Surface Structure of Crystalline and Amorphous Chromia Catalysts for the Selective Catalytic Reduction of Nitric Oxide

IV. Diffuse Reflectance FTIR Study of NO Adsorption and Reaction

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Adsorption of NO onto the *oxidized* surfaces of both crystalline and amorphous chromia results in the formation of nitrato complexes, by the reaction of NO with surface oxygen. Up to six differently bound species exhibiting different thermal stabilities have been identified. As the catalyst surfaces are saturated with adsorbed oxygen, the bound NO molecules are not decomposed: Upon heating, NO is molecularly desorbed, and neither formation of N_2O nor of N_2 is observed. *Reduced* chromia surfaces, which are partially depleted in surface oxygen, are more reactive towards NO. Decomposition of NO, to form N_2O and N_2, is taking place already at room temperature and is accompanied by a partial reoxidation of the catalyst surface. Nitrato complexes are the most abundant surface species also on the reduced chromia; signals of adsorbed mono- and dinitrosyl complexes are comparatively weak. This observation shows that NO preferentially binds to the Lewis basic surface oxygen ions. As a consequence of the decreased surface oxygen concentration, the coverage of *bridging* surface nitrate species (requiring two adjacent surface oxygens) is smaller than on the oxidized catalysts. The reaction of NO with surface hydroxyl groups, producing N_2 and NO_2^-, results in a minor concentration of $Cr-NO_2$ surface nitro complexes. On the reduced *amorphous* catalyst, extensive reoxidation of the surface accompanied by N_2O formation is observed between 311 and 411 K in temperature-programmed reaction and desorption (TPRD) experiments, while this process is observed to a much smaller extent on reduced *crystalline* chromia. Above 473 K, bridging and bidentate surface nitrates are the most abundant species on both morphologies. Further heating results in the decomposition of these nitrates yielding N_2, N_2O (on crystalline chromia only), and surface oxygen. © 1992 Academic Press, Inc.

INTRODUCTION

Chromia has recently attracted attention (*1, 2*) as an active catalyst material for the selective catalytic reduction (SCR) of NO with ammonia, in the presence of excess oxygen. Amorphous chromia, in particular, is characterized by high selectivities towards N_2. On crystalline chromia, higher concentrations of the undesired side product, N_2O, as well as partial consumption of the NH_3 reactant by direct oxidation reactions have been observed.

To elucidate the origins of these differences, the temperature-programmed reaction and desorption (TPRD) of NH_3 and NO has been studied both on crystalline and amorphous Cr_2O_3 (part I of this study, Ref. (*3*)). Diffuse reflectance FTIR (DRIFT) spectroscopy has been used to monitor the generation of coordinatively unsaturated sites on the catalyst surfaces upon thermal activation, the availability of weakly bound surface oxygen, and the influence of an oxidative treatment at 473–498 K (part II, Ref. (*4*)). FTIR *in situ* studies of ammonia adsorption and temperature-programmed desorption have revealed the presence of two types of Brønsted- and Lewis-acidic sites (part III, Ref. (*5*)). It was found that the

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concentration of strongly surface-bound NH_3 molecules, which are involved in direct oxidation reactions at higher temperatures, is significantly lower on amorphous chromia, as compared to α-Cr_2O_3.

In the present study, the adsorption of NO on the two types of chromia surfaces is studied by *in situ* DRIFT spectroscopy. Kugler *et al.* (6) have used NO adsorption to probe the Lewis acidic sites on the surface and have described an adsorbed oxygen-bound *cis*-N_2O_2 dimer. Ghiotti *et al.* (7) assigned the corresponding vibrational bands to a (nitrogen-bound) dinitrosyl complex; four types of these complexes have been identified by Conway *et al.* (8). Recently, these studies were supplemented by IR and ESR investigation of NO adsorption on CrO_x/ZrO_2 catalysts (9).

Several types of surface reactions of adsorbed NO molecules have been considered: Disproportionation reactions on zeolites, producing N_2O and NO_2 as the gas-phase products, were investigated by Chao and Lunsford (10); adsorbed nitrite, nitrate, and NO_2^+ ions have been detected. Nitrite as well as NO^- and $N_2O_2^-$ was also observed by Cerruti *et al.* (11) in a related study on MgO. Recently, evidence for the formation of nitrate ions upon NO adsorption has been obtained by Dines *et al.* (12, 13).

In the present study, the surface species produced upon adsorption of NO on crystalline and amorphous chromia are identified, and their importance is discussed in terms of the structural models derived for the chromia surfaces (4, 5). The thermal stability is assessed by thermal desorption experiments and is related to the selectivities of the catalyst surfaces that have been determined for the SCR reaction (1, 2).

EXPERIMENTAL

The preparation of the catalysts and the apparatus used have been described in detail in parts I and II of this study (3, 4). The oxidation or reduction treatment conditions and the NO adsorption conditions were identical to those used in part I (3). An oxidized state of the surface was established by thermal pretreatment at 623 K for one hour, followed by oxygen adsorption at 498 K for 1 hr. Reduced surfaces were prepared by heating samples in a flow of 6% H_2/Ar to 623 K, at which temperature they were held for 1 hr.

Prior to introduction of nitric oxide, background spectra have been accumulated at a resolution of 4 cm^{-1} both for the oxidized and reduced states of the surface. The spectra presented below in Figs. 1–10 are ratioed with respect to this background. These spectra will therefore only exhibit bands due to adsorbed NO, the products of NO reduction or oxidation, and changes in the background caused by NO adsorption or desorption.

In the TPRD experiments (3), the temperature was increased from 298 to 553 K at a rate of 2 K/min. As the desorption is a dynamic process which depends on the temperature scan rate, it appeared inappropriate to record the FTIR spectra at constant temperature, and to increase the temperature in rapid steps between accumulations. Rather, several scans (typically 100) were coadded while the temperature was being increased at a rate of 2 K/min. Therefore, a typical spectrum represents the state of the surface during TPRD as averaged over a 25-K interval.

For a sensitive representation of temperature-dependent changes in the population of surface species, ratios of two successive spectra of this kind have been calculated. These spectra have been labelled, e.g., by R (311 K)/R (336 K), which represents the ratio of the two spectra recorded at average temperatures of 311 and 336 K, as defined above. A *value* < *1* in the ratioed spectrum at a given wavenumber signifies *desorption:* An absorbing species, which decreases the surface reflectivity at the lower temperature, has been desorbed at the higher temperature, whereby the reflectivity is increased.
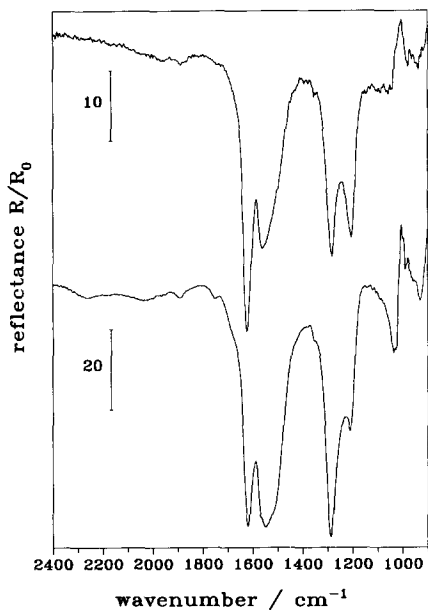
RESULTS

A. EXPERIMENTS ON OXIDIZED CHROMIA SURFACES

A.1. Adsorption of Nitric Oxide

Spectra of the oxidized surfaces of crystalline and amorphous chromia prior to NO adsorption have been presented and discussed in part II of this study (4). Changes in the IR spectrum caused by adsorption of NO at room temperature are shown in Fig. 1. On *crystalline* Cr_2O_3 (lower trace), an increase in surface reflectivity is observed at 1004, 980, and 950 cm^{-1}, with a new absorption appearing at 1040 cm^{-1}. Bands appearing above 1000 cm^{-1} are due to molecularly adsorbed NO and to surface nitrites and nitrates as discussed below. There are four dominant bands at 1285, 1210 (asymmetry towards lower wavenumbers), 1620, and 1550 cm^{-1}, which will be assigned to surface nitrates (11, 14, 15). The latter broad band

is composed of two overlapping features at 1570 and 1500 cm^{-1}. In addition, broad bands are noted around 2260 and 2040 cm^{-1}, as well as less intense peaks at 1750, 1895, and 1690 cm^{-1} (shoulder). A small peak at 1355 cm^{-1} is due to uncoordinated nitrate (14).

