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Infrared Study of Nitric Oxide Adsorbed on Silica-Supported Chromia

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The infrared spectrum of NO adsorbed on a 1.28% Cr sample supported on silica has bands at 1875, 1800, and 1745 cm^{-1}. The 1875 and 1745 cm^{-1} bands behave as if they arise from one discrete species. These two bands behave as a pair when the chromia concentration is varied or when the adsorption temperature is lowered to −78°C. On the basis of the position and intensity of the two infrared bands, the surface species producing the spectrum is predicted to be an N_2O_2 dimer. The 1800 cm^{-1} infrared band behaves differently from the other two bands and is attributed to monomeric NO.

INTRODUCTION

Nitric oxide has been used in surface investigations for many years. Because of its unique electronic properties and ease of detection it has been used to probe the surface of many catalysts. Much of this work appears in an excellent review (*1*).

Recently, there has been concern about the toxic qualities of nitric oxide in air and catalysts have been developed to reduce nitric oxide to nitrogen. These catalysts fall into two general classes. One class of catalysts, most often metal oxides, produces some nitrous oxide which appears to be an intermediate in the reduction to nitrogen (*2*). The other class of catalysts, most often metals, produces some ammonia which can be decomposed by high temperatures to nitrogen and hydrogen.

Chromia is selected in this study as an example of a nitric oxide reduction catalyst which involves the production of nitrous oxide. In an effort to understand the selectivity of chromia toward nitrous oxide formation, the adsorption of nitric oxide on chromia has been investigated by infrared spectroscopy. The chromia is supported on silica to stabilize the surface and to provide adequate infrared transmission.

This report is written in two parts. The first part involves the separation of infrared bands and their assignment to reasonable surface structures. The second part involves the elucidation of the structure and nature of the surface species by isotopic substitution.

EXPERIMENTAL

The chromia sample used in this study was prepared by impregnation of Cab-*o*-sil (Cabot Corporation, Boston) with a chromic nitrate solution. The sample is dried at room temperature prior to being ground and seived. Discs used in infrared studies were pressed under 1400 psi pressure into a stainless steel ring 2 cm in diameter. The average weight of these discs is 0.1 g.

In the standard activation procedure the

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[1] This study was initiated before the sudden death of Professor Richard J. Kokes. Any imperfections in this report are the responsibility of the other authors. We are saddened by the loss of a good friend and invaluable colleague.

sample is degassed as the temperature is raised from room temperature to 350°C. Then carbon monoxide is circulated over the sample at 350°C for 1 h with liquid nitrogen traps in the circulation loop to remove condensibles. After reduction, the sample is evacuated and the temperature raised to 400°C for 1 h, after which the sample is cooled.

The techniques and cells used in infrared experiments have been described previously (*3,4*). For spectra run at −78°C, the cell is cooled with a dry ice, trichloroethylene bath. About 5–10 Torr of helium is added to the cell to aid thermal conduction. A thermocouple in the infrared cell in contact with the edge of the disc is used to confirm the temperature. Heating by the infrared beam may occur inside the disc, however, so temperatures recorded should be viewed as approximate.

All tank gases used were purified by standard techniques. Carbon monoxide and nitric oxide were condensed and a center cut of the liquid was stored for use. Helium was purified by passage through an activated charcoal trap at −195°C. Nitric oxide, 98% ^{15}N, obtained from Merck, Sharp and Dohme was used as received. The isotopic purity was confirmed by infrared spectroscopy.

RESULTS

Nitric oxide adsorbs strongly on reduced samples of chromia supported on silica. When nitric oxide is adsorbed on a 10.8% Cr on silica sample, the infrared spectra show two bands, one strong band at 1745 cm^{-1} and one moderate band at 1875 cm^{-1} (Fig. 1). As nitric oxide is added to the sample in small doses, both bands grow. Since the band of moderate intensity is at the same position in the spectra as a band of the silica support, it is necessary to determine that this band is, in fact, due to nitric oxide and is not just an artifact due to changes in the support. In order to show that both bands are due to nitric oxide, ^{15}NO is used in place of ^{14}NO (Fig. 1).

