

The Nature of NO Adsorption on Chromia

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The interaction of nitric oxide with chromia catalysts has been investigated. Infrared spectra are reported which suggest that NO adsorbs in two forms: a *cis*-N₂O₂ dimer and a chelating NO₂ group. Two forms of surface sites have been postulated for these adsorbed species and have been confirmed by selective poisoning experiments with oxygen. Infrared observations are consistent with NO adsorption at chromium cations with either one or two coordination positions. This model has been supported by quantitative adsorption measurements.

INTRODUCTION

The adsorption of nitric oxide on supported chromia samples has recently been studied by infrared spectroscopy (1-4). Results reported from this laboratory have suggested that nitric oxide adsorbs both as a monomer and as a *cis*-N₂O₂ dimer on silica-supported chromia samples. The adsorption of nitric oxide has now been investigated on samples of unsupported chromia by infrared spectroscopy. The use of unsupported chromia samples extends the low frequency cutoff of the infrared spectrum from 1350 to 750 cm⁻¹. Infrared bands observed in this low frequency range together with bands which appear above 1350 cm⁻¹ provide information on the nature of both the adsorbed nitrogen oxide species and the chromia surface.

EXPERIMENTAL METHODS

The chromia sample used in this study was prepared by the thermal decomposition of ammonium dichromate (5,6). Three grams of this salt were heated in the side-arm of a 3 liter bulb which was evacuated by a mechanical pump with a liquid nitrogen trap in the line. The salt decomposed at 225-250°C. The product was a green, bulky powder that was washed and filtered to remove any unreacted salt. The

freshly prepared sample had a surface area of 140 m²/g, as measured by the BET method using argon. The discs used in the infrared studies were pressed under 2500 psi pressure into a stainless steel ring 2 cm in diameter. The average weight of these discs was 30 mg.

In the standard activation procedure for infrared studies, the sample was reduced with carbon monoxide at 450°C and then was evacuated at 450°C. Each step lasted for a minimum period of 1 hr. Longer periods of reduction or evacuation had little effect on the infrared measurements. This high temperature was not necessary to produce an active sample, since 350°C had been adequate for prior chromia/silica work, but instead was needed to remove a chemisorbed form of CO₂ which produced strong infrared bands at 1550 and 1350 cm⁻¹.

The sample used for quantitative adsorption measurements had an initial weight of 0.536 g. This sample was activated at 450°C in the same fashion as the discs used for infrared studies, and its surface area was determined to be 77 m²/g. After the sample had been activated several times, the surface area was remeasured and was found to have decreased to 59 m²/g. Because of the loss in surface area of this sample, it was subsequently

activated at 400°C, and the area then remained constant over the period when adsorption measurements were made.

The techniques and cells used for the infrared experiments have been discussed previously (7,8). For spectra run at -117°C, the cell was cooled with an ethyl bromide slush. Helium (5-10 Torr) was added to the cell to aid thermal conduction. Since heating of the sample disc by the infrared beam may occur, temperatures recorded should be viewed as approximate.

All tank gases used in this study were purified by standard techniques. Carbon monoxide, oxygen and argon 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 was condensed and purified by trap-to-trap distillation until the solid collected was completely white. Nitric oxide, 98% ^{15}N , obtained from Merck, Sharp and Dohme was used as received. The isotopic purity was confirmed by infrared spectroscopy.

RESULTS

The adsorption of nitric oxide on a reduced chromia sample at room temperature produced two prominent pairs of infrared bands: one pair at 1865 and 1735 cm^{-1} , and the other at 1285 and 1180 cm^{-1} . This spectrum is shown in Fig. 1. The higher frequency pair of bands has been observed on silica-supported chromia samples and is assigned to a *cis*- N_2O_2 dimer (1,2). The lower frequency pair of bands has also been reported by Cerruti and Guglielminotti (9), who attribute these bands to a chelating NO_2 group.

