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METAL-SUPPORT INTERACTIONS: THEIR EFFECTS UPON ADSORPTION, ELECTRONIC, AND ACTIVITY/SELECTIVITY PROPERTIES OF COBALT IN CO HYDROGENATION: FINAL PROGRESS REPORT FOR THE PERIOD APRIL 1, 1984 TO JULY 1, 1987

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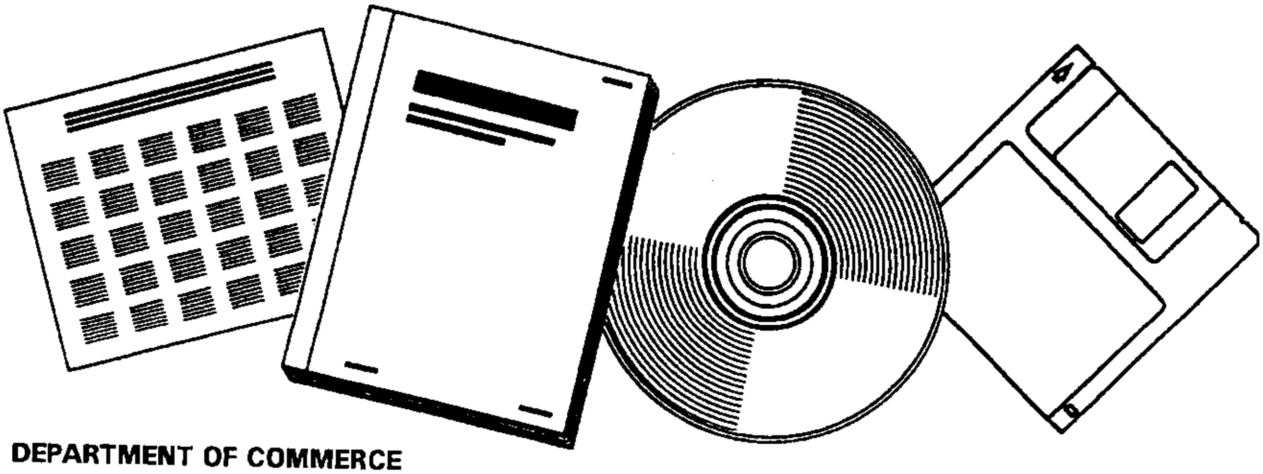

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METAL-SUPPORT INTERACTIONS: THEIR EFFECTS UPON ADSORPTION, ELECTRONIC, AND ACTIVITY/SELECTIVITY PROPERTIES OF COBALT IN CO HYDROGENATION

Final Progress Report
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by

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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 thee 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 three years, the BYU Catalysis Laboratory has been involved in an investigation of the interaction of cobalt (and to a lesser extent iron) metal(s) with alumina, silica, titania, and carbon. The results of this investigation over these past three years are summarized in this brief report.

II. Summary of Accomplishments During the Past Three Years

During the last three years of the contract, the effects of support and dispersion on the adsorption, activity/selectivity and electronic properties of supported cobalt and iron were investigated in two lab reactor studies, a TPD/TPR study, a Moessbauer spectroscopy study and a surface science investigation. Accomplishments during this period are summarized in Table 1, while some further details regarding each of these studies is provided below.

A. Lab Reactor Study of the Effects of Dispersion and Extent of Reduction on CO Hydrogenation Activity/Selectivity of Co/alumina. Activities and selectivities of cobalt/alumina catalysts for CO hydrogenation were determined as functions of metal loading (3-25%), reduction temperature (250-450^{o}C), and preparation (3 different preparations). Specific activities and average carbon number of the hydrocarbon product were found to vary significantly with metal loading, reduction temperature and preparation. These changes were also found to be linearly correlated with changes in dispersion indicating that CO hydrogenation on Co/alumina is apparently structure-sensitive. The changes in activity with dispersion can be explained by either (i) variations in the distribution of low and high coordination sites, (ii) preferential decoration of small crystallites in catalysts of low loading with support species, (iii) promotion by unreduced cobalt oxide, or (iv) preferential poisoning of high coordination sites by carbon. 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 either due to surface structural or support effects. High-molecular-weight products are favored by catalysts having high rates of propagation and low rates of termination. The results of this study were presented at the International PACCHEM 1984 Honolulu

