

## Effects of Support and Dispersion on the CO Hydrogenation Activity/Selectivity Properties of Cobalt

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Specific activities and selectivities of unsupported cobalt and cobalt supported on alumina, silica, titania, carbon, and magnesia carriers for CO hydrogenation were measured in a single-pass differential reactor at low conversions, 1 atm, and 175–350°C. The results indicate that specific activity and selectivity of cobalt vary with support, dispersion, metal loading, and preparation method. The order of decreasing CO hydrogenation activity 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 increasing dispersion. Product selectivity is best correlated with dispersion and extent of reduction, i.e., the molecular weight of hydrocarbon products is lower and the CO<sub>2</sub>/H<sub>2</sub>O ratio is higher for catalysts having higher dispersions and lower extents of reduction. This effect may be due to stable oxides in the well-dispersed, poorly reduced catalysts, which catalyze the water-gas-shift reaction thereby increasing the H<sub>2</sub>/CO ratio at the surface. In the Co/Al<sub>2</sub>O<sub>3</sub> system, activity and selectivity for high molecular weight hydrocarbons increase very significantly 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, 86 wt% of its hydrocarbon fraction is in the C<sub>5</sub>–C<sub>12</sub> (gasoline) range compared to 18 wt% for 3% Co/Al<sub>2</sub>O<sub>3</sub>.

### INTRODUCTION

Supported catalysts find widespread application in the oil, gas, and chemical industries. The purpose of the support in these catalysts 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. Until recently, the effects of support and dispersion on activity and selectivity of the active metal phase were generally assumed to be of secondary importance.

Recent investigations (1–8), however, have provided evidence that the support can significantly influence the morphology, adsorption, and activity/selectivity properties of the active phase, especially in well-dispersed systems. For example, a number of recent studies in this (5–8) and other laboratories (1–4) show that the stoichiometries and states of H<sub>2</sub> and CO adsorption on cobalt, nickel, and platinum as well as the

activity and selectivity properties of nickel in CO hydrogenation are markedly changed by strong interactions between the metal and supports such as Al<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub> and even SiO<sub>2</sub> at high dispersions.

Although effects of support on the activity of cobalt were reported by Sinfelt *et al.* (9) almost 2 decades ago, no definitive studies of such effects have been reported for cobalt catalysts in CO hydrogenation. Vannice (10–11) reported significantly different methanation turnover numbers for Co/SiO<sub>2</sub> and Co/Al<sub>2</sub>O<sub>3</sub> catalysts, however his work did not define the effects of dispersion or support on either the activity or selectivity properties of cobalt. Recent companion studies from this laboratory (7, 8) provide evidence that dispersion and support significantly affect the adsorption stoichiometries and states of H<sub>2</sub> and CO on cobalt. Because H<sub>2</sub> and CO are also reactants in CO hydrogenation, effects of dispersion and support on activity and selectivity are likewise expected.

Recent work from this laboratory (7, 8) also indicates that  $H_2$  adsorption on cobalt is highly activated and that previous studies of the specific activity of cobalt in which  $H_2$  adsorption was used to measure active site densities may have involved significant errors.

The purpose of this work was to determine the effects of alumina, silica, titania, magnesia, and carbon supports on the specific activity and selectivity properties of cobalt in CO hydrogenation. Effects of dispersion, metal loading, and catalyst preparation on the activity/selectivity behavior of cobalt were also investigated.

#### EXPERIMENTAL

*Materials.* The preparation of the cobalt catalysts used in this study is described elsewhere (8).  $Al_2O_3$ -,  $SiO_2$ -,  $TiO_2$ -, and MgO-supported cobalt catalysts were prepared by impregnation and controlled-pH precipitation techniques (8, 12). Carbon-supported catalysts were prepared by evaporative deposition (8, 13).

High purity hydrogen (99.99%) and carbon monoxide (99.99%) were obtained from Whitmore and Matheson. The hydrogen was further purified using a Deoxo catalyst (Englehard) followed by a Molecular Sieve 5A (Linde) trap. The CO was also passed through a molecular sieve trap to remove iron carbonyl.

*Apparatus and procedure.* Measurements of CO/ $H_2$  synthesis activity and selectivity were performed in a differential, fixed-bed Pyrex reactor (14). Reactant gas flow rates were held constant with Brooks mass flow controllers, and reactor temperatures were fixed using a temperature controller constructed in-house. Product gases were passed through a heated line to a Hewlett-Packard 5834A gas chromatograph for on-line analysis. Fixed gases ( $H_2$ ,  $N_2$ , CO,  $CH_4$ ,  $H_2O$ , and  $CO_2$ ) were separated in a 2-m packed column containing Carbosieve B. Hydrocarbons were separated in a 12-m capillary column coated

with methyl silicone, which provided excellent resolution of carbon numbers 1–30 and alcohols but poor resolution of olefins from paraffins (15). The Hewlett-Packard gas chromatograph was fully programmable and equipped with thermal conductivity and flame ionization detectors for analysis of fixed gases and hydrocarbons.

