

PHYSICAL PROPERTIES AND FISCHER-TROPSCH ACTIVITIES OF  $\text{Co}/\text{Al}_2\text{O}_3$   
CATALYSTS PREPARED FROM THE DECOMPOSITION OF  $\text{Co}_4(\text{CO})_{12}$

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ABSTRACT

Carbonyl-derived cobalt/alumina catalysts were prepared in an attempt to obtain supported cobalt Fischer-Tropsch catalysts which are both highly dispersed and highly reduced. Catalysts prepared from the decomposition of tetracobalt dodecacarbonyl on partially dehydroxylated alumina were found to have twice the dispersion and twice the extent of reduction of conventionally prepared catalysts, resulting in catalysts with higher active surface area. Catalyst dispersion was optimized at a reduction temperature of 350°C. The carbonyl-derived catalysts have slightly higher specific activities than corresponding conventional catalysts, while their selectivity properties are very similar. The carbonyl-derived catalysts are stable under reaction conditions, losing only about 13% of their initial activities after 24 hours of reaction.

INTRODUCTION

Supported cobalt catalysts are selective for important mid-range products, e.g. gasoline and diesel fuel, in Fischer-Tropsch synthesis. However, unlike supported noble metal catalysts, it has proven difficult to produce by conventional preparations cobalt catalysts which are both highly dispersed and highly reduced [1,2]. Conventional  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts are typically prepared by aqueous impregnation of cobalt (II) salts such as  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , drying or calcination to produce cobalt oxide precursors and finally reduction in hydrogen. These oxide precursors, however, are generally quite difficult to reduce because of their strong interaction with oxidic supports, especially at cobalt loadings below about 5 wt.%. Thus, conventionally prepared low loading cobalt catalysts (<5%Co) have high dispersions but low extents of reduction, while higher loading catalysts (>5%) have higher extents of reduction but low dispersions. In metal carbonyls, the metal is in the zero-valent state. Therefore, catalyst preparations using cobalt carbonyls should produce cobalt catalysts with higher extents of reduction; and, depending on the interaction of the carbonyl with the support, higher dispersions.

Burwell [3] and Brenner [4] have shown that hydroxyl groups on the surface of alumina supports act as adsorption sites for metal carbonyls (resulting in highly dispersed catalysts), but will oxidize the metal during decomposition. However, decomposing metal carbonyls on dehydroxylated aluminas can produce supported catalysts which are both low-valent and well

dispersed [4]. Burwell [3] speculates that the Lewis acid-Lewis base pair sites which exist on dehydroxylated aluminas are possible adsorption sites for metal carbonyls, and that decomposition of carbonyls on these sites may result in zero-valent supported metal.

In this study, catalysts prepared from the decomposition of  $\text{Co}_4(\text{CO})_{12}$  on partially dehydroxylated  $\gamma\text{-Al}_2\text{O}_3$  were investigated. The objectives of the study were to: (1) prepare carbonyl-derived, alumina-supported cobalt catalysts which are more highly reduced and more highly dispersed than conventionally prepared catalysts, (2) determine the effects of metal loading, reduction temperature, and preparation method on the extent of reduction and dispersion (fraction of metal atoms exposed) of the carbonyl-derived catalysts, and (3) determine Fischer-Tropsch activities and selectivities of these carbonyl-derived catalysts.

## EXPERIMENTAL

### Catalyst Preparation

Previously dried  $\gamma$ -alumina (Conoco, DISPAL M) was dehydroxylated under vacuum at  $650^\circ\text{C}$  for 16 hours;  $\text{Co}_4(\text{CO})_{12}$  was obtained from Strem Chemicals. The carbonyl-derived catalysts were prepared by a solvent reflux method in which 10-20 grams of partially dehydroxylated  $\gamma\text{-Al}_2\text{O}_3$  was mixed in a 250 ml solution of  $\text{Co}_4(\text{CO})_{12}$  and cyclohexane (or xylene) at  $80^\circ\text{C}$  for 48 hours. Excess solvent was poured off and the catalyst samples were dried by evacuation and then reduced in flowing hydrogen for 16 hours. The reduction temperature was attained with a ramp of  $5^\circ\text{C}/\text{min}$ . The carbonyl was expected to completely decompose during this reduction treatment. All catalyst preparation and handling steps were performed under inert atmosphere in a glove box or vacuum system to avoid oxidation of the cobalt.

