

Final Report
U.S. Department of Energy

Ionizing Radiation Induced Catalysis
on Metal Oxide Particles

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Executive Summary

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. Many currently proposed tank waste cleanup alternatives encounter potential safety and/or pretreatment problems associated with organics. 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.

This project focuses on a novel approach for destroying organics found in high-level mixed waste prevalent at DOE sites. In this project, we have studied the destruction of organics, such as those found in Hanford tank waste, using reduction/oxidation (redox) chemistry resulting from exposure of typical photocatalytic materials to ionizing radiation (e.g., gamma radiation). Conceptually, this process is an extension of photocatalytic processes known to occur with visible and ultraviolet (UV) light at the interfaces of metal oxide photocatalysts (such as titanium dioxide, TiO_2). In these processes, energy is absorbed by the photocatalyst from light resulting in electron being excited within the photocatalyst. The excited electrons become available for reaction with solution species such as water, while the ‘holes’ (electronic states in the photocatalyst previously occupied by the excited electron) then strip electrons from adsorbed organic species resulting in oxidative destruction of the organic. The energy separation between the hole and the excited electron reflects the redox capability of the excited electron/hole (e^-/h^+) pair, and is dictated by the energy of the incident light and the electronic properties of the photocatalyst. Unfortunately, application of visible or UV light to large scale photocatalytic processes is severely limited by their marginal transparency into most metal oxide catalysts. Additionally, the relatively weak photon energies of visible and UV light limit the types of metal oxide catalysts that can show results. The use of ionizing radiation overcomes optical transparency limitations associated with visible and UV light (e.g., gamma-rays penetrate much farther into materials than either visible or UV light) and permits the use of wider variety of metal oxide catalysts that opens the door to a potentially greater degree of redox capabilities than those photocatalysts that can only be used with visible or UV

light. The use of ionizing radiation offers several attractions. For example, the process operates at ambient temperature and pressure eliminating many safety concerns associated with hydrothermal or calcination approaches. The metal oxide catalysts are robust and stable in both radiation chemically corrosive environments. Another advantage of this approach is that conceptually no additional safety concerns other than those required for handling mixed waste should be required, and existing radiation sources available at the Hanford Site, specifically, ^{137}Cs capsules, could be employed

In the three 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_2 catalysts. Our results show that exposure of solutions containing EDTA and TiO_2 to gamma radiation resulted in significant catalytic destruction of EDTA over that observed in absence of TiO_2 . This is as the case under conditions that might be encountered with tank waste (high pH, high electrolyte concentration and with the presence of chelating cations such as strontium). The mechanism for this destruction however does not appear to be the same as that of UV-based photocatalysis. We have conducted similar studies on smaller probe organic molecules (such as ethanol, formic acid, and acetic acid). UV-based experiments do show significant destruction of these small organics, in agreement with the literature, whereas our results show that solution-phase radiolytic processes dominate those associated with the TiO_2 surface to the extent that any catalytic effects are not detected. Therefore, we conclude that organics can be destroyed over typical metal oxide photocatalysts using ionizing radiation as the light source. However, the mechanism and viability of this approach have not been determined.

On fundamental side, this project has significantly added to the fields understanding of how ionizing radiation interacts with metal oxides and initiates chemical processes at their interfaces. This project has been highly productive in term scientific output and collaborations. To date, this project has resulted in approximately 10 publications in peer reviewed journals, with at least 5 additional manuscripts under review or soon to be submitted. Results from these works have been presented at over 15 national and international scientific meetings and at invited talks at 5 academic institutions (Univ. of Washington, Univ. of Illinois, Univ. of Puerto Rico, Notre Dame Univ. and Texas A&M Univ.). As a result of this project, collaborative interactions have been developed

between PNNL and the following institutions: Univ. of Puerto Rico, Univ. of New Mexico, Univ. of Zurich and New Mexico Tech.

