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Studies of Cobalt Carbonyls on Oxide Supports. 4. Nitric Oxide Reactions with Cobalt Carbonyls

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Nitric oxide was reacted with the cobalt carbonyls $Co_2(CO)_8$ and $Co_4(CO)_{12}$ supported on silica, γ-alumina, Na-Y and Na-X zeolites, and magnesia. IR spectroscopy, manometry, mass spectrometry, and isotopic exchange experiments disclosed, in each case, the conversion of the supported carbonyl compound to an intermediate $Co(CO)_3NO$ (I) and then to a trinitrosyl of cobalt (II). The IR spectra observed for I on the supports agreed quite closely with those reported for the corresponding pure compound. Indeed, I could be added directly from the vapor phase to the supports where it displayed properties identical with those of the intermediate observed in the surface nitrosylation process. Although the intermediate was observed only fleetingly on the Na-X zeolite and not at all on γ-Al_2O_3 during the conversion of the starting carbonyl to II, direct addition of I to both these supports resulted in spontaneous conversion to II. Moreover, when NO was added to supported II formed in this manner, the IR spectrum of II increased 2–3-fold in intensity, indicating that "bare" cobalt atoms formed in the spontaneous conversion of I to II may be nitrosylated to yield more II. The identity of II is more ambiguous because it could not be extracted from any of the surfaces for direct comparison with appropriate cobalt nitrosyl species. Analogy with known preparative solution chemistry, comparison with reported IR spectra, and interpretation of observations of the gas phase above the surface species lead to the conclusion that II is the zerovalent $Co(NO)_3$ complex, although the possibility that it is $[Co(NO)_3]^{2+}$ cannot be ruled out.

Introduction

The current interest in supporting metal complexes on refractory oxide surfaces derives largely from the desire to form novel supported metal catalysts. As a result, studies of these systems have tended to focus on the properties of the materials after decomposition of the surface-bound metal complex to yield "supported metal", ignoring the nature of the chemical reactions between the complex and the oxide. Recent studies of the relatively labile cobalt carbonyls on a variety of oxide surfaces disclosed a rich molecular chemistry for these materials,[1-4] a chemistry not unlike that for the same compounds in solution, but in which different species may be stabilized and different processes accelerated due to the special nature of oxide surface.

These earlier cobalt carbonyl studies were limited to reactions involving CO after the starting cobalt carbonyl was sublimed onto the oxide. To further explore the molecular nature of reactions of cobalt carbonyls on oxide surfaces, we have reacted NO with the surface-deposited cobalt carbonyls to examine the degree to which this chemistry is parallel to or diverges from the molecular chemistry that occurs in solution. Because NO is easily manipulated in the gas phase, it may be added as a new ligand in these studies without contaminating the samples by contact with solvent. Also, because NO reacts with both zerovalent and oxidized cobalt but produces different products depending upon the cobalt oxidation state, it can serve as a probe of the oxidation state of surface-bound cobalt.

Mond and Wallis[5] originally synthesized $Co(CO)_3NO$ by the rapid and quantitative vapor phase reaction of $Co_2(CO)_8$ with NO. Alternatively, $Co(CO)_4^-$ in solution reacts with NO[6] or $NaNO_2$[7] to yield the same nitrosyl tricarbonyl complex. Interestingly, reaction of $Co_2(CO)_8$ with excess NO in hexane at room temperature produces a different product.

Burg[8] has reported that the reaction of $Co(CO)_3NO$ with low pressures of NO produces $Co(NO)_3$. The reaction is rapid and direct in sunlight at room temperature but requires several days in the dark at 60 °C. Higher temperatures and NO pressures (20 atm) in the absence of light yield more complex products such as $[Co_4(NO)_8(NO_2)_2(N_2O_2)]$[9] and $[Co(NO)_2(NO_2)]_n$.[10]

Different reactions with NO have been reported when cobalt is in a higher oxidation state. For example, hexamminecobalt(II) reacts with NO to produce pentamminenitrosylcobalt, which has been described as a complex of cobalt (III) and NO^-.[11,12] This product can disproportionate to N_2O and a nitro complex of cobalt(II). Lunsford[13,14] has observed a similar chemistry on zeolite-supportedf cobalt(II).

This study reports the results obtained from reaction of NO with cobalt carbonyls supported on silica, zeolites, alumina, and magnesia. IR spectra of the samples produced are compared with those that have been reported for NO and NO_2 complexes. This information and the stoichiometric insights gleaned from gas volumetric measurements lead to conclusions regarding the molecular NO complexes produced on the various surfaces.

