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Identification of Adsorbed Species of Nitric Oxide on Silica-Supported Chromia

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Infrared data have been interpreted as indicating an N_2O_2 dimer and an NO monomer as the surface species for nitric oxide adsorbed on silica-supported chromia. These assignments are reinforced by isotopic substitution experiments. The experimentally observed bands attributed to $^{15}N_2O_2$ and $^{14}N^{15}NO_2$ agree with those calculated from the assumption that the observed bands for ^{14}N species arise from the *cis* dimer of N_2O_2. Slow isotopic mixing in the dimer species is observed at −78°C and rapid mixing at 25°C.

INTRODUCTION

The results reported in part I of this work led to the suggestion that nitric oxide adsorbs on silica supported chromia as a *cis* N_2O_2 dimer. This surface species exhibits two infrared bands at 1875 and 1745 cm^{-1}. A third band at 1800 cm^{-1} is attributed to monomeric nitric oxide. These assignments may be tested by isotopic substitution experiments. The results of such experiments designed to elucidate the nature of the adsorbed species are reported here.

EXPERIMENTAL METHODS

The methods and material used in this study have been previously described.

RESULTS

A mixture of ^{14}NO and ^{15}NO should yield three dimers on the chromia surface: one dimer with two ^{14}N atoms, one dimer with two ^{15}N atoms and one dimer with one ^{14}N and one ^{15}N atom. If the infrared bands at 1875 and 1745 cm^{-1} observed in the ^{14}NO spectra are assigned to the $^{14}N_2O_2$ dimer, the frequencies of the other two dimers can be calculated. The methods outlined by Wilson, Decius, and Cross (*1*) are employed in the calculation of the frequencies presented in Table 1.

The spectrum of ^{15}NO adsorbed on the 1.28% Cr sample is shown in Fig. 1. The infrared bands are observed at 1840, 1767 and 1712 cm^{-1}. The bands observed at 1840 and 1712 cm^{-1} are in excellent agreement with the calculated positions of 1841 and 1711 cm^{-1} for the $^{15}N_2O_2$ dimer. From the results of ^{14}NO experiments, an ^{15}NO monomer is expected to have a band at 1768 cm^{-1}. This result is in excellent agreement with the infrared band observed at 1767 cm^{-1}.

The addition of a mixture of ^{14}NO and ^{15}NO to the silica supported chromia sample should produce a mixture of three dimers. If a premixed 1 : 1 dose of nitric oxides were added to the sample, all three dimers should be produced in a statistical distribution. Figure 2 shows the spectrum of a 1 : 1 mixture added to the 1.28% Cr sample. The maxima in the spectra are observed near 1855 and 1725 cm^{-1}. Both infrared bands appear to be made up of several components, as if a distribution of isotopic species were responsible for each band. Figure 3 shows a construction of two spectra. The first spectrum is the sum of ^{14}NO and ^{15}NO spectra. If no mixed

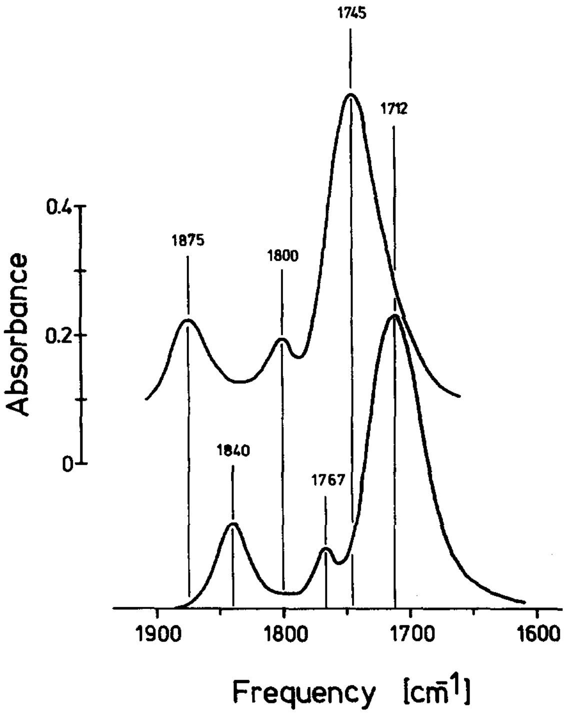

FIG. 1. Spectra of adsorbed ^{14}NO and ^{15}NO on 1.28% Cr sample. 0.15 cc of NO used for each spectrum.