NO adsorption onto *amorphous* chromia again causes an increase in reflectance around 1000 cm^{-1}. As with crystalline chromia, surface-coordinated nitrate species give rise to four dominant bands at 1205, 1285, 1620, and 1560 cm^{-1}, the latter with a pronounced shoulder towards lower wavenumbers. Weaker features are seen at 1355 (uncoordinated nitrate) and 1895 cm^{-1}.

A.2. Desorption of NO from Crystalline α-Cr_2O_3

The spectra in Fig. 2 were recorded while heating the sample at a rate of 2 K/min. As mentioned in the Experimental section, the spectra recorded during TPRD represent averages over a 25-K temperature interval. When comparing the bottom spectrum of Fig. 2 (labelled "311 K") recorded between 298 and 323 K with the room-temperature spectrum of Fig. 1, we note that no significant changes are occurring below 323 K.

Little desorption is occurring between 310 and 336 K. The spectrum R (311 K)/ R (336 K) exhibits only weak peaks at 1630, 1580, and 1200 cm^{-1}, the latter with a shoulder towards higher wavenumbers. In addition to these bands, the spectrum R (336 K)/ R (361 K) contains two decreasing absorptions at 1295 (dominant) and 1500 cm^{-1} (broad). Weaker features are seen at 1040 and above 2000 cm^{-1}.

In the temperature interval from 361 to 386 K, desorption occurs at a much higher rate, as may be seen from the intensity decrease of the corresponding bands (note calibration bars). In the spectral region corresponding to surface nitrates, a broad band at 1510 and a peak at 1290 cm^{-1} are dominant, with weaker features at 1625, 1585, 1220 (shoulder), and 1030 cm^{-1}. Above 1650 cm^{-1}, weak and broad IR bands of desorbing
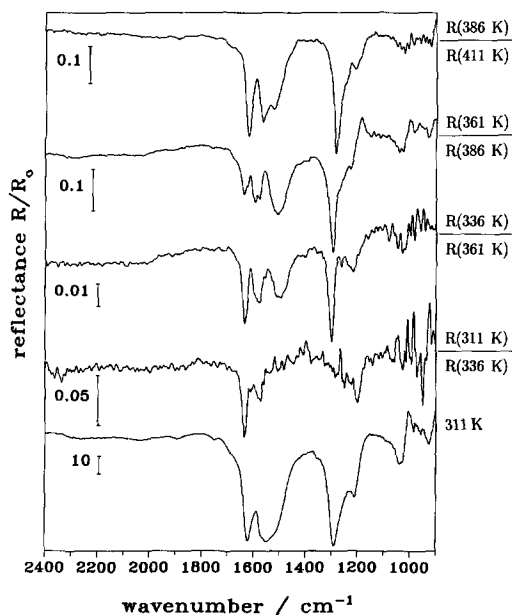
FIG. 2. Desorption of NO from *oxidized crystalline* α-Cr_2O_3. Spectra were recorded while the temperature was ramped at a rate of 2 K/min. Temperatures indicated correspond to the mean of a 25-K interval, as specified in the experimental section. In the upper four traces, the ratios of two spectra recorded in successive temperature intervals are presented. A negative-going peak indicates that the corresonding species is desorbing as the temperature is being increased. In the ratioed spectra, the sizes of the relative changes are indicated by the calibration bars.

species are detected at 1760, 1885, 2050, and 2285 cm^{-1}, which are seen more easily when the spectrum is plotted on an expanded scale. The surface reflectivity increases at 1185 cm^{-1}. In the temperature interval from 386 to 411 K, dominant decreasing peaks of surface nitrates are located at 1620, 1565, 1525 (shoulder), 1280, and 1210 cm^{-1}. A new feature at 1685 cm^{-1} and weak bands at 1890, 1750, and 1030 cm^{-1} are observed.

In the spectrum recorded at 411 K (Fig. 3, bottom trace), bands at 1620, 1550, 1280, and 1220 cm^{-1} due to surface nitrate species are still dominant. Weaker absorptions are located at 1040, 1360, 1430, 1685, and around 1890 cm^{-1}. Surface reflectivity at 1000 cm^{-1} is still increased as compared to the room-temperature background. Upon

further raising the temperature {ratioed spectrum R (411 K)/R (436 K)}, desorption of surface nitrate occurs {1615, 1550 (broad), 1281, and 1207 cm^{-1}}. Weaker bands of desorbing species are visible at 1690 and around 1030 cm^{-1}. In the ratioed spectrum R (461 K)/R (486 K) the peak at 1285 and the band at 1690 cm^{-1} are missing. The peak at 1550 cm^{-1} is much narrower, as compared to the preceding spectrum. A broad decreasing absorption is located around 2000 cm^{-1}. At even higher temperatures {R (486 K)/R (511 K) and R (536 K)/R (561 K)}, the desorption of surface nitrate goes to completion (peaks at 1610, 1550, and 1210 cm^{-1}). At the highest temperature studied (573 K), desorbing species give rise to bands at 1360, 1430, and 1950 cm^{-1}.

A.3. Desorption of NO from Amorphous Chromia

Spectra recorded on amorphous chromia during a TPRD run subsequent to NO adsorption at room temperature are presented
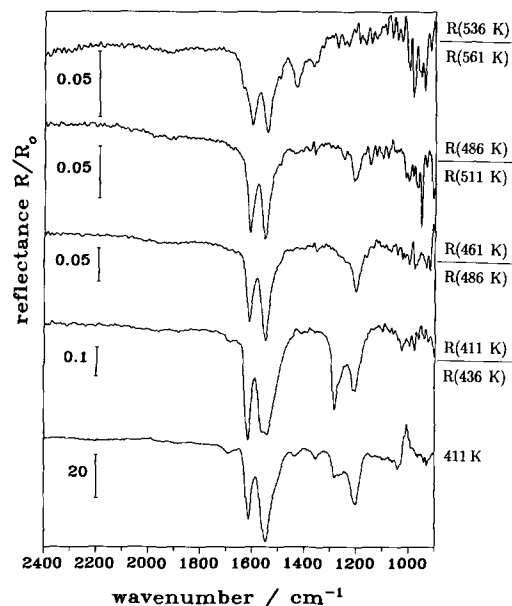

FIG. 3. Desorption of NO from oxidized crystalline α-Cr_2O_3. The temperature program of Fig. 2 is continued to higher temperatures.

in Figs. 4 and 5. The spectrum at 311 K is essentially unchanged as compared to 298 K, except for a slight sharpening of the 1550 cm^{-1} band due to desorption of a species absorbing at $\approx$ 1520 cm^{-1}.