As would be expected for two bands due to nitric oxide, substitution of ^{15}NO for ^{14}NO produced a shift in the position of both bands. The band of moderate intensity for ^{15}NO is no longer centered on a silica band but has moved to a position of lower frequency. The stronger band also shifts to lower frequency. Use of isotopic substitution shows that both bands in the

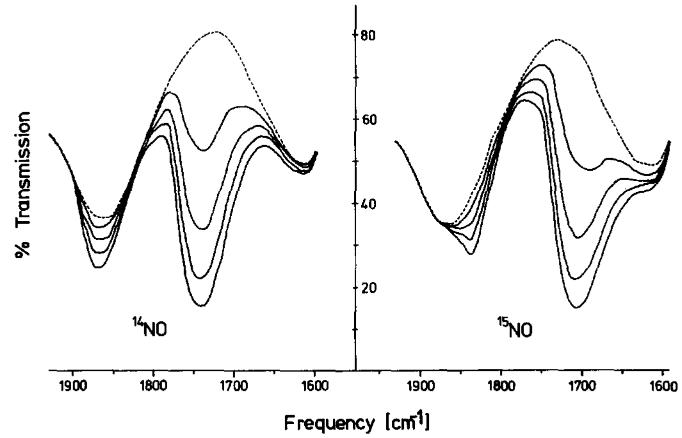


FIG. 1. Spectra of adsorbed ^{14}NO and ^{15}NO on 10.8% Cr sample. (----) shows chromia disc alone. NO is added in doses of ~0.06 cm^3 each.

TABLE 1
INTENSITY RATIO FOR 1875 AND 1745 cm^{-1} IR BANDS ON CHROMIA SAMPLES

	10.8% Cr sample		1.28% Cr sample		0.34% Cr sample
Number of doses	$\frac{I_{1875}}{I_{1745}}$	Surface coverage θ	$\frac{I_{1875}}{I_{1745}}$	Surface coverage θ	$\frac{I_{1875}}{I_{1745}}$
1	0.11	0.07	0.15	0.30	0.17
2	0.11	0.14	0.17	0.62	0.17
3	0.12	0.21	0.20	0.79	0.19
4	0.13	0.27	0.22	0.85	–

spectra are due to nitric oxide. Adsorption has little or no effect on the spectrum of the silica support.

The spectra in Fig. 1 have been plotted as absorbance in Fig. 2. Each spectrum involves approximately the same amount of nitric oxide, 0.219 cm^3 (STP) of ^{14}NO and 0.214 cm^3 (STP) of ^{15}NO, divided into four nearly equal doses. The two spectra show that when plotted as absorbance, the intensities of the ^{14}NO and ^{15}NO bands are nearly identical. These results seem reasonable, but are not obvious in Fig. 1 where the spectra are shown in percent transmission.

The spectra of Fig. 2 show that although the two nitric oxide bands grow at differing rates, the ratio of the intensities of the two bands remains nearly constant. This condition should be expected if both bands are due to the same adsorbed species. Careful integration of the two infrared bands shows that, indeed, the intensity ratio remains nearly constant. These ratios are included as part of Table 1. The difference in intensity of the two bands reflects the different extinction coefficients for the two normal modes of vibration involved.

In an effort to check the hypothesis that both infrared bands are due to the same adsorbed species, other supported chromia samples were prepared. 1.28% Cr and 0.34% Cr samples were made by the same procedure as was used in preparation of the 10.8% Cr sample. Figure 3 shows the spectra of nitric oxide adsorbed on these lower concentration samples. The same two bands at 1875 and 1745 cm^{-1} appear again on the lower concentration samples. In addition an infrared band is apparent between these two bands at 1800 cm^{-1}.

