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An Infrared Study of the Adsorption of NO on the Reduced and Oxidized Forms of Silica-Supported Ru

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The infrared spectra of NO adsorbed on the reduced and oxidized forms of supported Ru have been recorded. (An oxidized Ru sample was made by exposing a reduced sample to 50 Torr of O_2 at 325°C.) For NO adsorbed on an oxidized 6% Ru–silica sample, a strong sharp band at 1880 cm^{-1} is observed, and this band is assigned to $\nu_{(NO)}$ for NO adsorbed on an oxygen-perturbed Ru surface site. NO adsorbed on the oxidized form of Ru is stable both to evacuation up to temperatures of 325°C and to H_2 (g) up to temperatures of 200°C. When NO is adsorbed on a reduced 6% Ru–silica sample, N_2O (g) is detected, and the oxygen species formed in this reduction is adsorbed on the Ru–silica surface. Three bands are observed in the infrared spectra: a band at 1630 cm^{-1} assigned to $\nu_{(NO)}$ for $Ru^{\delta+}$–$NO^{\delta-}$, a band at 1820 cm^{-1} assigned to $\nu_{(NO)}$ for $Ru^{\delta-}$–$NO^{\delta+}$, and a band at 1860 cm^{-1} assigned to $\nu_{(NO)}$ for NO adsorbed on an oxygen-perturbed Ru surface site. When a reduced Ru–silica sample with full NO surface coverage is heated, we observe an intensification of the high-frequency NO band; however, if this sample is heated to 125°C in the presence of a reducing gas, i.e., H_2, the surface species react, and the frequencies of the infrared bands are shifted to lower wave numbers.

INTRODUCTION

There has been recent interest in the catalytic reduction of NO to N_2 without formation of undesirable byproducts, such as NH_3. It has been observed that supported Ru is an excellent catalyst for the direct reduction of NO to N_2 (*1–4*); furthermore, Taylor *et al.* (*5*) have reported that the N_2 selectivity is increased if an oxidized form of Ru is used. (This oxidized form of Ru was made by exposing a reduced sample to O_2 at elevated temperatures.) These authors found that Ru exhibited this "dual-state" behavior to a greater extent than the other noble metals, e.g., Pt or Pd; however, they were unable to explain this unusual behavior. In a recent gas-chromatographic study of the reduction of NO with CO and H_2 over a Ru catalyst, Voorhoeve and Trimble (*6*) suggested that the lower activity of the reduced form of Ru is due to the formation of a surface nitride which interferes with the NO reduction. To understand better the effect of an oxidizing environment on the catalytic activity of supported Ru, we have made an infrared study of the adsorption of NO on the reduced and oxidized forms of silica-supported Ru.

There have been several infrared studies of the adsorption of NO on various supported metal surfaces, and this area has been reviewed by Shelef and Kummer (*7*) and, more recently, by Shelef (*8*). Although there has been considerable interest in the adsorption of NO on the Ru surface, surprisingly, there has been no infrared study of the adsorption of NO on supported Ru.

Previously we made an infrared study of the adsorption of CO on the reduced and oxidized forms of silica-supported Ru,

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and we found that CO is adsorbed differently on these two forms of Ru (*9*). 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 bands at 2150 and 2080 cm^{-1}. For CO adsorbed on an oxidized 6% 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} was assigned to $\nu_{(CO)}$ for CO linearly adsorbed on a Ru surface site; the band at 2080 cm^{-1} was assigned to $\nu_{(CO)}$ for CO adsorbed on a Ru surface site perturbed by a nearby oxygen atom; and the band in the 2150 cm^{-1} region was assigned to $\nu_{(CO)}$ for CO adsorbed on a RuO surface site. To determine if NO is adsorbed differently on the reduced and oxidized forms of supported Ru, we studied the adsorption of NO and the stability of adsorbed NO on these two forms of silica-supported Ru.