Upon raising the temperature {R (311 K)/ R (336 K)}, incipient desorption is evident from the weak intensity decrease of bands at 1625, 1555, 1515 (broad), 1290 (dominant), and 1220 cm^{-1} (note intensity calibration bar). Minor features are located around 2000 and 1380 cm^{-1}. A further temperature increase {R (336 K)/R (361 K), R (361 K)/ R (386 K)} promotes the desorption of surface nitrates absorbing at 1520 cm^{-1}, while the bands at 1620 and 1560 cm^{-1} become dominant. We note an increase in reflectance around 996 cm^{-1}. At 386 K (top trace) the desorption of a surface species absorbing at $\approx$1950 cm^{-1} goes to completion.

The bottom trace of Fig. 5 (denoted "386 K") represents the spectrum recorded while heating the sample from 373 to 398 K. A dominant peak at 1620 cm^{-1} as well as weaker bands at 1560, 1280, and 1200 cm^{-1}
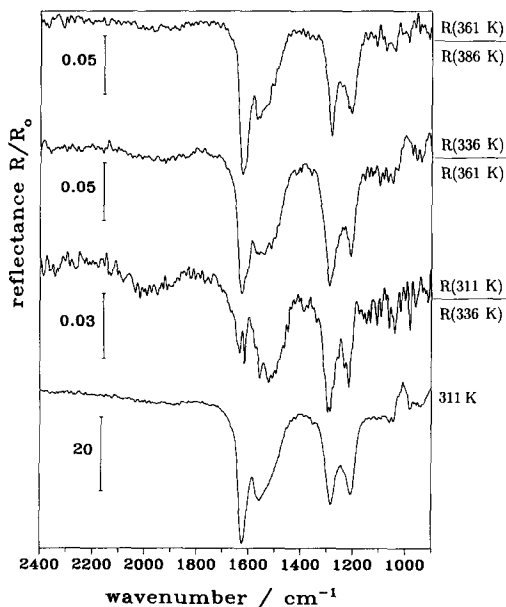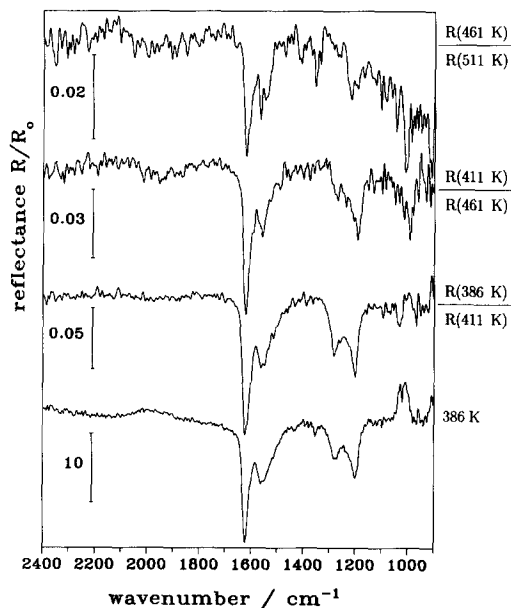

FIG. 5. Desorption of NO from oxidized amorphous chromia. The temperature program of Fig. 4 is continued to higher temperatures.

are due to surface nitrate species. A small peak at 1360 cm^{-1} is assigned (14) to free nitrate ions. "Negative" bands (reflectance increase) at $\approx$1010 and $\approx$2000 cm^{-1} are observed.

In the temperature interval from 398 to 423 K, desorption of surface nitrate gives rise to decreasing absorptions at 1620, 1555, 1280, and 1200 cm^{-1} {trace R (386 K)/R (411 K)}. At even higher temperatures {R (411 K)/R (461 K}, the desorption of the surface nitrate species absorbing at 1555 cm^{-1} gradually goes to completion. Broad bands of desorbing species are visible at 995 and around 2000 cm^{-1}. At the highest temperatures studied {R (461 K)/R (511 K)}, only minor intensity changes in the bands at 1620, 1560, and 1200 cm^{-1} due to desorption are still present.

B. EXPERIMENTS ON REDUCED CHROMIA SURFACES

B.1. Adsorption of NO

Diffuse reflectance spectra recorded after NO adsorption at room temperature for

FIG. 4. Desorption of NO from *oxidized amorphous* chromia. Conditions are the same as in Fig. 2.

1 hr (Fig. 6) again exhibit the characteristic vibrations of adsorbed nitrate species. For crystalline chromia (lower trace) dominant bands are located at 1610 (shoulder), 1570 (sh), 1540, 1490 (sh), 1285, and $\approx$1000 cm^{-1} (broad, extending from 950 to 1050 cm^{-1}). Smaller bands are noted around 2265, 1960, 1745, 1680 (sh), 1390, and 1125 cm^{-1}.

With amorphous chromia (Fig. 6, upper trace), five dominant bands at 1610 (sharp), 1570 (broad), 1420, 1285 (most intensive), and $\approx$1000 cm^{-1} are observed. Weaker broad features are seen around 2280, 2000, 1750, and 1210 cm^{-1} (shoulder).

B.2. Desorption of NO from Reduced Crystalline α-Cr₂O₃

In the temperature range between 298 and 323 K (Fig. 7, lowest trace), no substantial changes are recorded except for a sharpening of the broad 1000 cm^{-1} band, due to loss of absorbance at 1050 cm^{-1}. Raising the temperature to 348 K {R (311 K)/R (336 K)} causes the desorption of several surface spe-
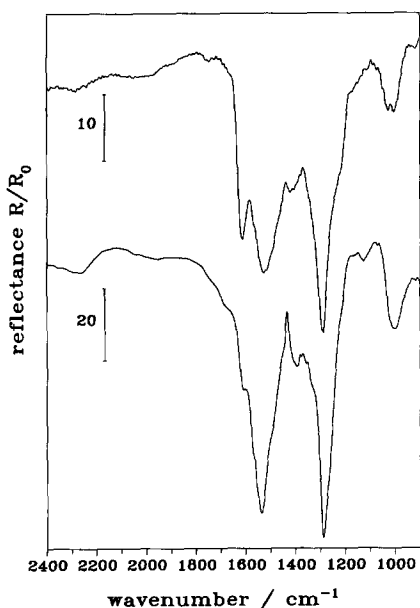

FIG. 7. Desorption of NO from the *reduced* surface of *crystalline* α-Cr₂O₃. Conditions are the same as in Fig. 2.

cies, as seen in the second trace of Fig. 7. Desorbing species are recognized by bands at 2285 (broad), 2040 (br), 1730, 1630, 1577, 1500, 1400, 1330 (sh), 1300, and 1030 cm^{-1}. An increase of surface reflectivity is noted at 1210 and 970 cm^{-1}. Further raising of the temperature renders a simpler ratioed spectrum {R (386 K)/R (411 K)}. In the range of surface nitrate absorptions, bands are located at 1620, 1565, 1510, 1285, and 1260 cm^{-1}. Weaker bands of desorbing species are seen at 2250 (br), 2000 (br), 1680, 1450, 1390, and at 1015 cm^{-1}. Upon increasing the temperature to 448 K {R (411 K)/R (436 K)}, signals at 2250 and 2000 cm^{-1} are no longer observed. The peaks of desorbing nitrate at 1600, 1530 (br), 1280, and 1215 cm^{-1} are dominating the spectrum. Weaker decreases of absorption are detected for the bands at 1680, 1450, and 1025 cm^{-1}.

