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Interactions of Cobalt Carbonyls with Oxide Surfaces

I. $(CO)_9Co_3CCH_3$ on Silicas, Aluminas, and Zeolites

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The adsorption and subsequent reactions of the cobalt cluster compound μ_3-ethylidine-tris-(tricarbonyl cobalt), **I**, on silica, alumina, and zeolite supports were investigated. The supports were pretreated, *in vacuo*, at temperatures between 295 and 700K. On silica, **I** appears to be physisorbed and reacts only slowly with O_2 to produce decarbonylated products. Adsorption on alumina produces physisorbed **I** and at least three cobalt carbonyl products of the reactions of **I** with the support. Aluminas pretreated at lower temperatures are the most reactive toward **I**, as evidenced by the greater tendency of **I** to react and form novel cobalt carbonyls on these aluminas. These reaction products are immediatley oxidized by O_2 to produce carbonate, bicarbonate, and oxidized cobalt. Compound **I** adsorbs at room temperature inside the supercages of a Na*Y* zeolite; it is subsequently converted, at elevated temperatures (350K), to the carbonyl species which were identified on alumina. Infrared and manometric data show that thermolysis and oxidation of **I** on zeolite ultimately lead to its total decarbonylation to produce carbonates, bicarbonates, and organic carbonyl fragments.

INTRODUCTION

A substantial body of work has now been reported in which metal carbonyl compounds were adsorbed upon oxide supports and the ensuing chemical and catalytic properties were investigated. Most of the carbonyls studied under these conditions were binary metal carbonyls, $M_x(CO)_y$, although there were exceptions (*1*). A collection of metal carbonyl compounds which are not binary and which have several properties commending them for study as oxide surface adsorbates are the compounds of general formula $(CO)_9Co_3CY$ (Fig. 1), where Y may be one of a variety of possible substituents. The notable properties of these compounds include: (1) the robust nature of the Co_3C kernel, as indicated by mass spectral fragmentation patterns (*2*); (2) the resistance to air oxidation for most members of the series (*3*); (3) the thermal stability of the compounds as solids and in solution; (4) the reported activity of one compound in this series as a hydroformylation catalyst (*4*); (5) the proposed ability of the apical carbon to act as a catalytic center through development of an intermediate carbonium ion or the important precursor species, acylium ion, $(CO)_9Co_3CCO^+$, (*3*); and (6) evidence that the Co_3C fragment may retain its integrity even during Co–Co bond rupture (*5*). Finally, members of this series with a light nonpolar Y group are volatile enough to be vacuum sublimed at room temperature. This allows them to be sublimed directly onto a pretreated oxide surface in order to avoid contamination of that surface by exposure to air or solvent.

As part of our continuing investigation of metal cluster carbonyls on oxide surfaces, we embarked upon a study of the compound $(CO)_9Co_3CCH_3$, μ_3-ethylidyne-tris-(tricarbonyl cobalt), **I**, adsorbed on several oxide supports. Because of the several sites for creation of an unsaturated metal atom and the special nature of the apical carbon, this compound might display properties on

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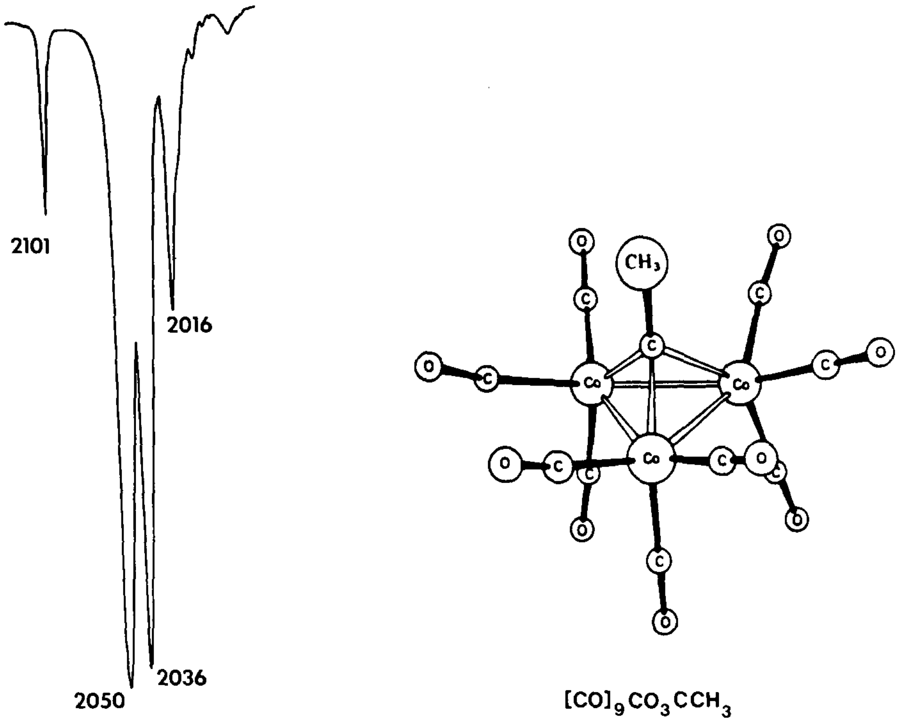


FIG. 1. Structure and ir solution spectrum of $(CO)_9Co_3CCH_3$. Solution spectrum obtained in *n*-pentane.

oxide support surfaces which are of catalytic interest.

The results are reported here for an ir and gas manometric study of **I** on silica gel, γ-alumina, and zeolite supports which were heated *in vacuo* prior to exposure to the subliming metal carbonyl; temperatures of the pretreatment varied from 295 to 700K.

EXPERIMENTAL

Compound **I** was prepared according to the general procedure of Seyferth *et al.* (*6*), by the reaction of 1,1,1-trichloroethane with dicobalt octacarbonyl:

$$H_3CCCl_3 + Co_2(CO)_8 \xrightarrow[40°C]{THF} (CO)_9Co_3CCH_3 + CoCl_2.$$

The reactants and the solvent were purified by appropriate distillation, recrystallization, or sublimation steps prior to the synthesis. The impure **I** product was purified by chromatography on silica gel using *n*-pentane as eluent. Infrared spectra and elemental analysis confirmed the purity. The *n*-pentane and *n*-heptane solvents used during this study were Mallinckrodt AR grade or better and were stored over sodium and purged with N_2 before use.