Experimental Section

Reagents. All gases were commercial grade and were purified by passage through appropriate packed columns for removal of water and O_2. Trap-to-trap distillation was used when necessary. Purity was judged on the basis of the mass spectrum. Isotopically enriched gases were purchased from Prochem Ltd. and were used as supplied. These included 99% enriched ^{13}CO and 99% enriched ^{15}NO. Solvents occasionally employed in extractions and wet synthesis were technical grade or better organics, such as cyclohexane and pentane, dried over metallic sodium. $Co_2(CO)_8$ was purchased from Pressure Chemical Co. Inc., and Strem Chemicals, Inc., and was occasionally vacuum sublimed, onto a liquid-N_2 cold finger, to separate it from nonvolatile decomposition products.

$Co(CO)_3NO$ Synthesis. $Co(CO)_3NO$ was synthesized from the reaction of NO with $Co_2(CO)_8$. A sample of $Co_2(CO)_8$ was transferred under dry oxygen-free nitrogen into a test-tube-reactor cell. The cell was then cooled to −57 °C (dry ice–actone bath) and the transfer gas evacuated. Typically, 100 Torr of NO was admitted into the cell, which was then warmed to room temperature. Within minutes the intensely yellow vapor of $Co(CO)_3NO$ formed and within a day or two most of the $Co_2(CO)_8$ had been converted into a dark red liquid suggestive of $Co(CO)_3NO$. The sample was purified by crystallization of the $Co(CO)_3NO$ vapor in a separate cold storage tube (−57 °C). Upon completion, excess NO was evacuated and the $Co(CO)_3NO$ refrigerated until needed. Purity of the product was judged by the infrared spectrum of the $Co(CO)_3NO$ vapor.

Support Materials. The five oxide support materials used in this work were obtained as fine powders from the manufacturer or were purchased

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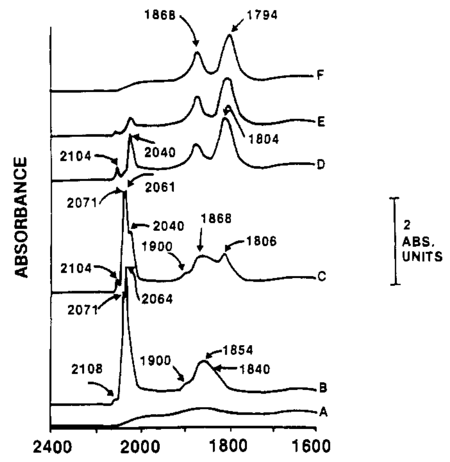

Figure 1. Change in IR spectra upon addition of NO to a Co_2/SiO_2 sample: (A) silica background spectrum; (B) spectrum of a freshly prepared Co_2/SiO_2 sample; (C) spectrum immediately following addition of 25 Torr of NO; (D) spectrum 12 h after NO addition; (E) spectrum 48 h after NO addition; (F) spectrum 96 h after NO addition.

as crystalline material and ground in a mortar and pestle to the desired mesh. Infrared wafers were pressed in a 1.25 in. diameter stainless-steel die. Each wafer was cut to accomodate the carriage of an infrared cell previously described.[1,2]

After preparing wafers or shards of the support materials, the following procedures were used prior to exposure to cobalt carbonyl.

For SiO_2 and Al_2O_3, the support was exposed to 40 Torr of O_2 at 400 °C for 1 h, followed by evacuation at 400 °C for a second hour and cooling in vacuo.

For Na–Y and Na–X, the support was heated to 400 °C by 100 °C increments in 10–20-min steps under 40 Torr of O_2. Heating was continued at 400 °C under O_2 for 1 h after which time the cell was evacuated at 400 °C for 3 h (Na–Y) or 8 h (Na–X) and then cooled in vacuo.

For MgO, the support was heated at 400 °C under O_2 for 2–4 h and then heated in vacuo at the same temperature for 2-4 h before cooling to room temperature.

There were some minor variations in this pretreatment from experiment to experiment, but this was not thought to alter the chemical properties of the support. In the case of Na–X it often was necessary to increase the dehydration time in order to successfully dehydrate the surface, as indicated by the IR band near 1650 cm^{-1} due to adsorbed H_2O. A support was considered experiment worthy when this band showed an absorbance of less than 0.03 unit. Pretreated wafers with overall absorbances greater than 1 absorbance unit were deemed too thick and discarded.