As nitric oxide is added in small doses

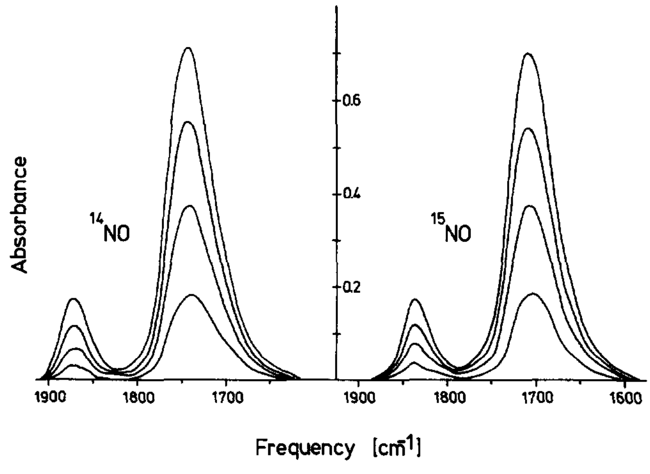


FIG. 2. Spectra of adsorbed ^{14}NO and ^{15}NO on 10.8% Cr sample.

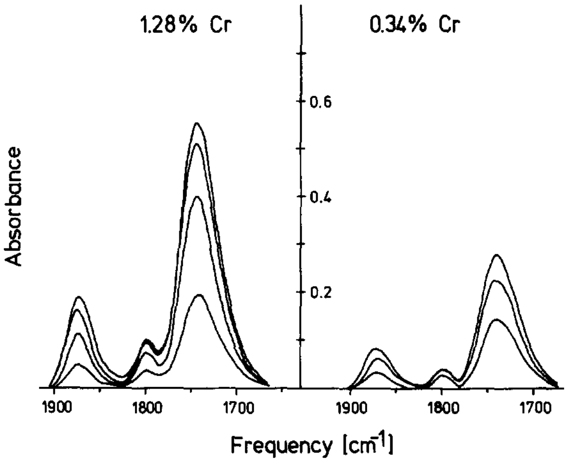


FIG. 3. Spectra of adsorbed NO on 1.28% Cr and 0.34% Cr samples. NO is added in doses of ~0.05 cm^3 to 1.28% Cr sample and ~0.03 cm^3 to 0.34% Cr sample.

to each of the low chromia concentration samples, the infrared bands increase in intensity. However, after several doses the 1800 cm^{-1} band appears to reach maximum intensity and any growth with additional dosage seems to be due to broadening of the 1745 cm^{-1} band. In the case of the 0.34% sample, there is no intensity change in the 1800 cm^{-1} band when a third dose of nitric oxide is added. After the 1800 cm^{-1} band reaches constant intensity, the bands at 1875 and 1745 cm^{-1} continue to grow. However, the 1875 and 1745 cm^{-1} bands soon reach maximum intensity also.

The ratio of the intensity of the 1875 cm^{-1} band to the intensity of the 1745 cm^{-1} band appears to remain nearly constant for the low chromia concentration samples. Careful integration of the infrared bands involved shows that the intensity ratio remains nearly constant for the 0.34% sample, but the ratio increases with each dose on the 1.28% sample. The data are given in Table 1. The intensity ratios are also higher for the 1.28% Cr and 0.34% Cr samples than the ratios observed on the 10.8% Cr sample.

The 1.28% Cr and 0.34% Cr samples were investigated with near saturation surface coverage. The 10.8% Cr sample was investigated with less than one third of the surface covered with nitric oxide. The capacity for nitric oxide on the 10.8% Cr sample was determined by separate isotherms. The capacity for nitric oxide on the 1.28% sample is estimated from Fig. 4 using the intensity of the 1745 cm^{-1} infrared band. Table 1 shows the fraction of the surface covered when the intensity ratio is determined. There is direct correlation between the intensity ratio and the surface coverage. Intermolecular interactions are most likely responsible for the small changes in intensity ratio. If both infrared bands are due to the same discrete species, the ratio of the two bands should remain constant in the absence of intermolecular interactions. With intermolecular interactions, small distortions of the adsorbed species should cause the intensity ratio to vary. This is likely to occur at high surface coverage.

