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Interactions of Cobalt Carbonyls with Oxide Surfaces. 2. Dicobalt Octacarbonyl and Tetracobalt Dodecacarbonyl on Silicas and Aluminas

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The reactions that ensue when $Co_2(CO)_8$ or $Co_4(CO)_{12}$ is sublimed onto silica, γ-alumina, or a silica–alumina have been studied by IR spectroscopy and gas manometry. On silica, $Co_2(CO)_8$ is converted at room temperature, in vacuo, to $Co_4(CO)_{12}$ with liberation of the requisite CO, but the reaction is completely inhibited by a low pressure of CO (<50 torr). IR spectra in the regions of surface hydroxyl and metal carbonyl vibrations show that adsorption of the cobalt carbonyls on the silica surfaces involves hydrogen bonding of surface hydroxyls to oxygens of bridging CO ligands. Very similar features are observed when the support is a silica–alumina, but some formation of novel oxygen-sensitive species, with $\nu(CO)$ bands in the 1900–2030-cm^{-1} region, occurs on this support. The aluminas present a very reactive surface for the cobalt carbonyls. Sublimation followed by evacuation leads, in each case, to rapid reactions, generating new metal carbonyl species, presumably sub-carbonyls, that may be carbonylated to redevelop surface-bound parent carbonyl. The chemistry observed on aluminas is independent of whether $Co_2(CO)_8$ or $Co_4(CO)_{12}$ is the cobalt carbonyl source; this suggests an initial conversion of the dicobalt compound to $Co_4(CO)_{12}$ followed by rapid reaction of this species to form products. Alumina pretreated by evacuation at room temperature [Al_2O_3 (295 K)] is most reactive toward the cobalt carbonyls, and somewhat different products are developed on this surface, including one identified as $Co(CO)_4^-$. The several surface-bound cobalt carbonyl species show varying sensitivities to O_2. The new species developed on the aluminas are oxidized almost instantly while the parent carbonyl species—$Co_2(CO)_8$ or $Co_4(CO)_{12}$—are less susceptible to oxidation. Oxidation produces CO_2 (or surface carbonates), releases CO, and oxidizes the cobalt. When the oxygen is $^{18}O^{18}O$, large quantities of $C^{18}O$ are released during oxidation. The surface-bound cobalt carbonyls all exchange readily with gas-phase ^{13}CO to produce fully exchanged materials. In some cases the ^{13}CO-exchanged products can be extracted from the oxide supports, providing pure fully exchanged compounds in solution.

Introduction

Cobalt carbonyl compounds and their derivatives have been of special significance in the field of homogeneous catalysis; Roelen's discovery in 1938[1] of the oxo (hydroformylation) reaction, which is the cobalt carbonyl catalyzed synthesis of aldehydes and alcohols from synthesis gas, is thought to mark the first widely used synthesis via metal carbonyl complexes. Cobalt carbonyls now are known to be homogeneous catalysts for many other reactions. Hydrocarbon reactions catalyzed by cobalt carbonyls include alkene isomerizations,[2] carbonylations of alkenes and alcohols,[3] and hydrogenations of aldehydes and ketones;[4,5] a cobalt carbonyl hydrocarbon, $(CO)_9Co_3CC_6H_5$, recently has been shown to be a hydroformylation catalyst.[6]

The various organic reactions catalyzed by the cobalt carbonyls, the reactivity of cobalt carbonyls toward a diversity of substrates, and the facile interconversions between the several cobalt carbonyl species have encouraged continued interest in these compounds. Among the best characterized binary members of this group are the mononuclear anion, $Co(CO)_4^-$, the dimorphic dicobalt compound, $Co_2(CO)_8$, and the tetranuclear cluster carbonyl, $Co_4(CO)_{12}$.

The recent spate of studies of metal carbonyls supported on refractory oxides has largely neglected the cobalt carbonyls. This may be partly due to the reactivity of these compounds toward oxygen, their tendency to decompose quickly in many solvents, and the aforementioned interconversions between the various cobalt carbonyl species, all of which could make loading of a particular cobalt carbonyl species on the support problematic and characterization of the supported carbonyl difficult. The reactivities and facile interconversions of these compounds commend them, though, for study as catalyst systems under conditions in which interactions with a support surface could stabilize catalytically active species. These considerations encouraged us to begin a series of studies of cobalt carbonyls on oxide supports. A first paper on this

subject reported the study of $(CO)_9Co_3CCH_3$ on several oxides.[7]

Brenner and Hucul,[8–10] using temperature-programmed decomposition (TPDE), have studied $Co_2(CO)_8$ and $Co_4(CO)_{12}$ on γ-Al_2O_3 and SiO_2. Thermal decomposition in flowing He produced small quantities of CH_4 ($\simeq 0.03$ mol/mol of Co), as well as H_2, CO, and CO_2 at temperatures up to 600 °C. Ichikawa[11,12] has studied hydroformylation of ethene and propene by mixed rhodium–cobalt clusters and by $Co_4(CO)_{12}$ on ZnO and found activity for each compound; the specific rate for $Co_4(CO)_{12}$ was ~20-fold less than that for $Rh_4(CO)_{12}/ZnO$, but the specificity for normal isomer formation was highest (90%) for the cobalt catalyst. In Ichikawa's study, the metal carbonyl was deposited onto the metal oxide from organic solution and pyrolyzed at 160 °C, in vacuo, prior to use as a catalyst. Anderson et al.[13] also studied the series of $Rh_nCo_{4-n}(CO)_{12}$ compounds, but few details regarding the $Co_4(CO)_{12}$ species were reported.

We report here the results of an IR and gas manometric study of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ on silica, a silica–alumina, and γ-alumina. After the desired in situ pretreatment of the

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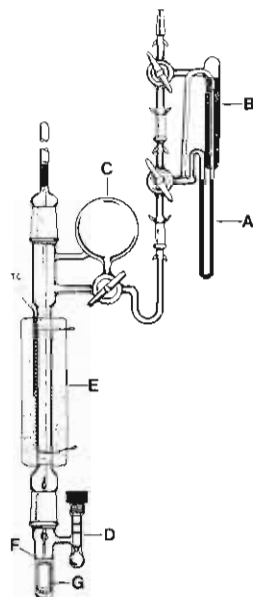†Present address: Department of Chemistry, University of Auckland, Auckland, New Zealand.

