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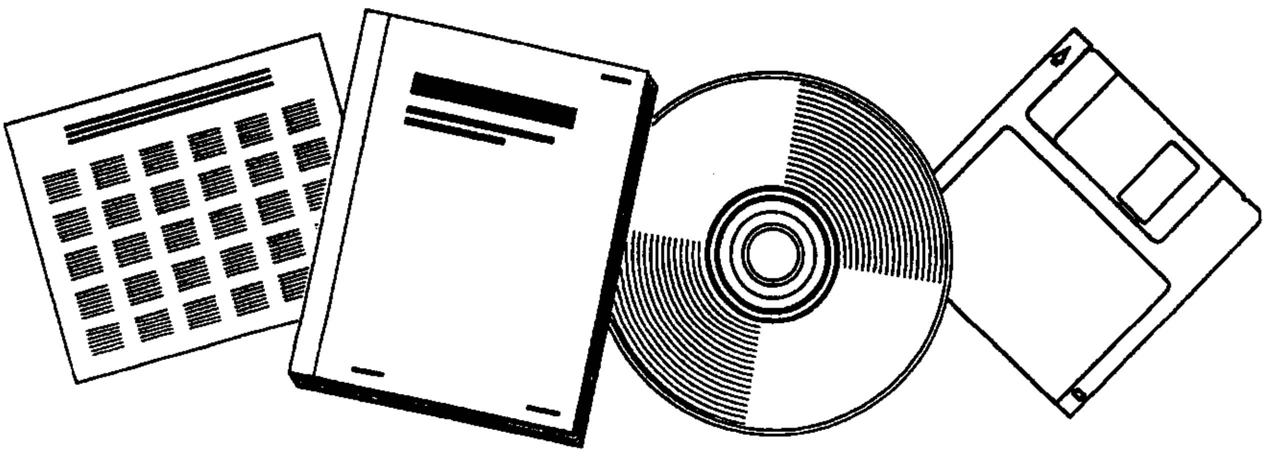

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METAL-SUPPORT INTERACTIONS: THEIR EFFECTS UPON ADSORPTION, ELECTRONIC, AND ACTIVITY/SELECTIVITY PROPERTIES OF COBALT IN CO HYDROGENATION

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For the Period April 1, 1982 to March 31, 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_2 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_2O_3, SiO_2, TiO_2, MgO, and carbon supports to determine physical and chemical, bulk and surface properties of each catalyst using BET, H_2 and CO chemisorption XRD, TEM, TPD, and TPR measurements.

During the past year, measurements of dispersion, extent of reduction, H_2 and CO adsorption stoichiometries, CO hydrogenation activity and selectivity, and H_2 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_2 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_2) 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_2 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_2, Al_2O_3, TiO_2, 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_2 adsorption stoichiometries of cobalt as a function of support and metal loading using conventional static H_2 adsorption, CO adsorption, and O_2 titration techniques (4,5).

2. Determine binding energies and binding states of CO and H_2 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_2

1. Catalyst Preparation. Cobalt catalysts were prepared on Al_2O_3, SiO_2, TiO_2, 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_2 at 400°C (Co/Al_2O_3 catalysts at 350°C).

2. Dispersion and Extent of Reduction Measurements. Cobalt metal dispersions were measured by H_2 adsorption at the temperature of maximum uptake determined from TPD (7,8, Section IIIB). Extents of reduction were measured by O_2 titration at 400°C, assuming formation of Co_3O_4 (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_2 (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[c]	Percentage Dispersion[d]	Average Crystallite Diameter (nm): H_2 Adsorption[c] d_s[e]	TEM d_s[e]	XRD d_v[f]	d_v[f]	CO/Co_s[g]
100% Co	100	0.26	285			0.4	
Co/SiO_2							
3%	75	11	8.7	1115		1.3	
10%	92	10	9.6	1216	12	0.7	
3[a]	4.6	20	4.8			1.2	
Co/Al_2O_3							
1%	11	34	2.8			0.4	
3%	22	10	9.4			1.1	
10%	34	9.9	9.7	1115		0.7	
15%	44	6.6	14	1417		1.0	
3%[a]	16	19	5.0			1.7	
Co/TiO_2							
3%	14	17	5.6			0.9	
10%	47	4.5	21	8.7	11	13	0.8
3%[a]	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%[b]	13	55	1.7			1.0	
10%[b]	47	36	2.7	3.4	3.8	20	0.7
Co/C (Spheron)							
3%[b]	9.3	86	1.1			1.1	
10%[b]	15	63	1.5		54	1.4	

[a] Controlled-pH precipitation; catalysts not designated were prepared by impregnation.

[b] Evaporative deposition.

[c] Calculated from O_2 titration of reduced sample at 673 K, assuming formation of Co_3O_4 (11).

