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An Infrared Study of the Interaction between Adsorbed CO and Adsorbed NO on Supported Ru and Supported Pt

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The interaction between CO and NO adsorbed on 6% Ru–silica and 6% Pt–silica samples at 25°C has been studied using infrared spectroscopy. When adsorbed CO is slowly displaced from a 6% Ru–silica surface by NO, we observe a new band at 2180 cm^{-1} in the infrared spectrum. The intensity of the band at 2180 cm^{-1} depended on the relative amounts of CO and NO adsorbed on the surface. In studies made using $C^{13}O$ and $N^{15}O$, we find that this new surface species contains both C and N atoms and that it is bound to the Ru surface through the N atom; thus, we conclude that the band at 2180 cm^{-1} is the antisymmetric stretching vibration of a surface isocyanate, Ru–NCO. When CO and NO are both adsorbed on a 6% Pt–silica sample, we do not observe a strong band in the 2200 cm^{-1} region. A mechanism is proposed for the formation of a surface isocyanate at 25°C on silica-supported Ru; the failure to observe isocyanate formation on silica-supported Pt is also discussed.

INTRODUCTION

The formation of a surface isocyanate in the high temperature reactions of CO and NO has been of recent interest in catalysis. In a simultaneous infrared and kinetic study of the reduction of NO by CO over CuO, London and Bell (*1*) observed a weak band in the 2260 cm^{-1} region. In their consideration of the reaction mechanism, they suggested that this band is due to the formation of a surface isocyanate. Unland (*2*) reported a strong band at 2263 cm^{-1} in an infrared study of the interaction of NO and CO at 400°C over supported Pt. He assigned this band to the antisymmetric stretching vibration of a surface isocyanate, $\nu_{a(NCO)}$. In more recent comparative studies of isocyanate formation over various supported noble metal catalysts (Pt, Pd, Rh, Ir, and Ru), Unland (*3*, *4*) observed the weakest band assigned to the surface isocyanate over supported Ru. It is known that Ru selectively reduces NO to N_2 with low NH_3 formation, whereas NH_3 is a major product in the NO reduction over Pt, Pd, Rh, and Ir (*5–8*); thus, Unland suggested that the formation of the surface isocyanate may be an intermediate step in NH_3 formation.

In these previous studies both investigators have reported the appearance of a band in the infrared spectrum which they have assigned to the antisymmetric stretching vibration of a surface isocyanate; however, neither author has investigated the mechanism whereby this surface species is formed. Since it may be possible to observe interactions between adsorbed molecules at lower temperatures, we have made an infrared study of the interaction between adsorbed CO and adsorbed NO on silica supported Ru and silica supported Pt at 25°C.

In earlier infrared studies we have characterized the adsorption of CO and NO on supported Ru (*9*, *10*). When CO is adsorbed on a reduced 6% Ru–silica sample, we observe a strong band at 2030 cm^{-1} and two weak high frequency CO bands at 2150 cm^{-1} and 2080 cm^{-1}. Furthermore, we find that the relative intensities of these three CO bands change when O_2 is added before or after the adsorption of CO. When CO is adsorbed on an oxidized Ru–silica sample, we observe a strong band at 2080 cm^{-1} and bands of medium intensity at 2135 and 2030 cm^{-1}. Thus the relative intensities of the three CO bands indicate whether the Ru surface is in a reduced or oxidized state. In this study the following band assignments were made: the band at 2030 cm^{-1} is assigned to $\nu_{(CO)}$ for CO linearly adsorbed on a Ru surface site, the band at 2080 cm^{-1} is assigned to $\nu_{(CO)}$ for CO adsorbed on an Ru surface site that is perturbed by a nearby oxygen atom and the band at 2150 cm^{-1} is assigned to $\nu_{(CO)}$ for CO adsorbed on a RuO surface site.

The adsorption of NO on silica supported Ru is complex; however, when NO is adsorbed on a 6% Ru–silica sample subjected to a 4-h reduction at 325°C, the dominant feature in the spectrum is a strong band that first appears at 1800 cm^{-1} and shifts to 1815 cm^{-1} with increasing surface coverage. We assign this band to the ν_{NO} for NO linearly adsorbed on a Ru surface site, Ru–NO.

The chemisorption of CO on silica supported Pt has been studied extensively and it is characterized by a single strong absorption band at 2070 cm^{-1} (*11*). In contrast to the numerous infrared studies of CO adsorption on supported Pt, there has been no recent study of NO adsorption on supported Pt; therefore, we have included the spectrum obtained when NO is adsorbed on silica-supported Pt in this report.

In this investigation we have made a comparative study of the stability and interaction of adsorbed CO and NO on silica-supported Ru and silica-supported Pt using infrared spectroscopy.

