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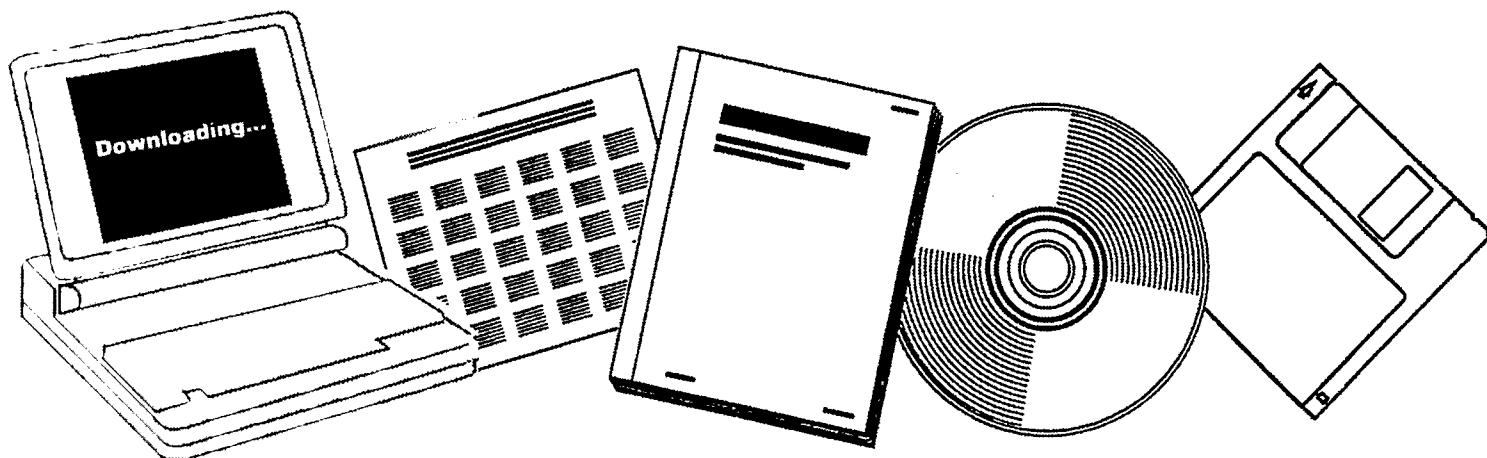
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**METAL-SUPPORT INTERACTIONS: THEIR EFFECTS  
UPON ADSORPTION, ELECTRONIC, AND  
ACTIVITY/SELECTIVITY PROPERTIES OF COBALT  
IN CO HYDROGENATION. FINAL PROGRESS  
REPORT, APRIL 1, 1982-SEPTEMBER 30, 1983**

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

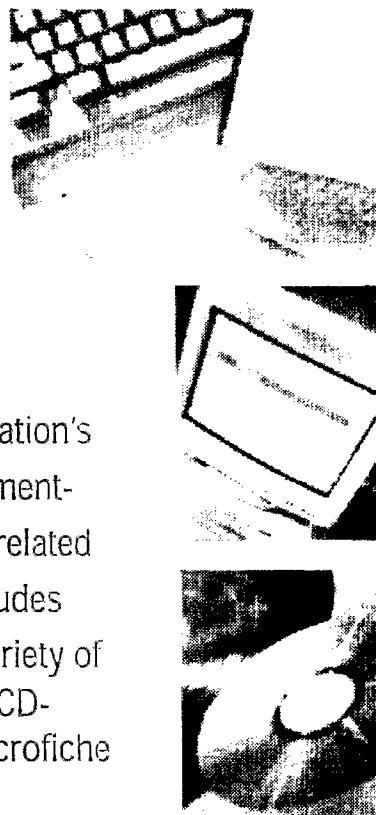
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METAL-SUPPORT INTERACTIONS: THEIR EFFECTS  
UPON ADSORPTION, ELECTRONIC, AND ACTIVITY/SELECTIVITY  
PROPERTIES OF COBALT IN CO HYDROGENATION

Final Progress Report  
For the Period April 1, 1982 to September 30, 1983

by

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## SUMMARY

The investigation of cobalt metal-support interactions and their effects upon adsorption and activity/selectivity properties of cobalt is described. The objectives of this research are to (i) determine the effects of cobalt-support interactions on dispersion, oxidation state and adsorption properties of cobalt; (ii) correlate the activity/ selectivity properties for hydrocarbon synthesis on cobalt with dispersion, oxidation state and behavior of adsorption of CO and H<sub>2</sub> and (iii) measure directly the extent of interaction of various supports with iron using Moessbauer Spectroscopy. The proposed work features a quantitative experimental investigation of Co on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, MgO, and carbon supports to determine physical and chemical, bulk and surface properties of each catalyst using BET, H<sub>2</sub> and CO chemisorption XRD, TEM, TPD, and TPR measurements.