[d] Based on total activated H_2 uptake; calculated from Equation 1.

[e] Surface mean diameter.

[f] Volume mean diameter.

[g] CO molecules adsorbed per surface cobalt atom.

3. Stoichiometries of H_2 and CO Adsorption. H_2 adsorption on cobalt was found to be activated and partially reversible. By comparison of cobalt crystallite diameters from H_2 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 nydrogen atom per cobalt surface atom. In the case of Co/TiO_2 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 submitted to 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_2 and CO on cobalt catalysts.

B. Study of Binding Energies and Binding States of CO and H_2 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_2 adsorption on a dozen selected catalysts from Table 1. A typical set of TPD spectra of H_2 from 10% Co/SiO_2 as a function of adsorption temperature is shown in Fig. 1. The amount of H_2 adsorbed increases through a maximum with increasing temperature. In other words, H_2 adsorption on Co/SiO_2 is highly activated. Similar results were obtained for the other catalyst systems. Activation energies for Co, Co/SiO_2, and Co/Al_2O_3 catalysts are summarized in Table 2. It is evident that the activation energy increases in the order Co, Co/SiO_2, Co/Al_2O_3; it also increases in the Co/SiO_2 system with decreasing loading.

The observation in this study that H_2 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.

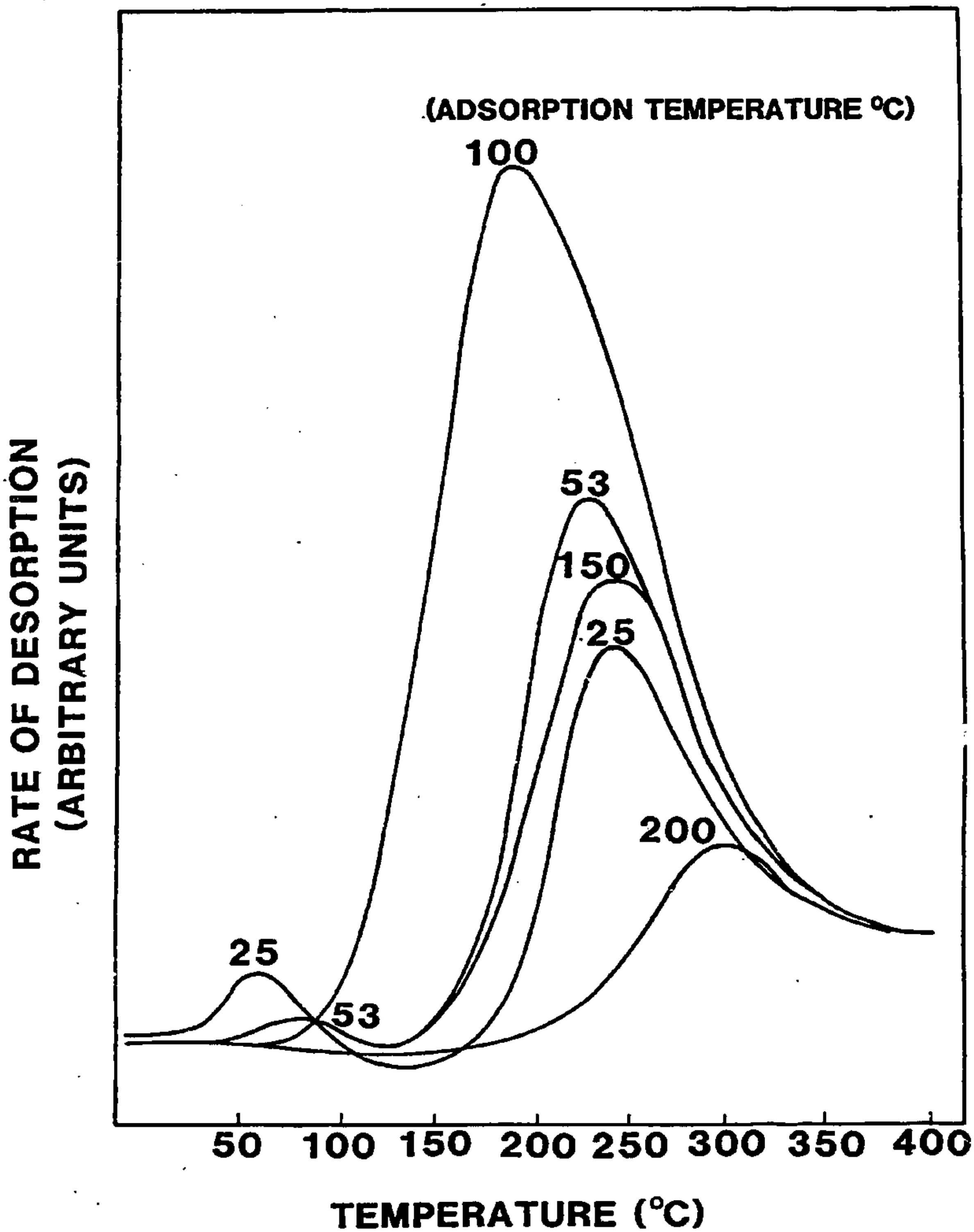

Figure 1. TPD spectra of H_2 from 10% Co/SiO_2 as a function of adsorption temperature.

