Project Title: **Investigation of the Origin of Catalytic Activity in Oxide-Supported Nanoparticle Gold**

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A. **Abstract**

Since Haruta's discovery in 1987 of the surprising catalytic activity of supported Au nanoparticles, we have seen a very large number of experimental and theoretical efforts to explain this activity and to fully understand the nature of the behavior of the responsible active sites. In 2011, we discovered that a **dual catalytic site** at the perimeter of ~3nm diameter Au particles supported on TiO_2 is responsible for oxidative catalytic activity. O_2 molecules bind with Au atoms and Ti^{4+} ions in the TiO_2 support and the weakened O-O bond dissociates at low temperatures, proceeding to produce O atoms which act as oxidizing agents for the test molecule, CO. The papers supported by DOE have built on this finding and have been concerned with two aspects of the behavior of Au/TiO_2 catalysts: (1). Mechanistic behavior of dual catalytic sites in the oxidation of organic molecules such as ethylene and acetic acid; (2). Studies of the electronic properties of the TiO_2 (110) single crystal in relation to its participation in charge transfer at the occupied dual catalytic site. A total of 20 papers have been produced through DOE support of this work. The papers combine IR spectroscopic investigations of Au/TiO_2 catalysts with surface science on the $TiO_2(110)$ and TiO_2 nanoparticle surfaces with modern density functional modeling. The primary goals of the work were to investigate the behavior of the dual Au/Ti^{4+} site for the partial oxidation of alcohols to acids, the hydrogenation of aldehydes and ketones to alcohols, and the condensation of oxygenate intermediates- all processes related to the utilization of biomass in the production of useful chemical energy sources.

B. Specific Objectives and Results

Abstracts of papers are listed below:

Vibrational Spectroscopic Observation of Weakly Bound Adsorbed Molecular Oxygen on Powdered Titanium Dioxide

(Published in J. Phys. Chem. in 2010)

The adsorption of O_2 from air is an essential step in the use of TiO_2 as a photo-oxidation catalyst. This work explores the properties of a weakly bound O_2 species which is probably the precursor to “active” O_2 needed for the photo-oxidation of molecules by TiO_2. Adsorbed molecular oxygen was observed via FTIR for the first time on nanosized TiO_2 particles. The observed O-O stretching mode frequency at 1550 cm^{-1} is identical to the Raman displacement of O_2 gas, showing that the interaction between the IR active O_2 molecules and TiO_2 is relatively weak. It is noteworthy that weak adsorption of O_2 on TiO_2 is accompanied by the development of a weak IR absorption band due to the production of a small dipole in the molecule. In addition, the constant ν_{O_2} observed for increasing coverage indicates that the O_2 molecules exhibit only small interactions with each other in the adsorbed layer. The adsorption enthalpy of O_2 on TiO_2 is measured to be between -16 to -21 kJ mol^{-1}. The O_2^- species formed by O_2 adsorbing on TiO_2 surface defect sites (likely to be the active O_2 in photochemistry), with a calculated vibrational frequency of 1097 cm^{-1}, is not observed in this work. The influence of coadsorbed CO, CO_2, and H_2O with the adsorbed O_2 species was also investigated. It isfound that when the adsorbed surface species, such as CO, CO_2, and excess H_2O, screen the TiO_2 surface electric field and TiO_2 surface dispersion forces, the IR active O_2 species are no longer observed.

Spectroscopic Observation of Dual Catalytic Sites During Oxidation of CO on a Au/TiO_2 Catalyst

(Published in Science in 2011)

The prevailing view of CO oxidation on gold-titanium oxide (Au/TiO_2) catalysts is that the reaction occurs on metal sites at the Au/TiO_2 interface. We observed dual catalytic sites at the perimeter of 3-nanometer Au particles supported on TiO_2 during CO oxidation. Infrared-kinetic measurements indicate that O-O bond scission is activated by the formation of a CO-O_2 complex at dual Ti-Au sites at the Au/TiO_2 interface. Density functional theory calculations, which provide the activation barriers for the formation and bond scission of the CO-O_2 complex, confirm this model as well as the measured apparent activation energy of 0.16 electron volt. The observation of sequential delivery and reaction of CO first from TiO_2 sites and then from Au sites indicates that catalytic activity occurs at the perimeter of Au nanoparticles.

