Infrared Observations of Rh—NCO and Si—NCO Species Formed During the Reduction of NO by CO over Silica-Supported Rhodium

WILLIAM C. HECKER[1] AND ALEXIS T. BELL

Department of Chemical Engineering, University of California, Berkeley, California 94720

Infrared studies of NO reduction by CO over Rh/SiO_2 give clear indication of the presence of Rh—NCO species characterized by a band at 2170–2200 cm^{-1}. The surface coverage by this species is greatest under conditions where the NO partial pressure is low and the CO partial pressure is high. The NCO Groups present on Rh are very unstable and decompose immediately when the reduction of NO ceases. The *in situ* infrared spectra also show evidence for Si—NCO groups characterized by bands at 2300 and 1460 cm^{-1}. These species appear to be formed by spillover of isocyanates from the rhodium microcrystallites onto the support. Once formed, the Si—NCO groups are quite stable and are not readily decomposed.

INTRODUCTION

In the last few years, there has been much discussion regarding the formation of isocyanate species (NCO) during the reaction of NO and CO over transition metal catalysts (*1–15*). In an early infrared investigation, Unland (*2–4*) studied the interaction of NO and CO at 673 K over five alumina-supported noble metal catalysts (Ru, Pt, Pd, Ir, Rh). For all five, he observed the formation of very intense and stable infrared bands at 2264 ± 5 cm^{-1}, which he assigned to isocyanate species bound to the metal (M—NCO). Weaker bands were also observed in the region of 2150–2200 cm^{-1}, which were tentatively assigned to an anionic isocyante species. More recent studies by Eley *et al.* (*16*), Morrow and Cody (*17*), Gillet *et al.* (*18*), Dalla Betta and Shelef (*5*), and Solymosi and Bansagi (*11*) have clearly established that the intense bands observed near 2265 cm^{-1} following the high temperature interaction of NO and CO on alumina-supported catalysts are due to isocyanate species bound to the alumina support and not the metal. Likewise, the intense band observed near 2300 cm^{-1}

following similar interactions on silica-supported catalysts is due to an isocyanate group attached to silica. This assignment is in good agreement with the spectrum of $Si(NCO)_4$, which exhibits a band at 2284 cm^{-1} for assymetric streching vibrations of the NCO group (*19*).

In other studies, the room temperature interaction of NO and CO on silica-supported Ru and Ni (*6–8*) produced bands at 2180–2200 cm^{-1}, which were assigned to Ru—NCO and Ni—NCO species, respectively. No bands at 2300 cm^{-1} were seen. Lorimer and Bell (*13*) obtained *in situ* infrared spectra during the reduction of NO by CO over a Pt/SiO_2 catalyst at 573 K. They observed an intense, stable band at 2300 cm^{-1} and a weak band at 2190 cm^{-1}. They assigned these to Si—NCO and Si—CN species, respectively. Solymosi and Sarkany (*12*) in a recent study of the interaction of NO and CO with a Rh/Al_2O_3 catalyst observed a weak band at 2270 cm^{-1} and a very weak band at 2195 cm^{-1}. These were assigned to Al—NCO and tentatively to Rh—NCO.

The results of two very recent studies help identify the band observed at 2150–2200 cm^{-1} in many of the studies cited above. Gorte *et al.* (*14*) adsorbed HNCO onto a Pt(110) surface and observed a band

at 2160 cm^{-1} using high resolution electron energy loss spectroscopy (EELS). However, the species represented by this band was very unstable, since most of it decomposed to nitrogen-containing surface fragments and CO by 264 K during temperature-programmed desorption. Rasko and Solymosi (15) studied the reaction of NO and CO, as well as the adsorption of HNCO, on unsupported Pt and observed a weak band at 2180 cm^{-1} in both cases. They assigned this band to a Pt—NCO species based partly on the results of isotopic labeling experiments. This band was again found to be fairly unstable as it disappeared above 310–330 K in the absence of both NO and CO (or HNCO) in the gas phase. Attempts by Rasko and Solymosi to observe this band on other unsupported noble metals, including Rh, were unsuccessful.

