

Nature of reactive O₂ and slow CO₂ evolution kinetics in CO oxidation by TiO₂ supported Au cluster

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Recent experiments on CO oxidation reaction using seven-atom Au clusters deposited on TiO₂ surface correlate CO₂ formation with oxygen associated with Au clusters. We perform first principles calculations using a seven-atom Au cluster supported on a reduced TiO₂ surface to explore potential candidates for the form of reactive oxygen. These calculations suggest a thermodynamically favorable path for O₂ diffusion along the surface Ti row, resulting in its dissociated state bound to Au cluster and TiO₂ surface. CO can approach along the same path and react with the O₂ so dissociated to form CO₂. The origin of the slow kinetic evolution of products observed in experiments is also investigated and is attributed to the strong binding of CO₂ simultaneously to the Au cluster and the surface. © 2006 American Institute of Physics.

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I. INTRODUCTION

Understanding the catalytic behavior of Au particles supported on TiO₂ has become a major area of experimental and computational research in surface science approach to heterogeneous catalysis.^{1–3} The system is particularly interesting as the Au bulk and surfaces are inert⁴ and the catalytic properties emerge at the nanoscale, a theme that is central to the science of nanotechnology. In comparison with the transition metals, the relative inertness of Au bulk and surfaces can be rationalized by the relatively high cohesive energy of Au bulk and the filling of the antibonding states during surface adsorption.⁴

The catalytic behavior of Au nanoparticles can be loosely classified into three regimes and it is possible that more than one mechanism may act together in different regimes. The first regime has the largest number of Au atoms in the spherical oxide supported Au nanoparticles which are prepared from the liquid phase.^{1–3} This regime is most relevant to industrial catalysis but the preparation method employed offers little chemical and morphological control at the atomistic level of the putative catalytically active centers.^{1–3} Even though the overall morphology of particles prepared from different methods may be similar, it is difficult to quantitatively assess the role played by different mechanisms. Different mechanisms have been considered including increased undercoordination of the nanoparticle^{5–7} due to increased surface-to-volume ratio and the effect of the support.^{1,8,9} Traditionally, the nature of support has been differentiated under two categories, reducible (catalytically active) and irreducible (inactive),³ but this classification has been questioned by recent experiments.¹⁰

The second regime is the planar oxide supported Au films that are vapor deposited on to an oxide surface.^{11,12} The films may grow via Volmer-Weber or Stranski-Krastanov

mode and the extent of control on the film thickness and particle size is determined by self-assembly characteristics of the metal particle and the oxide interface.¹³ This regime gives a better chemical control compared to the first regime, although some contaminants such as hydroxyl groups cannot be easily removed even in high vacuum conditions.¹⁴ One main mechanism that may contribute here is the quantum size effect,^{11,12} whereby a bilayer Au film has been suggested to be most active. Other effects such as undercoordination^{1,5,6,8,15–17} and strain^{17,18} may also play a role.

The third regime is comprised of very small nonmetallic particles, resulting from the effort to decrease coverage so as to reduce cost and enhance performance.^{19–21} In this regime, the catalytic activity seems to persist even when the particle contains as few as one to ten atoms depending on the metal investigated.^{19–21} A useful experimental method for analyzing such small nonmetallic particles is by depositing size selected metal clusters on the oxide support, a technique pioneered by Heiz and co-workers.²² This method has been extended to the Au-TiO₂ system by Anderson and co-workers^{21,23,24} and by Tong *et al.*,²⁵ which showed the Au clusters to exhibit strong size-dependent catalytic properties.^{21,23,24} The main focus towards the underlying mechanisms in this regime is on the undercoordination in the cluster,²⁶ nature of the defects,^{6,27,28} cluster charge,^{15,27,29} cluster fluxionality,³⁰ and role played by the support.⁷

The present computational study is concerned with the analysis of the experiments performed in the third regime. Previous computational studies have focused on establishing the role of defects and cluster charge,²⁰ nonmetallic to metallic transition of the cluster,³¹ cluster fluxionality³⁰ and undercoordination,^{6,7} support effects,³² and presence of more than one channel for the reaction.³² As the Au particle size is the smallest in this regime making it very fluxional, it is most likely that more than one mechanism may play a role in catalysis. Moreover, due to the small particle size, the dis-