EXPERIMENTAL

Materials

The 6% Ru–silica sample used in this study was prepared by impregnating Cab-o-sil, Grade M-5 (Cabot Corporation, Boston, Mass.), with an aqueous solution of $RuCl_3 \cdot CH_2O$ (Engelhard Industries). A detailed description of the preparation of sample pellets for use in infrared studies has been reported previously (*9*). The average crystallite size of the 6% Ru–silica sample used in this study was estimated as 60 Å. This particle size was determined from the (101) line of Ru using the Sherrer equation for X-ray line broadening.

Commercial H_2 was used in the reduction of the sample pellets and in several adsorption experiments. 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. C. P. Grade O_2 was further purified by passing it through a dry ice/acetone 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 trap 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. ^{15}NO (Bio-Rad Laboratories, reported 99% enriched in ^{15}N) was used without further purification. All gases were periodically checked for purity on a Dupont Model 104 mass spectrometer.

Techniques

The pretreatment procedure for the reduced form of the catalyst was as follows: evacuated for 1 h at 325°C, reduced in flowing H_2 (150 ml/min) for 6 h at 325°C, and evacuated for 2 h at 325°C. Reduction temperatures in excess of 350°C resulted in sintering of the sample. The oxidized form of the catalyst was made by exposing a pellet, reduced in the manner just described, to 50 Torr of O_2 for 15 sec. A higher O_2 pressure or longer exposure time resulted in severe scattering and a loss in transmittance of the infrared radiation. The reduced form of the catalyst can be regenerated from the oxidized form by a standard 6-h reduction.

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, 6% Ru–silica pellets 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 bands 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 analyses were made on a Dupont Model 104 mass spectrometer.

RESULTS AND DISCUSSION

The infrared spectra of the stepwise adsorption of NO on an oxidized 6% Ru–silica sample is shown in Fig. 1. With the first exposure to NO, we observe a sharp band at 1880 cm^{-1}, and we find that the intensity of this band increases with each subsequent addition of NO until full NO surface coverage is attained. No frequency shift is observed, and there are no low-frequency bands observed in the spectrum.

NO is very strongly adsorbed on the oxidized form of Ru. Desorption studies show that this adsorbed NO is stable to evacuation up to 325°C. Desorption studies at higher temperatures cannot be made because the Ru–silica samples sinter when heated to temperatures greater than 350°C. We also find that NO adsorbed on the oxidized form of supported Ru is stable to H_2 at elevated temperatures. When an oxidized Ru–silica sample with full NO surface coverage is heated to 200°C in the presence of 10 Torr of H_2 (g), we observe no change in the intensity or the frequency of the NO band at 1880 cm^{-1}. NO adsorbed on the oxidized form of Ru is stable to 10 Torr of O_2 at room temperature (25°C); the stability of adsorbed NO to O_2 at elevated temperatures cannot be determined, because the Ru–silica samples suffer an irreversible loss in the transmittance of the infrared radiation when they are heated in O_2 for 2 min or longer.

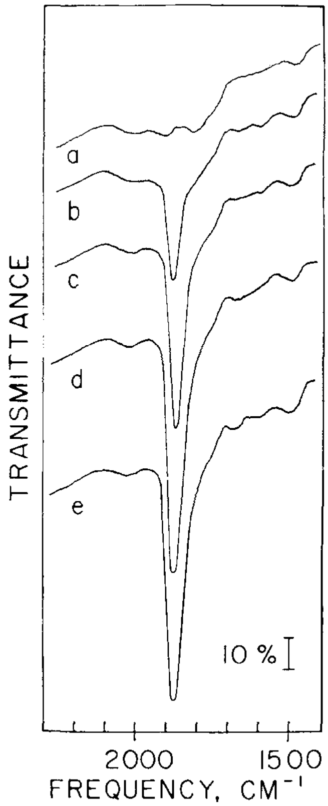

Fig. 1. Infrared spectra of NO adsorbed on an oxidized 6% Ru–silica sample at 25°C: (a) background, (b) first exposure to NO, (c) second exposure to NO, (d) third exposure to NO, (e) full NO surface coverage.