Research Objectives

This project was conducted to determine if ionizing radiation could be used to catalytically destroy organics over semiconducting metal oxide particles. We focussed primarily on the destruction of organic chelating agents, such as EDTA, which are known to hamper the separation of radionucleii (such as Sr or Am) from tank waste using current ion exchange methods. Our objective was to determine if ionizing radiation could be used to destroy the chelating capability of species such as EDTA, either by partially or completely decomposing the organic, in order to free radionucleii for efficient separation. Although a considerable amount of information is available in the open literature on the roles of visible/UV light in photocatalysis, little is known about the processes initiated by ionizing radiation. In this sense, the use of ionizing radiation is both novel, and may find an important niche in the pretreatment of mixed waste. An additional aim of the project was determine the mechanism(s) by which the radiocatalysis effect took place and compare it to what is know from visible and UV photocatalytic processes in the literature. The main outcome of this work is 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.

Methods and Results

Experiments are aimed at extending the body of knowledge about e^-/h^+ pair chemistry of semiconducting metal oxide 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 were conducted in two main areas: 1) details of the gamma-radiocatalytic destruction of EDTA over titanium dioxide photocatalysts, and 2) determination of the radiocatalysis mechanism by comparison with UV photocatalysis and electron-stimulated processes.

Gamma-Radiocatalysis of EDTA-Colloidal Metal Oxide Solutions

Studies on the radiocatalytic decomposition of ethylene diamine tetraacidic acid (EDTA, which is a complexing agent found in many Hanford waste tanks) were conducted using a ^{60}Co source. An increase in the G-value (defined as the number of events per 100 V of absorbed energy) for the

radiolytic destruction of EDTA was observed in the presence of colloidal TiO_2 and O_2 over that occurring in aqueous solution (from 2.4 to 3.7). The enhancement is obtained only when both TiO_2 and O_2 are present in solution. The estimated G-values for EDTA radiolysis on TiO_2 in the absence of O_2 (solution and headspace purged with dry N_2) are the same as the aqueous solution value (2.4). This indicates that the presence of an electron scavenger (O_2 in this case) is essential for organic (EDTA) radiocatalytic oxidation. The G-value for EDTA destruction in colloidal TiO_2 solutions is dependent on the TiO_2 powder concentration, as one should expect since the absorption of radiation is partitioned between the solution, with its G-value of 2.4 for EDTA destruction, and the TiO_2 particles. With a 0.02 M EDTA and 0.10 g/ml TiO_2 solution, we estimate that 91.5% of the radiation is absorbed by water, 7.8% by TiO_2 and 0.6% by EDTA. Therefore, the G-value for EDTA destruction from radiation absorbed by TiO_2 is probably considerably higher than the values we estimated based on the overall radiation absorbed.

We have observed that the radiocatalytic destruction of EDTA is very pH dependent. As the solution pH is increased (more basic solutions) the difference between the blank experiment (no TiO_2 present) and that with TiO_2 present becomes zero. We interpret this to mean that as the pH increases the surface charge on each TiO_2 particle becomes increasingly negative, and anionic species, such as EDTA, are unable to directly interact with the surface. This effect is significantly overcome if EDTA is complexed with a cation such as Sr^{2+} . We interpret this to mean that complexed EDTA is an electrostatically neutral solution species and is therefore insensitive to the negative charge on a TiO_2 particle at high pH. We have also observed that Cu^{2+} ions produce the same effect as Sr^{2+} , which is consistent with EDTA complexing with 2+ cations in general. This finding has great significance for the radio- and photo-catalytic destruction of complexants such as EDTA because pH effects can be negated. The effect is minimal at a pH of 5, where the surface charge on TiO_2 is close to zero. These results are also consistent with UV photooxidation studies conducted by Prof. Dayte's group at the University of New Mexico.

We have also characterized the solution and gas phase products from radiocatalytic destruction of EDTA over TiO_2 . Although several products are observed from solution radiolysis in the absence of TiO_2 , there is a significance increase in the yields of ED3A and formic acid, as well as a decrease in the yield of oxalic acid, when TiO_2 is present. Assuming that charge transfer occurring between the gamma ray excited TiO_2 surface and the adsorbed EDTA species is responsible for

EDTA decomposition, we expect that the anchoring group of the molecule is most susceptible to TiO_2 -mediated oxidation. Based on comparisons with the binding of carboxylic acids, such as formic acid and acetic acid, to TiO_2 , we expect that EDTA should bind to the surface through only one of its four carboxyl groups due to steric issues. Therefore, the production of ED3A is consistent with this model in that one acetate moiety is preferentially decomposed per EDTA molecule destroyed. The implications of this are significant. Since these functional groups are those that bind cations, one needs only to destroy these carboxylic acid groups in order to destroy the chelating capability of EDTA. The complete destruction of EDTA (to CO_2) is not necessary in order to free chelated cations into solution.