EXPERIMENTAL

Materials. The 6% Ru–silica sample used in this study was prepared by impregnating Cab-o-sil, Grade M-5 (Cabot Corp., Boston, Mass.) with an aqueous solution of $RuCl_3$–$3H_2O$ (Engelhardt Industries). A similar technique was used to prepare the 6% Pt–silica sample from $H_2PtCl_6 \cdot 6H_2O$ (Engelhardt Industries). A detailed description of the preparation of the sample pellets for use in infrared studies has been reported previously (*9*). The average crystallite size of both the 6% Ru–silica sample and the 6% Pt–silica sample was estimated as 60 Å. The particle size was determined by the Sherrer equation for X-ray line broadening using the (101) line of Ru and the (111) line of Pt.

Commercial H_2 was used in the reduction of the sample pellets. It was purified before use by passing it through a Deoxo unit to convert O_2 impurities to H_2O, which was then removed by a molecular sieve and a liquid N_2 trap. NO (Matheson Technical Grade) was first purified by a standard vacuum distillation; dissolved N_2 was removed by the freeze–thaw technique. In the freeze–thaw technique, the NO sample is first frozen at liquid N_2 temperatures (−196°C) and evacuated for 5 min. The liquid N_2 is then removed, the first portion is pumped off, and the remainder is stored for use in a 1-liter glass bulb. This process can be repeated several times until all N_2 impurities have been removed. $C^{13}O$, reported 90% enriched in C^{13} (Bio Rad Laboratories), and $N^{15}O$, reported 99% enriched in N^{15} (Bio Rad Laboratories), were both used without further purification. All gases were periodically checked for purity on a Dupont Model 104 mass spectrometer.

Techniques. Prior to the adsorption experiments, the Ru samples were subjected to the following pretreatment: evacuated for 1 h at 325°C, reduced in flowing H_2 (150 ml/min) for 4 h at 325°C and evacuated for 2 h at 325°C. Initially the Pt samples were subjected to the same pretreatment; however, we observed that a shorter reduction period of 2 h at 325°C was adequate for complete reduction of the Pt surface. Therefore, in subsequent experiments this shorter reduction period of 2 h was used; the evacuation procedure was the same as that used for the Ru samples.

The infrared cell and the adsorption apparatus have been described in an earlier report (*9*).

All infrared spectra were recorded at room temperature on a Perkin Elmer Model 521 infrared spectrometer using the double beam method. In the double beam mode of operation, identical pellets, e.g., 6% Pt–silica, are placed in both the sample and reference beams of the infrared spectrometer. The absorption bands due to the silica support in the sample beam are cancelled by the same absorption in the reference beam. In this way a relatively flat baseline is obtained from 4000 to 1300 cm^{-1}. Below 1300 cm^{-1} the silica support completely absorbs the infrared radiation.

All mass spectral analysis were made on a Dupont Model 104 mass spectrometer.

RESULTS AND DISCUSSION

Interaction between CO and NO on Supported Ru

In our initial infrared studies we determined the stability of adsorbed CO, CO(ads), to gaseous NO, and also the stability of NO, NO(ads), to gaseous CO. In the infrared spectrum obtained when a 6% Ru–silica sample with complete CO surface coverage was exposed to 5 Torr NO(g) at 25°C (excess CO(g) was previously removed by 15-min evacuation, whereas excess NO(g) is not evacuated), we observe a sharp decrease in the intensity of the CO band at 2080 cm^{-1} and note the appearance of a strong band at 1815 cm^{-1} due to NO(ads). There is no change in the intensities of the two high frequency CO bands at 2150 cm^{-1} and 2080 cm^{-1}, even after exposure to excess NO(g) for over 1 h. These spectra are illustrated in Fig. 1. The decrease in the intensity of the CO band at 2030 cm^{-1} in the presence of excess NO(g) suggest that CO linearly adsorbed on the Ru surface is either displaced by NO or it is oxidized to CO_2 in the presence of excess NO(g). In a previous study (*9*) we observed an increase in the intensities of the high frequency CO bands at 2150 and 2080 cm^{-1} when CO(ads) is oxidized to CO_2; thus, we conclude that CO(ads) is displaced from the Ru surface by NO(g). This observation is confirmed

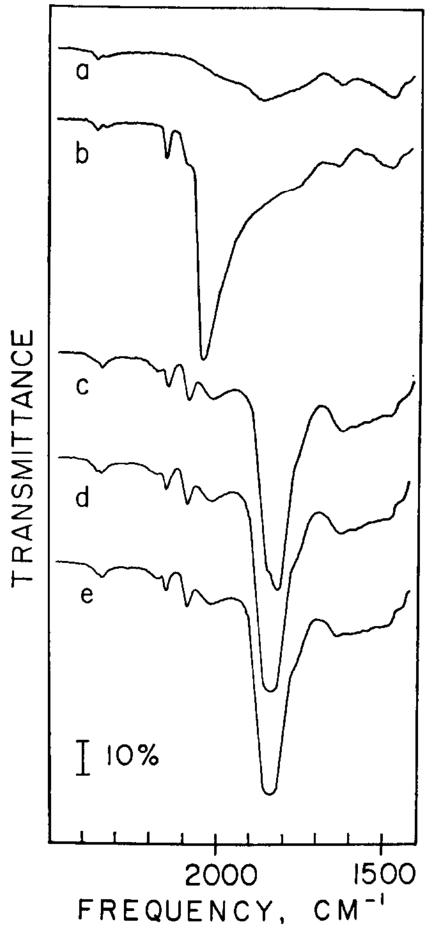


Fig. 1. Infrared spectra illustrating the displacement of adsorbed CO by excess NO(g) on a 6% Ru–silica sample at 25°C: (a) background; (b) full CO surface coverage followed by a 15-min evacuation; (c) 5 Torr of NO added, exposure time = 15 min; (d) exposed to 5 Torr of NO for 1 h; (e) cell evacuated for 15 min at 25°C.

