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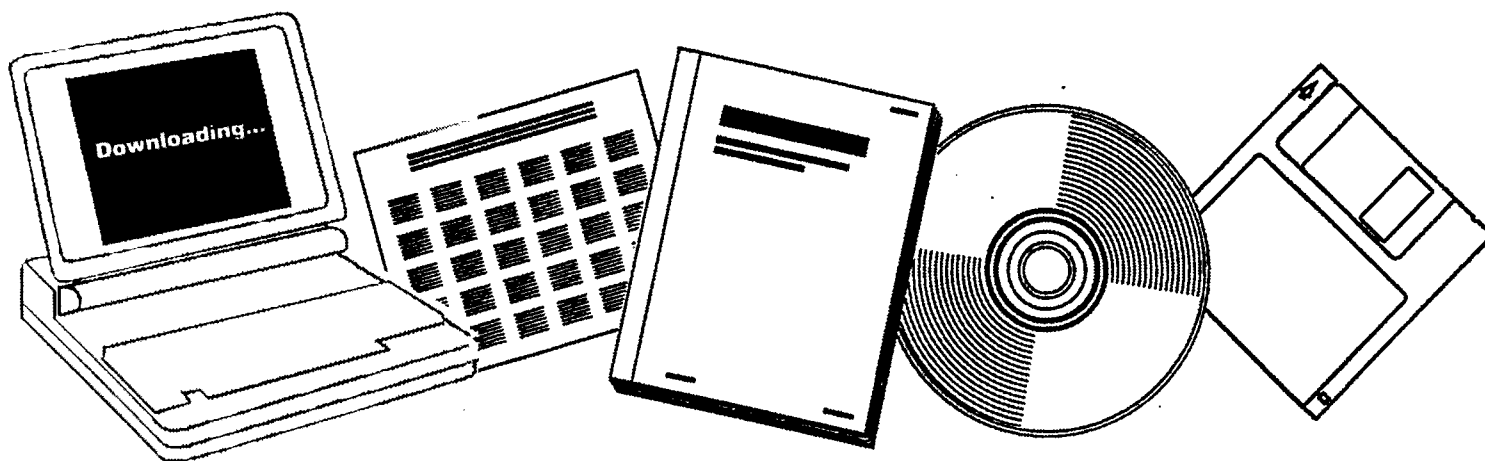
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**EFFECTS OF DISPERSION AND SUPPORT ON
ADSORPTION, CATALYTIC AND ELECTRONIC
PROPERTIES OF COBALT/ALUMINA CO
HYDROGENATION CATALYSTS: (TECHNICAL
PROGRESS REPORT)**

BRIGHAM YOUNG UNIV., PROVO, UT. DEPT. OF
CHEMICAL ENGINEERING

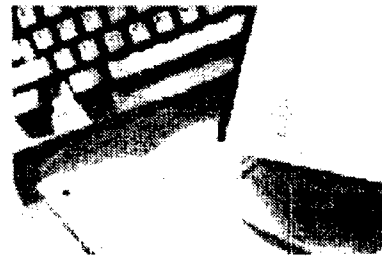
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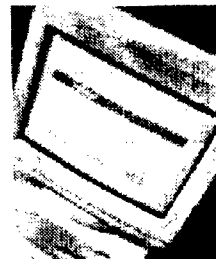
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Progress Report

RENEWAL PROPOSAL

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DEPARTMENT OF ENERGY
Office of Basic Energy Sciences
Division of Chemical Sciences

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

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ABSTRACT

The continued investigation of dispersion and metal-support interactions and their effects upon the adsorption, activity/selectivity, and electronic properties of the metal in cobalt/alumina (and to a lesser extent on iron/alumina) catalysts is proposed. The objectives of this research are to (i) determine the effects of surface structure and metal dispersion on the adsorption and catalytic properties of cobalt, and (ii) determine the effects of metal-support interactions, i.e. effects of decorating support species on metal crystallites and of direct electronic interactions between metal clusters and the support, on the adsorption, catalytic and electronic properties of cobalt supported on alumina.

