

Electron-Mediated CO Oxidation on the TiO₂(110) Surface during Electronic Excitation

Zhen Zhang and John T. Yates, Jr.*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904

Received July 13, 2010; E-mail: johnt@virginia.edu

Abstract: The role of electrons and holes in the electronically excited oxidation of adsorbed CO on TiO₂(110) has been investigated by tuning the surface electron and hole availability by the adsorption of Cl₂ or O₂. The presence of an electron acceptor (Cl₂ or O₂) on the TiO₂(110) surface causes upward band bending, increasing the excited hole availability and decreasing the excited electron availability in the near surface region. This enhances O₂ desorption and depresses CO₂ production during electronic excitation. This result gives clear evidence for the first time that the electronically excited CO oxidation reaction is caused by an electron-mediated process in contrast to O₂ desorption which is mediated by holes.

The electronic excitation of a semiconductor using either photons or electron impact results first in exciton formation followed quickly by separation of an electron–hole pair.^{1–3} The utility of the hot electron produced is related to its ability to tunnel from the conduction band (CB) to an adsorbed molecule which presents an empty orbital at the appropriate energy. Electron attachment to the adsorbed molecule can produce a temporary negative ion which can then undergo dissociative electron attachment (DEA) producing new products.⁴ The utility of the hole produced in the valence band (VB) is to accept an electron from a filled orbital of an adsorbed molecule causing subsequent chemical processes to also occur on the surface. Titanium dioxide is widely used as a photoactive material in which the two processes involving electron and hole charge carriers are balanced, maintaining charge neutrality during photoexcitation.^{2,5,6}

The manipulation of the rate of transport of photogenerated charge carriers from the bulk solid to adsorbed species on the surface is a powerful method for the control of surface processes induced by the electronic excitation of a semiconductor. Such control of charge carriers could be useful in enhancing photochemistry on TiO₂ particles as well as charge transport efficiency in photovoltaic cells. In previous work,⁷ we have shown that electron-withdrawing and electron-donating adsorbates on TiO₂(110) are able to strongly influence charge transport to the adsorbed O₂ molecule. This is postulated to occur by upward band bending for electron-acceptor surface modifiers and downward band bending for electron-donor surface modifiers, as shown in Figure 1. The upward and downward band bending processes are accompanied by mobile charge carrier displacements in the near surface region of the semiconductor.^{8–10}

The present study is carried out on an atomically clean TiO₂(110)-1×1 single crystal in ultrahigh vacuum (UHV) using traditional surface preparation and measurement methods used in surface science experiments. Accurate control of surface cleanliness and adsorbate coverage is achieved using these methods. The structure and surface defect density are well-known for this crystal which

was processed to contain 8–10% bridge-bond oxygen (BBO) vacancy defects to act as sites to bind molecular O₂. Thus the experiments differ from the usual TiO₂ particle-surface modification experiments, where small TiO₂ particles with unknown surface inhomogeneities are often employed, and where in such experiments surface impurities, particle size effects, and aqueous solvent effects are often present.

