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Structure Sensitivity and Its Effects on Product Distribution in CO Hydrogenation on Cobalt/Alumina

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Activities and selectivities of cobalt/alumina catalysts for CO hydrogenation were determined as a function of metal loading, reduction temperature, and preparation. Specific activities and average carbon numbers 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/Al_2O_3 is structure-sensitive. The changes in specific activity with dispersion can be explained by variations in the distribution of low and high coordination sites and by changes in the nature of adsorbed CO species available for reaction. High specific activity is apparently favored on sites to which CO is strongly coordinated. 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. High-molecular-weight products are favored by catalysts having high rates of propagation and low rates of termination.

INTRODUCTION

The considerable renewed interest during the past decade in indirect liquefaction of coal as a potential source of chemicals and fuels has stimulated a great deal of research activity directed toward the improvement of catalysts for this process. Recent investigations (*1–9*) provide evidence that support and metal dispersion can significantly influence the activity and selectivity of metals in CO hydrogenation. Reuel and Bartholomew (*8, 9*) recently reported that the specific activity of supported cobalt in CO hydrogenation decreases with increasing cobalt metal dispersion (i.e., the fraction of metal atoms exposed to the surface). King (*1*), Kellner and Bell (*4*), and Chen *et al.* (*7*) observed similar trends for supported ruthenium catalysts, while Storm and Boudart (*2*) and Jung *et al.* (*5*) reported the same effect for supported iron catalysts.

Effects of dispersion or metal crystallite size on hydrocarbon selectivity in CO hydrogenation were previously reported by Nijs and Jacobs (*3*), Kellner and Bell (*4*), and Reuel and Bartholomew (*8*). Nijs and Jacobs postulated that the size of hydrocarbons formed in Fischer–Tropsch synthesis could be limited by the size of metal crystallites in the catalysts; by incorporating the effects of particle size in the Anderson–Schulz–Flory model they were able to explain observed deviations from classical Anderson–Schulz–Flory kinetics in catalysts containing small metal crystallites. Kellner and Bell (*4*) observed that the average molecular weight of hydrocarbons produced during CO hydrogenation on Ru/alumina decreased with increasing dispersion in well-dispersed catalysts (having percentage dispersions greater than 70%); in catalysts having dispersions less than 70% the probability of chain growth was independent of dispersion. Reuel and Bartholomew (*8*) found that hydrocarbon product selectivity in CO hydrogenation on supported cobalt could be correlated with dispersion

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and extent of reduction; for example, they found that the average molecular weight of the hydrocarbon product increased linearly with decreasing log D (D = dispersion). However, because their selectivity data as well as those of previous workers (*3, 4*) were obtained after only short periods of reaction it was difficult to determine if these observations might be due to transient effects.

The objective of this work was to extend the study of Reuel and Bartholomew by investigating in greater depth and under steady-state conditions the effects of dispersion, extent of reduction, and catalyst preparation on the activity and selectivity behavior of cobalt/alumina catalysts in which loading, percentage reduction, reduction temperature, and method of preparation were more systematically varied. Based on these new data, a qualitative model of the factors which affect hydrocarbon product chain length in Fischer–Tropsch synthesis is proposed which accounts for the effects of dispersion, specific activity, and binding energy of the hydrocarbon product.

EXPERIMENTAL

Materials and catalyst preparation. A high-purity γ-alumina (Dispal-M, Sample No. 8032 H from Conoco) was used as the catalyst support. 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 (Engelhard) followed by a molecular sieve 5A (Linde) trap. The CO was also passed through a molecular sieve trap to remove iron carbonyl.

Co/Al_2O_3 catalysts containing 3 wt% cobalt were prepared by three methods: (i) impregnation with an aqueous solution of cobalt nitrate (*10, 11*), (ii) pH-controlled precipitation (*11–13*), and (iii) decomposition of $Co_4(CO)_{12}$ on dehydroxylated alumina during cyclohexane reflux (*14, 15*). The remainder of the catalysts was prepared by impregnation.

Chemisorption measurements. Gas adsorption measurements were performed in a conventional Pyrex vacuum apparatus described in previous studies (*10, 11*). Hydrogen adsorption uptakes were measured statically at 25°C after 45–60 min equilibration (*10, 11*). Since the adsorption of H_2 occurs at equilibrium or near equilibrium for Co/alumina catalysts under these conditions (*10*), it was not necessary to perform the adsorption measurements at elevated temperatures. Extents of reduction to cobalt metal were determined by oxygen titration at 400°C of reduced and evacuated catalysts (*10, 16*). Calculations of metal dispersion and extent of reduction were carried out as described previously (*10*).