Selected catalysts were previously prepared by conventional aqueous cobalt nitrate impregnation [2] and by dry mix sublimation [5]. Dry mix sublimation was performed by heating an intimate mixture of solid  $\text{Co}_4(\text{CO})_{12}$  with partially dehydroxylated alumina in an evacuated glass cell at  $80^\circ\text{C}$  for 24 hours. These catalysts were also reduced in flowing hydrogen for 16 hrs.

### Catalyst Testing

The cobalt loadings of the catalysts were determined by chemical analysis using atomic absorption spectroscopy. Hydrogen chemisorption was performed statically on reduced catalysts in a Pyrex volumetric adsorption apparatus. Since hydrogen adsorption on cobalt is an activated process [6], the hydrogen isotherms were measured after adsorbing hydrogen at  $350^\circ\text{C}$  and then cooling to room temperature. Extents of reduction were determined by oxygen titration at  $400^\circ\text{C}$ , where the reaction of reduced cobalt with oxygen was considered to proceed to  $\text{Co}_3\text{O}_4$ . Percent dispersions and extents of reduction were calculated according to the method of Bartholomew et al. [2,6].

Fischer-Tropsch activities and selectivities of selected catalysts were measured in a differential, fixed-bed Pyrex reactor. Experiments were performed at  $200^\circ\text{C}$  and 1 atm

pressure with a H<sub>2</sub>/CO ratio of 2. Reaction products were fed through heated lines to a gas chromatograph for on-line analysis. Hydrocarbon products were separated in a fused silica capillary column and analyzed by an FID, while fixed gases were separated in a packed column and detected by a TCD. The activity/selectivity data were obtained under steady-state conditions (after at least 24 hours run time) and at conversions of less than 10% (to maintain differential conditions). Activity tests were conducted within a relatively short time-frame at two or three higher temperatures to obtain the activation energies for CO conversion.

## RESULTS AND DISCUSSION

### Physical Properties of the Catalysts

Table 1 lists the physical properties of three carbonyl-derived catalysts of different wt% Co and compares them with two conventionally-prepared catalysts of Fu and Bartholomew [2] which have similar cobalt loadings and reduction temperatures. The carbonyl-derived catalysts of corresponding loadings have higher values of hydrogen uptake, % reduction, and % dispersion.

TABLE 1. Comparison of the chemical/physical properties of three carbonyl-derived catalysts with two conventionally-prepared catalysts: Effects of cobalt loading.

Catalyst code	Preparation method	Co wt%	Reduction temperature	Hydrogen uptake <sup>a</sup>	%R <sup>b</sup>	%D <sup>c</sup>
A	Cyclohexane reflux	3.0	350°C	31	44	29
B	"	4.0	350°C	33	28	34
C	"	9.7	350°C	84	67	15
Fu1 <sup>d</sup>	Aqueous Nitrate	3	375°C	11	28	15
Fu2 <sup>d</sup>	Impreg.	10	375°C	26	34	9

<sup>a</sup> Hydrogen uptake in  $\mu\text{mol/g}$

<sup>b</sup> Percent reduction

<sup>c</sup> Percent dispersion

<sup>d</sup> Data taken from Reference 2.

Dispersions of the carbonyl-derived and conventional catalysts are compared as a function of cobalt loading in Figure 1. The dispersion of the carbonyl-derived catalysts is consistently about twice that of the conventional catalysts.

