

REACTION KINETICS OVER SINGLE CRYSTAL CATALYSTS

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Research Scope and Objectives

The goal of this research is to develop an understanding of surface catalyzed reactions at the molecular level using the full complement of modern surface probes. Of primary importance are those reactions relating to the synthesis of hydrocarbons from H_2 and CO. The experimental work includes the determination of reaction kinetics of hydrocarbon formation and rearrangement over single crystal catalysts. An additional focus of this work is the elucidation of the mechanism by which catalytic poisoning and promotion takes place, particularly that relating to the catalytic chemistry of synthesis gas. A third experimental area of emphasis is in the simulation of oxide-supported-metal catalytic systems using a well-characterized, low surface area model system.

Description of Research Effort

Several reactions representative of important categories of catalytic systems have been studied on clean and chemically modified single crystal surfaces. These reactions are methanation of CO (I) and CO_2 (II), hydrogenolysis of ethane (III), hydrogenation of ethylene (IV), cyclopropane ring-opening (V), and hydrogenolysis (VI), and CO oxidation by O_2 (VII) and NO (VIII). For those reactions believed to be "structure insensitive" (I, II, IV, V, VII, and VIII) excellent correlations have been found between the kinetic results for single crystals and those observed for high-area supported catalysts. These include results for nickel, ruthenium, and rhodium catalysts. For the "structure sensitive" reaction of ethane hydrogenolysis, distinctly different rates are found for different crystal planes in contrast to the previously mentioned reactions. The reactivity differences of different facets has been ascribed to the variation of the spacings of the high coordination sites on the different surfaces.

Poisoning of the above reactions by ordered, submonolayer coverages of sulfur on nickel show large nonlinear effects for sulfur versus reactivity attenuation. These data suggest that the dominant influential effect of poisoning is an electronic one and one that extends over distances larger than the atomic radius of sulfur.

Additional studies have addressed the role of potassium promoters in nickel catalysts for methanation of CO and CO₂. Kinetic measurements of these reactions over a Ni(100) catalyst containing submonolayer quantities of potassium have been combined with detailed surface analysis before and after reaction. For CO methanation, potassium decreases the rate of methane formation and increases the rate of higher hydrocarbons relative to the clean surface. Similar results have been reported for supported nickel catalysts suggesting that support effects play a small role in catalytic promotion by potassium. For CO₂ methanation at certain reaction conditions not only is potassium observed to promote overall activity but is seen to compensate for the negative effects of sulfur.

Recent experiments have shown it possible to successfully simulate supported metal/oxide system using a low surface area model. Evaporated nickel at submonolayer coverage on a thin film of oxidized aluminum show a methanation activity identical (per nickel atom) to that of a high-area supported system. This convenient model should prove to be most useful in future experiments incorporating various vacuum spectroscopies.

Future Research

We are currently using several surface spectroscopies to study the nature of the surface electronic modification by impurity atoms such as sulfur and alkali metals. Ultraviolet photoelectron spectroscopy (UPS) is being used to monitor surface electronic state change induced by modifiers. X-ray photoelectron spectroscopy (XPS) is being employed to observe compensation effects of electronegative additives by electro-positive ones. Similarly, Auger electron spectroscopy (AES) studies are underway to probe the electronic perturbation by surface additives using techniques developed at Sandia. These studies are carried out in conjunction with kinetic studies over single crystals as well as simulated supported catalytic systems.