In summary, there now seems to be good agreement that infrared bands observed at 2265 and 2300 cm^{-1}, resulting from the interaction of NO and CO on alumina and silica-supported catalysts, respectively, are attributable to isocyanate groups attached to the support. Similar agreement on the assignment of an associated band at 2150–2200 cm^{-1} has not existed until lately. As noted above, studies on unsupported Pt suggest that this band can probably be assigned to an isocyanate species adsorbed on the metal (M—NCO). Since this species has been hard to observe, and since few of the studies to date have been done under reaction conditions, its chemistry is not well understood. Likewise, little is known about the relationship of isocyanate groups present on the metal and those attached to the support.

This paper reports on a study of the formation of isocyanate groups on a Rh/SiO$_2$ catalyst during the reduction of NO by CO. In situ infrared spectra show clear evidence for a Rh—NCO structure, as well as an Si—NCO structure. The temporal behavior of these species strongly suggest that NCO groups are formed on the Rh surface and then migrate onto the support. The ob-served dependence of NCO formation on reaction conditions can be interpreted with the aid of a simple mechanistic model.

EXPERIMENTAL

The experimental apparatus and procedure are identical to those described in Ref. (20). The reduction of NO by CO was carried out in a reactor designed to permit infrared spectra to be taken of species adsorbed on the catalyst. The reactor is connected to a gas recirculation loop, which is continuously supplied with fresh reactants. Products are continuously withdrawn from the loop and analyzed by gas chromatography (21). Infrared spectra were recorded using a Perkin–Elmer 467 dual-beam spectrometer.

A 4.6% Rh/SiO$_2$ catalyst was prepared by impregnation of Cab-O-Sil HS-5 with an aqueous solution of RhCl$_3 \cdot$3H$_2$O. The dried catalyst was calcined in air at 773 K and reduced in flowing hydrogen at 673 K. The rhodium dispersion, determined by H$_2$ chemisorption, was 38%. A 30-mm-diameter disk, weighing 0.125 g, was produced by pressing the reduced catalyst.

At the start of each experiment, the catalyst disk was reduced in the reactor in flowing H$_2$ for at least 2 h at 573 K. Following reduction, the reactants were fed to the reactor and analysis of the reaction products was begun immediately.

RESULTS AND DISCUSSION

The infrared spectra observed under reaction conditions were qualitatively different depending upon the conversion of NO. Spectrum A in Fig. 1 is representative of the spectra observed for NO conversions below 50%, and Spectrum B is representative of those observed at high NO conversions. While all of the bands seen in Spectrum A also appear in Spectrum B, the latter spectrum contains some additional features, and the relative intensities of those bands appearing in both spectra differ.

The bands at 2300 and 1460 cm^{-1} can be

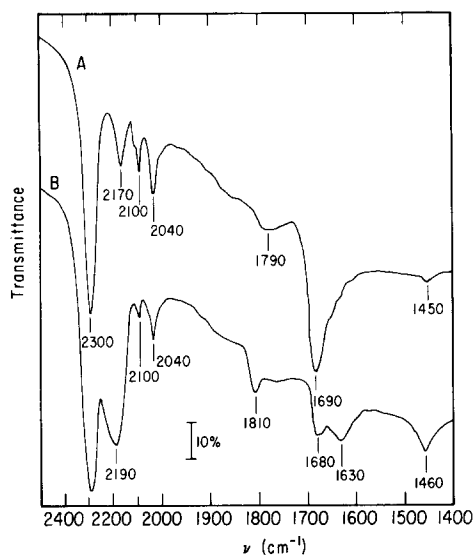FIG. 1. Infrared spectra observed at moderate and high NO conversion. Feed composition: $-P_{NO}^0 = 1.2 \times 10^{-2}$ atm, $P_{CO}^0 = 3.6 \times 10^{-2}$ atm; total pressure, 1.2 atm; gas flow rate, 200 STP cm^3/min; Spectrum A, $T = 500\,K$, $x_{NO} = 0.50$; Spectrum B, $T = 504$ K, $x_{NO} = 0.90$.

assigned to the asymmetric and symmetric stretching vibrations of Si—NCO. As was discussed in the Introduction, the high frequency band has been observed in a number of previous studies concerning the interaction of NO and CO over silica-supported Group VIII metals (1–15), and has also been observed when HNCO is decomposed on silica (11, 16, 18). The independence of the reported band position on the composition of the metal, and its close agreement with the position of the band produced by HNCO decomposition on silica, indicate quite clearly that the band at 2300 cm^{-1} is due to isocyanate groups present on the support. This assignment is further confirmed by the fact that the spectrum of the complex Si(NCO)$_4$ exhibits a strong band at 2284 cm^{-1} (19). The band at 1460 cm^{-1}, seen in Spectra A and B, is also assigned to Si—NCO groups based on the similarity of the position of this band to that observed at 1482 cm^{-1} for Si(NCO)$_4$ (19). It is noted further that the bands at 2300 and 1460 cm^{-1} were found to undergo a parallel growth, or diminishment, in in-

tensity, strongly suggesting that both features are attributable to a single species.