In a previous study on the adsorption of CO on the oxidized form of supported Ru, we observed a strong band at 2080 cm^{-1}, and we found that this species was strongly adsorbed on the Ru surface (*9*). This CO band at 2080 cm^{-1} was assigned to $\nu_{,CO}{}^3$ for CO adsorbed on an oxygen-perturbed Ru surface site. A similar assignment is reasonable for the strong band at 1880 cm^{-1} for NO adsorbed on the oxidized form of supported Ru, i.e., this band is $\nu_{,NO}{}^3$ for NO adsorbed on an oxygen-perturbed Ru surface site. (This is a tentative assignment, and all band assignments will be discussed in detail later.)

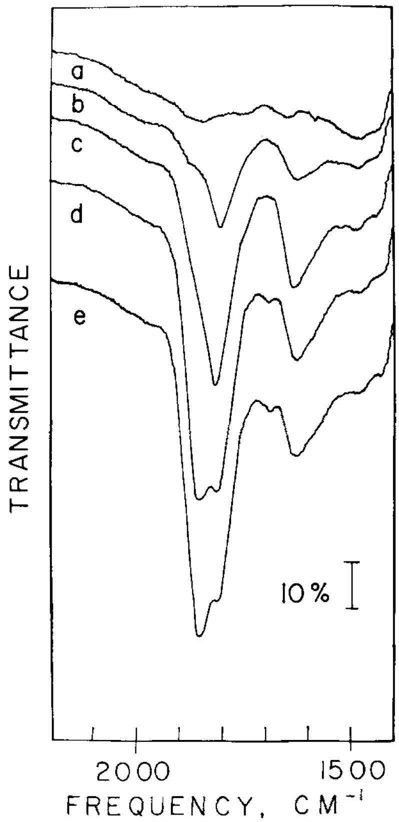

FIG. 2. Infrared spectra of NO adsorbed on a reduced 6% Ru–silica sample at 25°C: (a) background, (b) first exposure to NO, (c) second exposure to NO, (d) third exposure to NO, (e) full NO surface coverage.

To verify this band assignment, we studied the adsorption of NO on the reduced form of supported Ru. The spectra obtained of NO adsorbed on a reduced 6% Ru–silica sample as a function of surface coverage are shown in Fig. 2. After the initial exposure to NO, we observe two bands, a band at 1800 cm^{-1} which is asymmetric to the high-frequency side and a broad symmetric band centered at 1630 cm^{-1}. With the next addition of NO, we find that the intensities of both bands increase; the frequency of the band first observed at 1800 cm^{-1} shifts to 1820 cm^{-1}, whereas no frequency shift is observed for the band at 1630 cm^{-1} (Fig. 2b, c). After the third addition of NO we note development of a definite high-frequency NO band at 1860 cm^{-1}. At higher NO surface coverage and in the presence of excess NO, we find that the intensity of the band at 1860 cm^{-1} increases, whereas there is no change in the intensities of the bands at 1820 and 1630 cm^{-1} (Fig. 2d, e).

To characterize better this complex spectrum of NO adsorbed on the reduced form of Ru, we studied the desorption behavior of the various NO bands. These spectra are shown in Fig. 3. When a 6% Ru–silica sample with full NO surface coverage is evacuated for 12 h at 25°C, we observe no change in the infrared spectrum (Fig. 3b, c). When this sample is heated to 200°C and evacuated for 2 h,

