



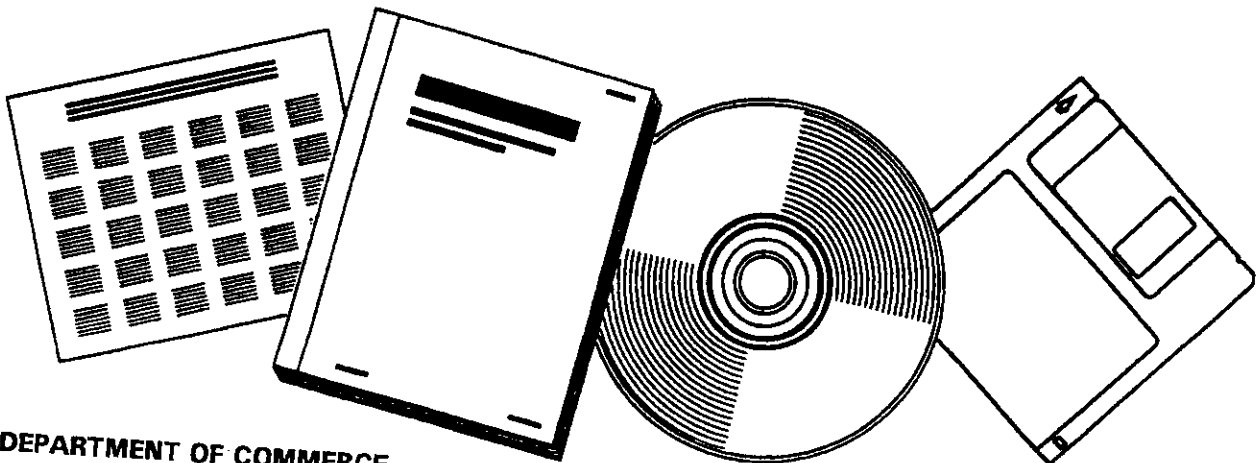
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**EFFECTS OF DISPERSION AND SUPPORT ON
ADSORPTION, CATALYTIC AND ELECTRONIC
PROPERTIES OF COBALT/ALUMINA CO
HYDROGENATION CATALYSTS: ANNUAL PROGRESS
REPORT, AUGUST 1, 1987-JULY 31, 1988**

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**EFFECTS OF DISPERSION AND SUPPORT ON ADSORPTION, CATALYTIC AND
ELECTRONIC PROPERTIES OF COBALT/ALUMINA CO HYDROGENATION CATALYSTS**

Annual Progress Report
For the period
August 1, 1987 to July 31, 1988

by

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ABSTRACT

An investigation of the effects of surface structure, dispersion, and support on the adsorption, catalytic, and electronic properties of cobalt/alumina is described, the objectives of which are to determine (1) the effects of surface structure and metal dispersion on the adsorption and catalytic properties of cobalt and (2) the effects of decorating support species on metal crystallites and of direct electronic interactions between metal clusters and support, on the adsorption, catalytic and electronic properties of cobalt supported on alumina. During the first year effects of surface structure and dispersion on the adsorption, activity/selectivity, and electronic properties of Co/W single crystal surfaces and alumina-supported cobalt were investigated in a surface science investigation, lab reactor studies, TPD/TPSR studies, and a Moessbauer spectroscopy study. The structure, stability, surface electronic properties, and chemisorptive properties of vapor-deposited cobalt overlayers (0-4 ML) on W(110) and W(100) were studied by Auger electron spectroscopy, low energy electron diffraction, work function changes, and temperature programmed desorption (TPD) of cobalt, hydrogen, and carbon monoxide. The CO chemisorptive properties of the two cobalt overlayers are quite different, CO adsorption being dissociative on the W(100) surface and nondissociative on the W(110) surface; comparison of the results with those for Ni/W(100) indicate that Co/W(100) dissociates CO as a result of electronic interaction with the tungsten substrate. Activities and selectivities of cobalt/alumina catalysts for CO hydrogenation prepared by decomposition of $\text{Co}_4(\text{CO})_{12}$ were determined as functions of metal loading, dispersion, and extent of reduction. Steady-state activity and product molecular weight were found to increase with increasing metal loading (decreasing dispersion and increasing extent of reduction). TPD/TPSR studies of supported cobalt catalysts prepared by conventional means were written up in a Ph.D. dissertation while new studies of carbonyl-derived catalysts were initiated. Moessbauer spectroscopy study of metal support effects in alumina-supported cobalt and iron catalysts were also initiated.

