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Catalysis Science and Technology

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Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Our objectives were to develop a multidisciplinary team and capabilities to develop a fundamental understanding of homogeneous, heterogeneous, and heterogenized catalysts. With the aid of theoretical chemistry approaches we explored and characterized the chemical reactivity and physical properties of a large number of catalytic systems.

Background and Research Objectives

Our objective was to discover new catalytic chemistry and understand the structure of catalysts that transform organic substrates into molecules having greater complexity. Our studies used the unique combination of capabilities from across the Laboratory in materials synthesis, organometallic chemistry, theoretical chemistry, neutron scattering, reaction chemistry, and nuclear magnetic resonance spectroscopy. We used these capabilities to answer key questions about catalyst structure and reactivity. Through this project, we not developed only a significant knowledge base but also formed a highly successful team of researchers.

Importance to LANL's Science and Technology Base and National R&D Needs

Many of the staff involved in this project now use the capabilities we have developed for approaching solutions to problems in such core mission areas of the Laboratory as the science of key weapons materials and processes. In addition, our research in various aspects of catalysis attracted interactions with industrial scientists, relationships and partnerships with our sister Laboratories were formed, and we forged a number of academic collaborations that will continue into the future.

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Scientific Approach and Accomplishments

We knit together a broad spectrum of disparate Laboratory capabilities into a focused effort in the study of catalytic materials and catalytic chemistry. Our objective was to develop new catalytic chemistry, theoretical techniques, and spectroscopic tools for the elucidation of structure and reactivity of catalysts. Our studies were focused in the following areas:

1). Solid state nuclear magnetic resonance and neutron scattering techniques for the elucidation of structure of site-isolated catalysts containing metal clusters and metal ions either in or on the zeolite framework. 2). Theoretical techniques to describe metal ions on or in the framework of aluminophosphates and zeolites. 3). Neutron scattering techniques for the determination of structure and of adsorbed molecules within the zeolite pores. 4). New catalytic chemistry in dense phase carbon dioxide. 5). New catalytic and stoichiometric chemistry of boration and diboration of unsaturated organic substrates. 6). Synthesis, catalytic activity, and deactivation of diphosphine rhodium cations on the surface of mesoporous silicas. These main areas of activity are outlined below, and the pertinent publications that were generated as a result of this research are referenced.

1). Structural studies of site-isolated catalysts. Neutron diffraction and solid state nuclear magnetic resonance studies of nanoporous zeolites containing dilute metal ions or metal clusters were undertaken to develop an understanding of the local structure of the catalytically important metal active sites. One such system that we focused on was TS-1, a titanium-containing molecular sieve that exhibits unusual activity and selectivity in the selective oxidation of hydrocarbons using aqueous hydrogen peroxide as oxidant. The active sites are known to be the dilute, site-isolated tetrahedral Ti ions isomorphously substituted into the zeolite framework. The structural details of the Ti siting has been the source of much controversy in the literature. Using neutron diffraction techniques, we solved the Ti siting for the first time. In contrast to the generally accepted prediction that the Ti is randomly distributed throughout the zeolite framework, we found that Ti is preferentially sited on just a few of the possible framework positions, with one being particularly favored. We also solved the siting of Fe in the related catalyst FeS-1, and found the iron is located on only one of the possible sites, and the preferred site is the same site as Ti most prefers. Semiempirical calculations on very large cluster models of TS-1 were also carried out to attempt to understand the preferential siting of Ti atoms at specific sites in the zeolite that we observed experimentally.

The possibility of a correlation between either substitution energies of Ti for Si at the 12 distinct sites or the interactions of cationic templates with Ti-OH anionic defect sites with the observed preference was examined. However, no correlation was observed for either supposition.[1]

In an attempt to study TS-1 by observing the Ti nuclear magnetic resonance (NMR) spectrum, we developed the capability and an understanding of Ti NMR in titanium silicate minerals.[2-4]

We have also investigated the local structure of Ti in TS-1 and other mesoporous Ti silicate catalysts and in Ti-substituted nanoporous aluminum phosphates using the influence of the paramagnetism of Ti(III) on Si-29 or P-31 NMR spectra.[5] We have used the paramagnetic influence of metals in $AlPO_4$ and TS-1 to obtain information about the state of the metal in substituted sieves. The hyperfine interaction produces shifts and broadening that are different from the dipole interaction, which obtains when the metal is simply exchanged in the pore. Our data strongly indicate that the titanium in TS-1 and in Ti-$AlPO_4$ is substituted in the framework.