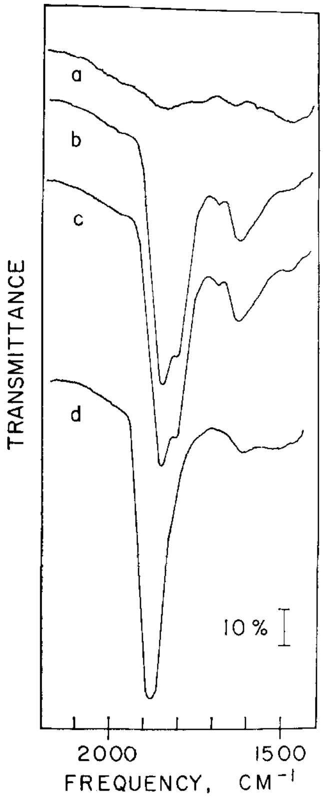

FIG. 3. Infrared spectra illustrating the desorption behavior of the NO bands observed on a reduced 6% Ru–silica sample: (a) background, (b) full NO surface coverage, (c) evacuated 12 h at 25°C, (d) evacuated 2 h at 200°C.

we observe a strong broad band at 1880 cm^{-1} and a weak band at 1630 cm^{-1} (Fig. 3d). Similar spectral changes are observed when a sample with full NO surface coverage is heated to 200°C without evacuation. Since we still observe a strong broad band at 1880 cm^{-1} after heating, it suggests that the NO surface species are not desorbed from the surface, but rather that heating the sample has changed the structure of the NO surface species.

In addition to recording the infrared spectra of NO adsorbed on the reduced and oxidized forms of Ru, we also made a mass spectral analysis of the gas-phase species present after excess NO (g) is added to the reduced and oxidized samples. For an oxidized Ru–silica sample, we observe only NO (g), whereas, for the reduced form, we find NO (g) and N_2O (g); no O_2 (g) or NO_2 (g) is detected. In the reduction of NO to N_2O, either O_2 or NO_2 must be formed; thus, the oxygen species formed in the reduction of NO is adsorbed on the surface of the reduced Ru–silica sample.

The results of these mass spectral analyses are helpful in our interpretation of the infrared spectra. In the infrared spectrum of NO adsorbed on the reduced form of Ru, we observe development of a high-frequency NO band at high NO surface coverage. Furthermore, we find an intensification of this high-frequency NO band when a reduced sample with full NO surface coverage is heated. A comparison of the frequency of this band (1860 cm^{-1}) and that of the band observed when NO is adsorbed on the oxidized form of Ru (1880 cm^{-1}) suggest that the band observed at 1860 cm^{-1} on the reduced Ru–silica sample is $\nu_{(NO)}$ for NO adsorbed on an oxygen perturbed Ru surface site. These sites are formed by the dissociation of NO during adsorption. It is reasonable to assume that, when a reduced sample with full NO surface coverage is heated, some of the adsorbed NO will dissociate further, and more oxygen-perturbed Ru surface sites will be formed. (On a highly oxidized Ru–silica sample, the NO band is observed at a higher frequency; this frequency shift is probably an electronic effect due to the presence of excess oxygen on the Ru surface.) The band at 1820 cm^{-1} could then be assigned to $\nu_{(NO)}$ for NO adsorbed on an unperturbed Ru surface site (similar assignments were made for CO adsorption on the reduced and oxidized forms of Ru); however, the presence of the low-frequency band at 1630 cm^{-1} and its apparent relationship with the band at 1820 cm^{-1} are unclear.

Since it is known that the bending vibration, ν_2, of H_2O absorbs in the 1625 cm^{-1} region *(10)*, it is necessary to determine if the band at 1630 cm^{-1} is due to the bending vibration of H_2O adsorbed on the silica support. If the band at 1630 cm^{-1} is due to adsorbed H_2O, we would not observe an isotope shift of this band with ^{15}NO; therefore, we recorded the spectrum obtained when ^{15}NO was adsorbed on a reduced 6% Ru–silica sample. When ^{15}NO is adsorbed on a reduced Ru–silica sample, we observe bands at 1835, 1790, and 1605 cm^{-1}. Thus, the species adsorbing at 1630 cm^{-1} with ^{14}NO does contain a N atom, and this band cannot be assigned to ν_2 for adsorbed H_2O.