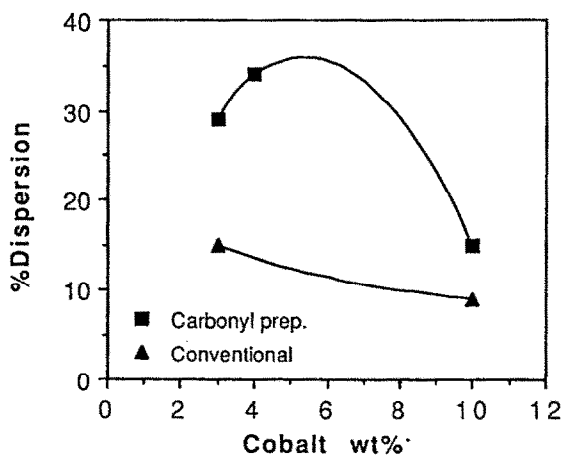


FIGURE. 1 Comparison of the dispersion of the carbonyl-derived catalysts with conventional catalysts.

The high dispersion of the carbonyl-derived catalysts suggests that  $\text{Co}_4(\text{CO})_{12}$  interacts strongly with the dehydroxylated alumina surface, possibly adsorbing on Lewis acid-Lewis base pair sites and then decomposing to form highly dispersed zero-valent metal, as discussed in the Introduction section.

Table 2 shows the effect of reduction temperature on hydrogen uptake, extent of reduction, and dispersion of the 3 wt% carbonyl-derived catalyst. Increasing the reduction temperature increases the extent of reduction as expected, while dispersion maximizes near 350°C.

TABLE 2. Effect of reduction temperature on the 3 wt% carbonyl-derived catalyst.

Catalyst code	Preparation method	Co wt%	Reduction temperature	Hydrogen uptake <sup>a</sup>	%R <sup>b</sup>	%D <sup>c</sup>
D	Cyclohexane reflux	3.0	300°C	24	42	23
A	"	3.0	350°C	31	44	29
E	"	3.0	400°C	38	96	16

<sup>a</sup> Hydrogen uptake in  $\mu\text{mol/g}$

<sup>b</sup> Percent reduction

<sup>c</sup> Percent dispersion

The increased extent of reduction of the carbonyl-derived catalysts is obviously the result of the preparation method which employs a precursor with the cobalt atom already in the zero-valent state, combined with the low concentration of surface hydroxyl groups present on the partially dehydroxylated alumina. The 96% extent of reduction for Catalyst E is quite remarkable, since generally in cobalt catalysts of 3-5% loading prepared by conventional techniques a large fraction of cobalt is found strongly coordinated in tetrahedral sites of alumina to form cobalt aluminate [7,8]. However, cobalt atoms must be in the +2 oxidation state to fit the tetrahedral sites, and starting with zero-valent cobalt may limit this reaction.

Table 3 lists the physical properties of three carbonyl-derived catalysts prepared by different methods. These catalysts were prepared at the same reduction temperatures, but unfortunately have different cobalt loadings. However, comparing these results with the results for similar weight loaded catalysts in Table 1 demonstrates that the cyclohexane reflux method produces catalysts which are both highly dispersed and highly reduced. This is probably the result of the cyclohexane reflux method producing a more intimate contact between the  $\text{Co}_4(\text{CO})_{12}$  and the dehydroxylated alumina.

TABLE 3. Effect of preparation method on three carbonyl-derived catalysts.

Catalyst code	Preparation method	Co wt%	Reduction temperature	Hydrogen uptake <sup>a</sup>	%R <sup>b</sup>	%D <sup>c</sup>
D	Cyclohexane reflux	3.0	300°C	24	42	23
F	Dry mix	3.7	300°C	27	27	24
G	Xylene reflux	10	300°C	31	59	6

<sup>a</sup> Hydrogen uptake in  $\mu\text{mol/g}$

<sup>b</sup> Percent reduction

<sup>c</sup> Percent dispersion

#### Activity/Selectivity Properties of the Catalysts

Table 4 lists activity/selectivity data at 200°C for two of the carbonyl-derived catalysts, and compares them with those for a conventional catalyst (Fu1). The Fischer-Tropsch activity/selectivity properties of the carbonyl-derived catalysts are quite similar to those of the conventional catalyst. At 200°C, the CO turnover frequency ( $N_{\text{CO}}$ ) and the activation energy ( $E_a$ ) are slightly but measurably higher than those of the conventional catalyst. The  $\text{CO}_2$  makes and olefin/paraffin ratios are also very similar to the conventional catalyst results, while the ASF propagation probabilities of the carbonyl-derived catalysts are somewhat higher.