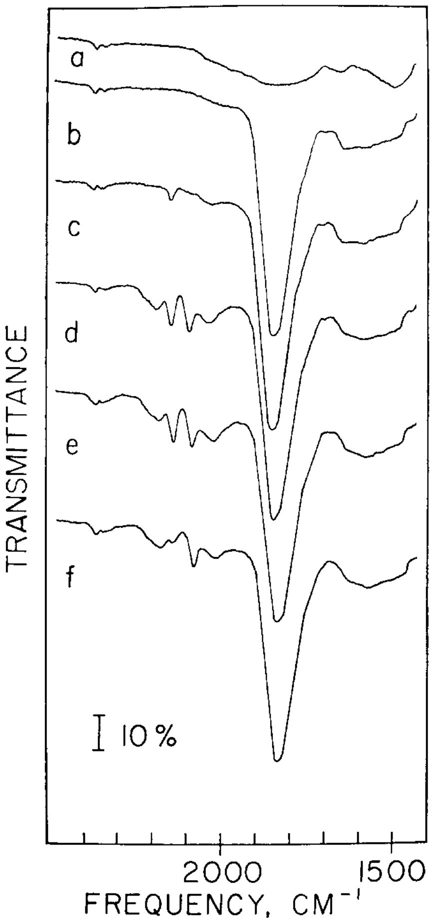


FIG. 2. Infrared spectra illustrating the effect of the addition of excess CO(g) to a 6% Ru–silica sample with full NO surface coverage: (a) background; (b) full NO surface coverage followed by a 15-min evacuation; (c) 5 Torr of CO added, exposure time = 15 min; (d) exposed to 5 Torr of CO for 30 min; (e) exposed to 5 Torr of CO for 24 h; (f) cell evacuated for 15 min at 25°C.

by a mass spectral analysis of the gas phase species present after excess NO(g) is added to the cell; only CO(g) and NO(g) are detected. In the infrared spectrum obtained after CO is displaced from the Ru surface by NO(g), we observe a weak broad band at 2180 cm^{-1} which is stable to room temperature evacuation.

We also observe this weak broad band at 2180 cm^{-1} in the infrared spectrum recorded when 5 Torr CO(g) is added to a 6% Ru–silica sample with full NO surface coverage at 25°C (excess NO(g) was previously removed by a 15-min evacuation whereas CO(g) is not evacuated). These spectra are shown in Fig. 2. In this case we observe no change in the intensity or the band shape of the NO adsorption band at 1815 cm^{-1}; however, we do observe three weak CO bands at 2135, 2080, and 2030 cm^{-1}. A weak broad band at 2135 cm^{-1} develops immediately after the addition of CO(g), whereas the bands at 2080 and 2030 cm^{-1} develop after a 30-min exposure to excess CO(g). No additional spectral changes are observed when this sample is exposed to CO(g) for 24 h. A mass spectral analysis of the gas phase species present after the addition of excess CO(g) reveal only CO(g); thus, adsorbed NO is stable to gaseous CO at 25°C.

To determine if any interactions occur when CO and NO are both present on the Ru surface, we recorded a series of spectra in which CO(ads) is slowly displaced from the Ru surface by small additions of NO(g). These spectra are illustrated in Fig. 3. Initially the Ru sample was exposed to 5 Torr of CO(g) and the cell was evacuated for 15 min (Fig. 3b). Small increments of NO(g) are then added to the cell; the cell is not evacuated until an excess of NO(g) is added. With each addition of NO(g) we observe a decrease in the intensity of the CO band at 2030 cm^{-1} and an increase in the intensity of the NO band at 1800 cm^{-1}; there is no change in the intensities of the high frequency CO bands at 2150 and 2080 cm^{-1}. After the first addition of NO, we note the appearance of the band at 2180 cm^{-1} and we find that the intensity of this band increases with each subsequent addition of NO (Fig. 3c–f).