Low-Temperature Catalytic H_2 Oxidation over Au Nanoparticle/TiO_2 Dual Perimeter Sites

(Published in Angew. Chem. Int. Ed. in 2011)

To our best knowledge, there are no reported theoretical studies on the $H_2 + O_2$ reaction that have considered the influence or involvement of the TiO_2 perimeter sites at the Au–TiO_2 interface. Herein, we use kinetic analyses together with in situ infrared spectroscopic studies and density functional theory (DFT) calculations to examine the activity of the Au sites as well as the Au and TiO_2 perimeter sites at the Au–TiO_2 interface and elucidate a plausible reaction mechanism. (We define a perimeter site as a Au or TiO_2 site at the external boundary between Au and TiO_2 surfaces. A dual perimeter site involves a Au perimeter site and a TiO_2 perimeter site that operate together during the catalytic reaction.) In summary, the active site for the $H_2 + O_2$ reaction over a Au/TiO_2 nanoparticle catalyst at low temperature was located at dual perimeter sites at the interface between Au and TiO_2. AnO_2-assisted H_2 dissociation through a Ti_OOH intermediate was proposed involving an early transition state. The calculated activation energies for sequential steps in the range 0.13–0.25 eV agree with the measured apparent activation energy of 0.22 eV.

Electric Charge of Single Au Atoms Adsorbed on TiO_2(110) and Associated Band Bending

(Published in J. Phys. Chem. C in 2011)

The influence of charge transfer from single Au atoms to TiO_2(110) on the photostimulated desorption (PSD) of $^{18}O_2$ has been studied using a measurement of the rate of hole transport which mediates PSD. Band bending effects observed experimentally and theoretically by density functional theory indicate that $Au^{\delta+}$ atoms are present. The presence of atomically dispersed Au on the TiO_2(110) surface with a constant coverage of preadsorbed $^{18}O_2$ depresses the photoinduced hole transport rate from the bulk to the TiO_2 surface and decreases the $^{18}O_2$ PSD yield. This indicates that single Au atoms donate a fraction of an electron to the surface, causing downward band bending. DFT calculations show that~0.2 electron transfers from single Au atoms to the O_2/TiO_2(110) surface and the valence and conduction bands bend ~0.6 eV downward. With increasing Au coverage, the positive charge per Au atom decreases due to the formation of small Au clusters.

Mechanistic Studies of Hydrogen Dissociation and Spillover on Au/TiO2: IR Spectroscopy of Coadsorbed CO and H-Donated Electrons

(Published in J. Phys. Chem. C in 2011)

Transmission Fourier transform infrared spectroscopy, coupled with CO adsorption, was used to study how the oxidation state of Au surface sites change during H_2 dissociation, migration, and electronic excitation of TiO_2 in a nanoparticulate Au/TiO_2 catalyst. Data reveals that atomic H, produced by H_2 dissociation on Au particles, readily hydroxylates the Au-O-Ti linkages around the periphery of the gold particles. Following passivation of peripheral sites, the H atoms diffuse into the bulk of the titania where they protonate the semiconductor, while donating an electron to shallow trapped (ST) states just below the conduction band (CB). The donated electrons effectively n-dope the semiconductor. By simultaneously monitoring changes in the infrared absorbance due to transitions involving ST electrons, free CB electrons, and the fundamental stretching mode of CO(a), we have found that the most active sites for hydrogen dissociation are Au_0 sites at the free step edges or other defect sites in the Au nanoparticles that are located away from the Au-O-Ti interface.