The spectrum recorded at 436 K (Fig. 8) still exhibits bands due to surface nitrate species. The band at $\approx$1000 cm^{-1} has become narrower and is peaking at 996 cm^{-1}. It is interesting to observe an increase of

FIG. 6. NO adsorption at room temperature on the *reduced* surfaces of crystalline α-Cr₂O₃ (lower trace) and of amorphous chromia (upper trace).

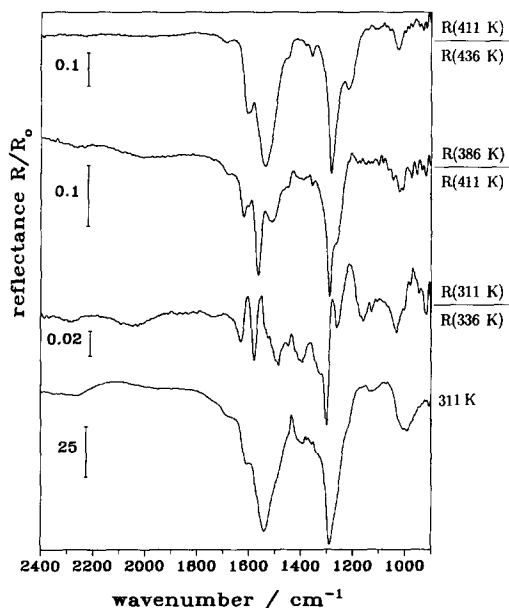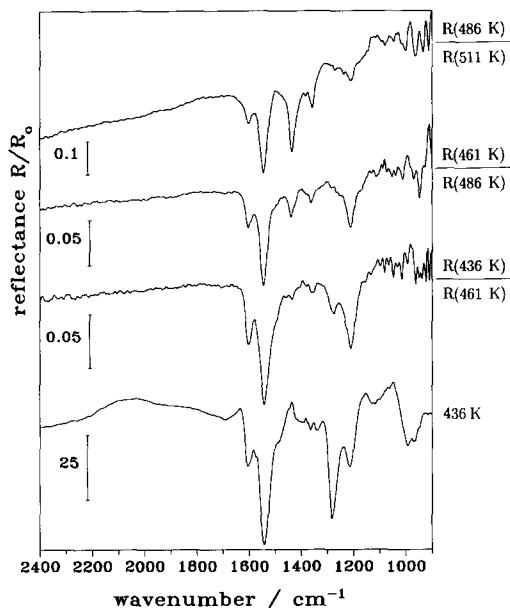FIG. 8. Desorption of NO from the *reduced* surface of *crystalline* α-Cr₂O₃. The temperature program of Fig. 7 is continued to higher temperatures.

reflectance in the form of two broad, overlapping bands around 1950 and 2100 cm⁻¹. The following series of spectra, which represent the desorption behavior in the temperature interval beween 448 and 583 K, indicate that the desorption of surface nitrates (bands at 1600, 1545, 1280, and 1210 cm⁻¹) approaches completion. The thermally most stable species absorbs at 1545 cm⁻¹ {cf. R (411 K)/R (436 K)}. Above 473 K, disappearing peaks at 1430 and 1360 cm⁻¹ become prominent.

B.3. Desorption of NO from Reduced Amorphous Cr₂O₃

Features of the 311 K spectrum in Fig. 9 agree with those discussed in Section B.1. When the temperature is raised to 361 K {R (336 K)/R (361 K)}, desorption of species occurs as indicated by bands at 2010 (broad), 1630, 1430 (broad), and 1315 cm⁻¹. At higher temperatures {R (361 K)/ R (386 K)} the broad band observed around 1430 cm⁻¹ in the preceding spectrum becomes asymmetric, with the maximum now

located at 1410 cm⁻¹. The decreasing peak at 1315 cm⁻¹ appears red-shifted to 1300 cm⁻¹. Upon heating to 423 K {R (386 K)/ R (411 K)} the decreasing signal around 1430 cm⁻¹ is strongly reduced, with the remaining main maxima at 1615, 1560, 1520, and 1290 cm⁻¹ due to surface nitrate.

Upon continuation of the temperature program (Fig. 10, bottom trace), the most significant feature is a dominant peak centered at 1000 cm⁻¹. In part II of this study (4) it has been demonstrated that absorptions in this spectral region are due to chromium–oxygen double bonds. The intensification of this band, which will be interpreted as a reoxidation of the surface, starts above 323 K (increase of reflectance around 1000 cm⁻¹ in Fig. 9) and continues up to the highest temperatures studied. Interestingly, this process is accompanied by a broad increase of surface reflectance around 2000 cm⁻¹. The ratioed spectra (second to forth traces in Fig. 10) exhibit bands at 1610, 1530, 1285, and 1215 cm⁻¹, due to desorption of surface nitrates. The
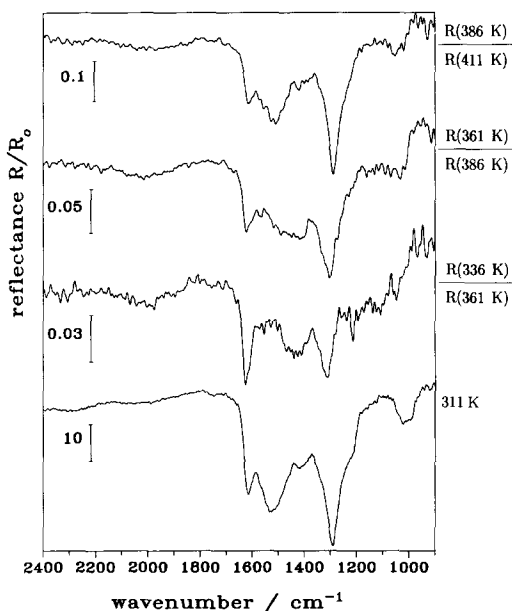

FIG. 9. Desorption of NO from the *reduced* surface of *amorphus* chromia. Conditions are the same as in Fig. 2.
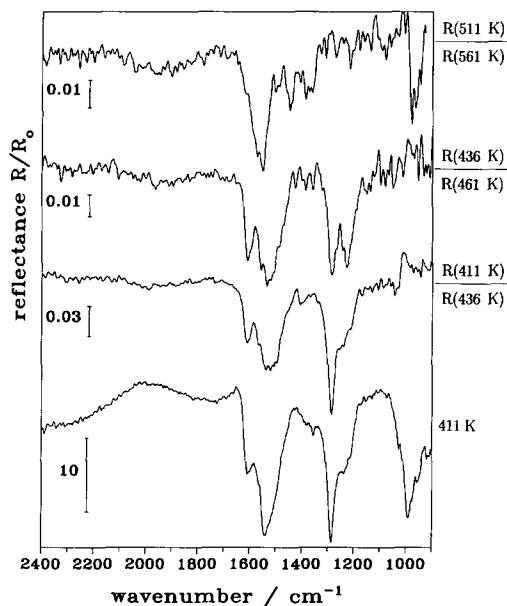
FIG. 10. Desorption of NO from the *reduced* surface of *amorphous* chromia. The temperature program of Fig. 9 is continued to higher temperatures.

species absorbing at 1530 cm^{-1} appears to be thermally most stable.

DISCUSSION

A. EXPERIMENTS ON OXIDIZED CHROMIA SURFACES

The spectroscopic results presented above will be correlated with the TPRD experiments reported in part I (3), which may be summarized as follows. On crystalline Cr_2O_3, nitric oxide desorbs over a broad temperature range, with maximum rate at 373 K and a long tail extending to high temperatures. No desorption of nitrogen or nitrous oxide is observed up to temperatures of 523 K. Small quantities of the latter product are desorbed at 623 K. In contrast, on the amorphous chromia the long tail of NO desorption is absent: the detected NO concentration practically drops to zero above 473 K. Again no reaction products of NO, such as N_2 or N_2O, are observed at temperatures below 573 K.

