Catal Lett (2007) 119:21–28
DOI 10.1007/s10562-007-9200-z

Recent Advances in Understanding CO Oxidation on Gold Nanoparticles Using Density Functional Theory

Ying Chen · Paul Crawford · P. Hu

Received: 25 June 2007 / Accepted: 2 July 2007 / Published online: 25 July 2007

Abstract Since the discovery of a series of Au-based catalysts by Haruta et al. considerable progress has been made in understanding the active role of Au in CO oxidation catalysis. This review provides a summary of recent theoretical work performed in this field; in particular it addresses DFT studies of CO oxidation catalysis over free and supported gold nanoparticles. Several properties of the Au particles have been found to contribute to their unique catalytic activity. Of these properties, the low-coordination state of the Au atoms is arguably the most pertinent, although other properties of the Au cluster atoms, such as electronic charge, cannot be ignored. The current consensuses regarding the mechanism for CO oxidation over Au-based catalysts is also discussed. Finally, water-enhanced catalysis of CO oxidation on Au clusters is summarized.

Keywords Density functional theory · Gold nanoparticles

1 Introduction

The interest in Au/oxide catalysts has grown significantly since the discovery by Haruta et al. that supported gold nanoparticles exhibited catalytic activity [1]. Despite the well-known inertness of bulk Au, nanosized particles of gold supported on various oxides [2–14], including two-layered gold islands on TiO_2 [15], were found to exhibit enhanced catalytic activity; particularly in the case of low-temperature CO oxidation [15–23]. The activity of CO oxidation was found to be very sensitive to the size of the Au particles and to the type of support. It is now generally accepted that an average particle diameter of less than 5 nm is necessary to obtain activity. Moreover, it has been demonstrated that Au supported on reducible oxides (TiO_2, Fe_2O_3) tends to be more active than Au supported on irreducible oxides (SiO_2, MgO) under similar conditions.

Ab initio quantum-mechanical simulations provide detailed insight at the atomic-level, and give direct evidence of mechanistic aspects of reactions [24–33]. This review is intended to summarize the accumulated results from DFT studies pertaining to CO oxidation on Au clusters and Au/oxide systems. DFT calculations have quantified a number of properties that contribute to the enhanced reactivity of small gold clusters: poorly-coordinated Au atoms [25], Au-oxide interface properties [27], charge donation from the support [31], strain effects [32], metal-insulator transition below a certain cluster size [33], and dynamic structural fluxionality [34(b)]. From this list, the low coordination state of the Au atoms and properties of the Au-oxide interface had the greatest influence on activity.

Recently, two reaction mechanisms for CO oxidation have been proposed: an Eley–Rideal mechanism on non-active supporting materials (MgO) [28, 29], and a Langmuir–Hinshelwood mechanism on active supporting materials (TiO_2) [27]. One of the major questions is whether the reaction occurs via O_2 dissociation, or direct reaction, namely, CO + O_2. The mechanistic scheme for CO oxidation on Au/oxide is shown in Fig. 1.

In addition, under normal reaction conditions, the role of water cannot be neglected. Extensive experimental studies [35–37] suggest that water can affect CO oxidation dramatically. More recently, a paper by Liu et al. [38] clarified the basic role of water in Au/TiO_2 systems in more detail. With regards to less active supporting materials, Bongiorno

Y. Chen · P. Crawford · P. Hu (✉)
School of Chemistry and Chemical Engineering,
The Queen's University of Belfast, Belfast BT9 5AG, UK
e-mail: p.hu@qub.ac.uk

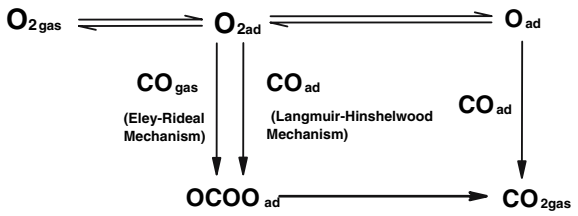

Fig. 1 General mechanism for CO oxidation on Au/oxide

and Landman [39] proposed that water can enhance the binding and activation of O_2, here MgO was used as the support.

This paper is organized as follows: In the next section a brief overview of the DFT approach is given. In the third section, we will summarize several properties of the Au/oxide system which contribute to the enhanced bonding energy of CO and O_2. In the subsequent section we will review the mechanism of CO oxidation over Au/oxide systems. The role of water in CO oxidation is examined in Sect. 5 and in the final section, some concluding remarks are given.

2 Computational Methodology

The last 10 years has seen an explosion in the application of first-principles computational modeling of catalytic reactions at surfaces. In the early 1970s, density functional theory (DFT) calculations were firstly employed in elementary simulations of surface phenomenon. These simple beginnings developed rapidly into more sophisticated modeling, due mainly to the vast increases in computer technology in the latter part of the last century. In DFT the focus is on the system's electron density rather than on the wave function. The working theory is a ground state theory, and is the result of the work of Hohenberg and Kohn, who showed that the ground state energy of an N electron system is a functional of its electron density [40, 41]. Within the framework of DFT, the problem of exchange-correlation (E_{xc}) is therefore conveniently addresses in terms of electron density. Indeed, there are many forms of functionals which relate E_{xc} to the systems electron density.