dimer were formed, the spectrum observed when a 1 : 1 mixture is added to the chromia sample should be the sum of the component spectra. This spectrum shows a plateau in the 1860 cm^{-1} region, in contrast to the observed spectrum. The second construction in Fig. 3 is for a statistical distribution of isotope species. The bands for the $^{14}N^{15}NO_2$ dimer are placed at the calculated positions and are assumed to have intensities similar to those of the symmetric dimers. The construction for a statistical distribution of three dimers has maxima at 1860 and 1725 cm^{-1}. When the spectrum of Fig. 2 is compared to the two constructions of spectra in Fig. 3, the observed spectrum of the 1 : 1 mixture is found to be very similar to that predicted for a statistical distribution of dimers.

The sequential addition of ^{14}NO and ^{15}NO to the 1.28% Cr sample at room temperature is shown in Fig. 4. The ^{15}NO

TABLE 1
CALCULATED FREQUENCIES FOR N_2O_2 DIMERS

	Symmetric mode (cm^{-1})	Asymmetric mode (cm^{-1})
O-^{14}N-^{14}N-O	1875	1745
O-^{15}N-^{15}N-O	1841	1711
O-^{14}N-^{15}N-O	1859	1726

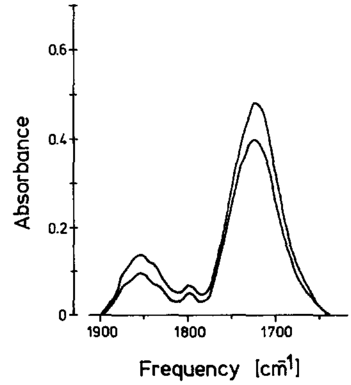

FIG. 2. Spectra of 1 : 1 mixture of ^{14}NO : ^{15}NO adsorbed on 1.28% Cr. 0.14 and 0.20 cc of the mixture used for the two spectra.

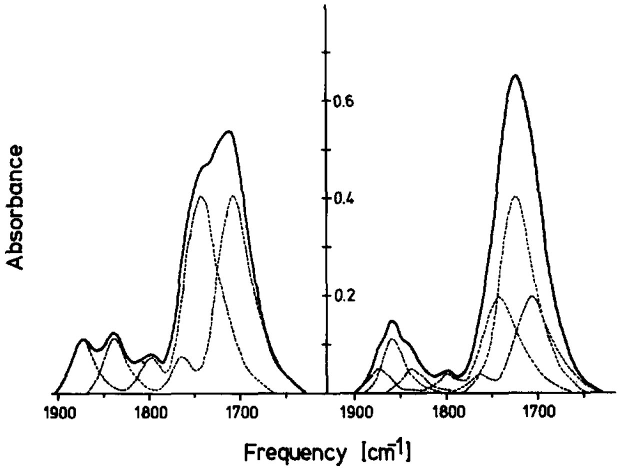

FIG. 3. Construction of possible spectra for 1 : 1 mixture of ^{14}NO : ^{15}NO. Left spectrum is sum of ^{14}NO and ^{15}NO spectra. Right spectrum is for statistical distribution of N_2O_2 dimers.