Measurements of dispersion, extent of reduction, H<sub>2</sub> and CO adsorption stoichiometries, CO hydrogenation activity and selectivity, and H<sub>2</sub> adsorption/desorption kinetics were conducted on 18 catalysts. Hydrogen adsorption was found to be highly activated and quite reversible; the adsorption stoichiometry corresponds to one hydrogen atom per surface cobalt atom. CO adsorption stoichiometries on the other hand vary considerably with support, dispersion, and preparation. Binding energies and adsorption states for H<sub>2</sub> on cobalt vary with support. Activity and selectivity in CO hydrogenation on cobalt vary with support, dispersion, and preparation. The specific activity and selectivity for heavier hydrocarbons decrease with increasing dispersion.

## I. INTRODUCTION

Most commercial metal catalysts 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 two-fold: (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. Metal-support interactions are primarily responsible for this stabilization, the degree of which varies with the metal/support system.

The effects of the support on activity and selectivity of the active catalytic phase have been assumed until recently to be of secondary importance. However, there is recent evidence (1-3) that strong metal-support interactions can dramatically

influence the activity/selectivity characteristics of noble and base metals in a number of reactions. They can likewise influence the manner in which reactant molecules adsorb on the metal. Particularly in base metal catalysts the metal-support interaction can determine the degree to which oxides can be reduced to the metallic state and the distribution of metal and metal oxide sites at the surface. Thus metal-support interactions can greatly influence the surface chemistry of a catalyst.

This report describes an investigation of the interaction of cobalt (and to lesser extent iron) metal(s) with a number of different supports, the strength of which is expected to vary over a wide range.

## II. OBJECTIVES AND APPROACH

### A. Objectives

This work involves a comprehensive, quantitative investigation of the effects of metal-support interactions on the surface, electronic and catalytic properties of cobalt (and to a lesser extent iron), the objectives of which are:

1. Determine the effects of cobalt-support interactions on dispersion, oxidation state, and adsorption properties (i.e. adsorption stoichiometries and binding states for CO and H<sub>2</sub>) of cobalt over a range of cobalt loading.
2. Correlate the activity/selectivity properties of hydrocarbon synthesis on cobalt with dispersion, oxidation state, behavior for adsorption of CO and H<sub>2</sub> and its strength of interaction with various supports.
3. Measure directly the extent of electronic interaction of iron, with various supports using Moessbauer Spectroscopy and correlate the degree of interaction with adsorption and activity/selectivity properties of the metal.

Cobalt has been chosen as the primary metal for study because of its importance in hydrotreating and coal-conversion reactions and because relatively little is known regarding its interaction with various supports. The materials to be used as supports include carbon, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and MgO. These particular supports are emphasized because (i) their extent of interaction with metals is believed to span a wide range from weak to very strong and (ii) all have commercial significance.

## B. Research Plan

In order to accomplish the above listed objectives the proposed work has been divided into four areas of study (four tasks) to be completed over a period of three years.

1. Prepare cobalt catalysts and determine the extent of reduction, dispersion, and CO and H<sub>2</sub> adsorption stoichiometries of cobalt as a function of support and metal loading using conventional static H<sub>2</sub> adsorption, CO adsorption, and O<sub>2</sub> titration techniques (4,5).

2. Determine binding energies and binding states of CO and H<sub>2</sub> on cobalt as a function of support and metal loading using temperature-programmed-desorption (TPD).

3. Measure specific activities and selectivities for hydrogenation of CO over cobalt on different supports by means of a differential laboratory reactor system.

4. Measure the effects of support on the electronic and chemical properties of iron using Moessbauer spectroscopy.

The experimental approach for each of these tasks was described in detail in our first annual report (6).