The Na–Y zeolite (a_s = 800 m^2/g, monolayer equivalent) was Linde SK-40 and Na–A was Linde 4A MS-409. Silicas were Davidson 923 gel (600 m^2/g) and Cabot Corporation M-5 Cab-O-Sil (200 m^2/g), while the γ-alumina was Akzo Chemie CK-300 (160 m^2/g). All oxide powders were washed with double-distilled water and then calcined in air prior to use. The powders were pressed into wafers using pressures up to 30,000 psi (γ-Al_2O_3). Wafer thicknesses were typically 0.33 ± 0.03 mm (5–10 mg/cm^2). The wafers could be used in the sample cell (Fig. 2) in the position for recording ir spectra or were broken into small chips to be placed in the quartz bucket portion of the sample cell during the gas manometric study. The pressed wafers were calcined in air at 400 or 800K (γ-Al_2O_3);

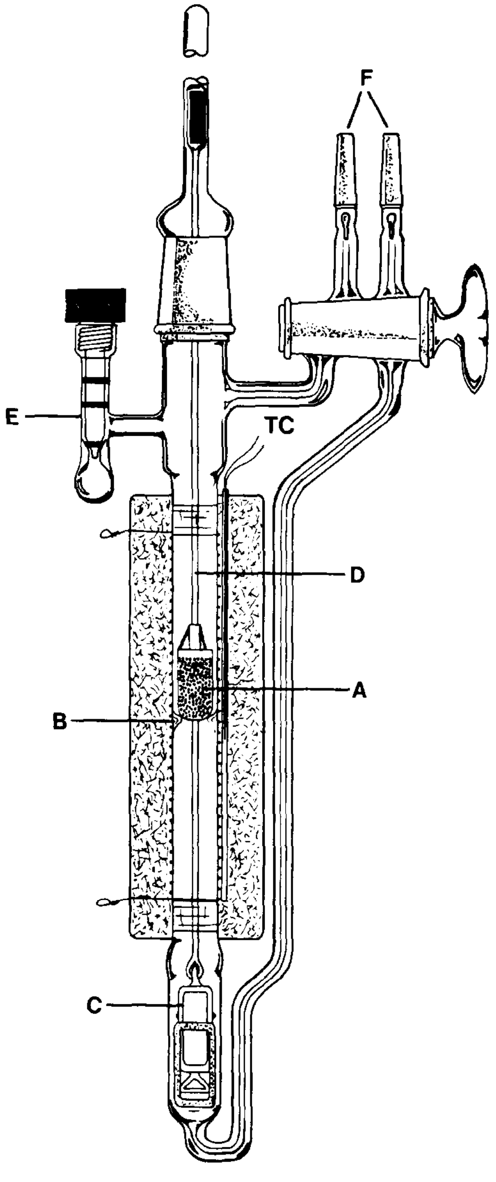


FIG. 2. Sample cell used for ir and manometric studies. Cross section is of bucket (A) within the tube oven section of the cell. The bucket rests on dimples (B) which prevent it from descending with the wafer holder (C) into the ir sampling region of the cell. The magnet extension rod (D) slides through the bucket. Using an external magnet, the rod and attached wafer holder may be raised until the holder contacts the bottom of the bucket. The entire assembly may then be raised until bucket and wafer samples are near the entrance to the sublimator (E). The sublimator consists of a modified size 0-3, teflon-in-glass, O-ring stopcock. The cell, as shown, may be used for recirculating gas studies and is attached to the gas handling system through $\$$ 10/30 joints (F).

they were then heated, *in situ*, under vacuum, at the desired pretreatment temperature before subliming the cobalt carbonyl onto the wafer surface.

Commercial grade gases used (viz., H_2, He, N_2, CO, CO_2, and O_2) were purified by passage through packed columns of $Mg(ClO_4)/P_2O_5$ and BASF R3-11 for removal of H_2O and oxygen, respectively, and by trap-to-trap distillations where appropriate. Isotopically enriched gases were purchased from Prochem, Ltd.; these were ^{13}CO (99.9%) and $^{18,18}O_2$ (99.8%).

Infrared spectra were obtained on a Beckman IR-12 and a Nicolet MX-1 Fourier transform ir spectrophotometer. Fourier transform spectra typically used 128 scans with a resolution of 2 cm^{-1}; longer scan times were used when better resolution or signal/noise ratio was required. The spectra on supports were obtained using the cell shown in Fig. 2 or other cells of more conventional design. The ir wafer could be positioned in the beam between KBr windows for recording spectra, in the oven region for pretreating the support or thermally decomposing the support/cobalt carbonyl sample, or proximate to the sublimation bulb for subliming the carbonyl onto the support.

Mass spectra were obtained using a Hitachi-Perkin-Elmer RMU 6D mass spectrometer or a Molytek Spectromass 80 RGA. Aliquots of gas were taken for analysis by the Hitachi spectrometer, while the RGA was used in-line between the gas source and the vacuum pumps.

Manometric measurements were conducted using a glass-metal hybrid high-vacuum system equipped with a BET-type gas adsorption measurement section. The vacuum system maintained pressures of 10^{-6} Torr. A mercury-filled gas buret served as the volume standard and for Toepler pumping gases into the calibrated volume section for the pressure measurements which used a Hg manometer-cathetometer combination. For manometry, the sample cell was used with the quartz bucket filled with chips of the oxide support wafers. The bucket filled with support chips was necessary to provide enough volume of gas to allow precise measurement of volume (pressure) changes during sample decomposition.

The precision limit for pressure measurements is conservatively estimated as ±0.1 Torr, and the volume of the vacuum system and sample cell totaled 160 cm^{-3}. A volume change of 0.02 CCNTP could, therefore, be observed. The vacuum system has a real leak rate of 2×10^{-7} Torr liters sec^{-1}, which corresponds to 0.01 CCNTP/day. The volume changes measured in experiments reported here were always in excess of 1.0 CCNTP: much larger than the sensitivity limit and leak rate.

The bucket sample and ir wafer were pretreated then raised into position for sublimation of **I** onto the support surfaces. The extent of loading was monitored by occasional recording of ir spectra. When the desired loading was obtained, any evolved gas (CO or CO_2) was expanded into the calibrated volume portion of the system for manometric measurement. Similar steps were followed with evacuation and with each thermal treatment of the sample.

Analysis for coablt on a given support was by atomic absorption using a Perkin–Elmer 360 spectrophotometer and by wet chemical analysis using an adaptation of the method developed by Clark (*7*) on samples solubilized by treatment with hot perchloric acid and hydrofluoric acid. The method gave linear response for samples containing microgram quantities of Co. Some analyses were also performed by Galbraith Laboraotries, Inc., Knoxville, Tennessee.

RESULTS

Infrared spectra obtained when **I** is added to the several support surfaces reflect the marked differences in reactivity of **I** toward these surfaces. Figures 3–8 display the spectra which develop with loading, subsequent evacuation, mild heating, and carbonylation or oxygenation of the silica, alumina, or zeolite supported cobalt carbonyl.

Adsorption on Silica

Adsorption of **I** on a silica gel surface results in a ν(CO) spectrum (Fig. 3) nearly identical to that of **I** in *n*-pentane, featuring ν(CO) bands at 2106, 2053, 2043, and 2021 (sh) cm^{-1}. Besides the ν(CO) bands, peaks at 1690, 1650, 1430, and 1370 cm^{-1} develop in the spectrum. Evacuation for several hours reduces the intensities of bands due to **I** and of all the lower frequency bands. As has been mentioned, **I**, as a solid or in solution, is relatively insensitive to oxygen. Addition of oxygen to the silica supported material, however, results in the gradual disappearance of all ν(CO) bands. This is accompanied by intensification of all four bands observed below 1700 cm^{-1} (spectrum 3D). This oxidation is attended by a color change from burgundy for the parent carbonyl on silica to grey for the oxidized form. The oxidized sample was then exposed to H_2 and CO at 675K, but no bands characteristic of cobalt carbonyl species were observed in the ir spectrum obtained after cooling the sample to room temperature.