A crude yet successful approach, proposed by Kohn and Sham, approximates $E_{xc}[\rho(\mathbf{r}_i)]$ as that of a homogeneous electron gas with a density equal to $\rho(\mathbf{r}_i)$; this approach is known as the local density approximation (LDA) [41]. The LDA is useful in cases where the electron density does not vary too fast. A more general approach, however, also considers the gradient of the electron density; this is the so-called generalized gradient approximation (GGA) [42, 43]. It has been demonstrated that GGA methods can calculate the geometry of molecular and extended systems to experimental accuracy, and bond energies to within a few percent error.

The supercell approach (the use of periodic boundary conditions), in which a unit cell is repeated periodically through 3-dimensional space, is commonly used to model extended systems. Thus, when modeling surfaces, we have slabs (consisting of atomic layers) with infinite surface area stacked one on top of each other. In taking this approach it is important to carefully consider the affect of slab thickness (number of atomic layers) and vacuum spacing between the slabs. It may also be important to examine the effect of relaxing the atomic layers [44].

The application of first principles density functional theory (DFT) to calculate adsorption energies and activation energies for surface chemical reaction has been reviewed by Hammer and Nørskov [45]. Calculated chemisorption energies provide information on the relative stability of adsorbates on the surface. In this review, chemisorption energies (E_{ad}) are defined as $E_{ad} = E_A + E_S - E_{A/S}$, where E_A, E_S, and $E_{A/S}$ are the total energies of the molecular in the gas phase, the clean surface or cluster and the chemisorption system, respectively. In optimizing the structure of a particular system we must firstly calculate the forces on the atoms in the initial guess structure, which are then minimized by numerical methods. Forces on atoms can be calculated using the Hellmann–Feynman theorem. There are several methods that are routinely employed to optimize geometries such as the BFGS scheme [44] and finite temperature molecular dynamics [44, 46]. To investigate a reaction mechanism, we need to consider the reaction pathway, e.g., the geometries of the initial state (IS), transition state (TS), and final state (FS), and the corresponding energetics. Location of the TS geometry is of particular importance, as its corresponding energy with respect to the IS determines the magnitude of the reaction barrier. The following two methods have been widely used in the study of chemical reactions: (i) the constrained minimization method [47]; and (ii) the nudged elastic band method [48].

3 CO and O_2 on Au Clusters

The first step of CO oxidation involves the adsorption of the molecular from the gas phase, such as CO. It is now known that most molecules cannot adsorb on pure gold. However, small gold clusters dispersed on various oxide supports exhibit remarkable activity for many reactions, especially for CO oxidation at or below room temperature. Several groups have suggested a number of explanations to account for this observation. They include the coordination state of the Au atoms, their electronic structure, support material, and strain.

3.1 The Role of Low-coordination Sites and Interfaces

By considering the catalytic activity of a number of Au systems toward CO oxidation as a function of average Au particle size, Lopez et al. [49] showed that the presence of a high concentration of under coordinated Au atoms is the dominant factor in the catalytic activity of Au nanoparticles. Indeed, by taking both electronic structural differences and geometrical configurations into account, they [25] adequately explained the remarkable difference in catalytic activity observed between small Au clusters and larger Au crystals.

3.1.1 CO Bonding

To evaluate the importance of coordination state, we have compiled a number of CO adsorption energies at different sites from a variety of Au clusters in the literature (summarized in Table 1). From Table 1, we can see that the effect of a low-coordination number is significant. CO bonds at corner and edge sites more strongly than at facet sites. In the first DFT study of CO adsorption on Au, Mavrikakis et al. [24] showed that Au step atoms on Au(211) have a stronger bonding potential than surface atoms on Au(111). Furthermore, Lopez et al. [49] found that CO adsorption on a Au_{10} cluster, where the most reactive Au atoms have a coordination number of 4, is up to 1 eV stronger than on a Au(111) surface, where the Au atoms have a coordination number of 9. Similarly, CO has been found to adsorb on Au(111) (E_{ad}(CO) = 0.17 eV) considerably more weakly than on surface defects (steps, adatoms and clusters) (E_{ad}(CO) > 1 eV) by Liu et al. [26]. It is suggested that in order for CO to adsorb with reasonable cohesion the coordination number of the gold atoms must not exceed eight [25]. Moreover, by investigating Au_{34} clusters, Molina and Hammer [28, 29] showed that decreasing the coordination number of the Au atoms can strengthen the CO binding, and that the edge sites can help CO diffusion. Therefore, under reaction conditions, CO is expected to be highly concentrated at the edges, corners and steps of the Au nanoparticles.

