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A Study of Catalysts Derived from Supported Cobalt Carbonyl Clusters: Carbon Monoxide Hydrogenation and XPS Analysis

GREGORY F. MEYERS and MICHAEL B. HALL*

Department of Chemistry, Texas A & M University, College Station, Tex. 77843, U.S.A.

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Abstract

The clusters $Co_2(CO)_8$, $CH_3CCo_3(CO)_9$, $Co_4(CO)_{12}$, or $Co_6(CO)_{15}^{2-}$, supported on γ-Al_2O_3, and $Co_4(CO)_{12}$ supported on dehydrated SiO_2–Al_2O_3, kieselguhr, Florisil, KOH–γ-Al_2O_3, molecular sieve 5 Å, or untreated ZnO, serve as precursors to catalysts for the hydrogenation of carbon monoxide. For the various clusters on γ-Al_2O_3, the initial activity of the prepared catalyst decreases with increasing precursor stability, however, the turnover number and product selectivities are similar under batch conditions at 250 °C. For catalysts derived from supported $Co_4(CO)_{12}$, the initial activity decreases with increasing basicity of the support. The turnover numbers and selectivities for the catalysts derived from $Co_4(CO)_{12}$ are similar for all supports except SiO_2–Al_2O_3, which exhibits a significantly greater turnover number. The enhanced activity of the silica–alumina support correlates well with the amount of reduced cobalt on the surface as measured by X-ray photoelectron spectroscopy. Product selectivity towards C_2–C_4 alkanes and alkenes is observed at lower reaction temperatures but at greatly diminished conversion.

Introduction

The decomposition of organometallic complexes [1], particularly metal carbonyls [2], onto inorganic oxides is a convenient route to highly disperse, supported metals for use as heterogeneous catalysts. These materials exhibit unusual activity [3] and selectivity [4–7] in many heterogeneous reactions including alkene hydrogenation, alkane hydrogenolysis, and CO/H_2 reactions.

One important question regarding the use of supported metal carbonyl clusters is whether or not the metal framework can exist intact on the surface under reaction conditions. Chemisorption of cluster carbonyls at room temperature may result in the formation of subcarbonyls [8], grafting via formation of metal hydrides [9], or oxidative addition of surface hydroxyl groups across metal–metal bonds [10]. The particular surface species depends on the support properties (acidity *versus* basicity and hydroxylated *versus* dehydroxylated) and to a lesser extent on the stability of the cluster toward oxidation or reduction. Decarbonylation at moderate temperatures (<120 °C) can decompose the clusters to partially oxidized mononuclear di- and tricarbonyl fragments [11–13]. More severe thermal treatment under H_2 or *in vacuo* results in both metal agglomeration (small particles typically <100 Å diameter) and metal oxidation [14–16]. The latter process is favored on hydroxylated supports. As a result of these processes catalysis by supported intact clusters has proved elusive for temperatures at which typical heterogeneous reactions are run**.

Previously we reported on a CO hydrogenation catalyst prepared by decarbonylation of $Co_4(CO)_{12}$ on γ-Al_2O_3 [18]. Kuznetsov *et al.* [11] studied the chemisorptive decomposition of $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and $Ru_6C(CO)_{17}$ cluster carbonyls on alumina and silica and observed that the same surface species formed regardless of precursor nuclearity. Synthesis gas conversion has been compared for supported osmium prepared from H_2OsCl_6, $Os(CO)_5$, $Os_3(CO)_{12}$, and $H_4Os_4(CO)_{12}$ on alumina [19]. Closely related to our study is the work by Ferkul *et al.* [20] who have compared catalysts prepared from $Co_2(CO)_8$ and $Co_4(CO)_{12}$ supported on alumina and silica. Blanchard and Bonnet [21] have compared a commercial Co/kieselguhr catalyst to $Co_2(CO)_8$ supported on a variety of supports for conversion of syngas. Here we extend our study of supported cobalt to explore the effects of precursor nuclearity and support material on carbon monoxide hydrogenation. We have investigated γ-Al_2O_3 supported catalysts prepared from $Co_2(CO)_8$, $CH_3CCo_3(CO)_9$, $Co_4(CO)_{12}$, or $Co_6(CO)_{15}^{2-}$ carbonyl clusters and $Co_4(CO)_{12}$ supported on SiO_2–Al_2O_3, kieselguhr, Florisil, KOH–γ-Al_2O_3, molecular sieve 5 Å, or ZnO. Catalytic reactions were carried out in a bomb reactor and the products distribution will differ from that of a flow reactor.

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*Author to whom correspondence should be addressed.

**IR studies provide evidence for intact cluster frames as part of catalytic cycles at low temperatures (<100 °C) [17].

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Experimental

Materials

$Co_2(CO)_8$ (Strem Chemicals) was purified by sublimation prior to use as catalyst precursor and for synthesis. $CH_3CCo_3(CO)_9$ [22]*, $Co_4(CO)_{12}$ [23], and $K_2[Co_6(CO)_{15}]$ [24], were prepared by literature methods. The neutral clusters were purified by vacuum sublimation and the purity of all precursors was checked by solution IR. Hexane (Fischer) and tetrahydrofuran (Fischer) were distilled under nitrogen over sodium benzophenone ketyl. For comparison, a more conventional cobalt catalyst was prepared by impregnation of five grams of γ-Al_2O_3 with 5.6 ml of a 2.6×10^{-1} M aqueous $Co(NO_3)_2$ (Fischer). The slurry was stirred for 16 h at room temperature, vacuum dried, calcined in air (35 psi) at 250 °C for 2 h, and reduced in hydrogen (45 psi) at 250 °C for 2 h prior to use.