Catalyst reduction. Catalyst samples of about 1 g were placed in a flow-through Pyrex cell (*17, 18*) and reduced in flowing hydrogen (99.99% Whitmore) at a space velocity of 2000 h^{-1}. Based on previous experience (*16*), the catalysts in this investigation were reduced directly in H_2 at a low heating rate (less than 5 K/min). The heating schedule also included holding the temperature constant for 15–20 min at 100 and 200°C, the temperatures at which water vaporizes and the nitrate decomposes.

Measurements of CO/H_2 synthesis activity and selectivity. Measurements of CO/H_2 synthesis activity and selectivity were performed in a differential, fixed-bed Pyrex reactor (*18*) at 1 atm, 200–250°C. 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 HP5834A for on-line analysis. Fixed gases (H_2, N_2, CO, CH_4, H_2, and CO_2) were separated in a 2-m packed column containing Carbosieve B. Hydrocarbons were separated in a 36-m capillary column coated with methyl silicone, which provided excellent resolution of carbon numbers 1-30 and alcohols and good resolution of olefins from paraffins. The Hewlett–Packard gas chromatograph

TABLE 1

Dispersion, Extent of Reduction, Specific Activity, and Kinetic Parameters for Co/Al_2O_3 Catalysts[a,b] as a Function of Metal Loading

Metal loading (%)	Extent of reduction (%)	H_2 adsorption uptake[c] (μmole/g)	D[d] (%)	N_{CO}[e] $\times 10^3$ (at 200°C)	E_{CO}[f] (kJ/mole)	A[f]
3	28	11	15	1.4	87	1.0×10^7
10	34	26	8.7	9.1	112	2.2×10^{10}
15	46	45.5	7.8	11.2	115	7.8×10^{10}
25	64	91	6.7	16.9	130	3.0×10^{12}

[a] All catalysts prepared by impregnation; reduction in flowing H_2 at 375°C for 20 h.

[b] Reaction conditions: 200, 225, and 250°C; $H_2/CO = 2$; 1 atm.

[c] Based on total hydrogen uptake (Refs. (*8–10*)).

[d] Cobalt metal dispersion calculated from the number of active sites and extent of reduction according to the relation $\%D = 1.179X/Wf$ where X = hydrogen uptake in μmole/g, W the wt% cobalt, and f the fraction of cobalt reduced to the metal.

[e] Turnover frequency for CO conversion, i.e., the number of CO molecules converted per catalytic site per second at 1 atm, $H_2/CO = 2$.

[f] Activation energy and preexponential factor for CO conversion determined from the temperature dependence of N_{CO}; based on three temperatures: 200, 225, and 250°C.

was fully programmable and equipped with thermal conductivity and flame ionization detectors for analysis of fixed gases and hydrocarbons. Space velocity and reaction temperature were varied in order to maintain CO conversions within the range of 5–10%. The apparatus and procedure used in this study are described in detail elsewhere (*19*). All data were obtained after 24–30 h of reaction, i.e., after steady-state conditions had been reached. All runs were repeated at least once; the precision or repeatibility of turnover frequency data was in the range ±5–15%.

Turnover frequencies, activation energies, and preexponential factors were based on the expression

$$N_{CO} = A'e^{-E/RT}P_{CO}^{x}P_{H_2}^{y} = Ae^{-E/RT}, \quad (1)$$

where N_{CO} = the turnover frequency (molecules CO converted per site per second), A = the effective preexponential factor which includes concentration factors (conversion was maintained at 5% and the H_2/CO ratio was always 2; hence the concentrations were assumed to be constant), and $E = E_{CO}$, the activation energy for CO conversion. The values of x and y in Eq. (1) were also assumed to be constant.

RESULTS

Hydrogen chemisorption uptakes, dispersions, and extents of reduction are listed in Table 1 and plotted in Fig. 1 for Co/alumina catalysts in which cobalt loading was varied from 3 to 25 wt%. Trends similar to those reported in previous studies (*8–10, 20*) are evident: (i) the extent of reduction increases with increasing metal loading, (ii)

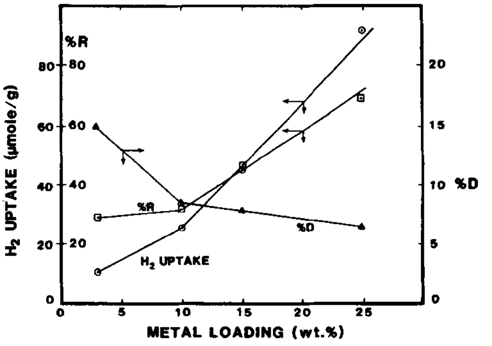

FIG. 1. Influence of metal loading on H_2 adsorption uptake, dispersion, and extent of reduction for Co/Al_2O_3 catalysts.

