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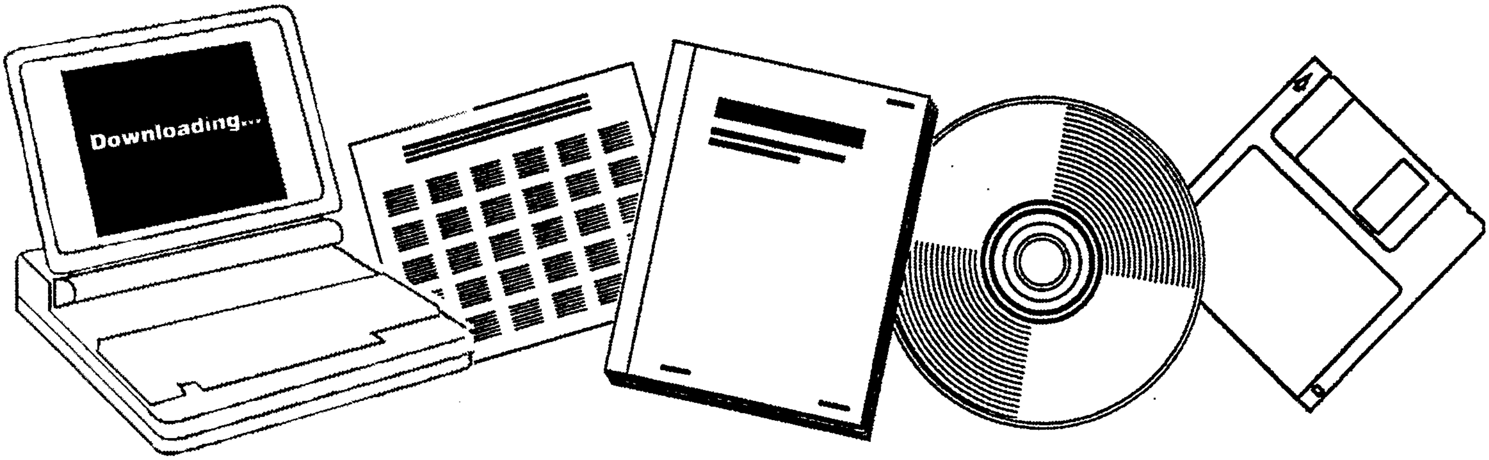

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METAL-SUPPORT INTERACTIONS: THEIR EFFECTS UPON ADSORPTION, ELECTRONIC, AND ACTIVITY/SELECTIVITY PROPERTIES OF COBALT IN CO HYDROGENATION

Annual Progress Report
For the Period April 1, 1984 to March 31, 1985

by

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prepared for

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Attention: Dr. Robert P. Eischens
Processes and Techniques Branch

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Introduction

During the past four 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 three years of investigation were summarized in a previously submitted final technical report [1] and in recently published papers [2-6]. 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 fourth year (first 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 effects of dispersion, extent of reduction, and preparation on activity/selectivity behavior of cobalt/alumina was investigated by Mr. Liu Fu, a visiting scholar from the Peoples Republic of China. Catalysts varying in loading from 3 to 25% were prepared by impregnation, while three 3% Co/alumina catalysts were prepared by impregnation, controlled-pH precipitation, and decomposition of a cobalt metal carbonyl. Specific activities and average carbon numbers of the hydrocarbon product were found to vary significantly with metal loading, reduction temperature and preparation. These changes were found to be linearly correlated with changes in dispersion indicating that CO hydrogenation on Co/alumina is structure-sensitive. The changes in specific activity with dispersion can be explained by variations in the distribution of low and high coordination sites and by changes in the nature of adsorbed CO species available for reaction. High specific activity is apparently favored on sites to which CO is strongly coordinated. Variations in the average carbon number of the product can be explained by changes in the rate of termination relative to the rate of propagation. High molecular weight products are favored by catalysts having high rates of propagation and low rates of termination.

The results of this investigation have been written up in two papers, which have been accepted by the Journal of Catalysis [7] and the Journal of C_1 Chemistry [8] (see attached preprints).

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. Candidate 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 these catalysts were found to increase with increasing metal loading or decreasing dispersion. The specific activities of 10% Fe/carbon and Fe/titania were about the same and comparable with values reported previously for Fe/silica and Fe/carbon catalysts [9,10]; however, the observed activities for Fe/titania from this study were significantly greater than reported earlier by Vannice for Fe/titania [11]. Interestingly enough, the specific activities of Fe/titania(LTR) and Fe/titania(HTR) were the same within experimental error. Selectivities for CO hydrogenation were in accordance with the Anderson-Schultz-Flory model (alpha = 0.65-0.70) and were independent of metal loading and dispersion.

The results of this study provide evidence that structure sensitivity and possibly the support affect the activity of iron in CO hydrogenation. The results of these measurements are being written up in an M.S. thesis and in two papers to which will be added the results of Moessbauer runs of the reduced catalysts, experiments which are currently in progress.

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 Mr. Lee redesigned and rebuilt our TPD system, incorporating an improved reactor design; he is presently designing necessary hardware and software to computer automate the mass spectrometer data collection system. Mr. Lee also devised a new general method for determining kinetic parameters from TPD spectra, which unlike previously reported methods [12,13], does not require the assumption that activation energy and preexponential factor for adsorption are independent of coverage.

During the past year an experimental plan for investigating the effects of support and dispersion on the kinetics of CO adsorption on cobalt was devised. TPD spectra for CO on Co/alumina, Co/silica, and Co/titania were obtained as a function of adsorption temperature and in the case of Co/titania as a function of reduction temperature. The results indicate that adsorption states and binding energies for CO on cobalt vary significantly with support; the spectra for Co/silica, consisting of one or two CO peaks and one CO_2 peak, are relatively simple, while those for Co/alumina and Co/titania are relatively more complex. The amount of CO desorbed from Co/titania decreases with increasing reduction temperature; after reduction at high temperatures (HTR state), no CO_2 desorption is observed, suggesting that the rate of CO dissociation is decreased. Treatment in oxygen, which reportedly destroys the HTR state [14], restores the CO desorption peaks; however, the CO_2 desorption peaks do not reappear!

During the coming year infrared experiments will be conducted on the same catalysts to determine the different kinds of CO species adsorbed as a function of support and reduction temperature. Both TPD and IR experiments will be conducted on a series of cobalt catalysts prepared from decomposition of metal carbonyls in which dispersion is varied over a wide range.

Investigation of the Effects of Support on the Electronic Properties of Cobalt and Iron. The study of cobalt catalysts by Moessbauer spectroscopy is being conducted by Mr. Loren Neubauer, a Ph.D. Candidate in Chemical Engineering. The study of iron catalysts was initiated by Mr. Val Jones and will be continued by Mr. Richard Jones, a senior in Chemical Engineering.

During the past year well-dispersed 1% Fe/carbon and 1% Fe/titania catalysts containing iron enriched to 90% in Fe^{57} were prepared. The facilities for preparing catalysts containing radioactive Co^{57} were designed, approved, and utilized in the preparation of a 1% Co/carbon. A special drive and optical bench for conducting cobalt Moessbauer were designed and constructed. Preliminary runs indicate that this equipment is working satisfactorily. During the coming year, Moessbauer spectra of the enriched iron and radioactive cobalt catalysts in the reduced state will be obtained to determine if electronic changes occur in the metal crystallites in these well-dispersed catalysts. Preparation and characterization by Moessbauer of additional cobalt catalysts on alumina and titania supports is planned.

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