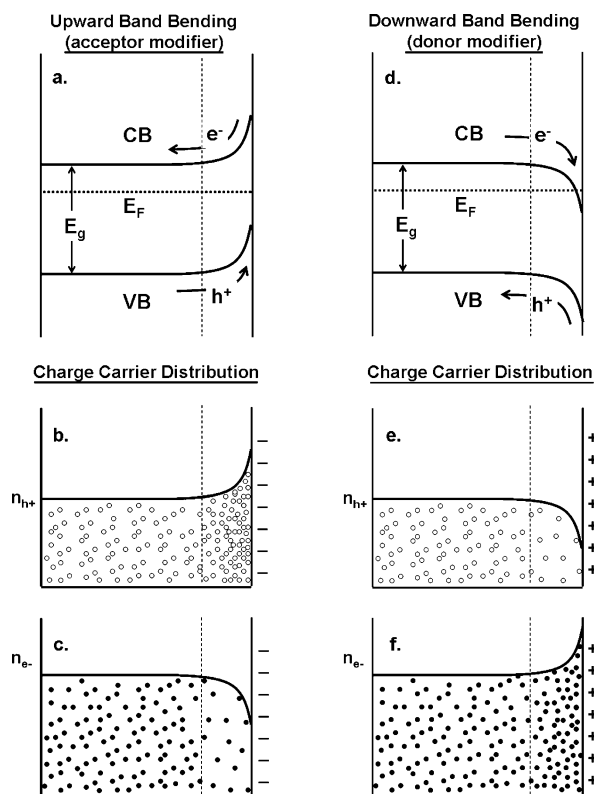


Figure 1. Role of (a) electron-acceptor and (d) electron-donor surface modifiers on band bending in an n-type semiconductor such as TiO₂. The TiO₂ is not electronically excited. The flow of electrons and holes for electronically excited TiO₂ is also indicated. For upward band bending: (b) hole density; (c) electron density. For downward band bending: (e) hole density; (f) electron density.

In this study we investigate the oxidation of adsorbed CO by adsorbed O₂ molecules on TiO₂(110) as induced by electronic excitation of the solid. We employ 100 eV electron bombardment which leads to electron and hole production in the near surface region of the crystal.¹¹ The CO oxidation reaction is well studied, especially by photon-induced excitation with ultraviolet light with photon energies above 3.1 eV, the bandgap energy of TiO₂.^{12–15} Our studies have shown that electron impact may also be used to produce electron–hole pairs in TiO₂ and that this method of excitation is very nearly equivalent to photon excitation of the TiO₂

since electron–hole pair production is involved in both cases.^{11,16} The behavior of O₂ chemisorbed on TiO₂(110) is also well studied.^{5,7,11,16–22} It has been found, both experimentally^{5,7,11,16–21} and theoretically,²² that the electronic desorption of O₂, originally adsorbed on BBO oxygen vacancy defect sites, is caused by holes produced either by UV excitation or by holes produced by 100 eV electron impact. The production of holes in TiO₂ may be accurately monitored by measuring the yield of desorbing O₂ molecules.^{11,16} We have found that the rate of the hole-mediated O₂ desorption process can be modified by adding either donor or acceptor molecules to the surface containing adsorbed O₂. Upward band bending, achieved by the chemisorption of Cl₂ (acceptor), has been found to enhance the initial rate of O₂ desorption by a factor of up to 25.⁷ Conversely, using methanol (donor), it has been found that the initial rate of O₂ desorption can be reduced to zero and it is postulated that downward band bending is responsible for this effect by limiting hole transport from the bulk to the surface.⁷

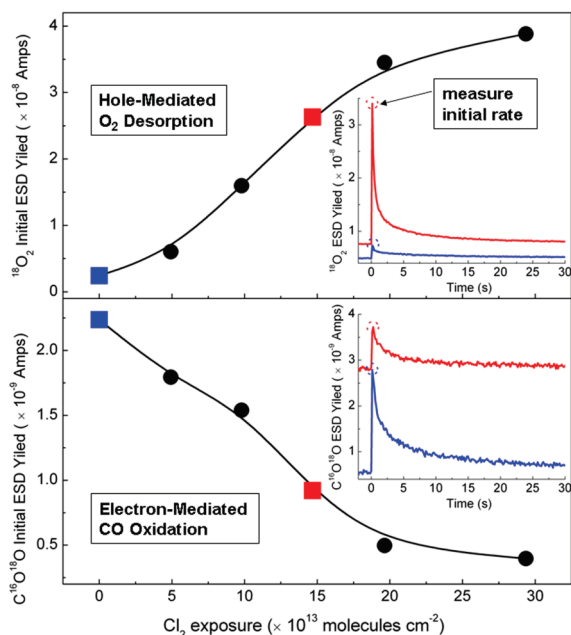


Figure 2. Plots of the initial yield of ¹⁸O₂ (upper panel) and C¹⁶O¹⁸O (lower panel) as a function of Cl₂ exposure during electronic excitation of a C¹⁶O + ¹⁸O₂ mixed layer. Inset shows the measurements by QMS for ¹⁸O₂ (upper panel) and C¹⁶O¹⁸O (lower panel) yields during electronic excitation in the presence of Cl₂ (blue curve, Cl₂ exposure: 0 molecules cm⁻²; red curve, Cl₂ exposure: 1.47 × 10¹⁴ molecules cm⁻²) on the C¹⁶O/¹⁸O₂/TiO₂(110) surface. ¹⁸O₂ exposure: 3.84 × 10¹³ molecules cm⁻²; C¹⁶O: exposure: 1.18 × 10¹⁴ molecules cm⁻², at 85 K. The electron bombardment is rapidly initiated at 0 s, and the initial desorption yields of ¹⁸O₂ and C¹⁶O¹⁸O are measured within the first 0.2 s (as shown in the dashed circles in the insets).

