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# Ionizing Radiation Induced Catalysis on Metal Oxide Particles

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## Research Objective

This project focuses on a novel approach for destroying organics found in high-level mixed waste prevalent at DOE sites. In this project, we propose that organics can be destroyed by using reduction/oxidation (redox) chemistry resulting from electron-hole ( $e^-/h^+$ ) pairs generated in stable, wide bandgap semiconductors via interactions with ionizing radiation. Conceptually, this process is an extension of visible and near-UV (ultraviolet) photocatalytic processes known to occur at the interfaces of narrow bandgap semiconductors in both solution and gas phases. In these processes, an electron is excited across the energy gap between the filled and empty states in the semiconductor. The excited electron does reductive chemistry and the hole (whence the electron was excited) does oxidative chemistry. The energy separation between the hole and the excited electron reflects the redox capability of the  $e^-/h^+$  pair, and is dictated by the energy of the absorbed photon and the bandgap of the material. The use of ionizing radiation overcomes optical transparency limitations associated with visible and near-UV illumination ( $\gamma$ -rays penetrate much farther into a solution than UV/Vis light), and permits the use of wider bandgap materials (such as  $ZrO_2$ ), which possess potentially greater redox capabilities than those with narrow bandgap materials.

Planned experiments are aimed at extending the body of knowledge about  $e^-/h^+$  pair chemistry of semiconducting metal oxide (MO) materials by examining the influence of surface structure, defects, and dopants on the photocatalytic activity of narrow bandgap materials ( $TiO_2$ ), and by expanding these studies to wider bandgap materials ( $ZrO_2$ ) that are virtually unexplored in terms of their  $e^-/h^+$  pair chemistry. Experiments are being conducted in three areas: 1)  $\gamma$ -radiocatalysis of reactant-colloidal MO solutions, 2) photoelectrochemical studies at model MO electrodes, and 3) photochemical studies in ultra-high vacuum (UHV) and high pressures on model MO surfaces. An outcome of this proposed work will be a more thorough evaluation of the use of ionizing radiation in the catalytic remediation of organics (and other problem species) in high-level mixed waste.

## Problem Statement

High-level radioactive waste storage tanks at DOE sites contain significant amounts of organic components (solid and liquid phases) in the form of solvents, extractants, complexing agents, process chemicals, cleaning agents, and a variety of miscellaneous compounds. These organics pose several safety and pretreatment concerns, particularly for the Hanford tank waste. All currently proposed tank waste cleanup alternatives encounter potential safety and/or pretreatment problems associated with organics, particularly Hanford tank waste. Remediation technologies are needed that significantly reduce the amounts of problem organics without resulting in toxic or flammable gas emissions and without requiring thermal treatments. These restrictions pose serious technological barriers for current organic destruction methods, which use oxidation achieved by thermal or chemical activation.

## Research Progress

### Probing the Mechanism of Radiocatalytic Oxidation and Reduction

In the first two years of this program, we examined in detail the radiocatalytic destruction of EDTA, a typical chelating agent found in DOE tank waste, over various TiO<sub>2</sub> catalysts. In the final year of this program, we have conducted similar studies on smaller probe organic molecules (such as ethanol, formic acid, and acetic acid). Our results show that solution-phase radiolytic processes dominate those associated with the TiO<sub>2</sub> surface to the extent that any catalytic effects are not detected. This contrasts with the catalytic destruction of EDTA, which was greater than solution-phase radiolysis. UV-based experiments did show significant destruction of these small organics, in agreement with the literature. The presence of platinumized TiO<sub>2</sub>, however, significantly increased the production of hydrogen during the destruction of these small organics, presumably through the interaction of solution-phase radicals with the catalyst surface.

A comparison of radiocatalytic and photocatalytic methods for the reduction of noble metal cations and for the decomposition of water has also been conducted. Specifically, the experiments were performed by irradiating carboxylic acid solutions containing H<sub>2</sub>PtCl<sub>6</sub>/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> with  $\gamma$ -rays from a <sup>60</sup>Co source and with UV light from a mercury lamp. The gas phase and liquid phase products were then analyzed using gas chromatography and high-performance liquid chromatography. Results show that the presence of the above catalysts and  $\gamma$ -irradiation significantly promotes the platinum ion reduction and hydrogen production. The  $\gamma$ -ray radiocatalytic generation of H<sub>2</sub> over platinumized TiO<sub>2</sub> is consistent with those obtained from UV photocatalysis. These results show that  $\gamma$ -irradiation of TiO<sub>2</sub> can simultaneously promote both reduction and oxidation, further suggesting that the e<sup>-</sup>/h<sup>+</sup> mechanism is in effect with  $\gamma$ -irradiation.