The assignment of infrared bands to a particular surface species may be tested by isotopic substitution experiments. The adsorption of ^{15}NO on the same chromia sample produced a pair of bands at 1830 and 1700 cm^{-1} , as well as a pair of bands at 1270 and 1155 cm^{-1} . This spectrum is

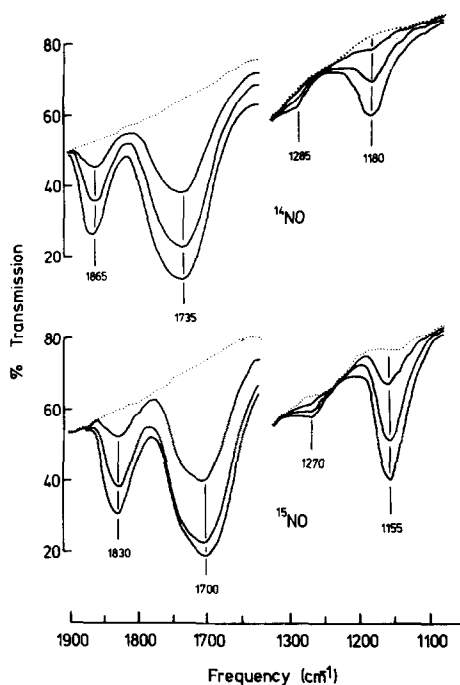


FIG. 1. Infrared spectra of ^{14}NO and ^{15}NO adsorbed on chromia. NO was added in increments of 0.12 cm^3 STP.

also shown in Fig. 1. The substitution of ^{15}N for ^{14}N caused each of the bands in the higher frequency pair to shift by 35 cm^{-1} , while the bands in the lower frequency pair shifted by unequal amounts. The 1285 cm^{-1} band shifted by 15 cm^{-1} to 1270 cm^{-1} , while the 1180 cm^{-1} band shifted by 25 cm^{-1} to 1155 cm^{-1} .

If the higher frequency bands in the ^{14}NO spectrum are assigned to the $^{14}\text{N}_2\text{O}_2$ dimer, and the lower frequency bands are assigned to a chelating $^{14}\text{NO}_2$ group, the frequencies for the corresponding ^{15}NO spectrum can be calculated. The methods outlined by Wilson *et al.* (10) have been employed in calculating the frequencies presented in Table 1. The calculated frequencies in Table 1 are in excellent agreement with the observed frequencies in the ^{15}NO spectrum. This agreement suggests that the addition of ^{15}NO to the reduced chromia sample produces $^{15}\text{N}_2\text{O}_2$ and $^{15}\text{NO}_2$ on the chromia surface.

TABLE 1
CALCULATED FREQUENCIES FOR NO₂ AND N₂O₂

| | Sym- metric mode (cm ⁻¹) | Δ_s (cm ⁻¹) | Asym- metric mode (cm ⁻¹) | Δ_{as} (cm ⁻¹) |
|---------------------------------------|---|-----------------------------------|--|--------------------------------------|
| O- ¹⁴ N-O | 1285 ^a | — | 1180 ^a | — |
| O- ¹⁵ N-O | 1267 | 18 | 1156 | 24 |
| O- ¹⁴ N- ¹⁴ N-O | 1865 ^a | — | 1735 ^a | — |
| O- ¹⁵ N- ¹⁵ N-O | 1831 | 34 | 1703 | 32 |
| O- ¹⁴ N- ¹⁵ N-O | 1850 | 15 | 1717 | 18 |

^a Observed frequency.

The infrared spectra resulting from the sequential addition of ¹⁴NO and ¹⁵NO to the chromia sample at -117°C are shown in Fig. 2. The ¹⁵NO was added first to a sample which had been precooled to -117°C. This is shown in spectrum a. Infrared bands are observed at 1825 and 1695 cm⁻¹. The pair of bands at lower frequencies did not appear. A dose of ¹⁴NO was then added to the ¹⁵NO at -117°C so that the isotopic ratio would be 1:1 on the chromia surface. This is shown in spectrum c. Since the spectra are plotted as absorbance, the spectrum of ¹⁵NO alone may be subtracted from the spectrum of the 1:1 mixture to yield spec-

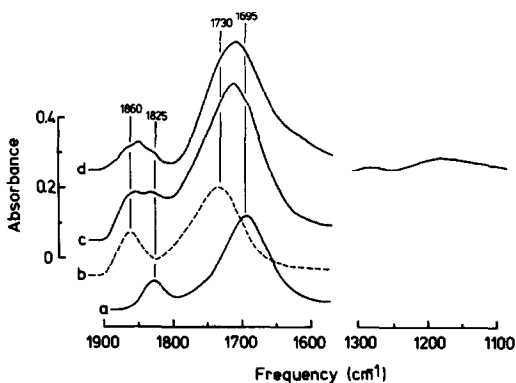


FIG. 2. Infrared spectra produced by the sequential addition of ¹⁵NO and ¹⁴NO to the chromia sample at -117°C. (a) 0.12 cm³ STP of ¹⁵NO was added to the sample at -117°C. ¹⁴NO was then added to this sample at -117°C so that the ratio was 1:1 in (c). (b) The difference between spectra (a) and (c). (d) Produced when the sample warmed to 25°C.

