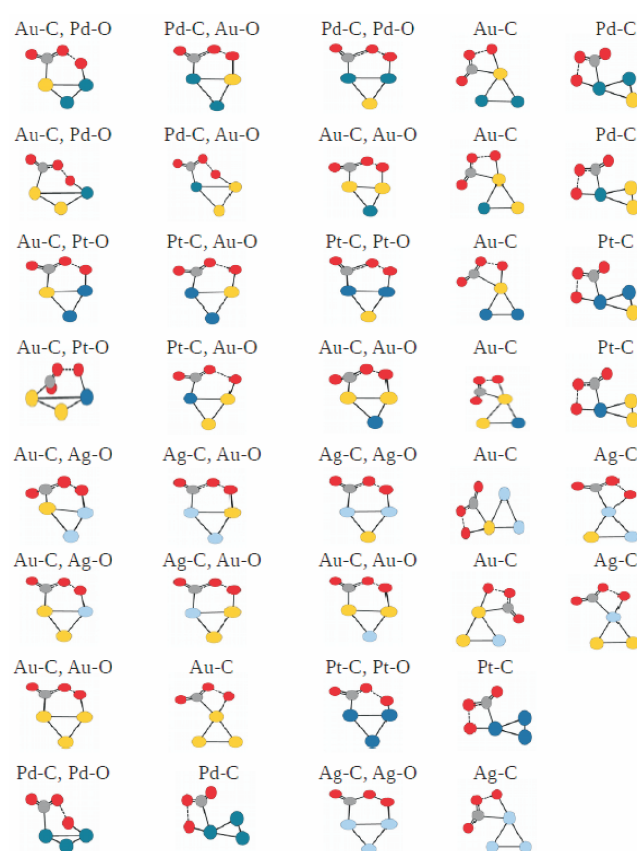


Fig. 2. Various possible reaction sites for Au, Ag, Pt and Pd based mono/bimetallic clusters.

atom is denoted by A-C where, C is for carbon atom and O₂ adsorption at B atom is indicated by B-O where, O symbolizes oxygen atom. The atom at which CO is adsorbed in case of ER mechanism and the combination of atoms at which CO and O₂ are co-adsorbed on cluster in case of LH mechanism show different behavior towards various properties of reaction pathway. Just like in case of transition state with gold cluster as catalyst, most of the transition states with

bimetallic clusters are thermodynamically more stable than the isolated reactants of the given reaction as shown in Fig. 3. It is important to mention here that the reference energy $E(\text{Ref})$ is taken to be the sum of energies of isolated reactants – corresponding cluster, CO and O_2 , for this analysis. Fig. 3 shows that the reaction can be catalyzed by most of the bimetallic clusters at ambient temperatures. The bimetallic clusters of gold-silver, gold-palladium, gold-platinum have transition states with CO adsorption occurring at Au, Pd and Pt atoms respectively for ER mechanism as the most energetically favorable ones. In case of LH mechanism, singly doped clusters show the most energetically favorable TS obtained when the reaction occurs at (Au-C, Ag-O) site for gold-silver clusters, (Au-O, Pd-C) site for gold-palladium clusters and (Au-O, Pt-C) site for gold-platinum clusters. In contrast to this, (Y-C, Y-O) reaction site for doubly doped clusters gives energetically most favourable transition state.