TABLE 2. Activation Energies and Heats of Adsorption and Desorption for H_2/Cobalt

Catalyst	E_{Aa} (kJ/mol)[a]	E_{Ad} (kJ/mol)[b]	$-\Delta H_a$[c]	Order of Desorption
This Study				
Unsupported Co	5.8	151	145±10	2
3% Co/SiO_2	43		--	--
10% Co/SiO_2	18	168	145±7	2
10% Co/Al_2O_3	39	144	105	2

[a]Activation energy for adsorption of H_2.

[b]Activation energy for desorption of H_2.

[c]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_2 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_2 adsorption on Co, Co/SiO_2, and Co/Al_2O_3 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_2 but is significantly lower (105 kJ/mol) for Co/Al_2O_3. Thus, the binding energy of H_2 on cobalt is clearly affected by metal-support interactions. Moreover, new low and high temperature states of H_2 are observed in the Co/TiO_2 and Co/carbon systems. The results of the H_2 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_2, and Co/Al_2O_3 catalysts 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_2, Co/SiO_2, Co/Al_2O_3, 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_2O_3 system, activity and selectivity for high molecular weight hydrocarbons increase with increasing cobalt loading. A 15% Co/Al_2O_3 is 20 times more active than 3% Co/Al_2O_3; moreover, 85 wt.% of its hydrocarbon fraction is in the C_5-C_{12} (gasoline) range!