A.1. Assignment of Spectral Features

$\nu(O-H)$ *stretching vibrations.* For *crystalline* chromia, bands were observed at 3610, 3570, and ≈ 3470 cm^{-1} (broad) after O_2 adsorption. The band at 3610 cm^{-1} has been assigned (4, 16) to isolated, nonacidic hydroxyl groups, while features at 3450 and 3250 cm^{-1} correspond to more acidic OH groups. Upon NO adsorption these bands appear downshifted to 3240 (broad, dominant), 3405, and 3505 cm^{-1}. This lowering of the vibrational frequency may be interpreted in terms of hydrogen bonding interactions between Cr–OH and NO; the affected hydroxyl groups must therefore be adjacent to NO adsorption sites, where surface nitrate species are created.

On the surface of *amorphous* chromia, a band at 3610 cm^{-1} and a very broad band around 3200 cm^{-1} have been observed after oxygen adsorption (4). Upon introduction of NO these bands are again shifted to lower wavenumbers, and a broad maximum centered at 3400 cm^{-1} is seen.

NO surface complexes. From the NO adsorption experiment on oxidized chromia surfaces (Fig. 1), the extent of NO bonding to coordinatively unsaturated chromium ions, and of its reaction with surface oxygen species, can be assessed. In the light of extensive studies of NO or NO_2 adsorption on metal oxide surfaces (11, 14, 15), the dominant bands observed subsequent to NO exposure on both oxidized and reduced chromia surfaces (range 1200–1630 cm^{-1} in Figs. 1 and 6) must be assigned to surface nitrate complexes, formed by the reaction of NO with surface oxygen ions. Thus NO chemisorption occurs mainly on Lewis-basic surface oxygen ions and only to a lesser extent by interaction of NO with coordinatively unsaturated, Lewis-acidic chromium ions.

During thermal pretreatment of α-Cr_2O_3, one- and twofold coordinatively unsaturated Cr ions are generated (cf. part II, Ref. (4)) which partly persist after oxygen adsorption at 473 K (5). The spectral region around 1000 cm^{-1} reveals the changes occurring at these sites upon NO adsorption.

TABLE 1

Surface Species Observed on Crystalline and Amorphous Chromia

Species	Vibrational frequency (cm^{-1})	Desorption temperature (K)			
		Oxidized surfaces		Reduced surfaces	
		$\alpha\text{-}Cr_2O_3$	am. Cr_2O_3	$\alpha\text{-}Cr_2O_2$	am. Cr_2O_3
Free NO_3^-	1360	573	523	523	523
Bridging NO_3^- I	1630/1200	373	373	373	373
Bridging NO_3^- II	1620/1210	573	473	573	500
Bidentate NO_3^- I	1580/1210	373	—	373	—
Bidentate NO_3^- II	1565/1280	573	473	573	500
Bidentate NO_3^- III	1525/1280	473	400	473	523
Monodentate NO_3^-	1490/1295	398	373	398	398
Nitrito Cr–ONO	1450/1025	—	—	473	—
Nitro Cr–NO_2	1400/1325	—	—	423	448
Chelate NO_2^-	1210	423	—	423	400
N_2O	2260	448	—	423	373
Dinitrosyl $(NO)_2$	1895/1750	480	—	480	—
Mononitrosyl NO	1685				
NO_2^+	≈ 2000				

In Fig. 1, an increase of surface reflectivity is observed at 1004 cm^{-1} {onefold coordinatively unsaturated sites (4, 16, 17)} and at 980/960 cm^{-1} {coodinatively saturated sites differentiated by ligand heterogeneity (16)}. A decrease in absorbance at these frequencies indicates that NO interacts both with coordinatively unsaturated Cr ions and with surface oxygens.

A.2. Crystalline Chromia: Interaction of NO with Surface Oxygen

Bands at 1620, 1550, 1285, and 1210 cm^{-1} in Figs. 1 and 6 are assigned to surface nitrate complexes characterized by different geometries, i.e., bridging, bidentate, and monodentate bonding. These assignments, which are based on a large body of literature (11, 14, 15), are summarized in Table 1. The bands are most easily grouped, and identified with the various nitrate complexes, by observing differences and correlations in the thermal desorption behavior.

Weak peaks at 1630 and 1585 cm^{-1} (Fig. 2) are seen to disappear already between 298 and 336 K. They are attributed to the high-

wavenumber components of the ν_3 vibrations for thermally unstable bridging and bidentate nitrate complexes, respectively (cf. Table 1). The corresponding low wavenumber components, at ≈ 1210 cm^{-1}, are not resolved.

Upon heating to 361 and 386 K (third and fourth traces in Fig. 2), intense bands of desorbing species are observed around 1500 and 1290 cm^{-1}. We tend to assign these features to the overlapping bands of monodentate nitrate {1490 cm^{-1} [$\nu_{as}(NO_2)$] and 1295 cm^{-1} ($\nu_s(NO_2)$)} and to bidentate nitrato species absorbing at 1560 cm^{-1} [$\nu(NO)$], 1525, and 1280 cm^{-1} (two components of split ν_3 vibration). The monodentate species desorbs below 398 K, as evidenced by a shift of the 1290 cm^{-1} peak down to 1280 cm^{-1} (Fig. 2). The peak at 1040 cm^{-1}, which has disappeared in parallel, is assigned to the $\nu_2(N–O)$ stretching vibration of monodentate nitrate.

In the temperature interval from 386 to 411 K (top trace of Fig. 2), the desorption of bridging nitrate {1620 and 1210 cm^{-1}, type II, Table 1} and of bidentate NO_3^- is domi-

nating {1560 and 1280 cm^{-1}, type II; 1525 and 1250 cm^{-1}, type III; cf. Table 1}. In agreement with the TPRD spectrum (3) where maximum rate of NO desorption had been found at 380 K, the strongest absorption decrease is observed in the temperature range between 361 and 386 K. The spectrum recorded at 411 K (Fig. 3, bottom trace) still features dominant bands due to surface nitrate. A small peak at 1360 cm^{-1}, which persists up to 573 K, is assigned to free, i.e., uncoordinated, nitrate ions (14).

After desorption of monodentate NO$_3^-$ has been completed, a small peak at 1430 cm^{-1} is clearly seen. Chao and Lunsford (10), who studied NO adsorption on Y-type zeolites, have assigned a band at 1420 cm^{-1} to a nitrito complex (M–ONO). For such complexes, IR absorptions are known in the 1465–1395 cm^{-1} range (14). Alternatively, the 1430 cm^{-1} feature could be attributed to a nitro complex (M–NO$_2$), which normally absorbs in the 1425 cm^{-1} range (11).

A comparison of the second and third traces in Fig. 3 demonstrates that the desorption of surface bidentate nitrate III {bands at 1525 and 1280 cm^{-1}, Table 1} is complete at about 480 K. Peaks at 1610, 1550, and 1200 cm^{-1} persist up to temperatures of 573 K, which prove the high thermal stability of the bridging (1610 cm^{-1}) and bidentate (1550 cm^{-1}) nitrato complexes on the surface of oxidized α-Cr$_2$O$_3$. At the highest temperatures studied (573 K, top trace in Fig. 3), free nitrate (1360 cm^{-1}) and nitro complexes (1430 cm^{-1}) are also being desorbed.