We extend the studies of the modification of hole- and electron-mediated processes on TiO₂(110) to the investigation of the role of charge carrier production on the CO oxidation reaction, finding that the oxidation process is **electron-mediated**. Until now, the role of the electron or hole in the CO oxidation has been unclear and contradictory results have been published. EPR^{23,24} and theoretical calculation²³ suggested that the active oxygen in the photocatalytic oxidation process is O₃⁻, formed by O₂ reacted with a hole center (O⁺), which is a hole-mediated process. In contradistinction, experiment and kinetics analysis^{25–27} showed that, in aqueous media (where water is chemically involved in the production of intermediate species), electron transfer to the O₂ may play an essential role in the photooxidation of organic compounds.

In this paper, by fine-tuning band bending at the TiO₂ surface using electron-acceptor adsorbates, and hence modifying the surface hole and electron availability and transport kinetics, we show that the oxidation of CO may be strongly modulated.

All the experiments have been carried out in a stainless UHV chamber with a base pressure lower than 3 × 10⁻¹¹ mbar, which has been described elsewhere.^{11,28} A clean TiO₂(110)-1 × 1 surface with ~8–10% of a monolayer of bridge-bonded oxygen vacancies can be reproducibly produced by Ar⁺ sputtering followed by annealing at 900 K in vacuum. The energy of the incident electrons from an electron gun (Kimball Physics ELG-2) is 100 eV with a flux of 6.8 × 10¹³ electrons cm⁻² s⁻¹. An absolutely calibrated capillary array doser²⁹ has been used to dose ¹⁸O₂ (99% isotopically pure), C¹⁶O, and Cl₂ (Sigma-Aldrich, >99.5%) to the surface. The rate of evolution of ¹⁸O₂ and C¹⁶O¹⁸O induced by the incident electrons was monitored by a line-of-sight quadrupole mass spectrometer (QMS) (UTI-100C) using 70 eV internal electron impact. All gas dosing and electron stimulated experiments have been done at 85 K. The TiO₂ crystal has been cleaned by sputter-annealing after each electron-excited experiment.

To investigate the influence of Cl₂ on the C¹⁶O oxidation by electron impact, various exposures of Cl₂ were dosed onto the TiO₂(110) surface following the exposure to a constant amount of ¹⁸O₂ (exposure: 3.84 × 10¹³ molecules cm⁻²) and to C¹⁶O (exposure: 1.18 × 10¹⁴ molecules cm⁻²) at 85 K. The insets of Figure 2 show the ¹⁸O₂ (upper panel) and C¹⁶O¹⁸O (lower panel) yields versus electron bombardment time. In the insets, Cl₂ exposures of 0 (blue curve) and 1.47 × 10¹⁴ molecules cm⁻² (red curve) were performed on the C¹⁶O/¹⁸O₂/TiO₂(110) covered surface. Similar to the ¹⁸O₂ yield, the C¹⁶O¹⁸O yield reaches a maximum value as the electron current is first established and then decreases monotonically over time. The **initial rates** of production of ¹⁸O₂ (upper panel) and C¹⁶O¹⁸O (lower panel) with various Cl₂ exposures are plotted in Figure 2. Measurement of the initial rate (during the first 0.2 s electron exposure) assures that significant electron-beam induced damage effects are not present. Consistent with our previous report,⁷ the ¹⁸O₂ desorption yield increases with the Cl₂ exposure over a range of exposure maximizing near ~1 ML of Cl₂ exposure. In contrast to the ¹⁸O₂ yield, the initial rate of C¹⁶O¹⁸O production decreases to near zero with the full Cl₂ exposure. The opposite trends of the yield of ¹⁸O₂ and C¹⁶O¹⁸O indicate that the electronic excitation mechanisms for the desorption of ¹⁸O₂ and for the production of C¹⁶O¹⁸O are different, as will be discussed later.

