

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

### I. Characterization by Temperature-Programmed Reaction and Desorption

H. E. CURRY-HYDE,<sup>1,\*</sup> HANS MUSCH, A. BAIKER,<sup>2,\*</sup>  
M. SCHRAML-MARTH,<sup>†</sup> AND A. WOKAUNT<sup>†</sup>

*\*Department of Chemical Engineering and Industrial Chemistry Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland; and †Physical Chemistry II, University of Bayreuth D-85580 Bayreuth, Germany*

Received February 27, 1991; revised July 29, 1991

Amorphous and crystalline chromia catalysts used for the selective catalytic reduction (SCR) of NO by NH<sub>3</sub> have been characterized using temperature-programmed reaction and desorption of preadsorbed NO and NH<sub>3</sub>. The acidity of the Lewis acid sites and the associated labile oxygen species are investigated using NH<sub>3</sub> as a probe molecule. The degree of coordinative unsaturation of these sites is inferred from the reactions of NO. The effects of reduction, oxidation, and SCR treatment on the state of the Lewis acid sites and the labile oxygen are discussed. Lewis acid sites on crystalline chromia are more acidic than those on amorphous chromia. Different labile oxygen species are discernable based on their oxidizing strengths and the products formed. All labile oxygen is readily removed by reduction; SCR treatment leads to the partial removal of labile oxygen from both morphologies of chromia. The degree of lability of the different oxygen species is related to the morphology of the chromia. The proportions of one- and twofold coordinatively unsaturated sites (1 and 2 c.u.s.) depends strongly on the morphology of the chromia and its pretreatment. Both types of sites show distinct differences in the acidity dependent on the morphology of the chromia. The most significant difference between the two morphologies is seen after SCR treatment. Crystalline chromia shows a very high density of 1 c.u.s. compared to amorphous chromia. These sites are generated from 2 c.u.s. by abstraction of oxygen from NO. Implications of these results on the SCR reaction are discussed. © 1992 Academic Press, Inc.

### 1. INTRODUCTION

It has been shown recently (1, 2) that amorphous chromia has unexpectedly high activity and selectivity at low temperature for the reduction of NO to N<sub>2</sub> by NH<sub>3</sub> in excess O<sub>2</sub> compared to that of crystalline  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>. The specific activity of the two morphologies of chromia showed that the rate of NO reduction to N<sub>2</sub> on the amorphous chromia surface is about four times higher than that on the crystalline chromia

surface. The amorphous chromia was found to selectively reduce NO to N<sub>2</sub> whereas the crystalline chromia produced N<sub>2</sub> and N<sub>2</sub>O together with a high degree of NH<sub>3</sub> oxidation. Other studies using  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> (3–5) confirm that in the crystalline state the chromia catalyst is nonselective to the production of N<sub>2</sub>, and in some cases a higher selectivity to N<sub>2</sub>O is reported. The differences in catalytic characteristics of the two catalysts were proposed to be due to the differences in their morphology.

The unusual catalytic properties of amorphous chromia have been known for some time (6), but have not been previously reported for the reduction of NO by NH<sub>3</sub> in O<sub>2</sub>. For this reason, little is known about the

<sup>1</sup> Present address: School of Chemical Engineering and Industrial Chemistry, University of New South Wales, PO Box 1, Kensington, 2033, Australia.

<sup>2</sup> To whom correspondence should be addressed.

interaction of the catalyst and the components NO, NH<sub>3</sub>, and O<sub>2</sub>, to which it is exposed. On the other hand  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>, in supported form and in its bulk state, has been studied using a variety of techniques. These studies have provided information about the adsorption sites on the  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> surface as well as the nature of the adsorbed species. NO (7-9) has been shown to be a useful probe molecule for the detection of Lewis acid sites. NH<sub>3</sub> (6, 10) has been used to detect a broad range of acidic sites and to determine the nature of the labile oxygen on the surface (11).

