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Catalysts for Hydrocarbon Oxidation

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Catalysts for Hydrocarbon Oxidation

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Abstract

This is the final report of a one-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). The focus of this project was elucidating structural aspects of a titanosilicate TS-1 that is an oxidation catalyst. We have prepared samples of TS-1 and used scanning electron microscopy, high resolution transmission electron microscopy, and ultraviolet-visible spectroscopy to examine the samples of TS-1 for amorphous titanium-containing phases that may confound the analysis of the neutron scattering data. We observed that the volume fraction of titanium-containing impurity phase(s) determined from electron microscopy did not correlate well with that amount determined by ultraviolet-visible diffuse-reflectance spectroscopy. We also designed, constructed, and tested a flow reactor that can be placed into the neutron flight path at the High Intensity Powder Diffractometer line at the Manual Lujan, Jr. Neutron Scattering Center. This reactor will allow for the observation of crystallographic changes of catalysts and other materials under reaction conditions.

Background and Research Objectives

Our general interest is in the investigation of the structure and reactivity of site-isolated solid catalysts that selectively oxidize hydrocarbon substrates to useful organic chemicals. In many site-isolated catalyst systems that are used in the industrial-scale preparation of organic chemicals of commerce, the structures of the active catalyst remain a mystery. This is because of the complex nature of these solid materials, and that the active sites are highly dilute in the solid matrix. There are few techniques for studying the local structure and chemistry of dilute sites within solid matrices. Also, the understanding of the mode of action of solid catalyst materials has been hampered because there are currently few, if any, techniques for probing the bulk and/or local structure of these materials under reaction conditions ($100^{\circ}\text{C} < T < 1000^{\circ}\text{C}$ and $1\text{ atm} < P < 15\text{ atm}$).

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The structural features and chemistry of a prototypical site-isolated oxidation catalyst, TS-1, are of interest to the catalysis community because of the unusual reactivity this catalyst exhibits. TS-1 selectively oxidizes hydrocarbon substrates to useful products at low temperatures and in aqueous media using hydrogen peroxide as the oxidant (see Reference 1 for a review of the current state of knowledge of TS-1 chemistry and structure). TS-1 is a microporous silicate with a small percentage of the silicon atoms replaced by Ti. It is believed that the Ti ions promote the oxidation chemistry via hydroperoxide intermediates, and that these intermediates are stabilized by being site isolated. Because of the low site population of Ti ions in the crystalline silicate host, the Ti sublattice is disordered and standard x-ray diffraction techniques are not useful in determining the location of Ti. Neutron scattering techniques appear to be useful in determining the location of Ti in the framework of TS-1, and in shedding light on the local structure surrounding the Ti ions. In order to perform these neutron diffraction studies, pure, well-characterized samples are required.

For this one-year project, our objectives were to synthesize samples of TS-1 and characterize them with a variety of techniques to allow us to better understand the nature of inactive Ti impurities that are not integral to the TS-1 structure and that interfere with our ability to better understand the structure of the titanium sites in the active catalyst. Another objective was to design, fabricate, and test a catalytic reactor that could be installed into the High Intensity Powder Diffractometer (HIPD) at the Manual Lujan, Jr. Neutron Scattering Center (MLNSC). This reactor was designed to be able to be heated to 250° C, cooled to -40° C, pressurized to several atmospheres, and allow for continuous flow of reactants to and products from the reactor. The reactor would then be lowered into the HIPD flight path such that neutron scattering data could be obtained from operating catalysts.

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

The research we performed relates to the Laboratory's complex experimentation and measurement competency. We develop instrumentation and techniques for the analysis of complex materials. These techniques are applicable to the studies of mission-oriented problems in interfacial phenomenon, aging, and defects in materials. Neutron scattering is a powerful capability for the study of catalysts, a capability that is currently underutilized by the catalysis community. Our research contributed additional capability to the utility of MLNSC for catalysis research that may have a positive impact on broadening the constituency of this national user facility.

The structure and function of disordered systems are important problems in a number of mission-oriented areas at the Laboratory and within the DOE complex. The study of a certain subclass of these materials that are catalysts is important to the development of new, more efficient catalysts. More efficient catalysts are desirable for the next generation of environmentally benign, energy efficient processes for industrial production of organic chemicals.

Scientific Approach and Accomplishments

We had two objectives, to synthesize samples of TS-1 suitable for neutron diffraction studies, and to design, build, and test a chemical reactor for performing in situ neutron diffraction. We attempted to prepare very pure samples of TS-1 for structural characterization studies. Samples of TS-1 were synthesized using hydrothermal techniques adapted from literature methods. The TS-1 zeolite samples that crystallized from the hydrothermal synthesis mixtures were characterized using standard x-ray diffraction techniques to assess the crystallinity and phase purity of the catalyst. To assure that the crystallized solids were catalytically active, we performed catalytic selective oxidation reactions using phenol as a substrate and hydrogen peroxide as the oxidant. Activity of the catalysts was assessed by comparing the conversion of phenol at 2 hours of reaction time at 80° C to that achieved by archival samples of authentic TS-1.