Loading of Supports. $Co_2(CO)_8$ and $Co(CO)_3NO$ were loaded onto the support materials by sublimation under a vacuum using the previously described cell.[1,2] Levels of loading of the cobalt carbonyls on supports were compared from experiment to experiment by infrared absorbance. Quantitative determination of loading levels was obtained from atomic absorption data and, in one case, by manometry and were, typically, 0.4–1.0%. Samples used for atomic absorption analysis were prepared by the method of Schneider.[1]

Spectra. Infrared spectra were recorded on Nicolet MX-1 and MX-10 Fourier transform infrared spectrometers accumulating 54 scans for a resolution of 2 cm^{-1}. Mass spectra were obtained with an Hitachi Perkin-Elmer RMU 6D mass spectrometer. Samples were analyzed as aliquots, typically at 70 eV. Atomic absorption measurements were recorded on a Perkin-Elmer 503 atomic absorption spectrometer.

Vacuum Systems and Manometric Measurements. Vacuum systems capable of a 10^{-6} Torr equilibrium pressure included a recirculation pump and a BET subsection. During some experiments the recirculation pump was used to more evenly deposit $Co(CO)_3NO$ vapor onto support materials.

Gas volumetric measurements were performed in the BET subsection of the vacuum line equipped with a U-trap. The volume of the reactor space was determined by expanding the system volume by calibrated increments and relating these increments to the corresponding decreases in pressure. Helium was used as the calibrant gas. Because it was necessary to know the partial pressure of each gas in a mixed-gas system, the difference in vapor pressures at liquid-N_2 temperatures was used to selectively condense NO and measure the pressure of CO alone.

Results and Discussion

Silica. Vacuum sublimation of $Co_2(CO)_8$ onto silica resulted in the conversion of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ with the simultaneous release of the requisite CO.[1,2] This addition changed the silica to an orange-brown color, and the infrared spectrum of the sample displayed bands characteristic of $Co_4(CO)_{12}$ adsorbed on silica. When NO ($P \sim 25$ Torr) was admitted to the infrared cell, the color of the support gradually faded to a light yellow-green. Figure 1 shows the effects of NO addition on the IR spectrum. After 12 h (Figure 1D) the $Co_4(CO)_{12}$ spectrum had been completely replaced by bands at 2104, 2040, 1868, and 1804 cm^{-1}. As the reaction continued, the 2104- and 2040-cm^{-1} bands diminished in intensity and the color of the sample changed again to brown. Finally, after 4 days the reaction ceased, leaving only bands at 1868 and 1794 cm^{-1}.

The shift of the 1804-cm^{-1} band to 1794 cm^{-1}, concomitant with the disappearance of the 2104- and 2040-cm^{-1} bands, suggests that bands at 2104, 2040, and near 1804 cm^{-1} belong to an intermediate species, while bands at 1868 and 1794 cm^{-1} belong to a final product. Figure 2C presents the subtraction of the spectrum in Figure 1F from that in Figure 1D in order to isolate the spectrum of the intermediate. The result is a set of bands at 2104, 2040, and 1812 cm^{-1} nearly matching those of gas-phase $Co(CO)_3NO$ (Figure 2A). The negative excursions in Figure 2C, near 1870 and 1790 cm^{-1}, correspond to the positions of the peaks in spectrum 1F. The growth of these peaks between spectra D and F in Figure 1 is shown by the negative peaks in the subtraction.