In the presence of excess NO(g), there is a slight decrease in the intensity of the band at 2180 cm^{-1}; however, some of the surface species adsorbing at 2180 cm^{-1} are stable to excess NO(g) for a period of 60 h at 25°C, as shown in Fig. 4. The C^{13}O isotope was used when these spectra were recorded; the significance of the isotope shifts will be discussed later. In these spectra we note the appearance of two new bands at 2275 and 1760 cm^{-1}. The formation of the band observed at 2275 cm^{-1} with $C^{13}O$ can be detected when $C^{12}O$ is used by noting a change in the contour of the P-branch of the gas phase band centered at 2349 cm^{-1}. This band is due to the antisymmetric stretching vibration, ν_3, of atmospheric $CO_2(g)$. When the infrared spectrometer is flushed with $N_2(g)$ to eliminate atmospheric absorption bands, we observe a weak band at 2340 cm^{-1}. We find that this band intensifies with each addition of NO (Fig. 3c–f) and that it is stable to excess NO(g) and room temperature evacuation (Fig. 4d, e). The band observed at 1760 cm^{-1} intensifies with time of exposure to NO(g); however, this band decreases sharply when the cell is evacuated for 30 min at room temperature (Fig. 4e).

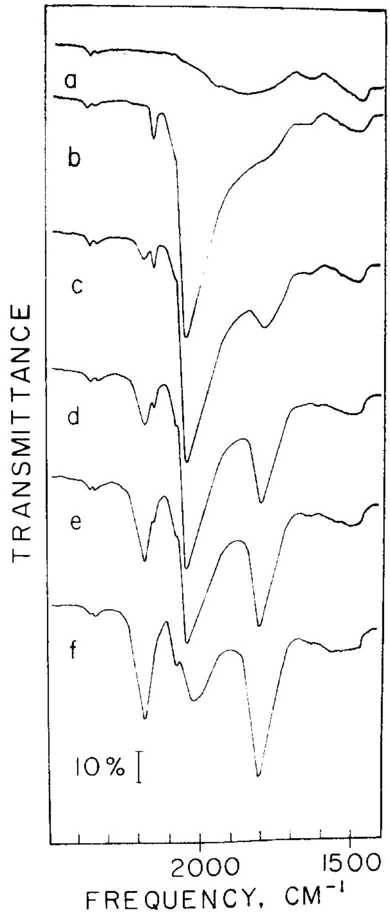


Fig. 3. Infrared spectra illustrating the stepwise displacement of adsorbed CO by NO on a 6% Ru–silica sample at 25°C: (a) background; (b) full CO surface coverage followed by a 15-min evacuation; (c) first addition of NO; (d) second addition of NO; (e) third addition of NO; (f) fourth addition of NO.

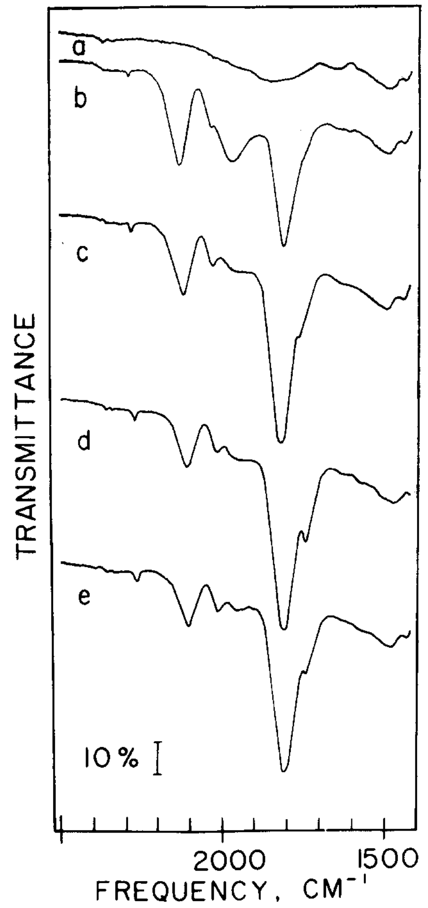


Fig. 4. Infrared spectra illustrating the effect of the addition of excess NO(g) after the stepwise displacement of adsorbed $C^{13}O$ by NO on a 6% Ru–silica sample at 25°C: (a) background; (b) partial displacement of adsorbed $C^{13}O$ by NO; (c) 5 Torr of NO added, exposure time = 30 min; (d) exposed to 5 Torr of NO for 60 h; (e) cell evacuated 30 min.

To gain a better understanding of the development of these new surface species, we recorded the spectrum obtained when CO(ads) and NO(ads) are allowed to inter-

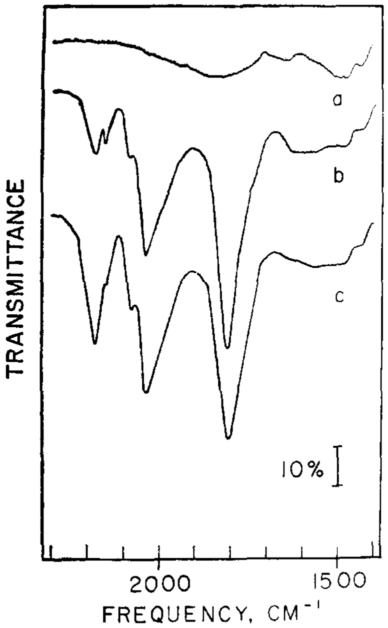


FIG. 5. Effect of time on the infrared spectrum of a 6% Ru-silica sample with CO and NO both adsorbed on the surface: (a) background; (b) partial displacement of adsorbed CO by NO; (c) exposure time = 1 hr.