Along this line, we have also shown that radiocatalytic reductive deposition of noble metals, such as Pt, onto TiO<sub>2</sub> can explain the generation of benzene from tetraphenylborate (TPB) in Savannah River waste tanks. Our studies show that radiation (either ionizing or not) is not required for TPB decomposition on noble metal impregnated TiO<sub>2</sub>; i.e., the thermal decomposition is highly facile even at room temperature. However, when noble metal ions, which are known to exist in the waste along with colloidal titanates, are irradiated they reductively precipitate on the titanates, opening the door for thermal decomposition of TPB.

## **Probing the Role of Surface Defects in Thermal and Photochemical Processes**

To understand better on a molecular level how redox processes occur on TiO<sub>2</sub> surfaces and how surface structure influences these processes, we have conducted a variety of UHV studies on model TiO<sub>2</sub> surfaces focusing on the role of defects in surface chemistry.

Because molecular oxygen is key in photo-oxidation processes, we have examined the interaction of molecular oxygen with the TiO<sub>2</sub>(110) surface using temperature programmed desorption (TPD), isotopic labeling studies, sticking probability measurements, and electron energy loss spectroscopy (ELS). Molecular oxygen does not adsorb on the TiO<sub>2</sub>(110) surface in the temperature range between 100 and 300K unless surface oxygen vacancy sites are present. These vacancy defects are generated by annealing the crystal at 850K and can be quantified reliably using water TPD. Adsorption of O<sub>2</sub> at 120K on a TiO<sub>2</sub>(110) surface with 8% oxygen vacancies (about 4 x 10<sup>13</sup> sites/cm<sup>2</sup>) occurs with an initial sticking probability of 0.5 to 0.6 that diminishes as the surface is saturated. The saturation coverage at 120K, as estimated by TPD uptake measurements, is approximately three times the surface vacancy population. Coverage-dependent TPD shows little or no O<sub>2</sub> desorption below a coverage of 4 x 10<sup>13</sup> molecules/cm<sup>2</sup> (the vacancy population), presumably due to dissociative filling of the vacancy sites in a 1:1 ratio. Above a coverage of 4 x 10<sup>13</sup> molecules/cm<sup>2</sup>, a first order O<sub>2</sub> TPD peak appears at 410K. Oxygen molecules in this peak do not scramble oxygen atoms with either the surface or with other co-adsorbed oxygen molecules. Sequential exposures of <sup>16</sup>O<sub>2</sub> and <sup>18</sup>O<sub>2</sub> at 120K indicate that each adsorbed O<sub>2</sub> molecule, irrespective of its adsorption sequence, has equivalent probabilities with respect to its neighbors to follow the two channels

(molecular and dissociative) suggesting that O<sub>2</sub> adsorption is not only precursor-mediated, as the sticking probability measurements indicate, but that all O<sub>2</sub> molecules reside in this precursor state at 120K. This precursor state may be associated with a weak 145K O<sub>2</sub> TPD state observed at high O<sub>2</sub> exposures. ELS measurements suggest charge transfer from the surface to the O<sub>2</sub> molecule based on disappearance of the vacancy loss feature at 0.8 eV and the appearance of a 2.8 eV loss that can be assigned to an adsorbed O<sub>2</sub><sup>-</sup> species based on comparisons with Ti-O<sub>2</sub> inorganic complexes in the literature. Using results from recent spin-polarized DFT calculations in the literature, we propose a model in which three O<sub>2</sub> molecules are bound in the vicinity of each vacancy site at 120K. For adsorption temperatures above 150K, the dissociation channel completely dominates and the surface adsorbs oxygen in a 1:1 ratio with each vacancy site. ELS measurements indicate that the vacancies are filled, and the remaining oxygen adatom, which is apparent in TPD, is transparent in ELS. Based on the variety of oxygen adsorption states observed in this study, further work is needed to determine which oxygen-related species play important roles in chemical and photochemical oxidation processes on TiO<sub>2</sub> surfaces.