Figure 3 displays the spectra obtained for **I** sublimed onto silica pretreated at 475K. Silica materials pretreated at different temperatures produced, when reacted with **I**, results essentially identical to those in Fig. 3.

Adsorption on γ-Alumina

In contrast with the silica results, the reactivity of **I** toward γ-alumina surfaces was greatly affected by the pretreatment temperature. Figures 4 and 5 show series of ir spectra for **I** sublimed onto γ-aluminas pretreated at 295K (Al_2O_3 (295K)) and 525K (Al_2O_3, (525K)), respectively. An alumina pretreated at 700K was also studied, but the results were nearly identical to those obtained for Al_2O_3 (525K). Upon contact with Al_2O_3 (295K), **I** is partially converted to new species with ν(CO) bands between

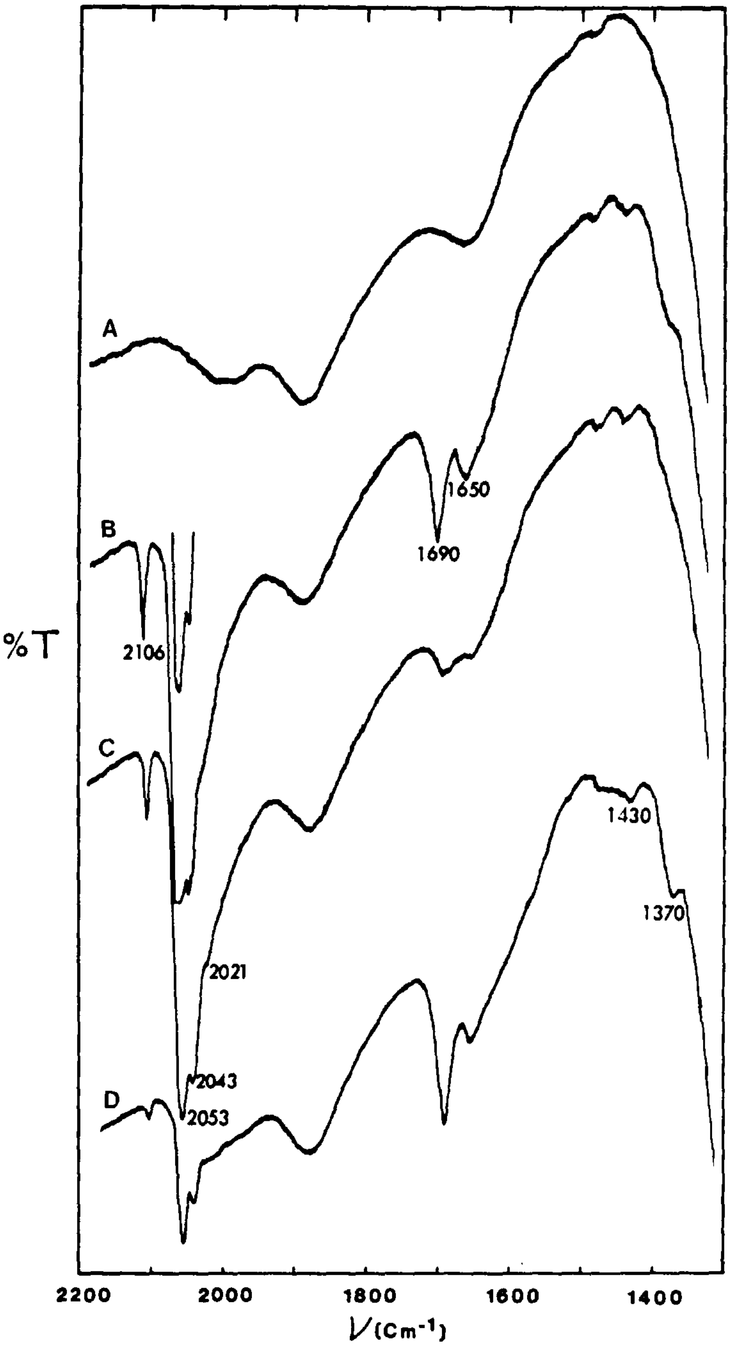


FIG. 3. Infrared transmittance spectra (1300–2200 cm^{-1}) for **I** sublimed onto silica which had been preheated, *in vacuo*, at 475K. Spectra are for (A) silica after preheating and before exposure to **I**; (B) sample after 45-sec exposure to subliming **I**; (C) sample evacuated 12 hr at room temperature; and (D) sample exposed to O_2 for 12 hr.