A.3. Crystalline Chromia: Reactions of NO with Coordinatively Unsaturated Cr Ions

Some features of lower intensity in Fig. 1 are due to the interaction of NO and its products with coordinatively unsaturated Cr ions. First, a broad band centered at 2260 cm^{-1} is observed on α-Cr$_2$O$_3$. Zecchina et al. (18) and Dines et al. (12) have studied the adsorption of N$_2$O on the surface of crystalline chromia; two bands at 2305 and 2238 cm^{-1} have been attributed to the nondissociative adsorption of N$_2$O, as a linear complex bound to a singly coordinatively unsaturated chromium site. The bond to the chromium centers can be established either through the terminal nitrogen (band at 2305 cm^{-1}) or through the terminal oxygen (band at 2238 cm^{-1}) of N$_2$O. The maximum of our band at 2260 cm^{-1} is just in between these two values, such that both complexes appear to be involved. These complexes are desorbing below 423 K (see, e.g., fourth trace in Fig. 2).

For the formation of N$_2$O, two reactions can be formulated. First, it is known that NO undergoes disproportionation at temperatures higher than 323 K and at elevated pressures, according to the reaction

$$3NO \rightarrow N_2O + NO_2, \qquad (1)$$

such that N$_2$O could have been already present in the reaction gas. A second mechanism is discussed in the Appendix.

Bands in the 1750–1900 cm^{-1} region have been observed upon NO adsorption on chromia/silica catalysts used for ethene polymerization (7, 8), and on reduced α-Cr$_2$O$_3$ (6). In the latter study, a doublet of bands at 1735 and 1865 cm^{-1} has been assigned to a cis-N$_2$O$_2$ dimer formed by adsorption of two NO molecules on a twofold coordinatively unsaturated Cr site. In contrast, Ghiotti et al. (7) and Conway et al. (8) have attributed bands in this frequency region to two types of dinitrosyl surface complexes, bound to coordinatively unsaturated Cr ions of different oxidation states.

In the present study, a weak doublet of bands is observed at 1895/1750 cm^{-1} after NO adsorption on oxidized α-Cr$_2$O$_3$, and to a lesser extent on the amorphous sample. However, the low intensity of these bands suggests that only a limited concentration of twofold coordinatively unsaturated sites exists on the surfaces of our preoxidized chromia samples. Desorption of the N$_2$O$_2$ dimer starts at about $\approx$350 K and is completed at 450 K.

Another small peak at 1685 cm^{-1} persists

up to 480 K. A band at this frequency has been reported by Erley (19) and Gardner *et al.* (20) upon adsorbing NO onto Ni(111) and Pt(100) surfaces, respectively. In accordance with these groups, the band is assigned to a mononitrosyl surface complex (NO adsorbed on a onefold coordinatively unsaturated Cr ion). No such mononitrosyl complex is formed on the surface of *amorphous* chromia.

A.4. Amorphous Chromia: Reactions of NO with Surface Oxygen

The assignment of spectral features resulting from the interaction of NO with oxidized amorphous chromia is analogous to the above discussion. However, some minor differences are worth mentioning. NO adsorbs on amorphous chromia to a much lesser extent than it does on crystalline chromia (cf. the TPRD spectra shown in Fig. 4 of part I of this study (3)). This observation is reproduced in the DRIFT spectrum of Fig. 1 (top trace), where the absorptions of NO exhibit half the intensity observed on α-Cr_2O_3 (note calibration bars). Again the dominant bands in the top spectrum of Fig. 1 are due to surface nitrate complexes, as detailed in Table 1. The concomitant consumption of surface oxygen ions is confirmed by the negative band around 1000 cm^{-1}.

As had been the case for the crystalline surface, a bridging (1630, 1200 cm^{-1}) and a monodentate (1500/1290 cm^{-1}) surface nitrate complex are desorbed at temperatures below 373 K (Fig. 4). Bidentate nitrate II (1555/1200 cm^{-1}) and nitrate III (1520/1285 cm^{-1}) show incipient desorption at 323 K (Fig. 4). The spectrum recorded while ramping the temperature from 373 to 398 K only exhibits bands due to bridging nitrate II (1620/1200 cm^{-1}) and to bidentate nitrates II and III (Fig. 5, bottom trace). The desorption of the latter surface complex is complete at about 400 K. Absorptions due to the most stable nitrate complexes (bridging, type II, and bidentate, type II) are now dominating the spectrum (second trace in Fig.

5). These surface species do, however, not possess the high thermal stability of their counterparts on crystalline chromia: At 473 K nearly all NO_3^- has disappeared, and only weak bands of desorbing species are seen in the 473 to 573 K interval (top trace in Fig. 5). This spectroscopic result is again in full agreement with the TPRD spectra in part I of this study (3).

A.5. Amorphous Chromia: Interaction with Coordinatively Unsaturated Cr Ions

Bands indicating a direct bonding of NO to coordinatively unsaturated Cr ions are encountered to a much lesser extent on the amorphous chromia. Weak and broad features at 1895 and 1750 cm^{-1} hint to minor amounts of the $(NO)_2$ dinitrosyl complex. As mentioned in part II (4), amorphous chromia possesses a much higher ability to retain its labile surface oxygen upon thermal treatment, as compared to crystalline chromia. Therefore, the population of one- and twofold coordinatively unsaturated Cr ions will be very small, and the spectral features associated with NO adsorption on these sites are correspondingly weak.

B. EXPERIMENTS ON REDUCED CHROMIA SURFACES

The temperature-programmed reaction and desorption of NO from the reduced surface of crystalline and amorphous chromia again takes place with maximum rate at 373 K on both morphologies (cf. part I, Ref. (3, Fig. 4)). However, on the reduced surfaces the desorption of NO is bimodal, with a second weaker maximum located around 423 to 473 K, especially pronounced on the crystalline sample. NO desorption slowly tails off on both morphologies and is complete at about 523 K.

In contrast to the oxidized surfaces, NO reacts to produce N_2 and N_2O on reduced surfaces. For *amorphous* chromia, no O_2 desorption has been observed in the course of TPRD in the temperature range between 298 and 650 K. Oxygen released from NO

upon N_2 and N_2O formation is therefore likely to reoxidize surface chromium ions, by filling coordinatively unsaturated Cr sites. Both the process producing N_2 and N_2O occur more readily, but to a lesser extent, on the amorphous chromia as compared to α-Cr_2O_3. For example, the reaction producing N_2 reaches maximum rate on the amorphous chromia at a temperature which is 50 K lower than on crystalline chromia.

On both morphologies, the sites that are catalyzing the decomposition of NO to yield N_2O, start to become active at temperatures 50 to 60 K lower than those associated with the production of N_2. In part I (3) it has been stated that decomposition to N_2O is favored, as only one oxygen atom must be accomodated on surface sites.

B.1. Assignment of Spectral Features

ν(O–H) stretching region. In contrast to oxygen covered chromia surfaces, the adsorption of NO on reduced chromia results in a dominant negative absorption band extending from 3620 to 3660 cm^{-1}, which suggests that hydroxyl groups have been consumed in a reaction between NO and Cr–OH. The corresponding spectra are not reproduced, but are available with the authors.

Zecchina et al.(16) have assigned a band between 900 and 1000 cm^{-1} on crystalline chromia to the deformational mode of surface hydroxyls. However, in this work we are observing an increase of surface reflectance at 830 cm^{-1} which is comparable in intensity and width to the negative feature around 3650 cm^{-1}. This correlation suggests that the latter band be associated with the deformational mode.

