JOURNAL OF CATALYSIS 49, 345–355 (1977)

Infrared Study of the Reactions between NO and CO and NO and H_2 on a Silica-Supported Ru Catalyst

ANATOLI A. DAVYDOV[1] AND ALEXIS T. BELL

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemical Engineering, University of California, Berkeley, California 94720

Received February 9, 1977

Observations of the interactions of NO with CO and H_2 on a silica-supported Ru catalyst have been performed using infrared spectroscopy. The formation of an isocyanate species was found when NO reacted with preadsorbed CO. When NO and CO interacted with the surface simultaneously, N_2O and CO_2 were formed in addition to the isocyanate species. Mechanisms for the formation of the isocyanate structure, N_2O, and CO_2 are proposed and discussed. Results of the interaction of NO with hydrogen (as D_2) showed that adsorbed NO reacted with D_2 to produce species containing N–D and O–D bonds.

INTRODUCTION

The surface chemistry involved in the reactions of NO with CO and H_2 over Ru is of interest because of its bearing on the performance of Ru as catalyst for the reduction of NO. In an infrared study of the interaction of NO with CO on alumina-supported noble metal catalysts Unland (*1–3*) observed the formation of an isocyanate species. The intensity of the isocyanate band was found to be correlated with the known ammonia-forming tendencies of noble metal catalysts. For Ru both the isocyanate band intensity and the selectivity toward producing ammonia were smaller than on Rh, Pd, Ir, or Pt. These observations led to the suggestion that the isocyanate species might act as an intermediate in the formation of ammonia. More recently, Brown and Gonzalez (*4*) reported studies of the adsorption and interaction of CO and NO on reduced and oxidized Ru supported on silica. They observed a band at 2180 cm^{-1} which they assigned to an isocyanate structure of the form $Ru^{\delta+}$–$NCO^{\delta-}$. A mechanism for the formation of the isocyanate group was proposed in which adsorbed NO reacts with two molecules of adsorbed CO. To date, no reports have been published concerning the interactions of NO with H_2.

In a previous study (*5*) we reported spectra for NO and CO adsorbed on a silica-supported Ru catalyst. A summary of the bands observed and their assignment to surface structures is given in Table 1. Both the mode and strength of adsorption were found to differ significantly depending upon the extent of oxidation of the Ru surface.

The present study was undertaken to develop a further understanding of the interaction between NO and CO and to obtain initial observations concerning the interaction between NO and H_2. Special attention was devoted to identifying the role of different forms of adsorbed NO and CO in forming the isocyanate structure.

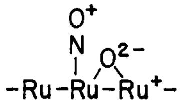
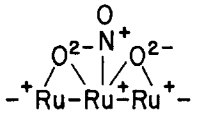
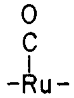
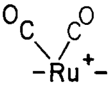
---

[1] Permanent address: Institute of Catalysis, Novosibirsk, USSR.

ISSN 0021-9517

TABLE 1

Assignment of Infrared Bands for Adsorbed NO and CO

State of Ru surface	Adsorbate	ν (cm^{-1})	Structure
Partially oxidized	$N^{14}O$ $N^{15}O$	1810–1815 1780–1785	
Partially or fully oxidized	$N^{14}O$ $N^{15}O$	1860–1875 1825–1840	
Reduced or partially oxidized	$C^{12}O$ $C^{13}O$	2030–2040 1980–1990	
Partially or fully oxidized	$C^{12}O$ $C^{13}O$	2070–2080, 2130–2140 2020–2030, 2080–2090	

Experiments were also performed to determine the thermal and chemical stability of the isocyanate structure.

EXPERIMENTAL

A 4% Ru on silica catalyst was prepared by impregnation from an aqueous solution of $RuCl_3 \cdot 3H_2O$. Details of catalyst preparation and reduction technique may be found in Ref. (*5*). For the infrared studies, about 100 mg of the reduced catalyst was pressed into a disk 29 mm in diameter using a pressure of 6000 psi.

The infrared cell and spectrometer used for this work have also been described previously (*5*). All of the spectra reported here were obtained at room temperature over the range of 3500 to 1300 cm^{-1}. To compensate for the infrared absorption of the silica support a catalyst disk was placed in the reference beam of the spectrometer.

Before each experiment the catalyst disk was pretreated in the infrared cell by heating in vacuum (10^{-5} to 10^{-6} Torr), reducing with H_2, and then further heating under vacuum. Pretreatment temperatures of 300 and 500°C were used and each phase of the pretreatment procedure lasted 2 h. In the present experiments no noticeable effect of pretreatment temperature was observed.

RESULTS AND DISCUSSION

Reactions of NO with CO

The interaction of CO with adsorbed NO was studied as a function of the procedure used for NO adsorption. Spectrum 1 in Fig. 1 shows two bands at 1860 and 1815 cm^{-1}, characteristics of NO adsorbed on an oxidized Ru surface, following NO adsorption at 25°C and subsequent evacuation of the gas at the same temperature. Introduction of CO results in the complete attenuation of the band at 1815 cm^{-1} and partial attenuation of the band at 1860 cm^{-1}. Concurrently, two bands appear at 2140 and 2080 cm^{-1}, associated with CO adsorbed on an oxidized Ru surface.