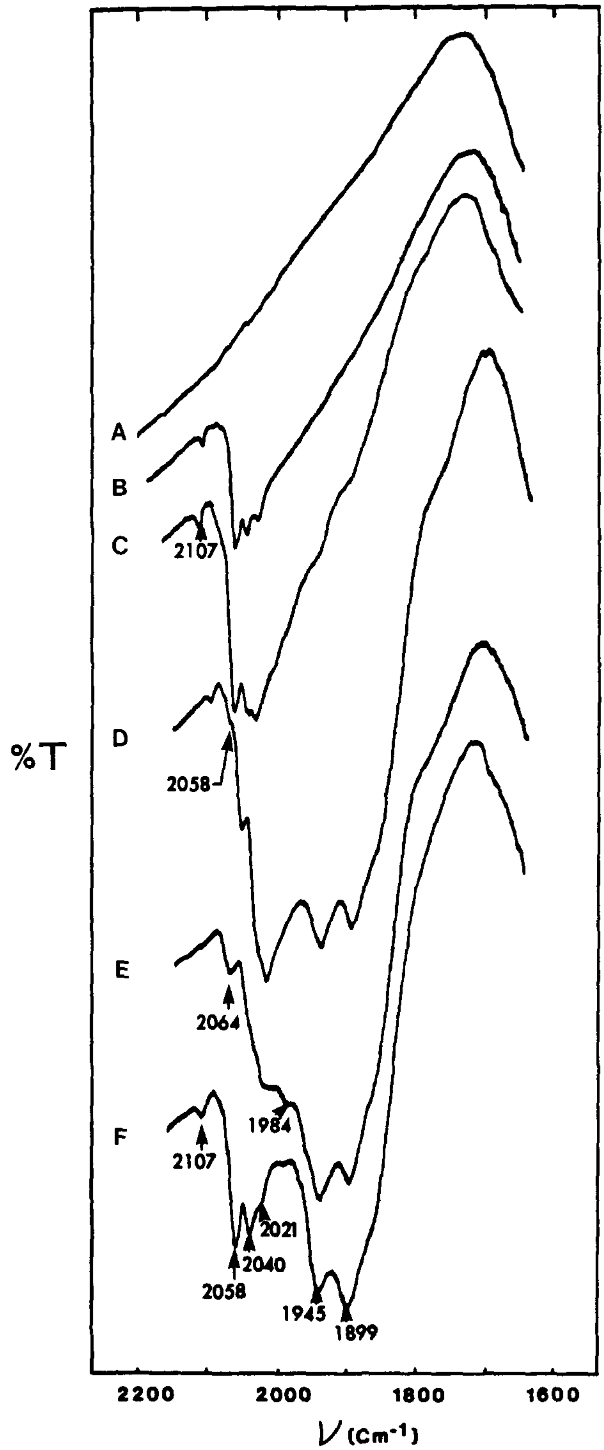


FIG. 4. Infrared transmittance spectra (1650–2150 cm^{-1}) of **I** sublimed onto γ-Al_2O_3 (295K). Spectra are of (A) alumina after pretreatment but before exposure to **I**; (B) sample after 4-min exposure to subliming **I**; (C) sample after 10-min exposure to **I**; (D) sample evacuated 8 hr; (E) sample evacuated 12 hr; and (F) sample exposed to 25 Torr CO for 1 hr.

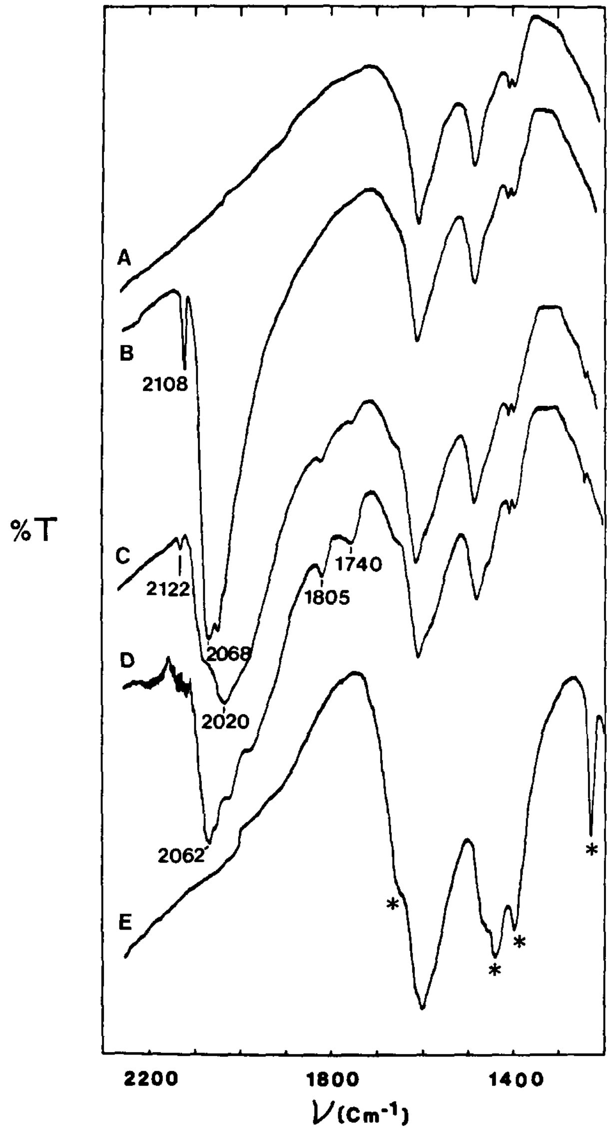


FIG. 5. Infrared transmittance spectra (1200–2200 cm^{-1}) of **I** sublimed onto γ-Al_2O_3 (525 K). Spectra are for (A) alumina prior to sublimation of **I** but after pretreatment; (B) sample after 10-min exposure to **I**; (C) sample after exposure to vacuum for 12 hr; (D) sample after introduction of 140 Torr CO; and (E) sample exposed to ^{13}CO and O_2. Bands marked * are due to surface carbonates.

1850 and 2020 cm^{-1}. Conversely, contact with Al_2O_3 (525K) results in an intense ν(CO) spectrum due primarily to **I** adsorbed on the alumina. Evacuation of both alumina samples evokes major spectral changes. The Al_2O_3 (295K) sample, after evacuation for several hours (spectrum 4E), displays intense bands at 2020, 1984, 1945, 1899, and 1875 (sh) cm^{-1}, as well as a broad weak feature between 1700 and 1800 cm^{-1}. Evacuation of the Al_2O_3 (525K) sample results in a spectrum which retains some features due to the parent carbonyl and displays a new intense peak near 2020 cm^{-1}, a broad ill-defined feature between 1850 and 2000 cm^{-1}, and weak bands at 1805 and 1740 cm^{-1}. Admission of CO to both samples effects the redevelopment of spectral features typical of adsorbed **I** (spectra 4F and 5D); in both cases, bands between 1980 and 2020 cm^{-1} are diminished, while bands in the region 1850–1970 cm^{-1} are either unaffected by CO or they intensify.

The reactivity of surface carbonyls toward oxygen is an important characteristic pertaining to their stability as surface species. Addition of oxygen to the sample cell containing the cobalt carbonyl on alumina causes the rapid disappearance of all $\nu(CO)$ bands not due to the parent **I** (ads). Figure 6 displays the spectra obtained in a series of experiments in which the Al_2O_3 (295K)