Impregnation of the TiO_2 catalyst with either a 1% (by weight) Pd or Pt salt, followed by reduction, had little or no effect on the rate of EDTA destruction versus that obtained in the absence of the metal. In fact, the rate decreased for the Pt case suggesting that the metal's presence may inhibit destruction, either by blocking sites or by trapping holes. No thermal decomposition of EDTA was observed at room temperature in the presence of the metal. This result indicates that expensive noble metals are not necessary for organic oxidation on TiO_2 by radiocatalysis.

Examination of the destruction of EDTA over colloidal ZrO_2 and Pt/ ZrO_2 catalysts was also briefly examined. Preliminary results indicate that, as expected based on the flat band positions of ZrO_2 relative to those of TiO_2 , ZrO_2 is not as effective as an oxidation catalyst, presumably because valence band holes in ZrO_2 are higher lying (less oxidizing). The rate of EDTA destruction on ZrO_2 was independent of the presence of Pt, and found to be about 10 - 20% less than that of TiO_2 .

Mechanism of Radiocatalysis

It is commonly held among photocatalytic researchers that the dominate mechanism associated with the semiconducting oxide photoeffect is the generation and subsequent chemistry of electron-hole pairs. Much has been made about the photoexcitation mechanism, charge carrier dynamics, surface and bulk trap states, effects of dopants in bending bands, and charge transfer processes occurring at the surface once electron-hole pairs are formed. Much of our effort has been focused on determining whether or not this accepted mechanism also applies to gamma ray radiocatalysis. Because we wish to determine the mechanism of radiocatalysis, we undertook studies aimed at smaller probe molecules. Our initial results indicate that small probe molecules such as formic

acid, acetic acid and ethanol are all insensitive to the presence of TiO_2 in the gamma ray experiments. That is, the extents of gamma ray radiolysis were the same for these molecules in solution regardless of the presence of TiO_2 . This result for formic acid is consistent with the EDTA experiments that show a gradual evolution of this species with increasing radiation dose implying that formic acid accumulates in solution without being further decomposed. However, this result is also surprising because UV photolysis conducted by us and in several published accounts indicate that small organics such as formic acid are rapidly photooxidized over TiO_2 . (As an aside, we have observed that impregnating TiO_2 with 0.5% Pt increases the rate of formic acid decomposition threefold over that of solution radiolysis. We believe this is a thermal effect because the yields of CO_2 produced are equivalent irrespective of the presence of gamma ray irradiation. During these gamma ray irradiation experiments we also observed significant yields of hydrogen gas that were not observed without platinized TiO_2 present or without irradiation. This hydrogen did not arise from photoreduction of water on the platinized TiO_2 since identical experiments in the absence of formic acid did not yield H_2 .)

In an effort to determine the role that other excitation mechanisms (other than the traditional e^-/h^+ mechanism) may play in the gamma ray experiments over TiO_2 , we have conducted controlled experiments with small organic molecules over TiO_2 single crystal surfaces in ultrahigh vacuum (UHV). One possible mechanism that might occur in solution is the effect of secondary electron induced chemistry resulting from absorption of the high energy radiation. For example, a Compton electron, formed by absorption of a gamma ray, can produce up to 10^4 100 eV electrons through subsequent ionization and loss processes. These electrons should be very effective at breaking bonds. In order to determine the cross sections, and thus the relative rates, for electron-induced decomposition of small organics on TiO_2 , we conducted a series of experiments focusing on the 100 eV electron irradiation of methanol on $\text{TiO}_2(110)$. These experiments were done in collaboration with Prof. Miguel Castro from the University of Puerto Rico.