3.1.2 O_2 Bonding

O_2 is observed to behave very much like CO over Au, in that it preferentially adsorbs at low-coordination sites. In Fig. 2, the adsorption energies are plotted as a function of the Au coordination number. Mavrikakis et al. [24] found that Au step edges increase both O and O_2 adsorption. This is in good agreement with the work of Xu and Mavrikakis [32]. Furthermore, calculations by Mills et al. [33] showed that oxygen molecules do not bind to flat facets of gold. However, placing small Au clusters on Au(111) did lead to O_2 binding. Moreover, work by Mills et al. [52] and Yoon et al. [34(a)] suggested moderate O_2-gold binding on very small Au_n clusters ($n < 8$). Conversely, Molina and Hammer [50, 51] placed molecular O_2 at a variety of sites around the Au_{34} and Au_{20} particles and found that binding of molecular O_2 is very weak (0 eV to –0.4 eV for Au_{34}, and 0 eV–0.15 eV for Au_{20}). Thus, it appears that molecular O_2 can bind more strongly on small Au_n clusters ($n < 8$) but only relatively weakly on larger Au particles; which is further evidence that the adsorption of O_2 is enhanced at under-coordinated gold atoms. Nonetheless, relative to CO adsorption, the binding energy of O_2 on gold clusters is relatively weak.

Some authors pointed out the special role of sites at the Au/support interface. The first DFT calculations of CO oxidation at the Au/TiO_2 interface were reported by Liu et al. [27]. They found that O_2 can adsorb more strongly (~0.6 eV) at the Au/TiO_2(110) interface than on pure Au. Recently, Liu et al. [53, 54] extended this work, and found that O_2 adsorption is greatly enhanced at the interface of Au/IrO_2 (1.42 eV) and Au/TiO_3/Mo(112) (>1.66 eV). By modeling a gold rod on TiO_2(110), Molina et al. [55] studied O_2 interface adsorption. They revealed that without gold clusters O_2 cannot adsorb on a perfect TiO_2(110), but at the Au/TiO_2 interface the O_2 adsorption is reasonably strong. More recently, using a gold cluster of 10 atoms supported on TiO_2(110), Remediakis et al. [56, 57] also reported that O_2 has a preference for binding in the contact area between the Au cluster and the Ti(5c) on the surface. Hence, on Au supported by TiO_2, the interface is far more

Table 1 Literature values of CO chemisorption energy (eV) at special adsorption sites on a number of Au clusters

Site	Au_{34}/MgO [50]	Au_{20} or Au_{20}/MgO [51]	Au_{12} [26]	Au_{10} [49]	Au surface [24, 26]		
					Au(111)	Au(211)	Au(221)
Corner sites	0.37–0.50	0.84	–	0.5	0.17	–	–
Edge sites (step)	0.15/0.30	0.54	1.25	–		$1.05^{(1/6\ ML)}$, $1.40^{(1/9\ ML)}$, 0.66 (bridge)	$1.00^{(1/8\ ML)}$, $1.31^{(1/12\ ML)}$
Facet sites	0.07–0.09	0.38	–	–	0.30 (atop)		

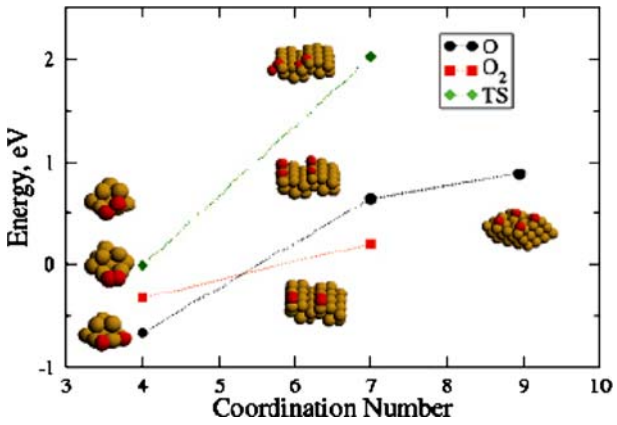

Fig. 2 Binding energy of molecular and atomic O relative to gas-phase O_2 plotted with respect to the coordination number of the Au atoms at the adsorption site. Yellow spheres represent Au atoms; red spheres represent O atoms (From Ref. [25])

favorable for O_2 adsorption than the low-coordinated sites of Au. This is, because the TiO_2 support can induce a significant electron transfer from the Au atom to the 2-π anti-bonding states of O_2 that sit at the interface between the metal and the oxide. Conversely, for an irreducible oxide like MgO, the O_2 bonding to the interface is relatively weaker and O_2 adsorption mainly depends on the formation of CO–O_2 complex at the interface [28, 29].