act on the Ru surface for an extended period of time. These spectra are shown in Fig. 5. The Ru sample was first exposed to 5 Torr of CO(g) and then evacuated for 15 min. A small amount of NO(g) is then added to the cell and the cell is not evacuated. Initially NO(g) displaces CO(ads) from the surface and we note the appearance of a weak band at 2180 cm^{-1} (Fig. 5b). When these surface species are left on the surface for 1 h, we observe a considerable enhancement in the band at 2180 cm^{-1} and a decrease in the intensity of the NO band at 1800 cm^{-1} (Fig. 5c). There is a slight increase in the intensity of the CO band at 2030 cm^{-1}, whereas there is no change in the high frequency CO bands at 2150 and 2080 cm^{-1}. We again note the appearance of a weak band at 2340 cm^{-1}; however, no band at 1760 cm^{-1} is observed. No further spectral changes occur when these surface species are left on the surface for 24 h. When this sample is evacuated for 30 min at room temperature, we observe no change in the infrared spectrum; furthermore, we find that all these adsorbed species; i.e., NO(ads), CO(ads), and the two surface species absorbing at 2340 and 2180 cm^{-1} are stable to evacuation up to temperatures of 150°C.

The observation that the intensity of the NO band at 1800 cm^{-1} decreases as the band at 2180 cm^{-1} intensifies suggests that chemisorbed NO is reacting to form this new surface species; however, the role of CO(ads) is unclear. We do not observe formation of a band at 2180 cm^{-1} when only NO is adsorbed on the surface; furthermore, only a weak band at 2180 cm^{-1} is formed when NO(ads) is contacted with excess CO(g) for 24 h at 25°C. These results suggest that CO and NO must both be present on the Ru surface for the species absorbing at 2180 cm^{-1} to form in appreciable amounts.

To verify these observations, the $C^{13}O$ and $N^{15}O$ isotopes were used to form the surface intermediate. The infrared spectrum obtained using $C^{13}O$ is illustrated in Fig. 4 and all the isotope shift data are summarized in Table 1. For the band observed at 2180 cm^{-1} with $C^{12}O$ and $N^{14}O$, we observe a frequency shift of 60 to 2120 cm^{-1} with $C^{13}O$, whereas for $N^{15}O$ a frequency shift of only 17 to 2163 cm^{-1} is observed. These results indicate that this surface species contains both C and N atoms; the greater frequency shift observed for $C^{13}O$ suggest bonding to the Ru surface through the N atom rather than the C atom. This observation is consistent with Ru chemistry, since it has been well established that Ru forms strong bonds with N-containing ligands (*12*).

A survey of the literature indicates that C–N stretching vibrations absorb in this frequency range. Our data suggest bonding to the Ru surface through the N atom rather than the C atom; thus, a surface isocyanate, Ru–NCO, and a surface isonitrile, Ru—N≡C, must both be con-

TABLE 1

Isotope Shift Data for Surface Species Formed with CO and NO Adsorbed on 6% Ru-silica

ν cm^{-1} $C^{12}O$ $N^{14}O$	ν cm^{-1} $C^{13}O$ $N^{14}O$	$\Delta\nu$ cm^{-1} $C^{13}O$–$C^{12}O$	ν cm^{-1} $C^{12}O$ $N^{15}O$	$\Delta\nu$ cm^{-1} $N^{14}O$–$N^{15}O$	Assignment
2340	2275	65	2340	0	Ru–O$\overset{\cdots}{-}$C$\cdots$O
2180	2120	60	2163	17	$Ru^{\delta+}$–$NCO^{\delta-}$
2150	2100	50	2150	0	RuO–CO
2080	2030	50	2080	0	Ru–CO (oxygen perturbed)
2030	1980	50	2030	0	Ru–CO
1815	1815	0	1785	30	$Ru^{\delta-}$–$NO^{\delta+}$
1760	1760	0	1730	30	Ru:NO or $Ru^{\delta+}$–$NO^{\delta-}$

sidered. Although Ru complexes with organic nitriles have been prepared (*13*), no stable Ru compound with a terminal isonitrile has been isolated; however, stable organic and inorganic isocyanate compounds have been prepared (*14–17*). Thus, we conclude that the band observed at 2180 cm^{-1} is the antisymmetric stretching vibration, $\nu_{a(NCO)}$, of a surface isocyanate, Ru–NCO. Hertzberg and Reid (*16*) have observed a strong band at 2246 cm^{-1} in an infrared study of HNCO (*s*) (in this case NCO covalently bound to the H atom), whereas Maki and Decius (*17*) have observed a strong band at 2163 cm^{-1} for K^+NCO^- (NCO^- ionically bound to K^+). These data suggest that the band observed at 2180 cm^{-1} is the antisymmetric stretching vibration of an isocyanate bound to a surface Ru atom with a partial positive charge, $Ru^{\delta+}$–$NCO^{\delta-}$.

