

Insights into Catalytic Oxidation at the Au/TiO₂ Dual Perimeter Sites

ISABEL X. GREEN,[†] WENJIE TANG,[‡] MATTHEW NEUROCK,^{‡,§}
AND JOHN T. YATES JR.^{*,‡,§}

[†]Department of Chemistry, University of Washington, Seattle, Washington 98104, United States, [‡]Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia 22904, United States, and [§]Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States

RECEIVED ON AUGUST 12, 2013

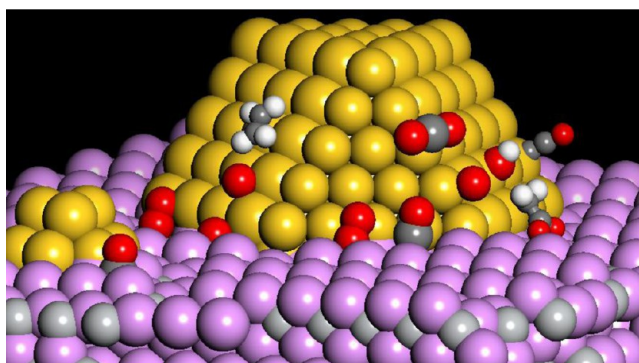
CONSPECTUS

Gold (Au) nanoparticles supported on reducible oxides such as TiO₂ demonstrate exceptional catalytic activity for a wide range of gas phase oxidation reactions such as CO oxidation, olefin epoxidation, and water gas shift catalysis. Scientists have recently shifted their hypotheses on the origin of the reactivity of these materials from the unique electronic properties and under-coordinated Au sites on nanometer-sized particles to bifunctional sites at the Au–support interface.

In this Account, we summarize our recent experimental and theoretical results to provide insights into the active sites and pathways that control oxidation over Au/TiO₂ catalysts. We provide transmission IR spectroscopic data that show the direct involvement of the Au–Ti⁴⁺ dual perimeter sites, and density functional theory results that connect the electronic properties at these sites to their reactivity and to plausible reaction mechanisms. We also show the importance of interfacial Au–Ti⁴⁺ sites in adsorbing and activating O₂ as a result of charge transfer from the Au into antibonding states on O₂ causing di-σ interactions with interfacial Au–Ti⁴⁺ sites. This results in apparent activation energies for O₂ activation of 0.16–0.60 eV thus allowing these materials to operate over a wide range of temperatures (110–420 K) and offering the ability also to control H–H, C–H, and C–O bond scission. At low temperatures (100–130 K), adsorbed O₂ directly reacts with co-adsorbed CO or H₂.

In addition, we observe the specific consumption of CO adsorbed on TiO₂. The more strongly held CO/Au species do not react at ~120 K due to high diffusion barriers that prevent them from reaching active interfacial sites. At higher temperatures, O₂ directly dissociates to form active oxygen adatoms (O*) on Au and TiO₂. These readily react with bound hydrocarbon intermediates via base-catalyzed nucleophilic attack on unsaturated C=O and C=C bonds or via activation of weakly acidic C–H or O–H bonds. We demonstrate that when the active Au–Ti⁴⁺ sites are pre-occupied by O*, the low temperature CO oxidation rate is reduced by a factor 22. We observe similar site blocking for H₂ oxidation by O₂, where the reaction at 210 K is quenched by ice formation. At higher temperatures (400–420 K), the O* generated at the perimeter sites is able to diffuse onto the Au particles, which then activate weakly acidic C–H bonds and assist in C–O bond scission. These sites allow for active conversion of adsorbed acetate intermediates on TiO₂ (CH₃COO/TiO₂) to a gold ketenylidene species (Au₂=C=C=O).

The consecutive C–H bond scission steps appear to proceed by the reaction with basic O* or OH* on the Au sites and C–O bond activation occurs at the Au–Ti⁴⁺ dual perimeter sites. There is a bound-intermediate transfer from the TiO₂ support to the Au sites during the course of reaction as the reactant (CH₃COO/TiO₂) and the product (Au₂=C=C=O) are bound to different sites. We demonstrate that IR spectroscopy is a powerful tool to follow surface catalytic reactions and provide kinetic information, while theory provides atomic scale insights into the mechanisms and the active sites that control catalytic oxidation.



1. Introduction

The stark contrast between the exceptional catalytic activity of nanometer Au particles supported on reducible metal

oxides such as TiO₂ and the inactivity of bulk Au has been the subject of considerable debate since its initial discovery 26 years ago by Haruta et al.^{1–4} By coupling IR

spectroscopy, kinetic studies, and theoretical calculations, we have been able to provide direct insights into the reactive intermediates and their specific sites at the interface, determine reaction pathways, and establish plausible reaction mechanisms. We focus herein on mechanisms for gas phase oxidation of different molecules over Au/TiO₂ to provide a framework for understanding different selective oxidation processes.

To locate the catalytic active sites on the Au/TiO₂ catalyst, we employed transmission IR spectroscopy, which provides real time information on the surface species evolution during catalytic reactions.^{5–7} Au nanoparticles with ~3 nm diameter supported on nanocrystalline TiO₂ powder^{8,9} were synthesized.^{10,11} By carefully selecting the reactions and experimental conditions, we were able to pinpoint the active sites for several catalytic oxidation reactions. The time-dependent spectroscopic measurements along with the information about the active intermediates and their specific adsorption sites at the Au/TiO₂ interface were used to guide the theoretical calculations. Detailed theoretical and experimental results were subsequently used to determine the reaction pathways that govern the selective oxidation of CO,^{12,13} H₂,¹⁴ acetate,¹⁵ and ethylene.¹⁶ The results indicate that molecular oxygen strongly binds to and is activated at the Au–Ti⁴⁺ dual perimeter sites of the Au/TiO₂ catalyst. At low temperatures, O₂ reacts directly with adsorbed molecules such as CO and H₂. At higher temperatures, O₂ dissociates to form active O* intermediates that diffuse along the support as well as onto and over the Au surface. These species are rather basic and act as nucleophiles that attack C=C or C=O substrate bonds or as Brønsted bases that activate O–H and C–H bonds. The basic properties of oxygen on Au surfaces have been subsequently used to describe a range of reactions carried out over bulk Au.^{17–19}

2. Adsorption and Activation of Oxygen

Important for all oxidation reactions over supported Au is the nature of the active sites for the adsorption of the oxidant, as well as the mechanism of activation. Nanometer Au particles on TiO₂ readily activate O₂ producing reactions with CO and other reactants even at cryogenic temperatures.^{13,14} The 3 nm experimental Au/TiO₂ clusters were modeled using a periodic three atom high and three atom wide Au nanorod on a rutile TiO₂(110) surface (Figure 1).²⁰ This model provides a reliable sampling of Au sites with different coordination numbers (CN) as well as the critical Au–O–Ti⁴⁺ interactions which couple the Au particles

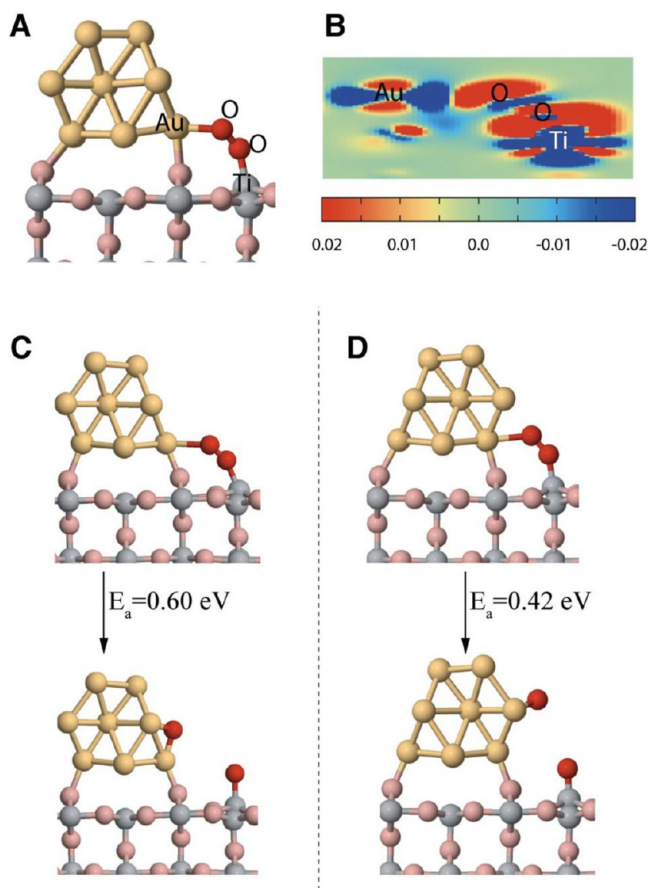


FIGURE 1. (A) The adsorption and activation of O₂ at the Au/TiO₂ catalyst results in di- σ bonding with Ti–Au dual sites. (B) Detailed charge analysis shows the charge transferred from Au to Ti is back-donated into $2\pi^*$ antibonding states of O₂. (C,D) The barriers for the activation at the Au–Ti⁴⁺ site. The model Au/TiO₂ catalyst herein is a Au nanorod structure on top of the TiO₂(110) surface. Adapted from refs 12 and 13.