Inhibition at Perimeter Sites of Au/TiO_2 Oxidation Catalyst by Reactant Oxygen

(Published in J. Am. Chem. Soc.in 2012)

TiO_2-supported gold nanoparticles exhibit surprising catalytic activity for oxidation reactions compared to noble bulk gold which is inactive. The catalytic activity is localized at the perimeter of the Au nanoparticles where Au atoms are atomically adjacent to the TiO_2 support. At these dual-catalytic sites an oxygen molecule is efficiently activated through chemical bonding to both

Au and Ti^{4+} sites. A significant inhibition by a factor of 22 in the CO oxidation reaction rate is observed at 120 K when the Au is preoxidized, caused by the oxygen-induced positive charge produced on the perimeter Au atoms. Theoretical calculations indicate that induced positive charge occurs in the Au atoms which are adjacent to chemisorbed oxygen atoms, almost doubling the activation energy for CO oxidation at the dual-catalytic sites in agreement with experiments. This is an example of self-inhibition in catalysis by a reactant species.

Localized Partial Oxidation of Acetic Acid at the Dual Perimeter Sites of the Au/TiO_2 Catalyst-Formation of Gold Ketenylidene

(Published in J. Am. Chem. Soc.in 2012)

Chemisorbed acetate species derived from the adsorption of acetic acid have been oxidized on a nano-Au/TiO_2 (~3 nm diameter Au) catalyst at 400 K in the presence of O_2(g). It was found that partial oxidation occurs to produce gold ketenylidene species, Au_2 =C=C=O. The reactive acetate intermediates are bound at the TiO_2 perimeter sites of the supported Au/TiO_2 catalyst. The ketenylidene species is identified by its measured characteristic stretching frequency $\nu(CO) = 2040\ cm^{-1}$ and by ^{13}C and ^{18}O isotopic substitution comparing to calculated frequencies found from density functional theory. The involvement of dual catalytic Ti^{4+} and Au perimeter sites is postulated on the basis of the absence of reaction on a similar nano-Au/SiO_2 catalyst. This observation excludes low coordination number Au sites as being active alone in the reaction. Upon raising the temperature to 473 K, the production of CO_2 and H_2O is observed as both acetate and ketenylidene species are further oxidized by O_2(g). The results show that partial oxidation of adsorbed acetate to adsorbed ketenylidyne can be cleanly carried out over Au/TiO_2 catalysts by control of temperature.

Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces

(Published in Chem. Rev. in 2012)

In this review, we focus on the principles of band bending and its effect on photochemistry and photocatalysis. This may be helpful to chemists and material scientists in the understanding of the photoexcitation process and the development of highly efficient photoactive materials and processes. The review is divided into three parts dealing with (1) the physical principles of band bending in semiconductors, (2) the measurement of band bending, and (3) the effects of band bending on photochemistry. The band bending concept is of course well established in semiconductor physics and has become one of the central concepts in electrochemistry and gas sensors.

Electron stimulated desorption, DIET, and photochemistry at surfaces: A personal recollection

(Published in J. Chem. Phys. in 2012)

A personal recollection of the beginning of the field of photochemistry on surfaces is given.

Direct Formation of Acetate from the Partial Oxidation of Ethylene on a Au/TiO_2 Catalyst

(Published in Top. Catal. in 2013)

The partial oxidation of ethylene to form adsorbed acetate on a Au/TiO_2 catalyst at temperatures as low as 370 K is reported here using Fourier transform infrared (FTIR) spectroscopy, gas chromatography-mass spectrometry (GC–MS) and density functional theory (DFT) calculations. Ethylene reacts with oxygen on Au/TiO_2 to produce acetate on the TiO_2 support as determined by the comparison with a blank TiO_2 and Au/SiO_2 catalyst. As shown by DFT calculations, O_2 dissociation occurs at the dual-perimeter Au–Ti^{4+} sites of Au/TiO_2 catalysts. Surprising, no ethylene oxide on the catalyst surface or in the gas phase is detected by either FTIR or GC–MS techniques at temperatures up to 673 K. The reaction pathway to ethylene oxide involves a higher barrier (~1.0–1.5 eV) than the pathway for acetate formation (~0.1–0.6 eV). The rate-limiting step to form adsorbed acetate was found to be the protonation of the $H_2C^*C(OH)O^*$ intermediate to produce the bound acetic acid. The theoretical initial deuterium kinetic isotope effect is ~3 which is consistent with the experimental data.

