

An Infrared Study of the Behavior of CO, NO, and CO + NO over Rh/Al₂O₃ Catalysts

RON DICTOR

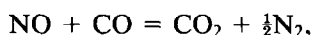
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Infrared spectroscopy was used to study the interaction of carbon monoxide and nitric oxide on a 0.475% Rh/Al₂O₃ catalyst. Both CO and NO readily adsorb on a prerduced catalyst surface. NO is not observed spectroscopically on preoxidized catalysts, yet isocyanate is produced during subsequent displacement by CO. The adsorption of CO on a preoxidized catalyst parallels the reduction of the catalyst. At temperatures in excess of 250°C and mixed feeds with CO/NO ≥ 1, a large buildup of isocyanate is observed on the support. At temperatures greater than 300°C an infrared band attributed to adsorbed cyanide ion is observed near 2150 cm⁻¹. Experiments involving displacement of NO by CO, displacement of CO by NO, and coadsorption of CO + NO show that contiguous rhodium surfaces are necessary for isocyanate production. Though the rhodium *gem*-dicarbonyl species, Rh(CO)₂, was observed, there was no experimental evidence demonstrating the presence of Rh(NO)₂ or Rh(NO)(CO) complexes. © 1988 Academic Press, Inc.

INTRODUCTION

One of the most important reactions occurring in automobile catalytic converters is that between NO and CO,



where the reactants are both undesirable pollutants. Rhodium is active for this reaction near stoichiometrically balanced compositions and is therefore included in the catalyst formulation. The reaction proceeds through NO dissociation, N atoms recombine or react with NO to form N₂, and CO reacts with adsorbed O atoms to form CO₂. Oh and co-workers recently compared the CO + NO reaction to the CO oxidation reaction (2CO + O₂ = 2CO₂) over Rh/Al₂O₃ catalysts and a Rh(111) single crystal (1). They found that the kinetics of the oxidation reaction were similar over the two catalysts whereas those of the CO-NO reaction were not.

Though several studies have been done on the interactions of CO and NO with catalyst surfaces, much uncertainty still exists regarding the identities and behaviors of surface species. Perhaps the best under-

stood of these interactions is that of CO with the Rh/Al₂O₃ surface (2-8). CO adsorbs molecularly to form at least three different surface species that are readily identified by infrared spectroscopy: linear carbonyl (2040-2070 cm⁻¹), bridged carbonyl (ca. 1850 cm⁻¹), and the *gem*-dicarbonyl (symmetric stretch 2100 cm⁻¹, asymmetric stretch 2030 cm⁻¹). The *gem*-dicarbonyl, Rh(CO)₂, is generally associated with isolated Rh¹⁺ sites, the bridged and linear species with a contiguous Rh⁰ surface.

Much less work has been done on the NO/Rh system and, as a consequence, there is more confusion over the nature of the surface species. NO adsorbs molecularly on rhodium surfaces and, under certain conditions, also dissociates (9, 10). Several nitrosyl species have been identified on Rh/Al₂O₃ catalysts and are characterized by infrared absorbance bands between 1600 and 2000 cm⁻¹. Arai and Tominaga assigned the nitrosyl species as NO⁺, NO, and NO⁻ (NO⁺ and NO⁻ having partial ionic character), which absorbed in the infrared at 1910, 1830, and 1740 cm⁻¹, respectively (6). More recently, Liang and

co-workers associated nitrosyl bands at 1912 and 1648 cm^{-1} with $\text{Rh}-\text{NO}^+$ and $\text{Rh}-\text{N}=\text{O}$ (bent NO), respectively (11). The authors also observed infrared bands at 1825 and 1743 cm^{-1} and assigned them to the symmetric and asymmetric stretches of a dinitrosyl species, $\text{Rh}(\text{NO})_2$. This latter assignment has been made by several groups (11-13) and contrasts with the earlier band assignments to neutral and negatively-charged NO adsorbates.

The interaction of CO and NO on supported catalyst surfaces often leads to the production of adsorbed isocyanate. Solymsi and co-workers have shown that the frequency at which isocyanate absorbs in the infrared is more dependent on the catalyst support than on the active metal component (14). Thus, isocyanate resides largely on the support. The dual-band appearance of isocyanate at 2230 and 2260 cm^{-1} is thought to arise from different coordination sites on the alumina surface (14). Additional bands have been observed in the CO + NO system at ~ 2180 and ~ 2150 cm^{-1} and are most often attributed to isocyanate adsorbed on the metal component and adsorbed cyanide ion, respectively (15-18). Very little evidence has been produced for this latter assignment.

The experimental procedures employed in this work are different from those used in most previous studies in that spectra were collected under (reactant gas) flowing conditions, and oxidations and reductions were done for extended periods of time. Dictor has shown that the pretreatment of $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts significantly affects the activity for the water-gas shift reaction (19), the activity being highly sensitive to oxidative pretreatments. It is shown here that the interactions of NO and CO with each other and with the catalysts are also highly sensitive to catalyst pretreatments.

