DFT Study of CO Oxidation Catalyzed by Au/TiO₂: Activity of Small Clusters*

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I. INTRODUCTION

Gold nanoparticles (≈ 3 nm in diameter) supported on metal oxides such as TiO₂ exhibit excellent catalytic activities toward low-T CO oxidation [1,2] and other important reactions [3]. Because gold generally lacks the ability to adsorb and activate O₂, it is viewed that reactions occur at the perimeter of a Au nanoparticle where it adjoins the oxide surface [4]. For a well-studied example of Au/TiO₂ at least, this has been supported by experiments showing the proportionality between the rate of CO oxidation and the length of the perimeter [5,6]. Yet, it is unclear whether this picture applies to supported clusters of smaller sizes (≈ 1 nm in diameter). This question is becoming more important with growing interest in the size- and shape-specific activity of small Au clusters [3].

In the field of heterogeneous catalysis, computational methods such as density-functional theory (DFT) [7,8] are indispensable for identifying reaction sites, active species, and reaction paths. There are now a number of DFT studies (and joint ones) on CO oxidation over Au/rutile TiO₂ [9-16]. Earlier DFT calculations for supported Au nanorods [9,10] have shown that O₂ adsorbs and activates on the pentacoordinate Ti site (Ti⁵c) of the oxide surface. This is because the strong positive field of the Ti cation lowers O₂ π⁺ states and induces electron transfer from the Au to O₂, resulting in Ti–O₂ ionic bonding and O₂ bond weakening; naturally, the TiO₂ surface itself is unable to adsorb O₂ in the absence of electron donors such as Au clusters and O vacancies. It is considered that O₂ adsorbs preferentially at the perimeter because of Au-O₂ ionic interactions [9,14], but adsorption on more remote sites ("off-perimeter") is possible. Indeed, a DFT study for TiO₂-supported Auₙ clusters (ₙ ≤ 7) [17] noted that O₂ adsorbs on a Ti⁵c site that is not directly next to a cluster. However, reactions by such O₂ have been neglected in most DFT studies.

In our previous work [18], we have examined CO oxidation over a TiO₂-supported Au nanorod by DFT and found that an off-perimeter O₂ reacts with CO(g) with an energy barrier of 0.57 eV; (g) denotes a gaseous molecule. The perimeter hypothesis still holds because an on-perimeter O₂ reacts with a Au-adsorbed CO (Au-CO) with a smaller barrier of 0.22 eV. The aim of the present DFT study is to examine how the balance between these on- and off-perimeter reactions changes when the supported Au particle is downsized to ≈ 1 nm. Since it is impractical to study all the possible sizes and shapes of Au clusters, we use a tetrahedral Au₁₀ as a model of small FCC clusters. This is a minimal FCC cluster and a building block for magic clusters such as 20-atom tetrahedron and 55-atom icosahedron. For comparison, we also briefly examine a truncated pyramidal Au₁₀ cluster.

The rest of this paper is organized as follows. Section II describes the details of calculation. Section III.A examines O₂ adsorption on Au₁₀/TiO₂ and finds that off-perimeter O₂ are nearly as stable as on-perimeter O₂. Section III.B examines CO oxidation on Au₁₀/TiO₂ and finds that an on-perimeter O₂ reacts with Au-CO with a very small barrier while an off-perimeter O₂ reacts with CO(g) with a barrier similar to that obtained for the supported rod. Section IV examines CO oxidation on Au₁₀/TiO₂ and finds that a carbonate is formed at the perimeter. Sec-

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tion V summarizes and concludes that $O_2 + CO$ reaction is much faster at the perimeter also for small clusters such as $Au_9$ and $Au_{10}$.