Methanol was chosen as the organic probe molecule for these experiments because it is the simplest organic that has no thermal decomposition on $\text{TiO}_2(110)$. Although we have not examined this species in gamma ray experiments, we expect that it behaves similarly to ethanol, which was not sensitive to gamma ray induced radiocatalysis over a TiO_2 suspension. Although about 30% of the methanol molecules decompose on $\text{TiO}_2(110)$, methanol is the only species that

desorbs from the surface on heating implying the recombination dominates additional thermal decomposition.

The $\text{TiO}_2(110)$ surface was prepared with molecular and dissociative species of methanol, and the sensitivity of each to electron irradiation was determined by monitoring the depletion of each in thermal desorption after electron exposure. Molecularly adsorbed methanol left no detectable carbon-containing fragments on the surface after activation with 100 eV electrons. Instead, the parent and/or its carbon-containing fragments were ejected from the surface leaving unoccupied surface sites. In contrast, electron irradiation of methoxyls resulted in adsorbed formaldehyde at the same respective binding sites. Formaldehyde molecules bound at vacancies were resistant to further electron induced decomposition, whereas those bound at non-vacancies were further decomposed (probably to gaseous CO). Cross section data indicates that although molecular methanol was decomposed with the lowest cross section ($1.7 \times 10^{-16} \text{ cm}^2$), its cross section was only a factor of 2.5 less than that for the gas phase dissociative ionization of methanol with 100 eV electrons. This indicates that the $\text{TiO}_2(110)$ does not significantly perturb the electronic structure of methanol, nor does it quench the excited states of methanol that result from electron impact ionization. The cross sections for methoxyl decomposition were approximately equivalent (about $5 \times 10^{-16} \text{ cm}^2$) indicating that the excited states of these more tightly bound fragments are also not significantly quenched by the $\text{TiO}_2(110)$ surface.

Although these large cross sections suggest that small organics like methanol should readily decompose on TiO_2 surfaces exposed to 100 eV electrons, it does not appear that the gamma ray studies show the same type of reactivity. This suggests that secondary electrons with energies above the ionization potentials of most organics (about 10 to 20 eV) are not generated in significant concentrations when TiO_2 suspension are irradiation with gamma rays.

We have also explored an alternative process that might explain photooxidation outside of the traditionally held electron-hole pair mechanism. It is well known that UV irradiation of TiO_2 materials results in photodesorption of oxygen from the surface of the oxide and the generation of Ti^{3+} -related surface defects. These photon generated defects have not been produced with sufficient surface concentrations to permit characterization, however it is also well known that oxygen vacancy sites can be made in the 0.05 to 0.15 ML coverage regime by thermal annealing. These vacancy defects are also associated with Ti^{3+} sites.

We have found that molecular oxygen adsorbed at these defect sites is very reactive for oxidation of C-H bonds in methanol generating formaldehyde. This process does not occur on $\text{TiO}_2(110)$ unless vacancy sites are available. These results provide incentive to consider alternative thermal and photochemical oxidation mechanisms that involve the interaction of organics and oxygen at surface defect sites. For example, ionizing radiation exposure may generate surface sites in which thermal reactions of molecular oxygen and organics can take place. We have investigated further the states of oxygen adsorbed on rutile TiO_2 by studying the interaction of light with adsorbed oxygen on $\text{TiO}_2(110)$. We find that 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 $\text{O}/\text{TiO}_2(110)$ system is explored. For thick overlayers (>4 monolayers), it is possible to generate via UV irradiation a previously unobserved oxygen TPD state that we believe is due to molecular oxygen trapped at the water – TiO_2 interface. Preliminary results indicate that this oxygen reacts with water to make a peroxo-like species that may be the same as the radical products many propose to be present at the surfaces of TiO_2 colloids exposed to UV light.

Working with Jürg Osterwalder at the University of Zurich, we have performed experiments mapping the 3-D Fermi surface of vacancy defects rutile $\text{TiO}_2(110)$ in order to better understand how molecules interact with them. Reduction of TiO_2 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_2 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_2) with the defective surface. For example, it was theoretically proposed, contrary to prior investigations, that the defect state for reduced TiO_2 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_2 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_2 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_2 .