The results of this and previously published studies strongly suggest that the band at 2170–2190 cm^{-1} observed in Fig. 1 is an isocyanate species adsorbed on the surface of the rhodium. In a recent study by Rasko and Solymosi (15) on unsupported Pt, a weak band was observed at 2180 cm^{-1} not only during reaction of NO and CO, but also upon adsorption of HNCO. Since no support was present, the band was assigned to Pt—NCO groups. Additional evidence for this point is provided by the study of Solymosi and Bansagi (11) in which Pt/SiO$_2$ and SiO$_2$ alone were treated with HNCO. For Pt/SiO$_2$, bands were seen at both 2313 and 2195 cm^{-1}, but only a single band at 2313 cm^{-1} was observed for SiO$_2$.

Additional evidence for the association of the band at 2170–2190 cm^{-1} with an M—NCO species can be developed by reference to the literature on transition-metal complexes. A list of NCO stretching frequencies for a number of Group VIII metal–isocyanate complexes is given in Table 1. These complexes all have isocyanate stretching frequencies between 2170 and 2230 cm^{-1}. It is also interesting to note that the frequencies for negatively charged

TABLE 1

Vibrational Frequencies in Transition-Metal Isocyanate Complexes

Complex	ν_{NCO} (cm^{-1})	Reference
[Fe(NCO)$_4$]$^{-2}$	2182	(29, 30)
[Fe(NCO)$_4$]$^-$	2171, 2208	(29)
[Co(NCO)$_4$]$^{-2}$	2179, 2217	(29, 30)
[Ni(NCO)$_4$]$^{-2}$	2186, 2237	(29)
[Pd(NCO)$_4$]$^{-2}$	2190–2200	(31)
Pd(bipy)(NCO)$_2$	2195–2215s	(32)
Pd(Ph$_3$P)(NCO)$_2$	2212–2218s	(32)
Pd(Ph$_3$As)$_2$(NCO)$_2$	2200–2210s	(32)
Pt(bipy)(NCO)$_2$	2215–2225s, 2240sh	(32)
Pt(Ph$_3$P)$_2$(NCO)$_2$	2200s, 2230sh	(32)
Pt(Ph$_3$As)$_2$(NCO)$_2$	2175–2205s, 2222sh	(32)
Rh(PPh$_3$)$_3$(NCO)	2230br	(33)

NCO species are slightly lower than those for neutral NCO species, and thus, more in line with the band observed here. This suggests that the present species might be more correctly written as Rh—NCO$^{\delta-}$.

The bands appearing between 2150 and 1600 cm^{-1} are identical to those reported previously by Hecker and Bell (20) and the assignment of these features to specific structures is discussed at length in their paper. In brief, the bands at 2100 and 2040 cm^{-1} are attributable to a rhodium dicarbonyl species, Rh(CO)$_2$. A small portion of the 2040 cm^{-1} can also be associated with a linear carbonyl of the form Rh—CO (22–25). The band appearing at 1790–1810 cm^{-1} is assigned to a Rh—NO structure, while bands in the region between 1690 and 1630 are assigned to structures of the form Rh—NO$^{\delta-}$. These assignments are based on the similarity of the band positions to those observed in rhodium nitrosyl complexes (26–28) and are consistent with interpretations given in other studies of NO on supported Rh (26, 27).

