

FT-IR Catalyst Studies

David M. Haaland
Division 1823
Sandia National Laboratories
Albuquerque, NM 87185

Research Scope and Objectives

The objective of the proposed research is to derive a basic understanding of the role of surface modifiers (both promoters and poisons) on the molecular processes occurring on the surface of supported catalysts during methanation and Fischer-Tropsch reactions. Fourier transform infrared spectroscopy (FT-IR) will be applied to adsorption and reaction studies on high surface area supported catalysts. These experiments will be performed in situ as a function of temperature, reactant concentrations, and level of modifier present in order to determine modifier-adsorbate, adsorbate-adsorbate, and metal-adsorbate interactions. The infrared results on these supported catalysts can then be correlated with the results being obtained at Sandia by ultra high vacuum (UHV) techniques on the effects of surface modifiers on single crystal metal surfaces. These data are needed not only to confirm the proposed mechanisms by which modifiers affect the methanation and Fischer-Tropsch reactions, but also to identify to what extent ultra high vacuum, single crystal data can be used for predicting the mechanisms and rates of these reactions on high surface area supported catalysts under realistic (commercial) reaction conditions. Recent experiments at Sandia and elsewhere have identified carbidic carbon as playing an important role in these same reaction systems. We would, therefore, also propose to use in situ FT-IR to study the reaction kinetics and surface reactant species generated when carbidic carbon is hydrogenated on a supported catalyst. By performing these studies with both modified and unmodified catalysts as a function of temperature, we hope to be able to determine the role of the modifiers on the basic reaction mechanisms which affect product selectivity and distribution.

Description of Research Effort

This research program does not start until October, 1984, and therefore, no experimental data is available at this time. However, the methods to be used will be similar to our earlier FT-IR catalyst studies on benzene hydrogenation and CO oxidation.

Future Research

This study will be undertaken to understand the mechanism of promotion and poisoning by several surface modifiers on supported metal catalysts. The results will then be correlated with those obtained previously at Sandia on Ni(100). Potassium promoted and sulfur poisoned silica supported Ni catalysts will be prepared for the study. Adsorbed CO from the synthesis gas will be used as a probe of the local environment. The frequency of

the C-O stretching vibration is very sensitive to the surrounding atomic environment. If the electronic ligand model of modifier adatoms is correct, then a decrease of the C-O frequency would be expected for an electro-positive promoter adatom and an increase in frequency would be expected for an electronegative adatom.

Since CO partially dissociates on a Ni surface to form carbidic carbon at higher temperatures, it is expected that the resulting electronegative carbon will also influence the bonding of adsorbed CO. Thus the extent of promotion by K may be partially compensated at reaction conditions by the presence of carbidic carbon. By performing the FT-IR studies of adsorbed CO as a function of temperature and promoter concentration, the extent of promoter compensation might be determined.

Finally, simultaneous kinetic data and surface coverage information can be obtained from FT-IR performed on modified and unmodified catalysts. Kinetic data and reaction intermediates can be determined during the hydrogenation of the carbidic carbon. If the surface species can be identified from their vibrational spectra and if these are shown to be active intermediates, then the basic mechanisms involved during the hydrogenation of carbidic carbon could be determined by this method. Of course, kinetic data will have to be obtained as a function of catalyst particle size to assure that the kinetic results are not influenced by mass diffusion limitations in these supported catalysts.