The proposed work will build on the accomplishments of the previous studies of cobalt and iron catalysts conducted during the past three years. It will feature comprehensive experimental investigations of (i) cobalt layers deposited on different single crystal surfaces of tungsten to determine the effects of surface structure and alumina decoration on the adsorption and catalytic properties of cobalt and (ii) highly dispersed cobalt/alumina catalysts prepared from decomposition of metal carbonyls on dehydroxylated alumina to determine the effects of dispersion and alumina decoration on the adsorption, activity/selectivity, and electronic properties of cobalt. The kinetics and energetics of adsorption will be studied by temperature-programmed desorption of CO and hydrogen, while the distribution and structures of CO species adsorbed will be studied by infrared spectroscopy. The effects of direct metal-support interactions on the electronic properties of well-dispersed metal clusters of cobalt and iron on alumina will be studied by Moessbauer spectroscopy. Activity/selectivity properties of these surfaces and catalysts in CO hydrogenation and ethane hydrogenolysis will be studied.

Completion of the proposed work will yield quantitative, definitive experimental data on the nature of structure-sensitivity of cobalt in CO hydrogenation and ethane hydrogenolysis and on the effects of support on the adsorption properties of cobalt for CO and hydrogen, the activity/selectivity behavior of cobalt in these reactions, and on the electronic properties of well-dispersed cobalt and iron clusters. These data will also provide a basis for controlling the activity/selectivity properties of cobalt and iron catalysts through choice of physical and chemical properties.

I. INTRODUCTION AND BACKGROUND

A. 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. In base metal catalysts the metal oxide-support interaction can determine the degree to which oxides can be reduced to the metallic state, the distribution of metal and metal oxide sites at the surface, and thus the surface chemistry. 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. For example, in most of the previous studies of structure-sensitivity of supported metals in CO hydrogenation [9-16], metal dispersion was varied by varying metal loading; thus, the observed "structure-sensitivity" could be attributed to either changes in dispersion or changes in metal-support interactions due to metal loading variations.

During the past two and one-half 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, summarized in a later section of this proposal, indicate that dispersion and metal-support interactions greatly influence CO and hydrogen adsorption properties and the CO hydrogenation activity/selectivity properties of cobalt and iron. The investigation of well-dispersed cobalt and iron clusters on alumina and carbon by Moessbauer spectroscopy indicates that the electronic properties of the metal are apparently altered by interaction with the support. Finally, a study of a cobalt surface using Auger spectroscopy and other surface science techniques indicates that the clean surface has the same activity for CO hydrogenation as observed for 10-15% cobalt/alumina catalysts, suggesting that metal-support effects rather than structure-sensitivity are responsible for the observed changes in activity with dispersion and metal loading in the

cobalt/alumina system [9,10].

This is a proposal to continue the investigation of structure-sensitivity and metal-support interactions an additional three years using cobalt surfaces and cobalt/alumina (and to a lesser extent iron/alumina) as model systems.

B. Background: Previous Work and Status of Present Knowledge

1. Structure Sensitivity, Dispersion, and Metal-Support Effects in CO Hydrogenation: Previous Work

a. Structure Sensitivity/Dispersion Effects. Most of the previous work dealing with effects of dispersion and surface structure in CO hydrogenation on Group VIII metals has been reviewed by McDonald and Boudart [2] and by Fu and Bartholomew [10].

According to Boudart [1] catalytic reactions are either structure-sensitive or structure-insensitive. In structure-sensitive reactions specific activity is a function of the geometric distribution of surface sites. This distribution may vary with metal loading, crystallite size, dispersion (fraction exposed), or preparation method. If the specific rate of a reaction varies with crystallite size, we may say that it is apparently structure sensitive. According to Boudart [1] there are a number of distinguishing features of structure sensitive reactions, namely they: (i) generally occur on large, multiple-atom sites, (ii) typically involve activation of C-C and N-N bonds, and (iii) involve substantial effects of alloying and poisoning on the rate of reaction. Manogue and Katzer [17] classified structure sensitive reactions into two groups: (i) primary structure-sensitive reactions involving changes in activity with changes in surface structure and (ii) secondary structure-sensitive reactions in which changes in activity are due to preferential contamination or poisoning of certain sites.

There are generally two methods which have been used to establish the structure sensitivity of a catalytic reaction. The first involves measuring activities of different single crystal surfaces of the same metal in which the surface structure has been varied. The second is to change the surface structure of metal crystallites in a supported metal catalyst by varying metal crystallite size. This latter method is based on the concept that concentrations of sites of low coordination number increase dramatically as particle size is decreased from 10 to 1 nm [18].