Frequency region of NO surface complexes. As with the oxidized surfaces of chromia, the dominant bands of Fig. 6 are due to surface nitrate complexes; bands due to bridging nitrato species (1610, 1200 cm^{-1}) are of significantly lower intensity, as compared to the oxidized samples. This can be understood in terms of geometrical reasons: upon reduction part of the surface oxygen

atoms is removed, and two- and onefold coordinatively unsaturated sites are generated (cf. part II, Ref. (4)). The probability for an NO molecule to establish bonds to two oxygen ions located at different Cr sites is therefore decreased. A compilation of desorbing surface nitrate species, together with their desorption temperatures, is given in Table 1, on which we now comment.

In the reduced state, NO and N_2O adsorbed at coordinatively unsaturated chromium sites are visible on both morphologies of chromia. The broad band observed around 2260 cm^{-1} in both spectra of Fig. 6 (particularly intense on the crystalline surface) is again attributed to N_2O adsorbed at onefold coordinatively unsaturated sites. Bands of adsorbed NO (dinitrosyl complex at 1750, mononitrosyl at 1685 cm^{-1}) are again weak on both surfaces. This observation would imply either that NO has a strong preference for the interaction with Lewis-basic surface oxygen ions, or that NO adsorbed at coordinatively unsaturated Cr sites is immediately decomposed to yield N_2O, N_2, or other products.

The latter interpretation is favored, as we are observing the decomposition of NO at ambient temperatures accompanied by a reoxidation of the surface, as suggested by intensive absorptions around 1000 cm^{-1} in both spectra of Fig. 6. In accordance with oxygen adsorption experiments reported in part II (4)), these bands are assigned to newly generated chromium–oxygen bonds with bond orders near two. The large width of these bands (950–1050 cm^{-1}) suggests, however, that ν(N–O) stretching vibrations of monodentate nitrates are contributing as well.

B.2. Crystalline Chromia: Desorption of NO

The validity of the latter statement can be verified in the spectra of Fig. 7 (NO desorption from α-Cr_2O_3), where decreasing absorptions at 1030, 1290, and 1490 cm^{-1} are observed, which have been assigned to a desorbing monodentate nitrate complex. In

addition, there are species desorbing up to a temperature of 436 K (top trace of Fig. 7) characterized by bands at 1450 (shoulder) and 1025 cm^{-1}, which according to literature (*11, 14, 15*), may be associated with a surface nitrito complex (Cr–ONO) known to adsorb below 473 K. An increase of surface reflectance at 1211 cm^{-1}, which is present in the difference spectra up to temperatures of 398 K, matches the frequency observed for a chelating NO$_2^-$ complex (*6, 11*). As with the oxidized samples, desorption of thermally unstable bridging (1630 cm^{-1}) and bidentate NO$_3^-$ (1580 cm^{-1}) occurs in the low-temperature regime. A doublet of bands at 1400 and 1325 cm^{-1} is assigned to a nitro complex (Cr–NO$_2$) desorbing below 423 K.

Thermal stabilities of adsorbed N$_2$O, di- and mononitrosyl surface complexes on the reduced surface are similar to the ones on preoxidized surfaces: desorption of N$_2$O and (NO)$_2$ already occurs at low temperatures (below 423 K), whereas the mononitrosyl complex absorbing at 1685 cm^{-1} desorbs only at 473 K (Fig. 7, top trace).

Simple desorption patterns are observed on the surface of reduced α-Cr$_2$O$_3$ at temperatures above 423 K (top trace in Fig. 7, Fig. 8). Bridging (1610/1215 cm^{-1}) and bidentate (1565/1525/1280 cm^{-1}) nitrate complexes are the prominent desorbing species. It is interesting to note that maximum rates of N$_2$ and N$_2$O desorption are observed in TPRD on crystalline chromia in the same temperature interval. Again bridging nitrate II (1605/1210 cm^{-1}) and bidentate nitrate II (1545/1280 cm^{-1}) are the thermally most stable species, persisting up to temperatures of 573 K on the surface (top trace in Fig. 8). Bands at 1430 and 1360 cm^{-1} at temperatures above 473 K are due to desorbing nitrite/nitro surface complexes and free nitrate ions, respectively.

B.3. Amorphous Chromia: Desorption of NO

Besides dominant bands due to surface nitrate (1610, 1570, 1525, 1285, 1210, and 1040 cm^{-1}, cf. Table 1), a broad band is observed at 1410 cm^{-1} (Fig. 9, bottom trace), which has not been detected with *oxidized* surfaces at room temperature. With *reduced* crystalline chromia, this vibration has been assigned to a nitro complex (Cr–NO$_2$), with a matching band at 1315 cm^{-1} (*11*). The desorption spectra of Fig. 9 reveal that this nitro complex is of low stability, desorbing below 448 K (second trace of Fig. 10, signal at 1400 cm^{-1}).

The appearance of surface nitro complexes, observed exclusively on reduced chromia, suggests a correlation with the consumption of hydroxyl groups upon adsorption of NO. One may formulate an overall reaction where NO adsorbed on coordinatively unsaturated Cr ions reacts with surface hydroxyl groups, and is transformed to surface bound nitrite and N$_2$,

$$6\,NO + 2\,OH^- \rightarrow 2\,H^+ + 4\,NO_2^- + N_2. \quad (2)$$
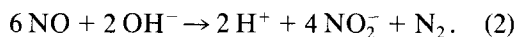
No surface nitro complexes are observed on *oxidized* samples at ambient temperatures. This may be explained by a lack of suitable adsorption sites, e.g., coordinatively unsaturated Cr ions in the vicinity of OH$^-$ groups. {As the concentration of surface OH$^-$ ligands is much higher on the oxidized surfaces, as demonstrated, e.g., by NH$_3$ adsorption, a minor consumption of OH$^-$ would not have shown up in the DRIFT spectrum of Fig. 1.}

The desorption of surface nitrate complexes closely follows the trend of thermal stabilities outlined above: Desorption of monodentate NO$_3^-$ occurs at temperatures below 398 K (1490/1295 cm^{-1}, overlapping with features of desorbing nitrite at 1410/1315 cm^{-1}), together with the desorption of bridging nitrate I (1625 cm^{-1}, cf. spectrum R (386 K)/R (361 K) in Fig. 9}. At higher temperatures (Figs. 9 and 10) dominant desorbing species are bridging nitrate II (1610 cm^{-1}), bidentate II (1560/1280 cm^{-1}) and bidentate III (1520/1290 cm^{-1}). This time the most stable desorbing nitrate species exhibits frequencies of 1530/1285 cm^{-1}; these values are in between the frequencies observed

for bidentate nitrates of types II and III (top trace in Fig. 10).

B.4. Reoxidation of the Surface

DRIFT spectra recorded *after* TPRD (not shown) exhibit broad and intense bands in the region of Cr=O stretching vibrations around 1000 cm^{-1}, both for reduced crystalline and amorphous chromia. These features give evidence for an extensive reoxidation of the chromia surfaces, by decomposition of NO into N$_2$ or N$_2$O.

Reoxidation of *crystalline* chromia *during* TPRD has only been observed in the temperature interval from 311 to 336 K (Fig. 7, second trace), as evidenced by a positive going peak around 1000 cm^{-1}. In the discussion of our results on oxidized surfaces, two reactions {(3) and (4)} have been formulated in the Appendix, which would account for the formation of N$_2$O, NO$_2^+$, and O^{2-} at oxygen deficient sites. As we do observe both a reoxidation of the surface and a decreasing band at 2000 cm^{-1}, assigned to adsorbed NO$_2^+$, the low-temperature desorption of N$_2$O observed around 373 K in TPRD of reduced α-Cr$_2$O$_3$ (Fig. 4 of part I) is tentatively assigned to the formation of N$_2$O at oxygen-deficient sites.