trum b. Spectrum b is the contribution produced by the dose of ¹⁴NO. The difference between the two spectra corresponds to the spectrum observed when ¹⁴NO alone was added to the chromia sample. This suggests that there was little mixing of the two doses of NO to form a ¹⁴N¹⁵NO₂ dimer at -117°C.

When the chromia sample with the 1:1 mixture of ¹⁴NO and ¹⁵NO was warmed from -117 to 25°C, the appearance of spectrum c changed, and spectrum d was produced. A band appeared at 1845 cm⁻¹, and the bands at 1860 and 1825 cm⁻¹ were of lower intensity. The shape of the band located at 1715 cm⁻¹ also changed slightly upon warming to room temperature. The positions of these new bands are in good agreement with the calculated frequencies for the ¹⁴N¹⁵NO₂ dimer given in Table 1. The changes in the spectrum upon warming to room temperature suggest that the doses of ¹⁴NO and ¹⁵NO mix to produce a statistical distribution of the three possible dimers. This conclusion is supported by the fact that spectrum d has been reproduced by the addition of a premixed dose of ¹⁴NO and ¹⁵NO in a 1:1 ratio to the chromia sample both at -117 and 25°C. These observations are consistent with previous results using silica-supported chromia samples.

When the nitric oxide added at -117°C was permitted to warm to room temperature, infrared bands appeared in the lower portion of the spectrum as shown in Fig. 2, spectrum d. This suggests that some of the nitric oxide reacted with oxygen in the chromia lattice to form the chelating NO₂ species.

The reaction of nitric oxide with oxygen on the chromia surface may be observed in the infrared spectra. The quantity of oxygen on the surface may be increased to facilitate this observation by adsorption of N₂O. Zecchina and co-workers (11) report that adsorption of N₂O on chromia is accompanied by some decomposition. This

decomposition leaves an oxygen atom with anionic character on the surface which produces an infrared band at 970 cm^{-1} , which is assigned to a chromium–oxygen stretching mode. The adsorbed N_2O may be removed afterwards by evacuation at room temperature. This procedure of adsorption and evacuation leaves the chromia surface with an increased oxygen content.

Figure 3 shows the results of nitric oxide interaction with oxygen on the chromia surface. Spectrum a was observed after 100 Torr of N_2O had been exposed to the chromia sample at room temperature for 1 hr and afterwards was removed by evacuation for 4 hr. A strong chromium–oxygen band was produced in the infrared spectrum at 970 cm^{-1} by N_2O decomposition. When the N_2O was removed by evacuation, the band at 970 cm^{-1} shifted to 985 cm^{-1} . This band is shown in spectrum a. Spectrum b resulted when 0.12 cm^3 STP of NO was added to the sample which had produced spectrum a. The intensity of the infrared band at 985 cm^{-1} decreased significantly. Concurrently, infrared bands appeared at 1285 and 1180 cm^{-1} with greater intensity than was observed without the N_2O pretreat-

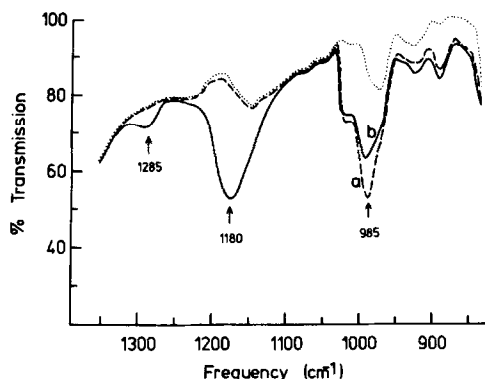


FIG. 3. Infrared spectra produced by the addition of NO to a chromia sample pretreated with N_2O . (a) Produced after 100 Torr of N_2O had been added and was removed afterwards by evacuation. (b) Observed when 0.12 cm^3 STP of NO was added to the sample after the N_2O pretreatment.

ment. The appearance of the strong NO_2 bands accompanied by the disappearance of the oxygen band strongly suggests that nitric oxide reacted with oxygen on the chromia surface to produce the chelating NO_2 species.