## III. ACCOMPLISHMENTS, RESULTS AND FUTURE PLANS

### A. Preparation and Measurement of Dispersion, Extent of Reduction and Adsorption Stoichiometries of CO and H<sub>2</sub>

1. Catalyst Preparation. Cobalt catalysts were prepared on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, and MgO supports by impregnation (and in selected cases by pH-controlled precipitation) and on carbon supports by evaporative deposition as described in our previous report (6). They were reduced in H<sub>2</sub> at 400°C (Co/Al<sub>2</sub>O<sub>3</sub> catalysts at 350°C).

2. Dispersion and Extent of Reduction Measurements. Cobalt metal dispersions were measured by H<sub>2</sub> adsorption at the temperature of maximum uptake determined from TPD (7,8, Section IIIB). Extents of reduction were measured by O<sub>2</sub> titration at 400°C, assuming formation of Co<sub>3</sub>O<sub>4</sub> (9,10). The results, summarized in Table 1, indicate that the cobalt in these catalysts was generally well-dispersed and, with the exceptions of Co/SiO<sub>2</sub> (impregnated) and unsupported cobalt, only partly reduced to the metal. The cobalt dispersions of Co/carbon catalysts were remarkably high.

TABLE 1. Extents of Reduction, Dispersions, and Average Crystallite Diameters for Supported and Unsupported Cobalt Catalysts

Catalyst	Percentage Reduction <sup>c</sup>	Percentage Dispersion <sup>d</sup>	Average Crystallite Diameter (nm)				CO/Co <sub>s</sub> <sup>g</sup>
			H <sub>2</sub> Adsorption <sup>c</sup> d <sub>s</sub> <sup>e</sup>	d <sub>s</sub> <sup>e</sup>	TEM d <sub>v</sub> <sup>f</sup>	XRD d <sub>v</sub> <sup>f</sup>	
100% Co	100	0.26	286				0.4
Co/SiO <sub>2</sub>							
3%	76	11	8.7	11	15		1.3
10%	92	10	9.6	12	16	12	0.7
3 <sup>a</sup>	4.6	20	4.8				1.2
Co/Al <sub>2</sub> O <sub>3</sub>							
1%	11	34	2.8				0.4
3%	22	10	9.4				1.1
10%	34	9.9	9.7	11	15		0.7
15%	44	6.6	14	14	17		1.0
3 <sup>a</sup>	16	19	5.0				1.7
Co/TiO <sub>2</sub>							
3%	14	17	5.6				0.9
10%	47	4.5	21	8.7	11	13	0.8
3 <sup>a</sup>	12	21	4.6				1.6
Co/MgO							
3%	11	2.1	45				2.3
10%	13	1.9	51				1.0
Co/C (Type UU)							
3 <sup>b</sup>	13	66	1.7				1.0
10 <sup>b</sup>	47	36	2.7	3.4	3.8	20	0.7
Co/C (Spheron)							
3 <sup>b</sup>	9.3	86	1.1				1.1
10 <sup>b</sup>	16	63	1.6			54	1.4

<sup>a</sup>Controlled-pH precipitation; catalysts not designated were prepared by impregnation.

<sup>b</sup>Evaporative deposition.

<sup>c</sup>Calculated from O<sub>2</sub> titration of reduced sample at 673 K, assuming formation of Co<sub>3</sub>O<sub>4</sub> (11).

<sup>d</sup>Based on total activated H<sub>2</sub> uptake; calculated from Equation 1.

<sup>e</sup>Surface mean diameter.

<sup>f</sup>Volume mean diameter.

<sup>g</sup>CO molecules adsorbed per surface cobalt atom.



3. Stoichiometries of H<sub>2</sub> and CO Adsorption. H<sub>2</sub> adsorption on cobalt was found to be activated and partially reversible. By comparison of cobalt crystallite diameters from H<sub>2</sub> adsorption with those from x-ray diffraction and transmission electron microscopy, it was determined that the total maximum adsorption on most cobalt catalysts corresponds to a monolayer of atomic hydrogen; i.e. hydrogen adsorbs dissociatively with a stoichiometry of one hydrogen atom per cobalt surface atom. In the case of Co/TiO<sub>2</sub> the stoichiometric adsorption ratio was about 0.5 atoms of hydrogen per surface cobalt atom. The CO adsorption ratio, on the other hand, varied from 0.4 to 2.3 molecules of CO per cobalt surface atom (see Table 1).