3.2 Charge Transfer Effect

There is one particular aspect which has been argued about extensively, namely, whether partially anionic ($Au^{\delta-}$) or partially cationic ($Au^{\delta+}$) gold atoms are responsible for the unique Au/oxide catalytic activity [2, 29, 30, 58–65]. As mentioned above, it is clear that CO will interact more strongly than O_2 with gold clusters regardless of the charge on Au. Therefore, taking the calculated O_2 binding energies as a measure of catalytic activity of the free anionic Au_n^- clusters, we have summarized the literature values of molecular oxygen adsorption energies in Table 2. The general results obtained by several groups [33, 34(a), 52, 61, 62, 64–65] are that negatively charged clusters containing an even number of atoms are more reactive, and bind O_2 more strongly than free neutral clusters. Interestingly, in the case of neutral clusters, an odd number of atoms are found to be more reactive. Indeed, from Table 2, we can see that oxygen binds most strongly to Au_2^- [63]. Additionally, Molina and Hammer [51] indicated that binding of O_2 is not feasible unless an Au_{20} cluster becomes negatively charged. Wells et al. [65] found that both of the oxygen atoms of O_2 prefer to be attached to the more negatively charged, near apex, gold atoms on Au_{10}^- and Au_{11}^- clusters.

It has been suggested that molecular oxygen obtains two electrons from the Au cluster to form a superoxo state (O^{2-}) which can react with a co-adsorbed CO molecule. From these studies, several conclusions have been drawn. For example, only clusters with an odd number of electrons can bind O_2; this appears to be linked to their ability to transfer one electron from an open shell to the molecule, while there is no electron transfer from a cationic Au cluster to O_2. Thus, for cationic Au clusters, only small Au_n ($n < 4$) clusters are found to provide moderate O_2 adsorption (E_{ad} = 0.2–0.6 eV) which is weaker than typical adsorption of O_2 on anionic clusters. It was suggested that the adsorption on cationic clusters may depend on a different mechanism [62]. Moreover, Prestianni et al. [60(a)] studied O_2 adsorption on neutral and positively charged Au_9 and Au_{13} clusters. They found that the adsorption of molecular oxygen in its singlet spin state is not favorable on cationic Au_9 clusters (–0.99 and –0.82 eV Au_9^+ and Au_9^{3+}, respectively); but triplet oxygen can bond to Au_9^{3+} (0.53–1.00 eV).

Table 2 Literature chemisorption energy values (eV) of molecular oxygen on anionic Au clusters

No.	Au_n [61]	Au_n^-			
		Molina and Hammer [61] (RPBE)	Millis et al. [33, 52] (PW91)	Yoon et al. [34(a)] (BO-LSD-MD)	Ding et al. [62] (PW91/B3LYP)
1	0.30	0.18	0.50		0.44/0.22
2	0.23	1.08	1.40	1.39	1.24/0.95
3	0.63	0.03	0.37	0.46	0.33/0.04
4	0.04	0.48	1.19	0.93–1.01	1.03/0.72
5	0.70	0.06	0.76	0.48, 0.61	0.44/0.07
6	0.04	0.77	1.15	1.02, 1.06	1.01/0.78
7	0.37	0.04	0.98	0.53	
8	0.06	0.49		0.87	
9	0.19	0.15			
10	0.00–0.10	0.19, 0.58			
11	0.14	0.12			

Generally, it seems that anionic Au clusters are more active than cationic clusters in CO oxidation. Under real reaction conditions, one can use two different catalyst modifiers: doping impurities like Na, and the use of supports with defects. Impurity-doping effects modify and control the electronic structure, and consequently the catalytic activity, of small Au clusters. An interesting finding by Molina and Hammer [51] is that the addition of endohedral Na dramatically improves the reactivity of the neutral Au_{20} cluster, and both CO and O_2 binding energies are systematically enhanced. Broqvist et al. [66] established a similar picture, namely that Na is found to be a promoter, enhancing both O_2 binding and OCOO formation. They also found that Cl acts as a poisoning species. Häkkinen et al. [34(b)] studied the effect of adding an electron donor (Sr) to small MgO-supported Au clusters. It was found that the addition of Sr significantly increased the amount of CO_2 produced per deposited cluster by enhancing both adsorption and activation of O_2 on the Sr-doped systems. Similarly, Graciani et al. [67] examined CO oxidation on an encapsulated cluster $V@Au_{12}^{-}$ and found that although the adsorption energy of O_2 was relatively week (0.3–0.4 eV), the cluster can uniquely bind a high number of oxygen molecules, which is a distinct advantage over pure gold clusters.

It has been speculated that surface defects may alter the electronic configuration of Au clusters and thus activate CO oxidation. Through a combined experimental and theoretical study, Yoon et al. [30] have demonstrated that the defects on MgO not only anchor the Au_8 nanoparticles but also play the role of active sites, controlling the (negative) charged state of the gold clusters and, consequently, the overall catalytic activity. Au_8 bound to the F center of the MgO is the smallest known gold heterogeneous catalyst that can oxidize CO at the low temperature, whereas, for larger Au clusters, charge is screened quite efficiently and its effect decays exponentially with distance form the charged center. Molina and Hammer [51] placed an Au_{20} cluster at either an MgO F- or an F^+-center where activity was found to be only slightly greater than the unsupported, neutral cluster. This finding is in accordance with the result of Remediakis and Lopez [57] which showed that reduced TiO_2(110) provided only a minimal reactivity.