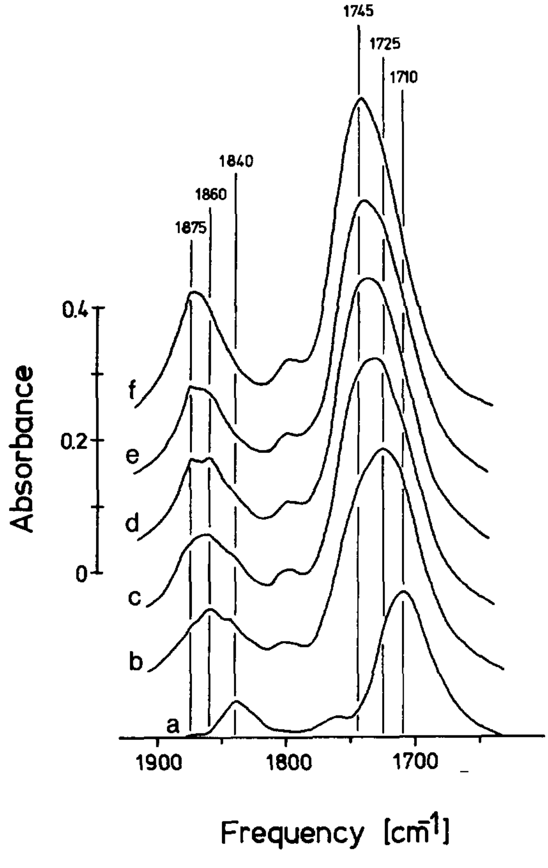

FIG. 4. Spectra for sequential addition of ^{15}NO and ^{14}NO to 1.28% Cr sample. (a) 0.07 cc of ^{15}NO added to sample. ^{14}NO is then added to this sample so that the ratio is 1 : 1 in (b), 2 : 1 in (c), 3 : 1 in (d), 4 : 1 in (e), and 20 : 1 in (f).

is added to the chromia sample first. Addition of ^{14}NO to the ^{15}NO so that the ratio is 1 : 1 produces a spectrum similar to that in Fig. 2 where a premixed dose of nitric oxides was added to the sample. The spectra are run immediately after each dose of ^{14}NO and show no change with time. Addition of a second dose of ^{14}NO so that the ratio of the isotopic species is 2 : 1 produces a spectrum similar to that expected for a statistical distribution of dimers. Addition of more ^{14}NO so that the ratio changes from 2 : 1 to 3 : 1 to 4 : 1 to 20 : 1 is reflected by changes in the spectra. Although the intensities of the infrared bands show little change after initial additions of ^{14}NO, the maxima of the two bands shift until at a 20 : 1 ratio the bands are similar to those observed for ^{14}NO alone.

The sequential addition of ^{14}NO and ^{15}NO to the 10.8% Cr sample at −78°C is shown in Fig. 5. The ^{15}NO is first added to the chromia sample precooled to −78°C. A dose of ^{14}NO is added to the ^{15}NO at −78°C so that their ratio is 1 : 1. The spectrum produced by the 1 : 1 mixture differs from the spectrum obtained at room temperature. In fact, the spectrum obtained at −78°C is very similar to the construction in Fig. 3 for no formation of mixed dimer. The difference between the spectrum of the 1 : 1 mixture and the spectrum of ^{15}NO alone is shown as a broken line. The difference between the two spectra is very similar to the spectrum of ^{14}NO alone in-