Supports

γ-Al_2O_3 pellets (100 m^2/g, 0.28–0.33 cc/g), SiO_2–Al_2O_3 pellets (425–50 m^2/g, 0.66 cc/g), kieselguhr pellets (2.4 m^2/g, 0.46 cc/g), and ZnO pellets (20 m^2/g, 0.25–0.35 cc/g) were purchased from Strem Chemicals**. Florisil (30–60 mesh) and molecular sieve 5 Å were purchased from Matheson, Coleman, and Bell. With the exception of ZnO, all support materials were extensively dried in a Vycor tube furnace at temperatures ranging from 520–660 °C in flowing oxygen for 18–24 h. They were evacuated at high temperature for 2 h followed by cool down in helium flow to room temperature. The tube furnace was fitted with vacuum stopcocks for passage into a Vacuum Atmospheres dry box (HE-493). KOH–γ-Al_2O_3 was prepared by stirring 20 g of untreated γ-Al_2O_3 with 150 ml of aqueous 1 M KOH solution for 3 h, filtering, and drying overnight at 120 °C. The oven-dried material was then loaded into the tube furnace and further dried at 560 °C for 16 h under helium flow and cooled to room temperature.

Catalyst Preparation and Reaction and Analysis

The preparation and handling of all catalyst materials was carried out in the dry box. Typically, 200–250 mg of metal carbonyl was dissolved in 100 ml of hexane (tetrahydrofuran was used for the $Co_6(CO)_{15}{}^{2-}$ salt). To this solution was added 5 g of support (giving a nominal metal loading of 1–2 wt% Co) and the mixture was stirred. The mixture was then loaded into a Parr 300 ml reactor (Parr Instrument Co.) The solvent was removed under vacuum at room temperature and the carbonyl precursor was then thermally decarbonylated *in vacuo* for an additional hour (heating rate about 14 °C/min up to a maximum temperature of 250 °C). The reactor was allowed to cool to room temperature and charged with 75 psi synthesis gas ($H_2/CO = 2.1$). The reactor was then heated to 250 °C (heating rate about 4 °C/min). Product sampling was obtained after a two hour period by expanding the bomb gases into a calibrated volume containing a syringe sampling port. Products were analyzed by GC on a Perkin-Elmer Sigma 3 gas chromatograph (FID) using dual 6-ft packed columns (Porapak Q) and a linear temperature program, 50 °C (2 min) then 50–175 °C at 15 °C/min. FID response factors were determined for the following gases: methane, ethylene, ethane, propylene, propane, n-butane. XPS spectra were recorded on an HP-5950A ESCA spectrometer using monochromatic Al Kα radiation. Sample preparation and analysis was similar to that for $Co_4(CO)_{12}/\gamma$-Al_2O_3 described previously [18]. Spectral deconvolution was performed using a Gaussian peak fit routine (Surface Science Laboratories) and atomic ratios were determined using cross-section data calculated for the HP instrument [25]. In this way the experimental Al/O ratio for dehydroxylated γ-Al_2O_3 was determined to be 0.650 in close agreement to the true value of 0.667.

Results and Discussion

Comparison of Precursor Nuclearity on γ-Al_2O_3

After the carbonyl precursors are deposited from solvent onto the γ-Al_2O_3, the color of the catalyst resembles that of the particular cluster used. Thus, catalysts prepared from $Co_2(CO)_8$ and $Co_4(CO)_{12}$ are initially golden brown; from $CH_3CCo_3(CO)_9$ are maroon; and from $Co_6(CO)_{15}{}^{2-}$ are dark green. The catalyst prepared by aqueous nitrate impregnation is pink. After thermal decarbonylation and one catalytic cycle all carbonyl based catalyst materials are grey in color.

Following thermal decarbonylation *in vacuo* at 250 °C the reactor is charged with 75 psi of synthesis gas ($H_2/CO = 2.1$). As the catalyst is heated the reactor pressure increases with temperature until the apparent conversion of CO begins. For the various supported precursors conversion begins over a temperature range of 100–150 °C and a pressure range of 70–80 psi. Based on the pressure–temperature profile the supported precursors may be ranked in the following decreasing order of initial activity:

$$Co_2(CO)_8 > Co_4(CO)_{12} > Co_6(CO)_{15}{}^{2-} \approx CH_3CCo_3(CO)_9 > Co(NO_3)_2$$

The initial activity decreases with increasing thermal stability of the carbonyl precursor.

In order to compare catalysts prepared from different precursors, several parameters were examined. Table I lists these parameters for the precursors on

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*The yield reported in ref. 22 was obtained only at THF reflux after 2 h.