Reaction of adsorbed NO with CO also causes the appearance of a new band at

2180 cm^{-1}. In an effort to determine whether this band should be assigned to an isocyanate species, experiments were conducted with isotopically labeled NO and CO. When $N^{15}O$ and $C^{12}O$ were used, the band observed at 2180 cm^{-1} was shifted to 2160 cm^{-1}. The use of $N^{15}O$ and $C^{13}O$ resulted in a further shift in the band position to 2110 cm^{-1}. These experiments confirm the presence of both nitrogen and carbon atoms in the adsorbed species. Based upon these observations and similar results reported by Brown and Gonzales (*4*) it was concluded that the band observed at 2180 cm^{-1} should be assigned to an isocyanate species of the form $Ru^{\delta+}{-}NCO^{\delta-}$.

When NO is adsorbed at 25°C and the gas is then evacuated from the cell while heating the catalyst to 100°C, spectrum 1 in Fig. 2 is obtained. By comparison with spectrum 1 in Fig. 1 the intensity of the band at 1860 cm^{-1} is greater while that at 1815 cm^{-1} is weaker. These features are characteristic of adsorption on a more highly oxidized surface. The introduction of CO produces changes in the spectrum similar to those observed in Fig. 1. As the partial pressure of CO is increased the intensities of the CO bands and the isocyanate band increase and the intensity of the NO band decreases.

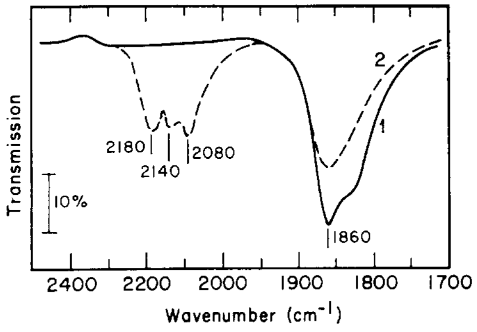


FIG. 1. Spectra of the interaction of CO with preadsorbed NO: (1) following adsorption of NO at 50 Torr and 25°C and subsequent evacuation at 25°C; (2) following addition of CO (60 Torr) at 25°C.

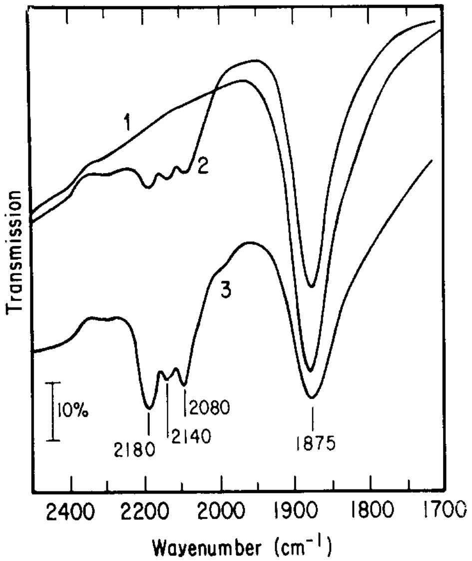


FIG. 2. Spectra of the interaction of CO with preadsorbed NO: (1) following adsorption of NO at 85 Torr and 25°C and subsequent evacuation at 100°C; (2) following addition of CO (44 Torr) at 25°C; (3) following addition of CO (100 Torr) at 25°C.

Adsorption of NO at high temperatures leads to a different sequence of observations than those shown in Figs. 1 and 2. Exposure of the catalyst to NO at 200°C and subsequent evacuation of the gas phase produces spectrum 1 in Fig. 3. The only feature present is a strong band at 1875 cm^{-1} characteristic of NO adsorbed on a fully oxidized surface. Subsequent introduction of CO at 25°C does not lead to the appearance of bands characteristic of CO or the isocyanate species. Adsorption of CO on oxidized centers and the formation of isocyanate species occurs only after the sample is heated in CO to 100°C. Increasing the temperature to 200°C results in a strong attenuation of the NO band, the appearance of a band at 2040 cm^{-1}, associated with CO adsorption on reduced sites, and an intensification of the isocyanate band. Further increasing the temperature to 300°C results in an almost complete elimination of the NO band, a strong intensification of the band characteristic of CO

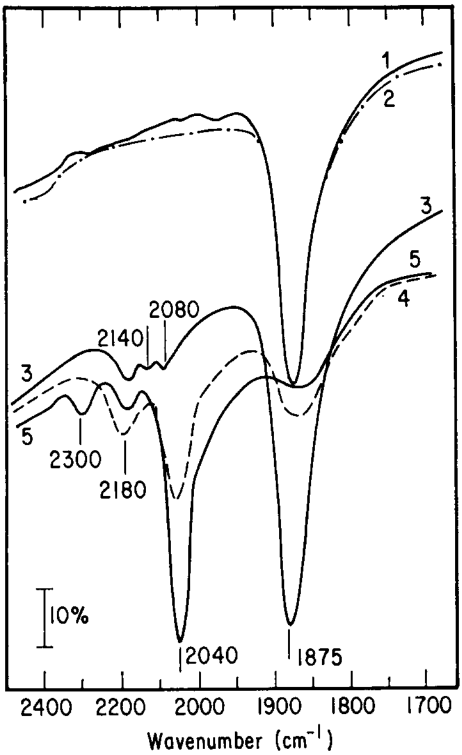


FIG. 3. Spectra of the interaction of CO with preadsorbed NO: (1) following adsorption of NO at 50 Torr and 200°C and subsequent evacuation at 25°C; (2) following addition of CO (70 Torr) at 25°C; (3) following heating in CO at 200°C; (4) following heating in CO at 300°C; (5) following heating in CO at 400°C.