Figure 1. High-vacuum IR cell with in-line Hg manometer (A) and 5-Å molecular sieve pump (B) attachments. Other important features: (C) gas storage bulb; (D) sublimator, which contained solid cobalt carbonyl; (E) quartz tube oven section; (F) wafer holder; (G) viewing ports with KBr windows affixed by epoxy cement. The cell is drawn to scale. For greater detail see ref 7c.

support material, the cobalt carbonyls were loaded on the support by subliming them against a vacuum or a low pressure of CO. This procedure avoids problems of reaction with dioxygen, contamination of the metal carbonyl or the surface by a solvent, and in some cases, undesired interconversions between $Co_2(CO)_8$ and $Co_4(CO)_{12}$.

Another paper[14] presents similar results for these same compounds adsorbed on zeolites and discusses a mechanism for the reactions of these cobalt carbonyls with oxide surfaces at ambient and elevated temperatures.

Experimental Section

Reagents. Dicobalt octacarbonyl was supplied by Pressure Chemical Co., Inc. The commercial material was purified by recrystallization from n-pentane, followed by sublimation under 10 torr of CO. The purified crystals were stored and transferred under CO. $Co_4(CO)_{12}$ was from Strem Chemicals, Inc., and was purified by dissolution in petroleum ether (Skellysolve C) and heating, under N_2, for several hours at 75 °C, followed by recrystallization. The black crystals were vacuum dried and stored under purified N_2. The IR spectrum of the crystals in n-hexane was free of any trace of bands due to $Co_2(CO)_8$.

The silicas used were Davison 923 (a_s = 600 m²/g, BET) and Cab-O-Sil M-5, supplied by Cabot Corp. (a_s = 200 m²/g, manufacturer's value). The alumina was Akzo Chemie CK-300 γ-Al_2O_3 (a_s = 160 m²/g, BET). The silica–alumina was supplied by Air Products, Houdry Division. It was a coprecipitate consisting of 88% silica and 12% alumina; the specific surface area was not determined for this support.

All oxides, as powders, were washed in doubly distilled water and dried in air at 125 °C. Wafers of the support material were pressed with a stainless-steel die at pressures up to 30 000 psi (γ-Al_2O_3). Wafer thicknesses were characteristically 5–10 mg/cm² ($\simeq$0.3 mm). The wafers were calcined in air at 400 K, except γ-Al_2O_3, which was calcined at 800 K. The pressed water disks were cut into 1.3 × 3.0 cm rectangles to be placed in the IR section of a gas cell or were cut into small squares or shards for surface area or gas manometry measurements. Once within the gas cell,[7] the wafers were heated,
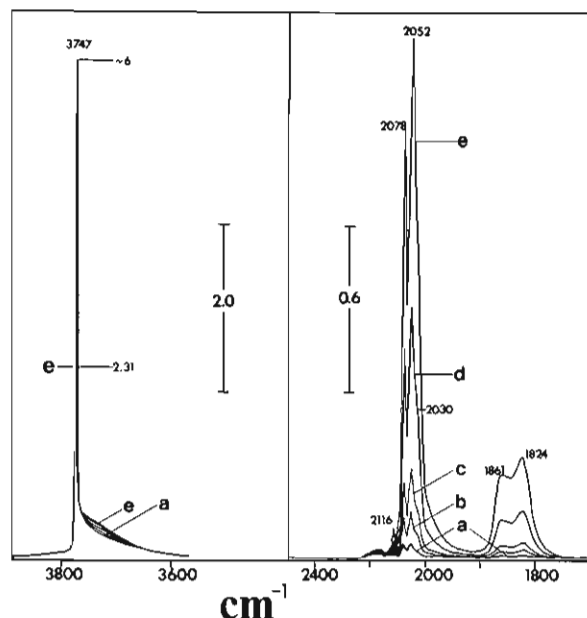

Figure 2. Difference IR absorbance spectra in the $\nu(CO)$ and $\nu(OH)$ regions for a Cab-O-Sil wafer previously heated, in vacuo, at 675 K and exposed to subliming $Co_2(CO)_8$ under 56 torr of CO for the following cumulative loading times (min): (a) 6; (b) 17; (c) 29; (d) 74; (e) 142.

in vacuo, at the desired pretreatment temperature for several hours.

Commercial grade gases used (viz. H_2, He, N_2, CO, CO_2, and O_2) were purified by passage through packed columns of $Mg(ClO_4)_2/P_2O_5$ and BASF R3-11 for removal of H_2O and O_2, respectively, and by trap-to-trap distillations, where appropriate. Isotopically enriched gases were purchased from Prochem, Ltd.; these were ^{13}CO (99.5 atom %) and $^{18}O^{18}O$ (99.8 atom %).

The solvents, n-pentane and n-heptane, used for recrystallizations and extractions and IR solvents were stored over Na and purged with N_2 before use.

Measurements. The IR gas cell shown in Figure 1 and those previously described[7,17] were used for deposition, manipulation, and IR spectral studies of the oxide-supported cobalt carbonyls. Following pretreatment in the oven section of the cell, the support was positioned opposite the entrance to the sublimator bulb and exposed to the cobalt carbonyl vapors. The adsorption of significant quantities of the cobalt carbonyls on the KBr cell windows was not a problem with this technique. This is partly because of the greater distance from the sublimator port to the windows but more importantly because the surface area of the support pellet was on the order of 10^4 greater than that of the windows. Absence of any problem of this kind was confirmed by blank IR spectra obtained after loading the pellet in the cell but before the pellet was positioned between the IR windows. No trace of $\nu(CO)$ bands could be observed under these conditions. Loading was monitored by recording the development of IR bands in the $\nu(CO)$ region. With the attached in-line manometer and molecular sieve sorption pump, the cell functioned as a self-contained gas manipulation system. This configuration, which was used routinely for the recording of sequential spectra, allowed the sample within the cell to remain fixed in the IR beam during gas pressure manipulations, controlled introduction of the cobalt carbonyls onto the pretreated oxide supports, and subsequent additions or removals of gases. IR spectra could thus be recorded and band intensities of all of the spectra compared without concern for errors associated with changing base lines due to removal of the cell from the spectrometer between spectra. The composite spectra shown in Figures 2, 4, and 5 were recorded using this technique.