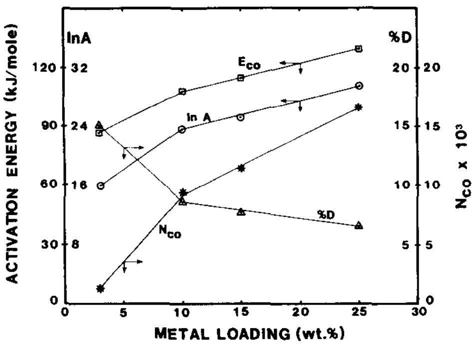

FIG. 2. Dispersion, turnover frequency, activation energy, and ln A for CO hydrogenation on Co/Al$_2$O$_3$ catalysts of different loading.

hydrogen adsorption uptake increases with increasing metal loading as expected, and (iii) dispersion decreases with increasing metal loading. These changes are linear at cobalt loadings above 10 wt% (see Fig. 1).

Also listed in Table 1 are specific activities in the form of turnover frequencies (the number of CO molecules converted per catalytic site per second) activation energies, and preexponential factors for CO hydrogenation on Co/alumina catalysts of different loadings. CO turnover frequencies, activation energies, and preexponential factors are plotted with values of dispersion as a function of cobalt metal loading in Fig. 2. Preexponential factors (on a logarithmic scale), activation energies, and turnover frequencies all increase with increasing metal loading and with decreasing dispersion; these changes are linear at metal loadings above 10%. In other words, there appears to be a good correlation of increasing CO hydrogenation activity with decreasing dispersion.

The effects of reduction temperature on the physical/chemical and catalytic properties of 3 wt% Co/alumina are shown by the data listed in Table 2 and the curves plotted in Figs. 3 and 4. Hydrogen adsorption uptakes increase linearly and extents of reduction increase nonlinearly with increasing reduction temperature, while cobalt metal dispersion passes through a maximum at a reduction temperature of about 350°C (see Fig. 3). In other words, there is an optimum reduction temperature for maximizing dispersion for a given catalyst. Preexponential factors (on a logarithmic scale) and activation energies increase linearly with increasing reduction temperature, while the turnover frequency like dispersion passes through a maximum (see Fig. 4). Thus, there is also a good correla-

TABLE 2

Dispersion, Extent of Reduction, Specific Activity, and Kinetic Parameters for 3% Co/Al$_2$O$_3$[a,b] as a Function of Reduction Temperature

Reduction temperature (°C)	H$_2$ uptake[c] (μmole/g)	Extent of reduction (%)	D[d] (%)	$N_{CO} \times 10^3$[e] (at 200°C)	E_{CO}[f] (kJ/mole)	A[f]
300	21.6	37	23	2.5	90	2.4×10^7
350	28.0	41	27	3.4	113	9.7×10^9
400	33.6	82.5	16	3.2	127	1.31×10^{11}

[a] Prepared by decomposition of Co$_4$(CO)$_{12}$ on dehydroxylated Al$_2$O$_3$ and reduction in flowing H$_2$ for 16 h at temperatures shown above.

[b] Reaction conditions: 200, 225, and 250°C; H$_2$/CO = 2; 1 atm.

[c] Total H$_2$ uptake measured at 298 K.

[d] Percentage dispersion (percentage exposed), see Footnote d in Table 1.

[e] Turnover frequency for CO conversion, i.e., the number of CO molecules converted per catalytic site per second at 1 atm, H$_2$/CO = 2, 200°C.

[f] Energies of activation and preexponential factors for CO conversion determined from the temperature dependence of N_{CO}; based on three temperatures: 200, 225, and 250°C.

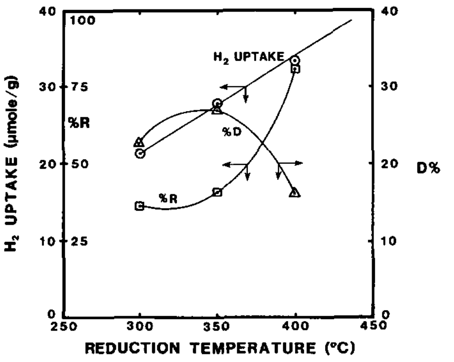

FIG. 3. Influence of reduction temperature on H_2 uptake, percentage reduction, and percentage dispersion of 3% Co/Al_2O_3.