The effect of temperature on the intensities of the Si—NCO (2300 cm^{-1}) and the Rh—NCO (2170–2190 cm^{-1}) bands is illustrated in Fig. 1. Spectrum A in Fig. 2 represents the baseline obtained prior to exposing the catalyst to NO and CO. Spectrum B taken after 22 h of reaction at 483 K, and at an NO conversion of 3%, shows small bands for each of the species. Increasing the temperature to 503 K causes an increase in the NO conversion to 16%, but produces no change in the intensity of the three bands (Spectrum C). However, when the temperature is increased further to 515 K, the NO conversion increases sharply to 86%, and both the Rh—NCO and Si—NCO bands rapidly intensify (Spectrum D). The Rh—CO band also increases substantially. After Spectrum D was recorded, the catalyst was maintained at 515 K for an additional 20 min, following which Spectrum E was recorded. It is clear from Spectrum E that the Si—NCO band grew rapidly during this interval, ultimately
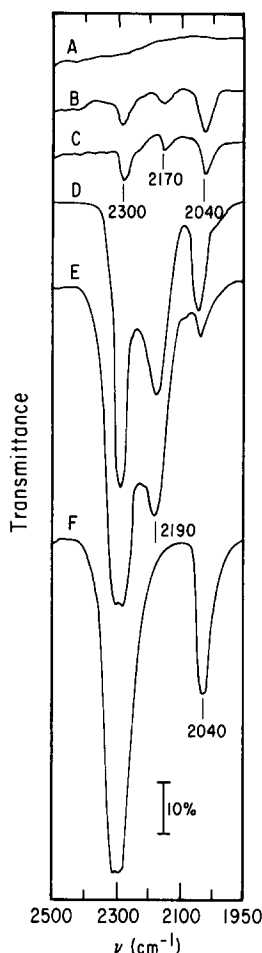

FIG. 2. Growth of isocyanate bands with increasing temperature. Feed composition—$P_{NO}^0 = 1.2 \times 10^{-2}$ atm, $P_{CO}^0 = 4.8 \times 10^{-2}$ atm; total pressure $- 1.2$ atm; gas flow rate, 200 STP cm^3/min. Spectrum A, background in helium at 483 K; Spectrum B, after 22 h of reaction at 483 K, $x_{NO} = 0.03$; Spectrum C, after 0.4 h of reaction at 503 K, $x_{NO} = 0.16$; Spectrum D, after 0.2 h at 515 K, $x_{NO} = 0.86$; Spectrum E, after 0.5 h at reaction at 515 K, $x_{NO} = 0.86$; Spectrum F, after 0.1 h in helium at 515 K.

reaching saturation intensity. The Rh—NCO band became only slightly more intense than before, and the Rh—CO band decreased to approximately the same intensity observed for this band at lower temperatures. After Spectrum E was recorded, the reaction was stopped by turning off the NO and CO feeds and purging the reactor with pure He. Six minutes (5.0 reactor space

times) after this change was made, Spectrum F was recorded. As can be seen, this change had no effect on the Si—NCO band, but caused the Rh—NCO band to disappear completely. Meanwhile, the Rh—CO band grew substantially larger. This increase was transitory, though, since subsequent spectra (not shown) indicated that the carbonyl band decayed significantly over the next 30 min. The sudden increase in the carbonyl band was probably due to the fact that the feed contained excess CO, and thus, when the feed to the recycle loop was discontinued, the NO was reacted away quickly, leaving an atmosphere of CO in helium over the catalyst for a brief time.

Figure 3 shows spectra recorded during NO reduction by CO over a fresh catalyst wafer at increasingly longer periods of time
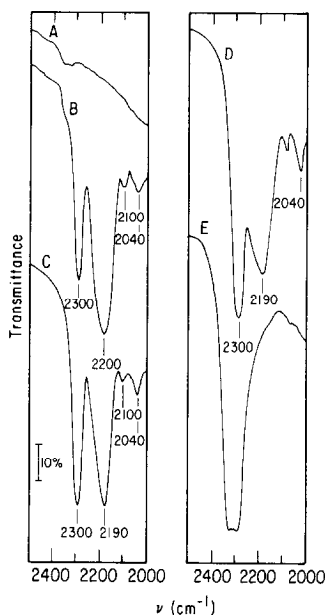

FIG. 3. Growth of isocyanate bands with time under conditions of high NO conversion: Feed composition—$P_{NO}^0 = 1.2 \times 10^{-2}$ atm, $P_{CO}^0 = 3.6 \times 10^{-2}$ atm; total pressure, 1.2 atm; gas flow rate, 200 STP cm³/min. Spectrum A, background in H₂ at 513 K; Spectrum B, after 17 min of reaction at 498 K, $x_{NO} = 0.85$; Spectrum C, after 40 min of reaction at 498 K, $x_{NO} = 0.75$; Spectrum D, after 65 min of reaction at 504 K, $x_{NO} = 0.90$; Spectrum E, after reduction of the catalyst in H₂ at 523 K, following 165 min of reaction.

