



# DFT study of catalytic activity of an ultrathin TiO<sub>2</sub>(110) layer covering Au(112): O<sub>2</sub> activation, CO oxidation, and replacing Au with Ag



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## ABSTRACT

As a model of Au-titania core-shell catalysts, an ultrathin rutile TiO<sub>2</sub>(110) layer inversely supported on Au(112) has been examined by DFT. O<sub>2</sub> adsorbs and activates on the pentacoordinate Ti site of rutile(110) as O<sub>2</sub> π\* orbitals accept electronic charge from the Au support via the oxide, as was found for Au/TiO<sub>2</sub>. O<sub>2</sub> reacts with CO to yield CO<sub>2</sub> and O, which then reacts with CO to yield CO<sub>2</sub> (barrier ~0.6 eV). O<sub>2</sub> adsorption weakens with increasing O<sub>2</sub> coverage and oxide thickness. The reactivity of O<sub>2</sub> changes negligibly even if we replace Au with Ag.

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## 1. Introduction

Gold is catalytically active toward numerous reactions including low-temperature CO oxidation if it is dispersed as nanoparticles onto metal oxides such as TiO<sub>2</sub> [1,2]. However, with a low-melting point and weak binding to the oxide support, Au nanoparticles are liable to sintering and deactivation at high temperatures. One solution is to coat them with oxide and immobilize them on another support material. For example, a durable NiO<sub>x</sub>/Au catalyst with such core-shell geometry has recently been developed for the production of methyl methacrylate [3]. Thus, the catalytic activity of oxide-coated Au nanoparticles deserves a close inspection.

The oxide-coated metal nanoparticles may have various facets and interfaces. As a first step, it is reasonable to model them as inverse catalysts [4,5], i.e., metal films covered partially or entirely with thin oxide deposits. In general, they exhibit catalytic activities via three mechanisms. First, the metal surface (or the perimeter of a metal/oxide interface [6]) serves as the active site as in the usual supported catalysts if the oxide overlayer is partial or permeable to reactants. Second, the oxide deposits may be structurally different from the bulk phase, exhibiting novel catalytic activities. Third, electrons from the metal support transfer via the oxide overlayer to activate reactants on its surface if the overlayer is very thin. O<sub>2</sub> activation by this mechanism

has been theoretically predicted for MgO(001)/Ag(001) [7,8] and experimentally observed on MgO(001)/Mo(001) [9].

Interestingly, the electron transfer via oxide is also invoked to explain the catalytic activity of rutile(110)-supported Au nanoparticles. Various DFT studies [10–17] find that O<sub>2</sub> adsorbs and activates on the pentacoordinate Ti site (Ti<sup>5c</sup>) of rutile(110) in the proximity of Au deposits. This is explained by electron transfer from the Au to O<sub>2</sub> via oxide [10,11]. This mechanism does not necessarily require direct bonding between O<sub>2</sub> and the Au. Indeed, our DFT calculation [18,19] finds that even Ti<sup>5c</sup> sites that are ~1 nm away from a Au deposit can activate O<sub>2</sub> for CO oxidation. Thus, a thin rutile(110) layer covering a Au surface may activate O<sub>2</sub> even if it blocks reactants from reaching the metal surface. With the metal surface protected from corrosion, Au may be replaced by less noble metals such as Ag.

In this DFT study, we verify the ability of such a rutile(110)/Au system to activate O<sub>2</sub> for CO oxidation. First, we show that the electronic effect of the oxide/metal interface extends to the surface if the oxide overlayer is very thin. Then, we examine O<sub>2</sub> adsorption and O–O bond activation due to electron transfer. Thereafter, we examine O<sub>2</sub> + CO and O + CO reactions. We also examine dependence on thickness and O<sub>2</sub> coverage. Lastly, we show that the reactivity of O<sub>2</sub> is essentially unaffected if Au is replaced by Ag.

## 2. Computational details

As in our previous studies on Au/TiO<sub>2</sub> [17–19], calculations were performed by a plane-wave DFT code (STATE [20]) within the generalized

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gradient approximation by Perdew, Burke, and Ernzerhof [21], using ultrasoft pseudopotentials [22] and a cutoff energy of 25 Ry. Spin-unpolarized states were calculated unless otherwise noted. Transition states (TS) were calculated by force inversion [23]. Conventions and analysis methods are described in the supplementary information (SI).