To gain a better understanding of the relationship of the various NO bands, we studied the effect of the addition of O_2 on a reduced Ru–silica sample with full and partial NO surface coverage. When 10 Torr of O_2 is added to a 6% Ru–silica sample with full NO surface coverage [excess NO (g) was previously removed by a 15-min evacuation, O_2 (g) was not evacuated], we observe no change in the infrared spectrum, even after exposure to excess O_2 for 2 h. (As noted previously, the Ru–silica samples cannot be heated in O_2; therefore, the stability of adsorbed NO to O_2 at elevated temperatures cannot

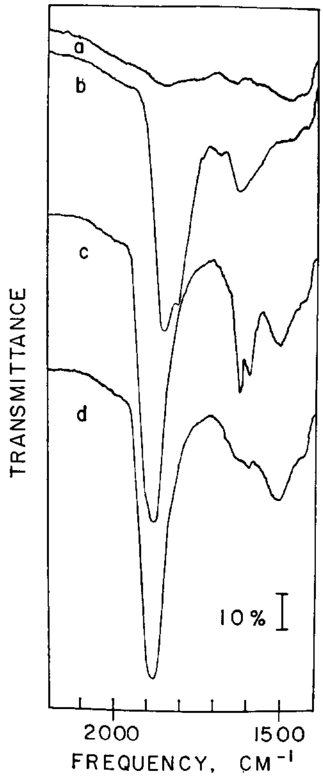

Fig. 4. Infrared spectra illustrating the changes in the adsorbed species following the oxidation of NO (g) to NO_2 (g) on a reduced 6% Ru–silica sample with full NO surface coverage: (a) background, (b) full NO surface coverage with excess NO (g) in cell, (c) 10 Torr of O_2 added, (d) cell evacuated 5 min.

be determined.) If excess NO (g) is not evacuated prior to the addition of O_2, NO (g) is oxidized to NO_2 (g), and we observe changes in the spectrum of the adsorbed species, as shown in Fig. 4. After the oxidation of NO (g) to NO_2 (g), we observe a strong band at 1870 cm^{-1} and a broad band at 1510 cm^{-1} (Fig. 4c). In related studies we find that the intensity of the band at 1510 cm^{-1} increases as the concentration of NO_2 (g) in the cell increases (*11*). This suggests that the band at 1510 cm^{-1} is due to the anti-symmetric stretching vibration, $\nu_{(asy)}$, of an adsorbed NO_2 surface; however, the formation of a surface nitrate cannot be eliminated from these data. In this spectrum, the presence of NO_2 (g) is confirmed by the appearance of the doublet at 1625 and 1597 cm^{-1}; these bands are the P- and R- branches of the anti-symmetric stretch, ν_3, of NO_2 (g). These bands are removed after a 5-min evacuation at 25°C, as shown in Fig. 4c, d; all other bands are stable to room-temperature evacuation.

We also studied the effect of the addition of O_2 to a sample with partial NO surface coverage. These results are shown in Fig. 5. After the first addition of NO, bands at 1810 and 1630 cm^{-1} are observed. When O_2 is added to this sample, we observe development of a high-frequency band at 1850 cm^{-1} (Fig. 5b, c). After evacuation of excess O_2 (g) from the cell, a trace amount of NO (g) was added, and we observed a strong band at 1870 cm^{-1}

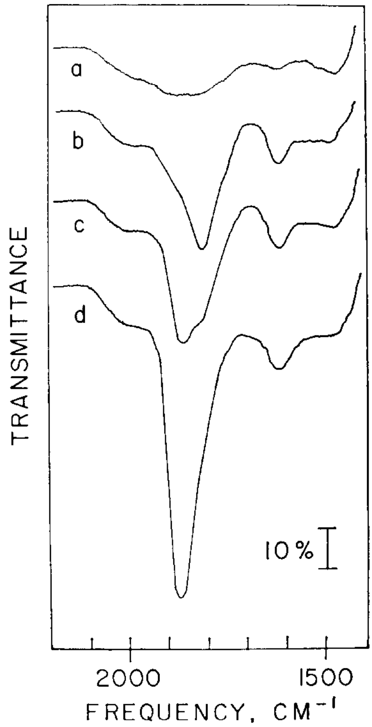

Fig. 5. Infrared spectra illustrating the effect of the addition of O_2 to a reduced 6% Ru–silica sample with partial NO surface coverage: (a) background, (b) first exposure to NO, (c) exposed to 5 Torr of O_2 and cell evacuated 15 min, (d) excess NO (g) added.