The results of the adsorption stoichiometry, dispersion, and extent of reduction measurements were recently accepted by the Journal of Catalysis for publication (9) and incorporated in an M.S. Thesis by Mr. Robert Reuel (11). These results comprise the first comprehensive study of the adsorption stoichiometries of H<sub>2</sub> and CO on cobalt catalysts.

#### B. Study of Binding Energies and Binding States of CO and H<sub>2</sub> on Cobalt Catalysts

Two TPD systems having thermal conductivity and mass spectrometer detectors were described in our previous report (6) and in an M.S. Thesis by Mr. John Zowtiak (12). The mass spectrometer system was constructed during the first year of this contract (6,12). Two kinds of TPD experiments were performed: (i) adsorption temperatures were varied to determine activation energies of adsorption and (iii) adsorbate coverages were varied to enable heats of adsorption to be determined (8).

Experiments of the first kind were conducted for H<sub>2</sub> adsorption on a dozen selected catalysts from Table 1. A typical set of TPD spectra of H<sub>2</sub> from 10% Co/SiO<sub>2</sub> as a function of adsorption temperature is shown in Fig. 1. The amount of H<sub>2</sub> adsorbed increases through a maximum with increasing temperature. In other words, H<sub>2</sub> adsorption on Co/SiO<sub>2</sub> is highly activated. Similar results were obtained for the other catalyst systems. Activation energies for Co, Co/SiO<sub>2</sub>, and Co/Al<sub>2</sub>O<sub>3</sub> catalysts are summarized in Table 2. It is evident that the activation energy increases in the order Co, Co/SiO<sub>2</sub>, Co/Al<sub>2</sub>O<sub>3</sub>; it also increases in the Co/SiO<sub>2</sub> system with decreasing loading.

The observation in this study that H<sub>2</sub> adsorption on cobalt is highly activated and that the extent of activation increases with increasing degrees of metal-support interaction has important implications for the science and practice of catalysis.