The appearance of two separate nitrogen oxide species on the chromia surface indicates that two different adsorption sites may exist. Figure 4 shows the results of an attempt to vary the populations of these adsorption sites. Spectrum a was observed when 0.12 cm^3 STP of NO was added to a freshly prepared chromia sample. Both nitrogen oxide species are shown to be present by this spectrum.

Spectrum b was observed when 0.12 cm^3 STP of NO was added to the chromia sample after the N_2O pretreatment, which produces additional oxygen atoms on the surface. The bands assigned to the N_2O_2 dimer have similar intensities in both spectra a and b; however, the intensities of the bands assigned to the NO_2 species have been greatly enhanced in spectrum b. When the number of surface oxygen atoms was increased by N_2O decomposition, the population of the NO_2 species formed by NO adsorption also increased.

Spectrum c was observed when 0.12

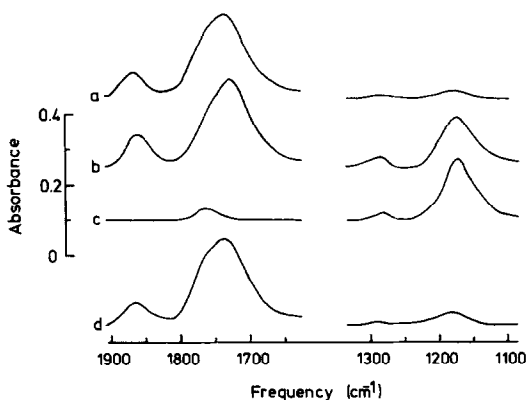


FIG. 4. Infrared spectra produced by the addition of 0.12 cm^3 STP of NO to chromia after various pretreatments: (a) NO added to reduced surface; (b) NO added after N_2O pretreatment; (c) NO added after O_2 pretreatment; (d) NO added to reduced surface.

cm³ STP of NO was added to the chromia sample after an oxygen pretreatment. Oxygen gas (10 Torr) was briefly exposed to a reduced chromia sample at room temperature. Excess oxygen was removed by evacuation for 1 hr. This procedure added pairs of oxygen atoms to the chromia surface. The strong infrared bands assigned to the N₂O₂ dimer did not appear after the oxygen treatment. A small band persisted at 1765 cm⁻¹ which could be responsible for the slight shoulder in spectra a, b, and d. This band could be produced by a small quantity of dimer in a slightly different environment or by a monomeric nitric oxide species. The infrared bands produced by the NO₂ species persisted and were relatively intense. Apparently, exposure to oxygen did not remove the adsorption sites responsible for NO₂ formation, but did block the positions where the dimer was adsorbed.

Spectrum d was observed when 0.12 cm³ STP of NO was added to the freshly reactivated chromia surface. This experiment was a repetition of the procedure used to produce spectrum a. The similarity of spectra a and d demonstrates that the effects of N₂O decomposition and oxygen adsorption have been eliminated by the procedure used to reactivate the sample.

The spectra in Fig. 4 show that the adsorption of oxygen gas on the chromia sample prior to NO adsorption prevented the formation of the N₂O₂ dimer. This result suggests that oxygen adsorbs on the same sites as the dimer. Quantitative measurement of the oxygen and nitric oxide adsorption can provide information on the distribution of adsorption sites.

Figure 5 shows isotherms for NO and O₂ adsorption on chromia at -78°C. Curve a shows the pressure dependence of NO adsorption on a reduced chromia sample. This sample was activated by a procedure similar to that used for the infrared experiments. After the determination of isotherm a, the sample was evacuated at -78°C for

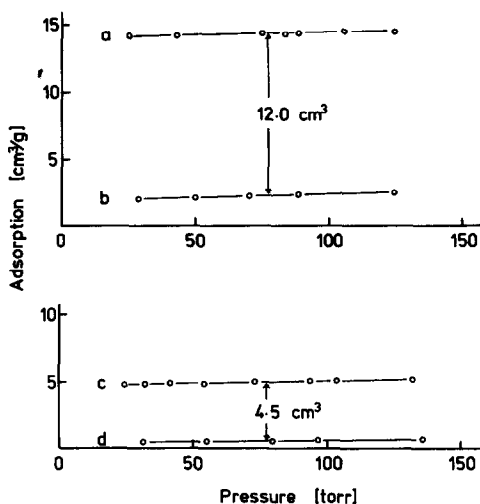


FIG. 5. NO (top) and O₂ (bottom) adsorption isotherms for chromia at -78°C: (a) NO adsorption on reduced surface; (b) NO adsorption after 2 hr evacuation at -78°C; (c) O₂ adsorption on reduced surface; (d) O₂ adsorption after 2 hr evacuation at -78°C.