I. INTRODUCTION

Cobalt, iron and nickel catalysts find wide application in the fuels and chemical industries, particularly in hydrogenation and hydrotreating reactions. Most commercial catalysts containing these metals consist of a metal or metal oxide phase dispersed throughout a high surface area ceramic carrier or "support." The purpose of the support is basically twofold: (i) to facilitate the preparation of a well-dispersed, high surface area catalytic phase and (ii) to stabilize the active phase against loss of surface area. The effects of surface structure, dispersion and support on activity and selectivity of the active catalytic phase were assumed until recent times to be of secondary importance. However, evidence published mostly in the past decade provides evidence that surface structure/dispersion [1-4] and metal-support interactions [5-8] can dramatically influence the adsorption and activity/selectivity properties of these metals in a number of reactions. While it is desirable to study separately the effects of surface structure, dispersion and metal-support interactions, it is experimentally difficult to achieve since these effects are often interrelated. During the past seven years, the BYU Catalysis Laboratory has been

involved in an investigation of the effects of surface structure, dispersion, and support on the adsorption, catalytic, and electronic properties of cobalt. A new phase of this work which emphasizes the effects of dispersion and support on the adsorption, catalytic and electronic properties of cobalt supported on alumina funded by the present grant was initiated August 1, 1987. The results of this investigation over these past year are summarized in this brief report.

II. RESEARCH SCOPE AND OBJECTIVES

An investigation of the effects of surface structure, dispersion, and support on the adsorption, catalytic, and electronic properties of cobalt/alumina is in progress, the objectives of which are to: (1) determine the effects of surface structure and metal dispersion on the adsorption and catalytic properties of cobalt and (2) determine the effects of decorating support species on metal crystallites and of direct electronic interactions between metal clusters and support, on the adsorption, catalytic and electronic properties of cobalt supported on alumina.

To accomplish the above-listed objectives the proposed work has been divided into three areas of investigation: (1) study of the effects of surface structure and support decoration on the adsorption and catalytic properties of cobalt monolayers deposited on W(100) and W(110) using TPD, LEED and AES spectroscopies, and *in situ* CO hydrogenation reaction measurements, (2) study of the effects of dispersion and support decoration on the CO adsorption/desorption and catalytic properties of well-dispersed cobalt/alumina and cobalt-tungsten/alumina using TPD and IR spectroscopies and lab reactor measurements, and (3) Moessbauer study of the effects of metal-support interactions and decoration on the electronic properties of well-dispersed cobalt/alumina and iron/alumina.

III. SUMMARY OF ACCOMPLISHMENTS DURING THE PAST YEAR

During the first year of the present grant, the effects of surface structure and dispersion on the adsorption, activity/selectivity and electronic properties of Co/W single crystal surfaces and alumina-supported cobalt were investigated in a surface science investigation, lab reactor studies, TPD/TPSR studies, and a Moessbauer spectroscopy study. Accomplishments during this period are summarized below.

A. Task 1: Study of Effects of Surface Structure and Support Decoration

Surface Science Investigation of the Adsorption and Catalytic Properties of Cobalt Overlayers on W(100) and W(110) Surfaces. The structure, stability, surface electronic properties, and chemisorptive properties of vapor-deposited cobalt overlayers (0-4 ML) on W(110) and W(100) were studied by Auger electron spectroscopy (AES), low energy electron diffraction (LEED), work function changes, and temperature programmed desorption (TPD) of cobalt, hydrogen, and carbon monoxide. The results indicate that the first layer of cobalt grows pseudomorphically with respect to the tungsten substrate, and is thermally stable to 1300 K. Second and subsequent layers grow layer-by-layer at 100 K, but form three-dimensional clusters above 400-500 K. The relative work functions of these surfaces are strongly dependent on temperature, coverage, and substrate geometry. The annealed

pseudomorphic monolayer of Co/W(100) has a positive work function change (+155 mV), indicating a net electronic charge transfer from the tungsten to the cobalt. The chemisorptive properties of the cobalt overlayers are quite different from those of planar cobalt surfaces, the former having two new binding states for hydrogen chemisorption and two sites for carbon monoxide dissociation. CO dissociates on cobalt-tungsten interfacial sites and on the pseudomorphic monolayer of Co/W(100). The pseudomorphic monolayer of Co/W(100) dissociates CO as a result of electronic interaction with the tungsten substrate, not because of geometric strain.