Mechanistic insights into the partial oxidation of acetic acid by O_2 at the dual perimeter sites of a Au/TiO_2 catalyst

(Published in Faraday Discuss. in 2013)

The unique interfacial sites of Au nanoparticles supported on TiO_2 are known to catalyze the activation of oxygen and it's addition to small molecules including H_2, CO, NO and propylene. Herein we extend these ideas and show that the unique Au–Ti dual perimeter sites that form at the Au/TiO_2 interface can also catalyze more demanding C–H and C–O bond activation reactions involved in the deoxygenation organic acids such as acetic acid. We have shown previously that acetic acid can be partially oxidized on a Au/TiO_2 catalyst to form a novel gold ketenylidene ($Au_2{=}C{=}C{=}O$) intermediate. In the present work we use in situ infrared spectroscopy and first-principle density functional theory (DFT) to examine the mechanism and the kinetics by which this reaction proceeds. The reaction was found to be localized at the dual perimeter sites of the Au/TiO_2 catalyst, where O_2 was activated. In contrast to Au/TiO_2, no ketenylidene formation was observed on a similar Au/SiO_2 catalyst or a TiO_2 blank sample. The reaction involves the activation of multiple C–H bonds as well as the C–O bond in the adsorbed CH_3COO species. C–O bond scission is postulated to occur at the TiO_2 sites, while C–H bond scission occurs on Au sites, both near the active Au–Ti^{4+} dual perimeter sites. $^{18}O_2$ isotopic labeling indicated that the O moiety of the ketenylidene species originates from the acetic acid during the oxidation process involving molecular O_2. The rate-limiting step was found to be the C–O bond scission resulting in an apparent overall activation energy of 1.72 eV as determined from DFT calculations. This is in very good agreement with the experimentally measured apparent activation energy of 1.7 ± 0.2 eV. A deuterium kinetic isotope effect of ~4 indicates that C–H bond activation is kinetically involved in the overall acetate oxidation reaction.

Defect-Electron Spreading on the TiO_2(110) Semiconductor Surface by Water Adsorption

(Published in J. Phys. Chem. Lett. in 2013)

The dissociative adsorption of water at oxygen-vacancy defect sites on the TiO_2(110) surface spatially redistributes the defect electron density originally present at subsurface sites near the defect sites. This redistribution of defect-electrons makes them more accessible to Ti^{4+} ions surrounding the defects. The redistribution of electron density decreases the O^+ desorption yield from surface lattice O_2^- ions in TiO_2, as excited by electron-stimulated desorption (ESD). A model in which OH formation on defect sites redistributes defect electrons to neighboring Ti^{4+} sites is proposed. This switches off the Knotek−Feibelman mechanism for ESD of O^+ ions from lattice sites. Conversely, enhanced O^+ reneutralization could also be induced by redistribution of defect electrons. The redistribution of surface electrons by adsorption is further verified by the use of donor and acceptor molecules that add or remove electron density.

Insights into Catalytic Oxidation at the Au/TiO_2 Dual Perimeter Sites

(Published in Acc.Chem. Res. 2014)

Gold (Au) nanoparticles supported on reducible oxides such as TiO_2 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/TiO_2 catalysts. We provide transmission IR spectroscopic data that show the direct involvement of the Au–Ti^{4+} 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–Ti^{4+} sites in adsorbing and activating O_2 as a result of charge transfer from the Au into antibonding states on O_2 causing di-σ interactions with interfacial Au–Ti^{4+} sites. This results in apparent activation energies for O_2 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 O_2 directly reacts with co-adsorbed CO or H_2.