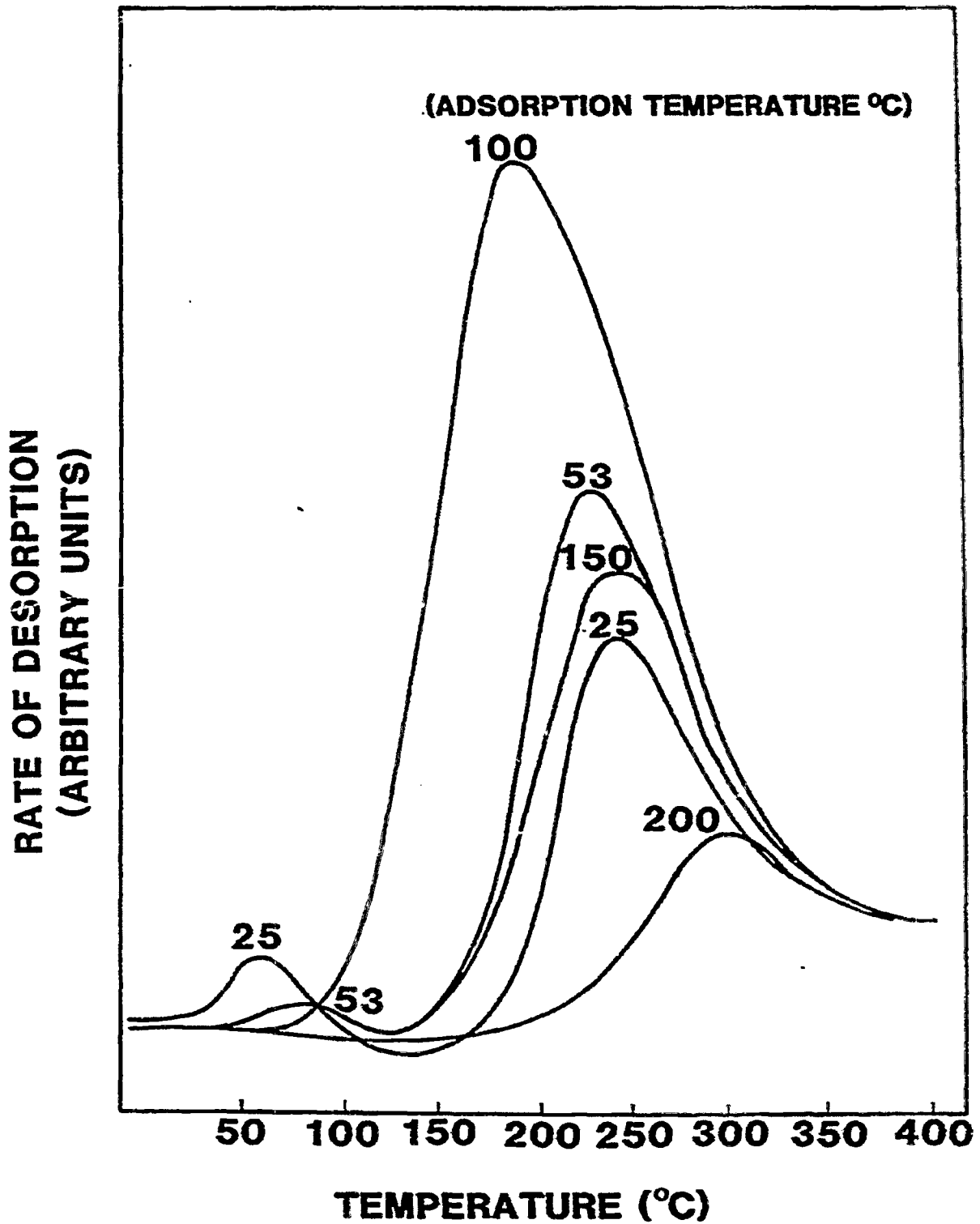


Figure 1. TPD spectra of H<sub>2</sub> from 10% Co/SiO<sub>2</sub> as a function of adsorption temperature.

TABLE 2. Activation Energies and Heats of Adsorption and Desorption for H<sub>2</sub>/Cobalt

<u>Catalyst</u>	<u>E<sub>Aa</sub> (kJ/mol)<sup>a</sup></u>	<u>E<sub>Ad</sub> (kJ/mol)<sup>b</sup></u>	<u>-ΔH<sub>a</sub><sup>c</sup></u>	<u>Order of Desorption</u>
<u>This Study</u>				
Unsupported Co	5.8	151	145±10	2
3% Co/SiO <sub>2</sub>	43	—	—	—
10% Co/SiO <sub>2</sub>	18	168	145±7	2
10% Co/Al <sub>2</sub> O <sub>3</sub>	39	144	105	2

<sup>a</sup>Activation energy for adsorption of H<sub>2</sub>.

<sup>b</sup>Activation energy for desorption of H<sub>2</sub>.

<sup>c</sup>Heat of adsorption;  $-\Delta H_a = E_{Ad} - E_{Aa}$ .

For example, previously determined cobalt surface areas and CO hydrogenation turnover frequencies for cobalt catalysts based on room temperature H<sub>2</sub> adsorption may be significantly in error. Moreover, previously measured desorption activation energy and heat of adsorption data are in error because the more energetic sites were not considered.

Heats of H<sub>2</sub> adsorption on Co, Co/SiO<sub>2</sub>, and Co/Al<sub>2</sub>O<sub>3</sub> obtained by varying coverage are also listed in Table 2. The heat of adsorption is approximately the same (145 kJ/mol) for unsupported cobalt and 10% Co/SiO<sub>2</sub> but is significantly lower (105 kJ/mol) for Co/Al<sub>2</sub>O<sub>3</sub>. Thus, the binding energy of H<sub>2</sub> on cobalt is clearly affected by metal-support interactions. Moreover, new low and high temperature states of H<sub>2</sub> are observed in the Co/TiO<sub>2</sub> and Co/carbon systems. The results of the H<sub>2</sub> TPD study were written up in two papers which have been accepted by the Journal of Catalysis (7,8) and in an M.S. Thesis (12).

Studies of CO desorption from Co, Co/SiO<sub>2</sub>, and Co/Al<sub>2</sub>O<sub>3</sub> catalysts (initiated by Mr. John Zowtiak and continued by Mr. Won Ho Lee, Ph.D. candidate) show the presence of two different adsorption states which vary in population according to support and possibly dispersion. Quantitative studies of CO desorption kinetics from these catalysts will continue during the remaining year of the contract.