to the support.^{12–16,21} The results from this Au model are consistent with those obtained on other types of models.^{20,22–25}

Oxygen can adsorb onto Au, onto the TiO₂ support, or at the Au/TiO₂ interface. DFT results indicate that O₂ does not strongly adsorb to terrace sites on TiO₂(110) since the binding energy is negligible, consistent with reported experimental results.²⁶ While O₂ can adsorb on Au, its binding is rather weak with adsorption energies of –0.16 to –0.51 eV depending upon the coordination number of the Au atoms involved. These values are significantly weaker than the adsorption energy of O₂ at the Au–Ti⁴⁺ dual perimeter, –1.01 eV (Figure 1).^{12,13,15} O₂ is stabilized at the Au–Ti⁴⁺ site via di- σ bonding, forming a Au–O–O–Ti intermediate. Theory clearly shows that there is direct electron transfer from Au to the Ti and subsequent charge transfer from the Ti into the $2\pi^*$ antibonding state of O₂, weakening the O–O bond (Figure 1B). This back-donation of electron density causes O₂ adsorption at the interfacial Ti⁴⁺ site and aids in

its activation, consistent with previous reports.^{20,22} The Au–O–O–Ti intermediate shown in Figure 1 is the active species in the anhydrous low temperature oxidation of CO, which occurs with a barrier of only 0.16 eV.^{12,13}

The Au–O–O–Ti intermediate is also very similar in character to the Au-peroxy (Au–OOH) species that forms at the ppm-level of water and rapidly oxidizes CO.²⁷ Both Ti and H donate charge (0.81 e[−] for Ti and 1 e[−] for H) into the 2π* state of O₂ and become ~Ti⁴⁺ and H⁺, respectively. This charge transfer increases the Au–OOH or Au–OOTi bonding and aids in O₂ activation. A detailed analysis of bond lengths for AuOOH (Au–O = 2.17 Å and O–O = 1.49 Å) and AuOOTi (Au–O = 2.24 Å and O–O = 1.44 Å) suggests that these intermediates are quite similar. The AuOOH and AuOOTi intermediates also show similar O–O stretching frequencies ($\nu_{\text{O–O}}(\text{AuOOH}) = 961 \text{ cm}^{-1}$ and $\nu_{\text{O–O}}(\text{AuOOTi}) = 874 \text{ cm}^{-1}$).

The high reactivity of AuOOH together with the strong similarities between AuOOH and AuOOTi indicate that the O–O bond of the AuOOTi complex can be activated at low temperatures, consistent with the observed activation barrier of 0.16 eV for the reaction with bound CO or by direct O₂ scission in the absence of a neighbor CO molecule at higher temperatures with activation barriers of 0.42–0.60 eV (depending on the CN of the Au).

Water is also a common oxidant often used to oxidize CO in the water gas shift reaction and aid in the CO oxidation with O₂.²⁸ Water is activated in a very similar manner to that of O₂ at the Au/TiO₂ interface. DFT calculations indicate that the adsorption of water at the interfacial Ti⁴⁺ site ($\Delta E_{\text{ads}} = -1.02 \text{ eV}$) is 0.22 and 0.80 eV stronger than that for the adsorption of water on Au or TiO₂ alone.²⁹ There is electron transfer from Au to the interfacial Ti⁴⁺ and subsequent transfer from Ti⁴⁺ into an antibonding σ^* O–H bond, which increases the adsorption energy of water and aids in O–H bond activation.

3. CO Oxidation

CO oxidation by O₂ over Au/TiO₂ occurs over a wide range of temperatures and involves different sites. From 2143 cm^{−1} for CO(g), the $\nu(\text{CO})$ blue shifts to ~2179 cm^{−1} when adsorbed on Ti⁴⁺ cationic sites (denoted later on as CO/Ti⁴⁺), red shifts to ~2106 cm^{−1} when adsorbed on Au⁰ sites (CO/Au⁰ or CO/Au), and red shifts to ~2126 cm^{−1} when adsorbed on Au^{δ+} (0 < δ < 1) cationic sites (CO/Au^{δ+}).^{12,13} It is also reported that the $\nu(\text{CO})$ for CO/Au³⁺ is ~2207 cm^{−130} and that for CO/Au^{δ−} is in the range of 2038–1900 cm^{−1}.³¹ These shifts lead to absorption bands more than 20 cm^{−1} apart and permit site identification and assignment of Au

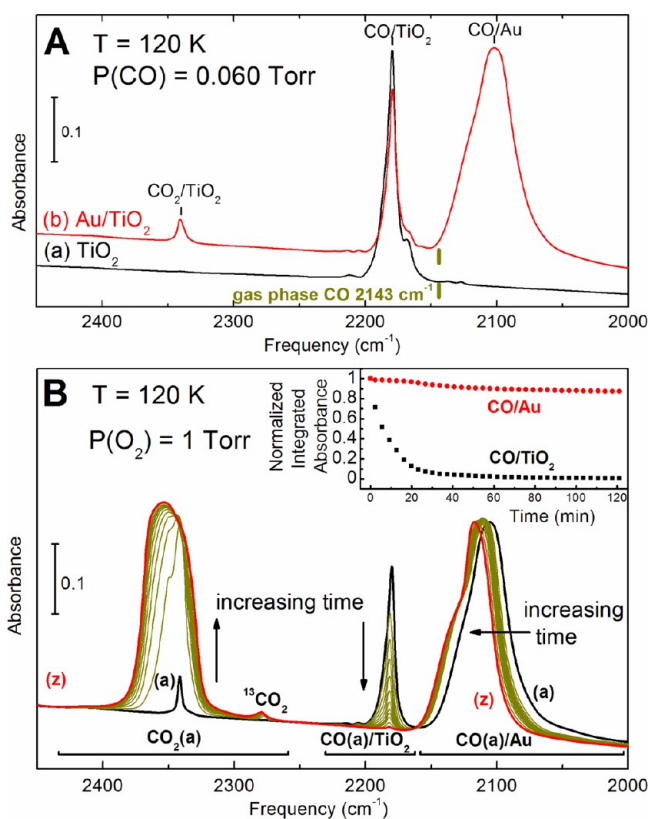


FIGURE 2. (A) IR spectra of saturated CO layer on (a) TiO₂ and (b) Au/TiO₂. (B) IR spectral development during the CO oxidation reaction on Au/TiO₂ from (a) before O₂ introduction to (z) after 120 min of reaction. Inset, plots of normalized integrated absorbance of CO/Au and CO/Ti⁴⁺ against time during the experiment. Adapted from ref 13.

gold charge states. In order to simplify the reaction mechanism and lowest energy pathways, we studied the CO oxidation reaction in the low temperature regime (110–130 K). It is important to note that while these studies provide direct molecular insights into the important O₂ bond scission and CO oxidation steps, the paths operating at the higher temperatures may be different.