EXPERIMENTAL

The infrared cell used in this investigation was developed by Hegedus and co-

workers and has previously been described in detail (20). It is composed of two 2 $\frac{3}{4}$ " vacuum flanges modified to include a gas inlet and gas outlet, a thermocouple which abuts the catalyst wafer, and two sapphire windows. The low-dead-volume inside of the reactor accommodates a pressed catalyst wafer supported in an aluminum holder. The sapphire windows of the reactor provide excellent infrared transmission through 1700 cm^{-1} , but the transmission falls to immeasurable levels by 1600 cm^{-1} . The reactor was wrapped with a heating tape, insulated, and mounted on an accessory for the Perkin-Elmer 180 spectrometer which was used in this study. All of the experiments were done under flow conditions, i.e., CO and/or NO carried in a He diluent were continuously passed through the reactor. Oxidations and reductions were done at atmospheric pressure by passing 5% O_2 or 5% H_2 , respectively, through the reactor cell. The feed compositions were made up by means of a gas manifold described in a previous publication (19).

The incipient wetness technique was used to make 0.475% $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts. The amine salt of rhodium dicarbonyl bromide, (*n*-but $_4\text{N}$) $_2\text{Rh}_2(\text{CO})_2\text{Br}_3$, was dissolved in acetone and used to wet low-density $\theta\text{-Al}_2\text{O}_3$ beads (Grace Chemical). The beads were first dried at room temperature, then calcined at 500°C for 2 h in air. They were then crushed and sieved to 100/170 mesh. Approximately 100 mg of powder was pressed into a wafer 0.2 mm thick, mounted on a wafer holder, and loaded into the reactor. All subsequent treatments were done *in situ*.

The spectrometer was used with a spectral slit width of 2 mm and a spectral resolution of 5 cm^{-1} . It was interfaced with a DEC Minc-11 computer which was used for collecting spectra. A typical scan from 2500 to 1600 cm^{-1} lasted 8 min; the times reported in the figures represent time between an event and the start of a scan. The grating change at

2000 cm⁻¹ is responsible for the apparent spectral features in several of the figures.

RESULTS

Adsorbed CO

The influence of oxidation and reduction catalyst pretreatments on CO chemisorption was investigated and the results are shown in Fig. 1. The spectrum of the catalyst that was oxidized overnight at 450°C (Figs. 1a–1e) took over 1 h to develop fully in 1% CO at 150°C. In contrast, that of the prerduced catalyst (Figs. 1f, 1g) developed almost instantly. The earliest features to appear on the preoxidized catalyst were the dicarbonyl bands at 2088 and 2022 cm⁻¹ followed later by the feature for linearly bonded CO at ~2060 cm⁻¹. It is possible that a band representing CO adsorbed

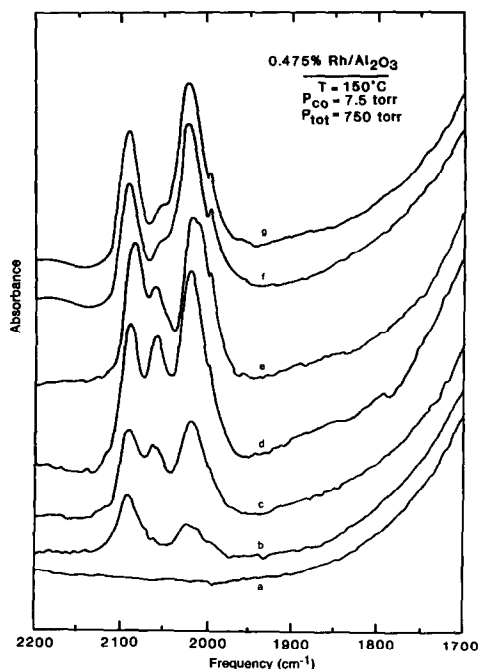


FIG. 1. Spectra following overnight oxidation at 450°C, 5% O₂, 1 atm. (a) Preceding introduction of CO; (b) immediately following introduction of CO; (c–e) after 15, 40, and 90 min, respectively. Spectra following overnight reduction at 450°C, 5% H₂, 1 atm. (f) Immediately following introduction of CO; (g) 35 min after introduction.