TABLE 4. Comparison of the Fischer-Tropsch activity/selectivity properties of carbonyl-derived catalysts with a conventionally prepared catalyst.

Catalyst	T <sub>rxn</sub> °C	N <sub>co</sub> <sup>a</sup>	E <sub>a</sub> <sup>b</sup>	wt% CO <sub>2</sub>	α <sup>c</sup>	olefin/paraffin
Carbonyl-derived:						
F 3.7% Co/Al <sub>2</sub> O <sub>3</sub>	200	2.6	26.5	4.0	0.78	0.8
B 4.0% Co/Al <sub>2</sub> O <sub>3</sub>	200	5.8	22.0	2.8	0.86	---
Conventional:						
Fu1 <sup>d</sup> 3% Co/Al <sub>2</sub> O <sub>3</sub>	200	1.4	20.8	5.2	0.70	0.6

<sup>a</sup> CO turnover frequency (x10<sup>3</sup>), molecules/site/s

<sup>b</sup> Activation energy, kcal/mole

<sup>c</sup> ASF propagation probability

<sup>d</sup> Data taken from Reference 2.

This paper is the first to report specific activity data on a site basis for carbonyl-derived Co/alumina. Several previous investigations [9-12] report CO hydrogenation activity data (mass basis) for carbonyl-derived cobalt/alumina catalysts. Two of these studies involved preparation of the catalyst from Co<sub>4</sub>(CO)<sub>12</sub> [10,12] while the others involved preparation from Co<sub>2</sub>(CO)<sub>8</sub>. Unfortunately, none of these papers reported the pretreatment of their support and particularly the temperature of dehydroxylation, which is critical in determining the properties of the catalyst; moreover, in none of the previous studies were active site concentrations and turnover frequencies determined. Thus, it is not possible to directly compare the specific activity data reported in this study with mass-based activities reported in these previous studies. However, it is possible to make a rough comparison of these activity data using formal turnover frequencies [13], i.e., activities based on the total number of cobalt atoms in the sample; naturally this doesn't account for differences in dispersion for the different catalysts. On this basis, the (TOF)<sub>f</sub> at 200°C for 4% Co/alumina from this study is 2 x 10<sup>-3</sup> s<sup>-1</sup> in excellent agreement with a value of 2.4 x 10<sup>-3</sup> for 2% Co/alumina [11] but only in fair agreement with values of 3 and 0.8 x 10<sup>-4</sup> [9,12] reported for similar catalysts; however, Ferkul et al. [10] reported negligible activity for their Co/alumina catalyst below 250°C. The wide variation in activity for these catalysts may relate to differences in the support preparation, since there is evidence that the activity of Fe/alumina catalysts prepared in similar fashion increases with increasing dehydroxylation temperature up to 973 K [14].

Contrary to expectations based on previous reports [13,15], the activity stability of the highly dispersed and reduced carbonyl-derived catalysts of this study is very good. The N<sub>co</sub> of Catalyst F drops only 13% from 3.0x10<sup>-3</sup> to 2.6x10<sup>-3</sup> after 24 hours of reaction. The activity decrease appears to line out after that time. The activity of Catalyst B also lines out after 24 hours of reaction. One of the reasons for the greater stability of catalysts in this study relative to the previous work [13,15] is the higher temperature of reduction which results in a thermally stable catalyst during reaction.

Hydrocarbon product distributions of the carbonyl-derived catalysts of this study follow standard Anderson-Schulz-Flory (ASF) kinetics, as shown in Figure 2.