Fig. 1 shows the inverse catalyst model we examined. The  $\text{TiO}_2(110)[001] \parallel \text{Au}(112)[110]$  orientation allows an excellent lattice match, and was observed when Au was deposited on  $\text{TiO}_2(110)$  at a high temperature (775 K) under ultrahigh vacuum conditions [24]. Each bridging oxygen ( $\text{O}^{\text{br}}$ ) at the bottom of the oxide layer sits above a Au step site. More justification for the interface structure of Fig. 1 is given in SI. The lattice parameters were fixed to those of  $\text{TiO}_2$  calculated theoretically ( $a = 467$  pm,  $c = 299$  pm). The default thickness was 2 L/2 L with over 1 nm of vacuum layer. The cell size was  $2 \times 4$ , where  $\times 4$  refers to the  $\text{TiO}_2[001]$  direction. The sampling  $k$ -point grid [25] was  $1 \times 4$  for the examination of various  $\text{O}_2$  adsorption configurations and  $1 \times 2$  for the study of reaction barriers and thickness dependence; refer to SI for more discussion. Although dipole correction and onsite Coulomb interaction correction were not used, some tests are described in SI.

### 3. Results and discussion

There is much debate about the charge state of oxide-supported Au clusters [26–30] because it depends sensitively on the size and shape of the clusters, the detailed structure of the interface, the oxidation state of the oxide, and the method of charge analysis. At least, Bader analysis on our planar system finds metal-to-oxide electron transfer, making the metal support slightly positive ( $+0.10 e/1 \times 1$ );  $e$  denotes unsigned elementary charge. The electronic charge is from the Au site at the interface, indicating the influence of anionic  $\text{O}^{\text{br}}$ . Most of the charge ( $-0.09 e$ ) is transferred to the bottom trilayer of the oxide. More important, the Au/oxide contact causes some electron density redistribution around the  $\text{Ti}^{5c}$  site of the front surface (Fig. 2(a)), enhancing its reactivity. Similar redistribution has been found around the  $\text{Ti}^{5c}$  site next to the Au/ $\text{TiO}_2(110)$  perimeter interface [12]. If the oxide thickness is increased to four trilayers, then the redistribution around the front  $\text{Ti}^{5c}$  site is less pronounced (Fig. 2(b)) although similar amount ( $-0.11 e/1 \times 1$ ) is transferred from the metal to the oxide. The electronic effect of the interface thus diminishes with increasing oxide thickness.

Further electron transfer to  $\text{O}_2$  allows it to adsorb on the cationic  $\text{Ti}^{5c}$  site (Fig. 3). Among the calculated geometries, the adsorption is strongest when  $\text{O}_2$  adsorbs sideon to  $\text{Ti}^{5c}$ . Spin-polarized calculation confirms that spin on  $\text{O}_2$  virtually vanishes.  $\text{O}_2$  bridging adjacent  $\text{Ti}^{5c}$  sites is nearly as stable as sideon  $\text{O}_2$ . The dissociation of bridge  $\text{O}_2$  into a pair of adjacent O adatoms [31] is energetically unfavorable by 0.11 eV and kinetically limited by an energy barrier of 1.04 eV. Sideon and bridge  $\text{O}_2$  carry similar negative charge, with their O–O bonds stretched substantially ( $>140$  pm) compared to that in the gas phase (125 pm, calculated). Projected density of states (PDOS) for sideon  $\text{O}_2$  shows  $\text{O } p_z$ – $\text{Ti } d_{yz}$  and  $\text{O } p_x$ – $\text{Ti } d_{xy}$  overlaps, indicating  $\pi$ -interaction between  $\text{O}_2 \pi_z^*$  and  $\text{Ti } d_{yz}$  and  $\delta$ -interaction between  $\text{O}_2 \pi_x^*$  and  $\text{Ti } d_{xy}$ , respectively (Fig. 4(a)). PDOS for bridge  $\text{O}_2$  shows  $\sigma$ -overlap between  $\text{O } p_z$  and  $\text{Ti } d_{yz}$ , with a small contribution from  $\text{Ti } d_{z^2}$ , as well as  $\pi$ -overlap between  $\text{O } p_x$  and  $\text{Ti } d_{xz}$  (Fig. 4(b)). Through these interactions,  $\text{O}_2$  receives electronic charge to both  $\pi^*$  orbitals. Indeed, the electron-density redistribution due to  $\text{O}_2$  shows a doughnut-shaped electron accumulation on each end of O–O (Fig. 3). Thus, sideon and bridge  $\text{O}_2$  are peroxide-like species. Compared to them,  $\text{O}_2$  attached endon to  $\text{Ti}^{5c}$  is much less stable, with less negative charge and a shorter O–O bond. Lastly,  $\text{O}_2$  barely adsorbs on the oxide layer ( $E_{\text{ad}} > -0.03$  eV) if the Au support is removed, remaining in a triplet state. Thus,  $\text{O}_2$  adsorption on  $\text{Ti}^{5c}$  and concomitant O–O bond activation are governed by electron transfer from the metal support to  $\text{O}_2 \pi^*$  via the oxide. Sideon and bridge  $\text{O}_2$  are basically identical to their counterpart ( $\text{Ti}-\text{O}_2$  and  $\text{Ti}-\text{OO}-\text{Ti}$ , respectively) on Au/rutile(110) [17], except that adsorption is somewhat weaker, reflecting the distance to cationic Au sites at the interface.