II. DETAILS OF CALCULATION

As in our previous work [18], total energies and optimized geometries were calculated by STATE [19], a plane-wave DFT code. This code has been applied to a wide range of systems including $Au/TiO_2$ [20,21]. Ultrasoft pseudopotentials [22] and the exchange-correlation functional by Perdew, Burke, and Ernzerhof [23] were used. Kohn-Sham orbitals and the charge density were expanded into plane waves up to the cutoff energies of 25 and 225 Ry, respectively. The number of valence electrons was 1, 4, 6, 10, and 11 for H, C, O, Ti, and Au, respectively. Unless otherwise noted, the spin unpolarized (polarized) state was calculated for a system with an even (odd) number of electrons. The transition state (TS) of a reaction was searched by constrained optimization and then refined by force inversion [24]. The initial and final states (IS/TS) of the reaction were found by relaxation from TS. If this resulted in the detachment of a molecule from the surface, then the desorption limit was identified as IS/TS, and its total energy was obtained as the sum of total energies of the gaseous molecule and the rest, calculated separately. The Bader method [25,26] was used to determine the charge (and spin charge) carried by each atom. Negative charge on O$_2$ and the O-O bond length were used as indicators of $O_2$ activation state. Note that the Bader charge may differ from the formal oxidation number, e.g., the Bader charge on O of TiO$_2$ is calculated to be -1.1 eV. The charge density was visualized using VESTA [27]. The total energy of a gaseous molecule was calculated using a 24-Bohr cubic cell; O$_2$ was calculated as a triplet.

Figure 1(a) shows the $Au_{10}/TiO_2$ model used in the present study. The rutile TiO$_2$(110) surface was represented as a four-trilayer slab placed in a $2 \times 4$ cell (sampled at $1 \times 2$ k-point mesh). The thickness of a vacuum layer was 1.39 nm. The atoms of the bottom trilayer were constrained to their bulk positions. A tetrahedral $Au_{10}$ cluster was placed on this surface with the orientation of $Au(111)[110] || TiO_2(110)[001]$. This choice reduces the lattice mismatch along the Au-Au bond to less than 2%. The average distance between the bottom facet of $Au_{10}$ and the uppermost Ti layer is calculated to be 0.31 nm, similar to 0.33 nm measured for Au nanoparticles deposited on TiO$_2$ [28]. Naturally, it is difficult to prove that this is the most stable geometry for the supported $Au_{10}$, but at least this is 0.24 eV more stable than a planar geometry shown in Fig. 1(b). The $Au_{10}/TiO_2$ model was obtained from $Au_{10}/TiO_2$ by removing the Au atom at the apex (Fig. 1(c)).

![Fig. 1. Models for a TiO$_2$(110)-supported Au cluster. (a) Tetrahedral $Au_{10}$. Indices for Ti$^{5c}$ sites are displayed in a plan view (right). (b) Planar $Au_{10}$. (c) Truncated pyramidal $Au_{10}$ (doublet).](http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/))

The adsorption energy is referenced to the desorption limit of $O_2$, CO, and/or $H_2O$. In our convention, a more stable state has more negative adsorption energy. Charge density difference due to $O_2$ adsorption was obtained as

$$\Delta \rho = \rho - \rho(Au_{10}/TiO_2) - \rho(O_2)$$

where $\rho$ is the charge density of the whole system, and $\rho(Au_{10}/TiO_2)$ and $\rho(O_2)$ are those of $Au_{10}/TiO_2$ and a spin-polarized $O_2$, respectively, calculated using the same cell and atomic coordinates as in the whole system.

The accuracy of the present calculation has been estimated as follows. The uncertainty associated with the cell size would be $\sim 0.06$ eV because difference in $O_2$ adsorption energies between Ti$^{2(3)}$ and Ti$^{2(1,2)}$ is 0.12, 0.16, and 0.06 eV for $2 \times 4$, $2 \times 5$, and $3 \times 4$ cells, respectively (all sampled at $1 \times 2$ k-point mesh). Dependence on the slab thickness and k-point mesh would be similar to that ($\sim 0.03$ eV) found for the supported rod [18].