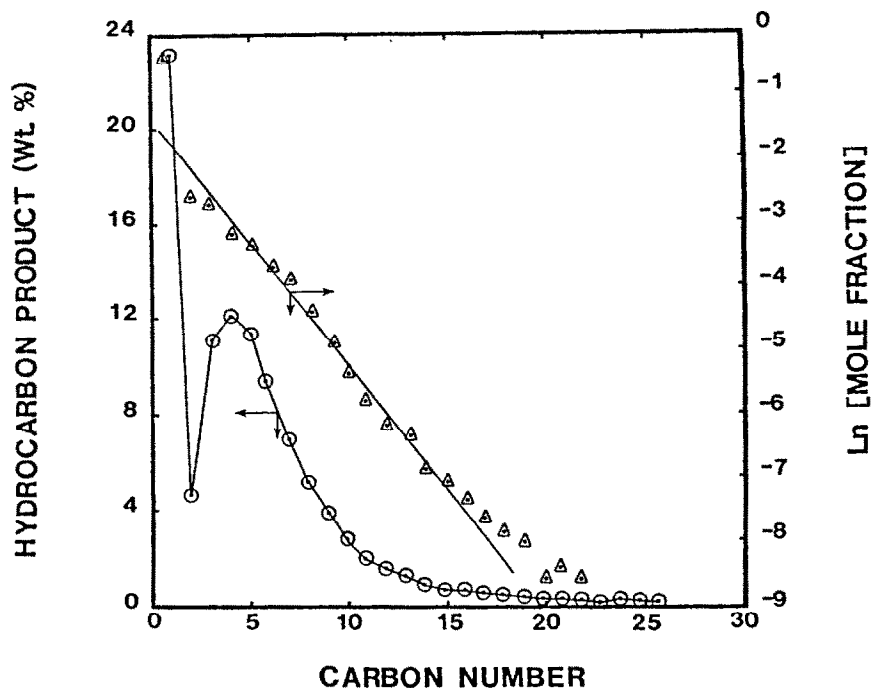


FIGURE 2. Hydrocarbon product distribution (○) and Anderson-Schulz-Flory plot (△) for carbonyl-derived 3.7% Co/Al<sub>2</sub>O<sub>3</sub> (Catalyst F).

The observation that selectivity properties of these carbonyl-derived catalysts are very similar to conventional catalysts contrasts with those of some previous investigators who reported unusual selectivities for cobalt [11] and iron [15] carbonyl-derived catalysts. For example, these investigators found high selectivities for low molecular weight olefins and non-ASF kinetic behavior; however these previous results were not obtained at steady-state as in this study.

Our results suggest that the principle advantage of carbonyl-derived catalysts over conventional catalysts is substantially higher active surface areas as evidenced by the higher hydrogen uptakes for the same loading of cobalt (see Table 1). This enhanced surface area is a result of increases in both dispersion and extent of reduction over conventional catalysts; moreover, it is maintained during reaction conditions.

## SUMMARY

1. Carbonyl-derived Co/alumina catalysts are substantially more highly dispersed and reduced than their conventionally prepared counterparts and thus have higher active surface areas. In this study, dispersions up to 34% and extents of reduction of up to 96% were observed for 3-4% Co/alumina.
2. Cobalt dispersion is maximized at a reduction temperature near 350°C. The cyclohexane reflux method is the most effective of those investigated for preparing catalysts of high dispersion and reduction.
3. That carbonyl-derived catalysts are well-dispersed suggests a strong interaction between  $\text{Co}_4(\text{CO})_{12}$  and some site on the partially dehydroxylated alumina, possibly Lewis acid-Lewis base pair sites. The high extents of reduction of carbonyl-derived catalysts result from the zero-valent state of the precursor metal atom combined with the low concentration of surface hydroxyl groups on the partially dehydroxylated alumina.
4. Carbonyl-derived catalysts have slightly higher specific activity than conventionally prepared catalysts, but retain the selectivity properties normally associated with supported cobalt catalysts.
5. Carbonyl-derived catalysts do not deactivate substantially during reaction conditions. Only a 13% loss in activity is observed after 24 hours of reaction.

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