Infrared spectra of the 1.28% Cr sample were taken with the surface saturated with nitric oxide. The sample was permitted to equilibrate with 30 Torr of nitric oxide for 30 min before the spectrum was recorded. The spectra are shown in Fig. 4 both as percent transmission and absorbance. The pressure in the cell was reduced after each spectrum was recorded. Reducing the ni-

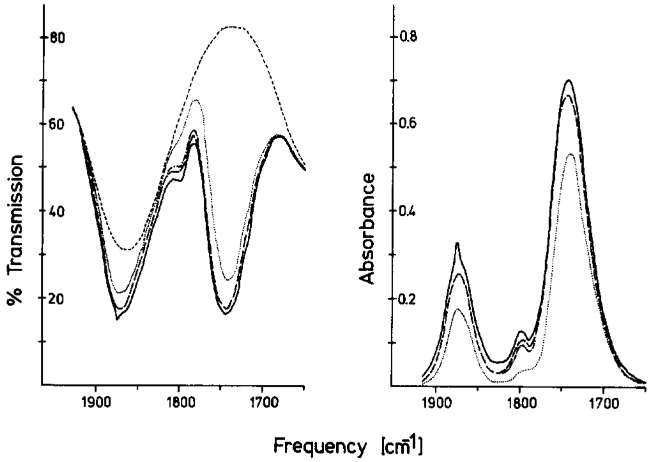


FIG. 4. Spectra of NO adsorbed on 1.28% Cr sample. (—) 30 Torr of NO in cell; (— —) 0.2 Torr of NO in cell; (-·-·-) change after 2 h evacuation; (·····) change after 12 h evacuation.

tric oxide pressure in the cell from 30 to 0.2 Torr has little effect on the infrared spectra except to remove the gas phase contribution. The Q-branch of the gas phase nitric oxide spectrum is most obvious at 1876 cm^{-1} and disappears when the pressure is reduced. The 1875 and 1745 cm^{-1} bands show broadening at the higher nitric oxide pressure, and this broadening disappears at the lower pressures. The changes on the wings of the 1745 cm^{-1} band make it appear that there is a change in the 1800 cm^{-1} band; however, the integrated intensity of the 1800 cm^{-1} band seems to remain nearly constant when the nitric oxide pressure is lowered from 30 to 0.2 Torr.

After the cell was evacuated for 2 h, the pressure in the vacuum system was measured at less than 1×10^{-6} Torr. The infrared spectrum shows little change as the pressure is reduced from 0.2 Torr. There is no change in the intensity of the 1875 and 1745 cm^{-1} bands. There is a small change in the intensity of the 1800 cm^{-1} band. Evacuation for an additional 12 h causes a decrease in the intensity of all three infrared bands. The 1800 cm^{-1} band almost disappears while the bands at 1875 and 1745 cm^{-1} have been reduced in intensity.

Addition and removal of nitric oxide from the 1.28% Cr sample show that the 1800 cm^{-1} band is caused by a separate adsorbed species. The 1800 cm^{-1} band seems to reach maximum intensity first when nitric oxide is added to the sample, and upon extended evacuation, the 1800 cm^{-1} band disappears while the other two bands persist. The infrared bands at 1875 and 1745 cm^{-1} behave as a pair both when nitric oxide is added to the sample and when the sample is evacuated.

When nitric oxide is added to the 10.8% Cr sample at −78°C (Fig. 5), the same two bands appear in the infrared spectra as were observed at room temperature. However, the intensity of the 1875 cm^{-1} band is greater than the intensity usually observed at room temperature. Careful integration of the spectra shows a higher intensity ratio at −78°C. These data are presented in Table 2. When the sample is

TABLE 2
INTENSITY RATIO OF IR BANDS

	10.8% Cr sample		1.28% Cr sample	
Number of doses	I_{1840}/I_{1710}	Sample temp. (°C)	I_{1875}/I_{1745}	Sample temp. (°C)
1	0.13	−78	0.15	−78
2	0.14	−78	0.17	−78
3	0.15	−78	0.20	−78
3	0.11	25	0.23	25

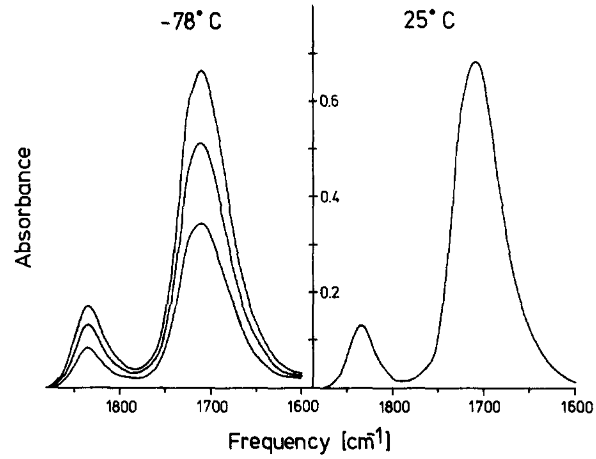


FIG. 5. Spectra of ^{15}NO adsorbed on 10.8% Cr sample at −78°C. NO is added in doses of ~0.04 cm^3 each. After adsorption at −78°C, sample warmed to 25°C.