Often it was possible to extract an adsorbed cobalt carbonyl from the oxide supports, with aliphatic hydrocarbons. Two techniques were employed. In the first, the cell's magnet travel tube was removed under positive N_2 pressure; the solvent was then introduced and later removed

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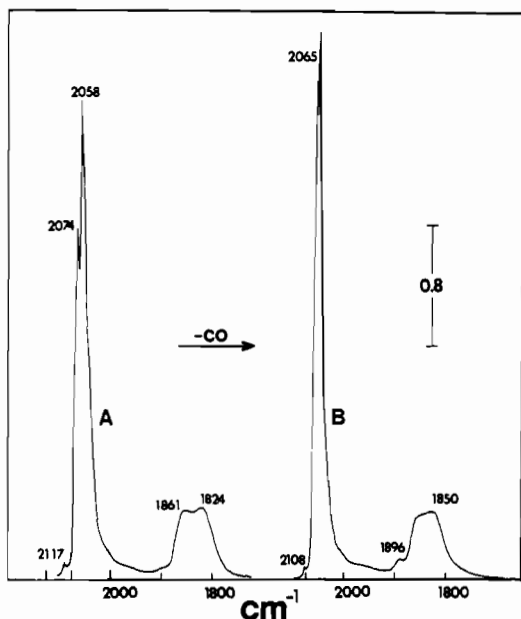
Figure 3. Difference IR absorbance spectra in the $\nu(CO)$ region showing conversion of $Co_2(CO)_8/SiO_2$ (A) to $Co_4(CO)_{12}/SiO_2$ (B) upon removal of CO from the gas cell.
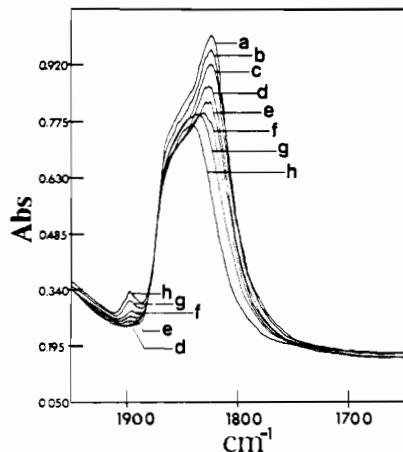

Figure 4. IR absorbance spectra in the $\nu(CO)$ region for bridging carbonyls showing the gradual conversion from $Co_2(CO)_8$ to $Co_4(CO)_{12}$ on the silica support as CO pressure is gradually reduced. CO pressures at which the spectra were recorded (torr): (a) 55; (b) 47; (c) 36; (d) 25; (e) 19; (f) 12; (g) 8; (h) 0.01.

Figure 5. Difference IR absorbance spectra in the $\nu(CO)$ region for $Co_2(CO)_8$ sublimed, in vacuo, onto silica–alumina that had been vacuum heated at 675 K. Spectra a–g show loading sequence as $Co_2(CO)_8$ is sublimed onto the support for the following cumulative times (min): (a) 15; (b) 40; (c) 56; (d) 93; (e) 118; (f) 132; (g) 206. The sublimator was closed at 132 min. Spectrum h shows conversion to $Co_4(CO)_{12}$ as CO was removed.

with hot perchloric acid and hydrofluoric acid.[19] The method gave a linear response for samples containing microgram quantities of Co used in this study. Loadings were typically 0.5–2.0% by weight cobalt corresponding to ~5–20% of a monolayer in these samples.

Gas handling and measurement were conducted in a glass–metal hybrid vacuum system equipped with a BET-type gas adsorption measurement section, a gas recirculation pump and loop, and a sampling loop with appending GC column leading to a TCD (Gow-Mac W2X with Re–W filaments). The GC column was packed with carbon molecular sieves (Carbospheres from Alltech Associates) that provide good separation of O_2, CO, CO_2, and CH_4. Column temperature was typically 115 °C, and the TCD cell temperature was 150 °C.

Pressure measurements, for BET determinations and manometry, used a manometer–cathetometer combination. A Hg-filled, mass-calibrated, gas buret served as the volume standard for manometry and as a means of Toepler pumping gases for their measurement.

Results

Adsorption. On Silicas. When $Co_2(CO)_8$ is sublimed in vacuo onto a silica support, the IR spectrum of the resulting sample indicates an immediate conversion to $Co_4(CO)_{12}$ has occurred. Indeed, $Co_4(CO)_{12}$ may be sublimed *directly* onto the same support to produce a sample with spectrum identical with that obtained by subliming $Co_2(CO)_8$. The only difference is the longer time required to obtain equivalent spectral intensity when the sparingly volatile $Co_4(CO)_{12}$ is the sublimate. When an IR wafer sample loaded in this manner with either cobalt carbonyl is immersed in *n*-pentane, by using Schlenk procedures, the IR spectrum of the resulting extract solution exactly matches that obtained for a sample in which $Co_4(CO)_{12}$ is directly dissolved in *n*-pentane, and the IR wafer now displays only a very weak $\nu(CO)$ spectrum due to residual cobalt carbonyl. The $\nu(CO)$ frequencies of this residual spectrum match those observed before extraction.

with the dissolved carbonyl with use of a long-needled syringe. The second method employed a Schlenk design solution well which, under a N_2 purge, replaced the bottom IR window section of the cell. Elaboration of this technique is provided elsewhere.[14]

IR spectra were recorded on Beckman IR-12 and Nicolet MX-1 Fourier transform infrared spectrophotometers. Spectra on the Beckman instrument were recorded after gain and slit adjustments brought the single-beam energy level to 50–60% in a nonabsorbing region near 2000 cm⁻¹ for a given sample. Scattering by the oxide wafers was sufficient to limit spectral resolution to 2–5 cm⁻¹ if sufficient energy was to enter the spectrophotometer. The Nicolet MX-1 spectra were, typically, the result of 128 interferograms. Spectral resolution was 2 cm⁻¹. Longer measurement times (480 scans) were used to resolve $\nu(OH)$ bands of the alumina and silica supports.