adsorbed on reduced sites, a slight attenuation of the isocyanate band, and the appearance of a new band at 2300 cm^{-1}. Similar results are obtained when NO adsorption is carried out at 400°C.

Positive assignment of the band at 2300 cm^{-1} was not possible since the appearance of the band was not reproducible. It was established, however, that the band appeared only during the interaction of NO with CO at high temperatures. Once formed the species responsible for the band was stable to evacuation up to a temperature of 500°C. Possible assignments of the band might be to either cyano or isocyano species (*6*).

To determine the effect of the sequence of interaction of NO and CO with the catalyst, experiments were conducted in which CO was preadsorbed and the catalyst was then contacted with NO. Spectrum 1 in Fig. 4 taken after the adsorption of CO and evacuation of the gas phase shows a strong CO band at 2040 cm^{-1} for adsorption on reduced sites and weaker bands at 2140 and 2080 cm^{-1} for adsorption on oxidized sites. Introduction of 1 Torr of NO causes an immediate displacement of the CO adsorbed on reduced sites and the appearance of NO bands at 1855 and 1815 cm^{-1}. With prolonged exposure to NO the intensity of the band observed at 1855 grows and the band shifts to 1860 cm^{-1}. Heating of the catalyst in NO results in an intensification of the NO band and a further shift in its position to 1875 cm^{-1}. Above 200°C all traces of the CO bands associated with oxidized sites are removed. It is significant to note that at no point in this sequence does an isocyanate band appear at 2180 cm^{-1}. A similar sequence of spectra was observed when the partial pressure of NO was reduced to 0.1 Torr.

The reaction of NO with CO adsorbed on an oxidized Ru surface was also examined. Spectrum 2 in Fig. 5, taken after exposure to CO and evacuation, shows

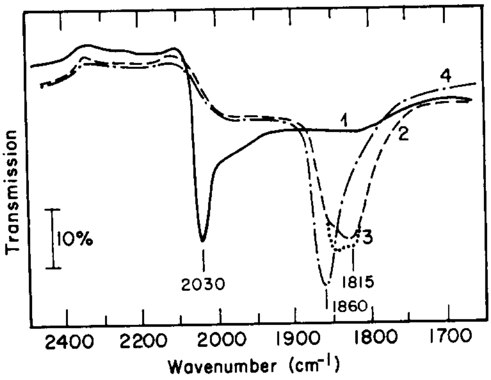


FIG. 4. Spectra of the interaction of NO with preadsorbed CO: (1) following adsorption of CO at 10 Torr and 25°C and subsequent evacuation at 25°C; (2) following addition of NO (1 Torr) at 25°C; (3) following exposure to NO for 30 min; (4) following heating in NO at 200°C.

bands at 2140 and 2080 cm^{-1} characteristic of CO adsorbed on oxidized sites. Subsequent introduction of NO leads to a significant attenuation of both bands and the appearance of a weak band at 1870 cm^{-1}. Here again no evidence was found for the formation of an isocyanate group.

The spectra shown in Fig. 6 characterize the adsorbed species present when the catalyst is exposed to an equimolar mixture of NO and CO. At 25°C spectrum 1 shows bands for CO and NO adsorbed on oxidized sites and a weak isocyanate band. Increasing the temperature to 100°C causes a shift of the NO band to higher frequencies indicating further oxidation of the Ru surface. When the temperature is further raised to 200°C a sequence of changes occurs: The position of the NO band is shifted even further upscale, the CO bands are eliminated, the intensity of the isocyanate band increases, and new bands appear at 2300, 2240, and 2210 cm^{-1}. The latter series of bands is easily removed upon evacuation at room temperature as shown in Fig. 7.

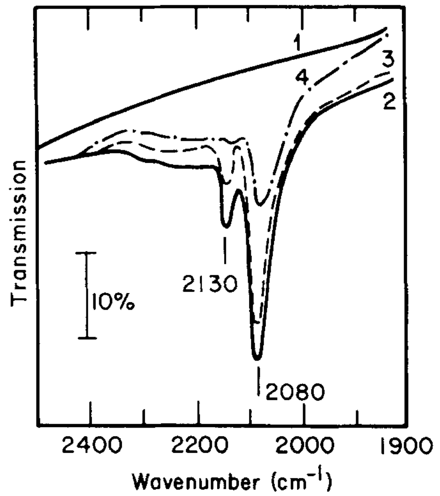


FIG. 5. Spectra of the interaction of NO with CO preadsorbed on an oxidized catalyst: (1) following catalyst oxidation in O_2 (100 Torr) at 200°C; (2) following CO adsorption at 8 Torr and 25°C; (3) following evacuation of CO at 25°C; (4) following addition of NO (10 Torr) at 25°C.