Studies using infrared spectroscopy have shown that the adsorption of NO on the surface of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> results in the formation of at least four adsorbed species. The sites responsible for this multiplicity of adsorption states are generally agreed to be the chromium ions in various coordination states. Adsorption on five-fold coordinated chromium ions leads to a linear mononitrosyl species (8) that could coordinate to a neighboring O<sup>2-</sup> ion to form a chelate complex (9). The form of the adsorbed complex formed on fourfold coordinated chromium ions is not agreed on. Kugler *et al.* (9) described the adsorbed species as a *cis*-N<sub>2</sub>O<sub>2</sub> dimer of NO. Ghiotti *et al.* (8) have, however, assigned the same infrared bands to *cis*-dinitrosyl species, whose characteristic bands are dependent on the pressure of NO. This study was, however, carried out using chromium oxide supported on silica with a 2+ oxidation state of the chromium ion. Other studies of supported chromia show that the 2+ state is readily stabilized by SiO<sub>2</sub> (12) and Al<sub>2</sub>O<sub>3</sub> (13) supports, whereas, on bulk chromia the oxidation state is not believed to go below 3+ (14, 15). This will clearly influence the adsorption site and could explain the discrepancy between the results of Kugler *et al.* (9) and Ghiotti *et al.* (8).

The studies using NH<sub>3</sub> have shown that the adsorption site is a chromium-oxygen ion couple (10) formed by the dehydroxyla-

tion of the chromia surface and the exposure of coordinatively unsaturated ions. Two adsorbed species appear to be formed, one through coordinative adsorption and the other through heterolytic dissociative adsorption. Temperature-programmed desorption of the adsorbed species indicates that two desorptions take place. The nature of the desorbing species was not determined. Temperature-programmed surface reaction studies (11) of oxygen-pretreated chromia indicate that two products, N<sub>2</sub> and N<sub>2</sub>O, are formed when preadsorbed NH<sub>3</sub> reacts with O<sub>s</sub>, a surface oxygen species. Other studies investigating the nature of the labile oxygen have found two species of oxygen present on the surface (16, 17) that are differentiated by the oxidizing power of the species.

It is clear from the above discussion that NO and NH<sub>3</sub> can be used as probe molecules to obtain information about the adsorption sites on the chromia surface. This information is a prerequisite to understanding the reason for the high activity and selectivity of the amorphous chromia surface compared to the crystalline chromia.

In the present work, the interaction of NO and NH<sub>3</sub> with differently pretreated chromia surfaces is studied using temperature-programmed reaction and desorption (TPRD) methods. Special emphasis is given to the elucidation of the different adsorption behaviors of these species on amorphous and crystalline chromia. In parts II and III (18, 19) of this series the knowledge gained by the surface reaction and desorption studies will be complemented using vibrational spectroscopy that provide more detailed insight into the structure of the adsorbed species and the changes of the surface structure induced by them.

## 2. EXPERIMENTAL

### *Catalyst Preparation*

The amorphous chromia catalyst was prepared by a slow addition over 10 h of 150 ml of 1 M ammonium solution in 700 ml of 0.071

mol/liter chromium nitrate solution. The crystalline chromia was prepared by rapid addition of 150 ml of 1 M ammonium solution over 30 min to 700 ml 0.071 mol/liter chromium nitrate solution. The resulting gel was washed thoroughly with distilled water, then dried at 60°C for 24 h before heating to 380°C in H<sub>2</sub> for 3 h. The crystalline chromia was olive green in color with a surface area of 86 m<sup>2</sup>/g and the amorphous chromia was dark green with a surface area of 254 m<sup>2</sup>/g. More details on the characterization of these catalysts have been reported previously (1, 2).

#### *Temperature-Programmed Reaction and Desorption*

TPRD was typically carried out using 100 mg of catalyst weighed into a micro-U-tube reactor. The following steps were then carried out before the TPRD was performed.