Mass spectra were obtained by transferring gas aliquots to a Hitachi RMU 6D mass spectrometer operating at 70-eV ionization energy or by using a Molytek Spectromass 80 RGA attached to the vacuum system.

The determination of cobalt on the oxide supports was by Galbraith Laboratories, Inc., and by in-house atomic absorption and colorimetric analyses. Atomic absorption measurements were made on a Perkin-Elmer 360 spectrophotometer. The colorimetric analysis used the method developed by Clark[18] on samples solubilized by treatment
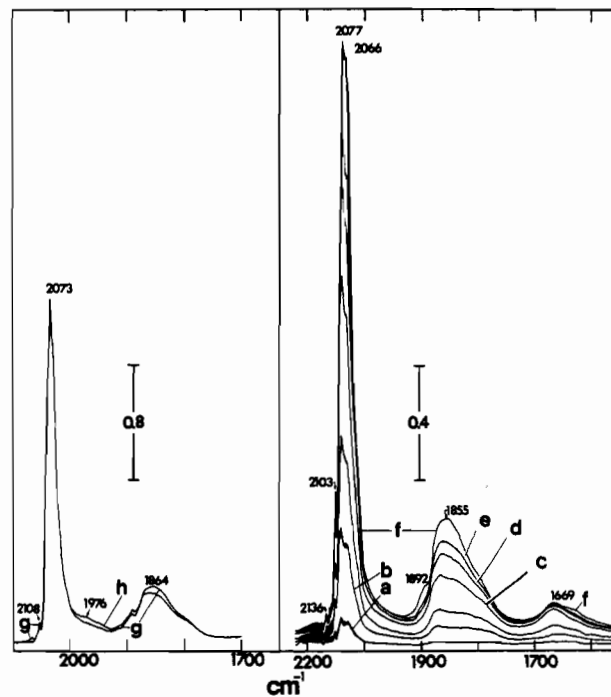
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Table I. Frequencies[a] Reported for $Co_2(CO)_8$ and $Co_4(CO)_{12}$ in Various Environments

	$\nu(CO)$ for $Co_2(CO)_8$	$\nu(CO)$ for $Co_4(CO)_{12}$
solid (Nujol mull)[b]	2112 (w), 2067 (s), 2063 (sh), 2054 (m), 2040 (s), 2029 (sh), 2021 (s), 1864 (m), 1854 (m)	2106 (w), 2067 (sh), 2062 (s), 2053 (s), 2036 (sh), 2027 (m), 1896 (w), 1857 (s)
alkane[c,d]	2112 (w), 2071 (s), 2044 (s), 2042 (s), 2035 (m), 2021 (s), 1867 (m), 1857 (m)	2104 (w), 2063 (s), 2054 (s), 2037 (m), 1898 (m), 1866 (m)
silica surface[b]	2116 (w), 2078 (s), 2052 (s), 2035 (sh), 1861 (m), 1824 (m)	2109 (w), 2072 (s), 2061 (sh), 1999 (sh), 1892 (w), 1846 (m)
silica–alumina surface[b]	2126 (w), 2077 (s), 2064 (s), 1850,[e] 1810[e]	2108 (w), 2073 (s), 1892 (w), 1859 (m)
alumina surface[e]	2127 (w), 2070 (s), 1795 (w)[e]	2108 (w), 2075 (s), 1795 w[e]
^{13}CO-substituted sample on silica		2052 (w), 2015 (s), 2007 (s), 1993 (sh), 1981 (m), 1849 (w), 1825 (s)

[a] Frequencies in cm^{-1}. [b] Frequencies from this work. [c] Alkane is *n*-hexane for $Co_2(CO)_8$ and *n*-pentane for $Co_4(CO)_{12}$. [d] Frequencies from K. Noack, *Spectrochim. Acta*, 19, 1925 (1963) for $Co_2(CO)_8$. [e] Bands were partially obscured by bands due to other species or were shoulders on bands due to other species.

Alternatively, $Co_2(CO)_8$ may be sublimed onto a silica wafer under CO (50 torr), and the IR spectrum of the resulting sample differs significantly—especially in the bridging $\nu(CO)$ region—from that obtained by sublimation under a vacuum. Removal of CO from this sample effects the rapid conversion to a sample with an IR spectrum typical of that of the Co_4-$(CO)_{12}/SiO_2$ sample obtained by sublimation under a vacuum.

Figure 2 shows a series of spectra obtained as dicobalt octacarbonyl is added to Cab-O-Sil under 56 torr of CO. The pattern of bands in Figure 2 closely resembles that for Co_2-$(CO)_8$ as a Nujol mull or in solution, but with some significant shifts in frequency. Table I, which compares the frequencies of various species on the supports with their frequencies in solution, shows the silica-supported $Co_2(CO)_8$ exhibits a shift of about 30 cm^{-1} to lower frequency for the B_2 bridging carbonyl band (1824 cm^{-1} in Figure 2) and smaller shifts (5–10 cm^{-1}) to higher frequency for the terminal carbonyl absorptions as compared with the same vibrational bands for the solution form.

The silica surface $\nu(OH)$ bands also are shown in Figure 2. A silica sample dehydrated at 675 K has a $\nu(OH)$ spectrum dominated by a sharp feature at 3747 cm^{-1}, which has been attributed to vibrations of isolated silanols.[15] ($Co_2(CO)_8$ is transparent in this region.) Adsorption of $Co_2(CO)_8$ reduces the intensity of this band, while a broad shoulder, centered at about 3680 cm^{-1}, develops.

Removal of CO from the cell prompts the conversion of the $\nu(CO)$ spectrum of $Co_2(CO)_8/SiO_2$ to that of $Co_4(CO)_{12}/$ SiO_2. The initial (56 torr of CO) and final (10^{-2} torr) spectra in the entire $\nu(CO)$ region are displayed in Figure 3, while the spectral changes in the bridging $\nu(CO)$ region, as CO is gradually removed from the cell, are shown in Figure 4. These spectra show that total conversion is not attained until P_{CO} is reduced below 7 torr.

The spectra shown in Figure 4, for each P_{CO}, were obtained within 2 min after reduction of the pressure to the measured value; no further spectral changes occurred with extended exposure of the sample to CO at this pressure. Despite this rapid conversion to the tetracobalt compound as the CO pressure was reduced, the reverse reaction could not be effected at a detectable rate even under more than 1 atm of CO.