**Surface areas and pore volume information supplied by the manufacturer.

TABLE I. CO/H_2 Conversion over Cobalt Precursors Supported on γ-Al_2O_3[a]

Precursor	Turnover number[b]	C Selectivity (%)[c]								n-C_4/i-C_4[f]
		C_1	C_2	C_3	C_4	C_5	C_6	$\bar{C}_n$[d]	$\bar{\alpha}$[e]	
$Co(NO_3)_2$	8.4(61)	75.1	10.8	7.0	4.1	2.7	0.3	1.2	0.33	10.2
$Co_2(CO)_8$	7.2(70)	51.0	14.2	15.1	9.5	6.6	3.9	1.5	0.49	17.3
$CH_3CCo_3(CO)_9$	10.0(81)	65.8	12.1	9.7	6.3	3.9	2.3	1.3	0.45	20.8
$Co_4(CO)_{12}$	9.2(79)	56.3	13.1	13.3	8.5	5.6	3.2	1.4	0.47	14.2
$Co_6(CO)_{15}^{2-}$	10.1(82)	60.2	13.1	12.0	7.3	4.7	2.7	1.3	0.46	11.4

[a] $H_2/CO = 2.1$ (75 psi total pressure), 250 °C, 2 h. [b] Turnover number = ΣnC_n mmol/mmol Co charged where n is the number of carbon atoms in hydrocarbon C_n. (The percent CO conversion at which turnovers were obtained) = 100 × ΣnC_n mmol/mmol CO charged. [c] C selectivity (%) = 100 × nC_n mmol/ΣnC_n mmol. [d] $\bar{C}_n$ (average carbon number) = ΣnC_n mmol/ΣC_n mmol. [e] Average value of the Flory parameter. [f] Normal butane/isobutane.

γ-Al_2O_3 after one F–T cycle. As a measure of overall activity for a run the total carbon turnover was determined. This represents the sum of mmol C (as hydrocarbon) formed per mmol Co charged for the two hour reaction period. The turnover numbers and conversions at which they were obtained indicate that the $Co_2(CO)_8$ precursor exhibits the lowest and the $Co_6(CO)_{15}^{2-}$ precursor the highest activity. If these values are normalized to 100% CO conversion, the average turnover becomes 12.1 ±1.3 indicating that the overall activity exhibits little dependence on the cobalt precursor used.

Under these batch conditions the catalysts based on cobalt carbonyls are less selective toward methane (51–65%) than the conventional cobalt nitrate based catalyst (75%) and are more selective toward higher hydrocarbons. All carbonyl based catalysts produced saturated linear and branched alkanes. The average carbon number, C_n, and the average chain growth probability, α, indicate the selectivity for higher molecular weight hydrocarbons. For all carbonyl precursors the mean value of C_n is 1.4 ±0.1 and of α is 0.47 ± 0.02 which are greater than the nitrate based catalyst. As with total carbon turnover, however, the extent of chain growth does not depend on the particular carbonyl used. The only unsaturate, propylene, was observed using the nitrate based catalyst and accounted for <1% of the C_3 fraction.

One factor which does depend on the precursor is the extent of isomerization in the synthesis. This is indicated by the n-butane/isobutane ratio shown in Table I. This ratio varies by a factor of two over the various precursors. Isomerization is the greatest using supported cobalt nitrate or the $Co_6(CO)_{15}^{2-}$ precursor and the least over the supported CH_3CCo_3-$(CO)_9$ precursor.

Comparison of Various Support Materials

We have supported $Co_4(CO)_{12}$ on a number of partially dehydroxylated supports. We were interested to see if any support effect was evident under our conditions. There is evidence to suggest that the Fischer–Tropsch synthesis is structure sensitive [26], and strong metal support interactions (SMSI) have been observed for catalysts supported on transition metal and rare earth oxides [27].

As before the order of initial activity for supported $Co_4(CO)_{12}$ can be ranked based on the temperature and pressure at which conversion begins. In general conversion began over a temperature range of 100–125 °C and pressures of 74–88 psi. For the various supports this decreasing order of initial activity is:

$$SiO_2\text{–}Al_2O_3 > \gamma\text{-}Al_2O_3 > KOH\text{–}\gamma\text{-}Al_2O_3 > \text{Florisil}$$
$$> \text{Kieselguhr} > ZnO\ \text{(untreated)}$$
$$> \text{molecular sieve } 5\ \text{Å}$$

This order parallels a decreasing order of support acidity. The Hammett acidity parameter, H_o, for silica–alumina calcined at 550 °C is –8.2 and that for silica–magnesia (like Florisil) calcined at the same temperature is +1.5 to –3.0 [28]. The pH of a 5% slurry of molecular sieve 5 Å is 10.5 [29]. In the present case the acidity is predominately in a Lewis sense owing to extensive drying of the supports.

Table II lists the reaction parameters for the various oxides used to support $Co_2(CO)_{12}$. The total carbon turnovers are similar for most supports used. The $Co_4(CO)_{12}/SiO_2$–Al_2O_3 catalysts is about 50% more active and the $Co_4(CO)_{12}/ZnO$ catalyst is about 50% less active than the other supports. The greater activity of $Co_2(CO)_8/SiO_2$–Al_2O_3 compared to $Co_2(CO)_8/Al_2O_3$ has previously been observed [30]. We have also observed a turnover enhancement of about 54% when the $Co_2(CO)_8$ precursor is supported on silica–alumina *versus* alumina. When the activities shown in Table II are normalized to 100% CO conversion the relative order of activity differs from the initial activities above, however, the relative differences between supports is less, the mean turnover number being 12.1 ± 1.7.