The results of previous studies of dispersion effects in CO hydrogenation are summarized in Table 1. In most of these studies metal dispersion was varied by varying metal loading. The same trend is observed in all of these studies, namely that of decreasing specific activity with decreasing particle size or increasing dispersion. While this phenomenon has been attributed to changes in surface structure with changes in particle size, it could be also explained by

TABLE 1

Previous studies of Dispersion-Activity
Correlations in CO Hydrogenation

<u>Catalysts</u>	<u>Variations in D(%)</u>	<u>Order of Mag. Variation in Activity</u>	<u>Activity-Dispersion Correlation</u>	<u>Ref.</u>
Co on alumina, silica, titania, magnesia, carbon	0.3-90	100	Linear decrease in log [initial TOF ^a] with increasing log D	9,35
3,10,15,25% Co/alumina	5-15	10	Linear decrease in steady state CO TOF with increasing D and metal loading	10,35
Fe/MgO	7-60	10	Increasing methane TOF with increasing crystallite diameter or decreasing D	11
2-5% Fe/carbon	2-100	40	Increasing initial CO TOF with increasing crystallite diameter or decreasing D	12
1-10% Fe/carbon	15-100	30	Increasing initial and steady-state CO TOFs with increasing crystallite diameter and decreasing metal loading	13
1-15% Ni/alumina	5-60%	5	Decreasing methane TOF with increasing D	14
Ru/alumina	30-82	60	Decreasing methane TOF with increasing D	16

^aCO TOF = CO turnover frequency or the number of CO molecules converted per adsorption site per second.

^bMethane TOF = methane turnover frequency or the number of methane molecules produced per adsorption site per second.

metal-support effects due to variations in metal loading, e.g. greater decoration of the metal by support species or a more intimate contact and greater extent of electronic interaction in small metal clusters (see discussion in the next section). Moreover, Goodman et al. [19] have shown that CO hydrogenation rates are the same for different low index planes of single crystal nickel and ruthenium, while Somorjai and coworkers [20-22] observed the same CO hydrogenation activity for single and polycrystals of iron and rhodium, these results suggesting that CO hydrogenation may be structure-insensitive. However, one must be cautious in drawing this conclusion from these results, since low index planes expose no edge or corner sites such as

those found in stepped planes or those believed to be present on the surface of small metal crystallites. The importance of studying stepped planes is emphasized by the results of Erley and Wagner [23] showing that CO dissociation is significantly more favorable on stepped planes relative to smooth planes of nickel.

Thus, the central question of why supported FT catalysts appear to be structure-sensitive has not yet been definitively addressed. The apparent decrease in activity with decreasing metal crystallite size may be attributed to: (i) primary structure sensitivity [1,17], (ii) selective self-poisoning by adsorbed carbon formed by CO dissociation [24], [iii] changes in the surface carbide level affecting the surface coverage of hydrogen to which the rate of reaction is proportional [25], (iv) metal support interactions in the form of decoration of metal crystallites by support species and/or (v) direct electronic interaction of small metal clusters with the support [6,7]. The main difficulty with the first theory is that a decrease in particle size would increase step site concentration, therewith increasing the rate of CO dissociation; thus, this theory predicts an increase in reaction rate with decreasing particle size, while the opposite trend is observed. Nevertheless, none of these possibilities can be ruled out based on presently available data.

b. Metal-Support Interactions. Metal-support interactions include a variety of phenomena involving the interaction of metal crystallites with a catalyst carrier or "support." Boudart [1] has classified metal-support interactions into 10 different types of which two, (i) the Schwab Effect II (direct electron transfer between metal and support) and (ii) decoration of a metal crystallite with support species, are probably most applicable to well-dispersed metal systems, although it is generally thought that for a support to electronically influence the properties of a metal (i.e. Schwab II Effect), the latter's crystallite diameter must be less than about 1-2 nm in diameter [1]. On the other hand, the decoration of metal crystallites by support species can lead to modifications of the metal surface in both small and large crystallites. In fact, decoration of metal surfaces by reduced TiO_x species has been experimentally observed in supported metal systems involving reducible supports such as titania and niobia following reduction in hydrogen at high temperatures [6,7]. Recent evidence [26-27] suggests that decoration effects may be a more general phenomenon, even in metal-support systems involving difficult-to-reduce supports such as alumina and silica. For example, Raupp and Dumesic [28] have demonstrated that the adsorption properties of nickel foils are modified by decoration with alumina, that is, the alumina decorant increases the binding energy of hydrogen while decreasing the binding energy of CO on nickel. Furthermore, the observed hydrogen adsorption kinetics and energetics on alumina-decorated nickel are very nearly the same as observed for hydrogen adsorption on nickel/alumina reduced at 450°C [29].