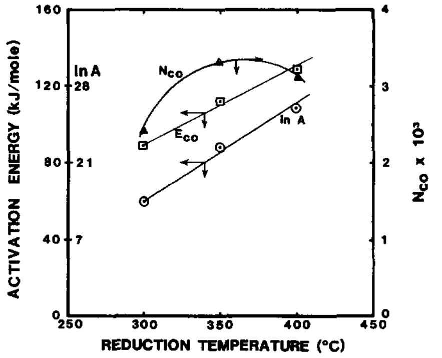

FIG. 4. Influence of reduction temperature on N_{CO}, E_{CO}, and ln A.

tion between specific activity and dispersion for catalysts reduced at different temperatures.

Effects of different catalyst preparation techniques on the physical/chemical and catalytic properties of 3 wt% Co/alumina are summarized by the data in Table 3. Hydrogen uptake and extent of reduction are clearly highest for the catalyst prepared from decomposition of $Co_4(CO)_{12}$ on dehydroxylated alumina. However, the activity and metal dispersion are highest for the catalyst prepared by pH-controlled precipitation. Again activity and dispersion appear to be well correlated.

Product distributions for CO hydrogenation on Co/alumina catalysts of different loadings, reduction temperatures, and preparations are listed in Table 4 as CO_2 selectivities (mole%), hydrocarbon group selectivities (wt%) and average carbon numbers (mole basis). Hydrocarbon product selectivity is defined here as the weight fraction of converted CO appearing as a given hydrocarbon product or product group. CO_2 selectivity is defined as the

TABLE 3

Dispersions, Extents of Reduction, Specific Activities and Kinetic Parameters for 3% Co/Al_2O_3 Catalysts[a,b] Prepared by Different Techniques

Preparation technique	H_2 uptake[c] (μmole/g)	Extent of reduction (%)	D (%)	$N_{CO} \times 10^3$[d] (at 225°C)	E_{CO}	A	r_t[e] $\times 10^3$ (at 225°C)
Prepared by impregnation	11.0	28	15	6.4	87	1.0×10^7	3.8
Prepared by pH-controlled precipitation	15.0	20	30	40	82	5.1×10^7	14
Prepared from reflux of $Co_4(CO)_{12}$	31.0	62	20	12.4	115	4.9×10^9	6.2

[a] Reduction in flowing H_2 at 375°C for 20 h.

[b] Reaction conditions: 200, 225, and 250°C; $H_2/CO = 2$; 1 atm.

[c] Total H_2 uptake measured at 298 K.

[d] Turnover frequency for CO conversion, i.e., the number of CO molecules converted per catalytic site per second at 1 atm, $H_2/CO = 2$, 225°C.

[e] Rate of termination (s^{-1}) calculated from Eq. (3) and experimental values of $\bar{n}$ assuming $r_p = N_{CO}$.

TABLE 4

Selectivity Data for Cobalt Catalysts of Different Metal Loading, Reduction Temperature, and Preparation

Catalyst description		Space velocity (h^{-1})	CO conversion (%)	CO_2[d] selectivity (%)	Hydrocarbon group selectivity[e] (wt%) C_1	C_2–C_4	C_5–C_{11}	C_{12+}	Weight ratio[f] of olefins to paraffins	Average[g] carbon number
Co/Al_2O_3[a] prepared by impregnating to different metal loadings	3%	150	5.2	1.3	16.5	23.6	54.5	5.4	0.6	3.1
	10%	500	5.7	0.6	14.5	22.4	57.1	5.9	0.5	4.0
	15%	750	7.2	0.5	9.5	12.6	71.4	6.5	0.3	4.6
	25%	1000	7.8	0.4	8.4	13.3	71.5	6.8	0.4	4.5
3% Co/Al_2O_3[b] prepared from metal carbonyl; different reduction temperatures	300°C	500	5.0	1.5	20.5	26.7	49.7	3.1	0.2	3.0
	350°C	750	5.8	1.4	21.9	29.3	44.9	4.3	0.5	2.8
	400°C	750	5.1	1.9	19.2	28.7	48.2	3.9	0.4	3.1
3% Co/Al_2O_3[c] different preparation techniques	Impregnation	500	5.8	1.7	23.4	30.3	44.5	1.7	0.6	2.7
	pH-controlled	750	5.9	2.3	20.0	26.0	51.0	2.5	0.5	3.9
	reflux of $Co_4(CO)_{12}$	600	6.3	1.4	18.1	30.2	49.9	1.8	0.4	3.0

[a] Reduced in flowing H_2 at 375°C for 20 h; selectivity data measured at 1 atm, $H_2/CO = 2$, and 200°C after 24–30 h of reaction.