Previous results^{7,8,30,31} have shown that O₂ is also an electron acceptor, capable of causing upward band bending when adsorbed on TiO₂. Thus, in the case of the electron-induced reaction of adsorbed O₂ and CO we have the possibility of the reactant, O₂, also being an electronic modifier of the photocatalyst surface by virtue of band bending which it induces. Figure 3 plots the effect of O₂ adsorption on the yield of desorbing O₂ in the top panel, where a mixture of adsorbed O₂ and CO is studied. The O₂ yield increases as the O₂ coverage increases for two reasons: (1) increasing O₂ coverage; (2) increasing upward band bending which promotes hole transport to the adsorbed O₂.⁷ In the bottom panel of Figure 3, it is seen that two effects are mixed when the production of CO₂ is simultaneously monitored. Initially, as the O₂ coverage is increased, the yield of CO₂ increases due to the coverage increase of the adsorbed O₂. However, at intermediate coverages of O₂, the rate of CO₂ production reaches a maximum and then decreases as the electronic effect of O₂ on electron transport **to itself** becomes dominant.

The results shown in Figures 2 and 3 may be rationalized on the following basis. The electron acceptor molecules, Cl₂ and O₂, when

adsorbed on $\text{TiO}_2(110)$, cause upward band bending at the CB and VB band edges. This results in an enhancement of hole transport to O_2 molecules upon excitation of the TiO_2 , resulting in the acceleration of the hole-mediated O_2 desorption process (Figures 2 and 3, upper panels). Concomitantly, the upward band bending produced by either Cl_2 or O_2 causes a diminution of the process mediated by electrons, namely the CO oxidation reaction (Figures 2 and 3, lower panels).

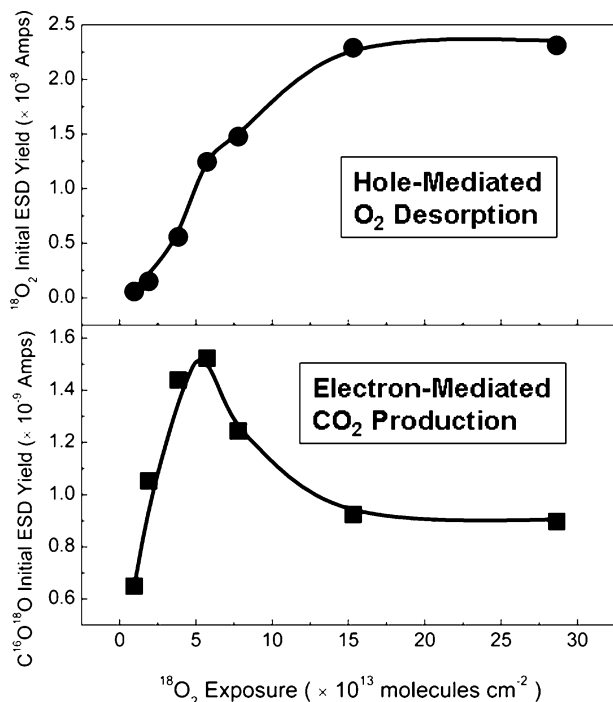


Figure 3. Plots of the initial yields of $^{18}\text{O}_2$ (upper panel) and $\text{C}^{16}\text{O}^{18}\text{O}$ (lower panel) as a function of $^{18}\text{O}_2$ exposure during electronic excitation of a C^{16}O layer. The preadsorbed C^{16}O exposure: 1.18×10^{14} molecules cm^{-2} at 85 K.

Figure 4 schematically shows the two electronically excited reactions of adsorbed oxygen which have been studied here, under conditions where electrons and holes stimulate different surface reactions. The upward band bending caused by either Cl_2 or O_2 adsorption results in the enhancement of the hole-mediated process leading to enhanced rates of O_2 desorption; at the same time, the electron-mediated CO oxidation process is diminished in rate as the process, driven by electrons from electron–hole pair formation in TiO_2 , is reduced by upward band bending.