The IR cell can mount two samples under the same experimental conditions allowing direct comparison.³² Figure 2A shows IR spectra for both the Au/TiO₂ surface and the TiO₂ blank surface saturated with adsorbed CO at 120 K. The CO/Ti⁴⁺ peak and the CO/Au peak are clearly distinguishable. A small CO₂/TiO₂ band is observed on the Au/TiO₂ but not on TiO₂. This band is due to the reaction of CO with traces of residual O₂ in the high-vacuum cell on Au/TiO₂. To investigate the surface species only, we evacuated the gas phase CO from the cell (leaving strongly bound CO and CO₂ species behind at 120 K) and introduced 1 Torr of O₂. Figure 2B shows the IR spectral evolution during 120 min: CO oxidation began immediately on the Au/TiO₂

surface, as indicated by the gradual disappearance of the CO/Ti⁴⁺ band and the growth of the CO₂/TiO₂ feature. At the same time, the CO/Au species is essentially unchanged indicating little participation in the reaction. The CO oxidation reaction is not detected on the blank TiO₂ sample. The difference in kinetics between CO/Ti⁴⁺ and CO/Au is shown in the inset of Figure 2B, where the normalized integrated absorbance for each CO species is plotted against reaction time. The main reactant is the CO/Ti⁴⁺ species, which is consumed within the first 40 min of the experiment, while only ~12% loss of the CO/Au species is observed over 120 min.

The kinetic discrimination between CO/Ti⁴⁺ and CO/Au is intriguing, especially when the CO/Ti⁴⁺ species do not react on the blank TiO₂ sample. It suggests that the CO oxidation reaction on the Au/TiO₂ catalyst is site specific and that the active region involves the Au nanoparticle as well as the TiO₂ support. The mobility of chemisorbed CO on Au and Ti⁴⁺ sites was examined by watching the disappearance rate of the two species when exposed to vacuum at elevated temperatures (140–160 K).^{5–7} The results showed that the CO/Ti⁴⁺ is more mobile than CO/Au at all temperatures examined. A Au/TiO₂ catalyst surface with only CO/Au species was created by thermally removing all the CO/Ti⁴⁺ species at 215 K. No reaction occurred upon exposing this CO/Au-only surface to 1 Torr of O₂ at 120 K.¹³ Thus, the nonreactivity of CO/Au species originates from the lack of mobility, preventing it from reaching the catalytic active zone located at the Au–Ti⁴⁺ dual perimeter sites.

CO oxidation experiments were carried out at different temperatures. The CO/Ti⁴⁺ species was found to be the main reactant, as shown in Figure 3A. The solid lines underneath the data points are the best first-order fits to the data indicating that the reaction is first-order in CO/Ti⁴⁺ coverage. The Arrhenius plot in Figure 3A is shown in black in Figure 3B; an apparent activation energy of 0.16 ± 0.01 eV is measured.

We have previously reported IR detection of weakly bound O₂ on TiO₂ at the exact Raman frequency of gas phase O₂, 1550 cm⁻¹.³³ However, a search for IR evidence of the activated O₂ species on Au/TiO₂ was inconclusive, since the only species detected was the unshifted weakly bound O₂. It is difficult to extract by IR how the Au–Ti⁴⁺ dual perimeter sites carry out the oxidation reaction. Theory provides insights into the most probable sites for adsorption and possible reaction paths and corresponding activation energies to compare with experiment.

The DFT results presented in section 2 indicate that direct dissociation of the O–O bond at the Au–Ti⁴⁺ dual perimeter

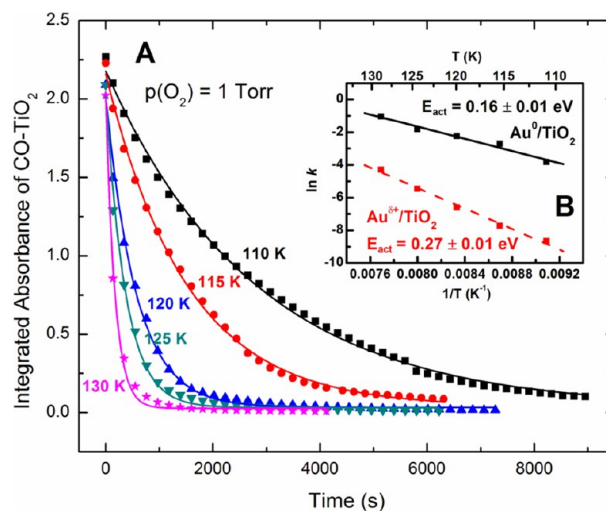


FIGURE 3. (A) Plots of the integrated absorbance of CO/Ti⁴⁺ against time at various temperatures fit to first-order kinetics. (B) Arrhenius plots for CO oxidation on the Au⁰/TiO₂ catalyst (red) and Au^{δ+}/TiO₂ catalyst (black). Adapted from ref 13.

sites can only proceed at temperatures above 215 K because the activation barriers are 0.42–0.60 eV depending upon the Au CN (Figure 1).¹² At low temperatures, O₂ instead reacts with CO bound to either perimeter Au or Ti⁴⁺ sites. CO does not bind to the Au terrace sites. While CO readily adsorbs onto the coordinatively unsaturated Au sites (–0.7 to –0.9 eV), it is too strongly held to the surface and does not react at the low temperatures (110–130 K) examined here. CO exhibits an adsorption energy of 0.4 eV on Ti sites and hence exhibits more rapid diffusion than that of Au. The only viable oxidation path at these low temperatures is via CO bound to surface Ti⁴⁺ sites, which exhibits a barrier of only 0.16 eV to react with O₂ at the Au–Ti⁴⁺ site. CO is continuously supplied to the interfacial Ti⁴⁺ sites via CO diffusion from different Ti sites with calculated diffusion barriers of 0.26 eV. CO oxidation thus proceeds by the formation of a CO–O₂ complex at the Au–Ti⁴⁺ site that readily dissociates to form CO₂ and atomic oxygen with a barrier of only 0.16 eV.

The DFT-calculated CO oxidation cycle shown in Figure 4 has activation barriers that range between 0.10 and 0.26 eV, well in line with the experimentally measured apparent activation energy of 0.16 eV. It is therefore difficult to establish a single rate-determining step among them because the barrier differences are small (~0.1 eV). However, the discrimination toward CO/Ti⁴⁺ species over CO/Au species suggests that the diffusion of CO over TiO₂ is an important step at very low temperatures.

We noted that at elevated temperatures ($T \geq 295$ K), the Au nanoparticles can oxidize in O₂ to make Au^{δ+} sites.¹²

