Catalytic Role of Metal Oxides in Gold-Based Catalysts: A First Principles Study of CO Oxidation on TiO_2 Supported Au

Zhi-Pan Liu,[1] Xue-Qing Gong,[1] Jorge Kohanoff,[2] Cristián Sanchez,[2] and P. Hu[1,*]
[1]*School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, United Kingdom*
[2]*Atomistic Simulation Group, School of Mathematics and Physics, The Queen's University Belfast,*
Belfast BT7 1NN, United Kingdom

(Received 4 August 2003; published 23 December 2003)

CO oxidation on TiO_2 supported Au has been studied using density functional theory calculations. Important catalytic roles of the oxide have been identified: (i) CO oxidation occurs at the interface between Au and the oxide with a very small barrier; and (ii) O_2 adsorption at the interface is the key step in the reaction. The physical origin of the oxide promotion effect has been further investigated: The oxide enhances electron transfer from the Au to the antibonding states of O_2, giving rise to (i) strong ionic bonding between the adsorbed O_2, Au, and the Ti cation; and (ii) a significant activation of O_2 towards CO oxidation.

DOI: 10.1103/PhysRevLett.91.266102 PACS numbers: 68.35.–p, 68.43.Bc

Gold can exhibit extremely high catalytic reactivity for many reactions when it is highly dispersed on metal oxides [1,2]. This is very surprising considering that gold is the most inert metal [3] and the oxides are poor catalysts for these reactions. As one of the most attractive catalytic systems in recent years, Au supported on metal oxides (Au/oxides) has been extensively studied. In particular, CO oxidation [4–12] on Au/oxides has been investigated in detail for its simplicity, as well as its technological importance. However, a fundamental issue, i.e., how oxides affect the reactivity of Au or vice versa, remains elusive. In this Letter, we aim at providing an insight into this issue.

Since the pioneer work of Haruta [1], a large volume of experimental works has been devoted to Au/oxides, and significant progress has been made [2]. These studies have shown that the catalytic reactivity of the Au-based systems is strongly dependent on the choice of oxide support. Generally, it is observed that Au supported on reducible oxides, such as TiO_2, has a higher reactivity compared to Au on irreducible oxides, such as MgO and SiO_2 [7,8]. In contrast, theoretical studies on the subject are limited. Several density functional theory (DFT) studies were carried out for O_2 and CO chemisorption and O_2 dissociation on unsupported Au clusters and extended surfaces [13–15]. Very recently, Molina and Hammer investigated thoroughly CO oxidation on Au/MgO and examined the effect of the Au cluster morphology using DFT [16]. The general consensus in the field is that CO can adsorb on Au while O_2 adsorption and dissociation on Au is difficult, which is consistent with the experimental findings that no adsorbed O atoms are detected during CO oxidation [2,6]. Here we present the first DFT study on CO oxidation on Au/TiO_2(110), attempting to answer the following questions: (i) Where and how is O_2 activated towards CO oxidation? (ii) Where and how does CO oxidation occur? (iii) What is the catalytic role of the metal oxide?

The modeling of chemical reactions occurring on composite systems (e.g., metal/oxide) from first principles is a challenging task due to their very large sizes. In this study, the SIESTA code [17] was used, in which the standard DFT supercell approach with the Perdew-Burke-Ernzerhof [18] form of the generalized gradient approximation functional is implemented and the Kohn-Sham orbitals are expanded in a localized basis set. Some of the structures and energetic results obtained with SIESTA were further checked by using the pseudopotential plane-wave CASTEP code [19] (see Table I). The calculation details are described in Ref. [21]. It was found that the agreement between the results obtained from the two codes is good (see Table I) [20].

The TiO_2(110) is modeled by a large unit cell [a (2×4) unit cell, 13.09 Å × 11.80 Å with slabs separated by more than 10 Å of vacuum]. The oxide slab contains six layers (in all 32 units of TiO_2 per slab) and the convergence of the adsorption energies is further checked by increasing to nine layers (48 units of TiO_2 per slab). Experimentally, Goodman *et al.* found that two-layer Au particles on TiO_2 have the highest activity [4]. Based on this, we have modeled the Au/TiO_2 system by adding a two-layer strip of Au on the TiO_2(110) substrate [Fig. 1(a)]. The size of the Au/TiO_2(110) cell used is believed to be large enough to describe the essential features of the metal/oxide interface. For the purpose of comparison, the Au strip without TiO_2(110), referred to as nonsupported Au hereafter, was also calculated. The structure of the Au/TiO_2(110) was determined by molecular dynamics and then geometry optimization using the methods described in Ref. [23]. The structure of the nonsupported Au was determined in a similar way.