TABLE 1: Summary of Accomplishments, 1984-87

Area of Study	Students/Scholar Participation	Most Significant Results	Most Significant Conclusions
Lab reactor study of the effects of dispersion and extent of reduction on CO hydrogenation activity/selectivity of Co/alumina	Liu Fu Visiting Scholar Peoples Republic of China	1. Steady-state activity and product molecular weight decrease linearly with increasing dispersion and decreasing metal loading. 2. Effects of extent of reduction on activity and selectivity are secondary.	1. Changes in specific activity may be due to either primary or secondary structure sensitivity. 2. High-molecular-weight products are favored on catalysts having high activity and high rates of propagation.
Lab reactor study of the effects of metal loading and dispersion on CO hydrogenation activity/selectivity of Fe/C and Fe/titania catalysts	Valient Jones M.S. Grad. Student	1. Initial and steady-state activities decrease with increasing dispersion and decreasing metal loading. 2. Activity decreases rapidly with time.	1. Changes in specific activity may be due to either primary structure sensitivity or metal-support interactions. 2. Rapid deactivation is due to carbon deposits formed during reaction.
TPD/TPR/IR study of the effects of support, metal loading and extent of reduction on CO adsorption kinetics and energetics of cobalt	Won Ho Lee Ph.D. Grad. Student	1. CO is more strongly adsorbed and dissociates more readily on cobalt/alumina catalysts of higher loading and of higher reduction temp. 2. Adsorption states and binding energies vary considerably with support.	Variations in CO adsorption kinetics and energetics may be due to primary or secondary structure sensitivity. Secondary effects due to carbon or support species contamination of the metal surface are favored
Moessbauer spectros. study of the effects of support, metal loading and extent of reduction on the chemical and magnetic properties of cobalt and iron on alumina, carbon and titania	Lawrence Neubauer Ph.D. Grad. Student	1. Superparamagnetic clusters of iron and cobalt are observed in well-dispersed iron and cobalt catalysts supported on alumina and carbon. The isomer shift of these clusters varies with reduction temperature and support. 2. The chemical states and extents of reduction of iron are highly dependent upon support.	The observed changes in isomer shift for Fe(0) suggest electronic transfer between support and well-dispersed metal clusters.
Auger/Surface science reaction study of clean unsupported cobalt	Wayne Goodman, Head Surface Science Div. Sandia Nat. Labs. Byron Johnson Ph.D. Candidate	1. CO hydrogenation activity and kinetics of a clean cobalt surface are similar to those for high loading cobalt/alumina. 2. Less than a monolayer of graphitic carbon forms on the cobalt surface during reaction; cobalt carbide is not formed.	1. The agreement of activities for unsupported and supported cobalt suggests that the reaction is not structure-sensitive; dispersion effects are probably due to contamination by carbon or support species. 2. The active surface for CO hydrogenation on cobalt is cobalt metal—not cobalt carbide.

meeting and published in three different journal articles [9-11].

B. Lab Reactor Study of The Effects of Dispersion and Extent of Reduction on CO Hydrogenation Activity/Selectivity of Iron/carbon and Iron Titania Catalysts. Well-dispersed 1, 3, 10% Fe/activated carbon catalysts by evaporative deposition of iron nitrate from a benzene/methanol solution. Hydrogen adsorption measurements were carried out with using a flow system with a thermal conductivity detector according to a new procedure developed as part of this contract [12]. From measurements of activity and selectivity for CO hydrogenation at 1 atm, $H_2/CO = 2$, and 450-530 K, it is evident that initial and steady-state specific activities and the olefin/paraffin ratio decrease with decreasing metal crystallite size. High olefin/paraffin selectivities were observed for these catalysts in agreement with previous workers, while the activity of well-dispersed Fe/C catalysts was found to decrease very significantly with time under typical FT synthesis conditions. The results of this work were presented at the 1986 National AIChE Meeting in New Orleans and published in a thesis [13] as well as in the Emmett memorial issue of the Journal of Physical Chemistry [14].