2 hr, and then isotherm b was determined. Longer periods of evacuation had little effect on the magnitude of isotherm b. Curves a and b are parallel lines whose difference is the quantity of irreversible NO adsorption at -78°C. This irreversible adsorption may be taken to represent the quantity of N₂O₂ and NO₂ on the chromia surface.

Curve c is an isotherm for O₂ adsorption on chromia at -78°C. After the determination of isotherm c, the sample was evacuated for 2 hr at -78°C, and isotherm d was determined. The difference between isotherms c and d is the amount of irreversible O₂ adsorption at -78°C. This irreversible O₂ adsorption may be taken as a measure of the N₂O₂ formation by assuming that each O₂ molecule occupied a position that would have accommodated an N₂O₂ dimer. The 4.5 cm³ STP of O₂ irreversibly adsorbed would occupy the same surface adsorption sites as 9.0 cm³ STP of NO. The remaining 3.0 cm³ STP of NO irreversibly adsorbed may be attributed to an NO₂ species.

The decomposition of N_2O was employed to add oxygen atoms to the chromia surface. This molecule decomposed immediately upon contacting the surface at room temperature. The decomposition probably occurred only at specific positions on the surface since additional reaction did not occur after the initial exposure. The amount of N_2O decomposition on a reduced surface can be greatly reduced by lowering the temperature to $-78^\circ C$. Infrared measurements have shown that adsorbed N_2O is stable on the chromia surface at low temperatures (12).

Figure 6 shows adsorption isotherms for N_2O on the chromia sample. Curve a is an isotherm for N_2O adsorption on a reduced chromia surface at $-78^\circ C$. N_2O adsorbed slowly at this temperature, and long periods of time were required for the adsorption measurement. The data shown in isotherm a were recorded after N_2O had been exposed to the chromia sample for a minimum period of 8 hr. The last data points were taken after 24 hr exposure. The reproducibility of the data indicates that little additional adsorption occurs after an initial 8 hr exposure to N_2O . At the end of the 24 hr measurement period, 0.3 cm^3 STP of nitrogen was found in the gas phase. Apparently this was produced by some N_2O decomposition.

The chromia sample used to obtain isotherm a was permitted to warm to room

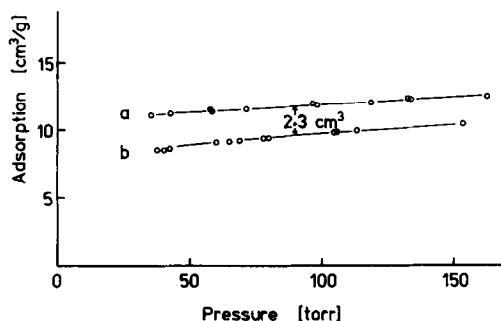


FIG. 6. N_2O adsorption isotherms for chromia at $-78^\circ C$: (a) N_2O adsorption on reduced surface; (b) N_2O adsorption after previous decomposition and evacuation at $25^\circ C$.

temperature for decomposition to occur. At room temperature, the sample was evacuated for 6 hr to remove adsorbed N_2O and afterwards was cooled to $-78^\circ C$ for measurement of isotherm b. Curve b shows N_2O adsorption on the chromia sample at $-78^\circ C$ after decomposition had occurred at room temperature. The difference between isotherms a and b is nearly constant over the pressure range investigated. This difference of 2.3 cm^3 STP should represent the quantity of N_2O that decomposed on the chromia surface at room temperature.