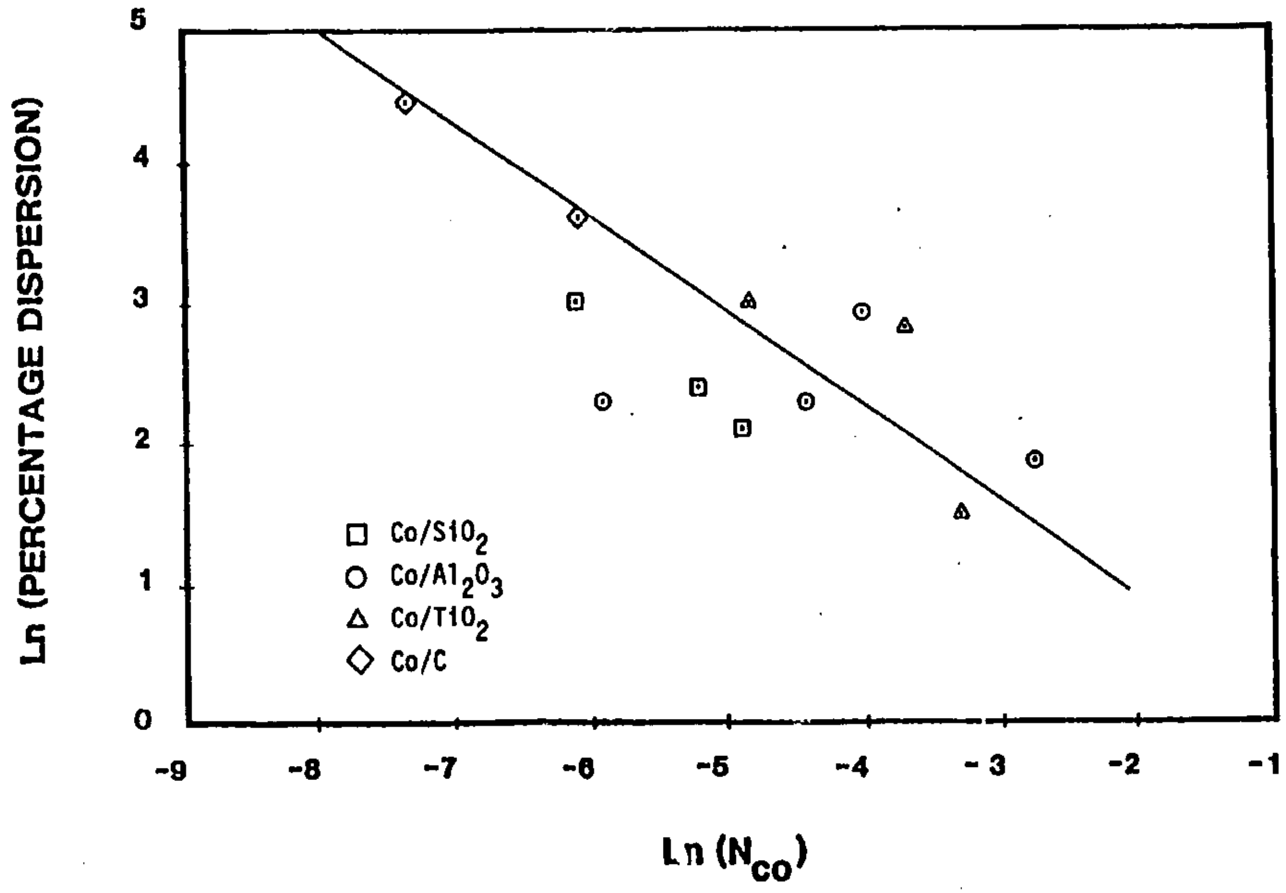

Figure 2. Dispersion versus CO turnover frequency for supported cobalt in CO hydrogenation (225°C, 1 atm).

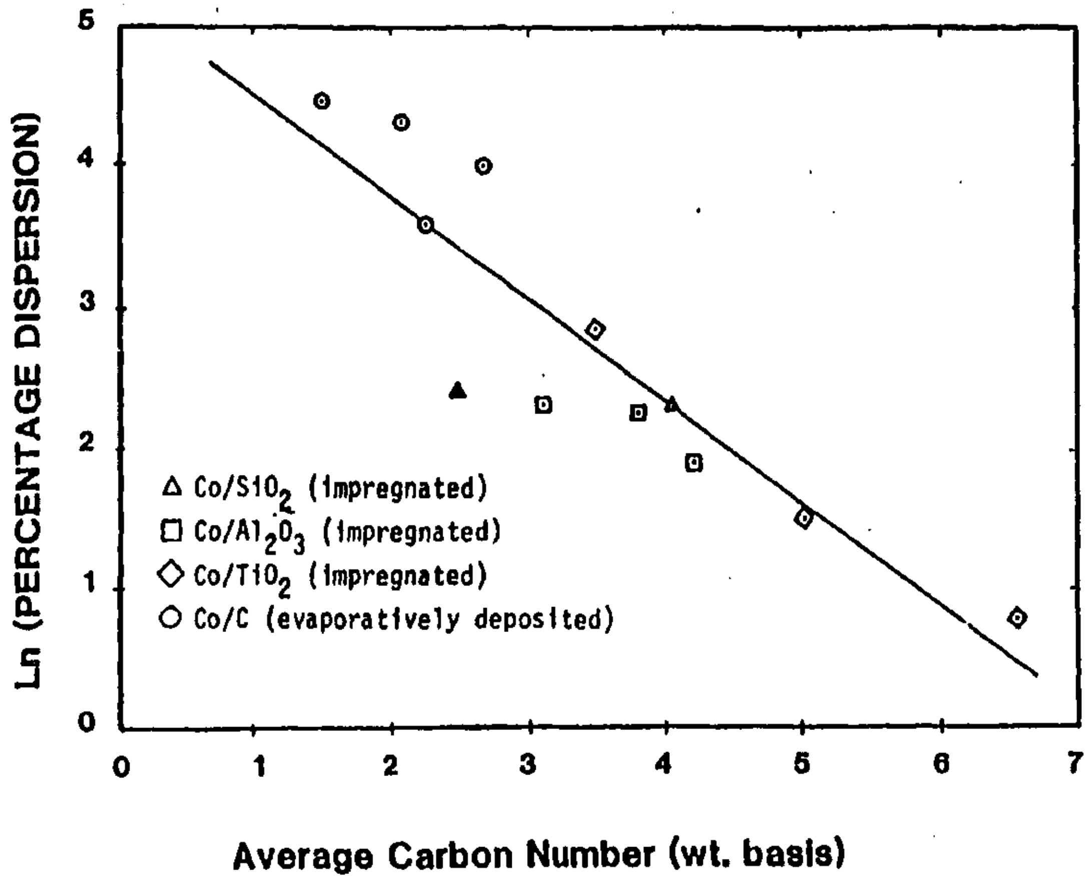

Figure 3. Dispersion versus average carbon number for supported cobalt in CO hydrogenation.

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 scientific literature.

D. Moessbauer Investigation of Supported Iron Catalysts

The investigation of well-dispersed Fe/C and Fe/TiO_2 was initiated only a few months ago by Mr. Val Jones, M.S. candidate. The objective is to determine how the support affects the electronic, chemical, and catalytic properties of well-dispersed iron. An Fe/C catalyst having a dispersion of 30% has been prepared by evaporative deposition. Preparation of well-dispersed Fe/TiO_2 from iron carbonyls is presently under investigation. Moessbauer analysis and CO hydrogenation activity/selectivity tests will be conducted on these catalysts during the remaining year of the contract.

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.

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