permitted to warm from −78°C to room temperature, the spectrum changes. On warming, the intensity of the 1875 cm^{-1} band is reduced and the intensity ratio returns to a normal level. When the sample is cooled from room temperature back to −78°C, there is no change observed in the spectrum.

If the 1875 cm^{-1} band were reflecting a desorption on warming from −78°C to room temperature, the desorbed material should be readsorbed immediately and the 1745 cm^{-1} band should increase in intensity. This is not the case. It seems more reasonable that at −78°C the nitric oxide is not well distributed over the chromia surface. Since the gas has its inlet on one side of the chromia disc, on adsorption the side closest to the inlet should have heavy coverage, while the side away from the inlet should have little adsorption. Intermolecular interactions in the heavy coverage areas should cause the intensity of the 1875 cm^{-1} band to increase. When the sample is permitted to warm to room temperature, the nitric oxide on the chromia surface is redistributed and the intensity of the 1875 cm^{-1} band returns to normal values.

When nitric oxide is adsorbed on a

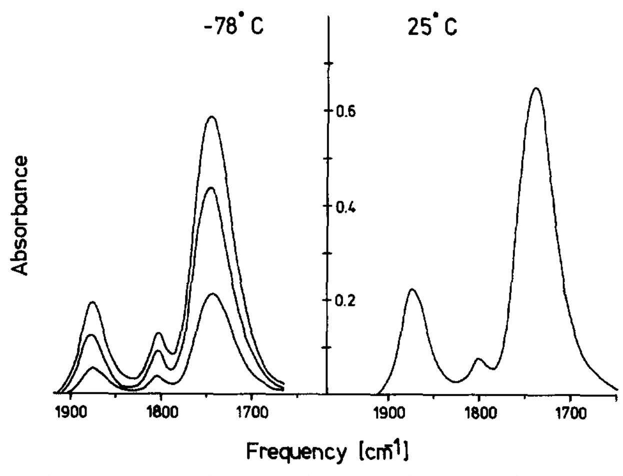


FIG. 6. Spectra of NO adsorbed on 1.28% Cr sample at −78°C. NO is added in doses of ~0.05 cm^3 each. After adsorption at −78°C, sample warmed to 25°C.

1.28% Cr sample at −78°C (Fig. 6), the pair of infrared bands at 1875 and 1745 cm^{-1} exhibits behavior like that observed at room temperature. With each dose of nitric oxide the intensity ratio is similar to that observed at room temperature (Table 2). This agreement should be expected because the sample is close to a saturated condition whether the sample is at room temperature or −78°C. However, the 1800 cm^{-1} band is more intense when nitric oxide is adsorbed at −78°C. When the sample is permitted to warm from −78°C to room temperature, the intensity of the 1800 cm^{-1} band decreases accompanied by an increase in the intensities of the 1875 and 1745 cm^{-1} bands. The changes in the spectra of the 1.28% Cr sample on warming from −78°C to room temperature reflect a redistribution of nitric oxide on the surface. The decrease in the 1800 cm^{-1} band accompanied by the increase in the 1875 and 1745 cm^{-1} bands emphasizes that the 1800 cm^{-1} band is caused by a single discrete species. The species responsible for the 1800 cm^{-1} band apparently reacts to form the species responsible for the 1875 and 1745 cm^{-1} bands.