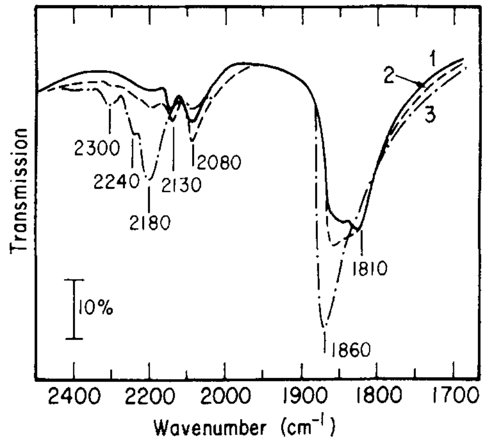


FIG. 6. Spectra of the interaction of NO and CO: (1) following the addition of NO (10 Torr) and CO (10 Torr) at 25°C; (2) following heating in the NO–CO mixture to 100°C; (3) following heating in the NO–CO mixture to 200°C.

In order to determine the nature of the new bands appearing upon interaction with gas mixtures, spectra were taken using isotopically labeled NO and CO. Figure 8 illustrates spectra obtained for a mixture containing $C^{13}O$ and $N^{14}O$. In this case the isocyanate band is shifted to 2120 cm^{-1} facilitating observation of bands in the region of 2400 to 2200 cm^{-1}. The bands observed at 2240 and 2210 cm^{-1} in Fig. 7

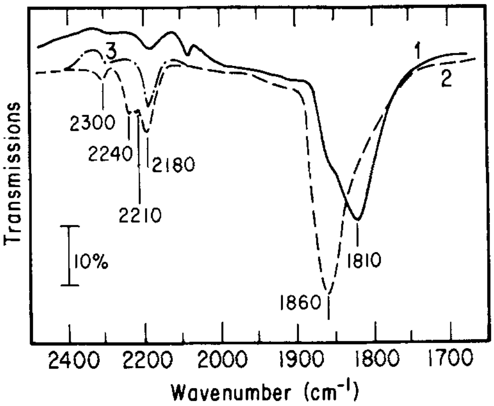


FIG. 7. Spectra of the interaction of NO and CO: (1) following addition of NO (20 Torr) and CO (20 Torr) at 25°C; (2) following heating in the NO–CO mixture to 200°C; (3) following evacuation at 25°C.

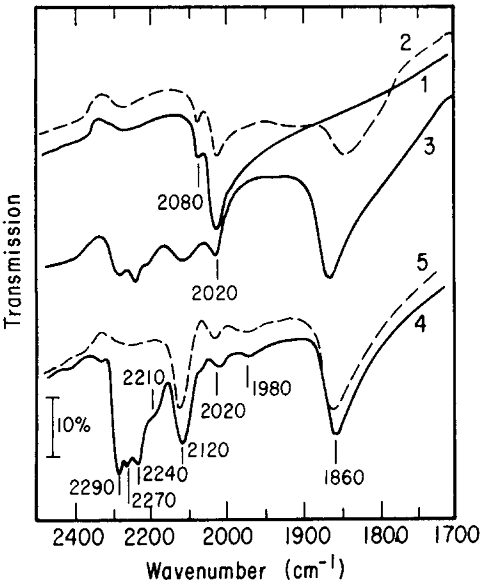


FIG. 8. Spectra of the interaction of $N^{14}O$ and $C^{13}O$ on an oxidized catalyst: (1) following catalyst oxidation in NO at 300°C, evacuation at 500°C, and addition of $C^{13}O$ (18 Torr) at 25°C; (2) following addition of $N^{14}O$ (18 Torr); (3) following heating in the $C^{13}O$–$N^{14}O$ mixture at 200°C; (4) following heating in the $C^{13}O$–$N^{14}O$ mixture at 300°C; (5) following evacuation at 25°C.

are observed here too. This indicates that the corresponding species involve nitrogen atoms but not carbon atoms. New bands are also observed at 2290 and 2270 cm^{-1}. When $N^{15}O$ is used instead of $N^{14}O$ these bands are observed again, indicating that the corresponding species contains carbon atoms but not nitrogen atoms.

The bands observed at 2240 and 2210 cm^{-1} in Figs. 7 and 8 lie in the range characteristic of vibrations in N_2O (*6*). To aid the assignment of these bands, experiments were performed in which a reduced Ru sample was exposed to N_2O. The spectra illustrated in Fig. 9 show a very weak band at 2300 cm^{-1} and very strong bands at 2240 and 2220 cm^{-1}. All three bands are easily removed upon evacuation of the gas phase. Based upon these observations and the work of Diamantis and Sparrow (*7*) concerning the coordination of N_2O in Ru complexes, the bands at 2240 and 2220 are assigned to N_2O weakly adsorbed through the oxygen atom. The weak band observed at 2300 cm^{-1} is possibly due to N_2O adsorbed through the nitrogen atom by analogy with observations of N_2O adsorption on chromia (*8*).