*Pretreatment.* The chromia was pretreated in one of three ways: (i) By reduction in 6% H<sub>2</sub>/Ar using a temperature program of 10°C/min from 25 to 380°C for 1 h (TPR); (ii) by oxidation in 7% O<sub>2</sub> using a temperature program of 10°C/min from 25 to 200°C for 1 h (TPO); or (iii) by using the catalyst to perform the reduction of NO with NH<sub>3</sub> in the presence of O<sub>2</sub> (SCR). After the pretreatment the catalyst was purged with He at 200°C for 1 h.

*Adsorption.* The probe molecule (NO or NH<sub>3</sub>) was then adsorbed from a flowing gas stream at 1 atm and 25°C. The mol fraction of the adsorbate was  $3.5 \times 10^{-3}$  (3500 ppm) in argon. Once equilibrium with the adsorbate was reached the gas stream was switched to pure Ar. This typically took place after 1 h. The pure Ar stream was flushed at 25°C for 30–60 min to purge the apparatus of free adsorbate after which the TPRD could be started.

*TPRD.* The temperature programmed reaction and desorption was performed by ramping the temperature of the furnace at 10°C/min from 25 to 380°C. An upper limit of 380°C was chosen to ensure that the surface

area and morphology of the amorphous chromia was not altered by the TPRD. A flow of 85 cm<sup>3</sup> (NTP)/min of Ar was passed through the catalyst bed in the micro-U-tube reactor. The evolved gases carried out of the reactor by the Ar stream were then analyzed continuously using a Balzers QMA 112A quadrupole mass spectrometer with an axial beam ion source and a 90° off-axis secondary electron multiplier. The effluent gas was sampled through a glass capillary at a rate of 8.9 cm<sup>3</sup> (NTP)/min. The mass spectrometer was controlled by a PC computer using the program QMACON (20) for the mathematical analysis of the data. With this arrangement the instrument was able to be calibrated, and quantitative analysis for NH<sub>3</sub>, H<sub>2</sub>O, N<sub>2</sub>, NO, O<sub>2</sub>, Ar, N<sub>2</sub>O was able to be performed. Analysis for NO<sub>2</sub> was also made; however, this could not be performed quantitatively due to fragmentation reactions that occur with the NO<sub>2</sub> on the hot ion source. More detailed descriptions of the analytical techniques and the apparatus will be reported elsewhere (20).

All the desorption rates reported in this paper have been calculated using the gas composition, as determined by the gas analysis, and the total flow from the exit of the reactor. The desorption rates have been referred to the surface area of the sample to facilitate the comparison of the two samples which have different surface areas. The desorption resulted in no more than 3000 ppm of desorbing gas in the Ar carrier gas stream; consequently the carrier gas flow rate could be regarded as being constant during the experiments.

### 3. RESULTS

#### 3.1 TPRD AFTER AMMONIA ADSORPTION

##### *Morphology Comparison*

*After oxidation.* In Fig. 1 (left) the TPRD after NH<sub>3</sub> adsorption are compared for both *amorphous* and *crystalline* chromia pretreated in oxygen. The desorption rates of NH<sub>3</sub>, N<sub>2</sub>, N<sub>2</sub>O, and H<sub>2</sub>O are plotted as a