In addition, we observe the specific consumption of CO adsorbed on TiO_2. 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, O_2 directly dissociates to form active oxygen adatoms (O*) on Au and TiO_2. 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–Ti^{4+} sites are pre-occupied by O*, the low temperature CO oxidation rate is reduced by a factor 22. We observe similar site blocking for H_2 oxidation by O_2, 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 TiO_2 (CH_3COO/TiO_2) to a gold ketenylidene species ($Au_2{=}C{=}C{=}O$).

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–Ti^{4+} dual perimeter sites. There is a bound-intermediate transfer from the TiO_2 support to the Au sites during the course of reaction as the reactant (CH_3COO/TiO_2) and the product ($Au_2{=}C{=}C{=}O$) 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.

Selective Catalytic Oxidative-Dehydrogenation of Carboxylic Acids—Acrylate and Crotonate Formation at the Au/TiO_2 Interface

(Published in JACS 2014)

The oxidative-dehydrogenation of carboxylic acids to selectively produce unsaturated acids at the second and third carbons regardless of alkyl chain length was found to occur on a Au/TiO_2 catalyst. Using transmission infrared spectroscopy (IR) and density functional theory (DFT), unsaturated acrylate ($H_2C{=}CHCOO$) and crotonate ($CH_3CH{=}CHCOO$) were observed to form from propionic acid (H_3CCH_2COOH) and butyric acid ($H_3CCH_2CH_2COOH$), respectively, on a catalyst with ∼3 nm diameter Au particles on TiO_2 at 400 K. Desorption experiments also show gas phase acrylic acid is produced. Isotopically labeled ^{13}C and ^{12}C propionic acid experiments along with DFT calculated frequency shifts confirm the formation of acrylate and crotonate. Experiments on pure TiO_2 confirmed that the unsaturated acids were not produced on the TiO_2 support alone, providing evidence that the sites for catalytic activity are at the dual Au–Ti^{4+} sites at the nanometer Au particles' perimeter. The DFT calculated energy barriers between 0.3 and 0.5 eV for the reaction pathway are consistent with the reaction occurring at 400 K on Au/TiO_2.

Electric Field Changes on Au Nanoparticles on Semiconductor Supports - The Molecular Voltmeter and Other Methods to Observe Adsorbate-Induced Charge-Transfer Effects in Au/TiO_2 Nanocatalysts

(Published in JACS 2015)

Infrared (IR) studies of Au/TiO_2 catalyst particles indicate that charge transfer from van der Waals bound donor or acceptor molecules on TiO_2 to or from Au occurs via transport of charge carriers in the semiconductor TiO_2 support. The $\Delta\nu_{CO}$ on Au is shown to be proportional to the polarizability of the TiO_2 support fully covered with donor or acceptor molecules, producing a proportional frequency shift in ν_{CO}. Charge transfer through TiO_2 is associated with the population of electron trap sites in the bandgap of TiO_2 and can be independently followed by changes in photoluminescence intensity and by shifts in the broad IR absorbance region for electron trap sites, which is also proportional to the polarizability of donors by IR excitation. Density functional theory calculations show that electron transfer from the donor molecules to TiO_2 and to supported Au particles produces a negative charge on the Au, whereas the transfer from the Au particles to the TiO_2 support into acceptor molecules results in a positive charge on the Au. These changes along with the magnitudes of the shifts are consistent with the Stark effect. A number of experiments show that the ∼3 nm Au particles act as "molecular voltmeters" in influencing $\Delta\nu_{CO}$. Insulator particles, such as SiO_2, do not display electron-transfer effects to Au particles on their surface. These studies are preliminary to doping studies of semiconductor-oxide particles by metal ions which modify Lewis acid/base oxide properties and possibly strongly modify the electron-transfer and catalytic activity of supported metal catalyst particles.