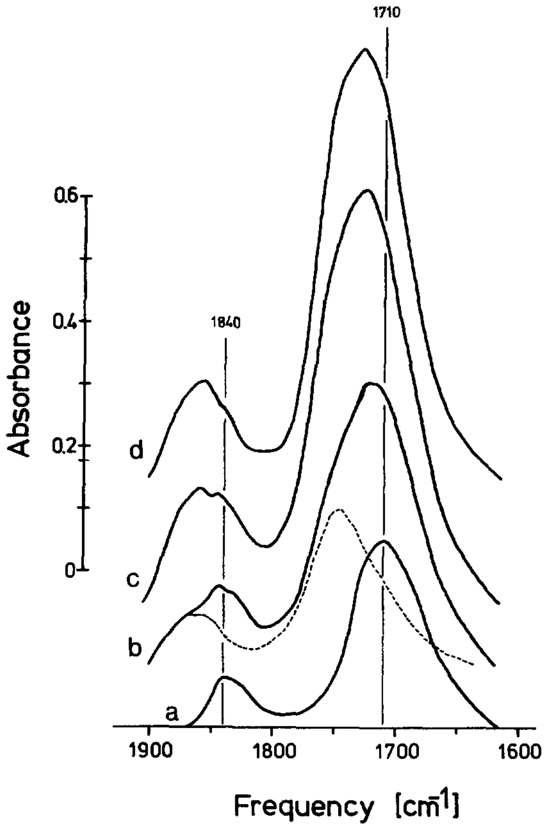

FIG. 5. Spectra for sequential addition of ^{15}NO and ^{14}NO to 10.8% Cr sample at −78°C. (a) 0.10 cc of ^{15}NO added to sample at −78°C. ^{14}NO is then added to this sample at −78°C so that the ratio is 1 : 1 in (b) and 2 : 1 in (c). (----) The difference between (a) and (b). (d) Spectrum of the 2 : 1 mixture after warming to 25°C.

dicating that little of the mixed dimer has been formed. Addition of a second dose of ^{14}NO to the chromia sample at −78°C produces a 2:1 mixture on the surface. The spectrum of the 2:1 mixture is also similar to that expected for little formation of the mixed dimer. The chromia sample with the 2:1 mixture of ^{14}NO and ^{15}NO is then warmed from −78 to 25°C. The intensity of the higher frequency bands decreases as was previously observed for the 10.8% Cr sample. In addition to a change in the intensity of the spectrum, there is a change in the position of the bands. The spectrum of the 2:1 mixture warmed from −78 to 25°C has the same appearance as the spectrum of the 2:1 mixture in Fig. 4 which was run at room temperature.

The addition of mixtures of ^{14}NO and ^{15}NO to the 1.28% Cr sample has little effect on the band assigned to a nitric oxide monomer. The 1800 cm^{-1} band assigned to ^{14}NO appears in Figs. 2 and 4. The band at 1767 cm^{-1} assigned to ^{15}NO is obscured whenever ^{14}NO is added to the sample. However, it is quite apparent in both Figs. 2 and 4 that no infrared band appears at a position intermediate to what is observed for the addition of ^{14}NO or ^{15}NO individually.

DISCUSSION

The results of this work suggest that nitric oxide adsorbs on supported chromia as an N_2O_2 dimer. Such a surface species is a four atom molecule with six normal modes of vibration. If the methods outlined by Wilson, Decius, and Cross are followed (*1*), a 6 × 6 secular determinant may be written whose solutions are the six possible frequencies of vibration. However, in the case of the N_2O_2 dimer, the determinant may be simplified since the N–O bonds are strong while other bonds are relatively weak. Hence, the normal modes of vibration which involve N–O stretching should have high frequencies while the other normal modes of vibration should have low frequencies. Smith, Keller and Johnston (*2*) have found this to be the case for condensed N_2O_2 where there are two frequencies in the 1700–1900 cm^{-1} range and the other four frequencies are below 500 cm^{-1}. By separating high and low frequencies, the secular determinant is diagonalized. The portion involving high frequencies may be solved separately in 2 × 2 size. The solutions are frequencies of normal modes which involve N–O stretch. This determinant is:

$$\begin{vmatrix} k_1(\mu_1+\mu_2)-4\pi^2\nu^2 & k_2(\mu_1+\mu_2) \\ k_2(\mu_3+\mu_4) & k_1(\mu_3+\mu_4)-4\pi^2\nu^2 \end{vmatrix}=0,$$

where k_1 is the force constant for the N–O stretch and k_2 is the coupling constant between the two N–O groups; μ_i is the reciprocal mass of the i-th atom and ν is the frequency of vibration.