### C. Measurement of Specific Activities and Selectivities for CO Hydrogenation on Supported Cobalt Catalysts

The catalysts listed in Table 1 were tested for activity and selectivity in CO hydrogenation using methods and equipment described in our first report (6). The results indicate that specific activity and selectivity of cobalt vary with support, dispersion, metal loading, and preparation method (10). The order of decreasing CO turnover frequency at 1 atm and 225°C for catalysts containing 3 wt.% cobalt is Co/TiO<sub>2</sub>, Co/SiO<sub>2</sub>, Co/Al<sub>2</sub>O<sub>3</sub>, Co/C, and Co/MgO. The specific activity of cobalt decreases significantly with decreasing dispersion (see Fig. 2). Product selectivity can be correlated with CO/H adsorption ratios; however, it is best correlated with dispersion (see Fig. 3). Fig. 3 shows that hydrocarbons of lower molecular weight are produced by catalysts of higher dispersion. In the Co/Al<sub>2</sub>O<sub>3</sub> system, activity and selectivity for high molecular weight hydrocarbons increase with increasing cobalt loading. A 15% Co/Al<sub>2</sub>O<sub>3</sub> is 20 times more active than 3% Co/Al<sub>2</sub>O<sub>3</sub>; moreover, 85 wt.% of its hydrocarbon fraction is in the C<sub>5</sub>-C<sub>12</sub> (gasoline) range!