under high NO conversion conditions. Even though the catalyst temperature under which the spectra were obtained varied slightly from one spectrum to the next, the NO conversions were fairly similar (ranging from 75 to 90% for Spectra B–D). Consequently, the changes observed are primarily due to the time that the catalyst was exposed to high conversion conditions. Spectrum A is a baseline spectrum obtained prior to initiation of reaction. Spectra B, C, and D are spectra obtained after 17, 40, and 65 min, respectively, of reaction at high conversion. Spectrum E was obtained in flowing hydrogen after the reactants were turned off, following 165 min of reaction under high conversion conditions. Spectra B–D indicate that the Rh—NCO band (2170 cm⁻¹) becomes intense very rapidly and essentially remains at the same high intensity as long as NO reduction by CO occurs at a high rate; however, as soon as the reactants are turned off, the Rh—NCO band disappears (Spectrum E). This instability of the Rh—NCO band, also seen in Fig. 2, was also observed when the flow of either NO or CO was curtailed. An interesting observation was made after stopping the flow of NO (but not CO) at the end of one run. As the Rh—NCO band disappeared, a small amount of N₂ was detected in the effluent from the reactor. This suggests the occurrence of the following overall reaction,

$$2Rh—NCO \rightarrow N_2 + 2CO + 2Rh$$
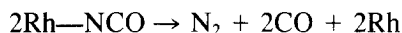
While the Rh—NCO band appears to grow and achieve a constant magnitude almost instantaneously, the Si—NCO band (2300 cm⁻¹) grows monotonically over the 165-min period represented in Fig. 3. Once formed, the Si—NCO is quite stable and is unaffected by displacement of the reactants with flowing hydrogen. In addition to the Rh—NCO and Si—NCO bands, Fig. 3 shows small CO bands at 2100 and 2040 cm⁻¹ (Spectra B–D). The intensity of these bands changes very little over the time in which Spectra B–D were obtained. When the flow of reactants was stopped and re-

placed with flowing hydrogen, the CO bands disappeared (Spectrum E).

As noted earlier, the Si—NCO species was found to be very stable. Treatments of the catalyst at temperatures up to 603K with several different gases (100% H_2, 2% NO, 2% O_2, 3% CO, and 3% H_2O) all failed to remove the Si—NCO bands. Only upon introduction of air into the reactor at 298 K did the Si—NCO bands eventually disappear. Figure 4 shows that the elimination of the Si—NCO species is a very slow process requiring as much as 40 h. It is also interesting to note that the attenuation of the Si—NCO band at 2300 cm^{-1} is accompanied by the appearance, and subsequent disappearance, of several new bands. These features can be identified as follows. The very weak band at 2170 cm^{-1} is attributed to Rh—NCO, the large bands at 2000 and 1860 cm^{-1} are due to carbonyl species (22–25), and the very strong bands at 1690 and 1630 cm^{-1} are due to nitrosyl species (26–28).
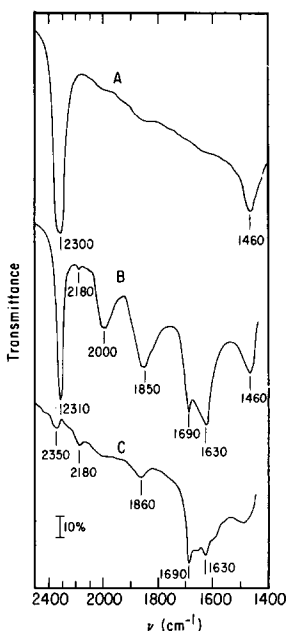
The intensities of the bands for

FIG. 4. Spectral changes occurring during the decomposition of Si—NCO species in air at 298 K. Spectrum A, background; Spectrum B, after 5.5 h; Spectrum C, after 40 h.

Rh—NCO and Rh—NO$^{\delta-}$ varied inversely in response to changes in the NO and CO partial pressures, as shown in Figs. 5 and 6. Figure 5 shows that with increasing NO partial pressure, the absorbance of the Rh—NCO band decreases and the absorbance of the Rh—NO$^{\delta-}$ band increases. The opposite trends are observed in Fig. 6 when the partial pressure of CO is increased at a constant NO partial pressure. These results suggest that the surface coverages by Rh—NO$^{\delta-}$ and Rh—NCO are closely related.

