

Final Report
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DESCRIPTION/ABSTRACT

The focus of this project is directed at the design of novel zeolite-based hybrid catalysts, based on encapsulated transition metal chelate complexes and metal oxo species. One goal is to achieve improved control over the active species in heterogeneous catalysis, as well as improved reactant and product selectivities. This is achieved by combining the catalytic activity of transition metal catalysts with the large surface area of microporous and mesoporous hosts. Furthermore, shape selectivity may be achieved through the well-defined pore structure of zeolites.

Several families of complexes have been studied, including nitrogen chelate complexes, chiral salen complexes, and supported molybdenum-oxo species. In the group of nitrogen-containing metal chelate complexes, some are derived from triazacyclononane, while others are derived from tetradentate cyclam-type ligands. These complexes have been studied in solution, encapsulated in the cages of zeolites, and attached to the channel walls of the novel mesoporous MCM-41-type materials. The latter approach is based on covalent grafting of the ligand to the host, followed by metalation. These heterogenized complexes show good activity in highly selective olefin epoxidation reactions.

Furthermore, we have investigated the encapsulation of *chiral* metal chelate complexes, including manganese salen complexes in the cages of EMT zeolite. This large-pore host allowed us to synthesize the entire complex in the zeolite in a multistep sequence. The epoxidation activity of these hybrid systems is truly encapsulated in the host cages: large substrate molecules such as cholesterol were not oxidized. Chiral epoxidation with enantiomeric excess of 80% was achieved.

Zeolite-supported molybdenum-oxo species have also been synthesized and investigated. These systems are also very active and selective epoxidation catalysts.

Comprehensive characterization with spectroscopic and structural techniques has been performed, including EXAFS (Extended X-Ray Absorption Fine Structure) spectroscopy utilizing synchrotron radiation, *in situ* FT-IR coupled to thermodesorption, Micro Raman, UV-NIR, and ESR spectroscopies. In these catalytic studies of hydrocarbon conversions we address issues including the location of catalytically active sites, stability against migration, and shape selectivity.

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