[b] Reduced at temperature shown above in flowing H_2 for 16 h; selectivity data measured at 1 atm, $H_2/CO = 2$, and 200°C after 24–30 h of reaction.

[c] Reduced in flowing H_2 at 375°C for 20 h; selectivity data measured at 1 atm, $H_2/CO = 2$, and 225°C after 24–30 h of reaction.

[d] CO_2 selectivity is the mole percentage of converted CO appearing as CO_2.

[e] Hydrocarbon group selectivity is based on total hydrocarbons in the product.

[f] Weight ratio of total olefins to total paraffins.

[g] Mole averaged carbon number.

mole fraction of converted CO appearing as CO_2. It is evident that CO_2 selectivities were almost negligibly small for this set of experiments (see Table 4). Hydrocarbon products consisted primarily of C_3–C_8 olefins and C_1–C_{15} paraffins. Representative hydrocarbon product distributions and Anderson–Schulz–Flory plots are shown in Figs. 5 and 6 for 3 and 15% Co/Al_2O_3 catalysts. Olefin production is maximum at C_3–C_6 carbon numbers for both catalysts while total hydrocarbon production is maximum at C_5–C_7 and C_8–C_{10} for 3 and 15% Co/Al_2O_3 catalysts, respectively. The probability of chain propagation α is clearly larger for the 15% Co/Al_2O_3 catalyst. Deviations on the low side from Anderson–Schulz–Flory kinetics are evident in both catalysts at carbon numbers 2 and 10–15.

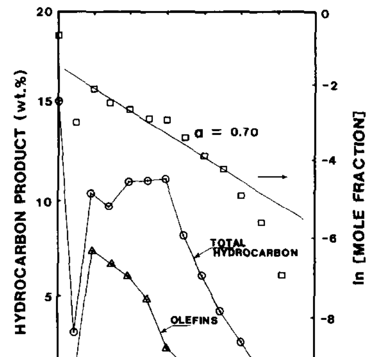

FIG. 5. Lower curves: Hydrocarbon product selectivity (wt%) for 3% Co/Al_2O_3 (prepared by impregnation and reduced at 375°C) at 200°C, 1 atm after 24 h of reaction. Upper curve: Anderson–Schulz–Flory plot for 3% Co/Al_2O_3 at 200°C, 1 atm after 24 h of reaction.

Correlations of dispersion with selectivity (in the form of average carbon number) are summarized in Fig. 7 for Co/alumina catalysts of different loading and reduction temperature. Linear correlations between dispersion and hydrocarbon selectivity are evident for both groups of catalysts; however, the trend for each is somewhat different. For example, the product carbon number for 3% Co/alumina catalysts reduced at different temperatures increases only very slightly with decreasing dispersion, i.e., the selectivity is relatively *insensitive* to

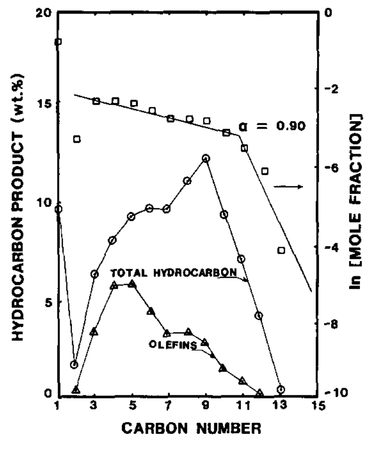

FIG. 6. Lower curves: Hydrocarbon product selectivity (wt%) for 15% Co/Al_2O_3 at 200°C, 1 atm after 24 h of reaction. Upper curve: Anderson–Schulz–Flory plot for 15% Co/Al_2O_3 at 200°C, 1 atm after 24 h of reaction.

changes in reduction temperature. The product molecular weight of catalysts of different loading increases significantly with *decreasing* dispersion for catalysts having dispersions greater than about 6–8%, the selectivity of catalysts having dispersion of 6–8% or less is apparently independent of dispersion. On the other hand, the product carbon number for the 3% Co/alumina catalysts prepared by different techniques increases with *increasing* dispersion (see Table 4).

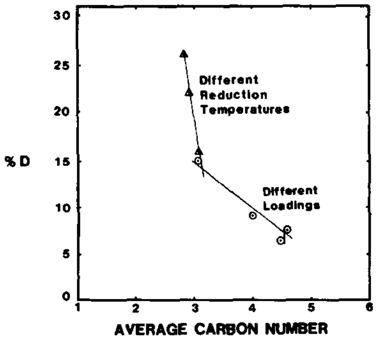

FIG. 7. Correlations of dispersion with average carbon number for Co/Al_2O_3 catalysts of different loading and reduction temperature. △, different reduction temperatures; ○, different loadings.