By means of postirradiation TPD, we have investigated further the states of oxygen adsorbed on rutile TiO<sub>2</sub>. Previous work has shown that annealing the (110) surface in vacuum produces isolated bridging oxygen vacancies, and that these vacancies are intimately connected with molecular and dissociative oxygen adsorption channels. We find that, at 120K, illumination of the oxygen exposed surface with photons having energies above the band gap (>3.6 eV) results in photodesorption of the molecularly bound oxygen, in contrast to the remaining oxygen destined for the dissociative channel. An unusual effect of water overlayers on the O/TiO<sub>2</sub>(110) system is explored. For thick overlayers (>2 mL), it is possible to generate via UV irradiation a previously unobserved oxygen TPD state.

We have also examined the interaction of these oxygen-related species with a simple organic species, methanol. The chemistry of methanol was explored on the vacuum-annealed TiO<sub>2</sub>(110) surface, with and without the presence of co-adsorbed water and oxygen, using TPD, high-resolution electron energy loss spectroscopy (HREELS), SSIMS, and low-energy electron diffraction (LEED). The vacuum-annealed TiO<sub>2</sub>(110) surface possessed about 8% oxygen vacancy sites, as determined with H<sub>2</sub>O TPD. Although evidence is presented for CH<sub>3</sub>OH dissociation to methoxyl groups on the vacuum-annealed TiO<sub>2</sub>(110) surface using SSIMS and HREELS, particularly at vacancy sites, the majority of the adlayer was molecularly adsorbed, evolving in TPD at 295K. Although no evidence of irreversible decomposition was found in the TPD, dissociative CH<sub>3</sub>OH adsorption at 135K on the vacuum-annealed TiO<sub>2</sub>(110) surface led to recombinative desorption states at 350 and 480K, corresponding to methoxyls adsorbed at non-vacancy and vacancy sites, respectively. Co-adsorbed water had little or no influence on the chemistry of CH<sub>3</sub>OH on the vacuum-annealed TiO<sub>2</sub>(110) surface; however, new channels of chemistry were observed when CH<sub>3</sub>OH was adsorbed on the surface after O<sub>2</sub> adsorption at various temperatures. In particular, O<sub>2</sub> exposure at 300K resulted in O adatoms (via dissociation at vacancies) that led to increased levels of CH<sub>3</sub>O-H bond cleavage. The higher surface coverage of methoxyl then resulted in a disproportionation reaction to form CH<sub>3</sub>OH and H<sub>2</sub>CO above 600K. In contrast, low temperature exposure of the vacuum-annealed TiO<sub>2</sub>(110) surface to O<sub>2</sub> resulted in low temperature state of O<sub>2</sub> (presumably an O<sub>2</sub><sup>-</sup> species) that oxidized CH<sub>3</sub>OH to H<sub>2</sub>CO by C-H bond cleavage. These results provide incentive to consider alternative thermal and photochemical oxidation mechanisms that involve the interaction of organics and oxygen at surface defect sites. We have begun EPR studies on TiO<sub>2</sub> to characterize both surface and bulk defects resulting from radiation.

Working with Jürg Osterwalder at the University of Zurich, we have performed experiments mapping the 3-D Fermi surface of rutile TiO<sub>2</sub>(110). Our recent investigations at Pacific Northwest National Laboratory suggest that the reduction of TiO<sub>2</sub> surfaces may be an important step in the radiation-induced chemistry that occurs under aqueous conditions. The reduction of TiO<sub>2</sub> results in the formation of a Fermi

surface. The Fermi surface is an important quantity because it determines many of the properties of the material (e.g., the chemical properties, the electrical and thermal conductivities, etc.). Also, recent theoretical investigations suggest that reduced TiO<sub>2</sub> has a spin-polarized state that is stabilized at defect sites. These theoretical investigations may provide insight into the chemistry of paramagnetic molecules (e.g., NO, O<sub>2</sub>) with the defective surface. For example, it was theoretically proposed, contrary to prior investigations, that the defect state for reduced TiO<sub>2</sub> is not localized on a single site. This has led to proposed structural models that suggest these delocalized states may, in fact, help stabilize the adsorption of molecules at the surface.

Experiments were performed on reduced TiO<sub>2</sub> to determine the dispersion of the defect state and perform Fermi-surface mapping, ultraviolet photoelectron diffraction, and x-ray photoelectron diffraction. Our preliminary results suggest that point defects such as oxygen vacancy sites, although localized entities from a structural perspective, have longer-ranging influence on the electronic structure of the TiO<sub>2</sub> surface. This delocalization of electrons at point defects has significant influence on the adsorption and reaction of molecules and may also influence the trapping of photoexcited charge carriers. We have measured the dispersion of the defect state along several different directions to experimentally investigate this effect. Results show that although the highest intensity along  $k_{\parallel}$  is at nearly -0.8 eV, a significant shift occurs from -0.9 to -0.8 eV at  $k_{\parallel} = 1.2$  to 1.5. This small but significant dispersion in the defect state is the first experimental evidence for delocalization of this state for reduced TiO<sub>2</sub>.

