Section IV

Summary of Major Accomplishments

Equipment and Instruments

During the period covered by this research grant, we have put in place and on-line the following equipment which was crucial to the progress made under this grant and continues to service research efforts in the departments of chemistry and chemical engineering here at University of Delaware:

1) Schlenk line for synthesis of air-sensitive materials under an inert environment. This apparatus was used in the synthesis of all the catalytic materials addressed in these studies.
2) Ammonia saturation and temperature programmed desorption unit. This apparatus was employed in the surface acidity characterization of many of the materials investigated in connection with this grant.
3) Transmission infrared (IR) cell. The cell was used in the pyridine adsorption infrared characterization of materials, investigation of the OH-region as a function of temperature, and investigation of the CO-region of the samples in high temperature CO and H_2 environments.
4) Low-pressure microreactor. The low-pressure reactor was employed in methanol dehydration probe reaction studies.
5) High-pressure reactor retrofitting. The high-pressure reactor was employed in all the CO hydrogenation testing of the catalytic materials.
6) Hydrogen chemisorption unit. This apparatus has been used throughout the course of the grant to quantify reactive surface area through H_2 and CO chemisorption on the catalytic materials synthesized in the course of our investigations

Scientific Progress

The three main sections of this report provide in-depth discussion of the scientific progress made during the period of this grant. In broad terms, (i) we have confirmed the synergy of the Rh-Mo combination for oxygenate production—both from materials in which the metals are sequentially chemisorbed and those in which the precursors are binuclear compounds containing rhodium and molybdenum, (ii) we have identified key features of the interactions between the transition-metal precursors and the alumina surface, and (iii) we have gathered evidence in support of our working hypothesis that the molybdenum in this system serves, primarily, to isolate and stabilize the active rhodium sites against agglomeration and consequent retrograde shifts in selectivity from oxygenates to hydrocarbons. More specifically, the following advances can be reiterated from the three manuscript sections of this report:

1) Bimetallic Rh-Mo/Al_2O_3 catalysts have been successfully synthesized from a homogenous, binuclear precursor, $(PPh_3)_2RhMo(CO)(\mu\text{-}CO)_2Cp$, and tested for CO and CO_2 hydrogenation.
2) Catalysts derived from binuclear precursors show superior selectivities for oxygenates to those derived from coadsorption of mononuclear complexes.
3) Analysis of global activation parameters of the binuclear- and mononuclear-derived Rh-Mo/Al_2O_3 catalysts suggest that the activation energies for CO and CO_2 conversion are markedly lower for the binuclear-derived materials.
4) Infrared analysis of the binuclear- and mononuclear- derived materials confirms that the Rh is present in a more highly dispersed mosaic on the binuclear-derived materials, as evidenced by the gem-dicarbonyl intensities on these samples. The IR results imply enhanced site-isolation of the Rh in the binuclear-derived materials.

5) Surface acidity of both native and metal-loaded aluminas have been quantified and controlled through KNO_3 doping. These materials have been characterized via methanol dehydration probe reaction studies, pyridine adsorption infrared spectroscopy, and ammonia saturation and temperature programmed desorption.
6) Dehydration activity of the KNO_3-doped samples was strongly correlated to their ultimate potassium loading and, hence, their Lewis acid character.
7) As has been suggested in the literature, $Mo(CO)_6$ precursors employed in this study appear to interact primarily with the non-acidic hydroxyl sites on the alumina surface during the sequential chemisorption used to synthesize these materials.
8) Upon adsorption of Rh subcarbonyls and their subsequent oxidation on the surface of Mo/Al_2O_3, the Lewis acidity of the materials is suppressed. This Rh-surface interaction suggests that the chemisorption of the active metal in this system occurs at Lewis acid centers of the surface.
9) $Rh-Mo/Al_2O_3$ catalysts, which have been prepared by sequential chemisorption (as opposed to coadsorption), have been tested for CO hydrogenation and compared directly to monometallic Rh/Al_2O_3 catalytic samples.
10) Promotion of Rh with preadsorbed Mo dramatically improves the activity and oxygenate selectivity of the Rh-catalyzed CO hydrogenation.
11) *In Situ* IR characterization and comparison of the $Rh-Mo/Al_2O_3$ and the Rh/Al_2O_3 materials, centering on analysis of the metal-carbonyl region, suggests that the Mo effectively hinders Rh agglomeration. This site-isolated Rh in the bimetallic system may, then, be responsible for the high oxygenate selectivity of these catalysts.

Major Presentations and Publications

Te, Mure, Lowenthal, Eric E., Foley, Henry C., "Comparative Study of Rh/Al_2O_3 and Rh-Mo/Al_2O_3 Catalysts", *Chemical Engineering Science* , submitted June 1994.

Te, Mure, Eric E. Lowenthal and Henry C. Foley, "Comparative Study of Rh/Al_2O_3 and Rh-Mo/Al_2O_3 Catalysts", poster to be presented at the 13th International Symposium on Chemical Reaction Engineering, Baltimore, Maryland, September 1994

Te, M., E. E. Lowenthal and H. C. Foley, "Evidence for Site Isolation in Rh-Mo Bimetallic Catalysts Derived from $CpRhMo(CO)_3(PPh_3)_2$", *Journal of Catalysis,* **146**, 591 (1994).

Lowenthal, E. E., S. Schwarz and H. C. Foley, "Surface Chemistry of Rh-Mo/γ-Al_2O_3: an Analysis of Surface Acidity", *Journal of Catalysis* , submitted April 1994.

Lowenthal, E. E. and H. C. Foley, "Bimetallic and Metal-Support Chemistries on Rh-Mo/γ-Al_2O_3", Presentation at Annual Meeting, American Institute of Chemical Engineers, St. Louis, Missouri, November 1993.

Lowenthal, E. E. and H. C. Foley, "Design of a High Activity, High Selectivity Alcohol Synthesis System: Secondary Dehydration and Site Isolation", Poster Presented at Biannual Meeting, North American Meeting of the Catalysis Society, Pittsburgh, Pennsylvania, May 1993.

Foley, H. C., M. Te and E. E. Lowenthal, "Rh-Mo Bimetallic Cluster-Derived Catalysts for CO Hydrogenation", Presentation at Annual Meeting, American Chemical Society, Petroleum Chemistry Symposium in Honor of Bruce C. Gates, Denver, Colorado, March 1993.