Catalyst samples of 1–2 g were reduced in  $H_2$  at 400°C for 16 h after which  $H_2$  and CO adsorption uptakes were measured by static methods (8). Following adsorption measurements, each catalyst was pretreated in flowing  $H_2$  at 300°C for 1 h to remove any adsorbed CO or carbonaceous deposits from its surface. Reactant gases consisting of  $H_2$  and CO, in a 2 to 1 ratio, were fed to the reactor at atmospheric pressure. Conversions were maintained between 5 and 10% to ensure that intrinsic rate data were obtained free of heat and mass transfer effects (16). Activity tests were conducted at three different temperatures from which CO and  $CH_4$  turnover numbers and activation energies were determined. Deactivation due to carbon deposits was prevented by cleaning the catalyst surface in  $H_2$  at 300°C for 20–30 min between tests at different temperatures, a method originally suggested by Sinfelt (17). The absence of deactivation effects was confirmed by experiments in which low temperature data were repeated after high temperature data had been obtained. Turnover frequencies and activation energies were based on the initial activities of fresh catalysts. Active site concentrations used to calculate turnover frequencies were based on monolayer  $H_2$  uptakes determined in our previous study (8). Since product distributions changed quite significantly during the first 30 min of reaction, they were measured after a near steady-state condition had been reached, i.e., within 2–3 h after the beginning of the run, as close to 225°C as feasible. In tests of 15% Co/ $SiO_2$  over longer periods of time (15–20 h), observed changes in selectivity after 2–3 h of reaction time were small (15, 18).

## RESULTS

Percentage CO conversions (to hydrocarbons and CO<sub>2</sub>) and gas hourly space velocities are listed in Table 1 at different reaction temperatures for CO hydrogenation on freshly reduced unsupported and supported cobalt catalysts. Space velocity and temperature were varied in order to maintain CO conversions near 5% and within the range of 2–10%. It was possible to obtain most of the conversion data in the temperature range of 200–250°C. However higher loading (10–15 wt%) Co/SiO<sub>2</sub>, Co/Al<sub>2</sub>O<sub>3</sub>, and Co/TiO<sub>2</sub> catalysts were sufficiently active to require testing at 175–215°C, while low loading (1–3 wt%) Co/Al<sub>2</sub>O<sub>3</sub>, Co/SiO<sub>2</sub> prepared by controlled-pH precipitation, 3 wt% Co/C catalysts, and Co/MgO catalysts were of sufficiently low activity to require conversion measurements at 250–350°C.

Specific activities in the form of turnover frequencies (number of molecules converted or produced per catalytic site per second) and activation energies for CO conversion and CH<sub>4</sub> production were calculated from the data in Table 1 and are listed in Table 2. Correlation coefficients of better than 0.999, from Arrhenius plots of turnover frequency, indicated high precision for these data. The reproducibility of specific activity for any given catalyst batch was better than ±15%.

At least three trends are apparent from the CO turnover frequency data in Table 2: (i) specific activities for each catalyst system increase with increasing cobalt content and decreasing dispersion, (ii) specific activities for catalysts prepared by controlled-pH precipitation are significantly different than those prepared by impregnation, i.e., lower for Co/SiO<sub>2</sub> and Co/TiO<sub>2</sub> and higher

TABLE 1

CO Conversions and Space Velocities at Different Temperatures during Activity Testing of Cobalt Catalysts in CO Hydrogenation

Catalyst	% CO Conversion, <sup>a</sup> space velocity (h <sup>-1</sup> ) at T(°C)								Miscellaneous
	175°C	200°C	225°C	250°C	275°C	300°C	325°C	350°C	
100% Co		4.5, 250	5.0, 800	5.8, 2000					
Co/SiO <sub>2</sub>									
3%			7.2, 250	6.2, 600					6.7, 900 (265°C)
10	8.2, 170	7.5, 500							5.3, 1200 (215°C)
3 <sup>b</sup>							1.2, 150	1.5, 170	2.2, 170 (400°C)
Co/Al <sub>2</sub> O <sub>3</sub>									<i>d</i>
1%									
3			6.7, 200	7.1, 500	7.6, 1300				
10	4.7, 150	5.6, 500	7.5, 1300						
15	6.9, 200	5.9, 2000							8.8, 3850 (215°C)
3 <sup>b</sup>		6.0, 170	10.6, 300	7.0, 1200					
Co/TiO <sub>2</sub>									
3%		6.2, 300	6.6, 1000	7.7, 2500					
10	3.6, 200	5.6, 900							6.8, 1700 (210°C)
3 <sup>b</sup>			11.2, 150	5.8, 2000					7.9, 500 (235°C)
Co/MgO									<i>d</i>
3%									
10						7.4, 200	7.5, 900	6.0, 3850	
Co/C (Type UU)									
3% <sup>c</sup>					2.0, 500	6.4, 700	8.8, 2000		
10 <sup>c</sup>	4.7, 150	9.2, 700	8.2, 6300						
Co/C (Spheron)									
3% <sup>c</sup>				7.4, 200	9.9, 800				6.4, 2000 (285°C)
10 <sup>c</sup>		6.0, 300	6.9, 1250						5.3, 800 (213°C)

<sup>a</sup> Percentage CO conversion at 1 atm, H<sub>2</sub>/CO = 2, temperature (°C), and space velocity (h<sup>-1</sup>) shown.