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tinction between active site arising due to fluxionality, Au/oxide interface, and cluster undercoordination/steps is harder to make. Here, we investigate two aspects of experiments performed using size selected Au clusters containing seven Au atoms that show the highest catalytic activity for CO₂ oxidation reaction, among the clusters deposited.^{21,23,24} In contrast to the previous experiments which used atomic oxygen,³³ these experiments used molecular oxygen and yet observed the formation of CO₂. These experimental studies suggest that the source of all the oxygen contributing to the formation of CO₂ originates from a form of reactive oxygen associated with the Au clusters after the molecular oxygen exposure.^{21,23,24} Furthermore, the nature of different modes of activated oxygen is of general interest in Au catalysis.³⁴ Therefore, as the first objective, we explore a possible candidate for the reactive form of oxygen indicated by these new experiments.^{21,24} Another intriguing feature of the experimental results is that the active Au clusters show a 300 ms delay in CO₂ evolution.^{21,24} Different factors that may contribute towards such a delay have been previously hypothesized.²⁴ Here, as the second objective, we investigate computationally the possible origin behind the slow product evolution kinetics observed in these experiments.^{21,24}

The present study suggests that there exists a thermodynamically favorable diffusion-reaction path for O₂ to approach the seven-atom Au cluster (Au₇) along the surface Ti row leading to a dissociated state of oxygen. The O₂ so dissociated has one oxygen atom in between the cluster and surface, bonding simultaneously to one Au atom in the cluster and one surface Ti atom, and the other oxygen atom above the cluster, bonding to the same Au atom in the cluster. As the dissociated O₂ is anchored to the cluster, CO can approach the O₂-cluster complex along the same surface Ti row, leading to a thermodynamically favorable reaction path for CO₂ formation. The present results may have wider applicability in the context of interpreting other experiments that also observe formation of CO₂ via oxidized Au intermediate even when molecular oxygen is employed.³⁵ Moreover, the CO₂ so formed is found to have a binding affinity of 0.73 eV to the Au cluster, which may be responsible for the experimentally observed 300 ms delay in CO₂ evolution.

II. COMPUTATIONAL METHODOLOGY AND ATOMISTIC MODEL OF THE SYSTEM

The calculations are performed using the pseudopotential³⁶ plane-wave total energy method,³⁷ as being commonly used for surface adsorption and surface cluster calculations. All atoms were allowed to relax in all the calculations. Exchange-correlation energy was calculated using the PW-91 generalized gradient approximation (GGA) functional.³⁸ The relaxation of electronic degrees of freedom was converged to within 10⁻⁴ eV per supercell and the ionic positions were optimized with the energy-convergence criterion of 10⁻³ eV of the total energy of the system. Test calculations carried out using Perdew-Burke-Ernzerhof (PBE) functional³⁹ did not affect the general conclusions. Spin polarization effects were also tested and did not contribute appreciably to total energies. Results for the bulk and smaller

surface unit cells were benchmarked with a previous study.⁴⁰ The bulk lattice parameters obtained in the present study is $a=4.649 \text{ \AA}$ with $c/a=0.64$, in good agreement with those obtained in previous experimental and computational studies.^{40,41} The formation enthalpy obtained in the present study is -10.29 eV, which is in reasonable agreement with the experimental value of -9.78 eV.⁴²

The characteristic structural features of the TiO₂ (110) surface are the “bridging” oxygen atoms that are twofold coordinated to the titanium atoms. There are two types of surface titanium atoms—fivefold coordinated (5-c) and six-fold coordinated (6-c). The twofold coordinated bridging oxygen atoms and the 5-c Ti atoms are more undercoordinated than other surface atoms and hence are the common reactive sites in the TiO₂ (110) surface.⁴³ Single point defects are easily created on the surface by the removal of bridging oxygen atoms, where the Au cluster prefer to nucleate.⁴⁴ The TiO₂ (110) surface with a single point oxygen defect was represented using a 2×4 supercell and by a three-layer slab containing a total of 48 Ti atoms and 95 oxygen atoms stacked together parallel to the [1̄10] plane and separated by a vacuum layer of 16.5 Å in between slabs. The supercell was sampled with a 2×2×1 special point mesh generated in the K space using Monkhorst-Pack technique,³⁷ and a plane-wave basis set with a cutoff of 420 eV was used for expansion of the wave function.