Reoxidation of *amorphous* chromia mainly occurs in the temperature range from 311 to 411 K, and to a lesser extent from 411 to 461 K, as evidenced by positive-going bands around 1000 cm^{-1} in the ratioed spectra of Figs. 9 and 10. Extensive reoxidation of the surface below 423 K can also be inferred from the strong rise in intensity of the Cr=O stretching band at 1000 cm^{-1} in the 411 K spectrum (bottom trace, Fig. 10), as compared to the 311 K spectrum (bottom trace, Fig. 9). This observation agrees well with the TPRD results of N$_2$O desorption from reduced amorphous chromia, where a maximum rate of N$_2$O desorption has been observed at 423 K.

On both morphologies of reduced chromia N$_2$ desorption occurs at higher temperatures (473 K for amorphous and 523 K for crystalline chromia) than N$_2$O desorption. In this temperature interval, the only surface species observed in the DRIFT spectra (Figs. 8 and 10) are surface nitrate complexes: bridging NO$_3^-$ absorbing at 1620/1200 cm^{-1}, and bidentate nitrates II and III with bands around 1550 and 1280 cm^{-1}. This suggests that at higher temperatures, N$_2$ is produced by the decomposition of the most stable surface nitrate complexes, according to Scheme 1. This process leads to a reoxidation of coordinatively unsaturated Cr ions, as has been demonstrated mainly for amorphous chromia (positive bands at 1000 cm^{-1} in the second and third traces of Fig. 10).

SUMMARY AND CONCLUSIONS

A. OXIDIZED CHROMIA SURFACES

The results of our spectroscopic experiments are in good agreement with the TPRD experiments for NO ad- and desorption on oxidized crystalline and amorphous chromia. Desorption of NO occurs up to 573 K on α-Cr$_2$O$_3$, and up to 473 K on amorphous chromia.

The most abundant species on both surfaces are nitrato complexes, formed by the reaction of NO with surface oxygens.
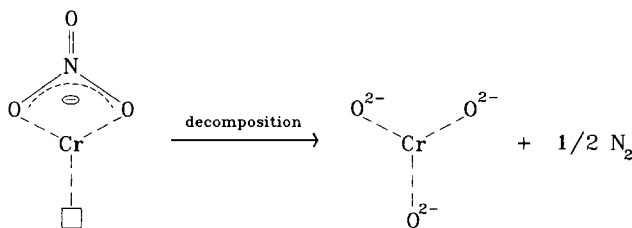
SCHEME 1

Up to six different surface nitrate complexes have been differentiated on the two morphologies (cf. Table 1), which exhibit widely different thermal stabilities. This spread in thermal stability distribution is the origin of the broad NO desorption bands observed in TPRD.

NO is *not* decomposed to N_2O or N_2 on the *oxidized* surfaces of crystalline and amorphous chromia. Both surfaces are saturated with surface oxygen, such that there is no driving force for a reoxidation of the surface by NO decomposition. Rather, NO is molecularly desorbed from both crystalline and amorphous surfaces. This process is depicted in Scheme 2.
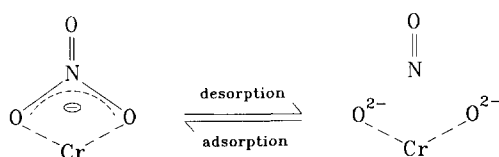
SCHEME 2

B. REDUCED SURFACES

Dominant bands appearing upon NO adsorption are again due to surface nitrate complexes. From this observation we conclude that even after reduction at 350°C in hydrogen for 1 hr, the surface oxygen concentration is sufficiently high to form the nitrates. Thus NO appears to preferentially react with the Lewis-basic surface oxygen ions. The lower intensity of the bands due to bridging nitrates, as compared to the oxidized surface state, demonstrates that significant amounts of oxygen have been removed from the surface by the reduction process.

NO decomposition, to yield N_2 and N_2O, already takes place during adsorption at room temperature, as can be inferred from increasing absorptions around 1000 cm^{-1} (cf. Fig. 6). This fact shows that the reduced surfaces are very reactive. Preferred reaction is suggested to occur at coordinatively unsaturated Cr ions, which leads to an im-

mediate reoxidation of the surface. As a consequence of the extended NO adsorption period of 1 hr, NO can also react with reoxidized surface sites formed in the first step mentioned above, to produce surface nitrates.

Bands due to adsorbed NO (both di- and mononitrosyl complexes, cf. Table 1) are found on both morphologies of chromia. Although the intensities are somewhat higher than the ones recorded on oxidized surfaces, the NO bands are still very weak as compared to the nitrate signals. This suggests that NO is immediately decomposed at coordinatively unsaturated Cr sites.

Hydroxyl groups are consumed upon NO adsorption onto reduced chromia. The concomitant formation of a surface nitro complex ($Cr-NO_2$), which is most dominant on amorphous chromia, has been attributed to a reaction of NO adsorbed at coordinatively unsaturated Cr sites with neighboring OH^- groups, to produce N_2 and NO_2^-.

In agreement with the TPRD of N_2O, extensive reoxidation is observed in the 311–411 K temperature interval on *reduced amorphous* chromia. For *crystalline* chromia, reoxidation has been observed to a much lesser extent in the 311–336 K interval.

At temperatures above 473 K, the thermally most stable species on both morphologies are bridging NO_3^- (type II) and bidentate NO_3^- (types II and III). N_2 desorption (on crystalline and amorphous chromia) and N_2O desorption (observed on crystalline chromia only) are the dominant processes in the corresponding TPRD experiment described in part I (*3*). This suggests that surface nitrates are decomposed at higher temperatures, to produce N_2, N_2O, and surface oxygen.

A weak reoxidation of the surface has been observed for amorphous chromia also at higher temperatures, but not for the crystalline morphology. This is explained in terms of the high affinity of amorphous chromia to bind oxygen at the surface (*1–5*).

APPENDIX: ASSIGNMENT OF BANDS AROUND 2000 cm^{-1}

On the oxidized surface of crystalline chromia (bottom trace of Fig. 1) a broad band is observed around 2000 cm^{-1}. This vibration can hardly be seen on the amorphous sample. From α-Cr$_2$O$_3$ the corresponding species desorbs at low temperatures (Fig. 2, third and fourth traces). A second burst of desorption is detected at this frequency at higher temperatures (Fig. 3, top trace).

Although on amorphous chromia this feature is hardly observable at ambient temperature, it desorbs throughout the entire temperature interval scanned in the spectra of Figs. 4 and 5, be it in a low quantity.

Chao and Lunsford (*10*) have studied the adsorption of small quantities of NO$_2$ onto Y-type zeolites and have assigned a broad band around 2000 cm^{-1} to an NO$_2^+$ surface species. As for the production of NO$_2^+$, two reactions may be formulated:

(a) Decomposition of surface nitrates would yield NO$_2^+$ and surface oxygen ions,

$$NO_3^- \rightarrow NO_2^+ + O^{2-}, \qquad (3)$$
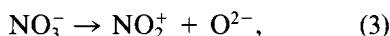
in a reaction which is likely to proceed at higher temperatures (cf. Figs. 3 and 5).

(b) A disproportionation reaction of NO at centers with an O^{2-} deficiency would yield both N$_2$O and NO$_2^+$, according to the overall reaction

$$8\ NO \rightarrow 3\ N_2O + 2\ NO_2^+ + O^{2-}. \quad (4)$$
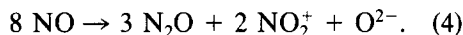
This process would account for the production and desorption of N$_2$O observed at temperatures above 523 K on both morphologies.

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