<sup>b</sup> Prepared by controlled-pH precipitation (Ref. (8)); catalysts not designated were prepared by impregnation.

<sup>c</sup> Prepared by evaporative deposition (Ref. (8)).

<sup>d</sup> No measurable activity at 400°C and below.

TABLE 2

Turnover Frequencies and Activation Energies for Conversion of CO and Production of CH<sub>4</sub> During CO Hydrogenation on Cobalt Catalysts

Catalyst	Total H <sub>2</sub> uptake <sup>a</sup> ( $\mu\text{mol/g}$ )	% Redn. <sup>a</sup>	% D <sup>a</sup>	$N_{\text{CO}} \times 10^3$ (s <sup>-1</sup> ) <sup>b</sup> at 225°C	$N_{\text{CH}_4} \times 10^3$ (s <sup>-1</sup> ) <sup>c</sup> at 225°C	$E_{\text{CO}}$ <sup>d</sup> (kJ/mol)	$E_{\text{CH}_4}$ <sup>e</sup> (kJ/mol)
100% Co	22	100	0.26	5.8	1.1	95	168
Co/SiO <sub>2</sub>							
3%	20	75	11	5.5	2.6	67	109
10	82	92	10	7.5 <sup>h</sup>	2.6 <sup>h</sup>	69	158
3 <sup>f</sup>	2.3	4.6	20	2.2 <sup>h</sup>	0.06 <sup>h</sup>	32	77
Co/Al <sub>2</sub> O <sub>3</sub>							
1%	3.2	11	34	<i>i</i>	<i>i</i>	<i>i</i>	<i>i</i>
3	5.6	22	10	2.8 <sup>h</sup>	0.8 <sup>h</sup>	96	137
10	29	34	9.9	12	3.8	98	143
15	37	44	6.6	63 <sup>h</sup>	8.0 <sup>h</sup>	146	295
3 <sup>f</sup>	7.8	16	19	18	2.6	87	139
Co/TiO <sub>2</sub>							
3%	6.1	14	17	25	6.1	96	167
10	18	47	4.5	38 <sup>h</sup>	24 <sup>h</sup>	142	250
3 <sup>f</sup>	7.6	12	21	7.8	5.1	173	236
Co/MgO							
3%	0.6	11	2.1	<i>i</i>	<i>i</i>	<i>i</i>	<i>i</i>
10	2.1	13	1.9	0.13 <sup>h</sup>	0.052 <sup>h</sup>	164	155
Co/C (Type UU)							
3% <sup>g</sup>	18	13	55	0.069 <sup>h</sup>	0.0048 <sup>h</sup>	157	178
10 <sup>g</sup>	143	47	36	2.2	0.62	176	183
Co/C (Spheron)							
3% <sup>g</sup>	21	9.3	86	0.64 <sup>h</sup>	0.30 <sup>h</sup>	153	167
10 <sup>g</sup>	84	15	63	5.9	3.8	121	175

<sup>a</sup> Total H<sub>2</sub> uptake, percent dispersion (percentage exposed), and percentage of reduction to cobalt metal measured in Ref. (8).

<sup>b</sup> Turnover frequency for CO conversion (to hydrocarbons and CO<sub>2</sub>), i.e., the number of CO molecules converted per catalytic site (based on total H<sub>2</sub> uptake) per second at 1 atm, H<sub>2</sub>/CO = 2, 225°C. These data were measured within a few minutes of the initiation of reaction and hence correspond to initial activities.

<sup>c</sup> Turnover frequency for CH<sub>4</sub> production, i.e., the number of CH<sub>4</sub> molecules produced per catalytic site (based on total H<sub>2</sub> uptake) per second at 1 atm, H<sub>2</sub>/CO = 2, 225°C.

<sup>d</sup> Activation energy for CO conversion based on the temperature dependence of  $N_{\text{CO}}$ ; based on at least three to four different temperatures.

<sup>e</sup> Activation energy for CH<sub>4</sub> production based on the temperature dependence of  $N_{\text{CH}_4}$ ; based on at least three to four different temperatures.

<sup>f</sup> Prepared by controlled-pH precipitation (Ref. (8)); catalysts not designated were prepared by impregnation.

<sup>g</sup> Prepared by evaporate deposition (Ref. (8)).

<sup>h</sup> Extrapolated values; in most cases the extrapolation was over a small (25–50°C) range of temperature.

<sup>i</sup> Inactive up to 400°C.

in the case of Co/Al<sub>2</sub>O<sub>3</sub>; and (iii) there are significant variations in specific activity with support, i.e., the order of decreasing activity at a 3 wt% loading level is Co/TiO<sub>2</sub> > Co/SiO<sub>2</sub>  $\cong$  100% Co > Co/Al<sub>2</sub>O<sub>3</sub> > Co/C (Spheron) > Co/C (Type UU) > Co/MgO.

The order of decreasing activity for 3 wt% precipitated catalysts is Co/Al<sub>2</sub>O<sub>3</sub> > Co/TiO<sub>2</sub> > Co/SiO<sub>2</sub>. Similar trends are evident for the CH<sub>4</sub> turnover frequencies; however, these data are less a measure of specific activity and more a measure of the selectiv-

ity for methane, since significant fractions of other hydrocarbons, CO<sub>2</sub>, and H<sub>2</sub>O are formed in CO hydrogenation on these catalysts under the conditions tested (see Table 3).

