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Ionizing Radiation Induced Catalysis on Metal Oxide Particles

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Research Objective

High-level radioactive waste storage tanks within 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. 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 utilize oxidation achieved by thermal or chemical activation.

This project focuses on using ionizing radiation (α,β,γ) to catalytically destroy organics over oxide materials through reduction/oxidation (redox) chemistry resulting from electron-hole (e^-/h^+) pair generation. Conceptually this process is an extension of visible and near-UV 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 (where the electron was excited from) 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 (γ-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.

Experiments have been aimed at understanding the mechanism(s) of γ-radiocatalysis and 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) 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.

Research Progress and Implications

We have observed that the yield of γ–ray induced destruction of EDTA in solution increased significantly if oxygen and a colloidal suspension of TiO_2 were present. Both oxygen and TiO_2 were necessary to see this increased EDTA destruction. Without TiO_2, about 19% of the EDTA in an aerated solution was destroyed after a 1 MRad γ–ray exposure, but with a 0.1 g/ml suspension of TiO_2 the level of EDTA destruction increased to near 50%. However, this process is very pH dependent. As the pH is increased the difference between the blank experiment (no TiO_2 present) and that with TiO_2 present becomes zero. This implies 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 overcome if EDTA is complexed with a cation such as Sr^{2+}. At a pH of 9 the level of EDTA destruction is approximately the same after a 1 MRad exposure with or without TiO_2. If the solution is made with 0.2 M in Sr^{2+} the level of EDTA destruction increases to about 25% after a 1 MRad exposure, while a 0.12 M solution increases the level to over 30%. 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 photoxidation studies conducted by Prof. Dayte's group at the University of New Mexico.

We have also undertaken to characterize 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 occuring between the γ–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.

Because formic acid was one of the major product of EDTA radiocatalysis and because we wish to better understand the mechanism of radiocatalysis, we have undertaken studies aimed at smaller probe molecules. Our initial results indicate that formic acid, acetic acid and ethanol are all insensitive to the presence of TiO_2 in the γ–ray experiments, that is, the extents of γ–ray radiolysis are 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 photoxidized over TiO_2.

Although we do not yet understand the absence of γ–ray induced radiocatalytic destruction of these small organics, 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 γ–ray irradiation. During these γ–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 various excitation mechanisms play in the γ–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 γ–ray, can produce up to 10^4 100 eV electrons through subsequent ionization and loss processes. These electrons should be very effect 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 $TiO_2(110)$. 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 $TiO_2(110)$. Molecularly adsorbed methanol on the $TiO_2(110)$ surface left no detectable carbon-containing fragments after irradiation with 100 eV electrons. In contrast, electron irradiation of methoxyl species resulted in adsorbed formaldehyde.

The cross section for 100 eV electron induced decomposition of molecularly adsorbed methanol was 1.7 x 10^{-16} cm^2 (only a factor of 2.5 less than that for the gas phase). This indicates that the $TiO_2(110)$ surface does not quench the excited states of methanol resulting from electron impact ionization. The cross sections for methoxyl decomposition was about 5 x 10^{-16} cm^2. These large cross sections suggest that small organics like methanol should readily decompose on TiO_2 surfaces exposured to 100 eV electrons, it does not appear that the γ–ray studies show the same type of reactivity. This suggests that secondary electrons with energies above the ionization potentials of most organics (above 10 to 20 eV) are not generated in significant concentrations when TiO_2 suspension are irradiation with γ-rays. The chemistry associated with less than 10 eV electrons has not been examined by our group, but is planned for the next year of this project.

Planned Activities

We will focus on the following areas in the next year:

We will continue studies aimed at determining the mechanism of the γ–ray radiocatalysis effect over TiO_2. These will include more studies involving small probe molecules, but also expanding into the area of photoreduction of metals. This effort will include looking at new TiO_2-based materials such as 10Å wide particles of anatase obtained from Dupont, and mesoporous materials grown in-house by Scott Elder.

We will begin work on ZrO_2. This will include growth of model ZrO_2 materials by molecular beam epitaxy that will be used to probe the photodynamics and charge carrier properties of wider bandgap materials.

We will continue probing the role of oxygen vacancies and reactive oxygen species in the photoxidation of organics over single crystal TiO_2 substrates. For example, we will further probe the oxidation of N_2 with oxygen adatoms and expand this work to consider organics such as acetone and propylene.

We will explore the ability of low energy (below 10 eV) electrons to activate adsorbed molecules, such as methanol, on the surface of $TiO_2(110)$.

Other Access To Information

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