As shown in Fig. 1, the optimized Au structure exhibits close-packed, (111)-like facets. The Au-Au distance in the structure is ~2.8 Å on average, slightly shorter than the calculated nearest neighbor distance in the Au bulk

TABLE I. Calculated adsorption energies (E_{ad}) and barriers (E_a) for the CO oxidation on Au/TiO$_2$(110) and nonsupported Au using SIESTA. The CASTEP results are listed in parenthesis for comparison [20]. All the energies are in eV.

		Au/TiO$_2$(110)	
	Nonsupported Au	Six-layer TiO$_2$	Nine-layer TiO$_2$[a]
$E_{ad}(O_2)$	0.07 (0.00)	0.86 (1.03[a])	0.60
$E_{ad}(CO)$	1.69	1.24	1.38
$E_a(O_2 \rightarrow 2O)$	> 2	0.52	
$E_a(CO + O_2 \rightarrow CO_2 + O)$	0.78 (0.73)	0.10	0.17

[a]The energy obtained using the structure born from the six-layer SIESTA calculation.

(2.93 Å). The Au strip binds to TiO$_2$(110) mainly through the bridging O (labeled as O$_{br}$ in Fig. 1) of the TiO$_2$(110). There are four Au-O$_{br}$ bonds per unit cell with a similar Au-O distance (~ 2.2 Å). The shortest distance between Au and the Ti atoms on the top layer of TiO$_2$(110) is about 3.9 Å, implying a weak interaction between Au and Ti. In fact, the adsorption energy of the Au strip on the TiO$_2$ is ~0.46 eV per Au-O$_{br}$ bond. This low adsorption energy is consistent with recent experimental and theoretical work for Au on defect-free TiO$_2$ [24,25].

The O$_2$ adsorption on Au/TiO$_2$ and nonsupported Au was then investigated and the results are listed in Table I. On Au/TiO$_2$(110), we considered O$_2$ adsorption at two different sites: site 1 (the interface) and site 2 (Au only), as labeled in Fig. 1(a). We found that the O$_2$ adsorption at site 1 is much more favorable ($E_{ad} = 0.86$ eV) than at site 2 ($E_{ad} = 0.05$ eV). For comparison, we calculated the O$_2$ adsorption energy on nonsupported Au at a position similar to site 2, and obtained a negligible value (Table I). These results strongly suggest that O$_2$ adsorption at the interface is highly favored with respect to adsorption on the Au. An important consequence of adsorption at the interface is that the O-O bond is largely stretched (O-O distance of 1.46 Å, compared to the calculated equilibrium gas phase value of 1.24 Å). Moreover, the O$_2$ molecule adsorbed at the interface is in a spin unpolarized state. In contrast, O$_2$ molecules adsorbed on nonsupported Au and on site 2 on Au/TiO$_2$(110) are spin polarized, with a shorter O-O distance close to that of gas phase O$_2$.

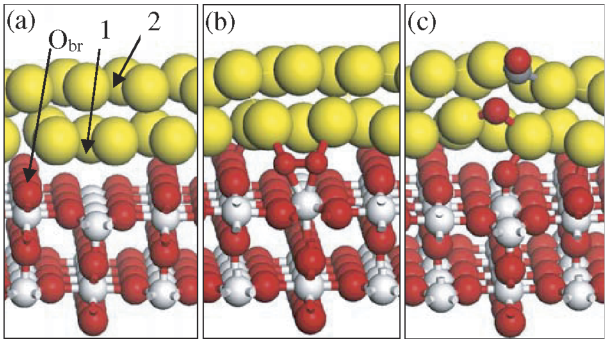

FIG. 1 (color online). The optimized structures of O$_2$/Au/TiO$_2$(110). (a) A side view at the interface of the optimized Au/TiO$_2$ system (site 1 and site 2 are defined in the text). (b) O$_2$ adsorption at the Au/TiO$_2$(110) interface. (c) The transition state for an adsorbed CO reacting with an O$_2$ at the interface.