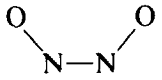
DISCUSSION

Infrared studies of nitric oxide adsorption on chromium containing solids have recently been made in other laboratories. Cerruti and Guglielminotti (*5*) use a sample of α-chromia prepared by the thermal decomposition of ammonium dichromate. These authors report the observation of three bands at 1875, 1800 and 1745 cm^{-1} (vs) which they assign to nitric oxide adsorbed on the Cr^{3+} cation. Naccache and Ben Taarit (*6*) used samples of chromium exchanged zeolites and observe infrared absorption bands at 1900 and 1780–1760 cm^{-1}. These authors assign the 1900 cm^{-1} band and part of the 1780–1760 cm^{-1} band to a complex which contains both bridging and terminal nitrosyl groups. The remainder of the 1780–1760 cm^{-1} band is assigned to terminal nitrosyl groups. Both nitric oxide species were assigned to adsorption on Cr^{2+} cations. Eley and co-workers (*7*) used chromium samples which are used commercially for polyethylene production. These samples consist of CrO_3 supported on silica. Eley and co-workers found nitric oxide adsorbed on their sample to produce infrared bands at 1740, ~ 1800, and ~ 1860 cm^{-1}. The absorption at 1800 cm^{-1} is assigned to a nitric oxide monomer adsorbed on a Cr^{4+} cation. The infrared bands at 1860 and 1740 cm^{-1} were each assigned to nitric oxide monomers, adsorbed on both Cr^{3+} and Cr^{5+} cations.

The infrared spectra of nitric oxide adsorbed on various chromium containing samples are very similar in appearance. In each case the spectrum has a very strong band in the vicinity of 1740 cm^{-1}. At about 130 cm^{-1} higher frequency than the very strong band is a band of lower intensity. Some samples show an infrared band at 1800 cm^{-1} while others do not. Although the spectra of all three investigators are very similar, the interpretations of these spectra differ greatly.

The results of this investigation show spectra of nitric oxide adsorbed on a chromium containing sample. There are three infrared bands observed in positions similar to those previously reported. However, the infrared bands at 1875 and 1745 cm^{-1} observed in this study have been found to behave as one discrete adsorbed species. Substitution of ^{15}NO for ^{14}NO has shown that both infrared bands shift their positions in a similar manner. Hence, both bands are probably caused by N–O stretching modes, coupled in some manner.

A reasonable model for the surface species responsible for the 1875 and 1745 cm^{-1} bands is an N_2O_2 dimer. The *cis*-form of the dimer has two infrared active normal modes of vibration which involve



N-O stretches. Such dimers have been isolated for infrared studies at low temperatures, usually in an inert matrix. Fateley, Bent, and Crawford (*8*) found that a *cis*-N_2O_2 dimer has infrared absorption bands at 1862 and 1768 cm^{-1} when condensed in an argon matrix. The 1862 cm^{-1} band is assigned to a symmetric stretching mode and the 1768 cm^{-1} band is assigned to an asymmetric stretching mode. The intensities of the two bands are very similar to those observed for nitric oxide adsorbed on chromia. The 1862 cm^{-1} symmetric stretch is of low intensity and the 1768 cm^{-1} asymmetric stretch is of higher intensity. The work of Fateley and coworkers also shows that the intensity ratio between the symmetric mode and the asymmetric mode increases as interaction between the dimers is increased. The intensity ratio is low when the concentration of nitric oxide is low in the matrix and the N_2O_2 dimers are isolated. However, the condensation of pure nitric oxide produces a dimer where the ratio between the bands is similar to what is reported on a saturated chromia surface (*6,7*). Guillory and Hunter (*9*) have investigated the N_2O_2 dimer at low temperatures in a nitrogen matrix. The spectrum of a *cis*-dimer with absorption bands at 1867 and 1768 cm^{-1} shows an intensity ratio similar to what is observed on a chromia surface. From their data we estimate the intensity ratio of the symmetric mode to the asymmetric mode to be 1/5. This is very similar to ratios reported in Tables 1 and 2.

The model of a *cis*-N_2O_2 dimer on the chromia surface explains the data well. It agrees with spectra of the dimer observed at low temperatures with respect to intensity and general position of the bands. The separation of the symmetric and asymmetric stretching modes in the matrix are ~ 90 cm^{-1} while those on the chromia surface are ~ 130 cm^{-1}. This variation reflects a difference in coupling between the N-O groups in two different environments. The changes in intensity of the symmetric mode as the surface is saturated are consistent with both the model and observations of N_2O_2 at low temperatures. If surface saturation causes the distance between the oxygen atoms of the dimer to be reduced, the resultant dipole of the symmetric stretching mode will increase. Such changes in geometry will be reflected by an increase in the intensity of the symmetric mode of vibration.