From previously cited work [5-8,13,26-29] there are two experimental approaches that have provided definitive information regarding metal support interactions: (i) recent Moessbauer spectroscopy studies of well-dispersed iron/support and cobalt/support systems which provide evidence of changes in the electronic and magnetic properties of 1-2 nm metal clusters due to their direct interaction with the support [13,30] and (ii) TPD and laboratory reaction studies of purposely decorated single crystals, films and supported metals [26-29] to determine the effects of support moieties on the adsorption and catalytic properties of these surfaces and which provide evidence that such additives either block adsorption sites and/or act as promoters or inhibitors.

Other than the work performed on this contract (summarized in the next section) there have been few reported investigations of cobalt-support and iron-support interactions. In work supported during the first three years of this contract Reuel and Bartholomew [9] investigated the effects of different supports, including alumina, silica, titania, magnesia and carbon, on the adsorption stoichiometries of hydrogen and CO and on the activity/selectivity properties of cobalt. Specific activities were found to vary over three orders of magnitude for cobalt on these different supports. Nevertheless, the specific activities apparently correlated well with metal dispersion varied by changing metal loading. Thus, it was not clear whether these differences in activity were due to primary structure sensitivity or to decoration or some other metal-support effect.

2. Summary of Accomplishments During the Past Three Years

Accomplishments during the first three years of this contract were summarized in a previous final progress report [31] and in journal publications [9,32-34]. These included the investigation of (i) effects of support on hydrogen adsorption/desorption kinetics on/from cobalt [32,33] and (ii) effects of support and dispersion on the adsorption and CO hydrogenation activity/selectivity properties of cobalt [9,34]. These studies provide evidence that metal-support effects and dispersion greatly influence the adsorption and activity/selectivity properties of cobalt.

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 2, 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 a function of metal loading (3-25%), reduction temperature (250-450°C), and preparation (3 different preparations).

TABLE 2: 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	Valent 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
Mossbauer spectrosc. 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.

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 [see Figs. 1 and 2]. The changes in activity with dispersion can be explained by either (i) variations in the distribution of low and high coordination sites or (ii) preferential decoration of small crystallites in catalysts of low loading with support species. 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 meeting and published in three different journal articles [10,35,36].

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 [37]. 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. While high olefin/paraffin selectivities were observed for these catalysts in agreement with previous workers [38-39], the activity of well-dispersed Fe/C catalysts was found to decrease very significantly with time under typical FT synthesis conditions, i.e. at a H_2/CO ratio of two. The results of this work were presented at the 1986 National AIChE Meeting in New Orleans and published in a thesis [40] as well as in the Emmett memorial issue of the Journal of Physical Chemistry [13].

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 summarized in Table 3 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 observed in other studies [26-28]. The results of this

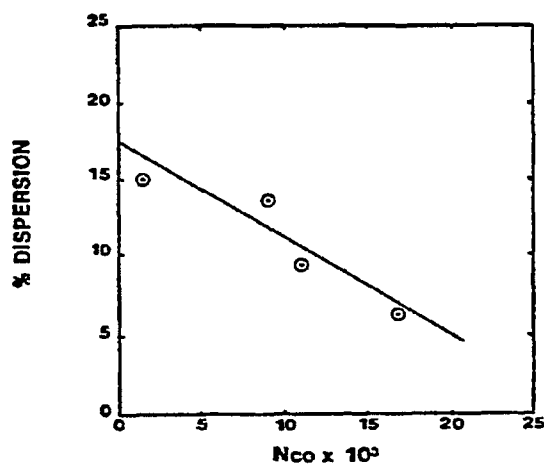


Fig. 1. Percentage dispersion vs. CO turnover frequency at 200°C, 1 atm for 3, 10, 15, 25% Co/Al₂O₃ catalysts after 20 h of reaction. (Ref. 35)