The intensity of the feature at the Fermi energy (E_f) can furthermore be monitored over the full 2π 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). We are currently conducting EPR studies on the bulk and surface defects on TiO_2 rutile, analyzing results from the surface mapping of defects on $\text{TiO}_2(110)$, and conducting studies on aluminum-doped TiO_2 .

Decomposition of Tetraphenylborate (TPB)

In an effort to assist in determining the source of benzene emission during Cs extraction from Savannah River tank wastes, we conducted a series of experiment involving sodium tetraphenylborate (TPB) radiolysis on colloidal TiO_2 . Titanates, previously used in sorption of Sr from solution, are among many constituents present in wastes being processed at Savannah River. We found that the rate of TPB destruction by gamma-irradiation is the same with or without TiO_2 , and there is no enhancement in the presence of O_2 . These results suggest that an e^-/h^+ pair mechanism is not involved in benzene generation, in agreement with results from Savannah River and Georgia Tech. TPB thermally decomposes at room temperature in the presence of either a TiO_2 - or ZrO_2 -supported Pt catalyst. The product yields (benzene and biphenyl) differ somewhat in the presence or absence of gamma-radiation suggesting radiolysis of the thermal products may take place.

Along this line, we have also shown that radiocatalytic reductive deposition of noble metals, such as Pt, onto TiO_2 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_2 ; 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.

Relevance, Impact and Technology Transfer

In order to address the impact of this research, the following questions have been offered by the EMSP as a guide. We have reproduced these questions below and offered our best answers to each.

a. *How does this new scientific knowledge focus on critical DOE environmental management problems?* Our goal was to explore a new method of destroying organics, such as chelating agents, which pose serious problems for pretreatment of HLW, especially with regards to ion exchange processes. We have also examined how radiolytic and thermal processes affect tank waste in our studies of TPB and EDTA.

b. *How will the new scientific knowledge that is generated by this project improve technologies and cleanup approaches to significantly reduce future costs, schedules, and risks and meet DOE compliance requirements?* The results of this study will not be employed in the near future for several reasons. First, the mechanism of the radiocatalysis effect is not well understood, so the conditions for optimal use are not known. Second, the experiments performed in this project were at the bench-top level, and scale-up studies are required before viability can be addressed. Third, only one organic (EDTA) and one photocatalyst (TiO_2) have been studied in detail. Therefore, since considerable more research is required, any benefits of radiocatalysis will not be realized in the short term.

c. *To what extent does the new scientific knowledge bridge the gap between broad fundamental research that has wide-ranging applications and the timeliness to meet needs-driven applied technology development?* Perhaps the greatest short-term benefit of this research is the realization that the interaction of radiation with metal oxides can have advantageous effects on destroying

organics. This, as mentioned in 'b', will not help solve today's problems, but is an investment in problems that may require novel solutions in the 5 to 10 year time span from the end of the project.

d. *What is the project's impact on individuals, laboratories, departments, and institutions? Will results be used? If so, how will they be used, by whom, and when?* Since the findings from these studies has been published in the open literature, the general effect of radiocatalysis is now available to be explored by other research groups. We know of at least one such group in this country that is currently exploring the potential radiocatalytic role of metal oxides, and expect that other groups will begin thinking of using ionizing radiation to promote chemistry at metal oxide surfaces.

e. *Are larger scale trials warranted? What difference has the project made? Now that the project is complete, what new capacity, equipment or expertise has been developed?* Because of this project, we have developed an expertise in the photochemical processes at model TiO_2 surfaces that few others in this country have obtained. This expertise is continuing to be recognized in terms of invited presentations, literature citations and collaborative interactions. Regarding large scale trials, there is a need for this, as mentioned above, but at present the short-term needs of EM leave little funding available to consider new technologies that can be applied on the 10+ year time scale.

f. *How have the scientific capabilities of collaborating scientists been improved?* Perhaps our greatest influence has been in influencing a number of research groups to study processes on photocatalysts such as TiO_2 .

g. *How has this research advanced our understanding in the area?* As mentioned in 'e', as a result of this project we have greatly increase the scientific visibility of PNNL in the areas of oxide surface chemistry and photocatalysis.

h. *What additional scientific or other hurdles must be overcome before the results of this project can be successfully applied to DOE Environmental Management problems?* The obvious problem

here is that resources are not available or are not committed to fully addressing the science needs of EM. This is particularly true for problems that are beyond the 3 year life cycle of a typical EMSP project.

i. *Have any other government agencies or private enterprises expressed interest in the project? Please provide contact information.* Yes, but perhaps not to such a degree that warrants serious consideration.