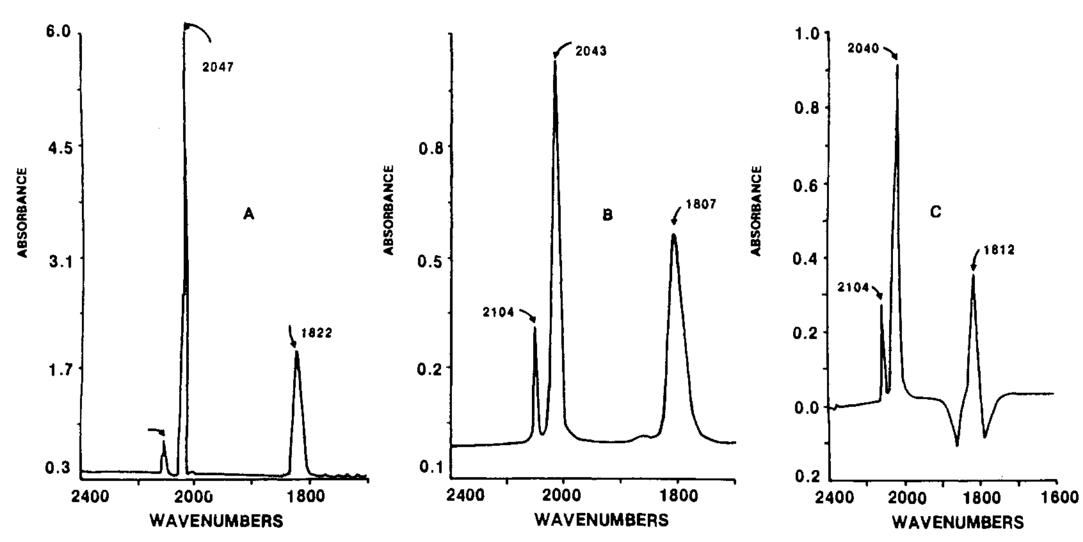

Figure 2. Comparison of silica-bound $Co(CO)_3NO$ with the gas-phase compound: (A) $Co(CO)_3NO$ gas-phase spectrum; (B) spectrum of $Co(CO)_3NO$ on SiO_2 surface. (C) difference spectrum obtained by subtraction of spectrum D from spectrum F in Figure 1.

The table compares the spectra of all nitrosylated cobalt complexes observed on the supports studied.

To confirm this identification, a sample of $Co(CO)_3NO$ vapor was loaded directly onto a silica support. The silica turned yellow in color and the infrared spectrum (Figure 2B) corresponded exactly to that developed initially upon exposure to NO of $Co_2(CO)_8$ adsorbed on SiO_2 (Co_2/SiO_2). $Co(CO)_3NO$ was very stable on silica but reacted slowly upon addition of NO to give the final product (1868 and 1794 cm^{-1}), as expected. It also could be removed in moments from the silica surface by room-temperature evacuation, suggesting that $Co(CO)_3NO$ is physically adsorbed on the support. The only significant difference between the observed IR frequencies of gas-phase $Co(CO)_3NO$ and adsorbed $Co(CO)_3NO$ is a 15-cm^{-1} shift in the ν(NO) band from 1822 cm^{-1} in the gas phase to 1807 cm^{-1} when adsorbed on silica.

Hydrogen bonding to this support may be studied in the ν(OH) region of the SiO_2 IR spectrum. Evidence of hydrogen bonding interaction is seen in the broadening and the downward shift of the ν(OH) band assigned to isolated surface hydroxyls when a high coverage of $Co(CO)_3NO$ is added.

The two ν(NO) bands of the final nitrosyl product (1868 and 1794 cm^{-1}) changed allometrically during NO addition, during heating under evacuation, and during renitrosylation experiments (vide infra), indicating these two bands are due to a single complex. Moreover, the frequencies closely match those at 1860 and 1795 cm^{-1} reported by Burg[8] for $Co(NO)_3$ in cyclohexane. Attempts to extract this material from the support with various organic solvents were unsuccessful.

Further evidence regarding the identity of the final NO complex was provided by manometry. $Co(CO)_3NO$ deposited on silica shards in a minimum volume reactor cell was allowed to react with a known quantity of NO. Measurements of CO evolution and NO adsorption provided a determination of the stoichiometry of the reaction of $Co(CO)_3NO$ with NO during complete conversion to the fully nitrosylated product.

The NO(ads)/CO(evolved) ratio was found to be 2.0/3.0, verifying eq 1 as the observed reaction.

$$2NO + Co(CO)_3NO \rightarrow Co(NO)_3 + 3CO \qquad (1)$$

Heating and evacuating the silica-supported $Co(NO)_3$ product at temperatures from 50 to 200 °C led to gradual intensity reduction of the 1868- and 1794-cm^{-1} bands. This loss was complete after the product was heated at 200 °C for 1 h. Addition of NO induced the return of the 1868- and 1794-cm^{-1} bands although not to the original intensity. Repetition of this process reduced the resulting ν(NO) band intensities with each cycle.

Exposure of supported $Co(NO)_3$ to O_2 or air demonstrated that, unlike the material prepared homogeneously, the supported material was relatively air stable for short periods (ca. 1 day).

Zeolites. Vacuum sublimation of $Co_2(CO)_8$ onto dehydrated Na–Y and Na–X zeolites results in formation of adsorbed $Co_4(CO)_{12}$ and a species identified as $Co(CO)_4^-$.[1,2] Reaction of NO with the Na–Y-supported cobalt carbonyls, prepared by sublimation of $Co_2(CO)_8$, proceeded much as the reactions of silica-supported carbonyls, except that the carbonyl spectrum of the partially nitrosylated intermediate had two bands not observed on the silica. Rapid conversion of the intermediate to $Co(NO)_3$, having ν(NO) bands at 1894 and 1810 cm^{-1}, followed. The Na–Y zeolite sample responded to heating/evacuation experiments in the same manner as the silica-supported nitrosyl product.