The product distribution in all cases is similar. Linear and branched alkanes are the sole hydrocarbon

TABLE II. CO/H_2 Conversion over $Co_4(CO)_{12}$ Supported on Various Oxides[a]

Support	Turnover number	C Selectivity (%)								n-C_4/i-C_4
		C_1	C_2	C_3	C_4	C_5	C_6	$\bar{C}_n$	$\bar{\alpha}$	
γ-Al_2O_3	9.2(79)	56.3	13.1	13.3	8.5	5.6	3.2	1.4	0.47	14.2
KOH–γ-Al_2O_3	8.0(66)	64.1	14.0	11.2	6.2	3.4	0.9	1.3	0.37	11.7
SiO_2–Al_2O_3	13.7(92)	61.8	11.3	11.8	8.3	4.3	2.4	1.3	0.46	2.3[c]
Florisil	8.9(83)	65.4	11.3	10.8	6.7	3.9	2.0	1.3	0.44	10.2
Kieselguhr	9.9(77)	69.6	11.4	9.3	4.9	3.2	1.6	1.2	0.42	14.1
Molecular sieve 5 Å	8.8(70)	63.5	13.6	11.8	6.1	3.1	2.0	1.3	0.42	12.5
ZnO[b]	4.5(47)	43.9	20.9	15.3	9.9	7.0	3.1	1.6	0.45	12.5

[a] Conditions and definitions as in Table I. [b] Used as received without pretreatment. [c] The same ratio is obtained for $Co_2(CO)_8$/SiO_2–Al_2O_3.

TABLE III. XPS Data of Supported Co Clusters Before and After Reaction

Sample	Treatment	Oxidized Co $2p_{3/2}$	Reduced Co $2p_{3/2}$	Reduced Co(%)[d]	'Actual' loading[e]	Surface at. ratios[f]
$CH_3CCo_3(CO)_9$/γ-Al_2O_3	decarb.[a]	780.5[c]	–	0	0.52	$CoC_{5.4}$
	F.T. (light)[b]	781.5	778.1	9	0.47	$CoC_{4.4}$
	F.T. (dark)[b]	781.5	778.7, 776.3	20	5.97	$CoC_{7.7}O_{1.9}$
$Co_4(CO)_{12}$/γ-Al_2O_3	decarb.	781.7	778.6	18	0.91	[g]
	F.T.	782.0	778.5	22	0.15	[g]
$Co_4(CO)_{12}$/SiO_2–Al_2O_3	decarb.	780.3	778.0	26	2.55	$CoC_{9.5}O_{12}$
	F.T.	780.2	777.9	37	1.04	$CoC_{44}O_{26}Al_{1.5}$

[a] Decarb. refers to a freshly decarbonylated sample as described in 'Experimental'. [b] F.T. refers to a sample after a carbon monoxide hydrogenation. Light and dark samples are described in the test. [c] Binding energies are ±0.2 eV and referenced to Al 2s at 119.0 eV. [d] Determined from spectral deconvolution using gaussian fit routine. [e] Weight percent cobalt (see text). Nominal loading is 1–2 wt% cobalt. [f] Residual ratios after subtracting contribution due to support. [g] C 1s spectra were not recorded. Samples showed no excess surface oxygen.

products and no olefins are observed. Carbon selectivities are similar for most supports. $Co_4(CO)_{12}$/kieselguhr is the most selective toward methane (70%) while $Co_4(CO)_{12}$/ZnO is the least selective (44%) and other supports show intermediate methane selectivity (56–65%).

These trends are reflected in C_n and α values as well, the largest C_n values occur with ZnO and γ-Al_2O_3 supports and the smallest with $Co_4(CO)_{12}$/kieselguhr*. In contrast, Van Hove *et al.* [30] observed unusual selectivity for $Co_2(CO)_8$ on alumina or silica–alumina supports which has uniformly small pore diameters. Assuming a cylindrical pore shape** the supports used in this study have average pore diameters ranging from small (56–66 Å for γ-Al_2O_3 and 29–31 Å for SiO_2–Al_2O_3) to extremely large (3830 Å for kieselguhr). At the high CO conversions and temperatures in our batch studies such pore size selectivity is apparently masked.

Interestingly, using KOH–γ-Al_2O_3 (compared to unpromoted γ-Al_2O_3) results in a catalyst which favors limited chain growth and lower activity (Table II) despite substantial evidence that potassium doping (on iron catalysts [31] and iron foils [32]) should have the opposite effect. Counterion potassium from $K_2[Co_6(CO)_{15}]$ apparently has no promotional effect on the $Co_6(CO)_{15}^{2-}$/γ-Al_2O_3 catalyst under our conditions (Table I)†.