Personnel Supported

(see cover page)

Publications

M. Li, W. Hebenstreit, U. Diebold, A.M. Tyryshkin, M.K. Bowman, G.G. Dunham and M.A. Henderson, "The Influence of the Bulk Reduction State on the Surface Structure and Morphology of Rutile TiO₂(110) Single Crystals," J. Phys. Chem. B, submitted.

C.L. Perkins and M.A. Henderson, "Photodesorption and Trapping of Molecular Oxygen at the TiO₂(110) – Water Ice Interface," J. Phys. Chem. B, to be submitted.

Y. Su "Preliminary Studies on the Degradation of Sodium Tetraphenylborate (TPB)," manuscript in preparation.

Y. Su "Radiocatalytic degradation of EDTA in colloidal TiO₂ suspensions", Env. Sci. & Tech., to be submitted.

Y. Su "Radiocatalytic Decomposition of Water over a ZrO₂ Catalyst", Env. Sci. & Tech., to be submitted.

G.S. Herman, Y. Gao, T.T. Tran, and J. Osterwalder, "X-ray Photoelectron Diffraction Study of an Anatase Thin Film: $\text{TiO}_2(001)$," *Surf. Sci.* **447** (2000) 201.

M.A. Henderson, S. Otero-Tapia and M.E. Castro, "The Chemistry of Methanol on the $\text{TiO}_2(110)$ Surface: The Influence of Vacancies and Coadsorbed Species," *Faraday Discuss.* 114 (1999) 313.

M.A. Henderson, W.S. Epling, C.L. Perkins, C.H.F. Peden, and U. Diebold, "Interaction of Molecular Oxygen with the Vacuum Annealed $\text{TiO}_2(110)$ Surface: Molecular and Dissociative Channels," *J. Phys. Chem. B* 103 (1999) 5328.

G.S. Herman, M.A. Henderson, K.A. Starkweather and E.P. McDaniel, "Mass-Spectrometry of Recoiled Ions and Secondary Ion Mass Spectrometry Investigation of Y-Stabilized $\text{ZrO}_2(100)$ and (110) ," *J. Vac. Sci. Technol. A* 17 (1999) 939.

W.S. Epling, C.H.F. Peden, M.A. Henderson and U. Diebold, "Evidence for Oxygen Adatoms on $\text{TiO}_2(110)$ Resulting from O_2 Dissociation at Vacancy Sites," *Surf. Sci.* 412-413 (1998) 333.

M.A. Henderson, S. Otero-Tapia and M.E. Castro "Electron Induced Decomposition of CH_3OH on the Vacuum Annealed Surface of $\text{TiO}_2(110)$," *Surf. Sci.* 412-413 (1998) 252.

Y. Su, Y. Wang, J.L. Daschbach, T.B. Fryberger, M.A. Henderson, J. Janata and C.H.F. Peden, "Gamma-Ray Destruction of EDTA Catalyzed by Titania," *J. Adv. Oxid. Technol.* 3 (1998) 63.

D.P. Taylor, W.C. Simpson, K. Knutsen, M.A. Henderson and T.M. Orlando, "Photon Stimulated Desorption of Cations from Yttria-Stabilized Cubic $\text{ZrO}_2(100)$," *Appl. Surf. Sci.* 102 (1998) 4536.

M. Alam, M.A. Henderson, P.D. Kaviratna, G.S. Herman and C.H.F. Peden, "Chromyl Chloride Chemistry at the $\text{TiO}_2(110)$ surface," *J. Phys. Chem. B* 102 (1998) 111.

Presentations

M.A. Henderson, 1999. "The Chemistry of Methanol on the $\text{TiO}_2(110)$: The Influence of Vacancies and Coadsorbed Species," 114th Faraday Discussion (The Surface Science of Metal Oxides), Ambleside, UK, **invited talk**.