Mechanistic Insights in the Catalytic Oxidation of Carboxylic Acids on Au/TiO_2 – Partial Oxidation of Propionic and Butyric Acid to Gold Ketenylidene through Unsaturated Acids

(Published in ACS Catalysis 2015)

The oxidative-dehydrogenation of model C_2-C_4 (acetic, propionic and butyric) carboxylic acids on Au/TiO_2 catalysts comprised of Au particles ~3 nm in size was investigated using transmission infrared (IR) spectroscopy and density functional theory (DFT). All three acids readily deprotonate to form their carboxylate analogs on the TiO_2 support which subsequently react to form a gold ketenylidene, $Au_2C=C=O$, intermediate along the way to their full oxidation. Hence the IR measurement of the kinetics of $Au_2C=C=O$ formation provides a surface spectroscopic method that kinetically probes alkyl group activation in the carboxylate intermediates that form. The reaction proceeds via the dissociative adsorption of the acid onto TiO_2, the adsorption and activation of O_2 at the dual perimeter sites on the Au particles (Au-O-O-Ti) and the subsequent activation of the □and □C-H bonds of the bound propionate and butyrate species by the weakly-bound and basic oxygen species on the Au to form acrylate and crotonate intermediates, respectively. These unsaturated carboxylates can readily oxidize via a nucleophilic attack of the C=C bond by a basic O species on Au thus promoting the activation of the $C_{□}$-$C_{□}$ bond and subsequent activation of the C-O bond of the carboxylate group. This occurs with an overall activation energy of 1.5-1.7 ± 0.2 eV, eventually producing the $Au_2C=C=O$ species for all three carboxylates. The results suggest that the decrease in the rate in moving from acetic to propionic to butyric acid is due to an increase in the free energy of activation for the formation of the $Au_2C=C=O$ species on Au/TiO_2 with an increasing size of the alkyl substituent.

The formation of $Au_2C=C=O$ proceeds for carboxylic acids that are longer than C_2 without a deuterium kinetic isotope effect, demonstrating that C-H bond scission is not involved in the rate-determining step; the rate instead appears to be controlled by C-O bond scission. The adsorbed $Au_2C=C=O$ intermediate species can be hydrogenated to produce ketene, $H_2C=C=O(g)$, with an activation energy of 0.21 ± 0.05 eV. These studies show that selective oxidative-dehydrogenation of the alkyl side chains of fatty acids can be catalyzed by nanoparticle Au/TiO_2 at temperatures near 400 K.

Defects on TiO_2 – Key Pathways to Important Surface Processes

(Published book chapter in Springer Series in Surface Sciences: Defects on Oxide Surfaces, 2015)

Defects govern most of the applications of TiO_2 in the fields of catalysis, photocatalysis and photoelectronics. In this chapter we present a general introduction to defects in solids. We then present surface science studies of point defects in TiO_2 and their influence on the chemistry and photochemistry behavior of TiO_2. The principles illustrated for TiO_2 apply also to other oxide-semiconductors and insulators.

Formation, Migration, and Reactivity of Au-CO Complexes on Gold Surfaces

(Published in J. Am. Chem. Soc. 2016)

We report experimental as well as theoretical evidence that suggests Au−CO complex formation upon the exposure of CO to active sites (step edges and threading dislocations) on a Au(111) surface. Room-temperature scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy, transmission infrared spectroscopy, and density functional theory calculations point to Au−CO complex formation and migration. Room-temperature STM of the Au(111) surface at CO pressures in the range from 10^{-8} to 10^{-4} Torr (dosage up to 10^{6} langmuir) indicates Au atom extraction from dislocation sites of the herringbone reconstruction, mobile Au−CO complex formation and diffusion, and Au adatom cluster formation on both elbows and step edges on the Au surface. The formation and mobility of the Au−CO complex result from the reduced Au−Au bonding at elbows and step edges leading to stronger Au−CO bonding and to the formation of a more positively charged CO ($CO^{\delta+}$) on Au. Our studies indicate that the mobile Au−CO complex is involved in the Au nanoparticle formation and reactivity, and that the positive charge on CO increases due to the stronger adsorption of CO at Au sites with lower coordination numbers.