The parameter which is most sensitive to the support used is the extent of isomerization. The n-butane/isobutane ratio varies by a factor of seven over all the supports. The smallest ratios are obtained

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*A commercial prereduced 25 wt% Co/kieselguhr catalyst (Strem Chemicals) under identical conditions produces methane exclusively (99.9%) with a turnover number of 0.98 at 72% CO conversion. Five percent weight Co on silica derived from $Co_2(CO)_8$ and $Co_4(CO)_{12}$ carbonyls produces methane as the sole hydrocarbon product under Fischer–Tropsch conditions above 300 °C.

**An average radius, r, where $r = 2V_g/S_g$. V_g and S_g are the pore volume and surface area per gram.

†Catalysts prepared from potassium salts of anionic iron carbonyls exhibit higher activity and selectivity over conventionally prepared catalysts prepared by impregnation of aqueous iron and potassium nitrate solutions, see ref. 33.

for $Co_4(CO)_{12}$ supported on $SiO_2-Al_2O_3$ (2.3) and Florisil (10.2). Both of these supports are used as commercial hydrogenolysis/isomerization catalysts suggesting a secondary role for these supports [34]. The ratio is the greatest on γ-Al_2O_3 (14.2) and kieselguhr (14.1).

XPS Studies

Earlier we reported in detail on the XPS of a $Co_4(CO)_{12}/\gamma$-Al_2O_3 catalyst [18]. Because the catalysts prepared from carbonyl clusters showed similar activity on γ-Al_2O_3 and enhanced activity on $SiO_2-Al_2O_3$, it was of interest to see if such differences would be reflected in cobalt XPS spectra.

Table III lists XPS data of three catalyst samples before and after one catalytic cycle. This Table compares the $CH_3CCo_3(CO)_9/\gamma$-Al_2O_3, the $Co_4(CO)_{12}/\gamma$-Al_2O_3, and the $Co_4(CO)_{12}/SiO_2-Al_2O_3$ catalysts. The Co $2p_{3/2}$ core level spectra for the three samples both before and after reaction are shown in Fig. 1.

Before reaction only oxidized cobalt is apparent (780.5 eV) on $CH_3CCo_3(CO)_9/\gamma$-Al_2O_3. Since the Co is already partially oxidized in this cluster [35], the decarbonylation and cluster breakdown might not result in any unoxidized metal. For $Co_4(CO)_{12}$ (cobalt formally zero-valent) supported on γ-Al_2O_3 or $SiO_2-Al_2O_3$ reduced cobalt is evident at 778.6 eV (18%) and 778.0 eV (26%), respectively. The balance of the cobalt is oxidized under thermal vacuum treatment owing to a surface redox reaction where the zero-valent metal is oxidized and surface protons are reduced [36].

After one catalytic cycle, the $CH_3CCo_3(CO)_9/\gamma$-Al_2O_3 catalyst gives rise to a visibly heterogeneous surface having light blue–grey and dark grey–black regions. The spectrum of the 'light' material exhibits a metal shoulder at 778.1 eV (9%). The spectrum of the 'dark' material shows zero-valent cobalt at 778.7 eV (14%) and a further reduced cobalt species evidenced by a low energy shoulder at 776.3 eV (6%). Based on IR studies Watters *et al.* [37] concluded that mononuclear $Co(CO)_4^-$ and perhaps polynuclear anionic cobalt clusters exist on the surface of $CH_3CCo_3(CO)_9/\gamma$-Al_2O_3. After one F–T cycle, the total percent of reduced cobalt on catalysts prepared from $CH_3CCo_3(CO)_9$ and $Co_4(CO)_{12}$ clusters on γ-Al_2O_3 is similar and accounts for the similar activity (Table I) of the two materials.

Hercules and Chin [38] have reported detailed surface studies on Co/Al_2O_3 catalysts to examine the effects of metal loading and calcination temperature on the reduction behavior of supported cobalt. In particular, a linear relationship between ESCA Co/Al intensity ratios *versus* percent cobalt loading was observed up to 10 wt% where monolayer coverage is complete. Table III includes the 'actual' cobalt loading calculated by applying a correction factor from the Hercules–Chin data to our observed Co/Al ratios. The post cycle 'dark' sample of $CH_3CCo_3(CO)_9/\gamma$-Al_2O_3 has a cobalt loading in excess of the nominal 1–2 wt% cobalt used to prepare the catalyst. Although the morphology of supported cobalt cannot be determined from XPS data the higher loading on this sample is perhaps associated with excess surface oxygen indicated by residual atomic ratios shown in Table III. In the case of $Co_4(CO)_{12}/\gamma$-Al_2O_3 catalysts the 'actual' cobalt loading is apparently decreased after one catalytic cycle. This decrease may reflect diffusion of cobalt into the support or may simply represent a diminished cobalt loading on this particular sample. The $Co_4(CO)_{12}/\gamma$-Al_2O_3 catalyst surface appeared visually homogeneous after one cycle.

XPS spectra of the catalysts prepared by supporting $Co_4(CO)_{12}$ on γ-Al_2O_3 and $SiO_2-Al_2O_3$ show that cobalt is much easier to reduce on the latter support which has a more pronounced metal peak at 777.9 eV (37%) while γ-Al_2O_3 has a weaker metal shoulder at 778.5 eV (22%). This result suggests a much weaker interaction between cobalt and the silica–alumina support. The ratio of percent metallic species of these two catalysts is 1.7 in very close agreement with the ratio of turnover numbers which is 1.5 for the two catalysts.