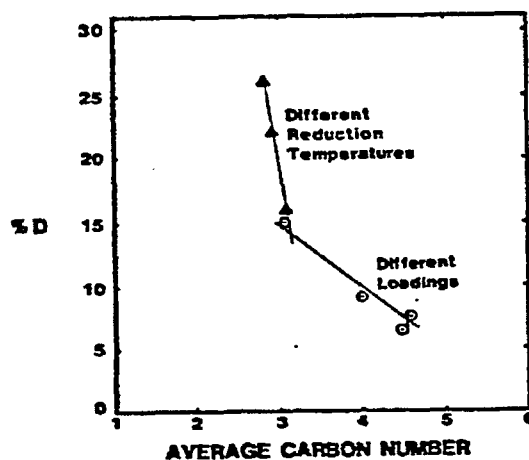


Fig. 2. Correlations of dispersion with average carbon number for Co/Al₂O₃ catalysts of $\circ$ different loadings and $\triangle$ reduction temperatures. (Ref. 10)

TABLE 3
Initial Turnover Frequencies and Activation Energies for CO Conversion During CO Hydrogenation on Fe/TiO₂ Catalysts

Catalyst	Percentage Dispersion	$N_{CO}^i \times 10^3 (s^{-1})^a$ at Temperature (K)			E_a^b (kJ/mol)
		473	493	513	
1% Fe/TiO ₂ ^c	54	—	—	—	—
3% Fe/TiO ₂	13.5	0.59	1.9	6.9	124
10% Fe/TiO ₂ (LT) ^d	9.1	0.62	4.7	25	186
10% Fe/TiO ₂ (HT) ^e	2.9	1.0	4.1	20	151

- a. Initial turnover frequency for CO conversion (to Hydrocarbons and CO₂); i.e., the number of CO molecules converted per catalytic site (based on H₂ uptakes) per second at H₂/CO = 2 and 1 atm.
b. Activation energy for CO conversion based on temperature dependence of N_{CO}^i .
c. Activity was too low to reproducibly detect up to 533 K.
d. After reduction at low temperature (523 K).
e. After reduction at high temperature (723 K).

work were published in an M.S. thesis [40] and are being prepared for journal publication [41].

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). A comprehensive TPD study of CO desorption from Co/alumina catalysts [42] indicates that CO is more strongly adsorbed and dissociates more readily (forming CO₂) on catalysts of higher loading and of higher reduction temperature (Figures 3 and 4). The corresponding TPR spectra for the same Co/alumina catalysts [43] contain two peaks indicative of either (i) two carbon intermediates having different reactivities or (ii) two kinds of sites of differing binding energies for reaction