It is well known that adsorbed O_2 species on BBO vacancy sites acquire a negative charge upon adsorption.^{7,8,22,30–36} We will assign these species as O_2^- superoxide species, based on theory^{22,34,35} and on observations by ESR^{33,36} and EELS.³² The chemisorbed O_2^- species, upon electron attachment in an electron-mediated process, produce the O_2^{2-} species, a peroxide ion well-known for its ability to cause oxidation. Peroxide ions participate in oxidation reactions with the production of O^{2-} , the oxide ion which has the formal oxidation number (-2), as do the oxygen moieties in CO_2 . Thus, because of the variable oxidation states available to oxygen, the reaction, driven by electrons interacting with O_2^- adsorbed species, results in the oxidation of CO, forming CO_2 .

These experiments demonstrate the dual role of adsorbed O_2 as a participant in both hole-driven and electron-driven surface processes on the TiO_2 surface. Depending on which charge carrier activates O_2^- , either $\text{O}_2(\text{g})$ (hole-mediated) or O_2^{2-} (electron-mediated) species are produced. The O_2^{2-} species act as oxidizing

agents for adsorbed CO as they are reduced to O^{2-} . It is likely that the electron-mediated process, leading to adsorbed O_2^- excitation to a peroxide, is also responsible for various photooxidation reactions involving organic molecules on TiO_2 under anhydrous condition; more complex electron-mediated oxidation chemistry occurs when water is present.^{25–27}

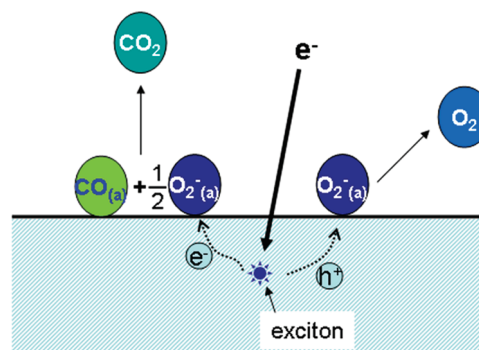


Figure 4. Schematic mechanism of O_2 desorption and CO oxidation on $\text{TiO}_2(110)$ during electronic excitation. Desorption of O_2^- as $\text{O}_2(\text{g})$ is induced by holes; Reaction of O_2^- to produce CO_2 is induced by excited electrons created in the TiO_2 .

In summary, the production of electrons and holes can be tuned using Cl_2 and O_2 as electron acceptors to cause upward band bending of the VB and CB of TiO_2 . A surface oxidation process (involving adsorbed oxygen), which depends on the excitation of electrons in the bulk TiO_2 , has been demonstrated, and it is shown that adsorbed acceptor molecules may be used as surface modifiers to modulate the rate of the oxidation process.

Acknowledgment. We acknowledge with thanks the support of the Army Research Office (ARO) under Grant W911NF-09-1-0371.