If the infrared bands at 1875 and 1745 cm^{-1} observed in the ^{14}NO spectrum are assigned to the $^{14}N_2O_2$ dimer, the values of the constants are calculated to be $k_1 = 14.41 \times 10^5$ dyn/cm and $k_2 = 1.05 \times 10^5$ dyn/cm. These values of the constants are used to calculate the frequencies in Table 1 for the other two dimers.

The infrared bands observed when nitric oxide is adsorbed on a chromium containing solid have been reported by several investigators (*3–6*). Each investigator interprets these infrared bands differently, but many interpretations follow the arguments proposed by Terenin and Roev (*7*) where each band is assigned to a nitric oxide monomer bound to the surface in some fashion. The present work shows that two of the infrared bands produced by nitric oxide on silica-supported chromia are not due to monomers on the surface.

The model of an N_2O_2 dimer on the surface is able to predict the frequencies observed when isotopic mixtures are added to the chromia sample. In order for a 1 : 1 mixture of ^{14}NO and ^{15}NO to produce infrared bands at 1860 and 1725 cm^{-1}, the adsorbed species must contain two N-O groups which are strongly coupled. A dimer on the surface should show a statistical distribution of isotopes when a premixed sample of nitric oxides is adsorbed. This is what happens. The observed spectrum is in agreement with the spectrum predicted for a statistical distribution of isotopes.

If all of the infrared bands observed were due to monomeric forms of adsorbed nitric oxide, the addition of a mixture of nitric oxides should produce the sum of the individual spectra. This appears to happen for the 1800 cm^{-1} band of ^{14}NO but clearly does not occur for the 1875 and 1745 cm^{-1} bands of ^{14}NO.

The use of isotopes substantiates the previous assignment of the infrared bands produced by the adsorption of nitric oxide on silica-supported chromia. The high and low frequency bands are most likely produced by an N_2O_2 dimer. The position and intensity of the two bands are consistent with observations at low temperature for the isolated dimer (*8*). The intensity ratio of the two bands changes with intermolecular interaction in the same fashion as those of the low temperature dimer (*8*). The position of the infrared bands can be predicted in the same fashion as those of the low temperature dimer (*9*). The statistical distribution of isotopes which occurs is consistent with the model of the dimer. The accumulation of evidence in favor of a dimer on the surface strongly suggests that this species is responsible for two of the infrared bands observed. The infrared band at the intermediate position in the spectrum was previously assigned to a nitric oxide monomer. This assignment has been substantiated by the constancy of the band when nitric oxide mixtures were added to the chromia sample.

The use of isotopically labeled compounds can provide information about the nature of the adsorbed species. Experiments by Twigg (*10*) and by Burwell *et al.* (*11*) have shown that adsorbed hydrogen species often have great mobility on a catalyst surface. A similar condition seems to be true with nitric oxide adsorbed on chromia.

The sequential addition of ^{14}NO and ^{15}NO to the chromia sample at room temperature produces spectra comparable to those expected for a statistical distribution of dimers. This implies that the adsorbed nitric oxide species have great mobility and that the dimer exchanges rapidly. As the ratio of isotopes increases from 1 : 1 to 20 : 1 the spectra of the adsorbed dimers reflect the isotope ratio immediately.

The sequential addition of ^{14}NO and ^{15}NO to the chromia sample at −78°C produces the spectrum of the symmetric dimers alone. It appears that rapid mixing and dimer exchange on the surface does not occur at this temperature. This result is consistent with indications in the preceding paper that the dimer has little mobility at −78°C. When the sample with nitric oxide on the surface is warmed to room temperature, the spectrum shows that the nitric oxide species have reached a statistical distribution on the surface. Hence, the exchange reaction becomes rapid by the time the sample reaches room temperature.

The exchange of N–O groups in the N_2O_2 dimer provides additional information about the surface species. The N–N bond in the dimer must be weak in order for exchange to occur rapidly at room temperature. In addition, the nitric oxide surface species must be very mobile. The fact that the N_2O_2 dimer persists during evacuation at room temperature suggests that the mobility does not involve the gas phase, but must involve a stable surface species, most likely the dimer.

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