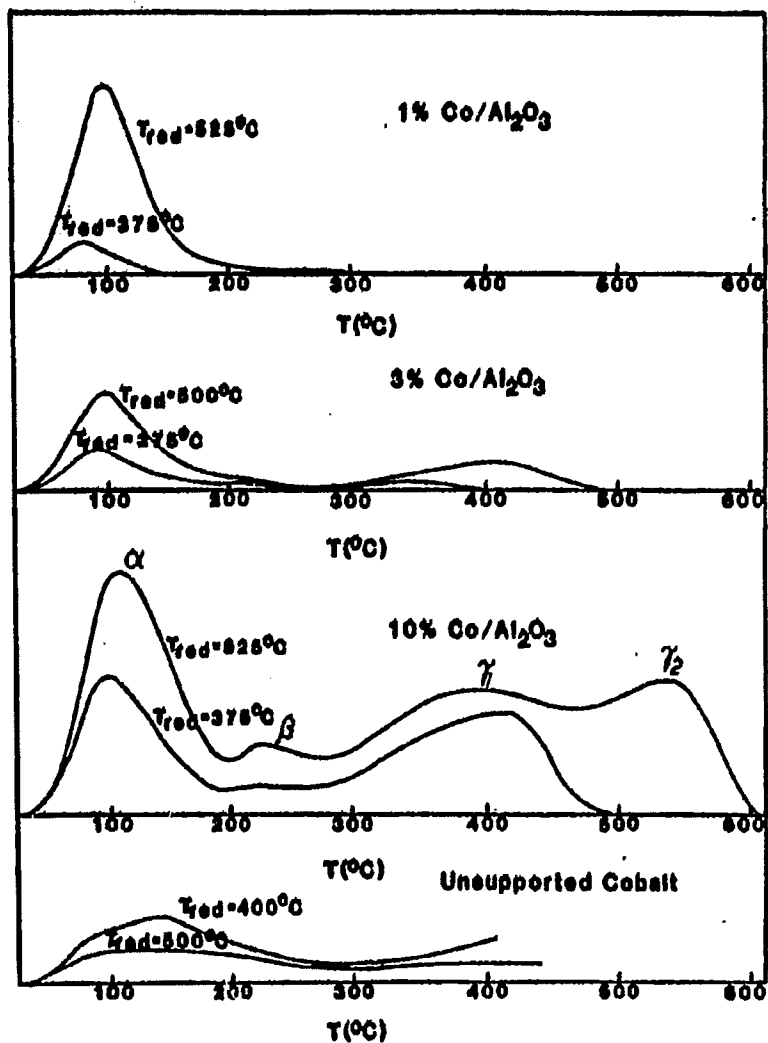


Fig. 3. TPD of CO from Co/Alumina catalysts following adsorption of CO at 25°C as a function of metal loading and reduction temperature. (Ref. 42)

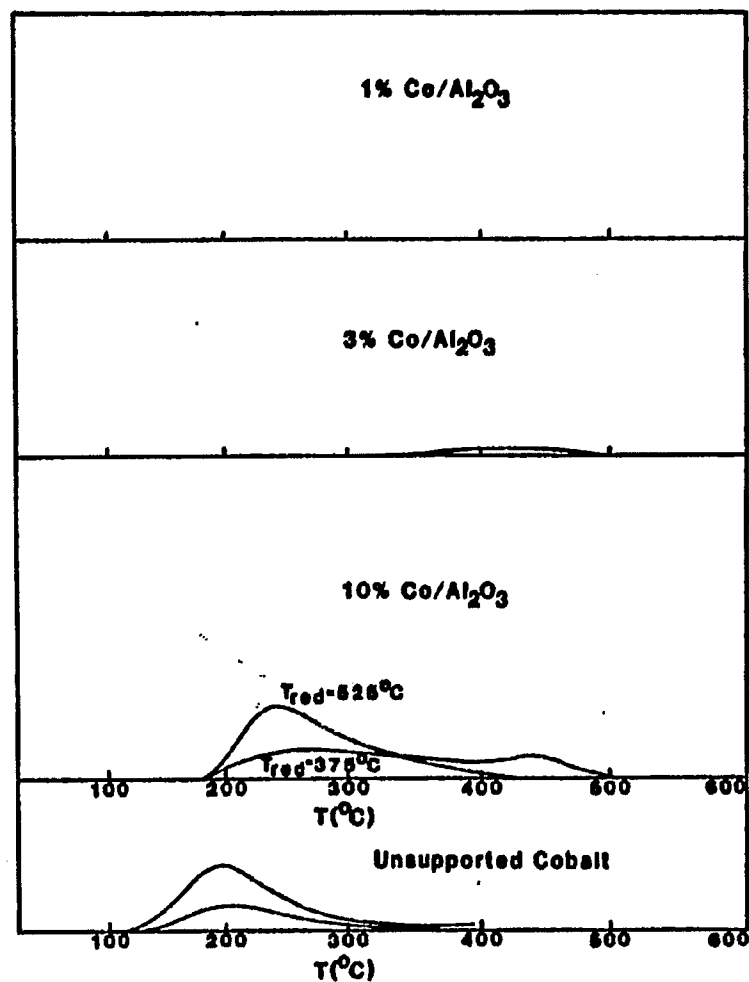


Fig. 4. TPD of CO₂ from Co/Alumina catalysts following adsorption of CO at 25°C as a function of metal loading and reduction temperature. (Ref. 42)

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. The results can be interpreted in terms of either a primary structure sensitivity involving two kinds of active sites or in terms of preferential decoration of the well-dispersed catalysts of low loading by support moieties.