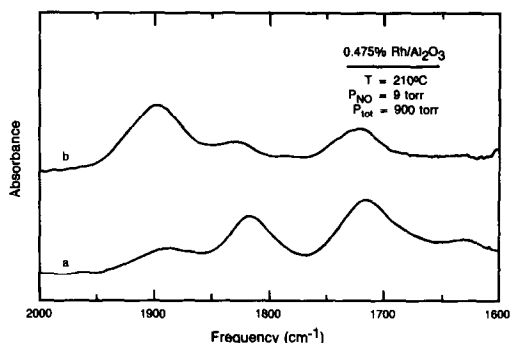


FIG. 2. Difference spectra following introduction of NO to catalyst reduced overnight at 450°C, 5% H₂, 1 atm. (a) Immediately following introduction of NO; (b) after 15 min.

on highly oxidized rhodium sites may contribute to the intensity of the high-frequency dicarbonyl band in curve 1b (8). Dictor has shown that the addition of H₂O to the feed suppresses the dicarbonyl features, increases the intensity of the bridge-bonded CO band (1850 cm⁻¹), and leaves the linear-CO band relatively unchanged (19). In dry systems the intensity of the band of bridge-bonded CO is usually low.

In Figs. 1f and 1g it can be seen that the linear CO band on the prerduced catalyst almost fully folded into the band from the asymmetric dicarbonyl stretch. The intensity of the linear-CO band relative to the dicarbonyl bands is lower in the case of the prerduced catalyst than for the preoxidized catalysts. The presence of the linear species was often difficult to confirm because of the variations in band position and intensity.

When CO was removed from the feed and the reactor purged with pure He, the linear and bridged CO features disappeared and the dicarbonyl bands remained. A small amount of O₂ in the feed produces similar results.

Adsorbed NO

The spectra in Fig. 2 were collected following introduction of 1% NO at 200°C to a wafer that had previously been reduced

overnight at 450°C. Three broad bands appeared between 1650 and 1950 cm^{-1} . Immediately following the introduction of NO, the bands at 1817 and 1716 cm^{-1} appeared, but the intensities of both peaks decreased and that of the band near 1890 cm^{-1} increased with time on stream. Increasing temperatures also favored the development of the 1890- cm^{-1} band; above 310°C only this band and its low-frequency shoulder (resulting from migration of the 1817- cm^{-1} band) were present.

In contrast with the results of Fig. 2, introduction of 1% NO to a catalyst that had been oxidized overnight at 450°C produced no absorption bands in the spectral range 2500–1600 cm^{-1} . However, NO or N atoms must have been present on the surface since a subsequent He purge and introduction of 1% CO led to the formation of isocyanate. This is discussed below.

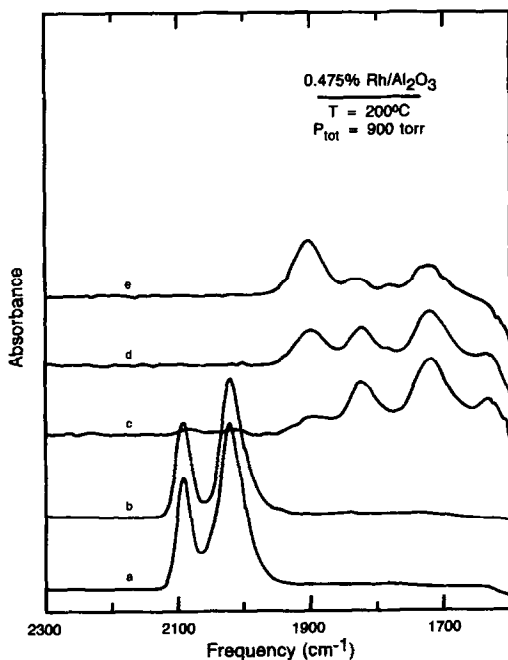


FIG. 3. Evolution of (difference) spectrum during displacement of preadsorbed CO by NO. Catalyst reduced 11 h in 5% H_2 , at 450°C, prior to experiments. (a) 1% CO flowing for 5 min; (b) following shut-off of CO; (c) immediately following introduction of NO; (d) after 10 min in flowing NO; (e) after 35 min in flowing NO.

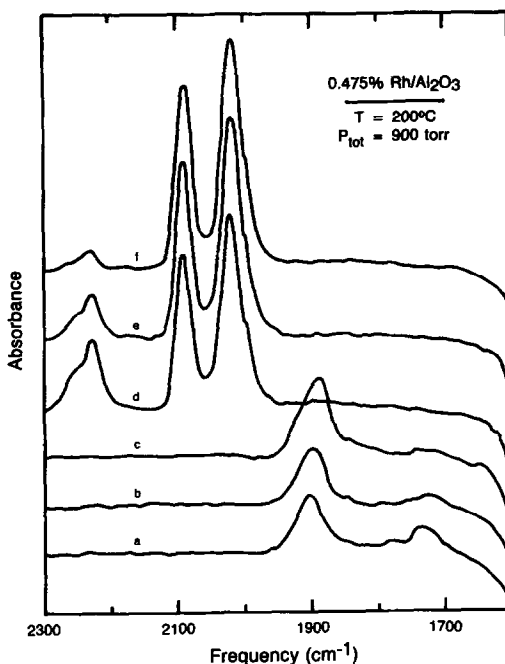


FIG. 4. Evolution of (difference) spectrum during displacement of preadsorbed NO by CO. Experiments follow those of Fig. 5. (a) 1% NO for 60 min; (b) immediately following shut-off of NO; (c) 20 min following shut-off of NO; (d) immediately following introduction of 1% CO; (e) 20 min following introduction of CO; (f) 70 min following introduction of CO.