Several trends are also evident from the activation energy data in Table 2: (i) energies of activation for CO conversion ( $E_{CO}$ ) and CH<sub>4</sub> production ( $E_{CH_4}$ ) generally increase with increasing loading except for cobalt on Spheron, (ii) values of  $E_{CH_4}$  are generally greater than values of  $E_{CO}$ , and

(iii) there are significant variations in values of  $E_{CO}$  with support and preparation. Indeed values of  $E_{CO}$  range from 32 kJ/mol for precipitated 3 wt% Co/SiO<sub>2</sub> to 176 kJ/mol for 10 wt% Co/C (Type UU).

Table 3 lists CO<sub>2</sub> selectivities (wt%) based on nonhydrocarbon products only and hydrocarbon group selectivities (in wt%) based on total hydrocarbon products only at 225°C (in a few cases at a higher temperature where catalytic activity was first observed or at a lower temperature to

TABLE 3  
Hydrocarbon and Carbon Dioxide/Water Product Distributions for Supported and Unsupported Cobalt Catalysts

Catalyst	Temp. (°C)	Weight percentage CO <sub>2</sub> selectivity <sup>a,b</sup>	Weight percentage hydrocarbon group selectivities <sup>a,c</sup>					Average carbon number <sup>d</sup>
			C <sub>1</sub>	C <sub>2</sub> -C <sub>4</sub>	C <sub>5</sub> -C <sub>12</sub>	C <sub>13+</sub>	Alcohols	
100% Co	225	0	29	42	28	0	1.1	3.4
Co/SiO <sub>2</sub>								
3%	225	41	47	34	15	0	3.9	2.5
10	225	0	29	27	42	0.2	1.3	4.0
3 <sup>e</sup>	325	33	99	1.1	0	0	0	1.0
Co/Al <sub>2</sub> O <sub>3</sub>								
1%	<sup>g</sup>	<sup>g</sup>	<sup>g</sup>	<sup>g</sup>	<sup>g</sup>	<sup>g</sup>	<sup>g</sup>	<sup>g</sup>
3	225	71	41	36	18	0	4.0	3.1
10	225	18	32	31	35	0.7	1.3	3.8
15	215	0	3.8	5.5	86	4.4	0	9.5
3 <sup>e</sup>	225	18	27	31	39	0	2.7	4.0
Co/TiO <sub>2</sub>								
3%	225	0	31	35	31	0	3.5	3.5
10	225	0	16	30	52	1.7	1.1	5.0
3 <sup>e</sup>	225	0	22	39	37	0	2.1	4.2
Co/MgO								
3%	<sup>g</sup>	<sup>g</sup>	<sup>g</sup>	<sup>g</sup>	<sup>g</sup>	<sup>g</sup>	<sup>g</sup>	<sup>g</sup>
10	300	36	55	39	6.2	0	0.6	1.9
Co/C (Type UU)								
3% <sup>f</sup>	275	84	30	54	16	0	0	2.7
10 <sup>f</sup>	225	44	53	31	16	0	0	2.3
Co/C (Spheron)								
3% <sup>f</sup>	250	24	85	8.1	7.0	0	0	1.5
10 <sup>f</sup>	225	8	66	23	11	0	0	2.1

<sup>a</sup> Measured at temperature shown above at H<sub>2</sub>/CO = 2, and 1 atm.

<sup>b</sup> Weight percentage of CO<sub>2</sub> in oxygen-containing, nonhydrocarbon products: CO<sub>2</sub>(10<sup>2</sup>)/(CO<sub>2</sub> + H<sub>2</sub>O).

<sup>c</sup> Weight percentage of hydrocarbon groups based on total hydrocarbons in the product.

<sup>d</sup> Weight averaged carbon number.

<sup>e</sup> Controlled-pH precipitation.

<sup>f</sup> Evaporative deposition.

<sup>g</sup> Inactive up to 400°C.

avoid lightoff as in the case of 15 wt% Co/Al<sub>2</sub>O<sub>3</sub>). Selected hydrocarbon product distributions are plotted in Figs. 1–3. It is evident that CO<sub>2</sub> selectivity generally decreases with increasing cobalt metal loading and extent of reduction. While CO<sub>2</sub> production over unsupported and titania-supported cobalt catalysts was not detectable, it was quite significant in the Co/MgO and Co/C catalyst systems (CO<sub>2</sub> selectivities of 8–84%).

Significant effects of support, metal loading, and preparation on hydrocarbon product distribution are evident from the data in Table 3 and Figs. 1–3. For example, production of heavier hydrocarbons increases with increasing metal loading, increasing extent of reduction and decreasing dispersion (except in the case of Co/C (Type UU)). Indeed, of the hydrocarbons produced by relatively well-reduced, poorly dispersed 15% Co/Al<sub>2</sub>O<sub>3</sub>, only 4% was methane and 96% hydrocarbons with two or more carbon atoms (86% in the C<sub>5</sub>–C<sub>12</sub> range) (see Table 3 and Fig. 3) while the poorly reduced, well-dispersed 3% Co/C (Type UU) catalyst produced unusually high C<sub>2</sub> and C<sub>3</sub> fractions.