The $Co_4(CO)_{12}/SiO_2-Al_2O_3$ catalyst shows excess surface carbon and oxygen both before and after one catalytic cycle. Additionally, excess aluminum is observed on the surface after one cycle (Table III). The FWHM of the Al 2s core level is significantly broader after reaction (4.5 eV) than before (3.5 eV). Although the former peak exhibits no asymmetry, the breadth of the peak suggests that more than one type of Al surface species is present. This is probably due to the conversion of some surface Lewis acid sites, $(\sigma\text{-}O^-)_3Al^{3+}$, to surface Bronsted sites, $(\sigma\text{-}O^-)_3\text{-}Al^{2+}\text{–}OH + H^+$, formed by reaction with water produced in the synthesis [39].

Temperature Effect on Selectivity

Both the precursor carbonyl cluster and support influence the extent of alkane isomerization under batch conditions at 250 °C. The product selectivities, however, are not dramatically different, partly because of the extremely high CO conversions (>60%) and partly because the catalytically active species is similar in all cases. Fischer–Tropsch catalysts derived from supported iron clusters have been shown to exhibit remarkable selectivities to low molecular weight olefins under differential (<7% CO conversion) flow conditions [6]. We therefore investigated the effect of lowering the reaction temperature (and therefore CO conversion) under batch conditions.

Table IV lists reaction parameters for three $Co_4(CO)_{12}/\gamma$-Al_2O_3 catalysts which were decarbonylated *in vacuo* at 250 °C and reacted with the

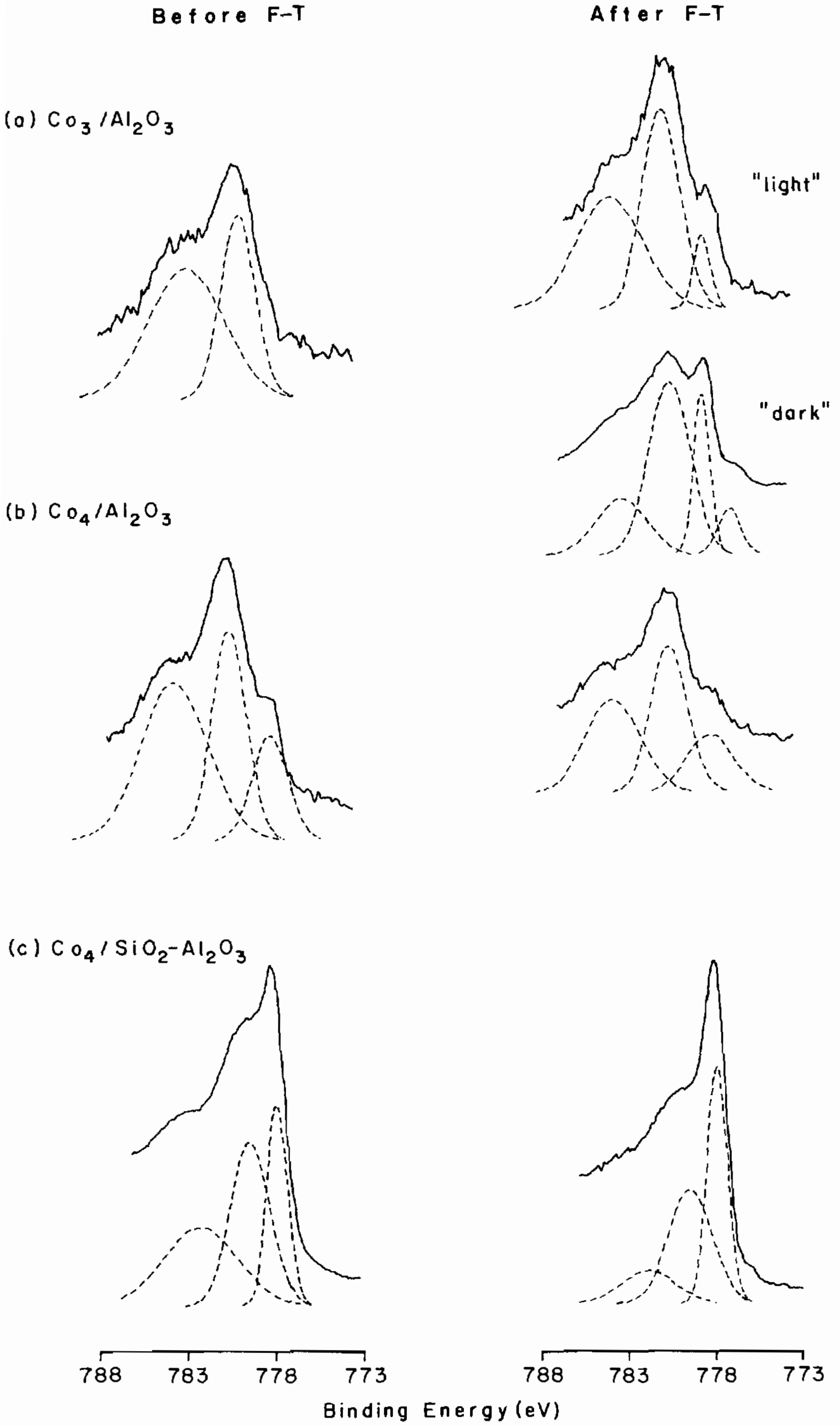

Fig. 1. Co $2p_{3/2}$ XPS spectra of (a) $CH_3CCo_3(CO)_9/\gamma$-Al_2O_3; (b) $Co_4(CO)_{12}/\gamma$-Al_2O_3; (c) $Co_4(CO)_{12}/SiO_2$–Al_2O_3 both before and after one catalytic cycle. In (a) 'light' and 'dark' refer to visible surface color. Spectral deconvolutions are indicated by dashed lines.

