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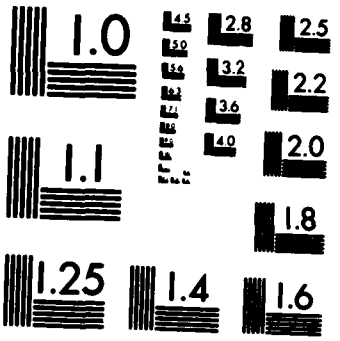

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18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Photocatalysis; semiconductor surfaces, selectivity, zeolites, clay, heteropolyoxoanions

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Sensitized interfacial photoreactivity has been investigated as a means for accomplishing unique chemical transformations. We have examined photoreactions on heteropolyoxoanions, on clays on native and modified form, and on zeolites of varying size, selectivity and catalyst loadings. We have investigated an array of reactions which occur with substantially different reaction pathways or do not occur at all in conventional homogeneous solutions. These include novel oxidative and/or reductive cleavages of organic substrates. Both mechanistic and synthetic studies of multi-functional molecules have been conducted.

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effective heterogeneous sensitizer for photoinduced singlet oxygen formation. The photogenerated singlet oxygen freely diffuses to solution where it reacts with normal reactivity.[7] The photocatalyst has high catalytic turnover and high stability. Zeolites X and Y can also be loaded with small particles of semiconductors. In the presence of sacrificial donors, these zeolites effectively evolve hydrogen from water.[8] Preliminary studies toward optimization of yield in such photoredox reactions were determined.

Loading of clays (kaolin or montmorillonite) with either protons or metals ions renders them effective as thermal isocatalysts and as three dimensional environments for controlled photochemical activation. Unfortunately, very low photoactivity was absorbed, so that clear preference for photochemical over thermal activation inside clays is lacking. The use of clays for cation radical induced Diels-Alder reactions produced significant accelerations compared to the neutral analogous reaction occurring in homogeneous solution, and the generation of protonated phenols to give visibility light activated cyclohexadienyl cations also occurs.[9]

List of Publications

1. "Photoactivation of Metal Oxide Surfaces: The Photocatalyzed Oxidation of Alcohols by Heteropolytungstates," M.A. Fox, R. Cardona, E. Gaillard, J. Am. Chem. Soc. 1987, 109, 6347.

2. "Charge Injection into Semiconductor Particles - Importance in Photocatalysis," M.A. Fox, Chim. Ind. (Milan) 1986, 68, 59; NATO Adv. Sci. Inst. Ser. 1986, 174, 363.

3. "Photocatalysis on Modified Semiconductor Surfaces and on Bipolar Photoelectrodes," M.A. Fox, Nouv. J. Chim. 1987, 11, 129.

4. "Effect of Cosolvent Additives on Relative Rates of Photooxidation on Semiconductor Surfaces," D.D. Sackett, M.A. Fox, J. Phys. Org. Chem. 1988, in press.

5. "Selectivity in the Semiconductor-Mediated Photooxidation of Polyols," M.A. Fox, H. Ogawa, P. Pichat, J.M. Hermann, M. Mozzanega, J. Org. Chem. 1987, submitted.

6. "Photooxidative Degradation Picolines on Metalized Semiconductor Particles," M.A. Fox, H. Ogawa, P. Pichat, J. Catal. 1987, submitted.

7. "Photoassisted Oxygenation of Olefins: An Exchanged Zeolite as a Heterogeneous Photosensitizer," T.L. Pettit and M.A. Fox, J. Phys. Chem. 1986, 90, 1353.

8. "Photochemical Hydrogen Generation on Zeolite-Encapsulated CdS Particles," M.A. Fox, T.L. Pettit, J. Phys. Chem. 1987, submitted.

Final Report

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Statement of the Problem Studied

Sensitized interfacial photoreactivity has been investigated as a means for accomplishing unique chemical transformations. We have examined photoreactions on heteropolyoxoanions, on clays on native and modified form, and on zeolites of varying size, selectivity and catalyst loadings. We have investigated an array of reactions which occur with substantially different reaction pathways or do not occur at all in conventional homogeneous solutions. These include novel oxidative and/or reductive cleavages of organic substrates. Both mechanistic and synthetic studies of multi-functional molecules have been conducted. These systems can service models for applications of this work in the clean-up of pollutant spills or contaminated water streams and in detoxification of purposely contaminated areas. The reactions allow chemical conversions under carefully controlled conditions so that these routes promise utility in the destruction of undesirable toxic agents.