The CO hydrogenation activity of the Co/W(100) surface was measured in the range of 100-500 Torr total pressure and 453-523 K at a H₂/CO ratio of 2/1. The specific activity per site was found to be an order of magnitude higher than that for polycrystalline cobalt [9]. This unusual result stimulated investigation of supported CoW/alumina catalysts discussed below.

B. Task 2: Study of Effects of Dispersion and Support Decoration on the CO Adsorption/Desorption and Catalytic Properties of Cobalt/alumina and CoW/alumina.

Lab Reactor Study of the Effects of Dispersion and Extent of Reduction on CO Hydrogenation Activity/Selectivity of Co/alumina and CoW/alumina. Activities and selectivities of cobalt/alumina catalysts for CO hydrogenation prepared by decomposition of Co₄(CO)₁₂ were determined as functions of metal loading (1-5%), dispersion (5-20%), and extent of reduction (38-95%). Steady-state activity and product molecular weight were found to increase with increasing metal loading (decreasing dispersion and increasing extent of reduction). These changes in specific activity may be due to either primary or secondary structure sensitivity [1]. Discrimination between these two effects will be attempted by varying dispersion while holding the extent of reduction constant.

TPD/TPSR/IR Study of the Effects of Support, Metal Loading, and Extent of Reduction on CO Adsorption Kinetics and Energetics of Cobalt. TPD/TPSR studies of CO and CO hydrogenation on cobalt catalysts supported on alumina, silica, titania, and magnesia prepared by conventional means were written up in a Ph.D. dissertation by Dr. Won Ho Lee [10] and 4-5 associated publications are in preparation. The TPD results indicate that CO is more strongly adsorbed and dissociates more readily (forming CO₂) on catalysts of higher loading and of higher reduction temperature. The corresponding H₂-CO TPSR spectra for the same Co/alumina catalysts contain two peaks indicative of two kinds of sites of differing binding energies for reaction intermediates. One of these sites is thought to be associated with large metal crystallites, the other with small metal clusters surrounded by cobalt aluminate or support species. The TPSR data also show a trend of increasing CO hydrogenation activity with increasing metal loading (and decreasing dispersion). Thus there is a correlation of higher activity for the catalysts which bind CO more strongly and on which CO dissociates more readily.

The adsorption/desorption kinetics and energetics of carbon monoxide on carbonyl-derived cobalt catalysts supported on alumina are being studied by temperature programmed desorption (TPD), while CO hydrogenation on these same catalysts are being studied by temperature programmed surface reaction (TPSR) as functions of dispersion and extent of reduction as a continuation of our previous study [10]. Thus far, a graduate student has been hired and trained in to operate the TPD/TPSR system; several

cobalt catalysts of varying dispersions have been prepared from carbonyl decomposition on dehydroxylated alumina, and the TPD system has been upgraded with a new Macintosh computer.

C. Task 3: Study of the Effects of Metal-Support Interactions and Decoration on the Electronic Properties of Well-Dispersed Cobalt/Alumina and Iron/Alumina. A Moessbauer spectroscopy study of metal-support interactions in alumina-supported cobalt and iron catalysts (1-5 wt.%) prepared by decomposition of the metal chlorides on partially dehydroxylated alumina and reduced at high temperatures to obtain well-reduced, highly dispersed metals is in progress. Thus far, a new graduate student has been hired and trained in the preparation of catalysts and the operation of the Moessbauer spectrometer. Several nonradioactive cobalt/alumina catalysts of varying dispersion and extent of reduction have been prepared and characterized by hydrogen adsorption and oxygen titration; radioactive Co^{57} chloride and isotopic Fe^{57} chloride have been ordered for the preparation of catalysts to be used in the emissions and transmission Moessbauer experiments.

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