More recently, Laursen and Linic reported a DFT study on the oxidation state of Au nanostructures deposited on reducible and irreducible supports [60(a)], their work has been helpful in explaining the following two questions: (i) is anionic $Au^{\delta-}$ or cationic $Au^{\delta+}$ responsible for the unique Au/oxide catalytic activity? Anionic Au is needed to adsorb and activate O_2. However, as oxygen's chemical potential is increased the electronic fingerprint of Au is reversed from anionic to cationic, which interacts with CO favorably in the process Au-oxygen bond formation. (ii) Why is Au which is supported on reducible oxides more active than Au which is supported on irreducible oxides under similar conditions? Irreducible oxides are characterized by a larger band gap which limits the charge transfer from irreducible oxides to Au. In contrast, the band gaps of reducible oxides are small, which promotes charge transfer to Au.

3.3 Other Effects

3.3.1 Effect of Strain

Recently, Giorgio et al. [67] measured experimentally the lattice constants of Au particles deposited on TiO_2, they found that the Au atoms adjusted their spacing to the substrate, and the lattice constant expand up to 12.5% with respect to the equilibrium value. In addition, Mavrikakis et al. [69], using DFT, showed that the surface reactivity of a number of transition metals increase with lattice expansion. Similarly, Xu and Mavrikakis [32] suggested that tensile strain enhances the adsorption of atomic and molecular oxygen (the adsorption energies of O_2 are 0.08 eV, 0.15 eV and 0.26 eV on 10%-stretched Au(111), unstretched Au(211) and 10%-stretched Au(211), respectively), due to a concurrent up-shift in the metal d-band centers.

3.3.2 Effect of Metal-insulator Transitions

Mills et al. compared the adsorption energy of O_2 at Au clusters deposited on Au(111) which have no band gap, with the adsorption energy on small isolated gas phase clusters, which are insulators with a large band gap [33]. The difference in adsorption energy of O_2 on an Au_2 dimer in the gas phase and an Au_2 dimer on Au(111) was found to be only 0.2 eV. Indeed, the geometries of the two systems were found to be very similar, and thus it was concluded that the existence of a band gap is not essential for the binding of O_2 on gold. Furthermore, as previously mentioned, the adsorption energy of oxygen to a negative or neutral cluster oscillates with the number of electrons in the cluster: it is large if the cluster has an odd number of electrons. However, calculations by Mills et al. do not show this effect: when O_2 binds to Au_n/Au(111)($n < 4$) the binding energy changes with n only slightly.

3.3.3 Effect of Dynamic Structural Fluxionality

The effect of dynamic structural fluxionality has been addressed by Häkkinen et al. [34(b)]. At finite temperatures, the small clusters can exhibit several structural forms (conformation) which can interconvert between one another. This capability of the small clusters may enhance the

rates of the chemical reaction, as each conformation has a slightly different catalytic activity. Namely, at finite temperatures, the conformers reach a dynamic equilibrium whereby reactive metastable forms perhaps dominate reactivity. Moreover, the cluster may adapt a structure so as to allow the reaction to evolve on the most favorable free-energy path. Häkkinen et al. [34(b)] illustrated this phenomenon by considering two conformations of the Au_8 cluster: it was found that O_2 binds more strongly on a so-called two-layered structure than on a second conformation which is thermodynamically more stable than the two-layered system. Interestingly, the two-layered system is shown to undergo a large structural transformation upon adsorption of O_2. Moreover, if they constrained the cluster to maintain its original geometry, it prevents the adsorption and activation of O_2.

4 CO Oxidation

Both experimental and theoretical work on CO oxidation has focused mainly on the late 4d and 5d metals. For reviews of CO oxidation on metal surface see references [70] and [71]. It has been generally accepted that CO oxidation over a metal surface follows the Langmuir–Hinshelwood mechanism. Here three elemental steps have been assumed to occur: (i) CO adsorption at the surface; (ii) molecular dissociation of O_2 at the surface; and (iii) reaction of CO with O to form CO_2 on surface.

However, Liu et al. [26] reported that it is not particularly easy to dissociate O_2 on pure Au, including flat and stepped Au surfaces, and several Au clusters (a barrier above 0.9 eV). Also rather large barriers have been calculated by Molina and Hammer [29] and Yoon et al. [34(a)] for O_2 dissociation at Au clusters supported by MgO(100) and at small unsupported Au clusters, respectively. On the other hand, Lopez and Nørskov [25] studied CO oxidation over an Au_{10} cluster. Here it was found that O_2 can readily dissociate at the corner sites (with a barrier of about 0.4 eV) but the energy barrier for this process is very sensitive to the geometry.