The effects on hydrocarbon product distribution of reducing 10% Co/Al<sub>2</sub>O<sub>3</sub> and 10% Co/TiO<sub>2</sub> at elevated temperature (525°C) are shown in Table 4. From these data it is evident that the fraction of heavier hydrocarbons increases with increasing extent of reduction and decreasing dispersion.

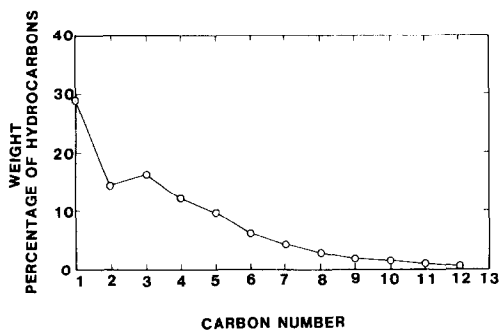


FIG. 1. Hydrocarbon product selectivity for unsupported cobalt at 225°C and atmospheric pressure.

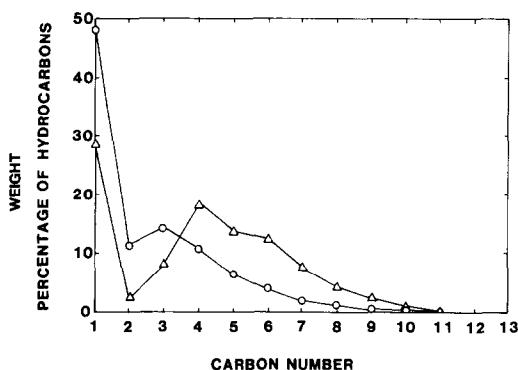


FIG. 2. Hydrocarbon product selectivity for impregnated Co/SiO<sub>2</sub> at 225°C and atmospheric pressure. O, 3% Co/SiO<sub>2</sub>; Δ, 10% Co/SiO<sub>2</sub>.

## DISCUSSION

### *Effects of Support, Metal Loading, Dispersion, and Preparation on Specific Activity of Cobalt*

In early studies of CO hydrogenation on cobalt catalysts (19–22), activities and product selectivities were determined under high conversion conditions; no consideration was given to determination of specific activities or of support and dispersion effects.

Recently, specific activity data were reported for CO hydrogenation on cobalt on silica and alumina (10, 11, 23–25). While none of these investigations was focused on providing a definitive treatment of support, loading, dispersion, and preparation effects, it is, nevertheless, useful to compare their results with those for corresponding catalysts from this investigation (see Table 5). The agreement of CO and CH<sub>4</sub> turnover numbers from this and previous studies to within a factor of 2 is remarkably good, particularly in view of differences in experimental technique for measuring reaction rates and catalytic surface areas among the different laboratories. Activation energies for Co/Al<sub>2</sub>O<sub>3</sub> are also in good agreement, while those for Co/SiO<sub>2</sub> determined in this study are lower, possibly due to differences in experimental conditions.

Activity data for the catalysts of low co-

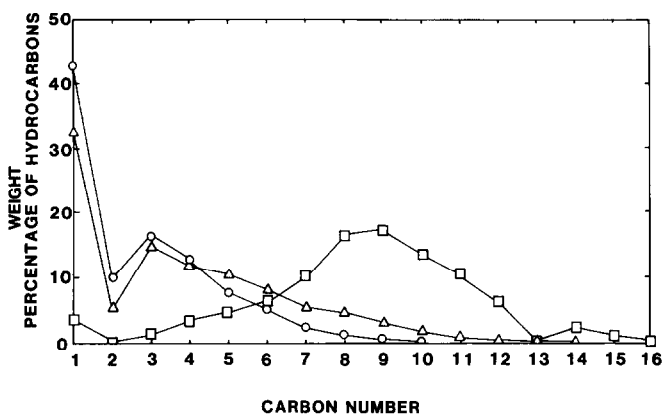


FIG. 3. Hydrocarbon product selectivity for impregnated Co/Al<sub>2</sub>O<sub>3</sub> at atmospheric pressure. ○, 3% Co/Al<sub>2</sub>O<sub>3</sub> at 225°C; △, 10% Co/Al<sub>2</sub>O<sub>3</sub> at 225°C; □, 15% Co/Al<sub>2</sub>O<sub>3</sub> at 215°C.

balt loading (e.g., 3 wt%) provide the best comparison of support effects since there is presumably a more intimate interaction of cobalt with the support (26). This comparison is particularly valid for the catalysts in this study because the dispersions of the 3% catalysts are nearly the same (especially in Co/Al<sub>2</sub>O<sub>3</sub>, Co/SiO<sub>2</sub>, and Co/TiO<sub>2</sub> systems). The data of this study (see Table 2) show that the CO hydrogenation activities of unsupported and silica supported cobalt are similar. However, the specific activity of 3% Co/TiO<sub>2</sub> is significantly higher than