A new form of chemisorbed photo- and electro-active atomic H species on the $TiO_2(110)$ surface

(Published in Surf. Sci. 2016)

Hydrogen adsorption on TiO_2 is of importance in chemical and photochemical reduction processes. Using several surface science methods,we clearly distinguish two kinds of H species on the surface of rutile $TiO_2(110)$-1 × 1. In contrast with the well-studied bridge-bonded OH species (α-H) originating from H_2O dissociation on the surface oxygen vacancy site on $TiO_2(110)$, atomic H adsorption on the $TiO_2(110)$ (denoted as β-H) exhibits special high sensitivity to the electronic excitation of the $TiO_2(110)$ by either electrons or UV photons. The formation of molecular H_2 gas by photoexcitation of β-H/$TiO_2(110)$ surfaces has been observed, which may shed light on the basic understanding of the processes of photocatalytic H_2 production by splitting water.

Anatase-Selective Photoluminescence Spectroscopy of P25 TiO_2 Nanoparticles: Different Effects of Oxygen Adsorption on the Band Bending of Anatase

(Published in J. Phys. Chem. C 2017)

Photoluminescence (PL) spectroscopy was used to infer that oxygen adsorption changes the band bending of the anatase phase of TiO_2 within P25 nanopowder in different ways. On the one hand, oxygen can adsorb through irreversible reaction with defects which reduces the intrinsic upward band bending at the TiO_2 surface and results in increased PL emission. On the other hand, oxygen exposure also leads to molecular chemisorption that yields an outermost negative charge at the surface which increases the upward band bending of TiO_2 and decreases the PL emission. Since band bending plays an active role in directing charge carrier migration to the surface, the finding that oxygen adsorption can have two different, and quite opposite, effects on the band bending of TiO_2 provides a new perspective on how oxygen may influence photocatalytic reaction efficiencies.

C. Special Recognitions of PI Yates

1. Associate Editor- Chemical Reviews (2013).
2. Gerhard Ertl Lecturer- Berlin (2013).

D. Human Resource Outcomes/ Current Affiliations

Zhen Zhang/ Asst Professor , Harbin Institute of Technology, China

Isabel Green/ Asst Professor, Dept. of Chemistry, Illinois State University, Normal, IL

Monica McEntee/ ORISE Postdoctoral Fellow, Edgewood Chemical Biological Center, MD

Ana Stevanovic/ Postdoc with Cynthia Friend, Dept. of Chemistry, Harvard University.MA