The experiments reported here clearly demonstrate that the rates of formation and decomposition of Rh—NCO and Si—NCO differ substantially. As shown in Fig. 3, the intensity of the Rh—NCO band increases rapidly to a steady state level while the intensity of the Si—NCO band continues to grow monotonically. The rate of growth of the Si—NCO species appears to be related to concentration of Rh—NCO species. The spectra presented in Figs. 2 and 3 suggest that when the flow of one or the other of the reactants is terminated, the Rh—NCO band rapidly disappears, while the band for the Si—NCO structure remains. These patterns suggest that isocyanate groups are formed on the surface of Rh microcrystallites and then spill over onto the support where they become firmly attached to silicon atoms. With time, an increasingly greater zone surrounding the microcrystallites is covered by isocyanate groups. Termination of NO reduction leads to a rapid decomposition of the Rh—NCO species, thereby terminating the driving force for further growth in the population of Si—NCO. The proposed interpretation is identical to that given by Lorimer and Bell (13) to explain formation of Si—NCO groups during the reduction of NO by CO over silica-supported Pt.

The formation and destruction of RH—NCO can be envisioned to involve the following steps.
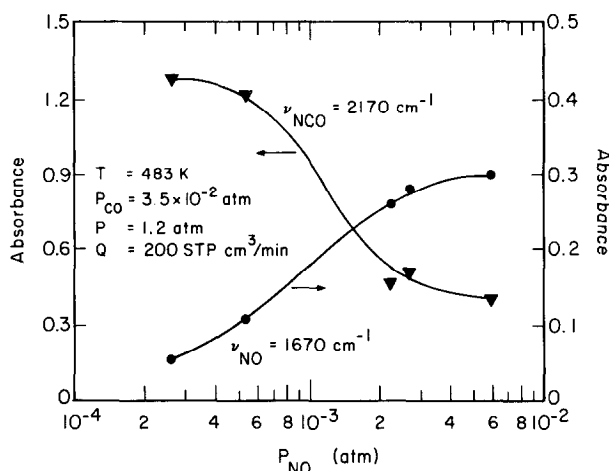
$$Rh—N + CO \rightleftarrows Rh—NCO$$

$$Rh—N + Rh—CO \rightleftarrows Rh—NCO + Rh$$
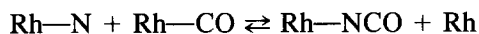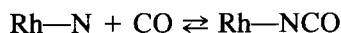
FIG. 5. Dependence of the absorbances for Rh—NCO and Rh—NO$^{\delta-}$ bands as a function of NO partial pressure.

Several authors (3, 8, 10, 12) have suggested that M—NCO groups are formed by the reaction of either gaseous or adsorbed CO with adsorbed nitrogen atoms produced by dissociative chemisorption of NO. In an effort to resolve the form of CO participating in the reaction, Davydov and Bell (8) performed a series of experiments using a Ru/SiO$_2$ catalyst. They found that Ru—NCO was formed when gaseous CO reacted with preadsorbed NO, but found no evidence of Ru—NCO formation when gaseous NO reacted with preadsorbed CO. These results led to the conclusion that gaseous CO is the preferred reactant for forming M—NCO groups. The decomposition of Pt—NCO groups present on a Pt(110) surface has been reported by Gorte et al. (14). Their work shows that Pt—NCO decomposes to produce nitrogen-containing surface fragments and CO. Similar chemistry has been observed in this study. As noted earlier, a small amount of N$_2$ was observed during the decomposition of Rh—NCO.