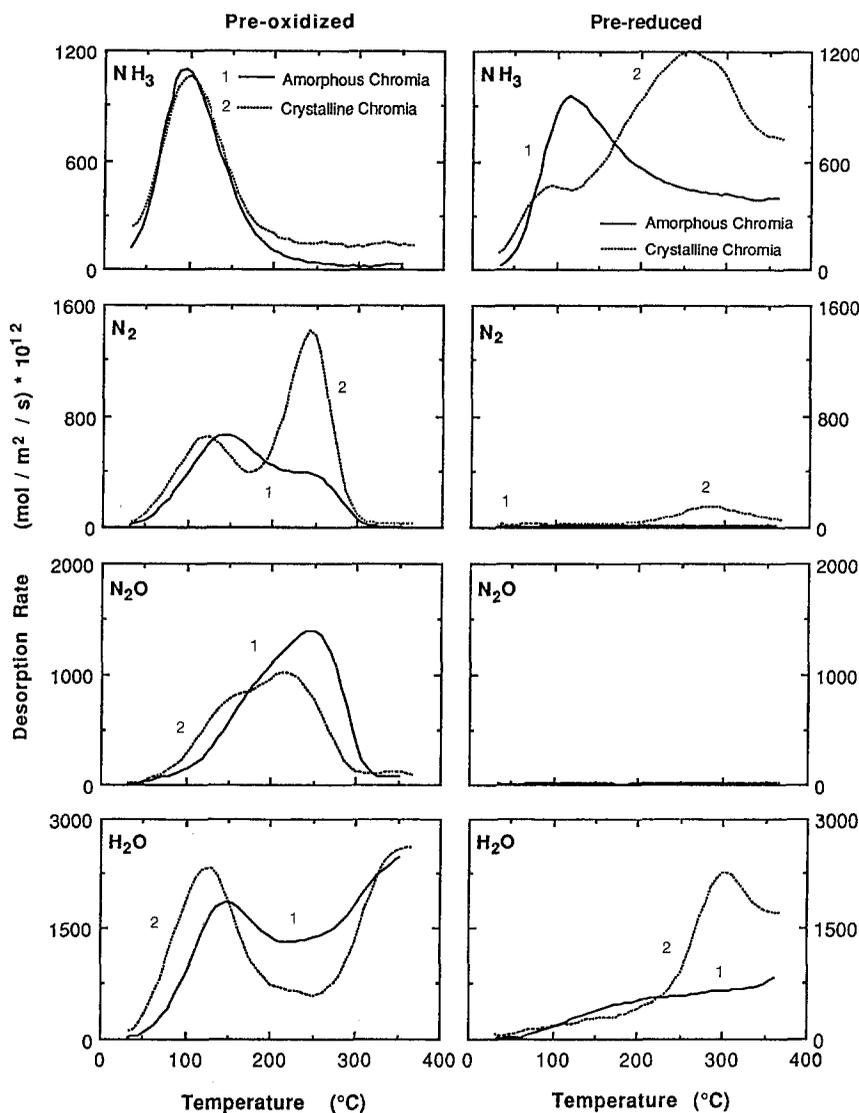


FIG. 1. The effect of morphology on the TPRD spectra after ammonia has been adsorbed on preoxidized (left) and prerduced (right) crystalline and amorphous chromia. Adsorption from carrier gas of 3500 ppm  $\text{NH}_3$  in Ar at 1 atm, temperature program rate at  $10^\circ\text{C}/\text{min}$  with Ar carrier gas flow rate at  $85 \text{ cm}^3$  (NTP)/min.

function of temperature.  $\text{NH}_3$  desorption occurs first with maximum rate at  $100^\circ\text{C}$ . The  $\text{NH}_3$  desorption rates, as a function of temperature, are the same on both morphologies of chromia.

Above  $100^\circ\text{C}$  the adsorbed  $\text{NH}_3$  begins to react with labile oxygen on the surface forming  $\text{N}_2$  and  $\text{N}_2\text{O}$ . Both the amorphous

and the crystalline chromia show two distinct  $\text{N}_2$  desorption rate maxima at  $115\text{--}140^\circ\text{C}$  and  $250^\circ\text{C}$ . On the amorphous chromia the low-temperature desorption of  $\text{N}_2$ , at  $140^\circ\text{C}$ , is dominant. On the crystalline chromia the high-temperature  $\text{N}_2$  desorption, at  $245^\circ\text{C}$ , is the dominant desorption mode. The desorption of  $\text{N}_2\text{O}$  appears to be

similar for both morphologies of chromia with the maximum rate occurring at 245°C for amorphous chromia and 212°C for crystalline chromia and with the broad shoulder occurring at 195 and 160°C, respectively. H<sub>2</sub>O desorption occurs together with the low-temperature NH<sub>3</sub> desorption; in addition, high-temperature desorption of H<sub>2</sub>O that is incomplete at 380°C takes place.