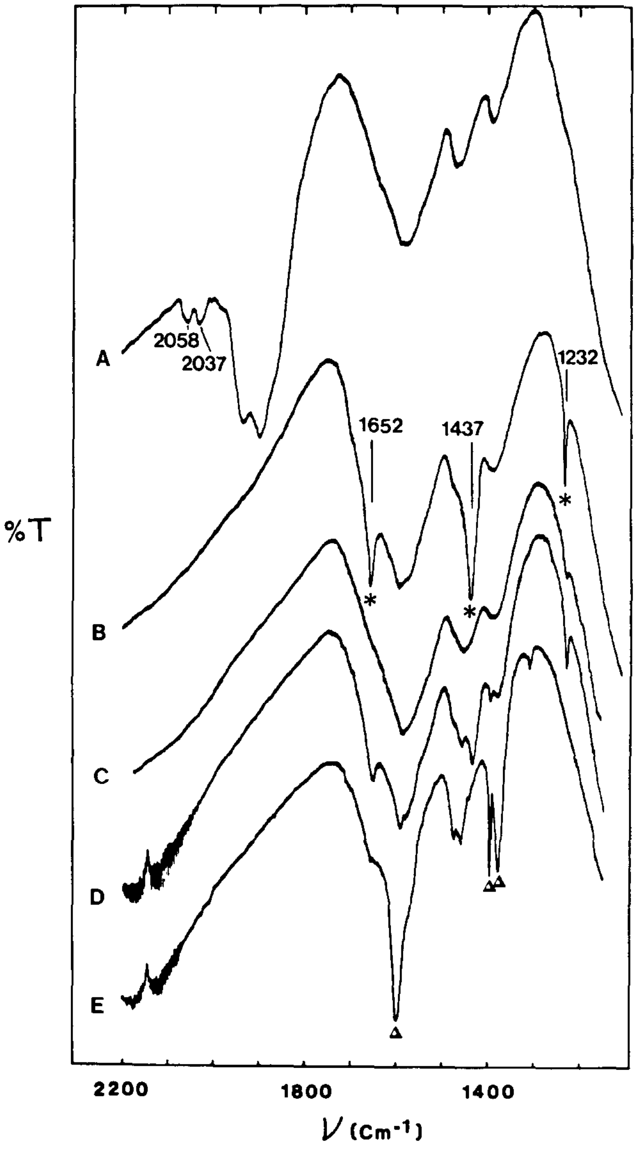


FIG. 6. Infrared transmittance spectra (1200–2200 cm^{-1}) of **I** sublimed onto γ-Al_2O_3 (295K). Spectra continue sequence of Fig. 4 and are for (A) sample as in Fig. 4F followed by thrice repeated cycles of evacuation of the cell and exposure to CO; (B) sample exposed to 350 Torr O_2; (C) sample evacuated to 10^{-6} Torr; (D) sample under 250 Torr CO; and (E) sample heated to 475K under CO. Bands marked * are due to surface carbonates and those marked Δ are due to formates.

sample was exposed to oxygen. Loss of ν(CO) bands due to reaction with O_2 is attended by development of three bands below 1700 cm^{-1}—at 1652, 1437, and 1232 cm^{-1} (spectrum 6B). These bands are typical of carbonate or bicarbonate adsorbed on alumina (*8*). Evacuation at room temperature removes the carbonate, as shown by the loss of these three bands. Heating the sample under CO at 375K results in the redevelopment of the carbonate spectrum and in the development of weak bands near 1600, 1400, and 1380 cm^{-1}, which have been assigned to formate on alumina (*9*). Increasing the temperature to 475K, with exposure to CO, greatly intensifies the formate bands, but the carbonate bands lose intensity. The formate production is not dependent upon the presence of cobalt species on the alumina surface as shown by experiments in which CO was heated above a cobalt free alumina to produce formate (*10*).

Spectrum 5E shows the results of an experiment in which the cobalt carbonyl species present on the Al_2O_3 (525K) sample after evacuation for several hours were exposed to a mixture of O_2 and ^{13}CO. The ν(CO) bands are quickly extinguished and bands due to carbonate containing ^{12}C or ^{13}C develop.

Adsorption of Na–Y Zeolite

Addition of **I** to Na–Y zeolite (525 or 475K) produces a deep pink sample and the ir spectrum A of Fig. 7. As a consequence of support crystallinity and the uniformity of adsorption sites, the adsorbate ir bands are sharper and, therefore, better defined than for the other supports used. The weak spectrum typified by the band at 2109 cm^{-1} is due to crystalline **I** adsorbed on zeolite surfaces. These bands are removed by brief evacuation. The four highest-frequency bands remaining in the spectrum, after evacuation, correspond to the four bands of **I** in solution, except that shifts of 10–20 cm^{-1} suggest relatively strong interactions between the cobalt carbonyl and the support. Heating the sample, *in vacuo*, results in the development of three broad bands near 2035, 1965, and 1780 cm^{-1} at the expense of the sharp bands due to **I** (ads). Finally, at 350K the spectrum is dominated by these three bands (Fig. 8, spectrum 8A). Admission of CO to the sample (spectrum 8B) regenerates some **I**, as indicated by a weak set of bands at 2120, 2073, 2040, and 2030 cm^{-1} and forms a new surface species with ν(CO) bands at 1876, 1906, and 1939 cm^{-1}. Heating at 425K under CO (spectrum 8C) does not affect the latter three bands but converts **I** back to the species with bands at 2035, 1965, and 1780 cm^{-1}. Admission of oxygen to the sample at this stage results in loss of all ν(CO) bands and the growth of bands at 1650 and 1378 due to surface carbonates on zeolite (*11*).

On the zeolite, as well as on silica and alumina, the fully oxidized sample may be reexposed to the vapor of **I** and the original spectrum (7A) develops. All subsequent steps–evacuation, heating, and treatment with CO or O_2—lead to spectra virtually identical with those observed prior to the first oxidation of the sample. Exposure of a fully oxidized sample to CO, only, does not regenerate any cobalt carbonyl species with detectable ir bands.

Gas Manometric and Mass Spectrometric Measurements

To better understand the reactions of **I** on the Na–Y zeolite surface, a gas manometric study was conducted in which the volumes of CO and CO_2 produced by thermal decomposition and O_2 oxidation of surface-adsorbed **I** were measured. Aliquots of gas-phase species were collected for mass spectral analysis during each phase of the measurement. The results of these measurements are given in Table I.

Heating a sample of **I** on Na–zeolite releases about 1 mole of CO per mole of $(CO)_9Co_3CCH_3$ sublimed onto the support as shown by the first two entries of Table 1. The ir spectrum of the sample at this point is dominated by bands of the new carbonyl