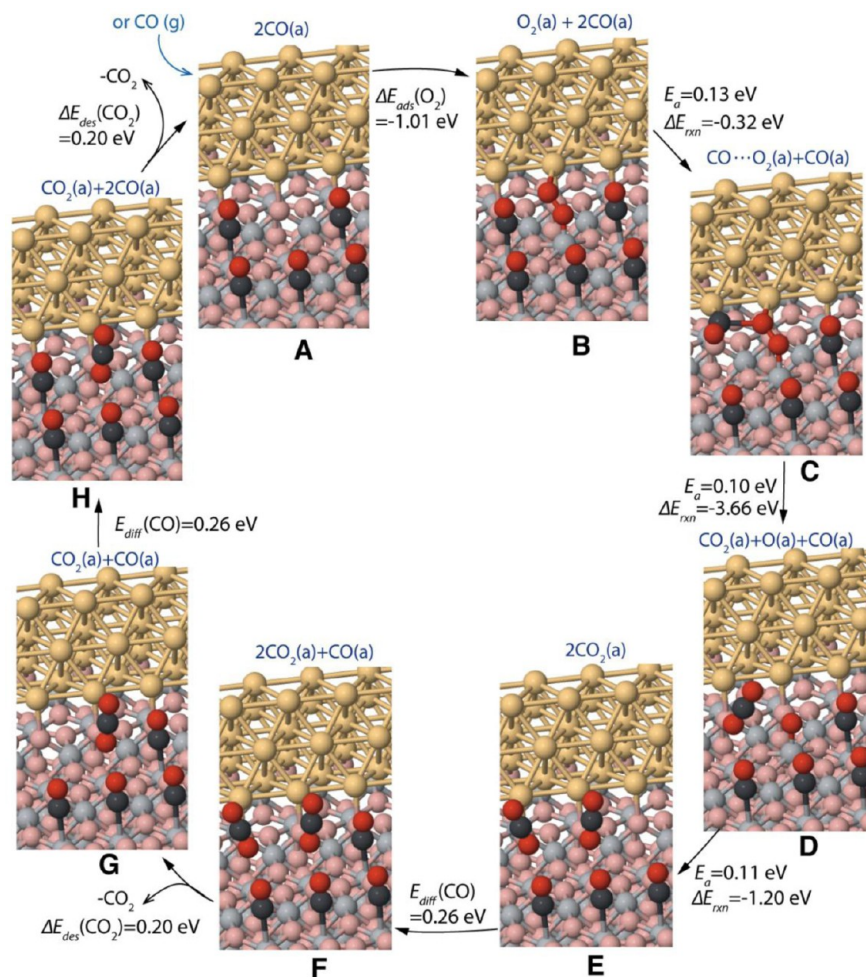


FIGURE 4. DFT-calculated cycle for the oxidation of CO at the Au–Ti⁴⁺ interface. Elementary steps include (A–B) O₂ adsorption, (B–C) O₂ and CO interaction; (C–D) CO* + O₂* reaction; (D–E) O* + CO* reaction; (E–F and G–H) diffusion of CO; (F–G and H–A) desorption of CO₂. ΔE_{ads} , E_a , E_{diff} , ΔE_{des} , and ΔE_{rxn} refer to the binding energy, activation barrier, diffusion barrier, desorption energy, and reaction enthalpy, respectively. Adapted ref 13.

Au oxidation is consistent with the moderate DFT-calculated barriers of 0.42–0.6 eV for the direct activation of O₂ reported. These preoxidized Au^{δ+} sites can be easily identified using IR measurements of $\nu(\text{CO})$. Au^{δ+} can be reduced back to Au⁰ by heating in CO. Figure 5 depicts the conversion of CO/Au^{δ+} to CO/Au⁰ as a function of increasing reduction temperature in CO. The frequency shift of CO was also directly captured by DFT calculations using the Au nanorod model by adding O adatoms next to the adsorbed CO species.¹²

We carried out low temperature CO oxidation reactions on this preoxidized Au^{δ+}/TiO₂ catalyst. Surprisingly, the reaction rate was diminished by a factor of 22 compared with the Au⁰/TiO₂ catalyst. The Arrhenius plot for CO oxidation over the Au^{δ+}/TiO₂ catalyst is shown in Figure 3B, where the apparent activation energy is measured to be 0.27 ± 0.01 eV (red). DFT simulations revealed that the

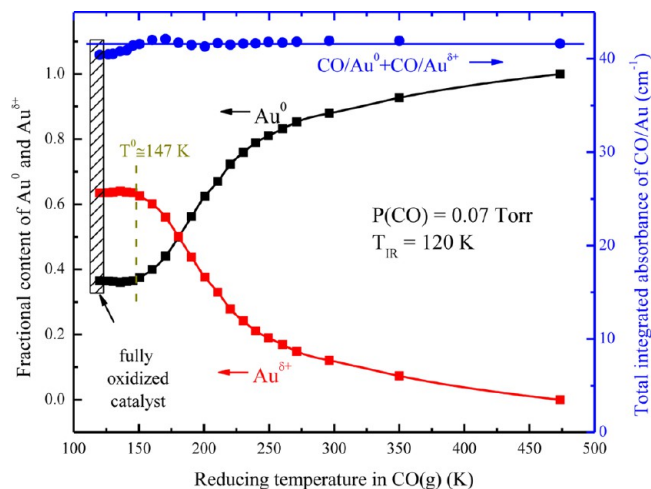


FIGURE 5. Plots of the total integrated absorbance of CO on Au species (right axis) and the CO/Au^{δ+} fractional conversion to CO/Au⁰ species (left axis) against catalyst reduction temperature in CO. Reprinted ref 12. Copyright 2012 American Chemical Society.

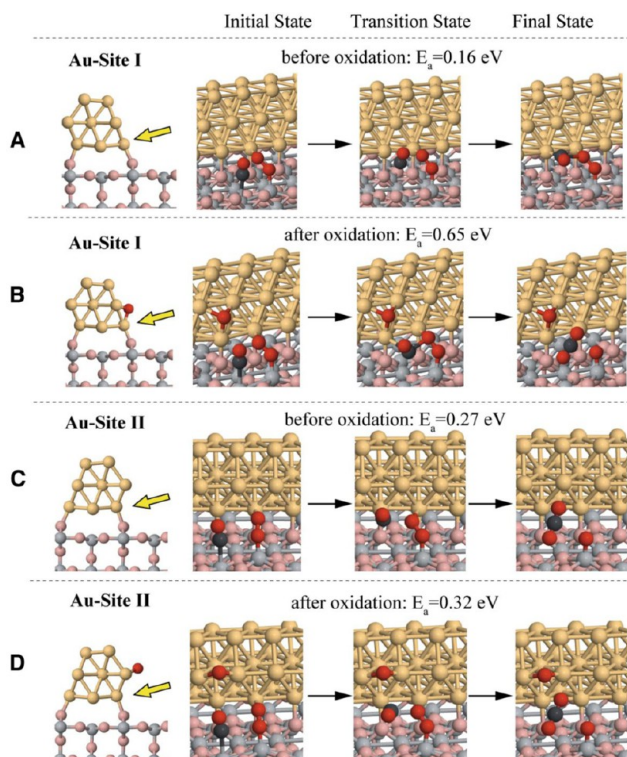


FIGURE 6. The inhibition of O₂ activation by O* at the Au–Ti⁴⁺ perimeter sites on a Au nanorod as calculated from DFT. (A, B) CO-assisted O₂ dissociation at Au-site I with CN = 6 (A) before and (B) after Au oxidation by an O*. (C, D) CO-assisted O₂ dissociation at Au-site II with CN = 7 (C) before and (D) after Au oxidation by an O*. Adapted ref 12.

increase in activation energy is the result of additional O adatoms that bind at the Au–Ti⁴⁺ dual perimeter sites increasing the CN of the active Au species and altering the charge transfer between Au and the neighboring Ti⁴⁺ sites (Figure 6).

The higher apparent activation energy measured on the Au^{δ+}/TiO₂ catalyst (0.27 eV experimentally in Figure 3B and 0.32 eV theoretically in Figure 6D) agrees with previously reported activation energies of 0.2–0.3 eV for CO oxidation on Au/TiO₂ catalysts measured at higher temperatures (200–350 K).^{34,35} This indicates that at temperatures above 200 K and in O₂ rich environments, the Au/TiO₂ catalyst surface is likely always partially covered with O adatoms, consistent with the 0.4–0.6 eV activation energy calculated for direct O₂ activation at the Au–Ti⁴⁺ dual perimeter. We also observed that CO can easily reduce the oxidized Au^{δ+} sites to Au⁰, at temperatures as low as 147 K (Figure 5, conversion onset).¹² In other words, the O adatoms generated at the Au–Ti⁴⁺ dual perimeter sites readily carry out CO oxidation at higher temperatures, where the mobility of CO species is no longer an issue. This argument is confirmed by

extending the Arrhenius plots shown in Figure 3B, where CO oxidation activity on the Au^{δ+} sites surpasses that on the Au⁰ sites at 198 K.

4. H₂ Oxidation: H–H Bond Activation

The oxidation activity of the dual catalytic Au–Ti⁴⁺ site extends to other oxidizable molecules, and H₂ is the simplest of these. Hydrogen can be activated on Au/TiO₂ alone or together with O₂. We have developed a method using the IR background change of TiO₂ to detect the electrons injected from dissociated hydrogen atoms, as shown in Figure 7A.^{14,36} After H₂ dissociation on the Au nanoparticles, the atomic H spills onto the TiO₂ support. The H atoms dissolved in the TiO₂ deliver electrons that are trapped in the conduction band edge (CBE) states. These trapped electrons absorb IR radiation producing a broad background rise (Figure 7B). The background rise is quenched immediately (Figure 7C) by traces of O₂, as H is oxidized by O₂ to form H₂O and the electrons in CBE states are drained. As the O₂ supply is cut off, the IR background rises again in an H₂ atmosphere on the H₂O covered surface (Figure 7D).