Figure 7 shows adsorption data for NO and O_2 after N_2O had been decomposed on the chromia surface. Isotherm a indicates the quantity of NO that adsorbed on a reduced chromia sample at $-78^\circ C$. This curve also appears in Fig. 5. Isotherm b shows the quantity of NO that adsorbed on the chromia surface at $-78^\circ C$ after the N_2O pretreatment. The difference between curves a and b is 2.5 cm^3 STP. This value closely corresponds to the 2.3 cm^3 STP of N_2O that decomposed on the sample. After isotherm b was measured, the

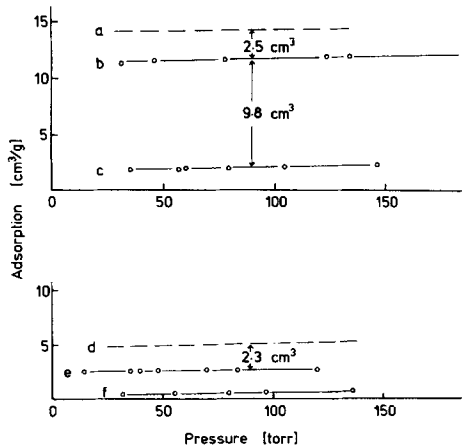


FIG. 7. NO (top) and O_2 (bottom) adsorption isotherms for chromia at $-78^\circ C$: (a) NO adsorption on reduced surface; (b) NO adsorption after N_2O pretreatment; (c) NO adsorption after 2 hr evacuation at $-78^\circ C$; (d) O_2 adsorption on reduced surface; (e) O_2 adsorption after N_2O pretreatment; (f) O_2 adsorption after 2 hr evacuation at $-78^\circ C$.

sample was evacuated for 2 hr at -78°C . Isotherm c was determined after evacuation. This quantity of reversible NO adsorption is very similar to the quantity of reversible NO adsorption reported for the reduced sample.

Isotherm d indicates the quantity of O_2 that adsorbed on the reduced chromia sample at -78°C . This curve also appears in Fig. 5. Isotherm e shows the quantity of O_2 that adsorbed on the chromia surface after the N_2O pretreatment. The difference between curves d and e is $2.3 \text{ cm}^3 \text{ STP}$. This is the same as the amount of N_2O that decomposed on the chromia surface. After measurement of isotherm e, the oxygen was evacuated for 2 hr at -78°C . Curve f shows the amount of O_2 that adsorbed at -78°C after the evacuation procedure.

The data in Fig. 7 indicate that the decrease in NO and O_2 adsorption after the N_2O pretreatment corresponds to the amount of N_2O that decomposed on the sample. The 1:1 relationship between the N_2O decomposition and the decrease in O_2 adsorption suggests that N_2O decomposed on a site that could have adsorbed O_2 . The decrease in NO adsorption after the N_2O pretreatment suggests that NO_2 might form at a position that could have accommodated the N_2O_2 dimer on a reduced surface.

Figure 8 shows the adsorption of NO on

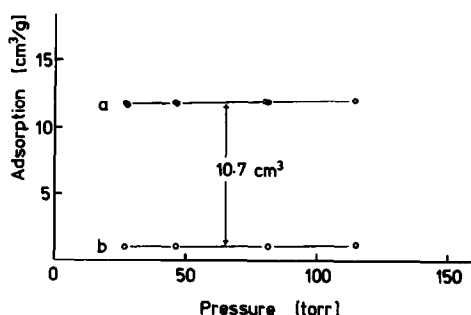


FIG. 8. NO adsorption isotherm for chromia at -78°C after O_2 pretreatment: (a) NO adsorption after O_2 pretreatment; (b) NO adsorption after 2 hr evacuation at -78°C .

the chromia surface after oxygen was adsorbed at -78°C and the reversible portion was removed by evacuation at the same temperature. Isotherm a is for NO that adsorbed on the chromia sample at -78°C after this oxygen pretreatment. Following the determination of curve a, the sample was evacuated for 2 hr at -78°C . Isotherm b was measured after the evacuation procedure. These two measurements show that $10.8 \text{ cm}^3 \text{ STP}$ of NO was irreversibly adsorbed on the sample that had previously adsorbed O_2 . Since infrared measurements in Fig. 4 have shown that the amount of N_2O_2 formation was drastically reduced by O_2 pretreatments, the NO on the surface must be primarily adsorbed as NO_2 . The large NO adsorption after the oxygen pretreatment demonstrates that oxygen atoms added to the chromia surface react with NO whether they were added in pairs by O_2 adsorption or individually by N_2O decomposition.