When a sample formed by direct contact of $Co(CO)_3NO$ vapor with Na–Y zeolite was evacuated at room temperature before any contact with NO, all ν(CO) bands gradually disappeared and $Co(NO)_3$ bands at 1894 and 1810 cm^{-1} developed (Figure 3), demonstrating spontaneous conversion to $Co(NO)_3$. In situ addition of NO to this sample induced further increases in the intensity of the two bands of $Co(NO)_3$, suggeting NO addition to previously "invisible" cobalt atoms on the surface.

The reactions on Na–X zeolite produced essentially the same results except that the final nitrosyl bands were shifted downward in frequency to 1886 and 1799 cm^{-1}. The reaction of NO with the supported cobalt carbonyls also produced observable amounts of NO_2^- (1260 cm^{-1}) and N_2O (2240 cm^{-1}) on the Na–X zeolite surface.

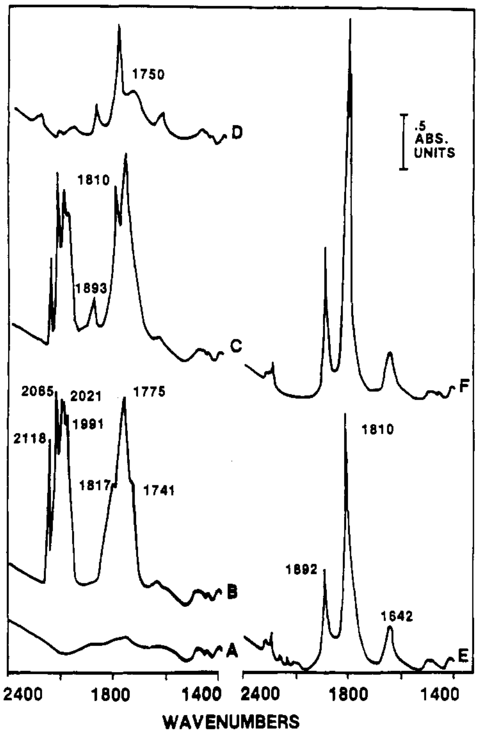

Figure 3. Sequence of spectra obtained by addition of $Co(CO)_3NO$ to Na–Y zeolite: (A) spectrum of pretreated Na–Y zeolite; (B) spectrum immediately following addition of $Co(CO)_3NO$; (C) spectrum following 3.5-h evacuation; (D) spectrum following 63-h evacuation; (E) spectrum following addition of NO for 0.5 h; (F) spectrum following addition of NO for 100 h. Spectra mimic those for NO addition to Co_2/Na–Y.

Direct addition of $Co(CO)_3NO$ to Na–X produced a sample with the same four ν(CO) bands but with different relative intensities than on Na–Y. These samples spontaneously reacted in an hour or two to yield supported $Co(NO)_3$ as well as NO_2^- and N_2O.

Comparison of the bands of "$Co(CO)_3NO$" species on Na–Y and Na–X suggests that there are *two* mixed carbonyl nitrosyl species present on these supports. Na–X and Na–Y differ only in aluminum content, which will determine the relative number and strength of Lewis acid and base sites. A study of acid and base properties by Barthomeuf[15] using pyridine and pyrrole demonstrated that Na–X possesses more basic sites than Na–Y. This difference between the supports can explain the difference in relative intensities of the "$Co(CO)_3NO$" species bands from Na–Y to Na–X. Both supports give rise to a pair of carbonyl bands at 2020 and 1990 cm^{-1}, with intensity ratios constant to one another in all experiments, and a second set at ca. 2120 and 2063, also with intensity ratios constant to one another. The intensity of one set relative to the other changes, however, from Na–Y to Na–X.

On the basis of similarity to gas-phase $Co(CO)_3NO$, the bands at ca. 2120 and 2063 (and 1817) cm^{-1} are attributed to adsorbed $Co(CO)_3NO$. Since the second species possesses two carbonyl stretches, but of lower frequencies, it is identified as $BCo(CO)_2NO$, where B is a surface base site. The intensities of the two $BCo(CO)_2NO$ bands increase over those of $Co(CO)_3NO$ on going from Na–Y to Na–X, as would be expected on going to a support with more and stronger basic sites. The NO stretch for $BCo(CO)_2NO$ also is support dependent, changing from 1776 cm^{-1} on Na–Y to 1755 cm^{-1} on Na–X.