DISCUSSION

Evidence for Structure Sensitivity: Effects of Metal Loading, Preparation, and Pretreatment on Specific Activity

The data of this study provide evidence of changes in specific, steady-state CO hydrogenation activity of cobalt/alumina with changes in dispersion (decreasing metal crystallite size) as a result of variations in metal loading, preparation, and pretreatment. Indeed, a 10-fold increase in specific activity is observed as metal loading is varied from 3 to 25% and metal dispersion decreases from 15 to 6.7% (see Table 1). Moreover, a sevenfold variation in CO turnover frequency is observed for 3% cobalt/alumina catalysts of different preparations in which dispersion varies from 15 to 30% (see Table 3). Thus, these data suggest that CO hydrogenation on cobalt/alumina is structure-sensitive under steady-state conditions (after 24–30 h of reaction). These results are consistent with the previous observation from this laboratory (*8*, *9*) of a 100-fold variation in initial activity with a 20-fold variation in dispersion for cobalt supported on alumina, silica, titania, and carbon.

Reasonably good correlations between dispersion and the kinetic parameters, E_{CO} and ln A, calculated from specific activity are evident for the data in Figs. 2 and 4. Indeed, it is probably more meaningful to correlate effects of structure sensitivity in terms of the basic kinetic parameters of which specific activity is composed (see Eq. (1)), since E_{CO} and A have great fundamental significance.

The preexponential or frequency factor A is generally related in surface reactions to the number of collisions occurring on the surface; this number is dependent upon the density of active surface sites. The observed variations in A with variations in dispersion could be due to changes in the relative distribution of sites having a specific geometry. Calculations by van Hardeveld and Hartog (*21*) demonstrate that the coordination numbers of surface atoms can vary a great deal with changes in metal crystallite size in the range of 1 to 10 nm, a range of relevance to this study. If the surface sites of high coordination number (planar sites) are the most active for CO hydrogenation, as proposed by Kellner and Bell (*4*), A and N_{CO} should decrease with increasing dispersion or decreasing metal crystallite size, since planar sites predominate in large particles while corner and edge sites predominate in very small crystallites. Indeed this is consistent with the observation in Fig. 2 of increasing ln A with decreasing dispersion for cobalt/alumina catalysts of different loading.

The activation energy, E_{CO}, is related to the changes in binding energy from reactants to the transition-state complex. Thus, it is a measure of the binding energy of reactants involved in the rate-determining step. The observed changes in E_{CO} with dispersion might be explained by (i) changes in the electronic structure induced by an increasing extent of interaction between support and metal with decreasing particle size or (ii) changes in the binding energy of reactant intermediates due to changes in surface structure with variations in particle size. The first hypothesis involving changes in electronic structure of the metal is unlikely, since the cobalt crystallites in the catalysts in this study involved average diameters in the range of 3 to 15 nm; according to previous theoretical studies (*22–24*), these crystallites are too large for their electronic structure to be affected by the metal–support contact. The second hypothesis of changes in binding energy due to variations in surface structure with changes in metal crystallites size is more plausible. Reuel and Bartholomew (*10*) observed a significant increase in the number of CO molecules adsorbing per cobalt surface atom with increasing dispersion, suggesting that bridged and linear forms of CO were predominant on poorly dispersed cobalt while subcarbonyl forms (two or three CO molecules adsorbed per metal surface atom) were prevalent on well-dispersed cobalt. On the basis of infrared measurements involving Ru/alumina, Kellner and Bell (*4*) concluded that linear CO species adsorb on metal sites active for CO hydrogenation, while subcarbonyl species adsorb on mainly inactive sites. It is reasonable to expect that in the case of cobalt the sites on which subcarbonyl species adsorb might be similarly less active than those involving linearly adsorbed species, since cobalt and ruthenium are chemically very similar. Thus the lower activity and the higher activation energy of well-dispersed cobalt would be explained in part by the prevalence of low-activity sites which bind to CO, carbon, and other carbon-containing reaction intermediates differently than the sites present in poorly dispersed cobalt.

While the evidence from this study favors correlating activity with dispersion, the possibility that unreduced cobalt present on the surfaces of cobalt crystallites to varying extents could account for the observed differences in activity and selectivity cannot be excluded. Nevertheless, this explanation is not supported by the observation in this study that changes in activity and selectivity due to changes in extent of reduction were relatively small (see Figs. 3 and 7). Moreover, this idea runs counter to observations by Chin and Hercules (*20*) providing evidence that cobalt metal and unreduced cobalt oxide in the form of a surface aluminate are likely two separate phases.