References

- (1) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69–96.
- (2) Linsebigler, A. L.; Lu, G. Q.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 735–758.
- (3) Mills, A.; Hunte, S. L. *J. Photochem. Photobiol., A* **1997**, *108*, 1–35.
- (4) Arumainayagam, C. R.; Lee, H.-L.; Nelson, R. B.; Haines, D. R.; Gunawardane, R. P. *Surf. Sci. Rep.* **2010**, *65*, 1–44.
- (5) Thompson, T. L.; Yates, J. T., Jr. *Chem. Rev.* **2006**, *106*, 4428–4453.
- (6) Yates, J. T., Jr.; Petek, P. *Chem. Rev.* **2006**, *106*, 4113–4115.
- (7) Zhang, Z.; Yates, J. T., Jr. *J. Phys. Chem. Lett.* **2010**, *1*, 2185–2188.
- (8) Diebold, U. *Surf. Sci. Rep.* **2003**, *48*, 53–229.
- (9) Henrich, V. E.; Cox, P. A. *The Surface Science of Metal Oxides*; Cambridge University Press: Cambridge, U.K., 1994; p 118–119.
- (10) Zangwill, A. *Physics at Surfaces*; Cambridge University Press: Cambridge, U.K., 1988; p 221–231.
- (11) Zhang, Z.; Yates, J. T., Jr. *J. Phys. Chem. C* **2010**, *114*, 3098–3101.
- (12) Linsebigler, A. L.; Lu, G. Q.; Yates, J. T., Jr. *J. Phys. Chem.* **1996**, *100*, 6631–6636.
- (13) Lu, G. Q.; Linsebigler, A. L.; Yates, J. T., Jr. *J. Chem. Phys.* **1995**, *102*, 3005–3008.
- (14) Linsebigler, A. L.; Rusu, C.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 5284–5289.
- (15) Petrik, N. G.; Kimmel, G. A. *J. Phys. Chem. Lett.* **2010**, *1*, 2508–2513.
- (16) Thompson, T. L.; Yates, J. T., Jr. *J. Phys. Chem. B* **2005**, *109*, 18230–18236.
- (17) Lu, G. Q.; Linsebigler, A. L.; Yates, J. T., Jr. *J. Chem. Phys.* **1995**, *102*, 4657–4662.
- (18) Thompson, T. L.; Yates, J. T., Jr. *J. Phys. Chem. B* **2006**, *110*, 7431–7435.
- (19) Sporleder, D.; Wilson, D. P.; White, M. G. *J. Phys. Chem. C* **2009**, *113*, 13180–13191.
- (20) Perkins, C. L.; Henderson, M. A. *J. Phys. Chem. B* **2001**, *105*, 3856–3863.
- (21) Petrik, N. G.; Kimmel, G. A. *J. Phys. Chem. Lett.* **2010**, *1*, 1758–1762.
- (22) de Lara-Castells, M. P.; Krause, J. L. *J. Chem. Phys.* **2003**, *118*, 5098–5105.
- (23) Anpo, M.; Kubokawa, Y.; Fujii, T.; Suzuki, S. *J. Phys. Chem.* **1984**, *88*, 2572–2575.
- (24) Einaga, H.; Ogata, A.; Futamura, S.; Ibusuki, T. *Chem. Phys. Lett.* **2001**, *338*, 303–307.

- (25) Schwitzgebel, J.; Ekerdt, J. G.; Gerischer, H.; Heller, A. *J. Phys. Chem.* **1995**, *99*, 5633–5638.
- (26) Gerischer, H.; Heller, A. *J. Phys. Chem.* **1991**, *95*, 5261–5267.
- (27) Heller, A. *Acc. Chem. Res.* **1995**, *28*, 503–508.
- (28) Lee, J.; Zhang, Z.; Yates, J. T., Jr. *Phys. Rev. B* **2009**, *79*, 081408(R).
- (29) Yates, J. T., Jr. *Experimental Innovations in Surface Science: A Guide to Practical Laboratory Methods and Instruments*; Springer: New York, 1998; pp 604–613.
- (30) Wendt, S.; Sprunger, P. T.; Lira, E.; Madsen, G. K. H.; Li, Z. S.; Hansen, J. Ø.; Matthiesen, J.; Blekinge-Rasmussen, A.; Lægsgaard, E.; Hammer, B.; Besenbacher, F. *Science* **2008**, *320*, 1755–1759.
- (31) Furube, A.; Asahi, T.; Masuhara, H.; Yamashita, H.; Anpo, M. *J. Phys. Chem. B* **1999**, *103*, 3120–3127.
- (32) Henderson, M. A.; Epling, W. S.; Perkins, C. L.; Peden, C. H. F.; Diebold, U. *J. Phys. Chem. B* **1999**, *103*, 5328–5337.
- (33) Anpo, M.; Che, M.; Fubini, B.; Garrone, E.; Giamello, E.; Paganini, M. C. *Top. Catal.* **1999**, *8*, 189–198.
- (34) de Lara-Castells, M. P.; Krause, J. L. *J. Chem. Phys.* **2001**, *115*, 4798–4810.
- (35) de Lara-Castells, M. P.; Krause, J. L. *Chem. Phys. Lett.* **2002**, *354*, 483–490.
- (36) Green, J.; Carter, E.; Murphy, D. M. *Chem. Phys. Lett.* **2009**, *477*, 340–344.

JA106207W