Confirmation of the straightforward conversion, on silica, of the dicobalt to the tetracobalt carbonyl compound (reaction 1) was obtained by manometric measurements that provided

$$2Co_2(CO)_8 \rightarrow Co_4(CO)_{12} + 4CO \qquad (1)$$
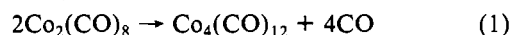
some insight into the stoichiometry of the reactions on the support surface. The experiment was conducted in two steps. In the first, $Co_2(CO)_8$ was added, by sublimation, to the silica gel under 50 torr of CO pressure. An IR wafer was present, in addition to the bulk sample, so the spectrum could be monitored during the loading process. The pressure in the cell then was reduced by Toepler expansion of the system until the

IR spectrum converted to that of $Co_4(CO)_{12}/SiO_2$. The CO in the system increased during this process by 5.4×10^{-5} mol. This was the CO evolved during the spontaneous room-temperature conversion to $Co_4(CO)_{12}$. Mass spectrometric analysis showed this gas contained only CO, and analysis of the sample for cobalt, after completion of the experiment, showed the presence of $4.8 \pm 0.4 \times 10^{-5}$ mol of Co in the sample. Thus, the conversion reaction generated 1.1 ± 0.1 mol of CO/mol of cobalt present, consistent with the stoichiometry of reaction 1.

The second part of the manometric experiment, conducted in two steps, involved thermal decomposition of $Co_4(CO)_{12}$ at 375 K followed by evolution of surface-adsorbed reaction products by heating to 685 K under oxygen. Heating to 375 K resulted in complete loss of $Co_4(CO)_{12}$, as demonstrated by the $\nu(CO)$ spectrum of the sample. This produced 12.8×10^{-5} mol of CO, which included a trace of CO_2. Heating to 685 K under O_2 released 3.6×10^{-5} mol of CO_2. The total gas evolved (CO and CO_2) as the sample was heated and the $Co_4(CO)_{12}$ decomposed and oxidized was 16.4×10^{-5} mol (3.4 ± 0.3 mol of C/mol of cobalt). This agrees with the stoichiometry expected for decomposition of $Co_4(CO)_{12}$. It is important to note also that the ratio of moles of carbon evolved during the room-temperature conversion to that evolved by heating to 685 K is 1:3, as required.

In a separate experiment, it was noted that extended evacuation (more than 6 h) of $Co_4(CO)_{12}/SiO_2$ converted the IR spectrum to one with just one broad feature near 2000 cm^{-1}. Subsequent exposure of this sample to 80 torr of CO regenerated an intense carbonyl spectrum, but this spectrum appeared to contain bands due to both $Co_4(CO)_{12}$ and $Co_2(CO)_8$. Evacuation converted this sample to one displaying only the spectrum of $Co_4(CO)_{12}$, but this spectrum also reverted gradually, after extended evacuation, to one with the single feature near 2000 cm^{-1}. Admission of O_2 to the sample resulted in the loss of all vestiges of $\nu(CO)$ bands in the IR spectrum.

A facile isotopic exchange of CO ligands has been observed for other metal carbonyl species on oxide supports.[7,17] The addition of 20 torr of ^{13}CO (99.5 atom % ^{13}C) to the sample cell containing $Co_4(CO)_{12}/SiO_2$, at room temperature, resulted in equilibrium exchange of CO ligands within 4 h. This $Co_4(^{13}CO)_{12}$ was extracted from a silica wafer into *n*-pentane. The IR spectrum of the solution obtained is entirely consistent with that expected for the isotopically exchanged form of the sample. This represents an easy method of isotopically enriching this cobalt carbonyl. It required only a small quantity (4.5 cm^{-3} of NTP) of highly enriched ^{13}CO for nearly total exchange, in 4 h, of about 0.2 mg of $Co_4(CO)_{12}$.

On Silica–Alumina. As for silica, the adsorption, by sublimation, of $Co_2(CO)_8$ onto a silica–alumina (SA) sample (88% SiO_2–12% Al_2O_3) shows inhibition of the conversion to Co_4-$(CO)_{12}$ when CO gas is present. Table I and Figure 5 may

be used to compare the frequencies of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ on SA to those recorded for the same compounds on silica. The most noteworthy aspect of the SA results is that 54 torr of CO appears to inhibit only partially the conversion to $Co_4(CO)_{12}$ on the SA surface. This is demonstrated by the development of the weak bridging band at 1892 cm^{-1}, due to $Co_4(CO)_{12}$, as the dicobalt compound is loaded on the SA. The terminal $\nu(CO)$ bands of the dicobalt species appear to be shifted upward more than for the same compound on silica; the bridging bands may shift downward, although this is difficult to determine from the spectra in this region, which are a composite of $Co_4(CO)_{12}$ and $Co_2(CO)_8$ bands. The spectra of the $\nu(OH)$ bands for isolated silanol groups show a shift of about 100 cm^{-1} when the dicobalt adsorbs; this is about 25 cm^{-1} greater than for the silica surface. The larger $\nu(OH)$ shift and larger upward shift of terminal $\nu(CO)$ bands both imply stronger H bonding through the bridging carbonyls to presumably more acidic groups on the silica/alumina surface.

The spectrum also shows the development of a weak set of bands between 1900 and 2000 cm^{-1} when in vacuo conversion to the tetracobalt cluster occurs. These seem to parallel bands observed for the cobalt carbonyls on γ-Al_2O_3, discussed below, and may, therefore, be due to chemistry at "alumina-like" sites on the SA. These bands disappear immediately when the sample is exposed to dioxygen, while the $Co_4(CO)_{12}$ bands disappear only after several hours of exposure to O_2.

A more remarkable observation during the study of the oxidation of $Co_4(CO)_{12}$ on the SA was made when the dioxygen was $^{18}O^{18}O$. The evolved gas, shown by mass spectral analysis to be mostly CO with a smaller amount of CO_2, was nearly 50% $C^{18}O$, indicating interactions between O_2 and CO that do not produce CO_2 but result in exchange of oxygen atoms.