M.A. Henderson, 1999. "Electron Induced Decomposition of Methanol on the Vacuum Annealed Surface of $\text{TiO}_2(110)$," Environmental Molecular Sciences Symposia and First Users' Meeting, Richland, WA.

M.A. Henderson, 1999. "Activation of molecular oxygen on $\text{TiO}_2(110)$ by reaction with bridging hydroxyls." First International Workshop on Oxide Surfaces, Elmau, Germany.

G.S. Herman, 1999 "Characterization of Oxide Surfaces by Mass-Spectroscopy of Recoiled Ions," Surface Analysis '99, Applied Surface Symposium, American Vacuum Society, Waukesha, WI.

G.S. Herman, 1999 "Anatase TiO_2 - A Structural Investigation by X-ray Photoelectron Diffraction," The Sixth International Conference on the Structure of Surfaces, Vancouver, BC.

C.L. Perkins, 1999 "Interactions of Oxygen, Water, and Defects on the $\text{TiO}_2(110)$ Surface", University of Illinois/Chicago Chemistry Department seminar, Chicago, IL, **invited talk**.

C.L. Perkins, 1999 "photoconversion of Adsorbed Oxygen States on $\text{TiO}_2(110)$ ", contributed poster presentation, Sixth International Conference on the Structure of Surfaces, Vancouver, Canada.

C.L. Perkins, 1999 "photoconversion of Adsorbed Oxygen States on $\text{TiO}_2(110)$ ", contributed oral presentation, 46th International Symposium of the American Vacuum Society, Seattle, WA.

C.L. Perkins, 1999 "Surface Chemistries of Group IV Oxides and Borides", Washington State University seminar, Richland, WA, **invited talk**.

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

Y. Su, 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.

M.A. Henderson, 1998. "Ionizing radiation induced catalysis: Radiocatalytic degradation of organic contaminants in TiO_2 suspensions." Notre Dame Radiation Laboratory, University of Notre Dame, South Bend, Indiana, **invited talk**.

M.A. Henderson, 1998. "Coadsorption studies with water: A small step toward understanding the surface chemical and photochemical properties of TiO_2 ." 45th National Symposium of the American Vacuum Society, Baltimore, **invited talk**.

M.A. Henderson, 1998. "Coadsorption studies with water and oxygen: A small step toward understanding the surface chemical and photochemical properties of TiO_2 ." Department of Chemistry, University of Puerto Rico, Mayaguez, Puerto Rico, **invited talk**.

M.A. Henderson, 1998 "Probing the Surface Chemistry of Single Crystal Metal Oxides with Water," 215th National Meeting of the American Chemical Society, Dallas, TX, **invited talk**.

C.H.F. Peden, 1998 "Water Adsorption and Reaction as a Probe of Oxide Surface Structure and Chemistry." Department of Chemistry, Texas A&M University (College Station, TX) April, 1998, **invited talk**.

M.A. Henderson, 1997. "Application of Static Secondary Ion Mass Spectrometry in Probing the Interaction of Water with Well-Defined Oxide Surfaces," SIMS XI, 11th International Conference on Secondary Ion Mass Spectrometry, Orlando.

Y. Su, 1997 "Radiocatalytic degradation of organic contaminants in colloidal TiO_2 and ZrO_2 suspensions," The Third International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air, Orlando, FL.

Y. Su, 1997 "Radiocatalytic degradation of organic contaminants in TiO_2 suspensions," 214th National Meeting of the American Chemical Society, Las Vegas, NV.

C.H.F. Peden, 1997 "The Growth, Structure and Surface Chemistry of Oxide Films as Model Surfaces." 17th National Congress of the Mexican Surface Science and Vacuum Society (Mazatlan, Mexico) September, **invited talk**.

Future Work

The following areas should be considered for future exploration of the radiocatalysis effect:

1. Determining the mechanism for the gamma radiocatalysis effect over TiO_2
2. Examination of other metal oxides photocatalysts
3. Probing the role of ionizing radiation in the photoreduction of metals
4. Comparing the effect of other sources of ionizing radiation such as X-rays, Compton electrons, beta particles, etc.
5. Scale up studies in order to determine viability of the radiocatalysis effect