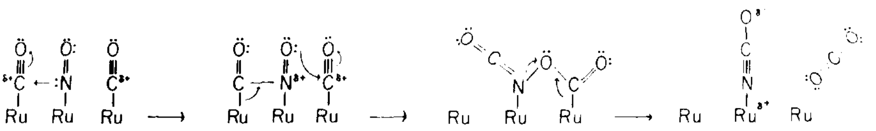
The isotope shift data also provides insight into the nature of the surface species absorbing at 2340 and 1760 cm^{-1}. For the band appearing at 1760 cm^{-1}, we observe an isotope shift of 30 to 1730 cm^{-1} with $N^{15}O$ and no shift with $C^{13}O$; thus, this surface species contains a N atom but no C atom. We observe an identical isotope shift of 30 cm^{-1} for the NO band observed at 1815 cm^{-1} (shifted to 1785 cm^{-1} with $N^{15}O$). This suggests that the band observed at 1760 cm^{-1} with $N^{14}O$ is due to the NO stretching vibration of adsorbed NO. The desorption behavior of this NO surface species (the intensity of this band decreased after a 30-min evacuation at 25°C) indicates that it is weakly adsorbed on the Ru surface. This suggests that NO is probably covalently bound to a Ru surface atom, Ru:NO. We only observe this band at 1760 cm^{-1} when the isocyanate band at 2180 cm^{-1} decreases in the presence of excess NO(g). No band at 1760 cm^{-1} is observed when NO is adsorbed on either the reduced or oxidized forms of supported Ru. Thus, this NO surface species must form as the surface isocyanate decomposes in the presence of excess NO(g).

The isotope shift data also reveal that the species absorbing at 2340 cm^{-1} contains a C atom but no N atom. As shown in Table 1, we observe an isotope shift of 65 cm^{-1} from 2340 to 2275 cm^{-1} with $C^{13}O$, whereas no shift is observed with $N^{15}O$. A frequency of 2340 cm^{-1} is higher than any reported for an adsorbed carbonyl surface species (*11*); however, the antisymmetric stretching vibration, ν_3, for CO_2(g) is observed at 2349 cm^{-1}. Furthermore, the observed isotope shift for this vibrational mode of CO_2(g) is 65 cm^{-1}; ν_3 for $C^{12}O_2$(g) is observed at 2349 cm^{-1}, whereas ν_3 for $C^{13}O_2$(g) is observed at 2284 cm^{-1} (*18*). From these data we conclude that the band at 2340 cm^{-1} is due to the antisymmetric stretching vibration, ν_3, of adsorbed CO_2, Ru–O$\overset{\cdots}{-}$C$\overset{\cdots}{-}$O. The presence of CO_2(g) is confirmed by a mass spectral analysis of the gas phase species present when the bands at 2340 and 2180 cm^{-1} reach their maximum intensities. We do not observe a band at 2340 cm^{-1} when $CO_2(g)$ is added to a reduced 6% Ru–silica sample at 25°C; thus, certain Ru surface sites must be activated for CO_2 adsorption during isocyanate formation.

Our results indicate that the adsorption of CO_2 on the Ru surface is related to isocyanate formation; furthermore, they indicate that CO and NO must both be adsorbed on the Ru surface for the isocyanate surface species to form in appreciable amounts. We observe that the band at 2180 cm^{-1} intensifies for only a limited time (1 h) when a specific amount of CO and NO are allowed to interact on the surface; this suggests that the surface isocyanate is formed by an interaction between CO(ads) and NO(ads) that are adjacent to each other on the Ru surface. Considering these facts, we propose the following mechanism to explain isocyanate formation: first, CO(ads) is displaced from the Ru surface by NO(g),

$$\text{Ru–CO} + \text{NO}(g) \rightarrow \text{Ru–NO} + \text{CO}(g).$$

This NO(ads) can interact with an adjacent CO surface species,



Finally, CO(g), which is displaced from the Ru surface when NO is initially added, or CO_2, which is formed during isocyanate formation, can readsorb on the vacant Ru surface sites. (These Ru surface sites can be activated for CO_2 adsorption by the presence of an isocyanate on an adjacent Ru site.)

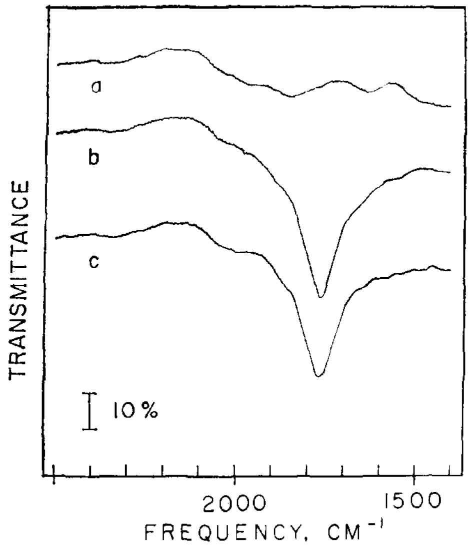


FIG. 6. Infrared spectrum of NO adsorbed on a 6% Pt–silica sample at 25°C: (a) background; (b) 5 Torr of NO added; (c) cell evacuated for 15 min at 25°C.