On Al_2O_3. γ-Alumina provides a much more reactive surface for the cobalt carbonyls than does either silica or the silica–alumina sample used. Figure 6 shows the series of spectra obtained when $Co_2(CO)_8$ was sublimed onto γ-Al_2O_3 pretreated at 775 K (γ-Al_2O_3 (775 K)). Carbon monoxide is evolved during this adsorption process, and the spectrum developed (Figure 6) is dominanted by bands not observed on silica or the SA sample. These new bands are near 2100, 2040, 2000, and 1960 cm^{-1}. Only the band near 2070 cm^{-1} and one of the bands in the bridging CO region, that at 1800 cm^{-1}, may be due to either $Co_2(CO)_8$ or $Co_4(CO)_{12}$ on the alumina surface. Extended evacuation of this sample (Figure 6C) results in the diminution of the bands at 2100 and 2040 cm^{-1} and development of a band at 2000 cm^{-1} but affects the other bands in the spectrum very little. Exposure to dioxygen of this and all other cobalt carbonyl samples on γ-alumina results in the loss of all $\nu(CO)$ bands in minutes. When $Co_4(CO)_{12}$ is sublimed directly onto γ-Al_2O_3, the spectra are identical with those shown in Figure 6 for which $Co_2(CO)_8$ was the starting material.

Reaction of both cobalt carbonyls with the alumina surfaces also generates a series of bands below 1700 cm^{-1}, which have been assigned to carbonate or bicarbonate on alumina.[16] These are at 1649, 1487, and 1240 cm^{-1}. They appear to result from oxidation of the cobalt carbonyl by reaction with the oxide surface at room temperature to form CO_2 which then adsorbs as a carbonate species. These bands also develop when an adsorbed cobalt carbonyl sample is exposed to dioxygen.

Similar IR spectral studies were conducted for $Co_2(CO)_8$ or $Co_4(CO)_{12}$ adsorbed on Al_2O_3 (525 K), Al_2O_3 (475 K), and Al_2O_3 (295 K). The same spectral features, with similar intensity ratios, are observed, but a band centered near 1900 cm^{-1}, which appears as only a weak shoulder on the side of the 1960-cm^{-1} peak in Figure 6B, becomes an important
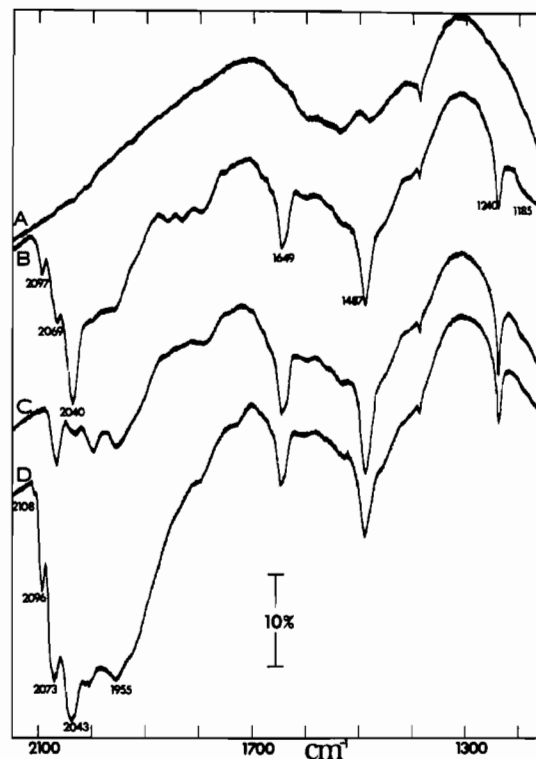

Figure 6. IR transmittance spectra in the region 1150–2200 cm^{-1} for $Co_2(CO)_8$ sublimed onto γ-Al_2O_3 (775 K). The spectra are recorded for (A) wafer of γ-Al_2O_3 that had been pretreated at 775 K, in vacuo, for 4 h, (B) wafer after exposure to subliming $Co_2(CO)_8$ for 5 min, (C) same sample as in (B) but after 8 h of room-temperature evacuation, and (D) sample after reexposure to $Co_2(CO)_8$ for 5 min at room temperature.

feature in the spectrum of $Co_2(CO)_8$ sublimed onto γ-Al_2O_3 (295 K). On the other hand, the carbonate bands are relatively weak in the spectrum on the latter support.

As with the silica-supported cobalt carbonyls, addition of ^{13}CO leads to exchange with all CO's of the surface carbonyl species. Not all the carbonyls exchange at the same rate, however, as demonstrated by the fact that a *limited* dose of ^{13}CO leaves some bands virtually unaffected. For example, addition of a small dose of ^{13}CO to a sample like that producing the spectrum in Figure 6B leaves the band at 2069 cm^{-1} unaffected, while all other $\nu(CO)$ bands in the spectrum appear to shift. Exposure for more than 1 h, though, to a stoichiometric excess of ^{13}CO also shifts the 2069-cm^{-1} band. This difference in exchange rates aids in identifying bands in the spectrum that are due to different types of carbonyl ligands.

Discussion and Conclusions

Silica Supports. Accumulated data for metal carbonyls on silica clearly establish this support surface as being much more passive toward the carbonyls than are aluminas, zeolites, and magnesia.[20] In many cases, the room-temperature addition of a metal carbonyl to a silica surface results in weak adsorption of the parent compound; conversion to other carbonyls or decomposition occurs only at elevated temperature (100 °C).

Sublimation, in vacuo, of $Co_2(CO)_8$ onto silica or silica-alumina surfaces results in nearly stoichiometric conversion of this compound to $Co_4(CO)_{12}$. This is evidenced by the IR spectrum that develops in the $\nu(CO)$ region; the spectrum closely resembles that of $Co_4(CO)_{12}$ in solution and is identical with the $\nu(CO)$ spectrum obtained when $Co_4(CO)_{12}$ is sublimed directly onto the same surface. This conclusion also is

(20) Bor, G.; Dietler, U. K. *J. Organomet. Chem.* **1980**, *191*, 295.

supported by the fact that $Co_4(CO)_{12}$ may be extracted from a silica surface displaying this $\nu(CO)$ spectrum, by the evolution of about 1 mol of CO/mol of cobalt deposited, consistent with reaction 1, and by the ultimate evolution of about 3 mol of carbon (as CO or CO_2)/mol of Co, upon subsequent heating and oxidation of the cobalt carbonyl deposited on the silica.