As in the case of silica, attempts to extract the completely nitrosylated complex were unsuccessful. Attempts to extract the mixed carbonylated nitrosylated complexes resulted in ligand loss.

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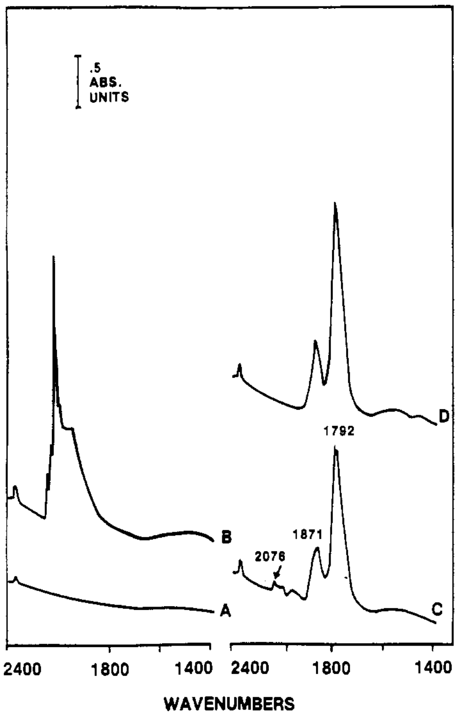

Figure 4. Sequence of spectra obtained upon NO addition (20 torr) to Co_2/γ-Al_2O_3: (A) spectrum of pretreated γ-Al_2O_3; (B) spectrum following sublimation of $Co_2(CO)_8$; (C) spectrum immediately following addition of NO; (D) spectrum following 1.5-days exposure to NO.

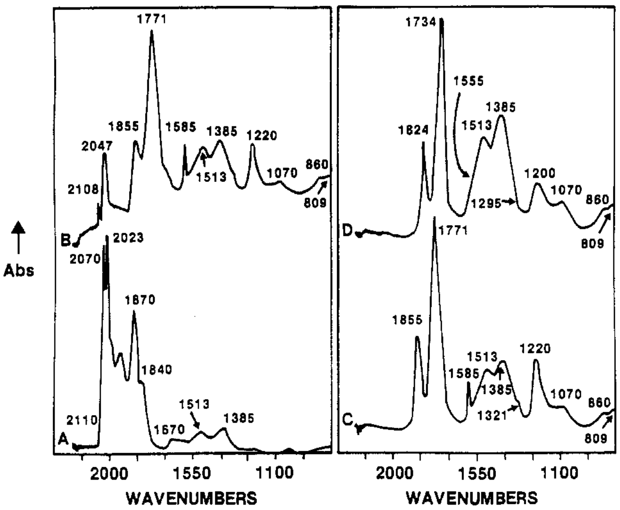

Figure 5. Sequence of IR spectra obtained upon addition of NO to Co_2/MgO: (A) spectrum following sublimation of $Co_2(CO)_8$ onto MgO; (B) spectrum after 15-min exposure to 35 Torr of NO; (C) spectrum after 1-day exposure to NO; (D) spectrum following brief evacuation and then exposure for 1 day to 30 Torr of ^{15}NO.

Alumina. The sublimation of $Co_2(CO)_8$ onto γ-alumina results in a variety of surface carbonyls.[1,2] Figure 4 presents a sequence of spectra showing the result of NO addition to these surface carbonyls. The γ-alumina support immediately turns brown, and the carbonyl stretches are replaced by nitrosyl bands at 1874 and 1790 cm^{-1}.

When $Co(CO)_3NO$ contacts the γ-alumina surface, only weak carbonyl bands are present, the main components being nitrosyl bands that develop immediately at 1874 and 1790 cm^{-1}. A brief evacuation removed all evidence of carbonyl species, but subsequent addition of NO resulted in further growth of the 1874- and 1790-cm^{-1} bands. Again, solvent extractions failed to remove this complex from the support.

Magnesia. The primary result of subliming $Co_2(CO)_8$ onto MgO is the development of $Co_4(CO)_{12}$ and $Co(CO)_4^-$ on the support.[3] Addition of NO yielded, within 15 min, the spectrum shown in Figure 5B, but after 1 day all ν(CO) peaks disappeared and only bands at 1855, 1771, 1585, 1321, and 1220 cm^{-1} remained (Figure 5C).