Specific activity data were also obtained under similar conditions for 1, 3, and 10% Fe/titania catalysts prepared by decomposition of iron pentacarbonyl on dehydroxylated titania. The results indicate that initial specific activity decreases with increasing dispersion and decreasing metal loading. The specific activity of 10% Fe/titania is apparently the same for catalysts reduced at 523 and 723 K respectively, although the dispersions of these two catalysts are significantly different. These changes in activity with metal loading and dispersion are best explained by preferential decoration of small metal crystallites with reduced TiO_x species. The results of this work were published in an M.S. thesis [13] and are being prepared for journal publication.

C. TPD/TPR/IR Study of the Effects of Support, Metal Loading, and Extent of Reduction on CO Adsorption Kinetics and Energetics of Cobalt. The adsorption/desorption kinetics and energetics of carbon monoxide on cobalt catalysts supported on alumina, silica, titania, and magnesia (loadings ranging from 1 to 15 wt.% cobalt) were studied by temperature programmed desorption (TPD), while CO hydrogenation on these same catalysts was studied by temperature programmed reaction (TPR). TPD study of CO desorption from Co/alumina catalysts indicates that CO is more strongly adsorbed and dissociates more readily (forming CO_2) on catalysts of higher loading and of higher reduction temperature. The corresponding TPR spectra for the same Co/alumina catalysts contain two peaks indicative of two kinds of sites of differing binding energies for reaction intermediates. These TPR data also show a trend of increasing 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.

A similar TPD/TPR study was conducted to determine the effects of loading and reduction temperature on the CO desorption kinetics and energetics and on the CO hydrogenation activity of 3 and 10% Co/titania. Chemisorption uptakes of CO were found to decrease with increasing reduction temperature (300-550°C) for both catalysts, the extent of suppression of CO adsorption being greater for the 3% cobalt catalysts. The temperature of the CO desorption rate maximum shifted to lower temperature and the rate of CO_2 formation decreased significantly with increasing reduction temperature. After catalysts reduced at 550°C were oxidized in 10% oxygen at 200°C or above, their adsorption capacities initially observed after reduction at 300°C were restored.

TPR spectra obtained during temperature-programmed reaction with hydrogen after CO adsorption on 10% Co/TiO_2 at room temperature, reveal two distinct methane peaks (A at about 150°C and B at 220-337°C) whose areas decrease with increasing reduction temperature and reduction time. While the position of Peak A remains unchanged, the position of Peak B shifts toward higher temperature (lower reaction rate) with increasing reduction temperature and time. These observed changes in CO desorption kinetics and CO hydrogenation rate on Co/titania with increasing reduction temperature and time are consistent with decoration of metal crystallites with a TiO_x species, occurring to a greater extent at higher reduction temperatures and times and which is reversed by treatment in oxygen.

TPD and TPR studies of cobalt on alumina, silica, and titania showed significant effects of support on CO binding states, binding energies and reactivities towards hydrogen. For example, during CO TPD, differences in the number and population of states and temperatures of rate maximum were observed for cobalt on these different supports. TPR spectra obtained after CO adsorption at room temperature revealed two sites for methanation for all three catalysts. However, the relative populations and positions of the methane peaks varied significantly with support. These results are probably most consistent with the presence of two kinds of metal sites, one in bulk metal crystallites and one in small clusters of metal surrounded by support or oxide.

The results of these TPD/TPR/IR studies have been presented at several meetings [15-18], are being prepared in a series of papers for publication and will be published in a doctoral dissertation [19].

D. Moessbauer Spectroscopy Study of the Effects of Support, Metal Loading, and Extent of Reduction on the Chemical and Magnetic Properties of Cobalt and Iron on Alumina, Carbon and Titania. A Moessbauer spectroscopy study of metal-support interactions in cobalt and iron catalysts (1-10 wt.%) supported by carbon, alumina, and titania was conducted [20]. Phase composition, extent of reduction to the metal, and changes in electronic and magnetic properties were measured as a function of metal loading, support, reduction temperature, and treatment in hydrogen, oxygen or synthesis gas. The most important results can be summarized as follows:

1. Reducibility of cobalt and iron to the metallic state is strongly dependent on support and metal loading; it decreases in the order M/titania, M/carbon, M/alumina and increases, as expected, with increasing metal loading. Supported cobalt is apparently more easily reducible than supported iron for a given support.