(Fig. 5d). The frequency and band shape of this band at 1870 cm^{-1} are similar to those observed when NO is adsorbed on the oxidized form of Ru. Thus, the appearance of the band in the 1870 cm^{-1} region is related to the presence of oxygen atoms on the Ru surface.

We have established that an oxidizing environment shifts the frequency of the NO bands to a higher wave number. We also wanted to determine the effect of a reducing gas on the infrared spectrum of adsorbed NO; therefore, we studied the effect of the addition of H_2 to a reduced Ru–silica sample with full NO surface coverage. These spectra are shown in Fig. 6. In these spectra, the ^{15}NO isotope was used; the significance of the isotope shifts has been discussed previously. When a reduced 6% Ru–silica sample is exposed to excess ^{15}NO (g), bands at 1835, 1790, and 1605 cm^{-1} are observed (Fig. 6b). After evacuation of excess ^{15}NO (g), the sample is exposed to 10 Torr of H_2 for 36 h at 25°C, and we observe no change in the infrared spectrum. When this sample is heated to 125°C for 1 h, we observe a broad band of medium intensity at 1800 cm^{-1} and a weak band at 1605 cm^{-1}. The relative intensities of these two bands at 1800 and 1605 cm^{-1} decrease sharply after the sample is heated in H_2 at 125°C for 1 h; thus, some of the adsorbed NO surface species have either reacted at 125°C in the presence of excess H_2 (g) or are displaced from the surface by the addition of H_2 (g) at 125°C. As noted previously, we found that NO adsorbed on the oxidized form of supported Ru was stable to 10 Torr of H_2 (g) up to temperatures of 200°C. Thus, NO adsorbed on a well-reduced Ru–silica sample is not as stable to H_2 (g) as NO adsorbed on an oxidized Ru–silica sample.

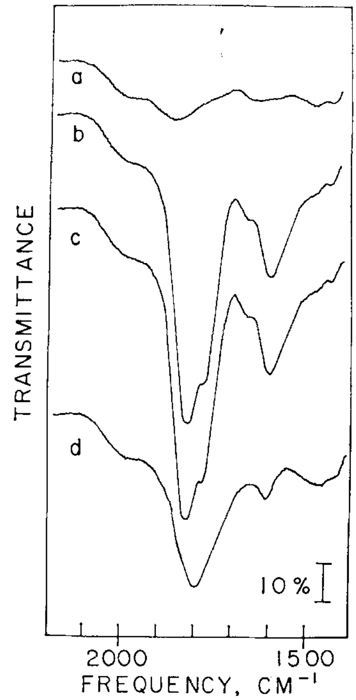

Fig. 6. Infrared spectra illustrating the effect of H_2 on a reduced 6% Ru–silica sample with full ^{15}NO surface coverage: (a) background, (b) full ^{15}NO surface coverage and evacuated 15 min, (c) 10 Torr of H_2 added, exposure time = 36 h, (d) heated to 125°C for 1 h.