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 [44]. 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 CO₂ formation decreased significantly with increasing reduction temperature. When the CO desorption peak area of 3% Co/titania was plotted against reduction time to the one-half power, two linear regions were observed, the first region having the larger slope. 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/TiO₂ 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. A linear relationship between the log of preexponential factors and activation energies for methanation, i.e., a rate compensation effect, was also observed. 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 [45] 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. Some of the TPD states have been correlated with CO species observed by IR spectroscopy. 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 support decoration effects.

The results of these TPD/TPR/IR studies have been presented at several meetings [46-49], are being prepared in a series of four papers for publication [44-45], and will be published in a doctoral dissertation [50].

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 [30]. 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 (see Figures 5 and 6).

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

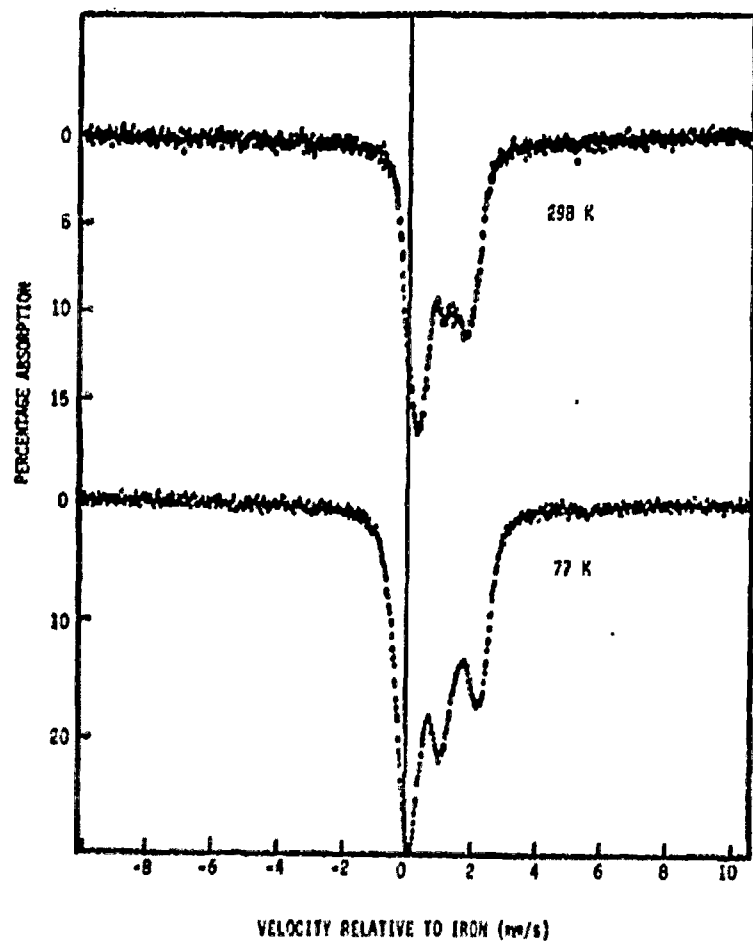


Fig. 5. Mössbauer spectra of 1% Fe^{57} /Carbon reduced in H_2 at 350°C . (Ref. 13)