III. $Au_{10}/TiO_2$ MODEL

A. $O_2$ adsorption

Earlier DFT studies [9,10,17,18] on TiO$_2$-supported Au clusters and nanorods have found that $O_2$ adsorbs strongly to the Ti$^{5c}$ site in a sideon configuration (Ti–O$_2$). This is also the case for $Au_{10}$: $O_2$ adsorbs sideon to the Ti$^{2(1)}$ site with a very strong adsorption energy of $-2.35$ eV (Fig. 2(a)). Strong $O_2$ activation can be seen in a substantial increase in the O-O bond length and negative charge carried by $O_2$. The upward displacement of Ti$^{5c}$ (by 95 pm) and the orientation of the O-O bond (47$^\circ$ with respect to TiO$_2[001]$) indicate strong orbital interactions between $O_2$ and Ti$^{5c}$. To analyze this further, we have calculated projected density of states (PDOS) for the Ti atom and the O of $O_2$ (Fig. 3(a)). An overlap between O $p_z$ and Ti $d_{z^2}$ states around $-1.4$ eV indicates a $\pi$-type interaction between the out-of-plane $O_2$ $\pi^*$ and Ti 3$d$ orbitals. An overlap between O $p_y$ and Ti $d_{xy}$ states around $-0.2$ eV indicates a $\delta$-type interaction between the in-plane $O_2$ $\pi^*$ and Ti 3$d$ orbitals; the diagonal ori-
tation of O-O is key to this interaction. With both π∗ orbitals lowered below the Fermi level, O2 is activated to a peroxide state. This can also be seen in the charge density difference due to O2 adsorption (Fig. 3(b)): As a result of electron transfer to both π∗ orbitals, a ring-shaped region of electron accumulation appears on each O of O2. A spin-polarized calculation also confirms that O2 is in a singlet state. We add that, in spite of the O-O bond weakening, O2 dissociation between two Ti sites is unlikely because the resulting configuration is much less stable (Fig. 2(d)).

O2 adsorbs at a dual perimeter site consisting of Ti(2,1) and Au sites (Ti-OO–Au) with a strong adsorption energy of -1.91 eV (Fig. 2(b)). O2 activation is not so strong as in Ti-O2. The striking feature of this configuration is that O2 extrudes a Au atom out of the cluster, causing the cluster to shrink by 10% along the TiO2[001] direction. Extrusion by O2 is barely noticeable on the Au rod [18] because a continuous structure would be unable to accommodate the resulting strain. Compared to the one on the rod model, the present Ti-OO–Au has a shorter Au-O2 distance (214 vs. 240 pm) and a more relaxed Ti–O–O bond angle (173° vs. 162°). As a result, the energy difference between Ti–O2 and Ti–OO–Au decreases from 0.71 eV [18] to 0.44 eV, although Ti–O2 is still the more stable configuration.

Compared to these Ti-adsorbed ones, O2 on the apex of Au10 is much less stable, with an adsorption energy of -0.51 eV (Fig. 2(c)). This O2 is barely activated, as can be seen in the O-O bond length and the charge and spin it carries. In addition, the positive charge induced on the top Au atom is small (+0.13e), indicating the weakness of the Au-O2 ionic bonding.

Having confirmed the greater stability of the sideon configuration, we now examine the relative stability between various Ti5c sites (Fig. 4). Ti(1–2)–O2 is practically degenerate with Ti(2,1)–O2 in spite of a contact with the Au cluster. Ti(1–3)–O2 is not directly next to the cluster, but is only marginally less stable than the on-perimeter ones. Ti(2,3)–O2 is slightly less stable than Ti(2,1)–O2. The O-O bond length and negative charge on O2 are sim-
FIG. 5. O₂ + CO reaction on and off the perimeter. (a–c) Ti(2,1)–O₂ reacting with Au–CO. (d–f) Ti(2,3)–O₂ reacting with CO(g). Adsorption energies, interatomic distances (pm), and Bader charges on O₂ and O adatoms are displayed in the figure. For a desorption state (marked with *), a snapshot is presented along with the energy at the desorption limit.

similar for all the Ti–O₂. The stability and activation state of Ti–O₂ thus depends weakly on distance to the Au cluster.

B. CO oxidation

As a typical example of CO oxidation on the perimeter of a Au cluster, we have examined a process whereby Ti(2,1)–O₂ reacts with CO adsorbed on the adjacent Au site (Figs. 5(a), (b), and (c)). As the figures show, CO approaches the left O of O₂ on its C end, extract the O to form CO₂, which desorbs spontaneously. The O adatom left on the Ti site is expected to react readily with CO [13]. Compared to the rod model [18], the calculated energy barrier for the Ti–O₂ + Au–CO step is smaller (0.13 vs. 0.22 eV). It is difficult to explain such a small difference, although a possible cause seems to be the extrusion of a Au atom by CO (Fig. 5(a)); extrusion by CO is noted in earlier work on free Au clusters [29]. In the Au₁₀ model, the Au atom is already extruded at IS, so it needs not be extruded further in going to TS. In the rod model, the corresponding Au atom must be extruded by 11 pm in going from IS to TS.

