

PROPERTIES OF LANTHANIDE OXIDES AS SUPPORTS
FOR TRANSITION METAL CATALYSTS

Michael P. Rosynek

Department of Chemistry
Texas A & M University
College Station, Texas 77843

Research Scope and Objectives

This research program involves a systematic investigation of the behaviors induced in dispersed transition metal catalysts by a series of lanthanide oxide supports, in comparison to those occurring with other, more conventional support materials. The lanthanide oxides selected for study provide appropriate variations in several important physical/chemical properties, including acid-base character and cationic multi-valency. The goals of the project are to attain an increased understanding of the general phenomenon of metal-support interactions, and to enable correlations to be made between physical/chemical properties of support materials and the catalytic behaviors of metals that are dispersed on their surfaces.

Description of Research Effort

Several previous studies have conclusively demonstrated that the catalytic, adsorption, and structural properties of dispersed transition metals may be significantly modified by variations in the nature of the support material employed. We have been investigating the effect of a variety of supports in influencing the catalytic behaviors of dispersed iron, cobalt, and nickel for two diagnostic reactions, viz., the hydrogenation of carbon monoxide and the multi-pathway conversion of n-paraffins. Particular emphasis has been placed on characterizing support-induced alterations in reaction selectivities.

We have observed that basic oxides, such as La_2O_3 and Eu_2O_3 , and other "electron-rich" supports, such as graphite, cause an overall increase in average hydrocarbon product chain length during CO hydrogenation over iron and cobalt at 200-300°C and one atmosphere pressure, when compared to the behaviors observed under identical reaction conditions with SiO_2 , Al_2O_3 , TiO_2 , and other neutral and acidic supports. Activity for the concurrent water-gas shift reaction may be markedly altered as well. An iron-graphite catalyst, for example, produced only 10-15% as much CO_2 during CO hydrogenation as did an Fe/ SiO_2 or Fe/ Al_2O_3 catalyst at similar CO conversions. Accompanying x-ray photoelectron spectroscopic studies of selected cobalt catalysts have indicated that marked differences in the ease and extent of reduction of surface cobalt occur among the various support materials investigated. A correlation appears to exist, moreover, between the

reducibility of surface metal and the observed hydrocarbon product chain length during CO hydrogenation. Although effects due to electron transfer between support and metal cannot be ruled out as contributing factors, the overall effect is attributed largely to support-induced differences in metal particle morphology.

A second diagnostic reaction that has been employed for these studies has been the multi-pathway conversion of n-paraffins, for which both dehydrocyclization to aromatic products and dehydrogenation/hydrogenolysis to shorter-chain hydrocarbons occur over nickel catalysts at 350-400°C. In this case, the electronic nature of the support appears not to play a significant role in determining reaction selectivity, but variations in both metal dispersion and total support surface area have pronounced effects on the observed product distributions. High surface area supports, such as charcoal and silica, caused increased selectivity to dehydrocyclization, while low surface area supports, such as lanthanide oxides and sintered silica, resulted primarily in dehydrogenation and hydrogenolysis reactions. This behavior is believed due to increased capability for deposition of two-dimensional, aromatic-like surface residues with increasing support surface area.

Future Research

We plan to extend our investigations of metal-support interactions involving lanthanide oxide supports to include various other Group VIII transition metal catalysts, particularly platinum and rhodium. It is our intention to characterize behavioral differences in these systems between typical poorly dispersed metals, such as iron and cobalt, and the more highly dispersed noble metals on selected supports.