Displacement: $\text{CO} \rightarrow \text{NO}$, $\text{NO} \rightarrow \text{CO}$

The introduction of 1% NO to a (reduced) catalyst that had previously been exposed to 1% CO was done at 200°C. As seen in Fig. 3, the carbonyl features were immediately suppressed while the nitrosyl bands appeared. The nitrosyl bands then behaved as seen above for NO introduced to a reduced catalyst, i.e., the intensity of the 1890- cm^{-1} band increased while that of the two lower-frequency bands decreased. The band near 1640 cm^{-1} may arise from the low transmission of the cell windows in this range, though its position does coincide with that of the bent Rh—NO feature reported by Liang and coworkers (11).

Reversing the order of introduction of gases produced contrasting behavior. Figure 4 shows the spectra that resulted from introducing CO to a reduced catalyst previ-

ously exposed to NO. The nitrosyl bands immediately disappeared and the carbonyl and isocyanate features developed. Similar observations were made when the experiment was repeated with an extensively oxidized catalyst. The results are shown in Fig. 5. It should be noted that for the oxidized catalyst, the nitrosyl features below 2000 cm⁻¹ were absent in the presence of 1% NO, and the isocyanate formed appeared to be more stable than that formed over the reduced catalyst. The appearance of isocyanate on a catalyst displaying no evidence of adsorbed NO suggests that NO was present in a dissociated state or its quantity and/or extinction coefficient made it difficult to detect. Another interesting observation is that isocyanate did not appear immediately on the oxidized catalyst whereas it did on the reduced catalyst. The first bands to appear on the oxidized catalyst were those of the dicarbonyl followed

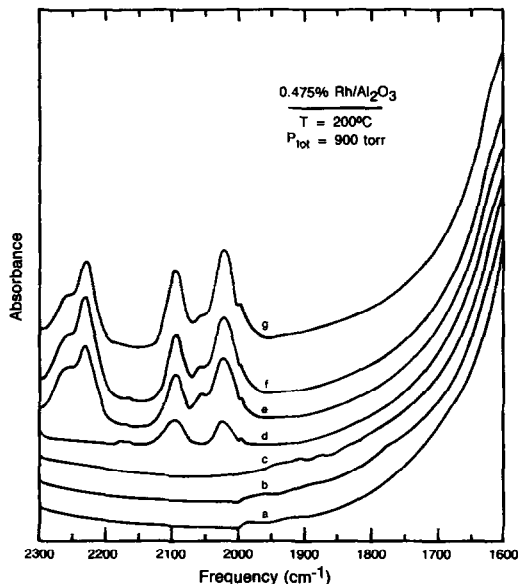


FIG. 5. Evolution of spectrum during displacement of preadsorbed NO by CO. Catalyst oxidized 14 h at 450°C, 5% O₂, 1 atm prior to experiments. (a) Blank; (b) immediately following introduction of 1% NO; (c) 25 min after introduction of NO; (d) immediately following He purge and introduction of 1% CO; (e-g) 10, 30, and 100 min following introduction of CO, respectively.

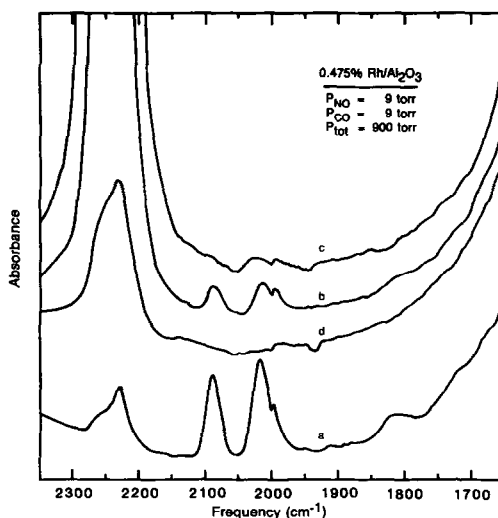


FIG. 6. Influence of temperature on spectrum for stoichiometric CO/NO feed mixture. (a) 200°C; (b) 250°C; (c) 300°C; (d) 350°C.

by the simultaneous appearance of the linear CO and isocyanate bands.