Both the IR background rise and the oxidation of H₂ to form H₂O indicate that the Au/TiO₂ catalyst is capable of dissociating the H–H bond. To accurately follow the kinetics, we carried out the Au/TiO₂ catalyzed H₂ oxidation reaction at 200–220 K, where H spillover is limited and all the H₂O produced is captured on the catalyst.¹⁴ By monitoring the H₂O build up (Figure 8) at different temperatures, we measured an apparent activation energy for H₂ oxidation of 0.22 ± 0.02 eV.

DFT simulations indicate that H₂ directly dissociates at low coordination Au sites (CN = 7) with an activation barrier of 0.48 eV. However, with the assistance of O₂ at the Au–Ti⁴⁺ dual perimeter site, the H–H bond scission barrier dropped to 0.16 eV resulting in the formation of a Ti–OOH peroxy species along with Au–H. The Ti–OOH intermediate subsequently dissociates to form Ti–O and a Ti–OH species with a barrier of 0.20 eV. The perimeter Ti–O species can easily activate another H₂ molecule with an activation energy of 0.13 eV, forming a second set of Ti–OH and Au–H bonds. The final hydrogenation of the two Ti–OH species by the Au–H species to form water exhibit activation barriers of 0.24 and 0.25 eV, respectively, in good agreement with the experimental apparent activation energy of 0.22 eV. The removal of H₂O from the perimeter sites requires an activation energy of 0.79 eV and is unlikely to occur at 200–220 K. This is consistent with the experimental observation that the

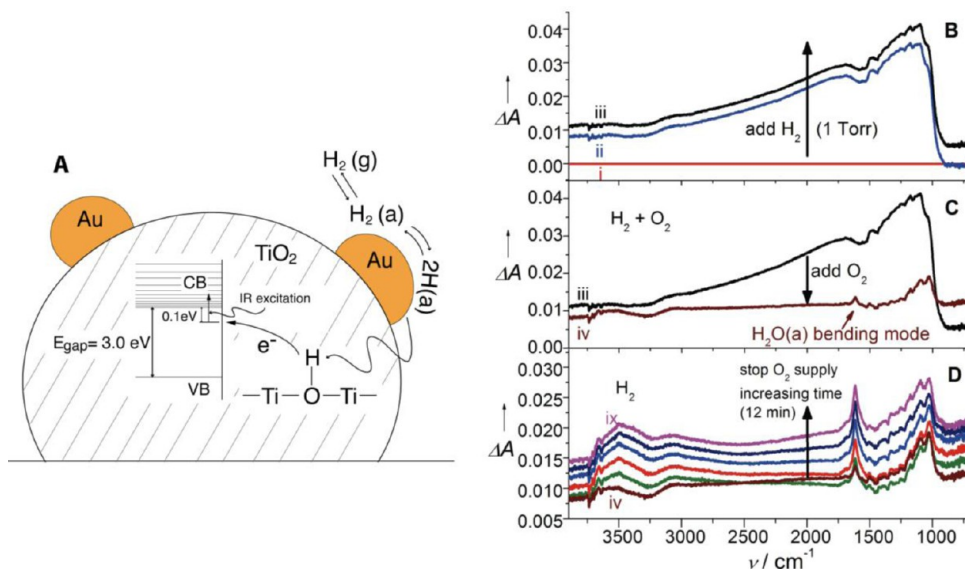


FIGURE 7. (A) Scheme of the H₂ spillover on the Au/TiO₂ catalyst and the IR excitation. (B) IR difference spectra of the CBE background shift caused by H₂ spillover on a Au/TiO₂ catalyst at 295 K. (C) Quenching of the background shift by O₂. (D) Continued background shift on H₂O covered Au/TiO₂ catalyst without O₂. Adapted from ref 14.

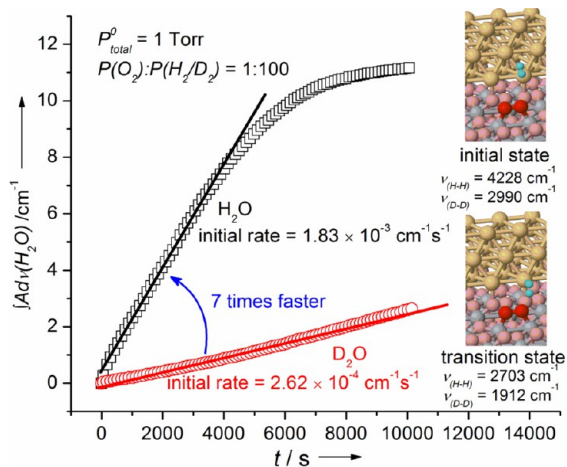


FIGURE 8. D₂ kinetic isotope effect for the oxidation of H₂ by O₂ over the Au/TiO₂ catalyst at 200 K. Inset, *ab initio* calculated initial-state and transition-state frequencies for the O₂-assisted H₂ dissociation process. Reprinted from ref 14. Copyright 2011 Wiley.

H₂ oxidation rate decreases to zero at high H₂O coverage (Figure 8).

The deuterium kinetic isotope effect was examined for the oxidation of H₂ over Au/TiO₂ to examine the transition state (TS) and probe the validity of the mechanistic findings from DFT. The measured k_H/k_D ratio reported in Figure 8 is equal to 7, which indicates an early TS (compared with 87 if the H–H bond is completely broken at a late TS). The DFT calculated initial state and TS frequencies are shown in the inset of Figure 8. A $k_H/k_D = 5$ is calculated from the DFT simulated frequencies, which is in good agreement with the experimental value.

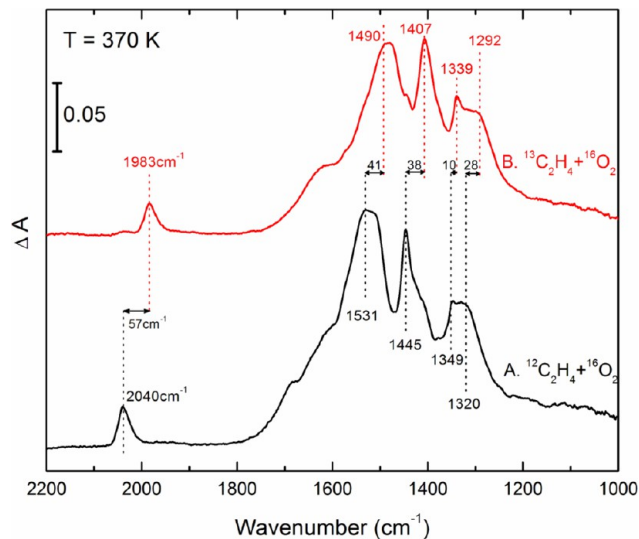


FIGURE 9. Oxidation product after 90 min of reaction of the mixture of 0.5 Torr isotopic labeled C₂H₄ and 0.5 Torr O₂ at 370 K on the Au/TiO₂ catalyst. (A) ¹²C₂H₄ study; (B) ¹³C₂H₄ study. Reprinted from ref 15. Copyright 2012 American Chemical Society.

5. C₂H₄ and Acetate Partial Oxidation: C–H and C–O Bond Scission

Herein we apply these ideas to the addition of oxygen to other unsaturated electrophiles such as C=C bonds and demanding C–H bond activation steps in selective oxidation of ethylene and acetate intermediates. More specifically, we examine the oxidation of ethylene to acetic acid and the subsequent partial oxidation of acetic acid to the ketyli-dene intermediate.