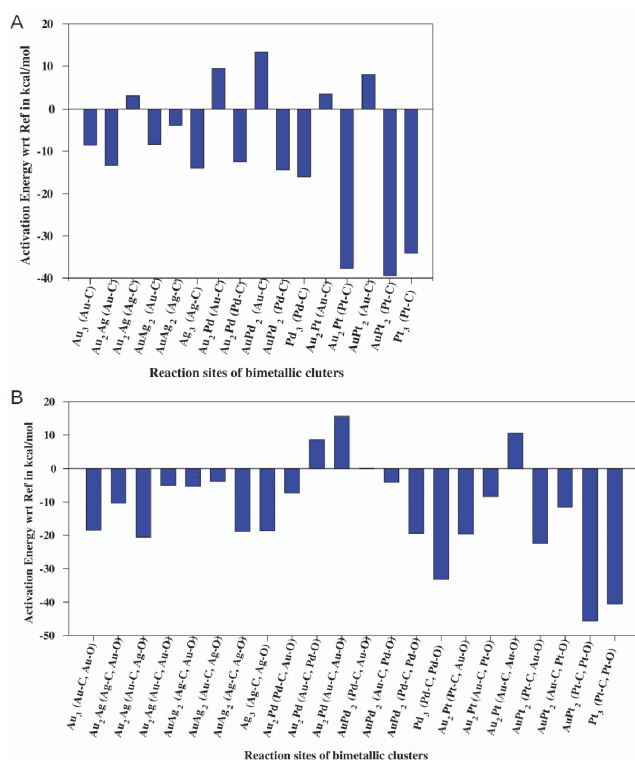


Fig. 3. The difference of energy (in kcal/mol) of the transition state $E(\text{TS})$ and the reference given by $E(\text{TS}) - E(\text{Ref})$ is analyzed for both (A) ER and (B) LH mechanisms on all clusters. The positive values in the figure show that the energy for such TS is higher with respect to the energy of corresponding isolated reactants and the negative values indicate that the corresponding TS is lower in energy with respect to the energy of isolated reactants.

But there are a few reaction sites which show positive values of transition state energy with respect to energy of isolated reactants. For a few ER pathways, this TS energy value with respect to the corresponding reference is positive for Au_2Ag at Ag site, $\text{Au}_2\text{Pd}/\text{Au}_2\text{Pt}$ at Au site and $\text{AuPd}_2/\text{AuPt}_2$ at Au site and that gives rise to high activation energy barrier for those pathways. Similarly, the energy of TS with respect to its reference is positive for LH pathway via (Au-C, Au-O) site in case of both Au_2Pd and Au_2Pt clusters. This shows that CO adsorption on gold atom and co-adsorption of CO and O_2 over Au-Au side of cluster reduces the catalytic efficiency of gold-palladium and gold-platinum trimers (refer Supplementary material for the PES). Hence, reaction site is very critical for a designed cluster to avoid the possibility of the reaction to take place via another pathway with a higher barrier height.

The CO_2 dissociation energy is also calculated for each reaction pathway by subtracting the energy of final products of half reaction (cluster with a nascent O attached and CO_2) from the energy of the Intermediate where CO_2 is formed on the cluster (Int2). The reaction pathway for Ag_3 has no energy barrier for CO_2 dissociation and the gold-silver trimers also show very low or no CO_2 dissociation energy barriers when CO is adsorbed at Au site. Most of the gold-palladium and gold-platinum clusters have very low CO_2 dissociation energy as compared to monometallic counterparts (refer Table 1), especially when CO is adsorbed at Au atom. Lesser CO_2 dissociation energy is endorsed by long metal- CO_2 bond

Table 1. Carbon dioxide dissociation energy values (E_{CO_2} in kcal/mol) and metal- CO_2 bond length ($R_{\text{M-CO}_2}$ in Å) for CO oxidation reaction on different catalysts. q_{transfer} is the charge transfer from cluster to CO_2 in a.u.

Cluster (Reaction site)	E_{CO_2}	$R_{\text{M-CO}_2}$	q_{transfer}
Au_2Ag (Ag-C, Au-O)	4.95	2.43	0.29
Au_2Ag (Au-C, Au-O)	1.21	2.68	0.31
AuAg_2 (Au-C, Ag-O)	0.72	2.76	–
AuAg_2 (Ag-C, Ag-O)	10.63	2.62	–
Au_2Pd (Pd-C, Au-O)	3.12	2.54	0.04
Au_2Pd (Au-C, Pd-O)	5.98	2.3	0.24
AuPd_2 (Pd-C, Au-O)	3.11	2.54	0.25
AuPd_2 (Au-C, Pd-O)	2.78	2.54	0.22
Au_2Pt (Pt-C, Au-O)	9.71	2.24	–0.11
Au_2Pt (Au-C, Pt-O)	3.76	2.45	0.42
AuPt_2 (Au-C, Pt-O)	3.58	2.46	0.21
AuPt_2 (Pt-C, Pt-O)	8.66	2.11	0.39