Interaction of CO + NO

The coadsorption and reaction of NO and CO on the Rh/Al₂O₃ catalyst produced complex spectra that were highly dependent on reaction temperature and reactant concentrations. In particular, notable differences were observed between lean conditions, NO/CO > 1, and rich conditions, NO/CO < 1.

The most prominent feature of all of the spectra collected at temperatures in excess of 250°C when CO/NO in the feed was ≥ 1 was the isocyanate band centered near 2230 cm⁻¹ with a high-frequency shoulder at 2260 cm⁻¹. An example of these features is shown in Fig. 6 for a set of back-to-back experiments in which feed composition remained unchanged as the reactor temperature was varied. The isocyanate bands first increased then decreased as the temperature was raised. This same behavior was observed when lean (1% CO, 2% NO) feeds were used, but under rich conditions the isocyanate feature continued to grow through 400°C. This can be seen in Fig. 7 for temperatures increasing from 250°C.

It can also be noted in Fig. 7 that a new peak develops from a low-frequency shoulder of the large isocyanate band. This band appears to be centered around $2130\text{--}2150\text{ cm}^{-1}$. It appeared consistently under rich conditions at temperatures in excess of 300°C . In an additional set of experiments this band was first developed at 400°C and then was eliminated when CO was removed from the feed. As shown in Fig. 8, the isocyanate feature lost its intensity much more rapidly than did this lower-frequency band.

On several occasions the low-frequency shoulder of the isocyanate band resolved into two bands after a switch to a lean feed. One band was the $2130\text{--}2150\text{ cm}^{-1}$ band and the other was centered near 2175 cm^{-1} . Though the results are inconclusive, it appeared that the presence of CO in the feed increased the likelihood of observing this additional band. Both bands are in the spectral region where one might expect to find adsorbed cyanide, —CN . To test the possibility that these peaks might indeed be adsorbed cyanide, HCN injections were made into the feed stream both under reaction

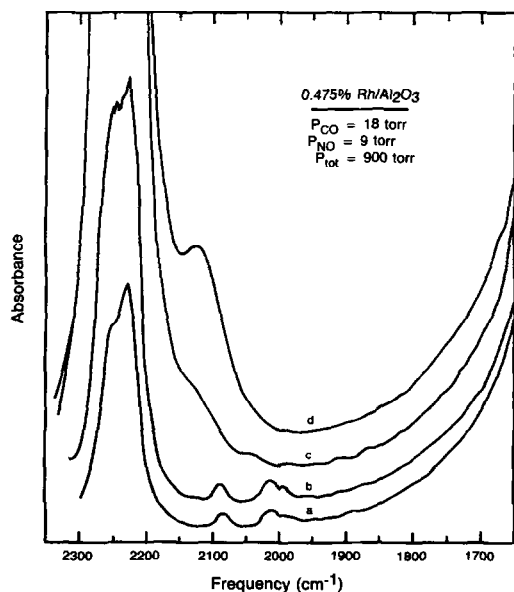


FIG. 7. Influence of temperature on spectrum for rich CO/NO feed mixture. (a) 250°C ; (b) additional 30 min at 250°C ; (c) 325°C ; (d) 400°C .

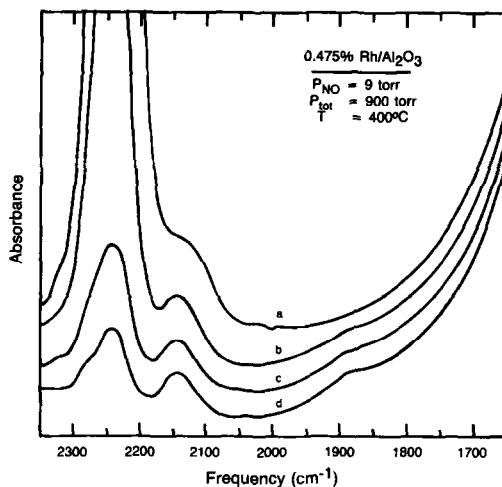


FIG. 8. Evolution of spectrum following switch from rich feed to NO only. (a) 1% NO + 2% CO; (b) immediately following CO shut-off; (c) 8 min after CO shut-off; (d) 16 min after CO shut-off. Distortion of baseline near 2300 cm^{-1} is due to CO_2 in spectrometer.

conditions and with an inert feed, at high and low temperatures. Under no circumstance did a new spectral feature develop or an existing feature get enhanced by the injection of HCN. The negative result of this experiment does not prove that the band is due to a species other than cyanide; it simply fails to confirm the identification.