There are several factors which can facilitate O_2 dissociation. Au-oxide interfaces are observed to promote dissociation e.g., at the Au-TiO_2(110) and Au-IrO_2 interface, the barriers are found to be 0.52 eV and 0.22 eV, respectively [27, 53]. Molina et al. [55] found that the presence of CO can induce dissociation, namely, O_2 can dissociate when it is near CO on Au/TiO_2(110). Interestingly, 10% tensile strain was found to lower the dissociation barrier from 1.12 eV to 0.63 eV over Au(211) [32]. On the other hand, Liu et al. [27] suggested that at low temperatures, the direct reaction of CO with O_2 to give CO_2 and an atomic O is preferential. Here, a very small barrier of 0.1 eV is observed at the Au/TiO_2(110) interface, which agrees well with the result of Molina et al. [55]. However, Lopez and Nørskov [25] found that the reactivity of the dissociative O_2 mechanism differed only marginally from that of the non-dissociative mechanism over an Au_{10} cluster.

Following from our discussion of CO and O_2 adsorption on Au clusters or Au/oxide systems, and the above, CO oxidation is now generally understood to occur over Au/oxide systems via the following mechanism: (i) CO adsorbs on dispersed gold clusters; (ii) molecular oxygen adsorbs at the interface; (iii) CO reacts with O_2 form CO_2 and CO_2 desorbs from the surface; and (iv) O is readily removed by another adsorbed CO to complete the reaction cycle. The reaction cycle is shown in Fig. 3 in which the barrier for the CO + O_2 reaction is according to the references [25, 27, 50].

5 Role of Water in CO Oxidation

It has been found experimentally that water can play a catalytic role in many reactions including CO oxidation over transition metals and Au/oxide systems [35–37]. DFT calculations of Gong et al. [72] showed that adsorbed H_2O can significantly promote CO oxidation on Pt(111) by lowering the reaction barrier from $E_a = 0.8$ eV to $E_a = 0.33$ eV. By a combination of STM and DFT studies, Schaub et al. [73] showed that water can react with oxygen vacancies on a TiO_2 surface to form two OH groups, which will consequently affect the interaction between the Au cluster and the support. Considering this observation, Lopez et al. [74] rationalized the effect of water on the activity of Au/TiO_2 as follows: water affects the interface

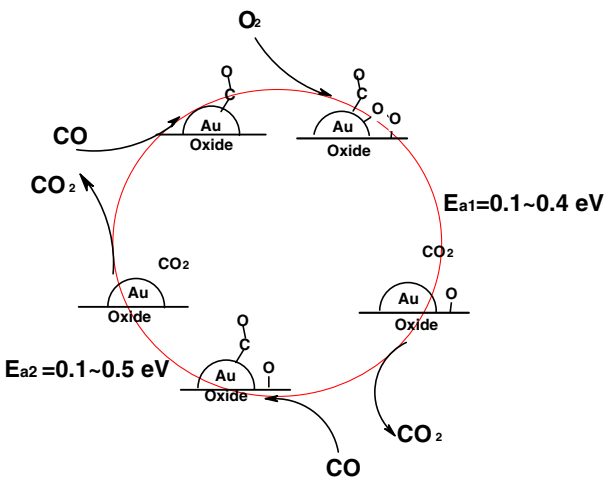

Fig. 3 Catalytic cycle for CO oxidation at the Au/oxide interface

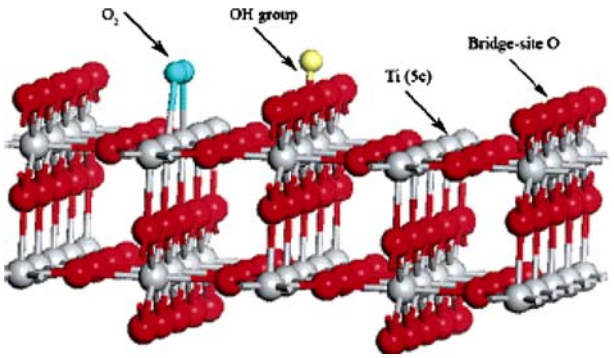

Fig. 4 Side view of O_2 adsorption on $TiO_2(110)$, $p(2 \times 4)$, in the presence of one OH group (From Ref. [38])

between Au and the support, which consequently influences the Au particle geometry. This modification in the geometry of the Au particles results in a change in concentration of active corner and edge atoms.

Liu et al. [38] have recently identified a water promoted mechanism which supplies O_2 for CO oxidation over $Au/TiO_2(110)$. Firstly, it was shown known that: (i) O_2 cannot adsorb on perfect $TiO_2(110)$; (ii) O_2 can adsorb strongly at an O vacancy on $TiO_2(110)$ (E_{ad} = 2.33 eV); (iii) O_2 can adsorb on $TiO_2(110)$ in the presence of OH with moderate chemisorption energy, 0.8 eV, shown in Fig. 4. Further investigations revealed that adsorbed O_2 could readily diffuse along the surface Ti (5c) atoms in the presence of OH so as to provide a supply of O_2 to the Au/TiO_2 interface for CO oxidation. The physical origin of these effects was also identified. Here, the charge supplied by the OH groups was found to be transferred to the adsorbed O_2.

