



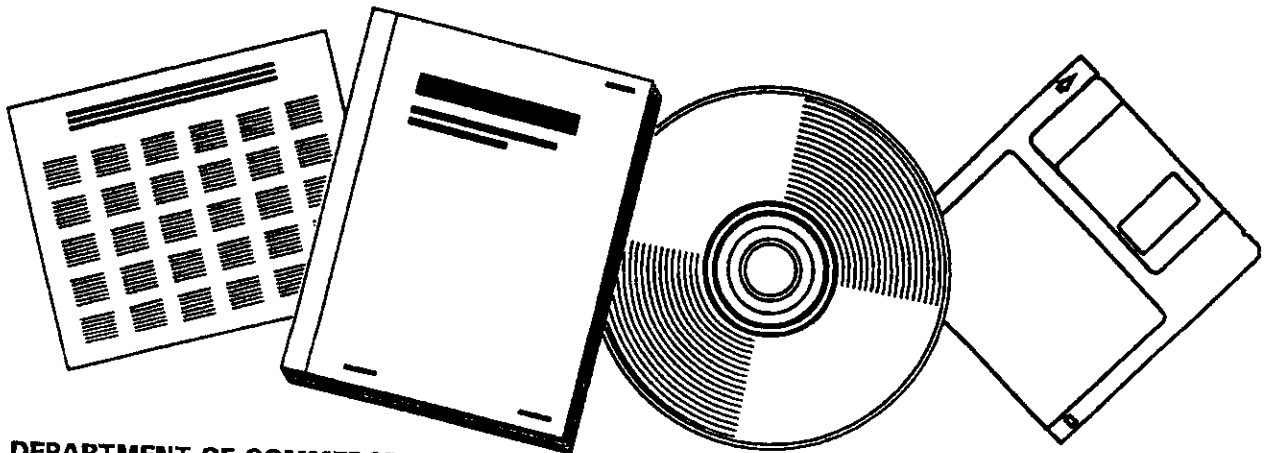
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**METAL-SUPPORT INTERACTIONS: THEIR EFFECTS
UPON ABSORPTION, ELECTRONIC, AND
ACTIVITY/SELECTIVITY PROPERTIES OF COBALT
IN CO HYDROGENATION. ANNUAL PROGRESS
REPORT, APRIL 1, 1985 - MARCH 31, 1986**

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METAL-SUPPORT INTERACTIONS: THEIR EFFECTS
UPON ADSORPTION, ELECTRONIC, AND ACTIVITY/SELECTIVITY
PROPERTIES OF COBALT IN CO HYDROGENATION

Annual Progress Report
For the Period April 1, 1985 to March 31, 1986

by

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prepared for

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Introduction

During the past five years the BYU Catalysis Laboratory has been involved in an investigation of the interactions of cobalt (and to a lesser extent iron) metal(s) with alumina, silica, titania, magnesia, and carbon supports. The results of the first four years of investigation were summarized in previously submitted technical reports [1,2] and in recently published papers [3-9]. Our contract was renewed for an additional three years starting April 1, 1984.

This work involves a comprehensive, quantitative investigation of the effects of metal-support interactions on the adsorption, catalytic, and electronic properties of cobalt (and to a lesser extent iron), the objectives of which are to determine: (i) effects of cobalt-support interactions and cobalt dispersion on the binding states, binding energies and species distribution of CO adsorbed on cobalt, (ii) the relation of dispersion and chemical state of cobalt to its activity/selectivity properties in CO hydrogenation, and (iii) the extent of electronic interaction of cobalt and iron with various supports.

This report briefly summarizes accomplishments during the fifth year (second year of the renewal contract) of this study.

Accomplishments and Results

Effects of Dispersion, Percent Reduction, and Preparation on the Activity/Selectivity Properties of Cobalt. The results of our investigation of the effects of dispersion, extent of reduction, and preparation on the activity/selectivity behavior of cobalt/alumina in CO hydrogenation were published in the Journal of Catalysis [8] and in C1 Molecule Chemistry [9] and presented at the International PACCHEM meeting in Honolulu [10], Advances in Catalytic Chemistry III [11], and at the Philadelphia Catalysis Club [12]. This work provides definitive evidence that CO hydrogenation on cobalt/alumina is structure-sensitive (activity is a function of dispersion) and that the product distribution changes with dispersion. However, it also raises some interesting important questions about the fundamental nature of this structure sensitivity.