Carbon monoxide, at pressures above 50 torr, completely suppresses the conversion of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ on the silica, but reduction of P_{CO} leads to rapid conversion of the dicobalt compound until, at pressures below 7 torr, complete conversion is achieved. Surprisingly, even though this conversion to $Co_4(CO)_{12}$ is quite rapid in the forward direction of reaction 1, direct reversal of the reaction does not occur at a detectable rate even at P_{CO} values in excess of 1 atm.

As is mentioned above, some $Co_2(CO)_8$ appeared to be regenerated by exposure to CO of a silica-supported intermediate—presumably a sub-carbonyl with a single broad band at 2000 cm^{-1}—which is formed by prolonged evacuation of a $Co_4(CO)_{12}/SiO_2$ sample. This suggests that Co_2/Co_4 conversion goes by way of a two-step mechanism requiring a species of reduced carbonyl composition (e.g., $Co(CO)_2 \cdot nS$ where S represents a surface site). This sub-carbonyl might not be present at the CO pressures under which direct regeneration of $Co_2(CO)_8/SiO_2$ from $Co_4(CO)_{12}/SiO_2$ was attempted in these experiments. Solution reactions converting $Co_2(CO)_8$ to $Co_4(CO)_{12}$ via disproportionation to mononuclear cationic and anionic cobalt species have been reported and discussed.[21-23] Similar reactions may connect the two neutral cobalt carbonyls on silica.

The nature of the interaction between a metal carbonyl and the oxide support surface may be studied by monitoring the $\nu(OH)$ region for changes that occur upon adsorption. The sharp $\nu(OH)$ band near 3750 cm^{-1} for partially dehydroxylated silicas provides a convenient indicator of adsorption effects on surface OH groups. Figure 2 shows the shift in $\nu(OH)$ observed as $Co_2(CO)_8$ adds to a partially dehydroxylated silica surface. This shift indicates rather weak H bonding. Indeed, a specific heat of adsorption of 1 kcal/mol of H bonds may be estimated on the basis of a correlation that has been established between $\Delta\nu(OH)$ and ΔQ_a for a series of adsorbates on silica.[24]

Hydrogen bonding to $Co_2(CO)_8$ would be favored to occur through the oxygens of the bridging carbonyls; these are the most basic carbonyl oxygens as demonstrated by their propensity toward formation of acid–base adducts with strong Lewis acids.[25] Such hydrogen bonding would explain the shifts in $\nu(CO)$ frequencies observed for $Co_2(CO)_8$ as it adds to silica; viz., the bridging $\nu(CO)$ band, of B_2 symmetry, is shifted 30 cm^{-1} to lower frequency, and the terminal CO frequencies move 5–10 cm^{-1} to higher frequencies. The downward shift for the bridging CO's is that expected for the direct effect of weak H bonding to those ligands, while the frequency shift for the terminal CO's is the indirect effect of shifting electron density from cobalt to the bridging CO ligands upon formation of the H bonds to the surface. Similar, though larger, effects on $\nu(OH)$ and $\nu(CO)$ have been reported for $Fe_3(CO)_{12}$ on H–Y zeolite,[26] and the following paper[14] discusses the same pattern of shifts in $\nu(CO)$ and $\nu(OH)$ frequencies for cobalt carbonyl on hydrogen zeolites. The

Table II. Assignment of $\nu(CO)$ Bands to Different Carbonyl Groups on Alumina Supports

species	$\nu(CO)$, cm^{-1}	species	$\nu(CO)$, cm^{-1}
$Co_4(CO)_{12}$	2108, 2075, 1795	α^c	2098, 2038
$Co_2(CO)_8$ ^{a}	2128, 2070, 1795	β^c	1995–2005, 1948–1955
$Co(CO)_4^-$ ^{b}	1940 (sh), 1900, 1870 (sh)		

^{a} The bands assigned to this species appear as weak features when a sample is loaded under 35 torr CO(g). ^{b} Present in significant quantities only on Al_2O_3 (295 K). ^{c} Assignment is based on spectra like those in Figure 6, spectra B–D.

magnitudes of the reported shifts are indicative of stronger H bonding with the zeolite. Similarly, the SA support exhibited $\Delta\nu(OH)$ values, upon H-bond formation with $Co_2(CO)_8$, that are 25 cm^{-1} greater than for the pure silica, and the shifts in $\nu(CO)$ for $Co_2(CO)_8$ on SA also appear larger than for the same compound on silica. It is important to note, however, that when reactivities with the surfaces are compared, two different types of surface reactivities are discussed. First, the initial interaction via H bonding that increases with the acidity of surface sites is observed. Second, chemical reactivity with the surfaces appears to be enhanced by strongly basic sites that may act as nucleophiles attacking carbonyl carbons.

Consistent with observations for cobalt carbonyls on more active supports (Al_2O_3 or MgO),[29] the new carbonyl species formed by prolonged evacuation or by thermal treatment of $Co_2(CO)_8$ or $Co_4(CO)_{12}$ on silica or SA, and represented by bands between 1900 and 2020 cm^{-1}, are rapidly oxidized by O_2, while the parent compounds ($Co_2(CO)_8$ and $Co_4(CO)_{12}$) are far less reactive toward O_2. The major species released during oxidation by O_2 is CO rather than CO_2. This may be rationalized by proposing a reaction in which the first oxidation step proceeds to form an oxidized cobalt complex and one CO ligand oxidized to CO_2 or CO_3^{2-}. The CO ligands remaining on the cationic cobalt carbonyl product would be labile and might be spontaneously evolved at the low pressures employed.

The detection of large quantities of $C^{18}O$, when the oxygen used for oxidation is $^{18}O^{18}O$, is more surprising. The same results are reported for reaction of $^{18}O^{18}O$ with cobalt carbonyl species on a zeolite, and an explanation is proposed in the report of those experiments.[14]

Finally, the facile exchange of CO ligands in $Co_4(CO)_{12}/SiO_2$ presents a ready means of preparing the totally exchanged form. The $\nu(CO)$ spectrum of $Co_4(^{13}CO)_{12}$ in n-heptane (Table I) represents the first reported for the fully ^{13}CO-exchanged compound. This facile exchange of CO ligands seems a common property of oxide-supported metal carbonyls and should be considered as a generally applicable approach to preparing isotopically exchanged metal carbonyls.