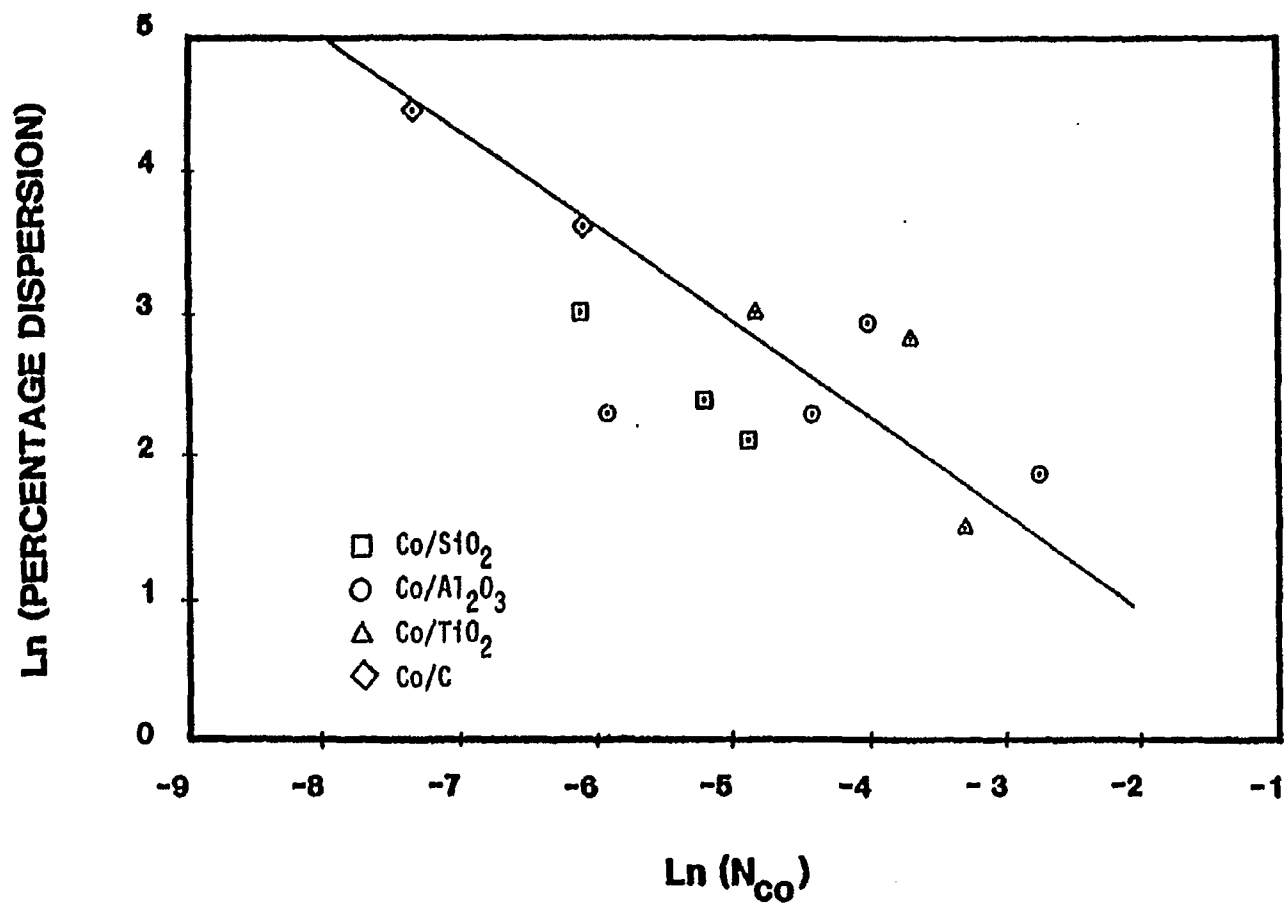


Figure 2. Dispersion versus CO turnover frequency for supported cobalt in CO hydrogenation (225°C, 1 atm).

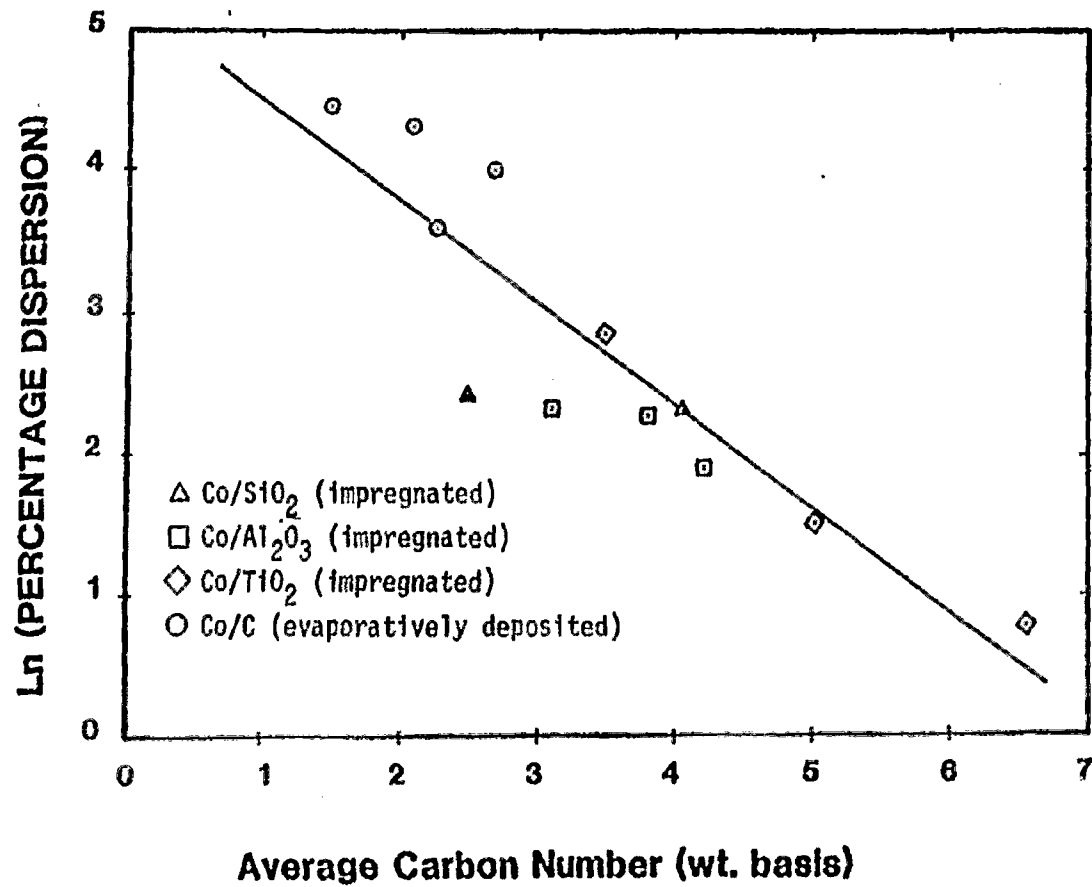


Figure 3. Dispersion versus average carbon number for supported cobalt in CO hydrogenation.