3% Co/SiO<sub>2</sub> while those of 3% Co/Al<sub>2</sub>O<sub>3</sub>, Co/MgO, and Co/C are lower. The trend of increasing activity in the series Co/Al<sub>2</sub>O<sub>3</sub>, Co/SiO<sub>2</sub>, Co/TiO<sub>2</sub> (at low loading) is the same trend observed for CO hydrogenation on corresponding nickel catalysts (3, 5). Moreover, our data for Co/SiO<sub>2</sub> and Co/Al<sub>2</sub>O<sub>3</sub> find agreement with those of Vannice (10, 11) (see Table 5), who reported a higher specific activity for Co/SiO<sub>2</sub> than Co/Al<sub>2</sub>O<sub>3</sub>. The higher specific activity of Co/TiO<sub>2</sub> may be a result of strong metal-support interactions as previously postulated for Ni/TiO<sub>2</sub> (3, 5, 6). Considering the low specific activity and poor dispersion of the cobalt-magnesia system, magnesia is apparently an undesirable support for promoting the activity of cobalt in CO hydrogenation, at least at low metal loadings. The low activity of the cobalt-carbon system is compensated for by its high dispersions and large activation energies which result in high rates of hydrocarbon production at elevated temperatures (250–275°C).

One of the significant observations from this work is that specific activities of Co/Al<sub>2</sub>O<sub>3</sub>, Co/SiO<sub>2</sub>, Co/TiO<sub>2</sub>, and Co/C catalysts (prepared by impregnation methods) increase with increasing metal loading and decreasing dispersion (Table 2 and Fig. 4). This effect is most noticeable in the case of Co/Al<sub>2</sub>O<sub>3</sub>; indeed, its activity increases 20-

TABLE 4

Effects of Extent of Reduction and Dispersion on Molecular Weight of Hydrocarbons Produced for Selected Cobalt Catalysts

Catalyst	Reduction temperature (°C)	Percentage reduction <sup>d</sup>	Percentage dispersion <sup>e</sup>	Average carbon number <sup>f</sup>
10% Co/Al <sub>2</sub> O <sub>3</sub>	375 <sup>a</sup>	34	9.9	3.8
10% Co/Al <sub>2</sub> O <sub>3</sub>	525 <sup>b</sup>	54	6.7	4.2
10% Co/TiO <sub>2</sub>	400 <sup>c</sup>	47	4.5	5.0
10% Co/TiO <sub>2</sub>	525 <sup>b</sup>	64	2.3	6.6

<sup>a</sup> Reduction in H<sub>2</sub> for 20 h at temperature shown.

<sup>b</sup> Reduction in H<sub>2</sub> for 2 h at temperature shown.

<sup>c</sup> Reduction in H<sub>2</sub> for 16 h at temperature shown.

<sup>d</sup> Percentage of cobalt reduced to the metal. Determined by O<sub>2</sub> titration at 400°C (Ref. (8)).

<sup>e</sup> Percentage of cobalt atoms exposed to surface. Based on total, activated H<sub>2</sub> adsorption (Ref. (8)).

<sup>f</sup> Average hydrocarbon chain length (weight basis).

TABLE 5  
Comparison of Turnover Numbers and Activation Energies with Literature Values

Catalyst	This study			Previous studies				
	$N_{\text{CO}} \times 10^3 \text{ s}^{-1}$ (225°C)	$N_{\text{CH}_4} \times 10^3 \text{ s}^{-1}$ (225°C)	$E_{\text{CO}}$ (kJ/mol)	$E_{\text{CH}_4}$ (kJ/mol)	$N_{\text{CO}} \times 10^3 \text{ s}^{-1}$ (225°C)	$N_{\text{CH}_4} \times 10^3 \text{ s}^{-1}$ (225°C)	$E_{\text{CO}}$ (kJ/mol)	$E_{\text{CH}_4}$ (kJ/mol)
3% Co/SiO <sub>2</sub>	5.5	2.6	67	109	7.9 <sup>a</sup> (23) 12 <sup>b</sup> (11)	3.6 <sup>c</sup> (23) 3.8 <sup>b</sup> (11)	131 <sup>a</sup> (23) 95 <sup>b</sup> (11)	149 <sup>a</sup> (23) 133 <sup>b</sup> (11)
3% Co/Al <sub>2</sub> O <sub>3</sub>	2.8	0.8	96	137	2.4 <sup>c</sup> (10)	1.7 <sup>c</sup> (10)	112 <sup>c</sup> (10) 106 <sup>d</sup> (25)	113 <sup>c</sup> (10)

<sup>a</sup> 5% Co/SiO<sub>2</sub>.

<sup>b</sup> 4% Co/SiO<sub>2</sub>.

<sup>c</sup> 2% Co/Al<sub>2</sub>O<sub>3</sub>.