DISCUSSION

The results of this study suggest that nitric oxide adsorbs on reduced chromia surfaces in two forms: an N_2O_2 dimer and a chelating NO_2 group. Each of these species has a pair of infrared bands in the observed spectrum. The bands at 1865 and 1735 cm^{-1} are assigned to the N_2O_2 dimer. This assignment is supported by the similarity of the bands in both intensity and position to those of the dimer isolated in a low-temperature, inert gas matrix (13,14). This assignment is also supported by isotopic substitution experiments which show that this surface species has two equivalent NO groups.

The infrared bands observed at 1285 and 1180 cm^{-1} are assigned to an NO_2 chelate. This assignment has been made by Cerruti and Guglielminotti (9) by comparing the positions and intensities of these bands to those of the NO_2 species in a nickel coordination complex (15). When NO reacts with individual oxygen atoms

on the chromia surface, these bands grow. This also suggests that they may be produced by an NO_2 group. The band intensities for this particular species are unusual. The asymmetric mode of vibration appears to be at a lower frequency than the symmetric mode of vibration. This observation has only been confirmed for a chelating NO_2 group. The results of isotopic substitution experiments confirm that the lower frequency is the asymmetric mode of vibration. The similarity of the observed and calculated frequencies for NO_2 strongly supports the identification of this

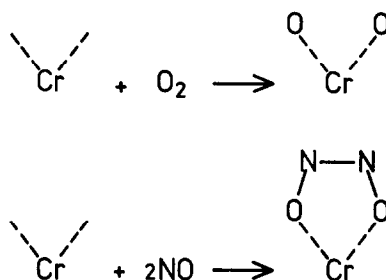
The calculation of frequencies for Table 1 employs the methods outlined by Wilson *et al.* (10). For each species the ^{14}NO spectrum has been used to calculate force constants for the molecule. A detailed description of the calculation for N_2O_2 has been given previously (2) and will not be repeated here. For N_2O_2 , the NO stretching force constant is 14.29×10^5 dyn/cm, and the coupling constant is 1.03×10^5 dyn/cm.

The frequencies calculated for the NO_2 species are based on the assumption that little coupling occurs between the stretching modes and the bending mode of the molecule. This assumption should be valid since the bending mode is at too low a frequency to be observed in the spectrum. The O-N-O bond angle was assumed to be 112° . This angle was reported for the same group in a nickel coordination complex (16). An error in the angle would affect the values calculated for the force constants but will do little to change the predicted frequencies. The values for the force constants used to calculate the NO_2 frequencies are 7.10×10^5 dyn/cm for the NO stretching force constant and 1.99×10^5 dyn/cm for the NO-NO coupling constant.

The formation of the N_2O_2 dimer and the NO_2 chelate on the chromia surface suggests that two different adsorption sites exist. This is confirmed by the addition of

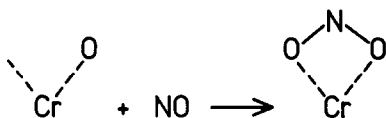
O_2 to the reduced chromia surface prior to NO adsorption. O_2 on the chromia surface prevents the formation of the N_2O_2 dimer but does not prevent the formation of the NO_2 species.

The adsorption of O_2 on the chromia surface must require a pair of coordination sites. Similarly, two adjacent coordination sites must be required to accommodate the N_2O_2 dimer. This suggests that these species may adsorb on a four-coordinate chromium cation. This adsorption may be represented as



The N_2O_2 dimer should fit into the chromia lattice. The closest oxygen-oxygen distance in α -chromia is 2.66 \AA (17), and the average oxygen-oxygen distance in solid N_2O_2 is 2.61 \AA (18).

The formation of the NO_2 chelate may occur on a five-coordinate chromium cation. This adsorption may be represented as

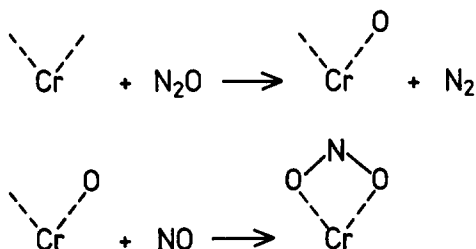


A crystal structure determination for an NO_2 chelate complex shows that the oxygen-oxygen distance is 2.1 \AA (16). This separation should also be compatible with the chromia lattice.