The intensity of the feature at the Fermi energy ( $E_f$ ) can furthermore be monitored over the full  $2\pi$  above the surface. Comparison of these results will be made to theoretical calculations. The calculations will provide information on the surface structure surrounding the defect state as well as the orbital that the electron occupies (i.e., which of the five 3-d orbitals).

## Planned Activities

We are currently conducting EPR studies on the bulk and surface defects on TiO<sub>2</sub> rutile, analyzing results from the surface mapping of defects on TiO<sub>2</sub>(110), and conducting studies on aluminum-doped TiO<sub>2</sub>. Other activities focus on writing (for publication) the results mentioned in this report before the end of this program in August of this year.

## Publications

Epling WS, CHF Peden, MA Henderson, and U Diebold. 1998. "Evidence for oxygen adatoms on TiO<sub>2</sub>(110) resulting from O<sub>2</sub> dissociation at vacancy sites." *Surf. Sci.* 412-413:333.

Henderson MA, WS Epling, CL Perkins, CHF Peden, and U Diebold. 1999. "Interaction of molecular oxygen with the vacuum annealed TiO<sub>2</sub>(110) surface: Molecular and dissociative channels." *J. Phys. Chem.* (in press).

Henderson MA, S Oretó-Tapia, and ME Castro. 1998. "Electron induced decomposition of CH<sub>3</sub>OH on the vacuum annealed surface of TiO<sub>2</sub>(110)." *Surf. Sci.* 412-413:252.

Henderson MA, S Otero-Tapia, and ME Castro. 1999. "The chemistry of methanol on the TiO<sub>2</sub>(110) surface: The influence of vacancies and coadsorbed species." *Phys. Chem. Chem. Phys.* (submitted).

Herman GS, MA Henderson, KA Starkweather, and EP McDaniel. 1999. "Mass-spectrometry of recoiled ions and secondary ion mass spectrometry investigation of Y-stabilized ZrO<sub>2</sub>(100) and (110)." *J. Vac. Sci. Technol. A* (in press).

Perkins CL and MA Henderson. 1999. "Photoconversion of adsorbed oxygen states on TiO<sub>2</sub>(110)" (in preparation).

Perkins CL and MA Henderson. 1999. "Reaction of molecular oxygen with bridging OH groups on TiO<sub>2</sub>(110)" (in preparation).

Su Y, Y Wang, JL Daschbach, TB Fryberger, MA Henderson, J Janata, and CHF Peden. 1998. "Gamma-ray destruction of EDTA catalyzed by titania." *J. Adv. Oxid. Technol.* 3:63.

Taylor DP, WC Simpson, K Knutsen, MA Henderson, and TM Orlando. 1998. "Photon stimulated desorption of cations from yttria-stabilized cubic ZrO<sub>2</sub>(100)." *Appl. Surf. Sci.* 102:4536.

## Presentations

Henderson MA. 1999. "Activation of molecular oxygen on TiO<sub>2</sub>(110) by reaction with bridging hydroxyls." First International Workshop on Oxide Surfaces, Elmau, Germany.

Henderson MA. 1998. "Ionizing radiation induced catalysis: Radiocatalytic degradation of organic contaminants in TiO<sub>2</sub> suspensions." Notre Dame Radiation Laboratory, University of Notre Dame, South Bend, Indiana (invited talk).

Henderson MA. 1998. "Coadsorption studies with water: A small step toward understanding the surface chemical and photochemical properties of TiO<sub>2</sub>." 45th National Symposium of the American Vacuum Society, Baltimore (invited talk).

Henderson MA. 1998. "Coadsorption studies with water and oxygen: A small step toward understanding the surface chemical and photochemical properties of TiO<sub>2</sub>." Department of Chemistry, University of Puerto Rico, Mayaguez, Puerto Rico (invited talk).

Su Y. May 2-6, 1999. "Radiocatalytic and photocatalytic studies of oxidation of organics and reduction of water." The 195th Meeting of the Electrochemical Society, Seattle.

Su Y. May 24-28, 1999. "Radiocatalytic and photocatalytic studies of metal ion reduction and water cleavage into hydrogen." The 5th International Conference on Advanced Oxidation Technologies for Water and Air Remediation, Albuquerque.