The bands observed at 2290 and 2270 cm^{-1} in the spectra taken with $C^{13}O$ can be assigned to $C^{13}O_2$ (*6*). A similar assignment was proposed by Brown and Gonzalez (*4*).

Because the formation of an isocyanate species is a characteristic feature of the interaction of NO with CO, experiments were conducted to determine the thermal and chemical stability of the isocyanate group. Figure 10 shows a series of spectra taken after desorption for 1 h at different temperatures. The band appearing at 2180 cm^{-1} is stable at 25°C and is attenuated only slightly when the desorption temperature is raised to 100°C. Further increase in the temperature to 200°C causes a complete elimination of the isocyanate band.

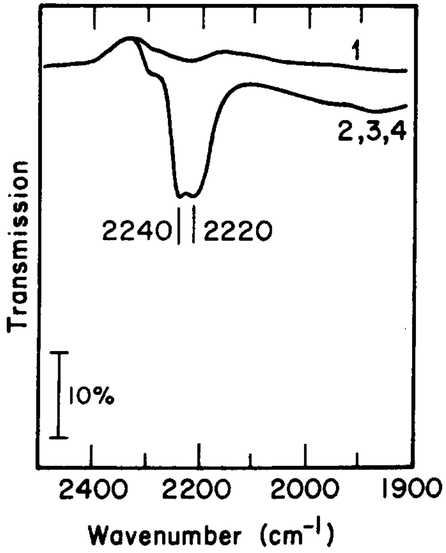


FIG. 9. Spectra of adsorbed N_2O: (1) background; (2) following addition of N_2O (8 Torr) at 25°C; (3) following heating in N_2O at 100°C; (4) following heating in N_2O at 200°C.

Spectra taken following the interaction of the isocyanate group with NO are shown in Fig. 11. It is apparent that beginning at 25°C the reaction of NO with the isocyanate group causes its gradual elimination from the surface. The extent of reaction is enhanced by raising the temperature to 100°C.

The observations reported above can now be considered in terms of the insight they provide regarding the reaction pathways of NO and CO on an Ru catalyst. Of particular interest are the mechanisms for the formation the isocyanate species and N_2O. The mechanism by which an oxidized Ru surface is reduced must also be considered.

In the present experiments the formation of an isocyanate species was observed when gas phase CO reacted with preadsorbed NO or when both CO and NO were present in the gas phase. No evidence for the formation of an isocyanate species was found when gas phase NO reacted with adsorbed CO. These observations lead us to propose that the isocyanate species is formed via a Rideal–Eley process involving adsorbed nitrogen atoms.

$$\text{Ru–N} + \text{CO} \rightarrow \text{R–NCO} \qquad (1)$$

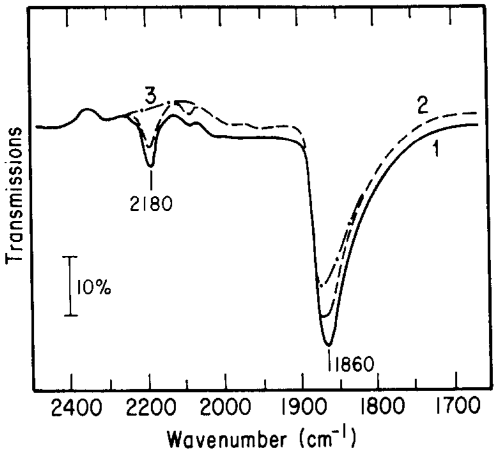


FIG. 10. Spectra illustrating the thermal stability of the isocyanate species: (1) following reaction in NO (10 Torr) and CO (10 Torr) at 200°C and subsequent evacuation at 25°C; (2) following evacuation at 100°C; (3) following evacuation at 200°C.

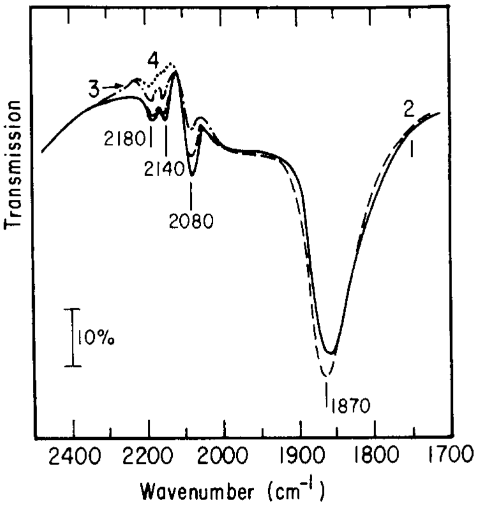
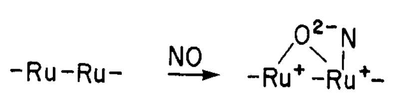


FIG. 11. Spectra illustrating the interaction of NO with the isocyanate species: (1) following reaction in NO (10 Torr) and CO (10 Torr) at 200°C and subsequent evacuation at 25°C; (2) following addition of NO (10 Torr) at 25°C; (3) following exposure to NO at 25°C for 12 h; (4) following heating in NO at 100°C.

