

PROJECT SUMMARY

Project ID: 54122
Project Title: A Broad Spectrum Catalytic System for Removal of Toxic Organics from Water by Deep Oxidation

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Number of Graduate Students/Post-doctorates: 2 graduate students, 1 post-doctorate

RESEARCH OBJECTIVE

Toxic organics in water and soil constitute an important environmental hazard. The objective of the research is the design of practical procedures for the removal of toxic organic pollutants by deep oxidation.

RESEARCH PROGRESS

This report summarizes the work performed in the course of a three year project.

In water, metallic palladium was found to catalyze the deep oxidation of a wide variety of functional organics by dioxygen at 80-90°C in the presence of carbon monoxide or dihydrogen.¹⁻³ Several classes of organic compounds were examined: benzene, phenol and substituted phenols, nitro and halo organics, organophosphorus, and organosulfur compounds. In every case, deep oxidation to carbon monoxide, carbon dioxide, and water occurred in high yields, resulting in up to several hundred turnovers over a 24 h period. For substrates susceptible to hydrogenation, the conversions were generally higher with dihydrogen than with carbon monoxide. For organophosphorus compounds, the system presents the first examples of catalytic cleavage of phosphorous-alkyl bonds.

It is clear from the results obtained that we have discovered an exceptionally versatile catalytic system for the deep oxidation of toxic organics in water. This system possesses several attractive features not found simultaneously in other reported systems. These are (a) the ability to directly utilize dioxygen as the oxidant, (b) the ability to carry out the deep oxidation of a particularly wide range of functional organics, and (c) the ease of recovery of the catalyst by simple filtration. While our understanding of the mechanistic steps involved in the oxidation is far from complete, preliminary studies indicate that the overall transformation encompasses three catalytic steps in tandem. The first is the water-gas shift reaction involving the oxidation of carbon monoxide to carbon dioxide with the simultaneous formation of dihydrogen. The second catalytic step involves the combination of dihydrogen with dioxygen to yield hydrogen peroxide (or its equivalent). The third step in the oxidation process involves the metal catalyzed oxidation of the substrate by the hydrogen peroxide equivalent.

Finally, we have achieved the oxidative degradation and chemical recycling of a wide range of polymeric materials under relatively mild conditions using nitrogen oxides and dioxygen.⁴ With the production of polymeric materials on the rise and landfill space at a premium, it becomes increasingly important to develop new techniques for reducing the amount of material lost to the landfill. While some condensation polymers are chemically recycled, there is very little, if any, recycling of addition polymers which constitute 75% by weight of all polymers manufactured. Using our procedure, a wide variety of addition and condensation polymers can be oxidatively degraded. In the particular cases

of polystyrene, high and low density polyethylene and, perhaps, polypropylene useful organics are produced in moderate to good yields.

PUBLICATIONS

1. "A Broad Spectrum Catalytic System for Removal of Toxic Organics from Water by Deep Oxidation Using Dioxygen as the Oxidant,"
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2. "The Deep Oxidation of Chemical Warfare Agent Models: Facile Catalytic Oxidative Cleavage of Phosphorus-Carbon and Sulfur-Carbon Bonds using Dioxygen,"
Terrence Hogan, Robert Simpson, Minren Lin, and Ayusman Sen,
Catal. Lett., **1997**, 49, 59.
3. "A Broad Spectrum Catalytic System for the Deep Oxidation of Toxic Organics in Aqueous Medium Using Dioxygen as the Oxidant,"
Anne Pifer, Terrence Hogan, Benjamin Snedeker, Robert Simpson, Minren Lin, Chengyu Shen, and Ayusman Sen,
J. Am. Chem. Soc., **1999**, 121, 7485.
4. "Chemical Recycling of Plastics to Useful Organics by Oxidative Degradation,"
Anne Pifer and Ayusman Sen,
Angew. Chem., Int. Ed., **1998**, 37, 3306.