Other models for a surface species responsible for the 1875 and 1745 cm^{-1} infrared bands do not fit the data as well. King and Bisnette (*10*) have prepared an inorganic chromium complex containing both bridging and terminal nitrosyl groups. The bridging group is assigned to a 1505 cm^{-1} infrared band and the terminal group to a 1672 cm^{-1} infrared band. Both infrared bands are strong. Other studies (*11,12*) with terminal and bridging nitrosyl groups show that the lower frequency is due to the bridging group and the intensity ratio reflects the number of bridging and terminal groups present. If nitric oxide were on the chromia surface as both bridging and terminal nitrosyl groups, there would have to be many more bridging groups than terminal groups present. If the concentration of the chromia in the sample were changed, the dispersion should change, and the appearance of the infrared spectrum should change also. When the chromium concentration in the sample is changed from 10.8% Cr to 0.34% Cr, the appearance of the 1875 and 1745 cm^{-1} bands remains constant. Terminal and bridging nitrosyl groups on a surface should also have different binding energies. If both types of binding took place on the chromia surface, the pair of infrared bands would not be expected to grow at the same rate when nitric oxide is added. Nor would the two infrared bands be expected to decrease at the same rate when the nitric oxide is removed. Hence, a model with bridging and terminal nitrosyl groups does not fit the data.

A surface nitric oxide species with a pair of nitrosyl ligands might also be considered as a reasonable source of the 1875 and 1745 cm^{-1} bands in the infrared spectrum. Inorganic dinitrosyl complexes have been investigated by several authors. Piper and Wilkinson (*13*) have observed chromium dinitrosyl complexes with infrared bands at ~ 1820 and ~ 1710 cm^{-1}. Cotton and Johnson (*14*) have investigated dinitrosyl tungsten and dinitrosyl molybdenum complexes with infrared bands at similar positions. These investigators find that the nitrosyl infrared bands are of nearly equal intensity in all of the dinitrosyl complexes studied. The similarity in intensity indicates that the nitrosyl groups are separated by an angle of ~90° (*15*). In order for a pair of nitrosyl groups on a chromia surface to agree with the intensity ratio observed, the separation angle would have to be ~ 140°. Hence, a dinitrosyl model does not seem adequate for a chromia surface species.

The experimental results indicate that the infrared band at 1800 cm^{-1} is due to a discrete species. If the infrared bands at 1875 and 1745 cm^{-1} are assigned to a nitric oxide dimer, the 1800 cm^{-1} band may be due to a nitric oxide monomer. This assignment is supported by the data shown in Fig. 6. When the nitric oxide adsorbed at −78°C on the 1.28% Cr sample warms to room temperature, the 1800 cm^{-1} band loses intensity while the 1875 cm^{-1} and 1745 cm^{-1} bands gain intensity. If more dimer is being formed on warming to room temperature, the species that disappears is most likely a monomer.

It is interesting that the 1800 cm^{-1} band is very apparent on the 1.28% Cr and 0.34% Cr samples, but does not appear on the 10.8% Cr sample. Presumably, the adsorption site that is related to the 1800 cm^{-1} nitrosyl band is in low concentration on the 10.8% Cr sample. Eley and coworkers (*7*) report an infrared band at 1800 cm^{-1} which can be removed under some reduction conditions. The same surface species may well be observed in this study. When the 1.28% sample is oxidized at 400°C for 2 h prior to reduction, the intensity of the 1800 cm^{-1} infrared band increases. However, the intensity of the band is not observed to vary when the reduction time is increased from 1 to 10 h. This variation of intensity of the 1800 cm^{-1} band with changes in chromia concentration and activation conditions seems to reflect the presence of a particular adsorption site.

The pair of infrared bands at 1875 and 1745 cm^{-1} show consistent appearance on all of the chromia samples investigated. This consistency which persists as nitric oxide is added or removed from the chromia samples indicates that both infrared bands are caused by the same adsorbed species, most probably an N_2O_2 dimer.

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