The dependence of Rh—NCO band intensity on the partial pressures of NO and CO can be interpreted with the aid of the reaction mechanism recently proposed by Hecker and Bell (20) to explain the kinetics of NO reduction by CO over Rh/SiO$_2$. The elementary steps involved in this mechanism are listed below. Since the justifications for selecting these reactions have been discussed previously at some length, they will not be repeated here.
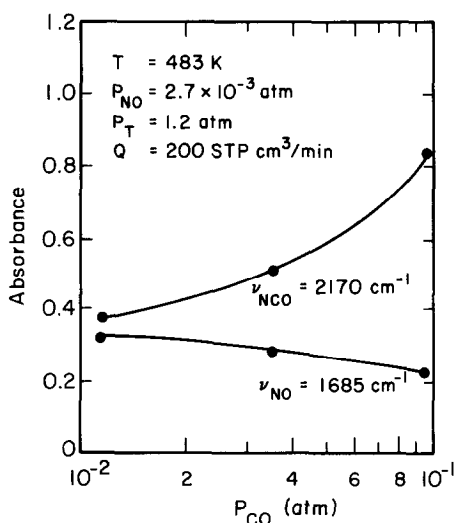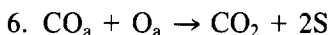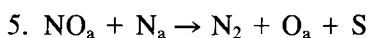
FIG. 6. Dependence of the absorbances for Rh—NCO and Rh—NO$^{\delta-}$ bands as a function of CO partial pressure.

1. NO + S $\rightleftarrows$ NO$_a$

2. CO + S $\rightleftarrows$ CO$_a$

3. NO$_a$ + S $\rightarrow$ N$_a$ + O$_a$

4. NO$_a$ + N$_a$ $\rightarrow$ N$_2$O + 2S

5. $NO_a + N_a \rightarrow N_2 + O_a + S$

6. $CO_a + O_a \rightarrow CO_2 + 2S$

If it is assumed that Rh—NCO is produced and consumed by

7. $N_a + CO \rightleftarrows NCO_a$

and that the spillover of Rh—NCO to the support does not significantly perturb the equilibrium, then

$$\theta_{NCO} = K_7 P_{CO} \theta_N \qquad (1)$$

where θ_{NCO} is the surface coverage by Rh—NCO, θ_N is the surface coverage by Rh—N, K_7 is the equilibrium constant for reaction 7, and P_{CO} is the partial pressure of CO. The coverage by adsorbed N atoms can be expressed as

$$\theta_N = \frac{k_3 \theta_v}{(k_4 + k_5)} \qquad (2)$$

where θ_v is the fraction of vacant sites and k_i is the rate coefficient for the ith elementary step. If reactions (1) and (2) are assumed to be at equilibrium as suggested by Hecker and Bell (20), and if it is assumed that the principal species covering the Rh surface are NO, CO, and NCO, then θ_v can be expressed as

$$\theta_v = [1 + K_1 P_{NO} + K_2 P_{CO} + K_7 k_3/(k_4 + k_5) P_{CO}]^{-1} \qquad (3)$$

Substitution of Eq. (3) into Eq. (2), and substitution of the result into Eq. (1) gives

θ_{NCO}

$$= \frac{K_7 k_3/(k_4 + k_5) P_{CO}}{1 + K_1 P_{NO} + [K_2 + K_7 k_3/(k_4 + k_5)] P_{CO}} \qquad (4)$$

Before discussing the correspondence of Eq. (4) to observation, it is desirable to derive an expression for the dependence of the surface coverage by NO on the partial pressures of NO and CO. Continuing with the assumption of equilibrium NO adsorption,

$$\theta_{NO} = K_1 P_{NO} \theta_v \qquad (5)$$

Substitution of Eq. (3) and Eq. (5) gives

θ_{NO}

$$= \frac{K_1 P_{NO}}{1 + K_1 P_{NO} + [K_2 + K_7 k_3/(k_4 + k_5)] P_{CO}} \qquad (6)$$

Equations (4) and (6) predict that θ_{NO} will increase, and θ_{NCO} will decrease, with increasing NO partial pressure. The reverse relationships are predicted for increasing CO partial pressure. As can be seen by inspection of Figs. 5 and 6, the trends predicted by Eqs. (4) and (6) are in good qualitative agreement with those observed experimentally.

CONCLUSIONS

It has been shown that during the reduction of NO by CO over Rh/SiO$_2$, an isocyanate group is formed on the surface of the rhodium microcrystallites. The Rh—NCO group is characterized by an infrared band at 2170–2190 cm^{-1}. The surface coverage of Rh by Rh—NCO is strongly dependent on reaction conditions and is greatest at low NO and high CO partial pressures. The coverage dependence of Rh—NCO, as well as that for adsorbed NO, can be rationalized on the basis of a reaction mechanism proposed to explain the reduction of NO. The formation of Rh—NCO groups is believed to occur via the reaction of atomically adsorbed nitrogen with gaseous CO. Under reaction conditions, the population of Rh—NCO rapidly achieves a steady state level. This population is readily destroyed, though, upon cessation of NO reduction, presumably as a consequence of the decomposition of Rh—NCO groups to form N$_2$ and CO.