In these spectra, the bands at 1820 and 1630 cm^{-1} appear to be related to a single adsorbed species, i.e., we find that the intensities of both bands increase or decrease at the same time. NO is known to exist as a dimer, N_2O_2, when NO is matrix-isolated at low temperatures; thus, we should consider if the bands at 1820 and 1630 cm^{-1} are due to the adsorption of an N_2O_2 dimer. The frequencies of the bands assigned to the matrix-isolated N_2O_2 dimer (*cis* form) were reported at 1862 and 1768 cm^{-1} by Fateley *et al.* (*14*); the weak band at 1862 cm^{-1} is assigned to the symmetric stretch, whereas the strong band at 1768 cm^{-1} is assigned to the antisymmetric stretch. Recently, Kugler *et al.* (*12*, *13*) have suggested that NO is adsorbed as an N_2O_2 dimer on silica-supported chromia. In their infrared study of the adsorption of NO on chromia, these authors observe a weak band at 1875 cm^{-1} and a strong band at 1745 cm^{-1}. From a detailed analysis of the ^{15}NO isotope shifts of these two bands, they concluded that the weak band at 1875 cm^{-1} is the symmetric stretch of the *cis* form of the N_2O_2 dimer, and the strong band at 1745 cm^{-1} is the anti-symmetric stretch of the N_2O_2 dimer. The frequencies and relative intensities of the two bands we observe for NO adsorbed on a reduced Ru–silica sample are different than those reported for the *cis* form of the N_2O_2 dimer, i.e., we observe a strong band at 1820 cm^{-1} and a weak band at 1630 cm^{-1}. Furthermore, the ^{15}NO isotope shifts of these two bands are different than those reported for the N_2O_2 dimer. Thus, the bands at 1820 and 1630 cm^{-1} are not due to the adsorption of the N_2O_2 dimer.

A survey of the literature of NO stretching vibrations in transition metal coordination compounds reveals that NO bands in the 1600 cm^{-1} region have been assigned to $\nu_{(NO)}$ for an anionic nitrosyl ligand, NO^-, whereas bands in the 1800 cm^{-1} region have been assigned to $\nu_{(NO)}$ for a cationic nitrosyl ligand, NO^+. This frequency shift is due to the transfer or acceptance of an electron into the π^* anti-bonding orbital of the NO ligand. If the NO ligand donates the π^* anti-bonding electron into an empty *d* orbital in the metal atom, the NO bond strength is increased, and $\nu_{(NO)}$ is observed at a higher wave number. The extent of this frequency shift is determined by the electron deficiency of the metal atom. If an electron is transferred from the metal atom into the π^* anti-bonding orbital of NO, the NO bond strength is decreased, and $\nu_{(NO)}$ is observed at a lower wave number.

It is known that Ru forms stable complexes with both NO^+ and NO^- ligands (*15*); furthermore, a dinitrosyl Ru complex, $[RuCl(NO)_2(P(C_6H_5)_3)]PF_6$, in which a single Ru atom is coordinated to both an NO^+ and an NO^- ligand has been prepared (*16*). In the infrared spectrum of this compound, the band at 1845 cm^{-1} was assigned to $\nu_{(NO)}$ for the NO^+ ligand, whereas the band at 1687 cm^{-1} was assigned to $\nu_{(NO)}$ for the NO^- ligand. The presence of the linear NO^+ ligand and the bent NO^- ligand in this compound was confirmed by an X-ray diffraction study.

From a consideration of these data, we conclude that the band at 1820 cm^{-1} is $\nu_{(NO)}$ for NO^+ adsorbed on the Ru surface, $Ru^{\delta-}$–$NO^{\delta+}$, whereas the band at 1630 cm^{-1} is $\nu_{(NO)}$ for NO^- adsorbed on a Ru surface site, $Ru^{\delta+}$–$NO^{\delta-}$. These two bands appear related to each other because the two oppositely charged NO surface species are weakly coupled, i.e., the adsorption of a charged NO^+ group on a Ru surface site, $Ru^{\delta-}$–$NO^{\delta+}$, can activate an adjacent site for the adsorption of an oppositely charged NO group, $Ru^{\delta+}$–$NO^{\delta-}$. In a previous infrared study of the interaction of CO and NO adsorbed on the Ru–silica surface, we found that the presence of a charged NCO^- group on a Ru surface site can activate an adjacent Ru site for the adsorption of CO_2 (*17*). Normally, CO_2 is not adsorbed on a Ru–silica sample at 25°C.