The arguments advanced above can explain the trend of decreasing activity with increasing dispersion observed for cobalt catalysts in which loading and reduction temperature were varied. However, they do not account for the observation of *increasing* activity with increasing dispersion observed for the 3% Co/alumina catalysts prepared by different techniques. In previous studies of cobalt and nickel catalysts (*10, 11*) significant variations in particle size distributions and CO adsorption stoichiometries with differences in preparation were observed. These variations may be indicators of significant differences in surface structure and binding energy of reaction intermediates due to differences in preparation. Butt *et al.* (*25*) have shown that preparation and pretreatment can very significantly affect the surface structure sensitivity of supported Pt, Pd, and Rh catalysts and under circumstances lead to opposite trends in activity with dispersion for the same catalyst.

Reuel and Bartholomew (*10*) observed that the ratio of strongly adsorbed CO to strongly adsorbed H_2 was significantly larger on 3% Co/alumina prepared by pH-controlled precipitation compared to 3% Co/alumina prepared by impregnation. According to Kellner and Bell (*4*) CO adsorbs more strongly on sites active for CO hydrogenation; thus, the fraction of available sites which are active for CO hydrogenation may be larger in the 3% Co/alumina catalyst prepared by pH-controlled precipitation relative to that prepared by impregnation.

Effects of Metal Loading, Preparation, and Pretreatment on Selectivity

The product distributions observed in this study for Co/alumina catalysts consisting primarily of paraffins, olefins, and water are, except for a few minor deviations, consistent with Anderson–Schulz–Flory kinetics and in line with product distributions previously reported for supported cobalt (*26–28*). Nevertheless, the data provide clear evidence of variations in average hydrocarbon chain length with differences in metal loading, preparation, and pretreatment. These changes in hydrocarbon chain length can be correlated with dispersion (see Fig. 7); however, the nature of these correlations is different for each group of catalysts in which either metal loading, pretreatment, or preparation was varied (see Table 3 and Fig. 7).

A careful analysis of these selectivity trends leads us to propose that the hydrocarbon chain length or average carbon number $\bar{n}$ of the hydrocarbon product in CO hydrogenation on cobalt is a function of two important factors:

$$\bar{n} = f_1(\text{chain propagation rate})\, f_2(\text{hydrocarbon residence time}). \quad (2)$$

The data from this study and the previous study of Reuel and Bartholomew (*8–9*) show that the average carbon number increases with increasing activity. It is also logical that the average chain length will be a function of the residence time of the growing hydrocarbon chain on the surface.

From Anderson–Schulz–Flory kinetics (*29, 30*) it can be shown that the average carbon number of the hydrocarbon product $\bar{n}$ is given by

$$\bar{n} = (r_p + r_t)/r_t = 1/(1 - \alpha), \quad (3)$$

where r_p is the rate of propagation for addition of a single carbon atom to a growing hydrocarbon chain, r_t is the rate of termination of chain growth, and α is the probability of chain growth. Generally in a chain reaction sequence at steady state the rate of propagation is much larger than the rate of termination, i.e., $r_p > r_t$. Thus the average carbon number is approximately

$$\bar{n} = r_p/r_t. \quad (4)$$

However, the rate of propagation r_p is proportional to the specific activity or turnover frequency N_{CO} while the rate of termination r_t is inversely proportional to the residence time of the hydrocarbon chain on the catalyst surface. Thus, f_1 (propagation rate) = N_{CO} and f_2(hydrocarbon residence time) = $1/r_t$ and the average carbon number is given by

$$\bar{n} = (N_{CO})\left(\frac{1}{r_t}\right). \quad (5)$$

In other words, changes in average carbon number depend on how propagation and termination rates change relative to each other.

The increase in average carbon number with decreasing dispersion observed for cobalt/alumina catalysts in which metal loading was varied (see Fig. 7) can be explained by changes in the strength of adsorption of carbon-containing intermediates with loading and dispersion. Recent adsorption, infrared, and TPD studies (*10*) are consistent with a shift from relatively weakly bound carbonyl species to strongly bound linear and bridged CO species with decreasing dispersion or increasing metal loading. It would be reasonable to expect that the metal–carbon bond strengths for adsorbed hydrocarbons would similarly increase with decreasing dispersion. This would lead to higher residence times and lower termination rates with decreasing dispersion. This would in accordance with Eqs. (4) and (5) lead to increasing average carbon number of the product with decreasing dispersion, as observed in this study (see Fig. 7).