The presence of molecularly adsorbed CO and NO was sensitive to temperature, as seen in Fig. 9. Upon introduction of 1% NO to the feed already containing 2% CO (at 150°C), all three nitrosyl bands appeared and the intensities of the dicarbonyl bands decreased. As the length of exposure increased, the band near 1890 cm^{-1} grew—possibly at the expense of the other NO bands but clearly not at the expense of the dicarbonyl bands, which remained nearly constant. As the temperature was increased to 200°C , all of the bands increased with the exception of the 1890 cm^{-1} band, which decreased. When the temperature was raised further, the intensities of all bands decreased. By 300°C all of the bands disappeared, but at 350°C the 1890 cm^{-1} band reappeared. Little isocyanate formed during the rise in temperature; this was typical

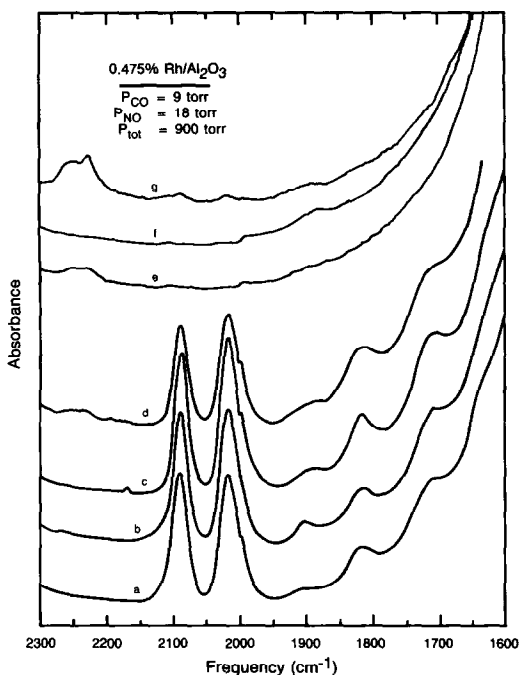


FIG. 9. Evolution of spectrum with increasing temperature under lean feed conditions. (a) Immediately following introduction of NO to feed at 150°C; (b) 30 min in mixed feed; (c) 200°C; (d) 250°C; (e) 300°C; (f) 350°C; (g) cooled back to 220°C.

of a very lean system. The removal of NO from the feed, though not shown in the figure, increased the intensity of the carbonyl bands.

Results qualitatively similar to those shown in Fig. 9 were obtained by simultaneously introducing CO and NO to the catalyst or by first introducing NO and then CO. In the latter case, the addition of CO not only suppressed the band near 1890 cm⁻¹ but increased the intensity of the two lower-intensity nitrosyl bands. This behavior was observed regularly when CO + NO feeds were used; increases or decreases of the intensity of the 1890-cm⁻¹ band were accompanied by the opposite effect on the lower-intensity bands. Higher concentrations of CO in the feed were more effective in suppressing the high-frequency NO band.

In situations where the linear (and also the bridged) carbonyl feature was present,

the addition of NO to the feed at low temperature fully erased these features. The net result was a spectrum showing the dicarbonyl bands and the nitrosyl bands with the 1890-cm⁻¹ band partially suppressed. Figure 10 shows these results for a system in which 1% NO is introduced to a catalyst resting in 1% CO at 150°C. A small amount of isocyanate is also formed at this low temperature.

One additional infrared band appears in many experiments and can be seen in Figs. 6 and 7. Under rich conditions a band of very low intensity develops near 2040 cm⁻¹ once the temperature exceeds 300°C. This band normally appeared following the disappearance of the two dicarbonyl bands. It was most prominent under conditions where the low-frequency shoulder of the isocyanate band developed. However, the shoulder appeared to develop independently of this peak.

DISCUSSION

Adsorbed CO

The sluggish development of the carbonyl spectrum over an extensively oxidized catalyst suggests that the catalyst must first be reduced by CO before adsorbing significant quantities of CO. Thus it

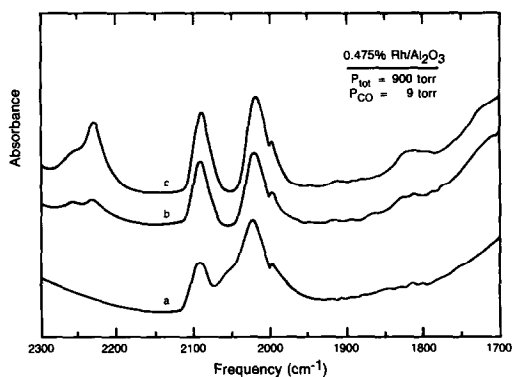


FIG. 10. Addition of NO to feed already containing CO. (a) CO only at 150°C; (b) 30 min following introduction of 1% NO to feed at 150°C; (c) CO + NO at 200°C. Note that the prominent feature at 2000 cm⁻¹ results from a grating change in the spectrometer.

is reasonable to expect the dicarbonyl feature to appear in advance of the linear- or bridged-CO bands since it is associated with Rh^{1+} ions and the others are associated with Rh^0 surfaces.