The two low-frequency NO bands at 1820 and 1630 cm^{-1} are assigned to $\nu_{(NO)}$ for $Ru^{\delta-}$–$NO^{\delta+}$ and $Ru^{\delta+}$–$NO^{\delta-}$, respectively. We also observe a high-frequency NO band at 1860 cm^{-1} when NO is adsorbed on a reduced Ru–silica sample; for NO adsorbed on an oxidized Ru–silica sample, a strong sharp band at 1880 cm^{-1} is observed. Previously, we tentatively assigned this band to $\nu_{(NO)}$ for NO adsorbed on a Ru surface site perturbed by a nearby oxygen atom. Our experimental results confirm this assignment. When a reduced sample with NO surface coverage is exposed to an oxidizing environment, the intensities of the two low-frequency NO bands at 1820 and 1630 cm^{-1} decrease, and a strong band in the 1870 cm^{-1} region is observed. The higher frequency of $\nu_{(NO)}$ for NO adsorbed on an oxygen-perturbed Ru surface site is consistent with previous considerations of NO bonding. The presence of oxygen atoms on the Ru surface would decrease the electron density of a Ru atom. Thus, the π^* anti-bonding electron of NO would be transferred more completely to the Ru atom. This would result in a stronger NO band and a shift of $\nu_{(NO)}$ to a higher wave number.

We find that repeated use of the same sample pellet changes the contour of the NO bands. When NO is adsorbed on a 6% Ru–silica sample reduced only once, we observe strong bands at 1860 and 1820 cm^{-1} and a band of medium intensity at 1630 cm^{-1}. For NO adsorbed on a 6% Ru–silica sample subjected to repeated adsorption, oxidation, and reduction sequences, we find that the doublet at 1860 and 1820 cm^{-1} is less intense and not as sharp and well-defined as that observed on a sample reduced only once; furthermore, only a weak broad band in the 1630 cm^{-1} region is observed. This suggests that repeated use of the same sample pellet for NO adsorption experiments has a sintering effect on the Ru surface; therefore, less intense infrared bands are observed.

This infrared study has provided valuable insight into the nature of NO adsorbed on the reduced and oxidized forms of supported Ru. When NO is adsorbed on a well-reduced 6% Ru–silica sample, we find that N_2O (g) is formed, and the oxygen species formed in this reduction is adsorbed on the Ru–silica surface. Three bands are observed in the infrared spectrum: a band at 1630 cm^{-1} assigned to $\nu_{(NO)}$ for $Ru^{\delta+}$–$NO^{\delta-}$, a band at 1820 cm^{-1} assigned to $\nu_{(NO)}$ for $Ru^{\delta-}$–$NO^{\delta+}$, and a band at 1860 cm^{-1} assigned to $\nu_{(NO)}$ for NO adsorbed on a Ru surface site perturbed by a nearby oxygen atom. When a reduced sample with full NO surface coverage is heated, we observe an intensification of the high-frequency NO band at 1860 cm^{-1} and note a decrease in the intensities of the bands at 1820 and 1630 cm^{-1}. However, if a Ru–silica sample with full NO surface coverage is heated in a reducing atmosphere, i.e., H_2, the frequencies of the NO bands are shifted to a lower wave number, and these adsorbed NO surface species are more reactive. For NO adsorbed on an oxidized 6% Ru–silica sample, we observe only one strong band at 1880 cm^{-1}, and this band is assigned to $\nu_{(NO)}$ for NO adsorbed on an oxygen-perturbed Ru surface site. In contrast to the reduced form of supported Ru, we find that NO is strongly adsorbed on an oxidized Ru–silica sample. This adsorbed NO is stable to evacuation up to temperatures of 325°C and is also stable to excess H_2 (g) up to temperatures of 200°C. This difference in the stability of NO adsorbed on the reduced and oxidized forms of supported Ru may account for the different activities that have been reported for these two forms of Ru catalyst.

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