The observation of increasing average carbon number with increasing dispersion due to differences in preparation (see Table 3) can likewise be explained by changes in binding energies and coverages of adsorbed hydrogen- and carbon-containing reaction intermediates. Reuel and Bartholomew (*9*, *10*) observed that hydrogen adsorption on 3% Co/alumina prepared by pH-controlled precipitation was more highly activated relative to 3% Co/alumina prepared by impregnation, while CO was more strongly adsorbed on the former catalyst. The combination of these two effects would predict a steady-state distribution of reaction intermediates richer in carbon and less concentrated in hydrogen in the case of the precipitated catalyst. This should in turn result in a lower termination rate relative to the propagation rate for the precipitated catalyst. Indeed, this is consistent with the termination rate data in Table 3. It would also be reasonable to expect higher metal–carbon bond strengths for adsorbed hydrocarbon intermediates on the precipitated catalyst, since CO is apparently more strongly adsorbed on this catalyst. This would likewise result in a lower termination rate relative to the propagation rate and thus (through Eqs. (4) and (5), lead to higher average carbon numbers for the product.

From the above discussion it is clear that most of the observed variations in hydrocarbon production distribution for CO hydrogenation on Co/alumina catalysts of different metal loadings, preparations, and pretreatments can be explained in terms of changes in the distribution of active surface sites and/or changes in adsorption strengths and residence times of adsorbed hydrocarbon chains. There are other points of view which should be mentioned.

Nijs and Jacobs (*3*) explained unusual product distributions obtained on a 2% Co/alumina catalyst (very similar to the 3% Co/alumina catalysts of this study) by a model stipulating that the maximum size of hydrocarbons formed in FT synthesis would be limited by the size of metal crystallites in the catalyst. Vanhove *et al.* (*31*) studied 2% Co/alumina catalyst having pore diameters ranging from 6.5 to 300 nm (the pore diameter of the alumina in this study would be about 14 nm). These workers postulated that the chain length of hydrocarbons formed during CO hydrogenation on these catalysts was limited by condensation and subsequent hydrogenolysis in the catalyst pores.

In analyzing the data obtained in this study we did not find it necessary or useful to invoke either of these models. The deviations from Anderson–Schulz–Flory kinetics observed for C_2 hydrocarbons can be explained by a partial hydrogenolysis of C_2 products to methane (*4*) or by a higher oligomerization rate of highly reactive C_2 hydrocarbons (esp. ethylene) to higher molecular weight hydrocarbons (*32*). The deviation for the C_{10+} products was found to be sensitive to reactant space velocity, reaction time, and the design of the sampling system; indeed, after redesigning our sampling/analysis system it was possible to obtain product distributions for 3–5% Co/alumina catalysts in which there were no deviations from Anderson–Schulz–Flory kinetics at carbon numbers of 10–20 (*15*).

These results suggest that the deviations are caused by partial adsorption and condensation of C_{10+} hydrocarbons in the pores of the support and even in heated lines of the sampling/analysis system rather than a result of particle size limitations as proposed by Nijs and Jacobs (*3*). The effects of similar experimental artifacts on the measurement of steady-state hydrocarbon product distributions were recently discussed by Jacobs and VanWouwe (*33*) and by Huff (*34*).

The data of this study are not consistent with the hypothesis of Vanhove *et al.* (*31*), involving condensation and hydrogenolysis of liquid hydrocarbons in the catalysts pores. All of the catalysts in this study were prepared from the same support and hence involved a single distribution of pore sizes; yet very significant differences were observed in the average carbon number of 3% Co/alumina catalysts prepared by different techniques. The model of Vanhove and coworkers would predict the same product distribution for all three catalysts. Moreover, the analysis of the data from this study leads to the conclusion that longer residence times of hydrocarbons leads to longer chains; the model of Vanhove and co-workers would lead to the opposite conclusion, since a longer residence time would favor hydrogenolysis reactions.

CONCLUSIONS

1. CO hydrogenation on supported cobalt is structure-sensitive. Its specific activity varies with changes in dispersion as a result of variations in metal loading, preparation, and pretreatment. Changes in specific activity are explained by variations in the distribution of low and high coordination sites and by changes in the nature of adsorbed CO species available for reaction. High specific activity is apparently favored on sites to which CO is strongly coordinated.

2. Hydrocarbon product selectivity in CO hydrogenation over cobalt varies with metal loading, preparation, and pretreatment. Variations in average hydrocarbon number can be explained by changes in the rate of termination relative to that for propagation. High-molecular-weight products are produced by catalysts having high rates of propagation and low rates of termination; these conditions are favored by sites on which carbon monoxide and other carbon-containing molecules are strongly adsorbed.

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