Here we present the first DFT study on CO oxidation on adsorbed O atoms are detected during CO oxidation [2,6]. which is consistent with the experimental findings that no contrast, theoretical studies on the subject are limited. very recently, Molina and Hammer investigated oxidation? (ii) Where and how does CO oxidation occur? (iii) What is the catalytic role of the metal oxide? 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) O₂ 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 O₂, giving rise to (i) strong ionic bonding between the adsorbed O₂, Au, and the Ti cation; and (ii) a significant activation of O₂ towards CO oxidation.

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 TiO₂, has a higher reactivity compared to Au on irreducible oxides, such as MgO and SiO₂ [7,8]. In contrast, theoretical studies on the subject are limited. Several density functional theory (DFT) studies were carried out for O₂ and CO chemisorption and O₂ 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 O₂ 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/TiO₂(110), attempting to answer the following questions: (i) Where and how is O₂ 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 TiO₂(110) is modeled by a large unit cell [a (2 x 4) unit cell, 13.09 Å x 11.80 Å with slabs separated by more than 10 Å of vacuum]. The oxide slab contains six layers (in all 32 units of TiO₂ per slab) and the convergence of the adsorption energies is further checked by increasing to nine layers (48 units of TiO₂ per slab). Experimentally, Goodman et al. found that two-layer Au particles on TiO₂ have the highest activity [4]. Based on this, we have modeled the Au/TiO₂ system by adding a two-layer strip of Au on the TiO₂(110) substrate [Fig. 1(a)]. The size of the Au/TiO₂(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 TiO₂(110), referred to as nonsupported Au hereafter, was also calculated. The structure of the Au/TiO₂(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.
Earium gas phase value of $E_{ad}$ (using SIESTA. The CASTEP results are listed in parenthesis for comparison [20]. All the energies are in eV.

There are four Au/O$_2$ bonds per unit cell with a similar Au-O distance ($\sim$ 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 $\sim$0.46 eV per Au-O$_{bn}$ 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$_2$.

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 ($E_{ad}$ > 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 orbitals 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. 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.](image-url)
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 ($2\pi$) 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 $2\pi$ 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$_2$ $2\pi$ and the Au Fermi energy, but the O$_2$ $2\pi$ 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...
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$_2$O$_5$ (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.

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[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).
[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$_2$ surface were relaxed, keeping the rest of the TiO$_2$ atoms fixed at their bulk-truncated positions.