Highly n-Type Titanium Oxide as an Electronically Active Support for Platinum in the Catalytic Oxidation of Carbon Monoxide

L. Robert Baker,‡† Antoine Hervier,‡† Hyungtak Seo,‡† Griffin Kennedy,‡† Kyriakos Komvopoulos,§ and Gabor A. Somorjai*‡†

1 Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
2 Department of Chemistry and 3 Department of Mechanical Engineering, University of California, Berkeley, California 94720, United States

3 Supporting Information

ABSTRACT: The role of the oxide-metal interface in determining the activity and selectivity of chemical reactions catalyzed by metal particles on an oxide support is an important topic in science and industry. A proposed mechanism for this strong metal–support interaction is electronic activation of surface adsorbates by charge carriers. Motivated by the goal of using electronic activation to drive nonthermal chemistry, we investigated the ability of the oxide support to mediate charge transfer. We report an approximately 2-fold increase in the turnover rate of catalytic carbon monoxide oxidation on platinum nanoparticles supported on stoichiometric titanium dioxide (TiO₂) when the TiO₂ is made highly n-type by fluorine (F) doping. However, for nonstoichiometric titanium oxide (TiOₓₓ<2) the effect of F on the turnover rate is negligible. Studies of the titanium oxide electronic structure show that the energy of free electrons in the oxide determines the rate of reaction. These results suggest that highly n-type TiO₂ electronically activates adsorbed oxygen (O) by electron spillover to form an active O⁻ intermediate.

INTRODUCTION

Although metals alone are often catalytically active, most industrial catalysts consist of metal particles supported on a porous oxide. This not only provides a high surface area for the heterogeneous catalyst, but as shown by many studies, the oxide support plays an important role in determining the activity and selectivity of the catalyst.¹–⁴ This phenomenon, known as the strong metal–support interaction (SMSI), has been widely studied and is an important topic in both science and industry.⁵

SMSI affects a wide range of catalytic reactions, including carbon monoxide (CO) and carbon dioxide (CO₂) hydrogenation,⁴–⁶ selective hydrogenation,⁷–⁹ and CO oxidation.¹⁰–¹３ Although not traditionally termed SMSI, the catalyst support also plays an important role in activating molecular oxygen for selective partial oxidation reactions. Industrially relevant examples include the synthesis of aldehydes from primary alcohols,¹⁴ the production of hydrogen peroxide from hydrogen,¹⁵–¹⁹ and the conversion of methane to synthesis gas.²⁰–²² In all of these cases, molecular oxygen is preferred over other oxygen donors due to cost, energy efficiency, and environmental concerns.¹⁴,²²

Titanium oxide is perhaps the best known example of an SMSI support.⁴,⁵ Additionally, titanium oxide is a common support for catalysts demonstrating high selectivity toward partial oxidation.¹⁴,¹⁸,²² The majority of proposed mechanisms for the role of titanium oxide fall into one of the following categories: (1) formation of active sites when the support wets (or “decorates”) the metal particle,²³,²⁴ (2) oxygen (O) activation and/or spillover from chemically active defects in the support,²⁵ and (3) electronic mediation through various forms of charge transfer.¹²,²⁶ Although each of these mechanisms can play an important role, this study focuses on the role of charge transfer and electronic mediation due to its importance in energy conversion reactions.

Previous studies have indicated that, at least in certain instances, catalytic oxidation reactions proceed by an electronically activated pathway.²⁷–³² Bonn et al.²⁷ showed that for CO oxidation on Ru, the activation of chemisorbed O occurs by charge transfer from the metal. Because the active O species cannot form thermally until well above the desorption temperature of CO, a temperature ramp of a CO/O₂ coadsorbed Ru surface produces CO and O₂ but not CO₂. However, a femtosecond laser pulse can produce very high electronic temperatures on the short time scale without significant lattice heating. This serves to activate the O without CO desorption, resulting in CO₂ formation.

Although fundamentally insightful, this type of experiment employing a femtosecond laser cannot be scaled for high turnover applications. Another approach to achieve electronic activation is to...
The electronic structure of the titanium oxide supports was characterized by XPS, spectroscopic ellipsometry, and measurements of surface conductivity and activation energy for charge transport.

XPS was used to analyze the chemical binding states of the titanium oxide films and the supported Pt catalysts both before and after reaction (Physical Electronics, PHI 5400 ESCA/XPS system with an Al anode source at 1486.6 eV). The analyzer was positioned at 50° relative to sample normal. All binding energies were calibrated to the Ti 2p peak state.