$$\text{Ru–} + \text{CO}(g) \rightarrow \text{Ru–CO}$$

or

$$\text{Ru–} + \text{CO}_2(g) \rightarrow \text{Ru–O}\cdots\text{C}\cdots\text{O}.$$

Interaction between CO and NO over Supported Pt

We have also made an infrared study of the adsorption and interaction of CO and NO on silica-supported Pt. Since there has been no recent infrared study of the chemisorption of NO on silica-supported Pt, initially we recorded the spectrum obtained when a 6% Pt–silica sample was exposed to 5 Torr of NO(g). In this spectrum, shown in Fig. 6, we observe a broad band centered at 1760 cm^{-1}, which is stable to room temperature evacuation. We assign this band to the NO stretching vibration of NO adsorbed on a Pt surface atom, Pt–NO.

When a trace amount of CO(g) is added

to a Pt sample with full NO surface coverage (excess NO(g) was previously removed by a 15-min evacuation whereas CO(g) is not evacuated), we observe a decrease in the intensity of the NO band at 1760 cm^{-1} and note the appearance of only one new band at 2050 cm^{-1} due to adsorbed CO, Pt–CO. These spectra are shown in Fig. 7. The NO(ads) and CO(ads) were then left on the Pt surface for 1 h; however, no new bands are observed in the infrared spectrum. After a second addition of CO(g), the CO band intensifies and shifts to 2060 cm^{-1}, whereas there is a decrease in the intensity of the NO band at 1760 cm^{-1}. Again, no new bands are observed when these surface species are left on the surface for 1 h (Fig. 7e, f). When excess CO(g) is added to the cell, only a strong sharp CO band at 2070 cm^{-1} is observed (Fig. 7g). A mass spectral analysis of the gas phase species present after excess CO(g) is added show only CO(g) and NO(g); thus, adsorbed NO is displaced from the Pt surface by CO.

When a Pt–silica sample with monolayer CO coverage is exposed to excess NO(g) (excess CO(g) was previously removed by a 15-min evacuation whereas NO(g) is not evacuated), we observe a slight decrease in the intensity of the CO band at 2070 cm^{-1} and note the appearance of a weak NO band at 1760 cm^{-1}. These spectra are illustrated in Fig. 8. This Pt sample was then exposed to excess NO for an extended period of time (48 h), and we observe a gradual decrease in the intensity of the CO band (with a resultant frequency shift). A mass spectral analysis of the gas phase species present after this sample is exposed to excess NO(g) for 48 h shows CO_2, N_2O, and NO (no CO is observed). These results indicate that chemisorbed CO is not displaced from the Pt surface by NO, but rather it is oxidized by excess NO to CO_2; i.e.,

$$Pt\text{–}CO + 2NO(g) \rightarrow N_2O(g) + CO_2(g).$$

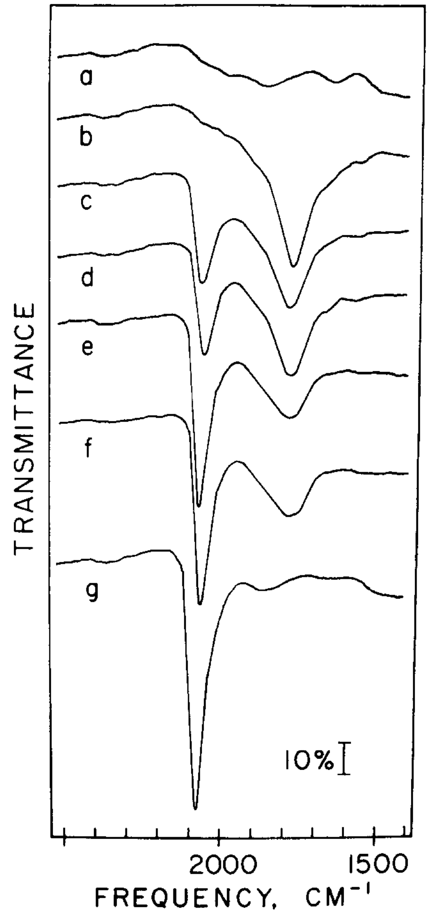


FIG. 7. Infrared spectra illustrating the stepwise displacement of adsorbed NO by CO on a 6% Pt–silica sample at 25°C: (a) background; (b) full NO surface coverage followed by a 15-min evacuation; (c) first addition of CO, exposure time = 15 min; (d) first addition of CO, exposure time = 1 h; (e) second addition of CO, exposure time = 15 min; (f) second addition of CO, exposure time = 1 h; (g) 5 Torr of CO added.