Table I. Summary of IR Frequencies of Observed Nitrosyl Species

species	support	infrared bands cm^{-1}
$Co(NO)_3$	silica	1868, 1794
	Na-Y	1892, 1811
	Na-X	1886, 1799
	alumina	1874, 1790
	MgO	1855, 1771
$Co(CO)_3NO$	silica	2104, 2040, 1807
	Na-Y	2118, 2066, 1817
	Na-X	2120, 2063 (1817)
	MgO	2108, 2047, 1810
$BCo(CO)_2NO$	Na-Y	2020, 1990, 1776
	Na-X	2020, 1990, 1755

Comparison of spectra B and C in Figure 5 shows a deepening of the minimum between 1770 and 1850 cm^{-1} that suggests a weak feature near 1810 cm^{-1} may be present in Figure 5B. A band near 1810 cm^{-1}, together with the ν(CO) bands at 2108 and 2047 cm^{-1}, again indicates the presence of $Co(CO)_3NO$ as an intermediate on the MgO surface during formation of $Co(NO)_3$ from cobalt carbonyl. Addition of ^{15}NO to the sample that produced the spectrum in Figure 5C resulted, after exposure for 1 day, in a spectrum displaying isotopic shifts of all the ν(NO) bands (Figure 5D). This isotopic effect is also obtained by the direct exposure of a Co_2/MgO sample to ^{15}NO to produce a spectrum with $\nu(^{15}NO)$ bands at 1824 (1855), 1782 ($\sim$1810), 1734 (1771), 1585 (1595), 1290 (1321), and 1196 (1220) cm^{-1}, where the frequencies in parenthesis are those of the corresponding band in the ^{14}NO spectrum.

Besides the development of the several bands due to nitrogen-containing species when the Co_2/MgO sample is exposed to NO, intensities of bands due to surface carbonate, at 1513, 1385, 1070, 860 and 809 cm^{-1}, increase markedly during exposure of the sample to NO. (Unlike the other supports, the relative IR transparency of the magnesia in the 800–1300-cm^{-1} region provided the opportunity to observe changes in that region on this support.)

In vacuo thermal treatment at 200 °C, for a sample like that containing the ^{15}N species shown in Figure 5D, resulted in the gradual loss of all ν(NO) bands. The higher frequency pair of bands (at 1824 and 1734 cm^{-1} for ^{15}NO and due to $Co(^{15}NO)_3$) disappeared allometrically followed by a slower loss of the features at 1290 and 1196 cm^{-1}. When this completely denitrosylated sample was exposed to ^{14}NO, very weak $Co(NO)_3$ bands reappeared, more intense features at 1321 and 1220 grew back within 1 day, and a weak band near 1585 cm^{-1} also gradually developed.

Assignment of the two bands of $Co(NO)_3$ on MgO (1855 and 1771 cm^{-1}) is quite straightforward on the basis of the results for the reaction of NO with cobalt carbonyls on other supports. The lower frequency vibrations involving nitrogen species (1321 and 1220 cm^{-1}) were not observed on other supports, except Na–X. Observation of these bands is at least partly due to the wider IR window with magnesia but may also be due to the different chemical nature of that support.

The metal complex, $[Co(NH_3)_5NO]^{2+}$, has its ν(NO) mode near 1650 cm^{-1}. The low frequency of the NO stretch in this complexes suggests that NO ligand is more like NO^- on Co(III). Thus, the 1595-cm^{-1} band in the present study may be due to a mononitrosyl complex of oxidized cobalt at the MgO surface.

The bands at 1220 and 1321 cm^{-1} are in the region of NO vibrations for free and complexed NO^- and NO_2^-.[16-18] The observation of loss, at 200 °C, of the species responsible for these bands is consistent with the ability to remove such species by

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evacuation at 200 °C[18] or to decompose cobalt nitro complexes on zeolite near 200 °C.[13]

Finally, when a thermally decomposed sample, from which all vestiges of ν(NO) bands have been removed, is exposed to fresh NO gas at room temperature, the major new species formed are the NO_2^- ion and some N_2O, suggesting the thermal decomposition produced a sample with cobalt primarily present in the oxidized form.

Conclusions

All cobalt species observed spectroscopically (Table I) were molecular complexes bound to oxide surfaces. In conjunction with earlier reports,[2] the results underscore the rich nature of the molecular chemistry of certain metal carbonyls on these oxides and illustrate not only differences in reactivity compared with the homogeneous phases but also among the various surfaces themselves.

The identification of the trinitrosyl species as the $Co(NO)_3$ complex of zerovalent cobalt is subject to some debate. Supporting this conclusion is the close correspondence of the ν(NO) IR spectrum with that reported by Sabherwal and Burg, the absence of any chemical evidence (viz., H_2 evolution) for oxidation of cobalt during the process of forming the trinitrosyl, and the close analogy to the reported synthesis of solid $Co(NO)_3$ by nitrosylation of $Co_2(CO)_8$ proceeding through the $Co(CO)_3NO$ intermediate.