Summary of Important Results

Progress has been made in three areas: photoinitiated redox reactions on heteropolyoxoanion surfaces and metal oxide semiconductors; photoinduced reactions induced by sensitizers held within zeolitic cages; and light activated reactions occurring inside clay layers.

Heteropolytungstates containing 1-30 tungsten atoms were compared in photocatalytic ability to semiconductor powders and single crystals of tungsten oxide. Evidence requiring precomplexation of organic substrates for effective photoinduced oxidation was obtained, and a striking variation in photocatalytic activity was observed as the surfaced properties of the heteropolytungstates were varied.[1] The conceptual mechanistic picture involved in the heteropolyoxo induced photooxidations are identical to those involved for charge injection at metal oxide surfaces.[2,3] Since the adsorption equilibria of a redox active molecule onto the photoactive catalyst was found to be determinative for efficient photoreaction, variation of solvent and surface properties induced profound effect on the quantum efficiency for these conversions.[4] Preferential adsorption effects were cited as the route source for selective oxidation of a primary over a secondary alcohol site in non-adjacent diols[5] and for the complete mineralization in the photooxidative destruction of adsorbed isomeric picolines.[6]

Selectivity in oxidative transformations could also be observed if the photoactive sensitizer was constrained to be held within the pores of zeolites. $Ru(bpy)_3^{2+}$-exchanged zeolite X or Y can act as an

9. "Competitive Reactions of Diene Cation Radicals Formed on Irradiated Metal Oxide Surfaces," M.A. Fox, J.N. Younathan, D.D. Sackett, Tetrahedron 1987, 43, 1643.

Meeting Presentations

1. "Photoreactivity on Heteropolyoxometallates," 1987 Conference on Chemical Defense Research, CRDEC, Aberdeen Proving Ground, Edgewood, MD, November 1987.

2. "Selective Organic Redox Reactions on Irradiated Semiconductor Particles," M.A. Fox, H. Ogawa, J. Muzyka, 1987 Fall Meeting, Electrochemical Society, Honolulu, HA, October 1987.

3. "Photocatalysis and Photosynthetic Reactions on Semiconductor Surfaces," M.A. Fox, New York Academy of Sciences, New York City, NY, November 1987.

4. "Photocatalytic Oxidation of Organic Substrates," NATO Advanced Studies Institute on Photochemistry, Cefalu, Sicily, September 1987.

5. "Selective Photoelectrochemical Dehydrogenation of Polyols," M.A. Fox, H. Ogawa, 193rd National Meeting, American Chemical Society, Denver, CO, April 1987.

6. "Future Trends," M.A. Fox, 1987 Florida Conference on Catalysis, Daytona Beach, FL, April 1987.

7. "Degradation of Organic Materials on Irradiated TiO_2 Particles," US Army CRDEC Workshop on Chemical Decontamination, Oxford, AL, March 1987.

8. "Surface Mediated Photochemistry," 1986 Scientific Conference on Chemical Defense Research, CRDEC, Aberdeen Proving Ground, MD, November 1986.

9. "Photochemistry of Zeolite Supported CdS," T.L. Pettit, M.A. Fox, 192nd ACS National Meeting, Anaheim, CA, September 1986.

Participating Scientific Personnel

Postdoctoral Associates: Y. L. Chow, C. J. Murphy

Students Receiving Degrees: T.L. Pettit, R. Cardona

Students in Pursuit of Advanced Degrees: D.A. Chandler, D.D. Sackett, B. Draper, G.A. Reitz

Dissertation Titles Involving Work Sponsored by this Grant

1. "Surface Mediated Photochemistry," T.L. Pettit, Ph.D., December 1986
2. "Photocatalytic Transformations of Organic Substrates in the Presence of Metal Salts," R. Cardona-Torres, Ph.D., June 1987

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