Alumina Surfaces. The chemistry that results from the addition of $Co_2(CO)_8$ or $Co_4(CO)_{12}$ to alumina is more complex than for these compounds on silica, although the spectrum for a given alumina support with a particular set of pretreatment conditions is independent of whether $Co_2(CO)_8$ or $Co_4(CO)_{12}$ is the source of the cobalt carbonyl. This observation implies $Co_2(CO)_8$ is converted to $Co_4(CO)_{12}$ on this support, as on silica and silica–alumina. The $Co_4(CO)_{12}$ that forms must, however, be rapidly converted to the several new species observed on the alumina.

The identical nature of samples prepared by sublimation of either $Co_2(CO)_8$ or $Co_4(CO)_{12}$ onto γ-Al_2O_3 is relevant to the report by Brenner and Hucul[8] for these compounds on this support. Their TPDE studies, if considered in terms of mol of evolved gas/mol of Co on the support, appear to be con-

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(22) Chini, P.; Albano, V. *J. Organomet. Chem.* **1968**, *15*, 433.
(23) Chini, P. *Pure Appl. Chem.* **1970**, *23*, 489.
(24) Kiselev, A. V. *Surf. Sci.* **1965**, *3*, 292.
(25) Shriver, D. F.; Alicki, A. *Coord. Chem. Rev.* **1972**, *8*.
(26) Ballivet-Tkatchenko, D.; Coudurier, G. *Inorg. Chem.* **1979**, *18*, 558.
(27) Wender, I.; Steinberg, H. W.; Orchin, M. *J. Am. Chem. Soc.* **1952**, *74*, 1216.
(28) Brown, T. L. *J. Mol. Catal.* **1981**, *12*, 41.

(29) Gopal, P.; Watters, K. L. *Proc. Int. Congr. Catal.* **1984**, *8*.

sistent, generally, with the identical nature of samples prepared by adding $Co_2(CO)_8$ or $Co_4(CO)_{12}$ to alumina.

The abundance of spectra recorded for samples with a variety of treatment histories and the observation of differing ^{13}CO exchange rates for different $\nu(CO)$ bands permit the identification of groups of bands that appear and disappear together under various treatments and shift at the same rate with sample exposure to ^{13}CO. Each of these bands or sets of bands may be assigned to a unique type of CO ligand. The sets of bands identified in this manner are listed in Table II. The types of CO's identified in Table II are not necessarily carbonyls on chemically different cobalt atoms. The identification of unique CO's depended, in part, on differing ^{13}CO exchange rates, and it is conceivable that different types of CO on the same cobalt (e.g., bridging and terminal CO's on a bi- or polynuclear species) might exchange at different rates, especially in view of the fact that adsorption on the surface might preclude some mechanisms for intramolecular exchange. On the other hand, bands that appear or disappear at different rates during evacuation, carbonylation, or oxidation must be due to CO ligands on chemically different cobalt atoms since oxidation or a change in the number of CO ligands for a given cobalt carbonyl species should change the $\nu(CO)$ values for all CO ligands bonded to that Co atom.

The previous report for the compound $(CO)_9Co_3CCH_3$ on several oxide supports identified $Co(CO)_4^-$ as a product of the reaction of that compound with Al_2O_3.[7] The $Co(CO)_4^-$ on alumina displayed a strong band near 1900 cm^{-1} with shoulders at about 1930 and 1870 cm^{-1}. (The presence of the shoulders was explained in terms of loss of strict tetrahedral symmetry due to surface adsorption.) This species may be formed by reactions of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ with alumina but, if so, is responsible for only a weak shoulder, near 1900 cm^{-1} in most spectra, on the side of the more intense broad band centered near 1950 cm^{-1}. The adsorption of $Co_2(CO)_8$ on Al_2O_3 (*295 K*) results, though, in a definite feature near 1900 cm^{-1} and a shoulder near 1870 cm^{-1}. This feature strongly resembles the bands assigned to $Co(CO)_4^-/Al_2O_3$ in the earlier study.

The Al_2O_3 (295 K) also displays less tendency to form surface carbonates upon reaction with $Co_2(CO)_8$ or $Co_4(CO)_{12}$. An increased propensity on Al_2O_3 (295 K), as compared with dehydrated aluminas, to form $Co(CO)_4^-$ and a diminished tendency to generate surface carbonates also was observed in reactions of $(CO)_9Co_3CCH_3$ with alumina surfaces.[7] Both differences may be explained by the presence of layers of water on Al_2O_3 (295 K). Reactions of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ with water are known to produce $Co(CO)_4^-$ from cobalt carbonyls.[27] The "wet" alumina may, therefore, favor this reaction. Meanwhile, the presence of water on the surface provides loosely bound oxygens that can add to CO in the initial oxidation reaction and be released as CO_2 rather than being bound to the surface as adsorbed carbonates. This would explain the reduced inclination of the wet support to form carbonates upon contact with the cobalt carbonyls. This feature of wet alumina surfaces has been discussed recently by Brown.[28]

The identities of species α and β of Table II are uncertain. The observed frequencies and the intensity ratios do not correspond directly to those of any reported cobalt carbonyl species. Bands like those observed between 1900 and 2030 cm^{-1} for the cobalt carbonyls on alumina seem unbiquitous to reactions of these carbonyls on active oxides. IR spectra for $Co_2(CO)_8$ sublimed onto Al_2O_3, zeolites,[14] and MgO[29] show, in each case, bands similar to those in Figure 6. These bands, formed on evacuation and/or heating below 150 °C, usually disappear upon addition of CO(g), and the parent carbonyl bands redevelop. The species responsible for the bands in the 1900–2030-cm^{-1} region are, then, reversibly related to the parent carbonyl. Sub-carbonyls such as $Co_n(CO)_{12-n}$ are implicated. Further discussion of the reactions on the oxide surface are provided in the following paper.[14]