Conversely, the O_2 adsorption energies at the interface between Au and irreducible oxides are relatively low. Thus, the rate-limiting step of CO oxidation on Au supported by irreducible oxides may be O_2 adsorption. Calculations by Bongiorno and Landman [39] showed that water can enhance O_2 adsorption on free and supported Au clusters through formation of a hydroperoxyl-like complex, whereby the O–O bond is weakened. Consequently the reaction with CO to form CO_2 may occur readily with a relatively low barrier of 0.5 eV.

6 Concluding Remarks

This article serves to summarize recent theoretical advances regarding CO oxidation over Au/oxide systems, a topical issue in catalysis. To date, electronic structure calculations based on DFT have been used extensively to study this reaction. The key points that this review intends to highlight include:

(i) The enhanced reactivity of small gold clusters stems from a number of important factors, namely, availability of under-coordinated Au atoms, e.g., step or edge atoms; Au-oxide interfacial effects; electronic charge on the Au atoms; strain; metal-insulator transition; and dynamic structural fluxionality.
(ii) The general mechanisms for CO oxidation over gold clusters.
(iii) The role of water in CO oxidation on gold-based catalysts.

References

1. Haruta M, Kobayashi T, Sano H, Yamada N (1987) Chem Lett 2:405
2. Fu Q, Saltsburg H, Flytzani-Stephanopoulos M (2003) Science 301:935
3. Haruta M (1997) Catal Today 36:153
4. Cosandey F, Madey TE (2001) Surf Rev Lett 8:73
5. Hammer B, Nørskov JK (1995) Nature 376:238
6. Over H, Kim YD, Seitsonen AP, Wendt S, Lundgren E, Schmid M, Varga P, Morgantem A, Ertl G (2000) Science 287:1474
7. Li J, Li X, Zhai H-J, Wang L-S (2003) Science 299:864
8. Arrii S, Morfin F, Renouprez AJ, Rousset JL (2004) J Am Chem Soc 126:1199
9. Shaikhutdinov SK, Meyer R, Naschitzki M, Baumerm M, Freund H-J (2003) Catal Lett 86:211
10. Kielbassa S, Kinne M, Behm RJ (2004) Langmuir 20:6644
11. Kielbassa S, Kinne M, Behm RJ (2004) J Phys Chem B 108:19184
12. Landon P, Collier PJ, Papworth AJ, Hutchings GJ (2002) Chem Comm 18:2058
13. Hodge NA, Kiely CJ, Whyman R, Siddiqui MRH, Hutchings GJ, Pankhurst QA, Wagner FE, Rajaram RR, Golunski SE (2002) Catal Today 72:133
14. Enache DI, Edwards JK, Landon P, Solsona-Espriu B, Carley AF, Herzing AA, Watanabe M, Kiely CJ, Knight DW, Hutchings GJ (2006) Science 311:362
15. Valden M, Lai X, Goodman DW (1998) Science 281:1647
16. Chen MS, Goodman DW (2004) Science 306:252
17. Choudhary TV, Goodman DW (2005) Appl Catal: A 291:32
18. Olson RM, Varganov S, Gordon MS, Metiu H, Chretien S, Piecuch P, Kowalski K, Kucharski SA, Musial M (2005) J Am Chem Soc 127:1049
19. Vijay A, Mills G, Metiu H (2005) J Chem Phys 118:6536
20. Hutchings GJ (2005) Catal Today 100:55
21. Canning NDS, Outka DA, Madix RJ (1984) Surf Sci 141:240
22. Haruta M, Tsubota S, Kobayashi T, Kageyama H, Genet MJ, Delmon B (1993) J Catal 144:175
23. Stampfl C, Scheffler M (1997) Phys Rev Lett 78:1500
24. Mavrikakis M, Stoltze P, Nørskov JK (2000) Catal Lett 64:101
25. Lopez N, Nørskov JK (2002) J Am Chem Soc 124:11262
26. Liu Z-P, Hu P, Alavi A (2002) J Am Chem Soc 124:14770
27. Liu Z-P, Gong X-Q, Kohanoff J, Sanchez C, Hu P (2003) Phys Rev Lett 91:266102
28. Molina LM, Hammer B (2003) Phys Rev Lett 90:206102
29. Molina LM, Hammer B (2004) Phys Rev B 69:155424
30. Yoon B, Häkkinen H, Landman U, Wörz AS, Antonietti JM, Abbet S, Judai K, Heiz U (2005) Science 307:403
31. Sanchez A, Abbet S, Heiz U, Schneider W-D, Hakkinen H, Baenett RN, Landman U (1999) J Phys Chem A 103:9573
32. Xu Y, Mavrikakis M (2003) J Phys Chem B 107:9298