We chose a seven-atom Au (Au₇) cluster as it has been observed to exhibit the highest activity for CO oxidation in the experiment.^{21,24} The cluster is placed above a missing bridging oxygen point defect as the defect sites has been implicated to be the nucleation centers for Au clusters⁴⁴ and also because of the importance of single point defects in catalytic activity.^{20,32} The clusters used in the mass selected cluster deposition experiments^{20,21,45} are smaller than the clusters used in the metal vapor deposition experiments.^{1,3,11} These relatively small clusters may be anticipated to be susceptible to structural changes in response to adsorption of reactants, and such a dynamical fluxionality of cluster has been shown to be important for catalytic activity.³⁰ But it remains largely unknown *a priori* what form of structure of the cluster would be most *catalytically* active. Computationally, it is also too demanding to exhaust all the possible structures and their associated catalytic activities for the Au₇ cluster on the TiO₂ surface. (Note that it is not necessarily true that the cluster of minimum-energy structure will have the highest reactivity.) Thus, we have opted to limit our investigations to a starting Au₇ cluster with a planar geometry, which was subsequently optimized before and after the molecular adsorption. This choice was partly made because the planar Au cluster was shown to have high stability in the gas phase.⁴⁶ Upon adsorption/reaction, the cluster was found to transform into a buckled structure. We note that the results we have so obtained will provide one particular form of reactive Au₇ cluster, without excluding other possible reactive cluster structures. The underlying mechanism we reveal from this particular choice may or may not be generally applicable to other cluster sizes and structures.

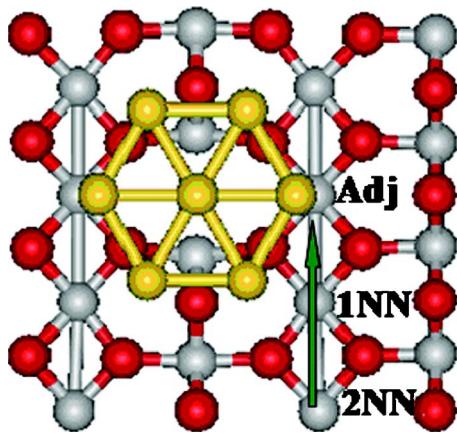


FIG. 1. (Top view) Diffusion-reaction path for reactants O₂ and CO along the surface 5-c Ti row of atoms. Adj, 1NN, and 2NN denote the Ti atoms over which geometry optimization were performed.

III. RESULTS AND DISCUSSION

In experiments,^{21,24} the TiO₂ supported Au₇ clusters are first dosed with excess of molecular oxygen and a part of O₂ is associated with the Au cluster. It is implicated that all the oxygen contributing to CO₂ formation originates from those associated with the Au cluster.²⁴ Hence, our first objective is to identify a potential candidate for the reactive form of the oxygen associated with the Au cluster. Energy minimizations were performed for a surface diffusion-reaction path along the row of 5-c Ti atoms, as indicated by an arrow in Fig. 1. This path is structurally less corrugated and is expected to be the diffusion path with the least barrier.⁴⁷ A set of O₂ structures was optimized by placing O₂ perpendicular to the surface on top/around three Ti atoms (2NN, 1NN, and Adj) along the path next to the Au₇ cluster, as indicated in Fig. 1. As the O₂ approaches the Au₇ cluster, the structure of cluster was also optimized simultaneously along with all other atoms. However, because these calculations are computationally very intensive, we obtained only a restricted phase space for O₂ diffusion (i.e., involving only three positions: 2NN, 1NN, and Adj), without mapping all the energy barriers and transition states along the diffusion path. Among many different geometries tested, the optimized structures with their corresponding energies at three positions are shown in Fig. 2. The energies are reported in reference to O₂ binding to a clean surface (which is ~0.23 eV relative to vacuum) as we are considering the driving force of O₂ diffusing towards the Au₇ cluster. Since the energy decreases considerably as the O₂ approaches the cluster (Fig. 2), it indicates an effective attractive interaction between the O₂ molecule and the Au₇ cluster. Most importantly, at the Adj position, the lowest en-