As an example of CO oxidation on an off-perimeter site, we have examined a direct reaction between Ti(2,3)–O₂ and CO(g) (Figs. 5(d), (e), and (f)). The calculated energy barrier of this reaction, 0.55 eV, is very close to 0.56 and 0.57 eV we obtained for Ti–O₂ + CO(g) reaction at the first and second nearest Ti site of the supported rod model, respectively [18]. Without CO activation by the Au [18], the reaction depends heavily on O₂ activation, as can be seen in O-O stretching and negative charge on O₂ at TS (Fig. 5(e)). Because the state of O₂ activation differs little between various Tiₙ sites (Fig. 4) and Au models, a similar barrier can be expected for Ti–O₂ + CO(g) reactions.

IV. Au₉/TiO₂ MODEL

For comparison, we have also examined CO oxidation over the Au₉ model. Results for Ti(2,1)–O₂ + Au–CO reaction are presented in Fig. 6(a). As is the case with Au₁₀, CO extracts the left O of O₂ to form CO₂. IS and TS are similar to those found for Au₁₀. In particular, O₂ is activated to a similar extent despite the odd number of electrons in the system; such a trend is also reported for Au₉ and Au₁₀ stripes [17]. As a result, the energy barrier (0.11 eV) is very close to that for Au₁₀. Furthermore, the calculated barrier for Ti(2,3)–O₂ + CO(g) reaction is again 0.55 eV. Thus, O₂ + CO reaction is faster at the perimeter also for Au₉.

However, CO₂ formed by the Ti(2,1)–O₂ + Au–CO reaction interacts differently with the cluster, combining with the remaining O adatom to form a carbonate, which is bound to two Au sites and the Ti(2,1) site (FS of Fig. 6(a)). Bader analysis indicates that an O adatom on Ti(2,1) receives the same amount of negative charge (−0.89e) whether the cluster is Au₁₀ or Au₉. On the other hand, the Au₉ cluster is in a spin-polarized state (Fig. 6(c)), with a spin charge of 0.87e, and so CO₂ does not detach from Au₉ as readily as it does from Au₁₀. This leaves some room for CO₂ to react with the O adatom. The implication is that a carbonate may form on odd-numbered clusters, although more calculations are needed for confirmation.

The decomposition of the carbonate into CO₂(g) and an O adatom is unfavorable by 0.39 eV. Thus, the carbonate may inhibit CO oxidation by rendering unavailable active Ti sites. Water may assist its decomposition [30] or prevent it from forming. Indeed, our calculations (Fig. 6(b)) indicate that, if H₂O is adsorbed on a Ti site next to O₂, the barrier of the Ti(2,1)–O₂ + Au–CO reaction does not change much (0.16 eV), but CO₂ desorbs instead of forming a carbonate. Apparently, hydrogen bonding with H₂O renders the O adatom less reactive with CO₂.

V. CONCLUSIONS

In this plane-wave DFT study, we have examined CO oxidation on a rutile TiO₂(110) surface supporting sub-nanometer Au clusters. We mainly studied tetrahedral Au₁₀ and also a truncated pyramidal Au₉. We have found that O₂ adsorbs sideon to a pentacoordinate Ti site (Ti–O₂), activated to a peroxide state. This O₂ is more stable than O₂ at a Ti–Au dual-perimeter site or O₂ on the apex of the cluster. Moreover, the stability of sideon O₂
depends weakly on distance to the Au cluster. Thus, O$_2$ adsorption is dominated by the interaction with Ti sites, although the Au cluster is still essential as an electron donor to O$_2$. The trend is similar to what we have found for the supported Au nanorod [18].

For Ti–O$_2$ + Au–CO reaction, similar barriers have been found for Au$_{10}$ and Au$_{110}$ (0.11 and 0.13 eV, respectively). These barriers are slightly lower than 0.22 eV found for the rod [18]. After the reaction, CO$_2$ desorbs from Au$_{110}$ while a carbonate forms on Au$_{10}$. We have also found that more remote Ti–O$_2$ reacts with CO(g) with a barrier of 0.55 eV on both Au$_{10}$ and Au$_{110}$. The barrier of this size appears to be universal for various Ti–O$_2$ and Au models.

In conclusion, O$_2$ + CO reaction is much faster at the perimeter even for small FCC clusters such as Au$_{10}$ and Au$_{110}$. However, the interaction of product CO$_2$ with the surface is more dependent on the size and shape of the cluster, sometimes yielding a carbonate.

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