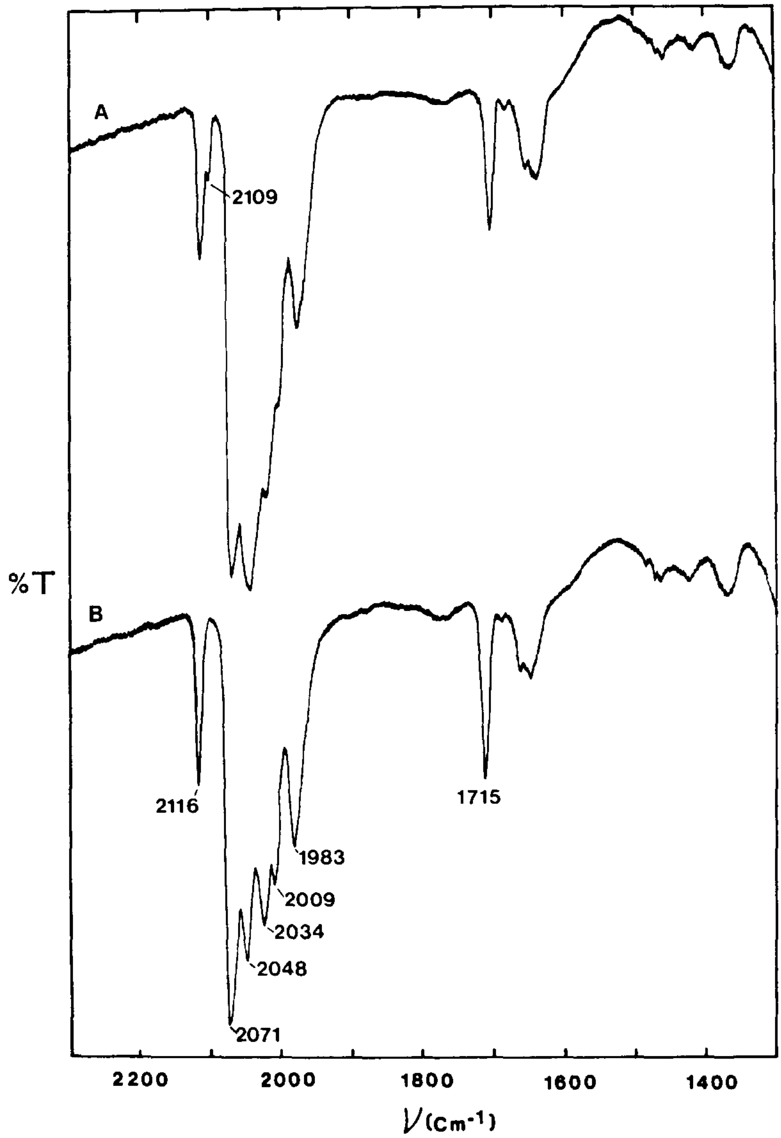


FIG. 7. Infrared transmittance spectra (1300–2300 cm^{-1}) of **I** sublimed onto Na–Y zeolite pretreated *in vacuo* at 475K. Spectra are for (A) sample after 90-sec exposure to subliming **I** and (B) sample after evacuation for 12 hr at 10^{-5} Torr.

species (spectrum 8A). The last two entries on Table 1 are for the same sample after exchange with ^{13}CO. When ^{13}CO is added to **I** on any of the oxide supports studied, the exchange with ^{12}CO is very slow for the adsorbed parent carbonyl but rapid for the species responsible for the ν(CO) bands between 1800 and 2040 cm^{-1}. The first two items in Table 1 are for the sample before exchange with ^{13}CO. After heating to 400K, to convert the parent compound to new carbonyl species, ^{13}CO was added to the system, with careful accounting of the volume of CO added; the ir spectrum changed at that point to that of a ^{13}CO-exchanged sample. The experimental steps in items 3 and 4 of the table were then completed. The total carbon released at the point where all carbonyl, carbonate, and carboxylate bands are expunged from the ir spectrum is 2.4 g-atoms of carbon per g-atom of Co detected on the support at the conclusion of the experiment. This means nearly 4 g-atoms of carbon per mole of initial complex (1.3 g-atoms per g-atom Co) are not accounted for in the volumetric measurements.

Mass spectral data in Table 1 show peaks for a sample of the evolved gas at *m/e* values of 12, 13, 16, 28, 29, 44, 45 which are appropriate for ^{12}CO, ^{13}CO, $^{12}CO_2$, $^{13}CO_2$ and fragments of these species. No spectral features suggestive of hydrocarbon species were detected.

DISCUSSION AND CONCLUSIONS

Examination of the patterns of spectral change as a particular sample of **I** on a support is processed through the several chemical and physical steps of loading, evacuation, mild heating, and exposure to CO or

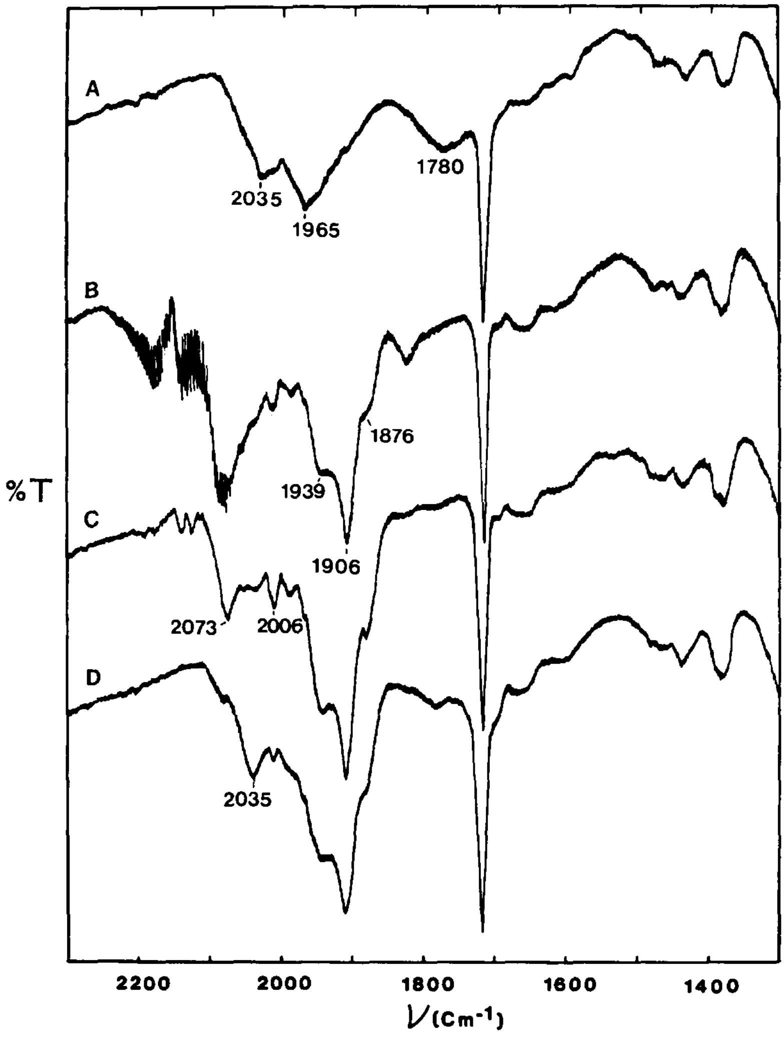


FIG. 8. Infrared transmittance spectra (1300–2300 cm^{-1}) of **I** sublimed onto Na–Y zeolite. These spectra continue sequence of Fig. 7 and are for (A) sample as in Fig. 7B then heated at 350K for 12 hr; (B) sample exposed to 100 Torr CO for 12 hr; (C) sample heated at 375K under 100 Torr CO followed by reduction of CO pressure to 15 Torr; and (D) sample heated at 425K under 75 Torr CO followed by evacuation of the cell.

TABLE 1

Data Obtained during Manometric Study

Item	Moles CO/g-atom Co[a] (moles CO/mole **I** deposited)	Mass spectral peaks[b] (*m*/*e*)	Reference ir spectrum
1. CO released during Co_3 deposition	0.009 (0.03)	12, 16, 18	A, Fig. 7
2. Total CO released upon heating Co_3/Na–Y sample to 400K	0.32 (0.96)	12, 16, 18	A, Fig. 8
3. CO released upon reaction of sample with O_2 at R.T.	1.25 (3.75)	12, 13, 16, 28, 29, 32	[c]
4. CO_2 released upon reaction of sample with O_2 at R.T. plus CO_2 released upon heating sample under O_2 at 525K (CO_2 trapped at LN_2)	0.82 (2.4)	12, 13, 16, 28, 29, 32, 44, 45	[d]
Total	2.4 (7.2)[e]		

[a] Manometric measurements are subject to a random error range of ±0.02 (moles × 10^4).