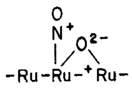
At least two routes can be envisioned for the formation of adsorbed nitrogen atoms. The first is the dissociative adsorption of NO on reduced portions of the catalyst surface, as illustrated by reaction (2).

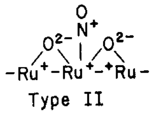

(2)

$$\text{-Ru-Ru-} \xrightarrow{\text{NO}} \overset{\text{O}^{2-}\ \text{N}}{\text{-Ru}^{+}\text{-Ru}^{+}\text{-}} \qquad (2)$$

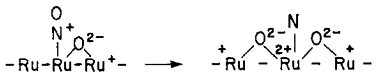
Studies by Ku *et al.* (*9*) on an $Ru(10\bar{1}0)$ surface have shown that NO will rapidly dissociate into separate oxygen and nitrogen phases. While experimental measurements of the activation energy for reaction (2) are not available, Miyazaki and Yasumori (*10*) have recently estimated a value of $\sim$3 kcal/mol. Evidence supporting a low activation energy for dissociative adsorption may also be found in the present studies. Figure 1 shows that exposure of a fully reduced Ru sample to NO at room temperature and subsequent adsorption of CO yields a spectrum in which only bands for CO adsorbed on oxidized Ru sites are present.

The second mechanism for forming surface nitrogen atoms involves the dissociation of molecularly adsorbed NO. We have previously proposed (*5*) that molecular adsorption leads to two surface structures, as illustrated below.


Type I


Type II

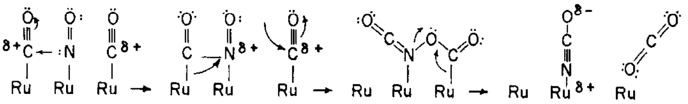
Type I adsorption is characteristic of a partially oxidized surface while type II adsorption is characteristic of a fully oxidized surface. Since NO adsorbed at type-II sites is largely surrounded by adsorbed oxygen atoms, dissociation should be precluded or at best very difficult. Dissociation of NO adsorbed at type I sites should be possible, however, since vacant sites are present near the adsorption center. An illustration of this dissociative process is given by reaction (3).


(3)

The occurrence of reaction (3) is supported by the spectra shown in Fig. 3. We recall that exposure of the catalyst to NO at 200°C leads to a spectrum characteristic of NO adsorption at type II sites. Subsequent contacting with CO at 25°C produces no change in the spectrum, indicating the absence of CO adsorption sites. When the temperature of interaction with CO is increased a partial reduction of the surface occurs which is evidenced by a decrease in intensity of the NO band, a shift of ν_{NO} to lower frequencies, and the appearance of CO bands. At the same time an isocyanate band appears. As the catalyst temperature is increased the intensity of the CO and isocyanate bands increases and the intensity of the NO band decreases. This sequence of observations can be explained by the fact that as the surface is reduced vacant Ru sites are produced adjacent to molecularly adsorbed NO. The appearance of these vacant sites makes it possible for the adsorbed NO to dissociate. This process produces surface nitrogen atoms which can, in turn, react with CO via reaction (1) to form isocyanate species. The spectra in Fig. 2 show that the intensity of isocyanate bands increases with increasing CO partial pressure.

It is of interest to note that our conclusions concerning the manner in which NO is adsorbed at high temperatures and the ability of adsorbed NO to dissociate are consistent with the observations of Ku *et al.* (*9*). In their study of NO adsorption on an $Ru(10\bar{1}0)$ surface they reported that prolonged exposure to NO at 200°C resulted in a saturation of the surface with atomically adsorbed oxygen and molecularly adsorbed NO. Nitrogen atoms produced on the surface through dissociative adsorption of NO were readily desorbed as N_2 at temperatures of 200°C and above. It was also observed that molecularly adsorbed NO could dissociate provided vacant sites were present adjacent to the adsorption site.

The mechanism of isocyanate formation proposed here differs significantly from that recently suggested by Brown and Gonzalez (*4*). They propose that adsorbed NO interacts with CO adsorbed on adjacent sites via the following sequence of steps.



To support this mechanism they note that appreciable amounts of the isocyanate species can be formed when adsorbed CO is allowed to interact with small doses of NO. Under these circumstances a part of the adsorbed CO is displaced by the NO and infrared bands are observed for adsorbed NO, CO, and –NCO.

We recall that in the present studies no evidence was observed to suggest that CO adsorbed on either reduced or oxidized sites could react with NO to form an isocyanate structure. Even when very low partial pressures of NO (~0.1 Torr) were used the CO adsorbed on reduced sites was immediately displaced by NO. In addition, it was observed that CO associated with oxidized sites was partially displaced upon interaction with NO at low temperatures and was completely removed from the surface at temperatures above 200°C, but without the formation of an isocyanate species. In view of these observations we must conclude that our results do not support the mechanism of isocyanate formation proposed by Brown and Gonzalez (*4*).