On the other hand, the failure to extract the neutral $Co(NO)_3$ species from any of the surfaces into an appropriate solvent raises some question about this assignment and suggests the species may be an ionic complex like $[Co(NO)_3]^{2+}$. However, although previous work has shown that some oxidized cobalt may be readily formed via room temperature disproportionation of $Co_2(CO)_8$ on some of the supports used,[1-3] the room-temperature formation of Co^{2+} from $Co_2(CO)_8$ on silica has not previously been reported, even though both $Co_2(CO)_8$ and $Co(CO)_3NO$ are spontaneously and stoichiometrically converted to the trinitrosyl complex on this support. The weight of evidence seems, therefore, to support the formation of a neutral cobalt trinitrosyl, and the succeeding discussion works from that conclusion.

The interaction of $Co(CO)_3NO$ with the various surfaces illustrates their different effects on reactivity. For example, the $Co(CO)_3NO$ intermediate is quite stable on silica, converting only slowly to $Co(NO)_3$, while on γ-alumina the $Co(CO)_3NO$ "intermediate" is hardly observed even when it is directly sublimed onto the surface.

When sublimed onto Na–Y and Na–X zeolites, $Co(CO)_3NO$ produces initially two different surface complexes, each characterized by two carbonyl vibrations. These are assigned as adsorbed $Co(CO)_3NO$ and $BCo(CO)_2NO$, where B is a surface base. This interpretation of the infrared patterns is based on differences in the relative intensities of the carbonyl bands for "$Co(CO)_3NO$" on Na–Y compared with "$Co(CO)_3NO$" on Na–X. Addition of NO to these complexes leads to rapid production of $Co(NO)_3$.

$Co(CO)_3NO$ and $BCo(CO)_2NO$ are not stable on Na–X and spontaneously disproportinate to form $Co(NO)_3$. These complexes, though stable on Na–Y, can be converted with facility to $Co(NO)_3$ by room-temperature evacuation. When exposed to alumina, $Co(CO)_3NO$ is converted immediately to $Co(NO)_3$. Addition of NO to any sample of supported $Co(NO)_3$ prepared by spontaneous in vacuo reaction of $Co(CO)_3NO$ on any of these surfaces results in an increase of the nitrosyl band intensities, indicating adsorption of NO on "bare" Co to yield more $Co(NO)_3$. Since nitrosylation of Co^{II}–Y and Co^{II}–X zeolites[16] results in infrared bands significantly different from those observed in this study and since no intermediates corresponding to the stable and oft reported dinitrosyl of Co(II) were observed under any conditions, it is concluded that this "invisible" Co is not simply supported Co(II). The $Co(CO)_3NO$ must react on these surfaces by releasing both NO and CO with the cobalt and then recombining with NO to form $Co(NO)_3$:

$$Co(CO)_3NO \rightarrow \text{“Co”} + 3CO + NO$$

$$\text{“Co”} + 3NO \rightarrow Co(NO)_3$$

The spontaneous conversion of $Co(CO)_3NO$ to $Co(NO)_3$ on Na–X, the direct reaction on Na–X of cobalt carbonyls with NO to form $Co(NO)_3$, and the formation of $Co(NO)_3$ on MgO all are accompanied by formation of other nitrogen oxides—probably N_2O and NO_2^-. These products were not observed on other supports, although the strong absorbance below 1300 cm^{-1} in the IR spectrum of γ-alumina may have precluded observation of these species in that case. It appears that the propensity toward formation of N_2O and NO_2^- is greatest for those cases with the lowest frequency ν(NO) bands (greater NO^- character) for the adsorbed cobalt carbonyl nitrosyl intermediates. A possible mechanism for N_2O and NO_2^- formation from nitrosyl complexes in homogeneous systems has been reviewed by McCleverty,[19] who proposed a scheme that which formally involves NO attack on coordinated NO^-.

The behavior observed in this study affirms the importance of surface interactions on the molecular chemistry of metal complexes. Further work with these systems will no doubt continue to reveal new and novel reactivity not known in homogeneous phases.

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Registry No. $Co(NO)_3$, 28484-23-3; $Co(CO)_3NO$, 14096-82-3; $Co_2(CO)_8$, 10210-68-1; $Co_4(CO)_{12}$, 17786-31-1; NO, 10102-43-9; $Co(CO)_4^-$, 14971-27-8; silica, 7631-86-9; magnesia, 1309-48-4; γ-alumina, 1344-28-1.

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[19] McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53.