[b] Mass spectra were recorded in the range $m/e = 10–60$ using a Spectromass 80 RGA. Peaks listed for items 3 and 4 reflect the fact that the decomposed surface species were predominantly ^{13}CO-exchanged carbonyls.

[c] The spectrum recorded after reacting the sample with O_2 showed the loss of all ν(CO) bands.

[d] The spectrum, recorded after heating the sample at 525K and Toepler pumping the cell, indicated the loss of all carbonate-like bands.

[e] The ratio of g-atoms carbon, released as CO or CO_2, to g-atoms Co on the zeolite was 2.40, whereas the stoichiometric C/Co ratio is 3.67 for $(CO)_9Co_3CCH_3$.

O_2 discloses the existence of four sets of ν(CO) bands. The bands of each set appear and disappear together in a series of experiments. At least three of these sets of bands are observed on both alumina and zeolite, showing that these carbonyl species are common to the reactions of **I** on both oxide support surfaces. These four sets of bands are listed in Table 2 and identified as **I** (ads), α, β, γ. Assignment of several bands to one species was made only after examination of spectra obtained for **I** on several samples of the same support material with the same pretreatment conditions.

TABLE 2

Frequencies of Cobalt Carbonyl Species on Oxide Supports ν(CO) Values[a]

Species	Silica	Alumina	Na–Y
I (ads)	2106, 2053 2043, 2021	2107, 2058, 2040, 2021	2116, 2071, 2048, 2034
α	—	1945, 1899, 1876(sh)	1939, 1903, 1876(sh)
β	—	≈2020[b]	2006, 1983[b]
γ	—	≈2040, 1980–1940, 1780[b]	≈2030, 1970, 1780[b]

[a] Frequencies given in cm^{-1}.

[b] Frequencies given for the β and for the γ species vary with identity of support and with pretreatment conditions.

Assignment of bands to **I** (ads) is quite straightforward. The intensity pattern and frequencies of this set of four bands are in agreement with the spectrum of **I** in *n*-hexane except for 5- to 20-cm^{-1} shifts due to interaction with the support.

The set of bands labeled α dominates the ir spectrum under certain conditions, as shown by spectra 4E,F for alumina and spectra 8B–D for the zeolite. Species α is believed to be $Co(CO)_4^-$ formed by reaction of **I** with the oxide surface. This conclusion is based upon the following observations:

1. Metal *cluster* carbonyls sublimed onto oxide supports produce substantial coloration of the support due to visible region electronic transitions between molecular orbitals centered primarily on the metal cluster nucleus. When samples of **I** on alumina or zeolite are converted to materials with ir spectra dominated by the three

bands of species α, however, the color of the sample fades to near white, implying that a mononuclear cobalt carbonyl is formed.

2. Addition of CO to a sample displaying the bands due to $Co(CO)_4^-$ does not seem to affect this species, as indicated by the absence of any change in the intensity of the bands assigned to it. This would be expected for this CO-saturated form of cobalt. The other two new species, β and γ, are converted back to **I** when CO is added.

3. α is the most sensitive, of the species listed in Table 2, to O_2.

4. Solution reactions of **I** and related compounds to yield $Co(CO)_4^-$ have been reported. Specifically, $(CO)_9Co_3CBr$ in CH_3OH produces Co(II) and $Co(CO)_4^-$, and **I** in methanolic NaOH yields $Co(CO)_4^-$ (*12*).

Consistent with *Td* geometry, $Co(CO)_4^-$ (aq) displays one ν(CO) ir band, of F_2 symmetry, centered at 1919 cm^{-1}. If the *Td* symmetry of the anion is reduced, however, as would be expected upon interaction with a support surface, the triply degenerate F_2 mode would be split to A_1 and E in C_{3V} symmetry or to A_1, B_1 and B_2 in C_{2V} symmetry, and the totally symmetric vibration (A_1 in *Td*) becomes ir active in both C_{3V} and C_{2V} symmetries. Thus $Co(CO)_4^-$ could have three (C_{3V}) or four (C_{2V}) ir active modes in the ν(CO) spectral region. Edgel *et al.* (*14*) have observed three ν(CO) bands, at 1889 (sh), 1886, and 1858 cm^{-1}, when $NaCo(CO)_4$ is dissolved in anhydrous THF. The rationale for the emergence of three bands in that study was symmetry reduction from *Td* to C_{3V} through ion pairing of $Co(CO)_4^-$ with Na^+ in the anhydrous solution.

Species β and γ are not as easily identified. They appear to be cobalt carbonyls which can add CO to regenerate **I** (see above). Indeed, the manometric results in Table 1 suggest the loss of at least 1 mole of CO per mole of **I** to produce a sample with bands due to β and γ. The band below 1800 cm^{-1} for γ suggests the presence of a bridging carbonyl ligand, although other possibilities, including the formation of polynuclear anionic carbonyls, cannot be excluded (*15*).

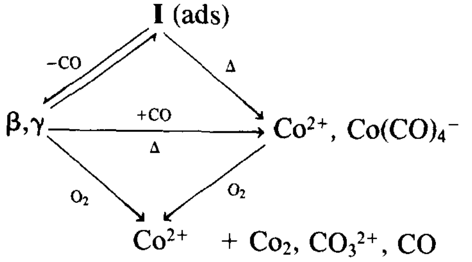
The reactivity of **I**, as measured by the tendency to form new cobalt carbonyl species on the supports, varies in the order

$$\gamma\text{-}Al_2O_3\ (295K) > \gamma\text{-}Al_2O_3\ (525K) > \text{NaY zeolite} \gg SiO_2.$$

This ordering of reactivity is based upon the spectra in Figs. 4–7. The relative unreactivity of silica toward the cobalt carbonyl is consistent with many reports in the literature regarding metal carbonyls on oxide supports. The primary effect of the silica surface upon **I** is a slightly enhanced reactivity toward oxygen and the slight tendency to form new carbonyl species, which is illustrated by the presence of very weak bands between 1950 and 2020 cm^{-1} (spectrum 3D).

That alumina is the most reactive of the surfaces toward **I** is demonstrated by the facile formation, on alumina, of species α, β, and γ upon evacuation of a cell containing **I** (ads) at room temperature. On the zeolite surfaces, reaction of **I** (ads) to form α, β, and γ does not occur readily until temperatures reach at least 350K. The greater reactivity of the unheated alumina, as compared to alumina pretreated at 525 or 700K, is of particular interest because it pertains to the identification of those oxide surface sites which react with the metal carbonyl. This enhanced reactivity of γ-Al_2O_3 (295K) has been reported previously (*16*) and has been further confirmed in investigations of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ on γ-alumina. Reasons for this difference in reactivity and a general discussion of the reactivity of cobalt carbonyls toward oxide surfaces are elaborated in the report of that study (*13*). Briefly, interaction and reaction of the cobalt carbonyls with oxide surfaces generally involves hydrogen bonding to surface hydroxyls through basic oxygens of metal carbonyls and attack by surface bases, $-OH^-$, or $-O^-$, upon electron-deficient carbonyl carbons metal atoms. The progress of such reactions is facilitated by loosely bound oxygens, as in a molecular water layer, which can be incorporated easily in -COOH ligands or evolved CO_2. Brown (*15*) has discussed the importance of this loosely bound water in reactions of metal carbonyls with oxide surfaces.