It is appropriate at this point to comment on the recent suggestion by Dalla Betta and Shelef (*11*) that the isocyanate species observed on transition metal catalysts resides on the support rather than the metal surface. We disagree with this interpretation for two reasons. The first is that the metal surface is a necessary component for the formation of the isocyanate species, since attempts to form this species on pure silica are not successful. Our second reason relates to the observations that the isocyanate species can be formed at 25°C and is strongly bonded to the surface. Unless the surface diffusion coefficient for the isocyanate species is high, one would not expect it to migrate from the metal surface to the support surface at 25°C.

The spectra shown in Figs. 10 and 11 indicate that the isocyanate species can be removed from the surface by thermal decomposition and that the presence of NO in the gas phase facilitates the removal process. While no clear definition of the reaction pathways is possible on the basis of the available evidence, reactions such as those listed below seem reasonable.

$$\mathrm{Ru{-}NCO} \rightarrow \mathrm{Ru{-}N} + \mathrm{CO} \tag{4}$$

$$\begin{aligned}\mathrm{Ru{-}NCO} + \mathrm{NO} &\rightarrow \mathrm{Ru} + \mathrm{N_2O} + \mathrm{CO}\\ &\rightarrow \mathrm{Ru} + \mathrm{N_2} + \mathrm{CO_2}\end{aligned} \tag{5}$$

$$\begin{aligned}&\mathrm{Ru{-}NCO} + \mathrm{Ru{-}NO}\\ &\quad\rightarrow 2\mathrm{Ru} + \mathrm{N_2O} + \mathrm{CO}\\ &\quad\rightarrow 2\mathrm{Ru} + \mathrm{N_2} + \mathrm{CO_2}\end{aligned} \tag{6}$$

The formation of N_2O is observed only in the case where NO and CO are present in the gas phase together. Several routes can be proposed to explain the appearance of this product

$$\mathrm{Ru{-}N} + \mathrm{NO} \rightarrow \mathrm{Ru} + \mathrm{N_2O} \tag{7}$$

$$\mathrm{Ru{-}N} + \mathrm{Ru{-}NO} \rightarrow 2\mathrm{Ru} + \mathrm{N_2O} \tag{8}$$

$$\begin{aligned}&\mathrm{Ru{-}NO} + \mathrm{Ru{-}NO}\\ &\quad\rightarrow \mathrm{Ru} + \mathrm{Ru{-}O} + \mathrm{N_2O}\end{aligned} \tag{9}$$

While the results presented here do not allow us to discriminate between these alternatives, several factors argue in favor of reaction (7). To begin with, bond energy–bond order (BEBO) estimates of the activation energies yield values of 10, 37, and 57 kcal/mol for reactions (7), (8), and (9), respectively (*12*). Use of these values in an absolute rate theory estimate (*13*) of the rates of reactions (7–9) leads to the conclusion that reaction (7) should represent the preferred reaction path, for the conditions of the present experiments. Secondly, Ku *et al.* (9) have observed that thermal desorption of NO from an Ru(10$\bar{1}$0) surface produces only NO, N_2, and O_2, but no N_2O. Furthermore, the peak in the NO desorption curve and the onset of the N_2 desorption curve both occur in the vicinity of 200°C. These results suggest that the activation energies for reactions (8) and (9) are higher than those associated with the thermal desorption of NO and N_2. In view

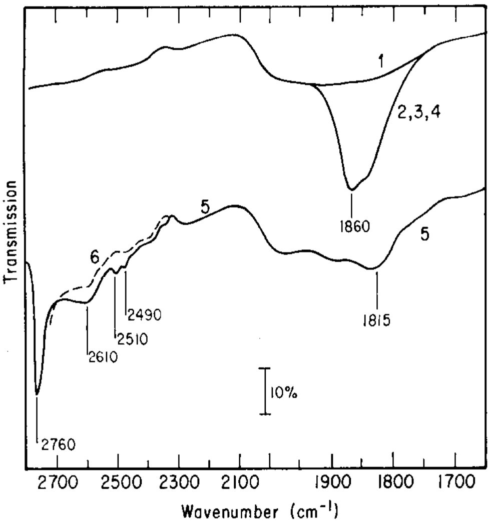


FIG. 12. Spectra of the interaction of D_2 with preadsorbed NO: (1) background; (2) following adsorption of NO (1 Torr) at 25°C; (3) following evacuation at 25°C; (4) following addition of D_2 (50 Torr) at 25°C; (5) following heating in D_2 at 100°C; (6) following evacuation at 25°C.

of these facts we are led to conclude that reaction (7) represents a preferred path for N_2O formation.

When NO and CO are present in the gas phase in equimolar concentrations we observe under reaction conditions that only NO is appreciably adsorbed on the catalyst surface. This is explained by the fact that NO adsorbs preferentially and is capable of displacing CO adsorbed at reduced sites. Since NO adsorption occurs dissociatively and causes an oxidation of the Ru surface, a constant reduction of the surface must occur in order for the reaction between NO and CO to continue. It is proposed that the dominant mode for the removal of adsorbed oxygen is reaction (10).

$$Ru^{\delta+}\text{–}O^{\delta-} + CO \rightarrow Ru + CO_2 \quad (10)$$

The principal argument favoring a Rideal–Eley process, such as reaction (10), over a Langmuir–Hinshelwood process involving adsorbed CO is the expectation of a significantly lower activation energy for the former process as is noted in the case of Pt (*14*).