usual synthesis gas charge at 250, 125 and 75 °C for a two hour period. As expected when the temperature of reaction is lowered the turnover and conversion decrease. The decreased CO conversion and temperature has a pronounced effect on selectivity as indicated by Table IV and shown in Fig. 2. In general, as

TABLE IV. Effect of Temperature on Synthesis over $Co_4(CO)_{12}/\gamma$-Al_2O_3[a]

Temperature (℃)	Turnover number	C Selectivity (%)[c]								$\bar{C}_n$	α	O/P[d]	%C C_2–C_4[e]
		C_1	$C_2^=$	C_2	$C_3^=$	C_3	C_4	C_5	C_6				
250	9.2(79)	56.3	0	13.1	0	13.3	8.5	5.6	3.2	1.4	0.47	0	34.9
125 + 250[b]	7.8(68)	45.3	0	11.3	0	15.3	12.4	9.7	6.0	1.6	0.56	0	39.0
125	5.3(53)	36.2	0.03	8.6	2.1	15.1	17.2	12.6	8.1	1.8	0.62	0.09	43.0
75	0.03(0.3)	21.9	1.5	16.6	11.2	12.6	20.4	12.5	3.4	2.1	0.50	0.48	62.3

[a] Conditions and definitions as in Table I. [b] Reaction run at 125 ℃ for 4 h and then heated to 250 ℃ for 1 h. [c] $C_2^=$ and $C_3^=$ correspond to ethylene and propylene, respectively. [d] Olefin/paraffin = $C_2^= + C_3^=/C_2^= + C_2 + C_3^= = + C_3$. [e] Sum of carbon selectivities for all C_2–C_4 hydrocarbons.

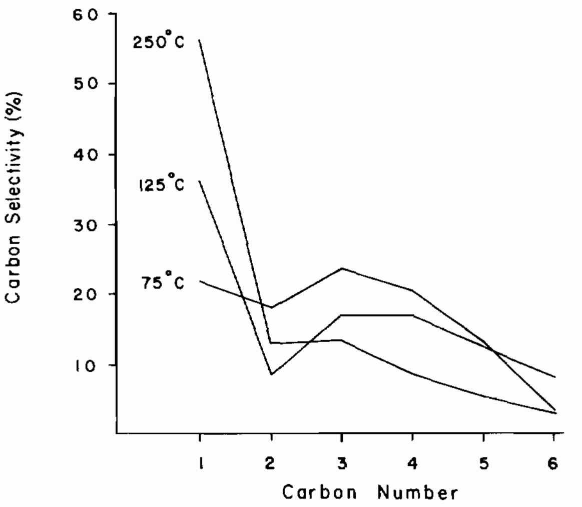

Fig. 2. Carbon selectivities over $Co_4(CO)_{12}/\gamma$-Al_2O_3 catalysts after one catalytic cycle at 250, 125 and 75 ℃.

the temperature is lowered the selectivity to higher molecular weight hydrocarbons increases as evidenced by increasing C_n. The most pronounced effect is in the C_2–C_4 region where carbon selectivities increase from 35% to 43% to 62% with decreasing temperature. In addition, ethylene and propylene are observed after reaction at 125 and 75 ℃ where olefin/paraffin ratios are 0.09 and 0.48, respectively. The lower selectivity to ethylene could be explained by the suggestion that ethylene is a primary product and undergoes secondary reaction to propylene as is observed for catalysts prepared from iron carbonyls supported on alumina or magnesia [40].

The above results suggest that secondary reactions are occurring in our reaction at 250 ℃. In particular, hydrogenolysis of higher molecular weight hydrocarbons or CH_2 deinsertion apparently occurs at higher temperatures. This is demonstrated by the second entry in Table IV where the catalyst used at 125 ℃ was recycled with a fresh charge of synthesis gas and run at 125 ℃ for 4 h and then heated to 250 ℃ for an additional hour. The reaction parameters are intermediate between those of reactions over fresh catalysts at 125 and 250 ℃.

Related Reactions

We have explored a limited number of secondary reactions which might alter product selectivities at high temperature and CO conversion. These reactions include carbon dioxide hydrogenation, ethylene hydrogenation and homologation, and n-butane hydrogenolysis. Carbon dioxide hydrogenation and alkane hydrogenolysis would be of only minor importance under the usual Fischer–Tropsch condition of high CO concentrations. However, since our reactions are run until the CO is depleted they might play a role in our product distribution. The reaction conditions and parameters are summarized in Table V.