We next studied CO oxidation on the O$_2$ preadsorbed systems. The main results are as follows. (i) Adsorption of CO on Au is quite strong (~1.7 eV) irrespective of the presence of the oxide. This is consistent with previous calculations and the experimental findings [6,13,15]. (ii) At the Au/TiO$_2$(110) interface, O$_2$ is able to dissociate with a low barrier (0.52 eV); however, on the nonsupported Au, O$_2$ dissociation is unfavorable ($E_a >$ 2 eV). (iii) At the Au/TiO$_2$(110) interface, the reaction $CO + O_2 \rightarrow CO_2 + O$ is favored by a very small barrier of 0.1 eV. The transition state for this reaction at the interface is depicted in Fig. 1(c). (iv) The same reaction on the nonsupported Au exhibits a much higher barrier (SIESTA, 0.78 eV; CASTEP, 0.73 eV). These results indicate that *CO oxidation on* Au/TiO$_2$(110) *can proceed with high efficiency without* O$_2$ *dissociation. However,* O$_2$ *dissociation at the interface is not excluded.* The low barrier of the CO + O$_2$ reaction at the interface can be explained by the fact that adsorbed O$_2$ is highly activated (the O-O bond being stretched).

Since the highly activated O$_2$ adsorption state at the interface appears to be responsible for the high reactivity of the Au/TiO$_2$ system, it is of interest to examine the bonding character of O$_2$ at the interface. We first calculated the charge density difference before and after O$_2$ adsorption: In Figs. 2(a) and 2(b), we present two contour plots of the density difference cutting through the bonding planes of O$_2$ with Ti and O$_2$ with Au, respectively. The charge density difference is constructed by subtracting the total electron densities of the O$_2$ adsorbed system (O$_2$/Au/TiO$_2$) from the densities of a free O$_2$ molecule and the Au/TiO$_2$ slab without modifying the atomic positions. Figure 2 shows that upon adsorption electrons flow into the O$_2$ 2π orbitals. As this is an antibonding state in O$_2$, the O-O bond weakens, leading to the increase of the bond distance. From Fig. 2(a), it is apparent that the 2π orbital is not the same as that of the free molecule but it is polarized along the Ti-O axis. This polarization is reasonable because the Ti atom is positively charged.

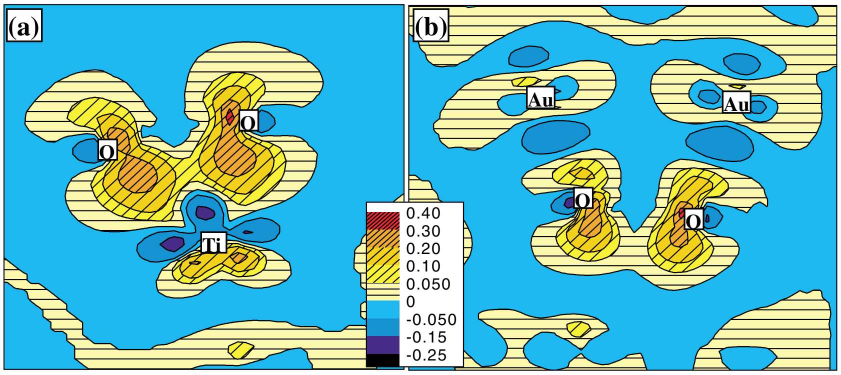

FIG. 2 (color online). Charge-density-difference contour plots showing the bonding of O_2 at the Au/TiO_2 interface. (a) O_2-Ti bonding plane and (b) O_2-Au bonding plane. The charge density difference is constructed by subtracting the electronic densities of O_2/Au/TiO_2(110) from the densities of an O_2 molecule and a clean Au/TiO_2(110), each in the same structure.

Since there is no obvious electron density accumulation in the O_2-Au or O_2-Ti bonding regions, we obtain an ionic-like bonding picture for the O_2 molecule at the Au/TiO_2 interface, with charge transfer and polarization.

A Mulliken population analysis strengthens this picture. The results show the following: For O_2 adsorbed at the Au/TiO_2 interface, (i) the Mulliken charges of the molecule are -0.72, while this number is reduced to -0.30 when adsorbed on the nonsupported Au; and (ii) the Mulliken charges of the oxide substrate are unaffected by O_2 adsorption, indicating that the extra charges on the O_2 molecule are provided by the Au. Therefore, TiO_2 enhances a charge transfer from Au to O_2 when O_2 is near the interface, but without transferring any charge itself. The O_2 at the interface is highly activated as its antibonding orbitals (2π) are being filled, and the O_2 bonding with the Au and Ti exhibits an ionic character.

