

## Spectroscopic and Kinetic Characterization of Metal Oxide and Sulfide Catalysts

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### Research Scope and Objective

The objective of this research is to provide a better fundamental understanding of catalysis by metal oxides and sulfides. The investigations being performed are primarily concerned with the examination of the nature of active catalyst phases or sites and with the exploration of the mechanisms of catalytic reactions. The experimental approaches include studies of preparation procedures, adsorption phenomena, and catalytic activity and selectivity. In investigating metal oxide and sulfide catalysts, however, two experimental approaches have been paramount. First, it has been an important goal of this research to provide a basis for relating the solid state chemistry of oxides and sulfides to their adsorptive and catalytic properties. For specific catalysts, this involves systematic variations in composition, oxidation state, or overall preparation technique. Extensive spectroscopic characterization of the structure and composition of catalysts is performed to provide a more fundamental understanding of the solid state. The second major emphasis of this research program has been to develop the experimental capability for performing in situ spectroscopic studies. In particular, laser Raman spectroscopy and Fourier transform infrared spectroscopy have been used to examine catalysts and adsorbed species under actual operating conditions. This typically involves measurements at elevated temperatures and pressures. Spectroscopic cells have been designed which permit spectroscopic and kinetic data to be obtained simultaneously.

### Description of Research Effort

Current research efforts are focusing on the catalytic properties of metal oxides and sulfides. The solid state chemistry of the catalysts being studied is similar; catalysts can be prepared with systematic variations in structure, composition, oxidation state, and surface properties. In addition, similar spectroscopic techniques can be used to characterize these catalysts, including laser Raman spectroscopy, Fourier transform infrared spectroscopy, x-ray diffraction, x-ray photoelectron spectroscopy, electron microscopy, and x-ray fluorescence.

The most important metal sulfide catalyst used in industry is the cobalt/nickel molybdate hydrodesulfurization catalyst. Despite the importance of this catalyst, the nature of the active phases or sites and the mechanisms for the desulfurization of important organosulfur compounds are not well understood. In order to understand the complex structure and composition of these catalysts, a systematic investigation of the preparation procedures has been performed. In situ laser Raman spectroscopy has been used extensively to characterize the oxidic and sulfided forms of cobalt molybdate on alumina catalysts. These studies have revealed the presence of a unique polymolybdate surface phase which dominates the oxide precursor state of the catalyst. Our in situ studies of the oxide-to-sulfide conversion of the catalyst were the first to identify the existence of oxysulfide phases on the surface of alumina; in addition, reduced phases could also be observed. Under vigorous sulfiding conditions, disordered molybdenum sulfide structures have been observed using the Raman technique. The Raman technique has been demonstrated

to be a very sensitive probe of these compounds; in situ techniques are also essential to the investigation of such air-sensitive catalysts. In addition to these recent advances, we have reported the first vibrational spectroscopy of hydrogen adsorbed on unsupported molybdenum sulfide catalysts. The Raman technique indicates that Mo-H bonds are formed at 25-350°C.

Recent work with hydrodesulfurization catalysts has focused on studies of unsupported catalysts--in order to better understand the structure, composition, and oxidation state revealed by our characterization of supported molybdenum catalysts. A new series of reduced molybdenum sulfide catalysts have been discovered based on chevrel phase compounds. These catalysts exhibit unusual selectivity for desulfurization compared to hydrogenation. Studies of the effect of oxidation state on catalytic activity and selectivity are also possible by performing systematic variations in the preparation of these compounds.

Selective oxidation catalysts based on the oxides of molybdenum, vanadium and tungsten are an important class of industrial catalysts. The mechanisms of selective oxidation reactions are typically complex: our current investigations of C<sub>4</sub> hydrocarbon oxidation to maleic anhydride include studies of oxidative dehydrogenation, oxygen insertion, and complete combustion. In addition, the catalysts involve multiple phases or various compositional ranges. Recent work has demonstrated that nonstoichiometric ratios of metals (excess molybdenum) produce much more active cobalt and nickel molybdate oxidation catalysts for 1-butene conversion to maleic anhydride. Current research is also focusing on the mechanism of this conversion; pulse and fixed bed reactors are presently being used. Investigations of the effect of oxidation state and defect structure on catalytic activity are being conducted using molybdenum shear structure compounds. These studies have indicated strong differences in catalytic activity for various steps in maleic anhydride synthesis. Recent work has also begun on V-P-O catalysts. We have successfully concluded the first systematic characterization of a series of model compounds for this catalyst system.

#### Future Research

The goal of this research program is to provide a better understanding of the solid state chemistry of oxide and sulfide catalysts and to develop an improved understanding of the mechanisms of hydrodesulfurization and selective oxidation reactions. Development of techniques such as laser Raman spectroscopy and Fourier transform infrared spectroscopy which can be used to perform in situ experiments is also an important goal of this research. Our hydrodesulfurization studies will continue to explore the unique activity of chevrel phase catalysts, with particular emphasis on the variation in molybdenum oxidation state which may be achieved through synthesis. In situ studies of the mechanism of thiophene hydrodesulfurization will also be performed using a new series of high pressure spectroscopic cells. A unique group of model organometallic compounds will be utilized in this investigation to identify adsorbed species or reaction intermediates. Selective oxidation experiments will focus on nonstoichiometric metal oxides which may also exhibit various oxidation states. This will permit new information about the relation between the solid state chemistry of oxides and their catalytic activity, selectivity, and stability. In order to study the mechanism of maleic anhydride in more detail, a multibed reactor will be used. In addition, in situ Fourier transform infrared spectroscopy studies will involve the adsorption of various potential maleic anhydride synthesis intermediates adsorbed on catalyst surfaces.