2. Small superparamagnetic clusters of iron or cobalt (1-2 nm) are the predominant phases in 1 and 3% Fe/carbon and 1% Co/carbon reduced at either 350 or 500°C; these tiny clusters are also present in 10% Fe/carbon, 1% Fe/alumina and 1% Co/alumina catalysts reduced under similar conditions. The isomer shifts of these clusters are positive (by 0.1-0.2 mm/s) for the carbon-supported catalysts suggesting a depletion of electron density of the metal nuclei, possibly due to transfer of electron density from the metal to the support; the isomer shifts of these clusters are negative (by 0.1-0.2 mm/s) for the

alumina-supported catalysts suggesting enhancement of electron density at the nuclei of metal atoms, possibly due to transfer of electrons from the support to the metal.

3. From the magnitudes of resonant (spectral) areas and temperature dependencies of these areas it is possible to deduce that metal clusters in 1% Fe/C and Co/C catalysts have high surface/bulk ratios and are bound tightly to the support (possibly as thin rafts). The corresponding 1% Fe/alumina and 1% Co/alumina catalysts have lower surface/bulk ratios and are less tightly bound to the support (possibly as three dimensional crystallites), while relatively large metal clusters in Fe/titania are least weakly bound to support. Nevertheless, these dense, 3-D clusters in Fe/titania apparently spread into thin rafts during high temperature reduction. The data are consistent with decoration of metal clusters by support moieties, this effect being more important at higher reduction temperatures and lower loadings.

4. After reduction the carbon-supported metals are easily oxidized at room temperature, while Co/alumina is relatively inert to oxidation, suggesting that the cobalt either migrates into the alumina or is decorated by a skin of alumina-like species. During exposure to synthesis gas supported iron catalysts, particularly Fe/carbon catalysts, readily form carbides and are easily deactivated, while little deactivation and insignificant carbide formation occurs on Co/alumina.

Thus, these results provide evidence that the fraction reduced to the metal and the surface chemistry, magnetic, and electrical properties of cobalt and iron metal crystallites can be greatly affected by the support. The observation of isomer shifts for superparamagnetic clusters of cobalt and iron which depend on the support probably constitutes the most convincing direct evidence todate for changes in the electronic properties of well-dispersed metal crystallites as a result of interaction with the support.

The results of this Moessbauer study have been detailed in a doctoral dissertation [20], while the results for Fe/carbon catalysts have been published in the Journal of Physical Chemistry [14]. Three other papers based on this work are in preparation.

E. Auger/Surface Science Reaction Study of Clean Unsupported Cobalt. This work, carried out by the PI during the Summer of 1986 at Sandia National Laboratories in collaboration with Wayne Goodman, involved the measurement of CO hydrogenation activity and selectivity of a clean cobalt surface as a function of temperature and reactant composition. The experimental procedure involved a cycle of oxidation and reduction treatments to remove carbon and sulfur from a polycrystalline cobalt surface (originally in the form of a single crystal but transformed by the cleaning procedure; surface cleanliness was checked by Auger electron spectroscopy(AES)) after which CO hydrogenation activity was measured in situ at a given temperature and starting composition in a batch reactor attached directly to the UHV system. From turnover frequency (TOF) versus temperature data at a H_2/CO ratio of two an activation energy of 110± 8.6 kJ/mole was obtained in very good agreement with that of 113± 18 reported for 2% Co/alumina by Vannice [21]. The observed TOF at 225°C of 22×10^{-3} is intermediate between values of 12 and 63×10^{-3} reported for 10 and 15% Co/alumina [9]. From rate data obtain for different CO and hydrogen concentrations, the reaction orders of hydrogen and CO were found to be 1.75 and -1.04 compared to values of 1.2 and -0.48 obtained by Vannice for Co/alumina [21]. After reaction the working surface of the cobalt catalyst was found to be cobalt metal covered by less than a monolayer of graphitic carbon.

Thus, the results of this study indicate that the active surface in CO hydrogenation is cobalt metal, not cobalt carbide, and that its activity is comparable to that of poorly dispersed 10-15% Co/alumina. The concentration and temperature dependencies for CO hydrogenation on clean cobalt are also comparable with those observed for cobalt/alumina. The agreement of CO hydrogenation activities for the unsupported polycrystalline cobalt and alumina-supported cobalt suggests that the reaction may not be structure-sensitive.

The results of this work have been submitted for presentation at the North American Catalysis Society Meeting [22] and are being prepared for publication.

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