Why then is it that TiO_2 promotes charge transfer from Au to O_2? The answer to this, which may be a fundamental issue regarding metal/oxide interfaces in general, can be found by analyzing the effect of TiO_2 on the electronic levels of the O_2 molecule and the Fermi level of the Au strip. Two calculations were performed by placing O_2 at two different distances from the TiO_2(110) surface. In structure (a), O_2/TiO_2, O_2 is 2.1 Å above the TiO_2(110) [the same structure as the optimized O_2/Au/TiO_2(110) without the Au strip]. Structure (b), $O_2 + TiO_2$, is the same as structure (a) but the O_2 is 6 Å away from the surface. When moving from structure (a) to structure (b), the 2π energy level of O_2 is lowered by 1.35 eV, as schematically shown in Fig. 3. In a similar way, the Fermi level of the Au + TiO_2 system is lowered only by 0.19 eV when the Au strip is brought into contact with the TiO_2 surface (the Au/TiO_2 system). Therefore, TiO_2(110) lowers both the energy levels of O_2 2π and the Au Fermi energy, but the O_2 2π orbitals are shifted to a larger extent, thus promoting the charge transfer from the Au.

The key point then is to understand why the O_2 molecule levels are more strongly affected than those of Au. There are several concurring factors for this to happen. First, the O_2 molecule is closer to the positively charged Ti ion than the atoms of the Au strip [see Fig. 1(b)]. Second, the Au feels an average electric field arising from both Ti and O atoms in the substrate, which is smaller than that of the Ti ion. In addition, this field is more efficiently screened by the electrons in the Au strip. Finally, the Au strip is a much bigger structure than the O_2 molecule, with a significant density of states at the Fermi level. Therefore, the Fermi energy is less sensitive to an external field.

In a previous paper, we reported a CO oxidation pathway in which there are three steps: (i) CO adsorbs on Au; (ii) a gas phase O_2 meets an adsorbed CO to form a complex of OC-OO on the Au; and (iii) the bond of OC-OO is strengthened while the bond in the O_2 is weakened, leading to CO_2 formation [15]. Molina and Hammer have identified a similar pathway on the interface of

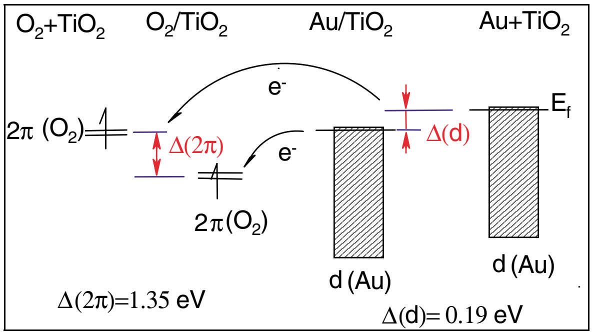

FIG. 3 (color online). Illustration of the energy level shifts of O_2 and Au on TiO_2. All the systems, $O_2 + TiO_2$, O_2/TiO_2, Au/TiO_2, and Au + TiO_2, have the same structure as the optimized O_2/Au/TiO_2 [Fig. 1(b)] except that in the O_2 + TiO_2 and O_2/TiO_2 systems the Au strip is removed and the O_2 is moved from the original position (2.1 Å above a Ti, O_2/TiO_2) to the vacuum (6 Å above the Ti, O_2/TiO_2); in the Au/TiO_2 and Au + TiO_2 systems the O_2 is removed and the Au strip is moved from the original position (3.9 Å above the Ti, Au/TiO_2) to the vacuum (7.9 Å above the Ti, Au + TiO_2).

Au/MgO very recently [16]. Although both pathways possess rather low barriers, there is a fundamental problem: The O_2 adsorption on Au is extremely weak (0.0–0.1 eV on pure Au [15,16] and 0.2 eV on Au/MgO [16]). Therefore, the probability of the formation of OC-OO complex is not high, if at all possible. Consequently, CO oxidation in these systems may not be favorable, consistent with experimental works [1,7]. In contrast, O_2 adsorption and activation, a critical step in any Au-based system, is facilitated by the presence of the Au/TiO_2 interface. The positively charged Ti atom induces a significant charge transfer from Au to O_2 which leads to (i) an ioniclike bonding between O_2-Ti and O_2-Au; and (ii) O_2 activation. This may be the key toward understanding the high activity of Au/oxide systems. Furthermore, our analysis indicates that there may be a relationship between the oxidation state (charge) of the oxide's metal ion, and its catalytic effect. Namely, oxides that possess ions with high oxidation states, such as TiO_2 (Ti^{+4}), V_2O_5 (V^{+5}), may have large promotion effects as they can induce a stronger electrostatic potential to promote charge transfer from Au to O_2. It should be emphasized that the potential induced by the positive ions decays quite rapidly away from the surface, and thus the strong catalytic effect of oxides may exist only at the interface.