In situ infrared spectra also show evidence of Si—NCO groups characterized by a bands at 2300 and 1460 cm^{-1}. These species appear to be formed via the spillover of isocyanate groups from the rhodium microcrystallites. Once formed, the Si—NCO groups are quite stable and do not undergo decomposition readily.

REFERENCES

1. London, J., and Bell, A. T., *J. Catal.* **31,** 32 (1973).
2. Unland, M. L., *Science* **179,** 567 (1973).
3. Unland, M. L., *J. Phys. Chem.* **77,** 1952 (1973).
4. Unland, M. L., *J. Catal.* **31,** 459 (1973).
5. Dalla Betta, R. A., and Shelef, M., *J. Mol. Catal.* **1,** 431 (1976).
6. Brown, M. F., and Gonzalez, R. D., *J. Catal.* **44,** 477 (1976).
7. Morrow, B. A., and Moran, L. E., *J. Phys. Chem.* **81,** 2667 (1977).
8. Davydov, A. A., and Bell, A. T., *J. Catal.* **49,** 345 (1977).
9. Voorhoeve, R. J. H., Trimble, L. E., and Freed, D. J., *Science* **200,** 759 (1978).
10. Voorhoeve, R. J. H., and Trimble, L. E., *J. Catal.* **54,** 269 (1978).
11. Solymosi, F., and Bansagi, T., *J. Phys. Chem.* **83,** 552 (1979).
12. Solymosi, F., and Sarkany, J., *Appl. Surf. Sci.* **3,** 68 (1979).
13. Lorimer, D., and Bell, A. T., *J. Catal.* **59,** 223 (1979).
14. Gorte, R. J., Schmidt, L. D., and Sexton, B. A., *J. Catal.* **67,** 387 (1981).
15. Rasko, J., and Solymosi, F., *J. Catal.* **71,** 219 (1981).
16. Eley, D. D., Kiwanuka, G. M., and Rochester, C. H., *J. Chem. Soc. Faraday Trans. 1,* **69,** 2062 (1973).
17. Morrow, B. A., and Cody, I. A., *J. Chem. Soc. Faraday Trans. 1,* **71,** 1021 (1975).
18. Guillet, A., Coudurier, M., and Donnet, J. B., *Bull. Soc. Chim. Fr.* **7–8,** 1563 (1975).
19. Miller, F. A., and Carlson, G. A., *Spectrochim. Acta* **17,** 977 (1961).
20. Hecker, W. C., and Bell, A. T., *J. Catal.* **84,** 200 (1983).
21. Hecker, W. C., and Bell, A. T., *Anal. Chem.* **53,** 817 (1981).
22. Yang, A. C., and Garland, C. W., *J. Phys. Chem.* **61,** 1504 (1957).
23. Yates, J. T., Duncan, T. M., Worley, S. D., and Vaughn, R. W., *J. Chem. Phys.* **70**(03), 1219 (1979).
24. Cavanagh, R. R., and Yates, J. T., *J. Chem. Phys.* **74**(7), 4150 (1981).
25. Rice, C. A., Worley, S. D., Curtis, C. W., Guin, J. A., and Tarrer, A. R., *J. Chem. Phys.* **74,** 6487 (1981).
26. Arai, H., and Tominaga, H., *J. Catal.* **43,** 131 (1976).
27. Solymosi, F., and Sarkany, J., *Appl. Surf. Sci.* **3,** 68 (1979).
28. Savatsky, B. J., and Bell, A. T., *ACS Symp. Ser.* **178,** 105 (1982).
29. Forster, D., and Goodgame, D. M. L., *J. Chem. Soc.* 262 (1965).
30. Chugtai, A. R., and Keller, R. M., *J. Inorg. Nucl. Chem.* **31,** 633 (1969).
31. Forster, D., and Goodgame, D. M. L., *J. Chem. Soc.* 1286 (1965).
32. Norbury, A. H., and Sinha, A. I. P., *J. Chem. Soc. A* 1598 (1968).
33. Anderson, S. J., and Norbury, A. H., *Chem. Commun.* 37 (1974).