Mr. Byron Johnson, a Ph.D. Candidate in Chemical Engineering, will explore these fundamental questions as part of his dissertation research in

collaboration with Dr. Wayne Goodman of Sandia Labs. His work will involve the preparation of highly dispersed cobalt/alumina catalysts via cobalt carbonyl decomposition on dehydroxylated alumina and the measurement of physical, chemical, and activity/selectivity properties for CO hydrogenation. The objective is to prepare a group of catalysts having a wide range of dispersion but all with high extents of reduction. This work will also involve the study of CO hydrogenation on different single crystal surfaces of cobalt at Sandia. Both Mr. Johnson and Dr. Bartholomew will spend 3-4 months at Sandia working with Dr. Goodman on this project.

Effects of Support and Dispersion on the Activity/Selectivity Properties of Iron. A study of the effects of support, metal loading, and dispersion on the CO hydrogenation activity/selectivity behavior of iron was conducted by Mr. Val Jones, M.S. Graduate in Chemical Engineering. Highly dispersed 1, 3, and 10 wt.% Fe/carbon and Fe/titania catalysts were prepared by nonaqueous evaporative deposition and decomposition of iron metal carbonyls respectively. Specific activities of the Fe/C catalysts were found to increase with increasing metal loading and decreasing dispersion. This behavior is attributed to geometrical effects. In the case of Fe/titania, the activation energy and selectivity for liquid hydrocarbons are lower for catalysts of low loading and for catalysts reduced at high temperature. This might be a result of electronic interaction between the iron and titania in the catalysts of low loading and/or decoration of the iron metal surface with reduced TiO_x species in the catalysts of low loading and high reduction temperature.

The results of this study have been written up in an M.S. thesis, will be presented at the New Orleans AIChE meeting [13] and are being written up in two papers to which will be added the results of Moessbauer runs of the reduced catalysts, experiments which have now been performed and are described below.

Effects of Support and Dispersion on the Binding States and Binding Energies of CO on Cobalt. The investigation by temperature-programmed desorption of the effects of support and dispersion on the binding states and binding energies of CO on cobalt is presently being conducted by Mr. Won Ho Lee, a Ph.D. Candidate in Chemical Engineering. During the past year the collection and reduction of data from the mass spectrometer TPD system was

computer automated. The kinetics of CO desorption from cobalt/alumina were studied as a function of cobalt loading and reduction temperature at a given loading. The results indicate that the adsorption site density of 1% Co/alumina increases with increasing reduction temperature up to about 550°C. The desorption order of CO also changes with reduction temperature in the same catalyst, suggesting that the distribution of sites is changing with reduction temperature. The desorption spectrum for CO on cobalt/alumina changes dramatically with cobalt loading. There is the appearance of new high temperature adsorption states in 3 and 10% catalysts which are not observed in the 1% cobalt/alumina, suggesting increasing binding energy of CO with increasing loading and decreasing dispersion. This behavior, in fact, provides a logical explanation for the structure sensitivity on these same catalysts observed by Fu [8].

During the coming year the TPD data will be combined with data from IR studies of the same catalysts and written up in papers.

Investigation of the Effects of Support on the Electronic Properties of Cobalt and Iron. The study of cobalt and iron catalysts by Moessbauer spectroscopy is being conducted by Mr. Loren Neubauer, a Ph.D. Candidate in Chemical Engineering.

During the past year well-dispersed 1 and 3 wt.% Co⁵⁷/carbon, Co⁵⁷/alumina and Fe⁵⁷/alumina catalysts were prepared using nonaqueous impregnation techniques. Moessbauer transmission spectra were obtained for the 1, 3 and 10% iron/carbon and 4% Fe/titania catalysts prepared by Val Jones and for the 1 and 3% Fe/alumina catalysts at temperatures ranging from 77 to 773 K after drying, reduction, reaction in CO/H₂, and room temperature exposure to air or hydrogen; emissions spectra were obtained for 1 and 3% Co⁵⁷/carbon and 1 and 3% Co⁵⁷/alumina catalysts under similar conditions. The spectra of the catalysts reduced at 350°C reveal the presence of superparamagnetic metallic clusters; moreover, significant isomer shifts are observed for these clusters (positive for the carbon supported catalysts and negative for the alumina-supported catalysts) indicating that their electronic structure is different from that observed for large ferromagnetic clusters. The fact that the electronic density of the metal varies with support suggests that these observed modifications in electronic behavior are a result of metal support interactions. To our knowledge, these are the first direct

measurements of changes in electronic structure of tiny supported clusters! Very significant changes in the Moessbauer spectra of the reduced catalysts upon room temperature exposure to first air and then hydrogen provide confirmation that they are very well-dispersed and that the chemistry of their surfaces is sensitive to the gas phase composition even at ambient temperature.

During the coming year the results of this work will be written up in a Ph.D. dissertation and in 2-3 journal articles.

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