<sup>d</sup> 6% Co/Al<sub>2</sub>O<sub>3</sub>.

fold as the metal loading increases from 3 to 15 wt% and dispersion decreases from 10 to 6.6%. This observation is consistent with previous studies (27, 28) in which loadings of 25 wt% cobalt on alumina provided optimal activity. This trend of increasing activity with increasing loading is probably an effect of changes in dispersion in view of a fair, but nevertheless unmistakable correlation of activity with dispersion (Fig. 4). Indeed, the data in Fig. 4 and Table 2 reveal a 100-fold decrease in the activity of cobalt as dispersion increases from 4.5 to 86% (about a factor of 20). This trend of decreasing activity with increasing dispersion is similar to that observed in previous studies of CO hydrogenation on supported Ni (5, 29), Ru (30), and Fe (31, 32). Whether this trend of decreasing activity with increasing dispersion is due to changes in surface structure with decreasing particle size or electronic modifications as a result of more intimate interactions of the small crystallites with the support, cannot be determined unambiguously on the basis of the presently available data.

#### *Effects of Dispersion, Metal Loading, Support, and Preparation on Product Selectivity of Cobalt*

Although the selectivity properties of cobalt catalysts have received considerable attention in previous investigations (10, 11, 19–23, 25, 28, 33–38), there are surprisingly few selectivity data reported for well-defined, unpromoted cobalt-support systems (10, 11, 23). Therefore, the results of this study provide new baseline information on the selectivity behavior of various supported cobalt systems. The product selectivities observed in this study for 3% Co/SiO<sub>2</sub> and 3% Co/Al<sub>2</sub>O<sub>3</sub> compare well with those reported by Amelse *et al.* (23) and Vannice (10, 11) for catalysts of similar loading and preparation, obtained under similar reaction conditions.

While high molecular weight hydrocarbons and water are reported to be typical products of CO hydrogenation on cobalt



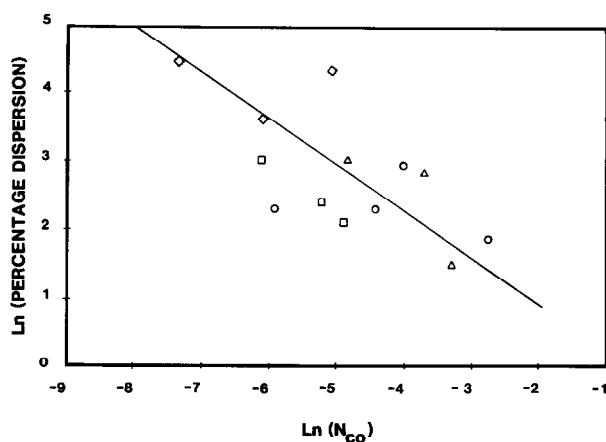


FIG. 4. Percentage dispersion vs CO turnover frequency at 225°C for impregnated, precipitated, and evaporatively deposited catalysts. □, Co/SiO<sub>2</sub>; ○, Co/Al<sub>2</sub>O<sub>3</sub>; △, Co/TiO<sub>2</sub>; ◇, Co/C.

(34), our results (Table 3) show that significant fractions of CO<sub>2</sub> are produced on highly-dispersed, poorly-reduced cobalt catalysts, a behavior more typical of iron catalysts (34, 35). The high selectivities of iron catalysts for CO<sub>2</sub> production are probably due to the presence of iron oxides which catalyze the water-gas-shift (WGS) reaction (39). Similarly, the high CO<sub>2</sub> selectivities of poorly reduced cobalt catalysts may be due to the abundance of stable surface oxides, e.g., cobalt spinels such as cobalt aluminate (26), which are inactive for CO hydrogenation but active for the WGS reaction (39).

While the hydrocarbon selectivity of cobalt clearly varies with support, loading, and preparation (Table 3), it is best correlated with dispersion; this is illustrated in Fig. 5 which shows that the average hydrocarbon chain length increases with decreasing dispersion. For example, highly dispersed carbon-supported cobalt produces large amounts of lighter hydrocarbons while moderately dispersed 10–15% Co/Al<sub>2</sub>O<sub>3</sub> catalysts produce heavier hydrocarbons. Moreover, by decreasing dispersion and increasing the extent of reduction of 10% Co/Al<sub>2</sub>O<sub>3</sub> and Co/TiO<sub>2</sub> (by reducing at elevated temperature), hydrocarbons of greater molecular weight are produced (see Table 4). Two exceptions to this trend are

poorly dispersed 10% Co/MgO and precipitated 3% Co/SiO<sub>2</sub> which produce lighter hydrocarbons, although this is easily explained by the fact that it was necessary to test these catalysts at relatively high temperatures where methane make is high. The effect of dispersion on selectivity is most dramatic in the Co/Al<sub>2</sub>O<sub>3</sub> system and leads to an unusual behavior in the case of 15% Co/Al<sub>2</sub>O<sub>3</sub> which displays an inordinately high selectivity (86 wt%) for gasoline-range hydrocarbons, a selectivity much higher than predicted by the Anderson/Schulz/

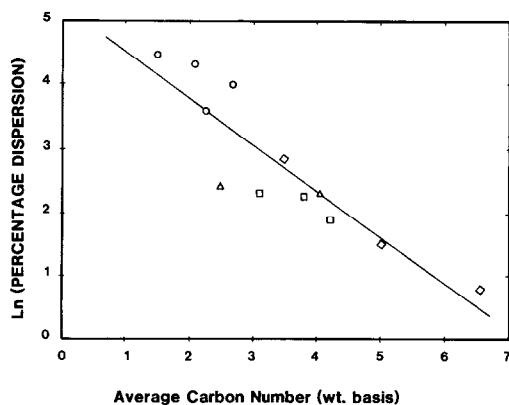


FIG. 5. Average carbon number of hydrocarbons produced at 225°C and 1 atm for 3 and 10 wt% supported cobalt catalysts as a function of dispersion. △, Co/SiO<sub>2</sub> (impregnated); □, Co/Al<sub>2</sub>O<sub>3</sub> (impregnated); ◇, Co/TiO<sub>2</sub> (impregnated); ○, Co/C (evaporatively deposited).