Interaction of NO and H_2

Studies of the interaction of hydrogen with NO were conducted using D_2 in order to facilitate the observation of N–H vibrations. Figure 12 illustrates a sequence of spectra characterizing the interaction of D_2 with adsorbed NO. Introduction of D_2 at 25°C produces no changes in the spectrum of adsorbed NO. Heating to 100°C leads to a strong attenuation of the NO band and the appearance of new bands at 2760, 2610, 2510, and 2490 cm^{-1}. Upon evacuation the bands at 2610, 2510, and 2490 disappear from the spectrum, suggesting that they are associated with weakly adsorbed species.

The assignment of the new bands observed in Fig. 12 can be made by comparison with published spectra (*6*, *15*). The band observed at 2760 cm^{-1} is readily associated with –OD groups formed on the surface of the silica support as a result of H–D exchange. The weak band appearing at 2610 cm^{-1} is assigned to D_2O while the bands appearing at 2510 and 2490 cm^{-1} are assigned to N–D variations in either $-ND_2$ or ND_3 (*6*).

Both D_2O and ND_3 are gaseous products of the reaction between NO and D_2. Since it is known that both products can adsorb on silica the possibility exists that the bands associated with these molecules are characteristic of adsorption on silica rather than on Ru. The present experiments do no allow us to discern between these two alternatives. We note, however, that Pozdnyakov and Filimonov (*16*) have observed broad bands at 3400–3345 and 3300–3250 cm^{-1} for NH_3 adsorbed on silica-supported Ru. These bands were not obtained when the support was exposed to NH_3, suggesting that the observed bands are attributable to NH_3 adsorption on the metal.

CONCLUSIONS

The present results lead to the conclusion that isocyanate species are formed on the surface of a Ru catalyst via a two-step process. In the first step adsorbed N atoms are produced by either dissociative adsorption of NO or dissociation of molecularly adsorbed NO. The adsorbed N atoms then react with gas phase CO to yield the isocyanate structure in the second step. The proposed reaction pathway is consistent with the available evidence concerning the adsorption of NO but differs from that previously proposed by Brown and Gonzalez (*4*) in that adsorbed CO does not participate in the reaction.

Investigations of the stability of the isocyanate species have revealed that it is rapidly removed from the catalyst surface at temperatures above 150°C. Reaction with gas phase NO facilitates the removal of the isocyanate species. However, the nature of the process and the reaction products have not been identified.

In studies performed with mixtures of NO and CO, N_2O, and CO_2 were observed as reaction products. It is proposed that both products are formed via Rideal–Eley processes involving the reactants in the gas phase and adsorbed N and O atoms. The validity of the proposed reaction mechanisms is supported through BEBO calculations of the activation energies for alternative processes.

Finally, it is concluded that the interaction of D_2 with NO leads to the appearance of adsorbed species containing O–D and N–D bonds, characteristic of D_2O and ND_2 or ND_3 species. These species are weakly bound and are easily removed by evacuation. It was not determined whether the observed species were adsorbed on the Ru surface or the surface of the silica support.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation (Grant GP-43728).

REFERENCES

1. Unland, M. L., *Science* **179**, 567 (1973).

2. Unland, M. L., *J. Phys. Chem.* **77**, 1952 (1973).

3. Unland, M. L., *J. Catal.* **31**, 459 (1973).

4. Brown, M. F., and Gonzalez, R. D., *J. Phys. Chem.* **80**, 1731 (1976); *J. Catal.* **44**, 477 (1976).

5. Davydov, A. A., and Bell, A. T., *J. Catal.* **49**, 332 (1977).

6. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed. Wiley Interscience, New York, 1970.

7. Diamantis A. A., and Sparrow, G. J., *J. Colloid Interface Sci.* **47**, 455 (1974).

8. Zecchina, A., Cerruti, L., and Borello, E., *J. Catal.* **25**, 55 (1972).

9. Ku, R., Gjostein, N. A., and Bonzel, H. P., *in* "The Catalytic Chemistry of Nitrogen Oxides" (R. L. Klimisch and J. G. Larson, Eds.). Plenum Press, New York, 1975.

10. Miyazaki, E., and Yasumori, I., *Surface Sci.* **57**, 755 (1976).

11. Dalla Betta, R. A., and Shelef, M., preprint submitted to *J. Catal.*

12. These calculations are similar to those reported by Weinberg, W. H., *J. Catal.* **28**, 459 (1973) and make use of bond energies for Ru=O and R≡N reported by Miyazaki, E., and Yasumuri, I., *Surface Sci.* **55**, 747 (1976).

13. Weinberg, W. H., *J. Catal.* **28**, 459 (1973).

14. Weinberg, W. H., and Merrill, R. P., *J. Catal.* **40**, 268 (1975).

15. Little, L. H., "Infrared Spectra of Adsorbed Species." Academic Press, New York, 1966.

16. Pozdnyakov, D. V., and Filimonov, F. N., *Kinet. Katal.* **13**, 475 (1972).