STUDIES OF SUPPORTED METAL CATALYSTS

Principal Investigator: David M. Hercules

Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

Research Scope and Objectives

The major objective of our research has been to characterize the binding of transition metals to catalytic supports and to study speciation of these metals on supports. The specific objectives of the research have been as follows: 1) To study the binding of Mo and W to alumina and other supports. 2) To study the binding of Co and Ni to alumina and other supports. 3) To study the effect of other transition metals on the binding of Co and Ni to supports. 4) To study the effect of preparation method and pretreatment on the nature of Co, Ni, Mo and W species on catalysts. 5) To study the interaction of Co and Ni with Mo and W on supports. 6) To study the effect of sulfiding on Co, Ni, W and Mo catalysts. 7) To correlate the above measurements with chemical activity of the catalysts for hydrodesulfurization reactions. 8) To determine the relative effectiveness of different spectroscopic techniques for studying the surfaces of supported heterogeneous catalysts.

Description of Research Effort

We have used a variety of spectroscopic techniques to study heterogeneous catalysts. These include: x-ray photoelectron spectroscopy (ESCA), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), low ion energy scattering spectroscopy (ISS), x-ray diffraction (XRD), laser Raman spectroscopy (LRS), extended x-ray absorption fine structure (EXAFS) and photoacoustic spectroscopy (PAS).

One of the major accomplishments of our work was to demonstrate the utility of using the combination of ESCA, ISS and LRS to study catalyst surfaces. Frequently, LRS and XRD can give structure specific information about bulk phases but ESCA can not; similarly, ESCA can give structural information about highly dispersed phases (monolayers) but LRS and XRD can not. In addition we have demonstrated a correlation between ESCA, EXAFS and PAS measurements on the same catalyst systems. This relates to the symmetry of the transition metals on the catalytic support. Valuable information can be obtained using this combination of techniques which can not be obtained from any one technique. We have been able to demonstrate a correlation between the reducibility of catalytic species measured by ESCA and the same quantity measured by more classical techniques.

We have been able to characterize nickel species on alumina and silica surfaces by varying the preparation method and nickel content of the catalysts. We have studied cobalt species on alumina and how these species are affected by the presence of molybdenum or zinc; also we have studied the effect of sulfiding. We have been able to study the speciation of molybdenum on an alumina catalyst to determine how Mo species are changed by sulfiding, by the presence of cobalt

or by changing the support (TiO_2). We have studied tungsten on alumina and have contrasted the catalytic species between Mo and W on the same support. We have carried out extensive photoacoustic measurements on Co and Ni systems to determine the site symmetry of cobalt and nickel supported on alumina.

Future Research

There are three major objectives for our future research. First, we will continue our systematic study of the influence of active-phase, promotors, supports and additive on the surface structure of catalysts in the active forms. Second, we will correlate surface structure of the active catalyst with its catalytic activity for a variety of reactions; primarily hydrodesulfurization. Third, using the above information we will attempt to tailor the activity and selectivity of catalysts for a given reaction.

Comprehensive characterization of supported catalysts requires detailed knowledge of four important parameters: the nature of the species on the surface; the dispersion of the supported phase; the nature of the interaction between the substrate and carrier; and the repartition of the deposited phase. The focus of our research will be to obtain information on these four parameters for the catalyst systems studied.

In order to obtain the information cited above, it will be necessary to use the combination of spectroscopic techniques (listed above) which probe both the surface and the bulk of the catalyst. The approach in our laboratory has been to use multiple spectroscopic techniques to obtain the necessary information about each of the important parameters above. These objectives will be achieved in the following way: First, the nature of the surface species will be elucidated by ESCA, SIMS, PAS, ISS, EXAFS and XRD. Second, the dispersion of the supported phase will be examined by EM and XRD. Third, information relating to the nature of the metal support interaction can be obtained primarily from ESCA binding energy measurements coupled with reduction studies. A combination of ESCA with hydrogen reduction has proved to be a powerful diagnostic tool. Fourth, indications about repartition of the supported phase can be obtained from ESCA intensity ratio measurements. A semiquanitative evaluation can be achieved using a microprobe attachment to an electron microscope. The combination of the two should be extremely fruitful.

In summary, the major objective of our research effort is to use an arsenal of highly sophisticated spectrosocpic techniques, coupled with more classical techniques, to fully characterize the nature of surface species of heterogeneous catalysts and their interaction with the catalyst surface. We will use this information to predict catalytic activity and to understand the selectivity and activity of catalysts in specific reactions.