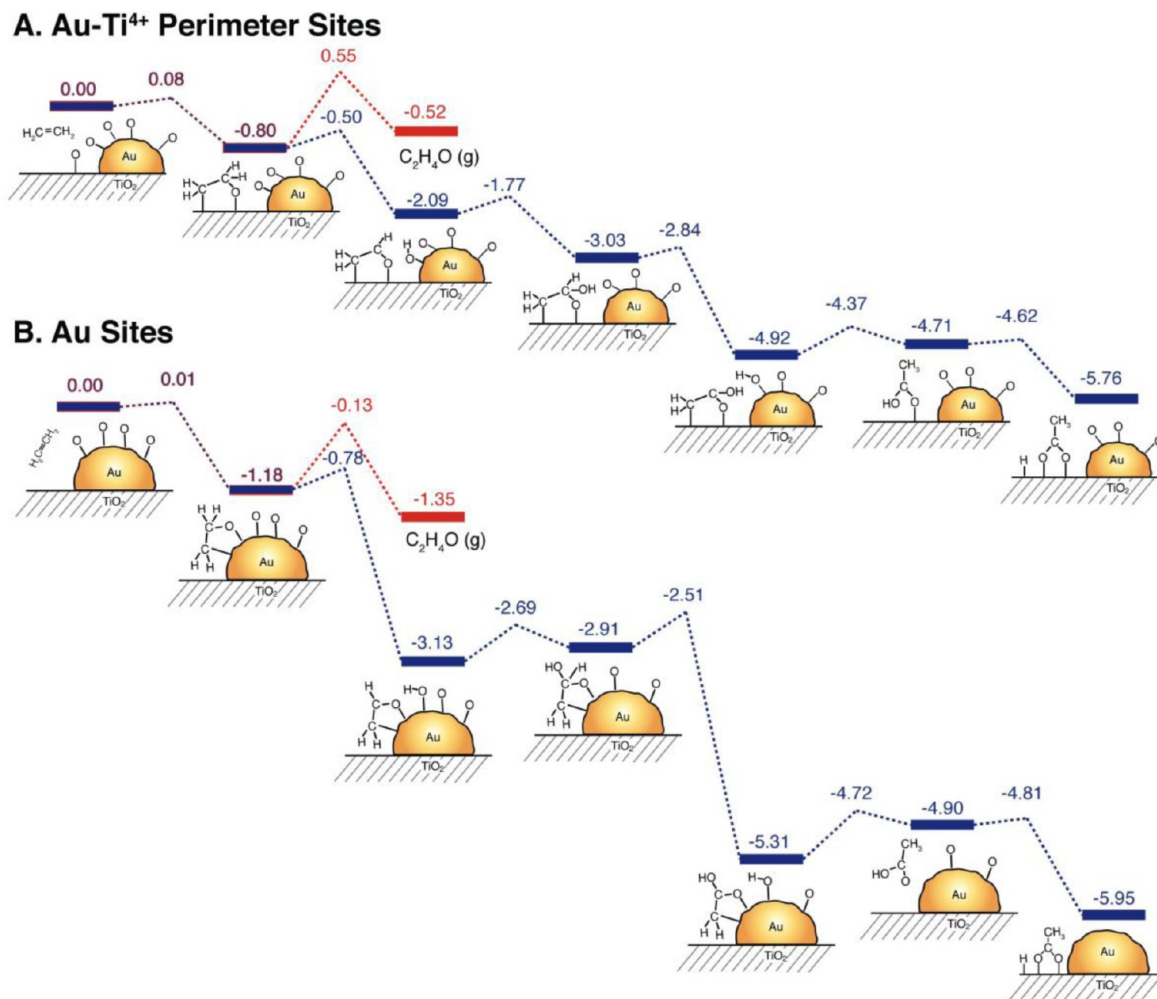


FIGURE 10. Potential energy diagram for the formation of EO and acetate, with respect to the gas phase C₂H₄. O* originate from the Au–Ti⁴⁺ dual perimeter sites. Adapted ref 16.

Ethylene is used as a model hydrocarbon reactant to demonstrate the role of the Au–Ti⁴⁺ dual perimeter sites in the selective oxidation of the C=C bond as well as in C–H bond activation.^{15,16,21}

When the Au/TiO₂ catalyst is exposed to a mixture of ¹²C₂H₄ and ¹⁶O₂ at 370 K, partial oxidation products begin to build up (Figure 9A). No reaction, however, was detected on either a Au/SiO₂ catalyst with similar Au nanoparticle size, or the TiO₂ blank sample, indicating that the unique Au–Ti⁴⁺ dual perimeter sites at the Au/TiO₂ interface are necessary for the reaction to proceed. Two partial oxidation products can be identified from Figure 9A: (1) acetate/TiO₂ ($\nu_{as}(\text{CO}_2)$ at 1531 cm⁻¹, $\nu_s(\text{CO}_2)$ at 1445 cm⁻¹, and $\delta(\text{CH}_3)$ at 1349 and 1320 cm⁻¹) and (2) Au ketenylidene (Au₂=C=C=O, $\nu(\text{CO})$ = 2040 cm⁻¹). Measurements with ¹³C₂H₄ shown in Figure 9B confirmed the frequency assignments for these species. Experiments that examine the partial oxidation of acetate intermediates on the Au/TiO₂ catalyst show that Au₂=C=C=O

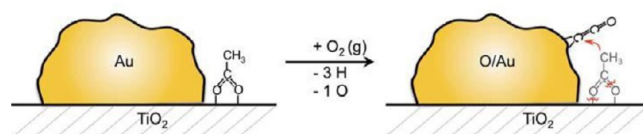


FIGURE 11. Scheme for the catalytic oxidation of CH₃COO/TiO₂ at the perimeter of the Au/TiO₂ catalyst, forming Au₂=C=C=O. Reprinted from ref 15. Copyright 2012 American Chemical Society.

is the secondary oxidation intermediate that results from the oxidation of acetate. As such, we examined the partial oxidation of C₂H₄ to acetate and the partial oxidation of acetate to ketenylidene separately.

The partial oxidation of ethylene to form ethylene oxide (EO) is a significant catalytic reaction on supported Ag nanoparticles.^{37,38} However, our IR study and an *ex situ* GC-MS study of the gas phase (detection limit ~0.01% EO in 1 Torr of gas) shows that no EO is produced either on the Au/TiO₂ catalyst surface or in the gas phase up to 673 K.¹⁶ This is consistent with other studies, which indicate that

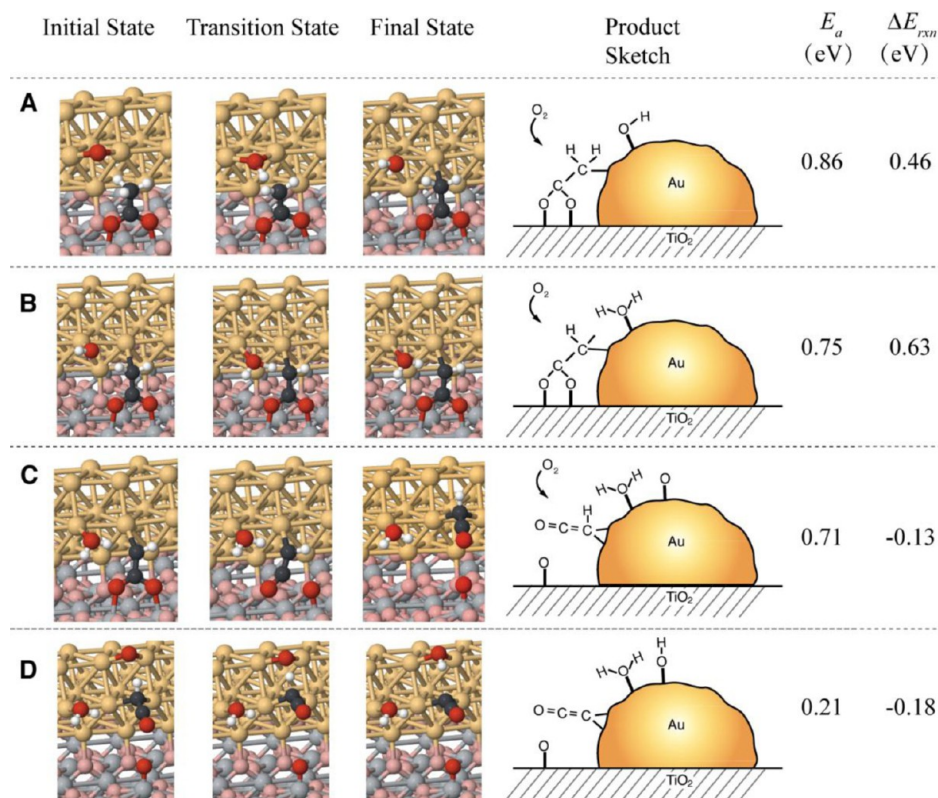


FIGURE 12. Key steps in the partial oxidation of acetate to ketenylidene at the Au–Ti⁴⁺ dual perimeter. Reprinted with permission from ref 21. Copyright 2013 Royal Society of Chemistry.