The carbonyl spectrum that develops following the introduction of CO to reduced rhodium catalysts is again dominated by the dicarbonyl bands, suggesting that the reduced catalyst was initially in the $1+$ state or that it oxidized from Rh^0 back to the $1+$ state following the introduction of CO. This latter possibility was suggested by Prins and co-workers (21) after they observed increases in Rh-Rh bond distances following the introduction of CO to a prerduced Rh/ Al_2O_3 catalyst. The infrared observations of Solymosi and Pasztor are in good agreement with this work (22). The authors found that the dicarbonyl bands developed slowly with increasing exposure time following introduction of CO to a reduced catalyst, apparently at the expense of the linear-CO band.

Adsorbed NO

In analogy to the rhodium dicarbonyl species, several groups have proposed the existence of the twin structure, $\text{Rh}(\text{NO})_2$, or the "fraternal twin" structure, $\text{Rh}(\text{NO})(\text{CO})$ (6, 11-13, 23). The dinitrosyl structure has stretching frequencies at 1825 and 1743 cm^{-1} , which correlate closely with two of the bands observed here (11). However, one expects the positions and relative intensities of the two bands to remain constant if they result from isolated $\text{Rh}(\text{NO})_2$ species. As seen in Figs. 2-4, changes have been observed in both quantities. Additionally, the introduction of NO to a CO-containing feed produces NO bands at 1817 and 1716 cm^{-1} with no significant diminution of the dicarbonyl features. Because of the competition for Rh^{1+} sites, the creation of $\text{Rh}(\text{NO})_2$ species is expected to be at the expense of $\text{Rh}(\text{CO})_2$ species.

Solymosi and Sarkany assigned bands at 2105 and 1760 cm^{-1} to the fraternal twin structure, $\text{Rh}(\text{NO})(\text{CO})$ (23). A feature at

2105 cm^{-1} would have increased the intensity of the high-frequency dicarbonyl band or appeared as a shoulder on that band, yet this feature was never observed. Similarly, a band at 1760 cm^{-1} was not observed in any of the displacement or mixed-feed experiments.

In light of the discussion above, the assignments of the 1890, 1817, and 1716 cm^{-1} bands as $\text{Rh}-\text{NO}^+$, $\text{Rh}-\text{NO}$, and $\text{Rh}-\text{NO}^-$, respectively, are acceptable. One might argue that the bands at 1817 and 1716 cm^{-1} are indeed due to dinitrosyl species and that their changes in position and intensity are caused by electronic and/or steric effects. However, the above assignments to the mononitrosyl species are most consistent with observations of the interactions between adsorbed NO and CO, an example of that being the apparent seesaw behavior between the 1890 and 1817/1716 cm^{-1} bands. This is discussed in detail below.

Infrared Bands: CO + NO

The frequency of the band near 2140 cm^{-1} is too high to be attributed to CO adsorbed on rhodium oxide, and bands in this region are most often assigned to $\text{M}-\text{NCO}$ (isocyanate on the metal), $\text{M}-\text{NCO}^-$ (isocyanate ion), or $-\text{CN}$ (cyanide on the metal or support). Hecker and Bell assigned a band in the 2170-2190 cm^{-1} region to $\text{Rh}-\text{NCO}$, observing that the band disappeared rapidly after the reactants were shut off (17). Unland originally assigned a band at 2148-2130 cm^{-1} to $\text{Pt}-\text{NCO}^-$ on the basis of isotope experiments (15). Solymosi and Rasko did a similar isotope exchange experiment using $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts and assigned a band at 2150 cm^{-1} to adsorbed cyanide ion (18).

The band appearing at 2150-2130 cm^{-1} in these experiments is interesting in that it develops only at high temperature and rich feed conditions yet remains relatively stable (compared to the band from isocyanate on the support) under oxidizing conditions. This would not be the expected behavior

for —NCO or —NCO⁻ adsorbed on the metal component. It is for this reason that a tentative assignment of this band to adsorbed cyanide ion is suggested. It is believed that cyanide is produced by removal of an O atom from adsorbed isocyanate. This would be consistent with our observation that the band appears at high temperatures and under CO-rich conditions.

The low-frequency shoulder of the isocyanate band sometimes resolved into two bands, the one which is believed to be due to cyanide and another near 2175 cm⁻¹. This latter band is assigned to Rh—NCO primarily on the basis of work by other groups (13, 17, 24, 25). The presence of CO enhanced the probability of observing this band. This is likely due to the dynamic equilibrium between isocyanate formation and decomposition (and migration) that is achieved in the presence of CO. Complete removal of CO from the feed halts production of isocyanate, and decomposition of the existing isocyanate is probably limited by the rate of diffusion from the support to the metal crystallites. In this latter case, little or no isocyanate will be present on the metal sites.