The results of the activity/selectivity study have been accepted by the Journal of Catalysis (10) and published in a thesis (11). The correlations of activity and selectivity with dispersion are very interesting and represent an important contribution to the understanding of selectivity in Fischer-Tropsch Synthesis.

#### D. Moessbauer Investigation of Supported Iron Catalysts

The objective is to determine how the support affects the electronic, chemical, and catalytic properties of well-dispersed iron. Over the past year Mr. Val Jones, M.S. candidate, prepared and characterized by  $H_2$  adsorption and  $O_2$  titration over a dozen Fe/C and Fe/ $TiO_2$  catalysts. Some of these catalysts have dispersions of 30% or greater. Moessbauer analysis and CO hydrogenation activity/selectivity tests will be conducted on these catalysts during the remaining months of the contract. In the case of Fe/ $TiO_2$  we intend to examine the effects of reduction temperature on the electronic and catalytic properties of iron.

#### IV. CONCLUSIONS

1. Hydrogen adsorption on cobalt is highly activated and partially reversible. Except in the case of Co/ $TiO_2$ , hydrogen adsorbs on unsupported and supported cobalt catalysts with a stoichiometry of one hydrogen atom per cobalt surface atom. The CO adsorption stoichiometry on the other hand varies considerably with support, metal loading, and preparation from 0.4 to 2.3 molecules of CO per cobalt surface atom.

2. The binding state and energetics of hydrogen adsorption on cobalt are a function of support. Activation energies for adsorption increase with increasing degrees of metal-support interaction. Heats of  $H_2$  adsorption on cobalt are the same (145 kJ/mol) for unsupported cobalt and 10% Co/ $SiO_2$  but lower (105 kJ/mol) in the case of 10% Co/ $Al_2O_3$ .

3. Activity and selectivity in CO hydrogenation on cobalt vary with dispersion, support, and preparation. Specific activity and the molecular weight of hydrocarbons both decrease with increasing dispersion.

REFERENCES

1. Tauster, S.J. and Fung, S.C., J. Catal. 55, 29 (1978).
2. Vannice, M.A. and Garten, R.C., J. Catal. 56, 236 (1979).
3. Bartholomew, C.H., Pannell, R.B., and Butler, J.L., J. Catal. 65, 335 (1980).
4. Bartholomew, C.H. and Farrauto, R.J., J. Catal. 45, 41 (1976).
5. Bartholomew, C.H. and Pannell, R.B., J. Catal. 65, 390 (1980).
6. Bartholomew, C.H., Reuel, R.C., and Zowtiak, J.M., Annual Progress Report to DOE-OER, DOE/ER/10855-1, April 30, 1982.
7. Zowtiak, J.M., Weatherbee, G.D., and Bartholomew, C.H., "Activated Adsorption of H<sub>2</sub> on Cobalt and Effects of Support Thereon," J. Catal. 82, 230 (1983).
8. Zowtiak, J.M. and Bartholomew, C.H., "The Kinetics of H<sub>2</sub> Adsorption on and Desorption from Cobalt and Effects of Support Thereon," J. Catal. 83, 107 (1983).
9. Reuel, R.C. and Bartholomew, C.H., "The Stoichiometries of H<sub>2</sub> and CO Adsorptions on Cobalt: Effects of Support and Preparation," J. Catal., in press, 1983.
10. Reuel, R.C. and Bartholomew, C.H., "Effects of Support and Dispersion on the CO Hydrogenation Activity and Selectivity Properties of Cobalt," J. Catal., in press, 1983.
11. Reuel, R.C., "Cobalt-Support Interactions: Their Effects on Adsorption and CO Hydrogenation Activity and Selectivity Properties," M.S. Thesis, Brigham Young University, April, 1983.
12. Zowtiak, J.M., "Metal-Support Interactions in Cobalt Catalysts: Their Effects on Adsorption/Desorption Kinetics for Hydrogen and Carbon Monoxide," M.S. Thesis, Brigham Young University, April 1983.



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