The real and imaginary parts of the complex dielectric constant, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, and absorption coefficients for titanium oxide samples were determined by visible-ultraviolet spectroscopic ellipsometry in a rotating compensator enhanced spectrometer. The monochromatic light source from a Xenon lamp at photon energies of 1.5–6 eV was used with spectral resolution of 15 meV.

To measure surface conductivity of the titanium oxide films, ohmic contact was made to the titanium oxide using thin film electrodes consisting of 10 nm Ti and 100 nm Au. All metals were deposited by electron beam evaporation. Measurements were made with a Keithley 2400 sourcemeter.

Reaction rates are reported in turnover frequency (TOF) as CO$_2$ molecules produced per Pt site per minute. All error bars represent the 95% confidence interval based on the rate of CO$_2$ production normalized to the estimated number of Pt sites. The number of Pt sites was estimated by assuming a uniform (111) surface coverage over the entire catalyst area. Although this calculation is approximate, it provides a consistent normalization to the catalyst area and yields a reasonable estimate of the absolute TOF.

**RESULTS AND DISCUSSION**

Figure 1 shows the effect of F on the reaction rate and on the surface conductivity of each stoichiometry. In the case of stoichiometric TiO$_2$, F doping increased the reaction rate by 61%, while F doping to TiO$_{1.7}$ and TiO$_{1.9}$ decreased the reaction rate by 21 and 8%, respectively. There is a surprising similarity between the effect of F on the turnover rate, and the effect of F on the surface conductivity of the titanium oxide support. As in the turnover rate measurements, F doping to TiO$_2$ dramatically increased (40-fold) the surface conductivity, while F doping to TiO$_{1.7}$ and to TiO$_{1.9}$ resulted in only a slight decrease (approximately 2-fold) in surface conductivity. We can explain these results by considering the electronic structure of stoichiometric and reduced titanium oxide. We characterized the electronic structure using two measurements: the activation energy of surface conduction and the optical absorption spectrum.
Figure 1. (A) Turnover frequencies (TOF) for CO oxidation on Pt nanoparticles supported on the six titanium oxide supports: TiO$_2$, TiO$_{1.9}$, and TiO$_{1.7}$, each with and without F insertion. Reaction occurred in 40 Torr CO, 100 Torr O$_2$, and 620 Torr He at 443 K. TOF data reflect the stable rate after ~30 min of deactivation. Error bars represent 95% confidence intervals. (B) Surface conductivity measurements for all six titanium oxide supports before Pt nanoparticle deposition. In the case of TiO$_2$, F insertion increased surface conductivity by a factor of 40 by acting as an extrinsic n-type donor. However, in the case of TiO$_{1.7}$ and TiO$_{1.9}$, F insertion slightly decreased the conductivity because F binds to Ti at O vacancy sites, resulting in the removal of subgap states that act as a transport channel in these samples. Note that TiO$_2$ with and without F is magnified by 10$^4$. This reflects the insulating nature of TiO$_2$ without the presence of a sub-band conduction channel. Comparison of panels A and B shows a surprising similarity between the effect of F on the TOF and on the surface conductivity.

To understand how the activation energy of transport relates to the electronic structure, it is necessary to consider the role of grain boundary defects in polycrystalline TiO$_2$. Grain boundaries produce defects in the band structure of titanium oxide with a localized defect state ~0.3 eV below the conduction band edge. Consequently, this is the activation energy for conduction in polycrystalline TiO$_2$ because electrons thermally trap and detrap at grain boundaries during transport. In contrast, O vacancies at high concentrations form a suboxide band structure at a reduced energy. This suboxide band shows semimetal, or nearly unactivated, electron transport.34

Figure 2A shows the activation energies for electron transport in TiO$_{1.7}$ and TiO$_2$. As expected, the highly reduced oxide shows low activation energy for conduction (0.07 eV) consistent with semimetal transport in a low-energy sub-band, while F-doped TiO$_2$ shows activation energy of 0.29 eV, consistent with conduction band transport across grain boundaries. TiO$_2$ without F was too insulating to accurately measure the activation energy of transport. However, F insertion into TiO$_{1.7}$ did not change the transport mechanism.

Figure 2B compares the optical absorption of TiO$_{1.7}$ and TiO$_2$. To illustrate the differences between these samples, we show the minimum excitation energy having a fixed absorption coefficient of 2 × 10$^4$ cm$^{-1}$. Full spectra are shown in Figure S3 (Supporting Information). We find that TiO$_{1.7}$ has a strong absorption located ~0.7 eV below the conduction band edge that arises from excitation of electron–hole pairs in the suboxide band. This measurement reflects the decrease in bandgap energy for the reduced oxide and shows the difference in the energy of free electrons in the two supports.