ergy structure of O₂ is found in a dissociated form. It has one oxygen atom above the cluster bonding to a Au atom and the other oxygen atom in between the cluster bonding simultaneously to a Au atom in the cluster and a surface 5-c Ti atom (Fig. 2, right panel). Thus, these structural intermediates in Fig. 2 would represent local minima in the potential energy surface for the entire diffusion-reaction channel of O₂ diffusing towards the Au₇ cluster and dissociatively adsorbing with one O atom in between the cluster and the TiO₂ surface. Although we have not computed barriers for this reaction-diffusion channel (which is a challenging problem requiring a more detailed study), the present calculations indicate that there exists a strong thermodynamic driving force for this process to take place. The O₂ driven to the cluster may then provide a source for activated oxygen reactants. The strong binding affinity of O₂ to the cluster may also lead to greater residence time for the active oxygen in the system and such a scenario has been observed in experiments.⁹

To qualitatively understand the dissociation of O₂ in terms of bonding energies, we performed a set of calculations with reactants and Au₇ cluster without the oxide support, but using the same atomic positions as obtained above on the oxide supported. We found that without oxide support, Au₇ cluster alone cannot dissociate O₂ molecule, the energy is higher by 1.34 eV in the dissociated state than in the undissociated state due to the large O₂ binding energy of 5.93 eV. This indicates that the oxide support plays a critical role in dissociating O₂ at the Adj position to the Au₇ cluster. The large binding energy of 8.14 eV for the dissociated O₂ to the Au₇ cluster on the oxide surface comes partly from two additional bond interactions as compared to the bare cluster: the O atom below the cluster bonding with a 5-c surface Ti atom (~1.7 eV as estimated from the formation enthalpy of TiO₂) and a Au atom bonding with a 5-c surface Ti atom on the other side of the cluster [see Fig. 2 right panel, ~1.4 eV as obtained from Au surface adsorption energy on TiO₂ (Ref. 48)]. However, we caution that the absolute value of the large binding energy of 8.37 we obtain here has contributions from bonding changes occurring in the slab and also possible overestimation by density functional theory. One correction that can be possible is to use a much thicker slab, which is unfortunately impractical at present due to limited computational resources. Nevertheless, we expect that the main conclusion of the existence of thermodynamic driving force for O₂ dissociation by TiO₂ supported Au₇ cluster will not be qualitatively affected by these possible sources of errors.

In experiments,^{21,24} the excess O₂ is purged and then is followed by pulse of CO. To simulate such a scenario, with the O₂ dissociated on the Au₇ cluster in the Adj position, as shown in Fig. 2 (right panel), CO is introduced along the 5-c Ti row of atoms. Far away from the cluster, CO binds to the surface Ti atoms predominantly via the C atom. As CO diffuses towards the cluster, it can bind to two possible under-coordinated binding sites: surface Ti atom and/or the edge sites of Au₇ cluster (Fig. 3). The tilted geometry of CO observed in the central panel of Fig. 3 (1NN position) is a result of C shifting from binding predominantly to the surface Ti atom to that of binding predominantly to the edge atom of the Au₇ cluster. We find that this diffusion-reaction path for

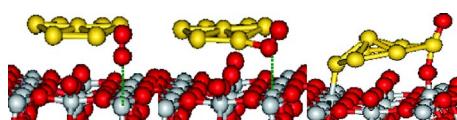


FIG. 2. (Side view) Structure (energy in eV with respect to O₂ adsorbed on a clean surface) of O₂ diffusing towards and reacting with the Au₇ cluster. Green lines mark the coordination of the O₂ to 5-c Ti. In leftmost structure (0.1), middle structure (1.27), and rightmost structure (8.37), the reactant is binding to 5-c Ti atom denoted as Adj, 2Au, and 3Au in Fig. 1, respectively.

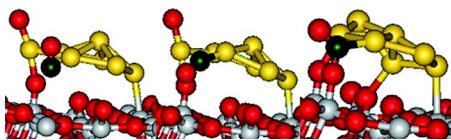


FIG. 3. (Perspective view) The structure (energy in eV with respect to CO adsorbed on a clean surface) of O_2 dissociated on the cluster as CO approaches the cluster to form CO_2 . Left figure (0.05) and middle figure (2.24) denotes CO in 2NN and 1NN positions, respectively. The right (6.19) figure denotes the final structure after CO_2 has been formed.

CO is also energetically downhill (energies are in reference to the CO adsorption energy on a clean TiO_2 which is 0.27 eV relative to vacuum).