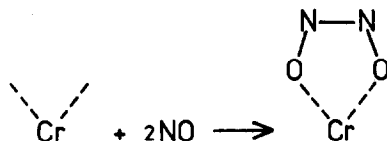
Quantitative adsorption measurements show that N_2O decomposes on some of the sites that adsorb O_2 . This would suggest that some of the four-coordinate chromium cations react with N_2O to become five-coordinate cations. This hy-

pothesis is supported by both infrared and quantitative measurement of NO adsorption after the N_2O decomposition.

A four-coordinate cation may decompose one N_2O molecule, then adsorb one NO molecule to form the NO_2 chelate as follows:



This would cause the population of NO_2 to be greater on the sample subjected to the N_2O pretreatment than on the reduced sample. Such an increase in NO_2 population has been observed by infrared spectroscopy. The same four-coordinate cation without N_2O pretreatment would adsorb two NO molecules to form the N_2O_2 dimer.



This would cause the NO adsorption to be greater on the reduced surface than on the surface pretreated with N_2O since two NO molecules would adsorb instead of one. The difference in NO adsorption between the two surfaces should correspond to the amount of N_2O decomposition. This has been observed by quantitative adsorption measurements.

The adsorption of oxygen on the chromia surface prevents the formation of the N_2O_2 dimer. However, the quantity of NO adsorption remains high after the O_2 pretreatment even though the N_2O_2 form is absent. In order for the NO adsorption to remain at a high level, the oxygen atoms added to the surface by O_2 adsorption

must react to form an NO_2 species. This may occur at a neighboring chromium cation.

Zecchina and co-workers (11) have proposed models for a completely dehydrated surface of α -chromia. Each coordination position on these surfaces is shared by two cations. If O_2 adsorbed at a four-coordinate cation, it would complete the coordination of that particular cation. However, this same oxygen molecule would make a neighboring cation five-coordinate and produce a site where the chelating NO_2 group can form.

The results of this study indicate that nitric oxide adsorbed on a chromia surface exists as either an N_2O_2 dimer or an NO_2 chelate. These two species form on different adsorption sites whose populations can be varied by the sample pretreatment. The systematic variation of the surface character by these pretreatment conditions has provided basic information to formulate a simple model for the surface adsorption sites.

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REFERENCES

1. Kugler, E. L., Kokes, R. J., and Gryder, J. W., *J. Catal.* **36**, 142 (1975).
2. Kugler, E. L., and Gryder, J. W., *J. Catal. J. Catal.* **36**, 152 (1975).
3. Eley, D. D., Rochester, C. H., and Scurrall, M. S., *J. Chem. Soc. Faraday I* **69**, 660 (1973).
4. Peri, J. B., *J. Phys. Chem.* **78**, 588 (1974).
5. Zecchina, A., Coluccia, S., Guglielminotti, E., and Ghiotti, G., *J. Phys. Chem.* **75**, 2774 (1971).
6. Harbard, E. H., and King, A., *J. Chem. Soc.* 955 (1938).
7. Dent, A. L., and Kokes, R. J., *J. Amer. Chem. Soc.* **92**, 6709 (1970).
8. Dixon, L. T., thesis, The Johns Hopkins Univ., Baltimore, MD, 1974.
9. Cerruti, L., and Guglielminotti, E., *Discuss. Faraday Soc.* **52**, 285 (1971).

10. Wilson, E. B., Jr., Decius, J. C., and Cross, P., "Molecular Vibrations." McGraw-Hill, New York, 1955.
11. Zecchina, A., Cerruti, L., and Borello, E., *J. Catal.* **25**, 55 (1972).
12. Kugler, E. L., and Gryder, J. W., *Proc. N. Amer. Meet. Catal. Soc. (Toronto) 1975*.
13. Fateley, W. G., Bent, H. A., and Crawford, B., Jr., *J. Chem. Phys.* **31**, 204 (1959).
14. Guillory, W. A., and Hunter, C. E., *J. Chem. Phys.* **50**, 3516 (1969).
15. Goodgame, D. M. L., and Hitchman, M. A., *Inorg. Chem.* **4**, 721 (1965).
16. Drew, M. G. B., and Rogers, D., *J. Chem. Soc. D* 476 (1965).
17. Graham, J., *J. Phys. Chem. Solids* **17**, 18 (1960).
18. Lipscomb, W. N., Wane, F. E., May, W. R., and Lippert, E. L., Jr., *Acta Crystallogr.* **14**, 1100 (1961).