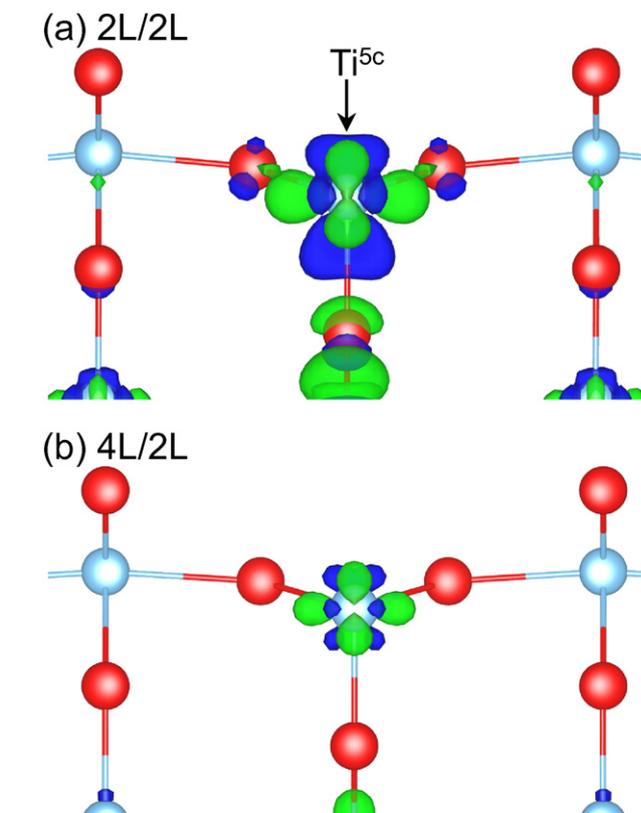


Fig. 2. Electron accumulation (green or light) and depletion (blue or dark) around front  $\text{Ti}^{5c}$  due to Au/oxide contact. Iso-surface at  $0.0005 e/\text{Bohr}^3$ .

Fig. 5 shows the transition states when CO attacks  $\text{O}_2$  directly from the gas phase. Both sideon and bridge  $\text{O}_2$  are reactive to CO without prior dissociation. The TS geometries indicate that the barriers are due to  $\text{O}_2 \cdots \text{CO}$  repulsion and the cost of stretching O–O and O– $\text{Ti}^{5c}$  bonds. On Au/ $\text{TiO}_2$ ,  $\text{O}_2 + \text{CO}(\text{g})$  reaction barriers are 0.55 eV for sideon  $\text{O}_2$  and 0.45 eV for bridge  $\text{O}_2$  [17]. Thus, the reactivity of  $\text{O}_2$  is essentially unchanged between the two systems. The difference arises at the Au/oxide perimeter, where CO is activated on a Au site and reacts with sideon  $\text{O}_2$  with a lower barrier ( $<0.3$  eV) [17–19]. For the same reason, partially covered Au nanoparticles are expected to show better CO oxidation performance than fully covered ones.

The above reaction leaves an O adatom on the  $\text{Ti}^{5c}$  site (Fig. 3(e)). Negative charge comparable to that on sideon  $\text{O}_2$  is now concentrated on a single O. The O– $\text{Ti}^{5c}$  bond is shortened as a result. Fig. 5(c) shows the transition state when CO attacks the O adatom from the gas phase

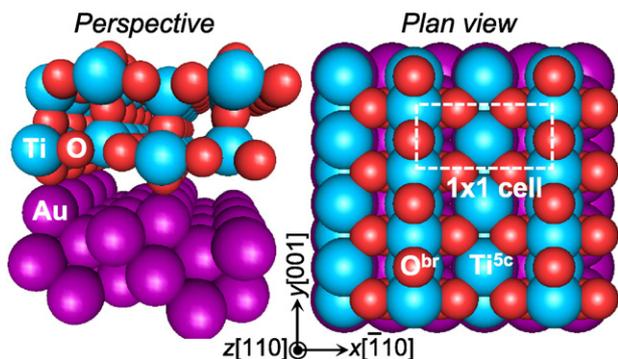


Fig. 1. Rutile(110) 2 L/Au(112) 2 L model ( $2 \times 4$  cell).

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