Au/TiO₂ is a poor catalyst for EO formation.³⁹ Detailed DFT calculations were carried out to examine the selective oxidation pathways for ethylene to EO and acetate on Au/TiO₂.

As was shown, the Au–Ti⁴⁺ perimeter sites readily activate O₂ directly with barriers of 0.4–0.62 eV when the reaction is carried out at high temperatures. The O adatoms (O*) that are generated at the dual perimeter sites can diffuse to other Au or Ti sites on Au/TiO₂ because the barriers for O* diffusion on Au and TiO₂ range from 0.2 to 0.7 eV, depending on the specific nature of the sites (Ti vs Au and the CN of each Au site).^{12,13} Under the experimental conditions used ($T \geq 370$ K in O₂), there is likely a significant surface coverage of O adatoms that can carry out oxidation. The O/Au and OH/Au species that form extract charge from the d-band of the Au to form basic O^{δ-}/Au and OH^{δ-}/Au species that are weakly held to the surface. As such, they act as nucleophiles and attack C=C and C=O bonds of surface intermediates and also catalyze the activation of weakly acidic O–H and C–H bonds.

The results (Figure 10) indicate that C₂H₄ adsorbs weakly on Au as well as on Ti⁴⁺ and can readily be oxidized by O* species that are present on the Ti⁴⁺ and Au sites, respectively, with barriers that are similar. The acetate that is

produced via the dissociative adsorption of acetic acid ($\Delta H_{rxn} = -1.05$ eV), however, is much more strongly bound to sites on the TiO₂ support than to sites on Au ($\Delta E_{ads} = 0.00$ eV, $\Delta H_{rxn} = +0.04$ eV), consistent with the IR observation that acetate adsorbs solely on TiO₂.²¹ The first oxidation step involving the formation the H₂C*–CH₂O* oxymetallacycle intermediate (* indicates bonding to Au/TiO₂) at the catalyst perimeter proceeds via a nucleophilic attack by the weakly bound O atom on the weakly held C₂H₄ species. As shown in Figure 10, the activation barrier to form EO(g) from the H₂C*–CH₂O* intermediate is 1.05–1.35 eV. Comparing the two oxidation routes, on both Au–Ti⁴⁺ perimeter sites and Au sites, Figure 10 shows that the EO route is energetically unfavorable compared with the acetate route.

The partial oxidation of acetate/TiO₂ to form Au₂CCO at the Au/TiO₂ interface provides further insights into the unique role of Au and Ti⁴⁺ sites in causing catalytic transformations as this reaction requires both C–H as well as C–O activation and a change in the active site as the reactant CH₃COO⁻ starts at Ti⁴⁺ sites on TiO₂ but results in a product Au₂=C=C=O that is bound solely to the Au sites (Figure 11).

The key steps (Figure 12) to produce Au₂=C=C=O are addressed in refs 15 and 21. The process takes place at the

Au–Ti⁴⁺ dual perimeter sites, involving three C–H bond scission steps on Au sites and C–O bond scission at the TiO₂ sites. Au₂=C=C=O is identified from the $\nu(\text{CO})$ and from ¹³C and ¹⁸O isotopic shifts, which agree well with DFT calculated shifts.

6. Conclusion

IR spectroscopy together with first-principle DFT calculations provides direct insight into the active sites at the Au/TiO₂ interface and their role in catalyzing different oxidation reactions. The unique Au–Ti⁴⁺ site at the Au/TiO₂ interface is critical in activating O₂ because it allows for electron transfer from Au to Ti and subsequent electron transfer into 2 π^* antibonding states of O₂, aiding in O–O bond activation. Adsorption of O₂ occurs via di- σ bonding to Au and Ti⁴⁺ to form a Au–O–O–Ti⁴⁺ state that is similar to the active Au-peroxy (AuOOH) complex formed in the presence of O₂ and water. The basic O/Au and O/Ti species at the Au–Ti⁴⁺ interface extract electron density from the substrate. As such, they readily attack bound C=O and C=C containing species and activate C–H and O–H bonds, thus catalyzing partial oxidation.

We have focused on the properties of the Au–Ti⁴⁺ dual site, which occurs at the perimeter of Au nanoparticles supported on TiO₂. These sites easily activate O₂, and our study of four oxidative reactions have shown the wide utility of the dual site in a range of partial and full oxidative reactions.

We acknowledge support from U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-09ER16080) and the FIRST Energy Research Frontier Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, XSEDE computing resources (Texas Advanced Computing Center/San Diego Supercomputer Center), and AES Graduate Fellowship in Energy Research at UVA for I. Green.

BIOGRAPHICAL INFORMATION

Isabel Xiaoye Green received her B. S. in Chemistry and B. A. in Economics from Peking University in 2007 and her Ph.D. in 2012 at the University of Virginia working under Dr. John T. Yates, Jr., in high vacuum transmission IR spectroscopic studies of surface reactions and surface adsorbent diffusion/desorption on powdered materials. She is currently a postdoctoral fellow at the University of Washington, studying under Dr. Charles T. Campbell on Single Crystal Absorption Calorimetry.

Wenjie Tang received her B. S. in Chemistry from the University of Science and Technology of China in 2005 and Ph.D. in Chemistry from the University of Texas under the guidance of Dr. Graeme Henkelman in 2010. Currently, she is a research scientist in the group of Dr. Matthew Neurock at the University of Virginia.

Her research interests include the development and application of methods for studying the electronic properties of materials and reactions in surface science and catalysis.

Matthew Neurock is the Alice M. and Guy A. Wilson Professor of Chemical Engineering and Professor of Chemistry at the University of Virginia. He joined the faculty in Chemical Engineering at the University of Virginia in 1995. He has received various awards for his research in Computational Catalysis including the 2007 R. H. Wilhelm Award in Chemical Reaction Engineering and the 2005 Paul H. Emmett Award in Fundamental Catalysis from the North American Catalysis Society. He has coauthored over 200 publications, 2 patents, and 2 books and is currently an editor for the *Journal of Catalysis*.

John T. Yates, Jr., is a physical chemist specializing in surface chemistry. He has spent 30 years in academia, first as R. K. Mellon Professor and founding Director of the Surface Science Center at the University of Pittsburgh (Departments of Chemistry and Physics) and as a Shannon Research Fellow and Professor at the University of Virginia (Departments of Chemistry and Chemical Engineering). Prior to academia, he was a research staff member at the National Bureau of Standards (now NIST) in the Physical Chemistry Division. His work has encompassed many aspects of surface chemistry through experimental studies of the properties of adsorbed layers on metals, semiconductors, and insulators using advanced measurement methods. He is the author of over 750 research publications, several books, and numerous reviews. He has received a number of awards from the ACS and the AVS. In 1995, he was elected to the National Academy of Sciences. In 2013, he was awarded the Ertl Lectureship at the Fritz Haber Institute in Berlin.

FOOTNOTES

The authors declare no competing financial interest.

REFERENCES

- Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Novel gold catalysts for the oxidation of carbon monoxide. *Chem. Lett.* **1987**, *2*, 405–408.
- Meyer, R.; Lemire, C.; Shaikhutdinov, S. K.; Freund, H.-J. Surface chemistry of catalysis by gold. *Gold Bull.* **2004**, *37*, 72.
- Chen, M. S.; Goodman, D. W. The structure of catalytically active gold on titania. *Science* **2004**, *306*, 252–255.
- Akita, T.; Kohyama, M.; Haruta, M. Electron microscopy study of gold nanoparticles deposited on transition metal oxides. *Acc. Chem. Res.* **2013**, *46*, 1773–1782.
- Green, I. X.; Buda, C.; Zhang, Z.; Neurock, M.; Yates, J. T., Jr. IR spectroscopic measurement of diffusion kinetics of chemisorbed pyridine through TiO₂ particles. *J. Phys. Chem. C* **2010**, *114*, 16649–16659.
- Wang, X.; Kim, S.; Buda, C.; Neurock, M.; Koper, O. B.; Yates, J. T., Jr. Direct spectroscopic observation of the role of humidity in surface diffusion through an ionic adsorbent powder. The behavior of adsorbed pyridine on nanocrystalline MgO. *J. Phys. Chem. C* **2009**, *113*, 2228–2234.
- Kim, S.; Wang, X.; Buda, C.; Neurock, M.; Koper, O. B.; Yates, J. T., Jr. IR spectroscopic measurement of diffusion kinetics of chemisorbed pyridine through nanocrystalline MgO particles. The involvement of surface defect sites in slow diffusion. *J. Phys. Chem. C* **2009**, *113*, 2219–2227.
- Valden, M.; Lai, X.; Goodman, D. W. Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties. *Science* **1998**, *281*, 1647–1650.
- Haruta, M. Size- and support-dependency in the catalysis of gold. *Catal. Today* **1997**, *36*, 153–166.
- Zanella, R.; Giorgio, S.; Henry, C. R.; Louis, C. Alternative methods for the preparation of gold nanoparticles supported on TiO₂. *J. Phys. Chem. B* **2002**, *106*, 7634–7642.