As Table V indicates, CO_2 is readily reduced under batch conditions with turnover and conversion comparable to that observed for CO reduction over $Co_4(CO)_{12}/\gamma$-Al_2O_3. The apparent conversion temperature is 125 ℃. The CO_2 reduction is highly selective toward methane formation (79%) with a small C_n value (1.1) due, in part, to a higher hydrogen ratio used for the reaction. Both ethylene and propylene are observed as minor products and this may be due to a shorter reaction period (1 h). Methane selectivity has been observed in CO_2 reduction over supported Ru derived from ruthenium cluster carbonyls [20].

Freshly prepared catalysts are extremely active for ethylene hydrogenation at room temperature. As Table V shows virtually all of the hydrogen charged is consumed to make ethane with 97% selectivity in a period of about one minute. High olefin hydrogenation activity is a general feature of catalysts prepared from metal carbonyls [3]. Thus, in the presence of H_2 alone at low temperature and short contact times or under H_2/CO atmosphere at high temperatures and longer contact times olefins are readily hydrogenated over supported cluster catalysts. At lower temperatures under H_2/CO, however, low

TABLE V. Related Reactions of $Co_4(CO)_{12}/\gamma\text{-}Al_2O_3$

Temperature (℃)	Turnover number	C Selectivity (%)								$\bar{C}_n$	Conversion temperature (℃)[g]
		C_1	$C_2^=$	C_2	$C_3^=$	C_3	C_4	C_5	C_6		
CO_2 reduction[a]	7.8(79)	78.9	0.16	10.7	0.73	5.5	2.6	1.0	0.54	1.1	125
C_2H_4 hydrog.[b]	29.0(70)	0.23	[e]	96.8	0.33	0.61	1.6	0.08	0.04	2.0	22
C_2H_4 homolog.[c]	0.32(0.7)	0.70	[e]	0	2.8	0	68.0	9.0	18.0	4.1	100
n-C_4H_{10} crack.[d]	23.2(39)	61.5	0	15.1	0	21.0	1.5[f]	0.78	0.07	1.3	>150

[a] H_2/CO_2 = 3.4 (75 psi), 200 ℃, 1 h. [b] H_2/C_2H_4 = 0.67 (75 psi), 22 ℃, 1 min. [c] 45 psi C_2H_4, 100 ℃, 2 h over catalyst used in [b]. [d] H_2/n-C_4H_{10} = 0.52, 250 ℃, 2 h. [e] Neglected in determining selectivity. [f] Isobutane in excess of that present in n-C_4H_{10} charged. [g] Temperature at which apparent conversion begins.

molecular weight olefins are much more stable toward hydrogenation. In the absence of CO or H_2, ethylene will homologate to form C_4 (68%) and C_6 (18%) hydrocarbons at 100 ℃ although the conversion at this temperature is quite low (Table V, third entry).

As was expected, freshly prepared $Co_4(CO)_{12}/\gamma\text{-}Al_2O_3$ is active for alkane hydrogenolysis. Table V lists reaction parameters for n-butane cracking. The apparent conversion begins above 150 ℃ with moderate conversion (39%). The cracking pattern is highly selective toward methane (62%) in spite of a H_2/n-C_4H_{10} ratio equal to 0.52. The high selectivity toward methane may be due to CH_2 deinsertion occurring rather than hydrogenolysis. Similar methane selectivity is observed for n-heptane hydrogenolysis over silica supported $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ carbonyl clusters [5]. The authors correlated the selectivity with the small Rh crystallites (<30 Å diameter) formed on the catalyst. Electron micrographs of $Co_4(CO)_{12}/\gamma\text{-}Al_2O_3$ before and after one F–T cycle show no visible cobalt crystallites at magnification X258000 suggesting that small cobalt particles may be responsible for methane selectivity.

Conclusions

The various cobalt carbonyl precursors supported on $\gamma\text{-}Al_2O_3$ exhibit similar activity and selectivity for CO reduction at high temperatures and CO conversions. Although differences in initial activity are observed for the various precursors, these differences are not very significant for the overall catalytic reaction. Our results suggest that similar active sites are produced by a wide variety of carbonyl cluster precursors. The decomposition of the carbonyls under syn-gas atmosphere gives rise to small metal particles of cobalt. In fact, Iwasawa *et al.* [41] have observed the conversion of surface $Co_2(CO)_8$ to Co_4 subcarbonyl species on both silica and alumina surfaces under moderate thermal treatment (<40 ℃ *in vacuo*). On alumina, more extensive heating or exposure to oxygen gives rise to Co_4O_4 surface clusters and Co(II) ions. Under reducing conditions these 'oxo' clusters may serve as sites for metal agglomeration.

Of all the supports used in this study, a silica–alumina support produces a catalyst which is more active and this activity correlates with the percent reduced cobalt on the support as measured by XPS. This suggests a weaker interaction of cobalt with this support.

The role of secondary reactions, in particular alkane hydrogenolysis and CO_2 reduction, could be important in determining product selectivity at high temperature and high CO conversion. At lower reaction temperature and lower conversion, catalysts prepared from cobalt carbonyls are selective in forming low molecular weight alkanes and alkenes.

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