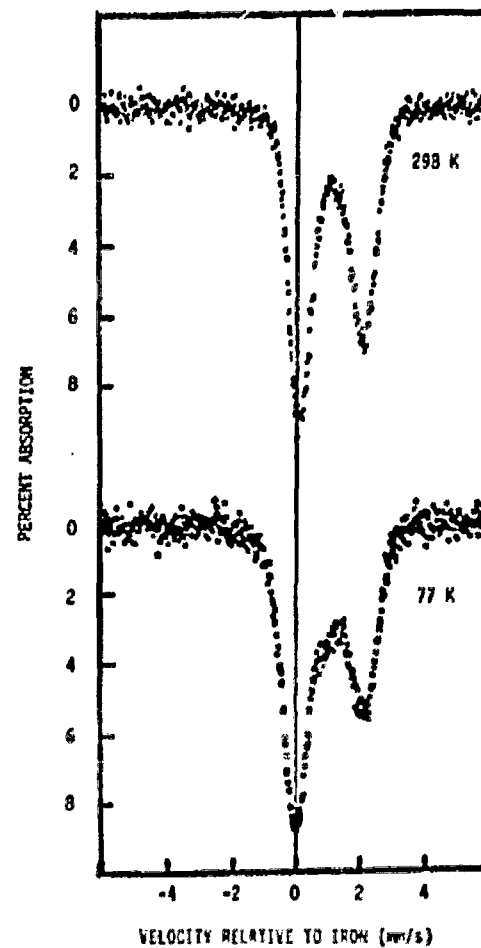


Fig. 6. Mössbauer spectra of 1% Fe^{57} /Alumina reduced in H_2 at 350°C . (Ref. 52)

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 to date 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 [30], while the results for Fe/carbon catalysts have been published in the Journal of Physical Chemistry [13]. Three other papers based on this work are in preparation [41,51-52].

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 [53]. From turnover frequency (TOF) versus temperature data at a H_2/CO ratio of two (Fig.7)

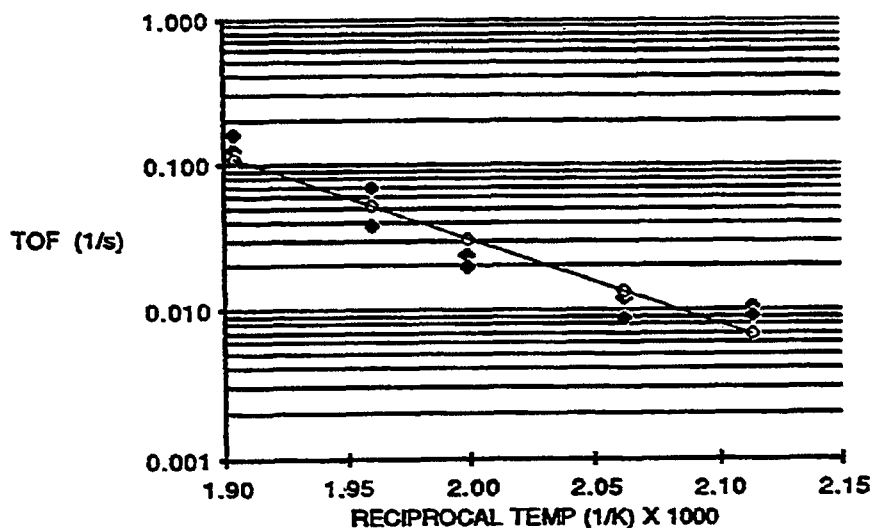


Fig. 7. Temperature dependence of CO hydrogenation rate on clean polycrystalline cobalt, $H_2/CO = 2$.

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 [55]. 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 [54]. 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 [55] and are being prepared for publication [56].

3. Present Status of Knowledge

From the brief review of previous work and the summary of accomplishments in connection with this contract during the past 3 years, it is clear that metal loading, support and dispersion can greatly influence the CO hydrogenation activity/selectivity properties of cobalt and iron. Indeed, activities for cobalt catalysts can vary over four orders of magnitude due to support effects [9] and over two orders of magnitude as a result of variations in metal loading and/or dispersion [9,10]. These results suggest the possibility that CO hydrogenation on cobalt and iron catalysts is structure sensitive [1,2,10]. Yet, since most of the previous studies of dispersion effects [9-16] also involved variations in metal loading, it is not clear whether these effects are a result of structure sensitivity or due to metal-support effects such as decoration. Moreover, the agreement of CO hydrogenation activities for clean unsupported cobalt and poorly-dispersed Co/alumina suggests that the reaction is not structure sensitive. Nevertheless, the surface science study [56] was not conclusive, since the polycrystalline surface involved mainly the basal planes of cobalt, while a study of stepped planes might uncover a structural dependence for the reaction similar to that observed for CO dissociation on stepped planes [57].

Accordingly, the need is clear for a careful study of the structure-sensitivity of cobalt and iron catalysts in CO hydrogenation which includes the following elements:

1. A study of smooth and stepped cobalt and iron surfaces to determine the role of primary surface structure in CO hydrogenation; it should also include the investigation of the same surfaces purposely decorated with support species to determine the possible role of decoration. The possible influence of surface carbon levels on the rate of reaction [19] should also be

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