Analytical electron microscopy was performed to identify crystalline and non-crystalline impurities. The non-crystalline impurities contained little silicon, and are best described as agglomerates of nanophase titania. The volume fraction of these non-crystalline titania aggregates was compared with ultraviolet-visible diffuse-reflectance (DR-UV-Vis) spectroscopy results. The DR-UV-Vis spectroscopy yields a bulk estimate of octahedral Ti ions that absorb below 370 nm versus four-coordinate Ti ions that absorb below 210 nm. The ratio of absorbance at 210 and 370 nm was compared to the volume fraction of titania aggregates as found by electron microscopy. No correlation was found between the two methods, perhaps because of poor statistics associated with the limited number of regions that can be analyzed by electron microscopy.

Analytical electron microscopy of individual crystallites from a preparation of TS-1 indicated that the crystallites had a distribution of Si/Ti atomic ratios, to the point where some crystallites contained no Ti whatsoever. This was observed from a number of different preparations. This inhomogeneous distribution of titanium contents can be rationalized in terms of the relative rates of reactivity of the silicon- and titanium-containing

precursors compared to the rate of nucleation of crystalline material. The titanium-containing precursors are significantly more reactive than the silicon-containing precursors, and are probably converted into crystalline TS-1 early in the reaction sequence. This leaves the reaction mixture depleted in reactive Ti species, and the material that crystallizes subsequently is increasingly depleted in Ti, to the point where the last material to crystallize contains no Ti. This effect, to our knowledge, has not been noted in the extensive literature of TS-1.

The "best" samples, as determined by DR-UV-Vis, x-ray diffraction, Si-29 nuclear magnetic resonance, and electron microscopy were then soaked in D₂O to remove residual protons, dried, and given to our collaborators doing neutron scattering studies of TS-1.

Our second objective was to design, construct, and test a catalytic reactor for performing in situ neutron diffraction studies. The design requirements were to allow us to operate at moderately low temperatures for adsorption studies to moderately high temperatures for reaction studies, be suitable to operate at moderate pressures, and allow for reactants to flow into and products out of the reactor. The reactor configuration had to adapt to the vacuum well of the HIPD at MLNSC. The construction had to incorporate appropriate neutron shields, and a reactor fabricated of a material that would give rise to negligible background contributions to the diffracted beam.

Our design (Figure 1) consists of a conventional plug flow reactor using a thin-walled vanadium metal reactor tube of identical dimensions as for vanadium sample cans used for conventional, static neutron diffraction at MLNSC. The design could also be adapted to using a sapphire tube cut off-axis to minimize Bragg reflections. Sapphire would be useful in cases where vanadium could react with reagents or products of the reaction. The reactor tube is heated within a boron nitride cavity using cartridge heaters, and can reach a temperature of 550° C. The boron nitride furnace block/collimator has cutouts at appropriate take-off angles to allow the scattered beam to impinge upon the detectors at HIPD. The vanadium reactor tube is thermally coupled to a copper block that can be chilled to below ambient temperatures, or to allow for rapid cooling of the reactor from high temperatures. This reactor configuration gives us the ability to treat samples in situ and to cycle reaction conditions without having to remount a sample following ex-situ (off line) processing. This is a key advantage to observing and understanding coordination changes at the active sites of these catalyst materials, and could be useful for studies of other classes of materials as well.

After complete bench testing of the reactor unit, we mounted the fixture into the vacuum well of HIPD during the Fall 1996 run cycle at MLNSC, and acquired data as a function of temperature while passing D₂O steam through the reactor. We were able to

verify the operation of the reactor in the neutron flight path, and successfully acquired scattering data at a number of temperatures.

Analysis of the neutron scattering data obtained from in situ steaming of TS-1 indicated that there was a small piece of boron nitride in the flight path that gave rise to small BN Bragg peaks in the diffraction pattern. This problem can readily be solved. Qualitative analysis of the data indicates that TS-1 undergoes significant structural rearrangement at elevated temperatures under steam. This is anticipated to occur readily, as aluminum ions are known to be readily removed from the framework of the analogous aluminum-containing zeolite under similar conditions.

In summary, we successfully prepared well-characterized TS-1 suitable for neutron scattering studies, and developed an in-situ reactor fixture for neutron scattering studies of solid materials at HIPD.

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Figure 1. Schematic of the reactor fixture for in situ neutron scattering studies at HIPD.