Figure 3A is a diagram of the two band structures of stoichiometric and reduced titanium oxide based on the above measurements. In the cases of both TiO$_{1.7}$ and TiO$_{1.9}$, F doping decreased the surface conductivity. The reason for this is that F binds to Ti at the sites of O vacancies resulting in passivation of defect states. Conduction in these samples occurs primarily in the suboxide band structure induced by the high concentration of O vacancies. Consequently, a decrease in the O vacancy concentration partially removes the conduction channel in these two samples. However, F insertion in the TiO$_2$ sample increased conductivity by a factor of 40. This is because F acts as an extrinsic n-type donor in metal oxide semiconductors, increasing the concentration of free electrons in the conduction band of TiO$_2$.35

Assuming a reaction mechanism where the rate-limiting step is activated by a conduction band electron from the titanium oxide support, the electronic structure of the titanium oxide explains the observed trend in reactivity. In the case of TiO$_{1.7}$ and TiO$_{1.9}$, the presence of F decreased the surface electron density in the oxide support resulting in a slightly reduced reaction rate. However, because the majority of electrons in these supports reside in the suboxide band at an energy that is presumably too low to induce chemistry, changes in electron density have a minimal effect on the reaction rate. In the case of TiO$_2$ where free carriers reside in the conduction band from which they can spill over to adsorbates, an increase of surface electron density...
induced by F correlates with a significant increase in catalytic activity by electronic activation.

We propose that the mechanism for electronic activation is electron spillover from TiO₂ to adsorbed O to form an activated O⁻ intermediate that readily reacts with CO. This is depicted schematically in Figure 3B. In the case of O vacancy doping, the energy of the suboxide band is 0.5–1.0 eV below the conduction band edge. This energy is much higher than kT (≥13 kT at a reaction temperature of 443 K). Consequently, a reaction pathway that is electronically activated by free carriers in the conduction band of TiO₂ would not be thermally accessible until a temperature of ~6000 K. However, because F insertion to TiO₂ increases the surface concentration of free electrons without formation of any midgap states, free electrons reside in the actual conduction band making this material an electronically active support for CO oxidation.

XPS and reaction kinetics provide evidence that electronic activation by the F-doped support occurs by electron spillover to surface O. Fresh catalysts prepared and treated under reaction conditions for 1 h at 373, 473, or 573 K showed significant changes in the O 1s spectrum that correlate with deactivation of the undoped catalyst. Figure 4A shows the O 1s XPS spectrum for the Pt/TiO₂ catalyst as-deposited (As-dep) and after 1 h under reaction conditions at 373, 473, and 573 K. The growth of surface O at high binding energy (∼532.5 eV) occurs with increasing reaction temperature. (B) Turnover frequency (TOF) data revealing the role of surface O to deactivate the undoped catalyst for CO oxidation. Following reaction at elevated temperature, the catalyst deactivated by a factor of 4. Removal of surface O by 100 Torr CO at 523 K restored the initial activity. Treatment in 100 Torr O₂ at 523 K again produced surface O resulting in deactivation. (C) Turnover frequency (TOF) data showing a change in catalyst activity at 443 K over 1 h. In all cases except for the Pt/TiO₂ – F, the catalyst deactivated over this time. This is attributed to the build-up of surface O. However, in the case of Pt supported on F-doped TiO₂, the activity increased by 49% during the reaction, indicating that the highly n-type support can electronically activate surface O as it forms for reaction with CO. Although not shown, F doping to the TiO₁.₇ and TiO₁.₉ catalysts did not result in a rate increase with time, suggesting the inability of electrons in the suboxide band to activate surface O.

Figure 3. (A) Band diagram depicting two types of transport in titanium oxide. Sub-band defect states in the reduced oxide provide a semimetal transport channel. In stoichiometric TiO₂ transport occurs in the actual conduction band. Because of grain boundary defects, conduction band transport is thermally activated as charges trap and detraps at grain boundaries. Although semimetal transport in the sub-band states is several orders higher than true conduction band transport, the carrier energy is 0.5 eV higher than kT (≈1.0 eV) below the conduction band edge. At this low energy, the electrons cannot activate surface O for reaction with CO. However, in stoichiometric TiO₂, electrons reside in the true conduction band. Charge transfer from the conduction band results in electronic activation of surface O for CO₂ formation.