The adsorption energies of CO binding to the clean surface via C (as discussed above) versus O are 0.27 and ~ 0 eV, respectively. Hence, far away from the clusters, the possibility of CO binding to surface via O is negligible. However, as the CO with C binding to the surface 5-c Ti diffuses towards the vicinity of the cluster, the C moves up to bind with Au while O flips down below the C, as shown in the central panel of Fig. 3. Finally, CO_2 forms by C forming another bond with the O in the dissociated oxygen anchored above the cluster, and in the meantime the flipped-down O in the CO forming a bond with surface Ti, as shown in the central panel of Fig. 3. We have also performed additional calculations to enforce a CO, with O binding to surface Ti, to diffuse towards the cluster. The energy is also found downhill, eventually leading to the same final stable structures in the vicinity of the cluster, but this pathway has a higher energy state *a priori* to the reaction.

Thus, our calculated dissociated state of O_2 , as shown in Fig. 2 (right panel), provides a potential candidate for the reactive form of O_2 molecule implicated in the experiments. It is interesting to consider these results in the context of experiments that deposit neutral Au atoms onto multilayer of molecular oxygen, which lead to the formation of oxidized Au intermediate and further production of CO_2 at temperatures as low as 35 K.³⁵ The spectroscopic signature of dissociated molecular O_2 at the Adj position might be similar to the oxidized Au observed in these experiments.

Another interesting experimental observation is that CO_2 evolves only after ~ 300 ms of the CO pulse. So, our second objective is to shed some light on the possible cause for such slow kinetics of reaction product CO_2 evolution. Two hypotheses were suggested,²⁴ which are partially assessed by our calculations. First, the slow kinetics could be caused by the existence of high-energy barriers for the reactants to approach the cluster. However, the restricted energy landscape for both O_2 and CO as calculated does not provide evidence for such a scenario. Second, the slow kinetics could result from a larger binding affinity of the product, i.e., CO_2 to the cluster or surface. Indeed, this seems to be consistent with our calculations, which show the binding energy of the CO_2 as formed above in Fig. 3 (right panel) is 0.73 eV lower than that of a CO_2 in the clean surface. This makes it relatively difficult for the CO_2 to dissociate from the cluster and diffuse away from the cluster before eventual desorption from the surface. The observed 300 ms delay of product evolution corresponds to a barrier of ~ 0.8 eV. The calculated binding

energy of 0.73 eV seemed to agree surprisingly well with the measured barrier of 0.8 eV, but we must caution that such a quantitative agreement might not be as reliable considering the known error in binding energy calculated by density functional method. Nevertheless, more importantly, the calculation provides at least qualitatively a possible explanation for the observed slow kinetics of CO_2 removal from the catalytically active site.

The relatively high binding energy of CO_2 can be rationalized by the binding geometry of CO_2 to the Au_7 cluster and the surface simultaneously. The CO_2 forms two bonds, one to the surface via the O atom and a second bond between the C atom and the undercoordinated Au atom at the Au_7 cluster edge. An interesting question is if this particular mode of binding of CO_2 results from the specific diffusion-reaction pathway that we have revealed here on TiO_2 surface and may not be generally available when CO_2 is absorbed on to a Au_7 cluster. In such a scenario, there might be different binding affinities of CO_2 than what we found here, and the possible conversion among different CO_2 adsorption states will be an interesting subject of study. Furthermore, it is also important to note that the present calculation suggests only a thermodynamic driving force for O_2 diffusion and CO_2 formation but it does not address the nature of activation barriers that may be present in such a process. Such a study to obtain the kinetic barrier will be computationally more formidable due to the large system size and the complex nature of transition states for diffusion-reaction pathway.

IV. CONCLUSIONS

Using a model Au_7 cluster, we demonstrate a potential pathway for diffusion-dissociation of O_2 along a row of surface Ti atoms towards the cluster. This form of oxygen may be a candidate for the reactive form of oxygen observed in experiments. Our computational results suggest that there exist a thermodynamic driving force for CO to approach along the Ti row of atoms to react with the dissociated O_2 to form CO_2 . Furthermore, a relatively high binding energy of CO_2 to the Au_7 cluster may provide a possible explanation for the observed slow kinetics of reaction product (CO_2) evolution. We believe that the two mechanistic findings from our computational studies of the Au_7 cluster may have some general implications in the catalytic activity of Au clusters on oxide surfaces.

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