An NO gas phase molecule can then adsorb on the vacant Pt surface site,

$$Pt\text{–} + NO(g) \rightarrow Pt\text{–}NO.$$

During this reaction we observe the appearance of a weak broad band at 2180 cm^{-1} that is stable to room temperature evacuation. Several attempts were made to increase the intensity of the band appearing at 2180 cm^{-1}, e.g., different ratios of CO and NO were adsorbed on the Pt surface: how-

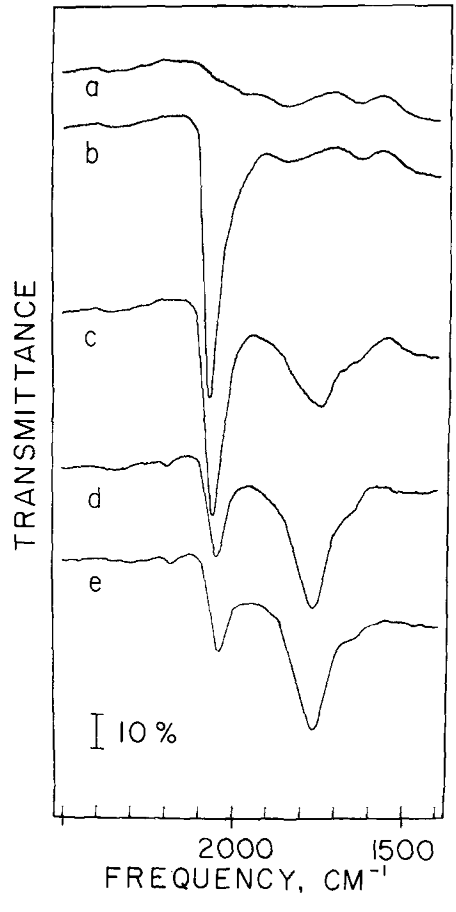


FIG. 8. Infrared spectra illustrating the effect of the addition of excess NO to a 6% Pt–silica sample with full CO surface coverage at 25°C: (a) background; (b) full CO surface coverage followed by a 15-min evacuation; (c) 5 Torr of NO added, exposure time = 15 min; (d) exposed 5 Torr of NO for 24 h; (e) exposed to 5 Torr of NO for 48 h, and cell evacuated for 15 min at 25°C.

ever, we were unable to form the strong sharp band at 2180 cm^{-1}, that is characteristic of the surface isocyanate.

The failure to observe the formation of an isocyanate on the Pt surface is not surprising if a mechanism analogous to that proposed for isocyanate formation on a Ru–silica surface is considered. In that mechanism, adjacent NO(ads) and CO(ads) molecules interact to form an N–C bond; however, in this process an M–C bond must be broken (the M–N bond is not broken). It is well known that CO is strongly adsorbed on the Pt surface, whereas NO is only weakly adsorbed, i.e., a strong Pt–C bond and a weak Pt–N bond. Therefore, at 25°C one would not expect the Pt–C bond to be broken so that the isocyanate surface species can form. In contrast to the Pt surface, NO is strongly adsorbed on a Ru surface, whereas CO is only weakly adsorbed, i.e., a strong Ru–N bond and a weak Ru–C bond. In this case one can envision that Ru–C bonds are easily broken so that the surface isocyanate can form.

Recently, Unland (*3*, *4*) has suggested that the formation of a surface isocyanate is an intermediate step in NH_3 formation. In a high temperature study of isocyanate formation on various alumina supported noble metal catalysts, Unland observed a strong isocyanate band on supported Pt, Pd, Rh, and Ir, whereas for supported Ru, he observed only a weak isocyanate band. This isocyanate band appeared in the 2260 cm^{-1} region of the infrared spectrum. He suggested that the failure to observe a strong isocyanate band on supported Ru may account for its unusual catalytic properties, i.e., the selective reduction of NO to N_2 with low NH_3 formation. We are able to form a surface isocyanate at 25°C on silica-supported Ru, whereas for silica-supported Pt we cannot form this species. Since Unland performed his experiments at 400°C, we feel that the high temperature sintered the Ru–alumina pellets and, therefore, less intense infrared bands were observed. It should be noted that Unland observed weak CO absorption bands in his infrared study, whereas other authors have reported strong infrared bands for CO adsorption on supported Ru (*9*). We find that sintering of the Ru–silica sample does occur at temperatures greater than 350°C.

In this infrared study we observe the formation of a surface isocyanate on silica-supported Ru, when CO(ads) is slowly displaced from the surface by NO(g). This surface isocyanate was identified by the appearance of a strong band at 2180 cm^{-1}, which was found to shift with both $C^{13}O$ and $N^{15}O$. Our data indicate that this surface isocyanate is formed by an interaction between CO(ads) and NO(ads) that are adjacent to each other on the Ru surface, and that $CO_2(g)$ is formed during the reaction. In studies made using silica-supported Pt, we were unable to form the surface isocyanate even when various amounts of CO and NO were adsorbed on the Pt surface. These results are reasonable when the different adsorption characteristics of the Pt and Ru are considered, i.e., the relative stability of adsorbed CO and adsorbed NO on these two different surfaces. This study has provided valuable insight into the mechanism of isocyanate formation on silica-supported Ru.

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