The band appearing near 2040 cm⁻¹ is assigned to a linear-CO feature since it occurs under rich conditions and its appearance does not parallel the development of any other peak. It should be recognized that a weak feature like this would probably not appear in a pulse experiment in which the partial pressures of the reactants are very low.

Interaction of CO and NO

The collective results of this study work together to create a simple yet consistent scheme for how CO and NO interact with the catalyst surface and with each other. It is in the context of this scheme that the remaining experimental results will be discussed.

It is apparent from the results of Figs. 2 and 3 that NO dissociates on a reduced rhodium surface but not on an oxidized sur-

face. In Fig. 4 it is seen that isocyanate forms immediately following the introduction of CO to an extensively reduced catalyst previously exposed to NO. This suggests that nitrogen atoms were present and available, that NO had dissociated. In contrast, the oxidized catalyst experienced an induction period following exposure to CO. The catalyst first reduced from a high oxidation state (as evidenced by the initial appearance of the dicarbonyl bands *followed* by the appearance of the linear-CO feature) before isocyanate appeared. Thus it may be inferred that a reduced rhodium surface is needed for both NO dissociation and isocyanate formation. The reverse experiment, displacement of preadsorbed CO by NO, produced no isocyanate and suggests that NO displaced CO before it could react with it. This has been observed repeatedly in the literature (6, 13, 18). It is interesting that Fig. 3 shows NO displacing primarily dicarbonyl CO. One would expect isocyanate formation at these sites given the mechanism of Rochester *et al.* (13) and Solymosi and Sarkany (23) showing interaction between CO and NO on a Rh(NO)(CO) ("fraternal twin") complex. The absence of isocyanate suggests that the dicarbonyl sites are not sites of chemical interaction between NO and CO.

The spectra obtained when NO + CO feeds were used reinforce the conclusions just reached. Figures 6, 9, and 10 show that the linear- and bridged-CO features are suppressed in the presence of NO. This again suggests that the interaction of NO and CO occurs on a contiguous rhodium surface and not on isolated sites.

The behavior of the nitrosyl features can also be explained in the context of the above scheme. As NO dissociates on a reduced rhodium surface, oxygen atoms begin to assert an electron-withdrawing effect on rhodium which in turn is passed on to the molecularly adsorbed NO molecules. As this proceeds, the NO molecules which first adsorbed as neutral or (net) negatively charged species become slightly positively

charged. This is followed spectroscopically by the growth of the 1890-cm^{-1} band and the disappearance of the 1817- and 1716-cm^{-1} bands with either time on stream or increases in temperature. If the oxygen atoms are removed from the surface, as through reaction with CO to form CO_2 , the surface is less oxidized and the intensity of the Rh-NO^+ band diminishes. Thus we see the basis of the seesawing effect between the 1890-cm^{-1} band and those at 1817 and 1716 cm^{-1} : the intensities of the bands increase or decrease as a function of the oxygen content of the surface.

The extent to which NO can oxidize a rhodium catalyst at 200°C is shown qualitatively in Fig. 4. Despite the length of time on stream and the strong development of the 1890-cm^{-1} band, the catalyst appears to be only lightly oxidized since the introduction of CO causes immediate spectral changes. This is also consistent with the fact that NO could not be observed on the extensively oxidized catalyst (Fig. 5).

SUMMARY

Carbon monoxide adsorbs nondissociatively on $\text{Rh/Al}_2\text{O}_3$ catalysts in three forms identifiable by infrared spectroscopy: gem-dicarbonyl (2088 and 2022 cm^{-1}), linear ($2040\text{--}2060\text{ cm}^{-1}$), and bridged (1870 cm^{-1}). Extensively oxidized catalysts must first be reduced before they show features of adsorbed CO. Three infrared bands between 1950 and 1650 cm^{-1} are attributable to molecularly adsorbed NO: Rh-NO^+ (1890 cm^{-1}), Rh-NO (1817 cm^{-1}), and Rh-NO^- (1716 cm^{-1}). NO dissociates on reduced rhodium surfaces and thereby lightly oxidizes the catalyst, favoring development of Rh-NO^+ .

Under reaction conditions with $\text{CO/NO} \geq 1$ and temperatures greater than 250°C , a tremendous buildup of isocyanate is observed on the support. Under rich conditions above 300°C an infrared band assigned by other workers to adsorbed cyanide is formed near 2150 cm^{-1} and is

more stable when the feed is made lean, than is the band due to isocyanate. Experiments involving displacement of CO by NO, displacement of NO by CO, and coadsorption of $\text{CO} + \text{NO}$ show that contiguous rhodium surfaces are necessary for isocyanate production and that isocyanate is not produced at isolated Rh^{1+} (dicarbonyl) sites. There was no experimental evidence to suggest that $\text{Rh}(\text{NO})_2$ or $\text{Rh}(\text{NO})(\text{CO})$ complexes are formed.

ACKNOWLEDGMENT

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