E. DOE Funded Publications

1. X. Green, and J. T. Yates, "Vibrational Spectroscopic Observation of Weakly Bound Adsorbed Molecular Oxygen on Powdered Titanium Dioxide", J. Phys. Chem. C **114**, 11924-11930 (2010)
2. X. Green, W. J. Tang, M. Neurock, and J. T. Yates, "Spectroscopic Observation of Dual Catalytic Sites During Oxidation of CO on a Au/TiO_2 Catalyst", Science **333**, 736-739 (2011)
3. I. X. Green, W. J. Tang, M. Neurock, and J. T. Yates, "Low-Temperature Catalytic H_2 Oxidation over Au Nanoparticle/TiO_2 Dual Perimeter Sites", Angew. Chem. Int. Ed. **50**, 10186-10189 (2011)
4. Z. Zhang, W. J. Tang, M. Neurock, and J. T. Yates, "Electric Charge of Single Au Atoms Adsorbed on TiO_2(110) and Associated Band Bending", J. Phys. Chem. C **115**, 23848-23853 (2011)
5. D. A. Panayotov, S. P. Burrows, J. T. Yates, and J. R. Morris, "Mechanistic Studies of Hydrogen Dissociation and Spillover on Au/TiO2: IR Spectroscopy of Coadsorbed CO and H-Donated Electrons", J. Phys. Chem. C **115**, 22400-22408 (2011)
6. X. Green, W. J. Tang, M. McEntee, M. Neurock, and J. T. Yates, "Inhibition at Perimeter Sites of Au/TiO_2 Oxidation Catalyst by Reactant Oxygen", J. Am. Chem. Soc. **134**, 12717-12723 (2012)
7. X. Green, W. J. Tang, M. Neurock, and J. T. Yates, "Localized Partial Oxidation of Acetic Acid at the Dual Perimeter Sites of the Au/TiO_2 Catalyst-Formation of Gold Ketenylidene", J. Am. Chem. Soc. **134**, 13569-13572 (2012)
8. Z. Zhang, and J. T. Yates, "Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces", Chem. Rev. **112**, 5520-5551 (2012)
9. J. T. Yates, "Electron stimulated desorption, DIET, and photochemistry at surfaces: A personal recollection", J. Chem. Phys. **137** (2012)
10. X. Green, M. McEntee, W. J. Tang, M. Neurock, and J. T. Yates, "Direct Formation of Acetate from the Partial Oxidation of Ethylene on a Au/TiO_2 Catalyst", Top. Catal. **56**, 1512-1524 (2013)
11. X. Green, W. J. Tang, M. Neurock, and J. T. Yates, "Mechanistic insights into the partial oxidation of acetic acid by O_2 at the dual perimeter sites of a Au/TiO_2 catalyst", Faraday Discuss. **162**, 247-265 (2013)
12. Z. Zhang, K. Cao, and J. T. Yates, "Defect-Electron Spreading on the TiO_2(110) Semiconductor Surface by Water Adsorption", J. Phys. Chem. Lett. **4**, 674-679 (2013)

13. X. Green, W. J. Tang, M. Neurock, and J. T. Yates, "Insights into Catalytic Oxidation at the Au/TiO_2 Dual Perimeter Sites", Acc. Chem. Res. **47**, 805-815 (2014)
14. M. McEntee, W. J. Tang, M. Neurock, and J. T. Yates, "Selective Catalytic Oxidative-Dehydrogenation of Carboxylic Acids-Acrylate and Crotonate Formation at the Au/TiO_2 Interface", J. Am. Chem. Soc. **136**, 5116-5120 (2014)
15. M. McEntee, A. Stevanovic, W. J. Tang, M. Neurock, and J. T. Yates, "Electric Field Changes on Au Nanoparticles on Semiconductor Supports - The Molecular Voltmeter and Other Methods to Observe Adsorbate-Induced Charge-Transfer Effects in Au/TiO_2 Nanocatalysts", J. Am. Chem. Soc. **137**, 1972-1982 (2015)
16. M. McEntee, W. Tang, M. Neurock, and J. T. Yates, "Mechanistic Insights into the Catalytic Oxidation of Carboxylic Acids on Au/TiO_2: Partial Oxidation of Propionic and Butyric Acid to Gold Ketenylidene through Unsaturated Acids", ACS Catalysis **5**, 744-753 (2015)
17. J. T. Yates, and Z. Zhang, "Defects on TiO_2 - Key Pathways to Important Surface Processes" in *Springer Series in Surface Sciences: Defects on Oxide Surfaces*, eds. J. Jupille, and G. Thornton (Springer, Berlin, 2015)
18. J. Wang, M. McEntee, W. J. Tang, M. Neurock, A. P. Baddorf, P. Maksymovych, and J. T. Yates, "Formation, Migration, and Reactivity of Au-CO Complexes on Gold Surfaces", J. Am. Chem. Soc. **138**, 1518-1526 (2016)
19. Z. Zhang, and J. T. Yates, "A new form of chemisorbed photo- and electro-active atomic H species on the TiO_2(110) surface", Surf. Sci. **652**, 195-199 (2016)
20. S. L. Ma, M. E. Reish, Z. Zhang, I. Harrison, and J. T. Yates, "Anatase-Selective Photoluminescence Spectroscopy of P25 TiO_2 Nanoparticles: Different Effects of Oxygen Adsorption on the Band Bending of Anatase", J. Phys. Chem. C **121**, 1263-1271 (2017)