A general reaction scheme for **I** on alumina and zeolite is given below. This scheme is based on the spectral observations and manometric data.



Once the $Co(CO)_4^-$ is formed, it does not convert back to β, γ, or **I** (ads), but remains on the surface until exposed to oxygen. The presence of an anion in this scheme requires, or course, the availability of a counterion. This may be Co^{2+} formed in the reactions, Na^+ ions in the zeolite, or, on alumina, the bare aluminum ions left after reaction of surface oxygens or hydroxyls with the cobalt carbonyl.

The development of bands assigned to surface carbonates is a feature associated with the adsorption and subsequent reactions of **I** on alumina and zeolite support surfaces. On alumina these bands are at 1652, 1437, and 1232 cm^{-1}, and on Na–Y zeolite they are observed at 1649 and 1378 cm^{-1}. These observed frequencies are in good agreement with those reported in the literature for carbonate on the respective surfaces. Intense carbonate bands generally develop upon admission of O_2 to a sample displaying $\nu(CO)$ bands typical of $Co(CO)_4^-$ and species β and γ. The concomitant disappearance of the $\nu(CO)$ bands connotes oxidation of the carbonyl species to cobalt ions and CO_2 or carbonate. Significant quantities of CO (nearly 4 moles per mole of **I** adsorbed—Table 1) are also released upon exposure to O_2. This may be explained by proposing a stepwise process leading to a cobalt carbonyl with cobalt in a positive oxidation state; the labile CO ligands on this species could then be evolved spontaneously at the low pressures employed.

One additional ir feature, not discussed heretofore, is a band near 1715 cm^{-1} (and sometimes 1685 cm^{-1}) on zeolite and 1690 cm^{-1} on silica. This band develops immediately upon adsorption of **I** on the supports. Within the limits of experimental data recorded for the two systems, the chemical behavior of the species responsible for the 1713-cm^{-1} band on zeolite is quite like that for the 1690-cm^{-1} species on silica. A possible assignment for the 1690-cm^{-1} band on silica is to formic acid. It is known that this acid adsorbs on silica as the protonated acid with an intense $\nu(CO)$ band near 1700 cm^{-1} (*17*). Acetic acid is also a candidate, having a $\nu(CO)$ band in the same region. The same species adsorbed on zeolite explains the 1715-cm^{-1} band on that support.

The 1715/1690 cm^{-1}-band could also be assigned to adsorbed aldehyde or ketone, both of which display $\nu(CO)$ bands in the 1700 cm^{-1} region. Acetone has been reported to adsorb fairly strongly on silica supports *via* hydrogen bonding through a silanol hydrogen and the carbonyl oxygen. Frequencies for the C–O stretch of the adsorbed acetone have been reported in the range of 1719–1690 cm^{-1} (*18*). Aldehydes and ketones adsorbed on zeolites are thought to interact strongly with the exchangeable cations, surface hydroxyls, and dehydroxylated framework sites *via* the C=O group (*19*). For example, a 1715-cm^{-1} band observed in the spectrum of adsorbed acetone on Y-zeolites has been attributed to a hydrogen-bonded C=O. In contrast to its adsorption on silica, acetone on zeolites is not easily removed by R.T. evacuation. The species responsible for the 1715-cm^{-1} band on zeolite in this study is also not removed by vaccum desorption. Finally, a 1370-cm^{-1} band has been observed in the spectrum of acetone adsorbed on silica and has been assigned to a bending mode of the CH_3 group (*18*). This could explain the band near 1370 cm^{-1} for oxidized samples on both silica and zeolite supports.

It is noteworthy that no 1700-cm^{-1}-region band is observed upon the exposure of γ-Al_2O_3 (R.T., 525 or 700K) to **I**. There are at least two possible explanations. One is simply that no species with a band in the 1700-cm^{-1} region is produced upon the initial interaction of Co_3 with γ-Al_2O_3. This is not consistent, however, with the otherwise close parallel between the chemistries of the cobalt carbonyl species on alumina and zeolite. A second explanation is that a 1700-cm^{-1} species is produced but is immediately decomposed on the Al_2O_3 surface. It is known that aldehydes and ketones are oxidized by alumina at R.T., producing surface carbonates.

The formation of a hydrocarbon compound—be it acid, aldehyde, or ketone—would explain the failure to detect the stoichiometric quantity of carbon upon decomposition of **I** on the various surfaces. The fate of the $-C-CH_3$ portion of **I** was not determined in any of the spectroscopic or manometric experiments employed in this research.

Another question addressed during the zeolite studies was whether **I** was adsorbed within the zeolite supercages or was only on the exterior surfaces. Cobalt analyses of several zeolite samples used for the ir experiments showed loadings of 1–2% w/w Co. Monolayer coverage of **I** on the external surfaces, which are about 1% of the total equivalent area of a zeolite (*20*), would produce Co loadings of <0.5%. A 1–2% loading into the internal surfaces of the zeolite corresponds to about one Co_3 cluster molecule per unit cell (one Co_3 cluster for every eight supercages). This loading level and the fact that the weak bands of spectrum 7A, which apparently are due to **I** adsorbed on the exterior zeolite surfaces, are quickly lost upon evacuation provide strong evidence for adsorption of **I** within the zeolite supercages of the Na–Y zeolite. Further support for this conclusion derives from an experiment in which **I** was sublimed onto Na–A zeolite with supercage apertures of ~0.4 nm, too small to admit **I**, which has a kinetic diameter estimated at 0.9 nm. Sublimation for several hours results in a weak ir spectrum nearly matching that of **I** in *n*-pentane. This spectrum disappears upon brief evacuation of the sample cell. Thus when **I** is unable to enter the zeolite supercages it is easily removed from the support and no conversion to other carbonyl species is observed.

In conclusion, the compound $(CO)_9Co_3CCH_3$ displays greatly varying reactivity toward the surfaces employed in this study. Silica provides a very passive surface, while γ-alumina, pretreated at room temperature, is very reactive toward this compound. Reversible equilibria involving CO exist between **I** and at least two surface species on alumina and Na–Y zeolite, and all three of these may be thermally converted to $Co(CO)_4^-$ and cobalt ions. The parent compound is fairly resistant to oxidation on all supports, while the new species formed by reaction with the support react quickly with O_2 to produce totally decarbonylated cobalt species, CO, CO_2, and surface carbonates. Some evidence also exists for the formation of organic carbonyls, presumably from the $-C-CH_3$ portion of the tricobalt parent compound.

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