Flory model (40) and much higher than previously reported for a promoted 15% Co/Al<sub>2</sub>O<sub>3</sub> (33).

Although hydrocarbon product selectivity is best correlated with dispersion (Fig. 5), it also correlates with metal loading, extent of reduction, and CO<sub>2</sub> selectivity; that is, the average carbon number of the hydrocarbon product also decreases with decreasing extent of reduction, decreasing metal loading, and increasing CO<sub>2</sub> selectivity (compare Tables 2 and 3). Conceivably all of these effects could be related in a fundamental way. For example, it is clear that dispersion increases and extent of reduction decreases with decreasing metal loading. Thus, the well-dispersed, low loading catalysts contain a larger fraction of stable, unreduced oxide phases capable of catalyzing the WGS reaction and thereby increasing the H<sub>2</sub>/CO ratio at the catalyst surface relative to well-reduced catalysts. Higher H<sub>2</sub>/CO ratios at the surface would promote the formation of lighter hydrocarbon products such as methane.

The data from this study provide a foundation for comparing the selectivities of cobalt on different supports independent of metal loading and to some extent dispersion. The comparison is most valid for 3% Co/SiO<sub>2</sub>, Co/Al<sub>2</sub>O<sub>3</sub>, and Co/TiO<sub>2</sub> catalysts, since these catalysts have similar dispersions and low metal contents. A comparison of product selectivities of these catalysts (Table 3) reveals very similar selectivity behavior for 3% Co/SiO<sub>2</sub> and Co/Al<sub>2</sub>O<sub>3</sub>. However, the methane make for Co/TiO<sub>2</sub> is lower and its production of C<sub>5</sub>–C<sub>12</sub> hydrocarbons is higher than for 3% Co/SiO<sub>2</sub> and Co/Al<sub>2</sub>O<sub>3</sub> catalysts (see Table 3). This may be a result of relatively strong interactions between cobalt and the titania support. A greater production of high molecular weight hydrocarbons by Ni/TiO<sub>2</sub> relative to Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> observed in previous studies (3, 5) was attributed to strong metal support interactions in the Ni/TiO<sub>2</sub> system.

The data of this study show that signifi-

cantly different selectivity behavior is observed for catalysts of the same support and loading prepared by impregnation and controlled-pH precipitation. The preparation of Ni/SiO<sub>2</sub> by controlled-pH precipitation has been demonstrated as a route to more highly dispersed catalysts having sharp crystallite distributions (5, 6). Ni/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by this technique have significantly lower extents of reduction (5, 6). Similarly, precipitated Co/SiO<sub>2</sub>, Co/Al<sub>2</sub>O<sub>3</sub>, and Co/TiO<sub>2</sub> are more difficult to reduce and have higher dispersions than corresponding impregnated catalysts (see Table 2). However, precipitated Co/Al<sub>2</sub>O<sub>3</sub> and Co/TiO<sub>2</sub> catalysts produce heavier hydrocarbons despite their higher dispersions and lower extents of reduction (see Tables 2 and 3). Precipitated Co/SiO<sub>2</sub> produces lighter hydrocarbons because of the high temperature (325°C) necessary to activate it.

#### CONCLUSIONS

1. The specific activity of cobalt in CO hydrogenation is a function of support, dispersion, metal loading, and preparation.

2. The order of decreasing CO hydrogenation activity 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 > Co/MgO.

3. The specific activity of cobalt in CO hydrogenation decreases significantly with increasing dispersion. Indeed, approximately a 100-fold decrease in activity is observed with a 20-fold increase in dispersion.

4. Product selectivity of cobalt in CO hydrogenation is also a function of support, dispersion, metal loading, and preparation. However, hydrocarbon and CO<sub>2</sub> product distributions are best correlated with dispersion and extent of reduction, i.e., lower molecular weight hydrocarbon products and higher product ratios of CO<sub>2</sub>/H<sub>2</sub>O are observed for catalysts having higher dispersions and lower extents of reduction. This effect may be due to the abundance of stable, oxide surface phases in the well-dispersed, poorly reduced catalysts capable of

catalyzing the water-gas-shift reaction and thereby increasing the  $H_2/CO$  ratio at the surface.

5. In the  $Co/Al_2O_3$  system, activity and selectivity for high molecular weight hydrocarbons increase dramatically with increasing cobalt loading. For example, 15%  $Co/Al_2O_3$  is 20 times more active than 3%  $Co/Al_2O_3$ ; moreover, 86 wt% of its hydrocarbon fraction is in the  $C_5-C_{12}$  (gasoline) range compared to 18 wt% for the 3%  $Co/Al_2O_3$ .

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