33. Mills G, Gordon MS, Metiu H (2003) J Chem Phys 118:4198
34. (a) Yoon B, Häkkinen H, Landman U (2003) J Phys Chem A 107:4066; (b) Häkkinen H, Abbet S, Sanchez A, Heiz U, Landman U (2003) Angew Chem, Int Ed 42:1297
35. (a) Kung HH, Kung MC, Costello CK (2003) J Catal 216:425; (b) Bergeld J, Kasemo B, Chakarov DV (2001) Surf Sci 495:L815
36. Sanchez-Castillo MA, Couto C, Kim WB, Dumesic JA (2004) Angew Chem, Int Ed 43:1140
37. Daté M, Okumura M, Tsubota S, Haruta M (2004) Angew Chem, Int Ed 43:2129
38. Liu LM, McAllister B, Ye HQ, Hu P (2006) J Am Chem Soc 128:4017
39. Bongiorno A, Landman U (2005) Phys Rev Lett 95:106102
40. Hohenberg P, Kohn W (1964) Phys Rev 136:864B
41. Kohn W, Sham L (1965) Phys Rev 140:1133A
42. Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiolhais C (1992) Phys Rev B 46:6671
43. Perdew JP, Burke K, Ernzerhof M (1996) Phys Rev Lett 77:3865
44. (a) Barnett RN, Landman U (1993) Phys Rev B 48:2081; (b) Fletcher R (1985) Practical methods of optimization, 2nd edn. John Wiley & Sons, Chichester; (c) Car R, Parrinello M (1985) Phys Rev Lett 55:2471
45. Hammer B, Nørskov JK (2000) Adv Catal 45:71
46. Payne MC, Teter MP, Allan DC, Arias TA, Joannopouls JD (1992) Rev Mod Phys 64:1045
47. Alavi A, Hu P, Deutsch T, Silvestrelli PL, Hutter J (1998) Phys Rev Lett 80:3650
48. Ulitsky A, Elber R (1990) J Chem Phys 92:1510
49. Lopez N, Janssens TVW, Clausen BS, Xu Y, Mavrikakis M, Bligaard T, Nørskov JK (2004) J Catal 223:232
50. Molina LM, Hammer B (2005) App Catal A 291:21
51. Molina LM, Hammer B (2005) J Catal 233:399
52. Mills G, Gordon MS, Metiu H (2002) Chem Phys Lett 359:493
53. Liu Z-P, Jenkins SJ, King DA (2004) Phys Rev Lett 93:156102
54. Liu Z-P (2006) Phys Rev B 73:1
55. Molina LM, Rasmussen MD, Hammer B (2004) J Chem Phys 120:7673
56. Remediakis IN, Lopez N, Nørskov JK (2005) Angew Chem, Int Ed 44:1824
57. Remediakis IN, Lopez N (2005) Appl Catal A 291:13
58. Minato T, Susaki T, Shiraki S, Kato HS, Kawai M, Alika K (2004) Surf Sci 566:1012
59. Guzman J, Gates BC (2004) J Am Chem Soc 126:2672
60. (a) Prestianni A, Martorana A, Labat F, Ciofini I, Adamo C (2006) J Phys Chem B 110:12240; (b) Laursen S, Linic S (2006) Phys Rev Lett 97:026101
61. Molina LM, Hammer B (2005) J Chem Phys 123:161104
62. Ding X, Li Z, J.Yang, Hou JG, Zhu Q (2004) J Chem Phys 120:9594
63. (a) Häkkinen H, Landman U (2001) J Am Chem Soc 123:9704; (b) Socaciu LD, Hagen J, Bernhardt TM, Wöste L, Heiz U, Häkkinen H, Landman U (2003) J Am Chem Soc 125:10437
64. Okumura M, Kitagawa Y, Haruta M, Yamaguchi K (2001) Chem Phys Lett 346:163
65. Wells DH Jr, Delgass WN, Thomson KT (2002) J Chem Phys 117:10597
66. Broqvist P, Molina LM, Grönbeck H, Hammer B (2004) J Catal 227:217
67. Graciani J, Oviedo J, Sanz JF (2006) J Phys Chem B 110:11600
68. Giorgio S, Henry CR, Pauwels B, van Tendeloo G (2000) Mater Sci Eng A 297:197
69. Mavrikakis M, Hammer B, Nørskov JK (1998) Phys Rev Lett 81:2819
70. Liu Z-P, Hu P (2004) Topics Catal 28:71
71. Liu Z-P (2004) Pure Appl Chem 76:2069
72. Gong X-G, Hu P, Raval R (2003) J Chem Phys 119:6324
73. Schaub R, Thostrup P, Lopez N, Lægsgaard E, Stensgaard I, Nørskov JK, Besenbacher F (2001) Phys Rev Lett 87:266104
74. Lopez N, Nørskov JK, Janssens TVW, Carlsson A, Puig-Molina A, Clausen BS, Grunwaldt J-D (2004) J Catal 225:86