Figure 4. (A) O 1s XPS spectrum for the Pt/TiO₂ catalyst as-deposited (As-dep) and after 1 h under reaction conditions at 373, 473, and 573 K. The growth of surface O at high binding energy (∼532.5 eV) occurs with increasing reaction temperature. (B) Turnover frequency (TOF) data revealing the role of surface O to deactivate the undoped catalyst for CO oxidation. Following reaction at elevated temperature, the catalyst deactivated by a factor of 4. Removal of surface O by 100 Torr CO at 523 K restored the initial activity. Treatment in 100 Torr O₂ at 523 K again produced surface O resulting in deactivation. (C) Turnover frequency (TOF) data showing a change in catalyst activity at 443 K over 1 h. In all cases except for the Pt/TiO₂ – F, the catalyst deactivated over this time. This is attributed to the build-up of surface O. However, in the case of Pt supported on F-doped TiO₂, the activity increased by 49% during the reaction, indicating that the highly n-type support can electronically activate surface O as it forms for reaction with CO. Although not shown, F doping to the TiO₁.₇ and TiO₁.₉ catalysts did not result in a rate increase with time, suggesting the inability of electrons in the suboxide band to activate surface O.
phenomenon. Surface O may bind and localize free electrons in the titanium oxide support that are necessary for activating the catalytic reaction. This suggests that O activation is rate limiting for CO oxidation and is consistent with the idea that electronic activation by the F-doped TiO$_2$ sample occurs by electron spillover to adsorbed O to form an activated O$^-$ intermediate. Figure 4C provides further evidence for this theory.

Figure 4C shows time-dependent reaction rate measurements for Pt on each TiO$_x$ stoichiometry and on F-doped TiO$_2$. Each undoped catalyst deactivated by 20–36% during 1 h under reaction conditions. However, Pt supported on F-doped TiO$_2$ showed a 49% rate increase. We propose that these kinetics correspond to the formation of surface O during the reaction and the ability or inability of electrons from the oxide support to activate it for CO$_2$ formation. The high energy of the electrons in the F-doped stoichiometric support is responsible for enhancing the catalytic activity by electron spillover. However, this effect cannot occur with catalysts containing high concentrations of O vacancies. Although there is a high density of free carriers in these supports, they are trapped in the suboxide band structure.

We also investigated the stability of F in reaction conditions at 373, 473, and 573 K. XPS showed that F concentration decreased with increasing reaction temperature and was undetectable after 1 h at 573 K. Figure S4 (Supporting Information) shows the F to Ti atomic ratio for F-doped TiO$_2$ as fabricated and after 1 h in reaction conditions at each of the three treatment temperatures. Although the surface F concentration began to decrease even at 473 K, it was still present at significant levels. Consequently, we safely assume that F remained in the support throughout the duration of the reaction rate measurements shown above which took place at 443 K.

**CONCLUSIONS**

We achieved approximately 2-fold increase in the reaction rate of CO oxidation on a Pt/TiO$_2$ catalyst when the TiO$_2$ is made n-type by F doping. A correlation of this effect with the electronic structure of titanium oxide indicates that the mechanism responsible for increased catalytic activity is activation of surface O by electron spillover from the oxide support.

Noting that certain catalytic reactions proceed by charged intermediates, it seems intuitive that hot carriers can activate nonthermal reaction pathways by spillover to surface adsorbates. Hot carriers are difficult to generate in a metal catalyst because of their fast relaxation times. However, n-type doping of oxide semiconductors is a feasible method for supplying charges of controlled energy to a catalytic interface. This unique utility of oxides also enlightens the properties of an oxide used to support metal clusters strongly influences the activity and selectivity of the catalyst system.

This result demonstrates that tuning the electronic structure of metal-oxide semiconductors used as catalyst supports can provide access to reaction pathways that on other catalysts would not be thermally accessible. This ability implicates applications in many other charge mediated processes, including energy conversion reactions, electrochemical processes, solid acid/base catalysis, and selective partial oxidation chemistry.

**REFERENCES**

(17) Fu, Q.; Saltsburg, H.; Flytzani-Stephanopoulos, M. Science 2003, 301, 935.
(23) Haruta, M. CATTECH 2002, 6, 102.

**AUTHOR INFORMATION**

*Corresponding Author*

E-mail: somorjai@berkeley.edu.

**ACKNOWLEDGMENT**

Deposition and processing of titanium oxide films took place in the Marvell Nanolab at the University of California, Berkeley (UCB). X-ray photoelectron spectroscopy and scattering electron microscopy took place in the Molecular Foundry at Lawrence Berkeley National Lab. This work was funded by the Helios Solar Energy Research Center and by the Chemical Sciences Division, which are supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 and by the UCB—KAUST Academic Excellence Alliance (AEA) Program.

**ASSOCIATED CONTENT**

$\text{Supporting Information.}$ Additional information and figures. This material is available free of charge via the Internet at http://pubs.acs.org.