Additional activities in the area of site-isolated catalysts have been in the study of small metal clusters in zeolites using solid state ^{129}Xe nuclear magnetic resonance as a function of temperature. In order to understand the results, we first had to develop an understanding of how Xe interacts with the walls of zeolites in the absence of the metal clusters.[6,7] Using this knowledge, we studied the interaction of Xe with zeolites containing small metal clusters. The results have indicated relative preferences for Xe interactions with the walls of the zeolite vs. metal clusters of differing sizes within the constrained microporous environment.[8]

2). In our exploration of the structure of site-isolated oxidation catalysts, we have used theoretical chemistry studies to probe the features of Co ions in inorganic frameworks, specifically the nanoporous aluminum phosphates, and the interaction of dioxygen (O_2) with the Co. These studies were benchmarked against X-ray absorption fine structure data and known molecular analogs of Co-O_2 complexes.[9-11]

We have also performed a series of cluster calculations on models of the zeolite TS-1 in order to understand the steps involved in the selective oxidation of hydrocarbons at the Ti center.

Transition states and activation barriers for various reaction pathways were determined for the epoxidation of ethylene.

3). As part of our effort to develop methods for characterizing site-isolated catalysts we have carried out neutron diffraction studies to assess the utility of pair-distribution function (PDF) analysis of diffraction data for this purpose. While an experiment designed to locate metal clusters in zeolite NaY was unsuccessful because of their very low concentration, we have been able to obtain local structural information on the location of adsorbed chloroform by means of a differential PDF between normal and deuterated adsorbed chloroform in zeolite NaY.[12] This study is complementary to previous work that we have done on similar systems using vibrational spectroscopies such as Raman and inelastic neutron spectroscopies in concert with computational modeling to determine local structural features of adsorbates in nanoporous environments.[13,14]

In the area of homogeneous catalysis and supported homogeneous catalysis, we developed new fields of metal catalyzed boration and diboration of unsaturated organic compounds.[15] These are new routes to functionalized compounds that can be further elaborated for use in complex organic reactions for the preparation of agrochemicals, pharmaceuticals, and other high-value specialty chemicals. We have also developed new catalytic chemistry in supercritical fluids that offer novel reactivity and selectivity in addition to novel means of separating reactants, products, and catalysts at the end of the reaction.[16] These areas are outlined below:

4). We investigated the selective oxidation of hydrocarbons substrates under liquid and supercritical fluid conditions. These represent some of the first studies demonstrating the utility of supercritical carbon dioxide as a useful, environmentally benign solvent for performing chemical catalysis of useful reactions. Rates and selectivities of epoxidation in liquid and supercritical carbon dioxide were found to be equivalent or enhanced in some cases to that found in conventional solvents.[17,18]

Another class of catalytic reactions that form carbon-carbon bonds were performed in supercritical carbon dioxide, and were found to proceed with high conversion and selectivity.[19]

More recently, we performed initial studies of homogeneous catalysis in supercritical carbon dioxide (hydroboration, hydrogenation, hydroformylation) using partially fluorinated phosphines as ligands for Rh(I) catalysts. This is the first demonstration of hydroboration in supercritical carbon dioxide and we are able to get good to excellent regiocontrol using styrene derivatives as substrates. Additional research is ongoing.

In addition, a variety of new metallophosphenium complexes of Rh, Pt, and Ru have been synthesized, and we have shown that careful design of the NR2 substituents on phosphorus leads to control of the steric and electronic nature of the phosphenium ligand, that may manifest itself as control over the electrophilic nature of the metal complex. The utility of these novel compounds awaits further investigation. A single crystal X-ray structure of one such complex has been determined. This work is ongoing, and will be published in due time.

In the area of supported homogeneous catalysis, we investigated the mode of binding of a molecular rhodium cationic complex onto silica surfaces, including the surface of mesoporous silicas. We discovered a highly efficient, simple method of binding the rhodium cation using off-the shelf reagents. We learned that the silica surface interacts with the counteranion of the rhodium cationic complex, and this is responsible for sequestering of the active rhodium complex to the surface. The choice of counteranion is crucial. We believe that the formation of hydrogen bonds between surface silanols and the counteranion are involved, and so the choice of a good hydrogen bond acceptor as counteranion leads to successful immobilization of the rhodium complex cation to the surface. We found that the trifluoromethylsulfonate anion led to a stable, heterogenized catalytic system for the efficient, selective enantioselective hydrogenation of enamide esters using chiral phosphine – rhodium cations.[20,21]

In addition to the focus areas above, we also made contributions to the literature in other areas, such as in the area of understanding the stability, structure, spectroscopy, and reactivity of zeolite catalysts,[22-26] and in the generation of topical overview papers for journals.[16,27,28]

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