In summary, our DFT calculations have identified an important catalytic role of metal oxides in Au/oxide catalysts. Our results show clearly that TiO_2 is not only a support to provide a means of spreading out Au particles over a large surface area, but also a promoter for CO oxidation. The positively charged Ti at the interface enhances electron transfer from the supported Au to the 2π orbitals of adsorbed O_2. As a result, O_2 is highly activated and CO oxidation at the interface occurs via a CO + O_2 mechanism with a very low barrier.

We gratefully acknowledge the UKCP for computing time in T3E and the Supercomputing Center in Ireland for computing time in IBM-SP and HP Itanium 2 cluster.

---

*Author to whom correspondence should be addressed. Electronic address: P.Hu@qub.ac.uk

[1] M. Haruta, Catal. Today **36**, 153 (1997).
[2] F. Cosandey and T. E. Madey, Surf. Rev. Lett. **8**, 73 (2001).
[3] B. Hammer and J. K. Norskov, Nature (London) **376**, 238 (1995).
[4] M. Valden, X. Lai, and D.W. Goodman, Science **281**, 1647 (1998).
[5] N. D. S. Canning, D. A. Outka, and R. J. Madix, Surf. Sci. **141**, 240 (1984).
[6] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet, and B. Delmon, J. Catal. **144**, 175 (1993).
[7] M. Schubert, S. Hackenberg, A. C. van Veen, M. Muhler, V. Plzak, and R. J. Behm, J. Catal. **197**, 113 (2001).
[8] R. J. H. Grisel and B. E. Nieuwenhuys, J. Catal. **199**, 48 (2001).
[9] J. D. Grunwaldt, C. Kiener, C. Wogerbauer, and A. Baiker, J. Catal. **186**, 458 (1999).
[10] H. Liu, A. I. Kozlov, A. P. Kozlova, T. Shido, and Y. Iwasawa, Phys. Chem. Chem. Phys. **1**, 2851 (1999).
[11] V. A. Bondzie, S. C. Parker, and C. T. Campbell, J. Vac. Sci. Technol. A **17**, 1717 (1999).
[12] C. Stampfl and M. Scheffler, Phys. Rev. Lett. **78**, 1500 (1997).
[13] M. Mavrikakis, P. Stoltze, and J. K. Norskov, Catal. Lett. **64**, 101 (2000).
[14] G. Mills, M. S. Gordon, and H. Meitu, Chem. Phys. Lett. **359**, 493 (2002).
[15] Z.-P. Liu, P. Hu, and A. Alavi, J. Am. Chem. Soc. **124**, 7499 (2002).
[16] L. M. Molina and B. Hammer, Phys. Rev. Lett. **90**, 206102 (2003).
[17] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys. Condens. Matter **14**, 2745 (2002).
[18] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[19] M. C. Payne *et al.*, Rev. Mod. Phys. **64**, 1045 (1992).
[20] We have checked the accuracy of SIESTA by calculating barriers (E_a) of chemical reactions on different metals. In general, SIESTA can reproduce the plane-wave results obtained with CASTEP to an accuracy of a few percent. For example, for CO oxidation on Pt(111), a well-defined model system, E_a from SIESTA is 0.79 eV, consistent with the 0.80 eV barrier from CASTEP.
[21] The CASTEP [19] calculation setup is the same as that reported in our previous papers [15,22]. In the SIESTA [17] calculations, Troullier-Martins norm-conserving scalar relativistic pseudopotentials were used. The semicore states ($3s$, $3p$) for Ti were treated explicitly. A double zeta plus polarization basis set was employed (except for Ti semicore states, for which a minimal set was employed). The energy cutoff for the real space grid used to represent the density was 120 Ry. The localization radii of the basis functions were determined from an energy shift of 0.025 eV (see Ref. [17] for details).
[22] Z.-P. Liu and P. Hu, J. Am. Chem. Soc. **125**, 1958 (2003).
[23] To obtain a physically meaningful structure for the Au/TiO_2 composite system, Nose thermostat molecular dynamics simulation ($T = 200$ K, 5 fs/step, 500 steps) was performed. Five low energy structures were selected and each one was further optimized by a conjugate gradients procedure. The lowest energy structure was then used for all subsequent studies. In all calculations, the Au atoms and the top three layers of $TiO_2(110)$ surface were relaxed, keeping the rest of the TiO_2 atoms fixed at their bulk-truncated positions.
[24] N. Lopez and J. K. Norskov, Surf. Sci. **515**, 175 (2002).
[25] E. Wahlstrom *et al.*, Phys. Rev. Lett. **90**, 026101 (2003).