- 11 Bond, G. C.; Louis, C.; Thompson, D. T. *Catalysis by Gold*; Imperial College Press: London, 2006; Vol. 6.
- 12 Green, I. X.; Tang, W.; McEntee, M.; Neurock, M.; Yates, J. T. Inhibition at perimeter sites of Au/TiO₂ oxidation catalyst by reactant oxygen. *J. Am. Chem. Soc.* **2012**, *134*, 12717–12723.
- 13 Green, I. X.; Tang, W.; Neurock, M.; Yates, J. T., Jr. Spectroscopic observation of dual catalytic sites during oxidation of CO on a Au/TiO₂ Catalyst. *Science* **2011**, *333*, 736–739.
- 14 Green, I. X.; Tang, W.; Neurock, M.; Yates, J. T., Jr. Low-temperature catalytic H₂ oxidation over Au nanoparticle/TiO₂ dual perimeter sites. *Angew. Chem., Int. Ed.* **2011**, *50*, 10186–10189.
- 15 Green, I. X.; Tang, W.; Neurock, M.; Yates, J. T., Jr. Localized partial oxidation of acetic acid at the dual perimeter sites of the Au/TiO₂ catalyst—formation of gold ketenylidene. *J. Am. Chem. Soc.* **2012**, *134*, 13569–13572.
- 16 Green, I. X.; McEntee, M.; Tang, W.; Neurock, M.; Yates, J. T., Jr. Direct formation of acetate from the partial oxidation of ethylene on a Au/TiO₂ catalyst. *Top. Catal.* **2013**, *56*, 1512–1524.
- 17 Madix, R. J.; Roberts, J. T. *Surface Reactions*; Springer-Verlag: Berlin, 1994.
- 18 Zope, B. N.; Hibbitts, D. D.; Neurock, M.; Davis, R. J. Reactivity of the gold/water interface during selective oxidation catalysis. *Science* **2010**, *330*, 74–78.
- 19 Liu, X.; Madix, R. J.; Friend, C. M. Unraveling molecular transformations on surfaces: a critical comparison of oxidation reactions on coinage metals. *Chem. Soc. Rev.* **2008**, *37*, 2243–2261.
- 20 Molina, L. M.; Rasmussen, M. D.; Hammer, B. Adsorption of O₂ and oxidation of CO at Au nanoparticles supported by TiO₂(110). *J. Chem. Phys.* **2004**, *120*, 7673–7680.
- 21 Green, I. X.; Tang, W.; Neurock, M.; Yates, J. T., Jr. Mechanistic insights into the partial oxidation of acetic acid by O₂ at the dual perimeter sites of a Au/TiO₂ catalyst. *Faraday Discuss.* **2013**, *162*, 247–265.
- 22 Liu, Z.-P.; Gong, X.-Q.; Kohanoff, J.; Sanchez, C.; Hu, P. Catalytic role of metal oxides in gold-based catalysts: A first principles study of CO oxidation on TiO₂ supported Au. *Phys. Rev. Lett.* **2003**, *91*, No. 266102.
- 23 Remediakis, I. N.; Lopez, N.; Nørskov, J. K. CO oxidation on rutile-supported Au nanoparticles. *Angew. Chem., Int. Ed.* **2005**, *44*, 1824–1826.
- 24 Wang, Y.-G.; Yoon, Y.; Glezakou, V.-A.; Li, J.; Rousseau, R. The role of reducible oxide—metal cluster charge transfer in catalytic processes: New insights on the catalytic mechanism of CO oxidation on Au/TiO₂ from ab initio molecular dynamics. *J. Am. Chem. Soc.* **2013**, *135*, 10673–10683.
- 25 Ganesh, P.; Kent, P. R. C.; Veith, G. M. Role of hydroxyl groups on the stability and catalytic activity of Au clusters on a rutile surface. *J. Phys. Chem. Lett.* **2011**, *2*, 2918–2924.
- 26 Pan, J.-M.; Maschhoff, B. L.; Diebold, U.; Madey, T. E. Interaction of water, oxygen, and hydrogen with TiO₂(110) surfaces having different defect densities. *J. Vac. Sci. Technol., A* **1992**, *10*, 2470–2476.
- 27 Ojeda, M.; Zhan, B.-Z.; Iglesia, E. Mechanistic interpretation of CO oxidation turnover rates on supported Au clusters. *J. Catal.* **2012**, *285*, 92–102.
- 28 Williams, W. D.; Shekhar, M.; Lee, W.-S.; Kispersky, V.; Delgass, W. N.; Ribeiro, F. H.; Kim, S. M.; Stach, E. A.; Miller, J. T.; Allard, L. F. Metallic corner atoms in gold clusters supported on rutile are the dominant active site during water–gas shift catalysis. *J. Am. Chem. Soc.* **2010**, *132*, 14018–14020.
- 29 Shekhar, M.; Lee, W.; Akatay, M.; Maciel, L.; Tang, W.; Miller, J. T.; Stach, E. A.; Neurock, M.; Delgass, W. N.; Ribeiro, F. H. *J. Catal.* **2013**, in preparation.
- 30 Mihaylov, M.; Knözinger, H.; Hadjivanov, K.; Gates, B. C. Characterization of the oxidation states of supported gold species by IR spectroscopy of adsorbed CO. *Chem. Ing. Tech.* **2007**, *79*, 795–806.
- 31 Boccuzzi, F.; Chiorino, A.; Manzoli, M. FTIR study of the electronic effects of CO adsorbed on gold nanoparticles supported on titania. *Surf. Sci.* **2000**, *454–456*, 942–946.
- 32 Basu, P.; Ballinger, T. H.; Yates, J. T., Jr. Wide temperature range IR spectroscopy cell for studies of adsorption and desorption on high area solids. *Rev. Sci. Instrum.* **1988**, *59*, 1321–1327.
- 33 Green, I. X.; Yates, J. T., Jr. Vibrational spectroscopic observation of weakly bound adsorbed molecular oxygen on powdered titanium dioxide. *J. Phys. Chem. C* **2010**, *114*, 11924–11930.
- 34 Daté, M.; Okumura, M.; Tsubota, S.; Haruta, M. Vital role of moisture in the catalytic activity of supported gold nanoparticles. *Angew. Chem., Int. Ed.* **2004**, *43*, 2129–2132.
- 35 Long, C. G.; Gilbertson, J. D.; Vijayaraghavan, G.; Stevenson, K. J.; Pursell, C. J.; Chandler, B. D. Kinetic evaluation of highly active supported gold catalysts prepared from monolayer-protected clusters. *J. Am. Chem. Soc.* **2008**, *130*, 10103–10115.
- 36 Panayotov, D. A.; Yates, J. T., Jr. Depletion of conduction band electrons in TiO₂ by water chemisorption - IR spectroscopic studies of the independence of Ti-OH frequencies on electron concentration. *Chem. Phys. Lett.* **2005**, *410*, 11–17.
- 37 Force, E. L.; Bell, A. T. Infrared spectra of adsorbed species present during the oxidation of ethylene over silver. *J. Catal.* **1975**, *38*, 440–460.
- 38 Kilty, P. A.; Sachtler, W. M. H. The mechanism of the selective oxidation of ethylene to ethylene oxide. *Catal. Rev.: Sci. Eng.* **1974**, *10*, 1–16.
- 39 Huang, J.; Haruta, M. Gas-phase propene epoxidation over coinage metal catalysts. *Res. Chem. Intermed.* **2012**, *38*, 1–24.