*After reducing.* Figure 1 (right) compares the TPRD spectra after NH<sub>3</sub> adsorption on previously reduced amorphous and crystalline chromia. The NH<sub>3</sub> appears to be adsorbed with two strengths on both morphologies of the reduced chromia. The weakest bound NH<sub>3</sub>, which desorbs with maximum rate at 100°C, is dominant on the amorphous chromia. The strongest bound state, which has a desorption rate maximum at 260°C, dominates on the crystalline chromia. No reactions of NH<sub>3</sub> with labile oxygen occur on either sample between 25 and 380°C. H<sub>2</sub>O desorption from the reduced chromia occurs at high temperature only with the crystalline chromia showing a distinct desorption at 300°C.

#### *Pretreatment Comparison*

*On amorphous chromia.* Figure 2 (left) compares the TPRD spectra after adsorption of NH<sub>3</sub> on amorphous chromia pretreated by SCR, reduction, or oxidation. The characteristics of NH<sub>3</sub> desorption from SCR pretreated amorphous chromia appear to be intermediate to the NH<sub>3</sub> desorption after the oxidation and reduction pretreatments. The high-temperature desorption tail found for the *reduced* chromia is not reproduced on the SCR-pretreated chromia.

The N<sub>2</sub> desorption produced by the reaction of NH<sub>3</sub> with labile oxygen occurs only at high temperature ( $T_{\max}$  at 290°C) on the SCR-pretreated chromia, two desorption maxima are observed at 150 and 250°C from the *preoxidized* chromia, and no N<sub>2</sub> desorption is found from the *prereduced* sample. The desorption of N<sub>2</sub>O from the SCR-pretreated chromia occurs in a similar temperature range ( $T_{\max}$  at 250°C) to the preoxidized

chromia, but at a significantly lower rate. The prereduced chromia, by comparison, indicates no oxidation of NH<sub>3</sub> to N<sub>2</sub>O. Only the SCR and preoxidized chromia show low-temperature H<sub>2</sub>O desorptions and all pretreatments show an increasing background of water at high temperature.

*On crystalline chromia.* Figure 2 (right) shows the TPRD after NH<sub>3</sub> adsorption for crystalline chromia after SCR, reduction, and oxidation pretreatments. NH<sub>3</sub> appears to be weakest bound on the preoxidized crystalline chromia and desorbs from a single adsorption state with maximum rate at 100°C. On the prereduced crystalline chromia, the NH<sub>3</sub> desorbs from two adsorption states. A small proportion is weakly bound and desorbs with maximum rate at 90°C and the major fraction is strongly bound and desorbs with maximum rate at 260°C. On the SCR-pretreated chromia NH<sub>3</sub> appears to desorb from both adsorption states with equal rates.

On the SCR-pretreated crystalline chromia, oxidation of NH<sub>3</sub> to N<sub>2</sub> occurs only at high temperature ( $T_{\max}$  at 210°C), whereas on the preoxidized crystalline chromia, oxidation occurs with two rate maxima at 120 and 240°C. On the reduced crystalline chromia oxidation of NH<sub>3</sub> to N<sub>2</sub> does not occur to any significant extent. Oxidation of NH<sub>3</sub> to N<sub>2</sub>O does not appear to take place on the crystalline chromia after SCR or reduction pretreatment; however, after oxidation the reaction occurs readily and two rate maxima are observed at 150 and 220°C. Only the oxidized chromia shows a low-temperature desorption of H<sub>2</sub>O; however, both the reduced and SCR-treated chromia show high-temperature desorptions. All pretreatments show an increasing background of H<sub>2</sub>O desorption taking place at high temperature.

Figure 3 presents the total amounts of each component desorbed per square meter surface area between 25 and 380°C. These have been determined by integration of the desorption peaks. Figure 3a shows that the oxidized and the SCR-pretreated samples of

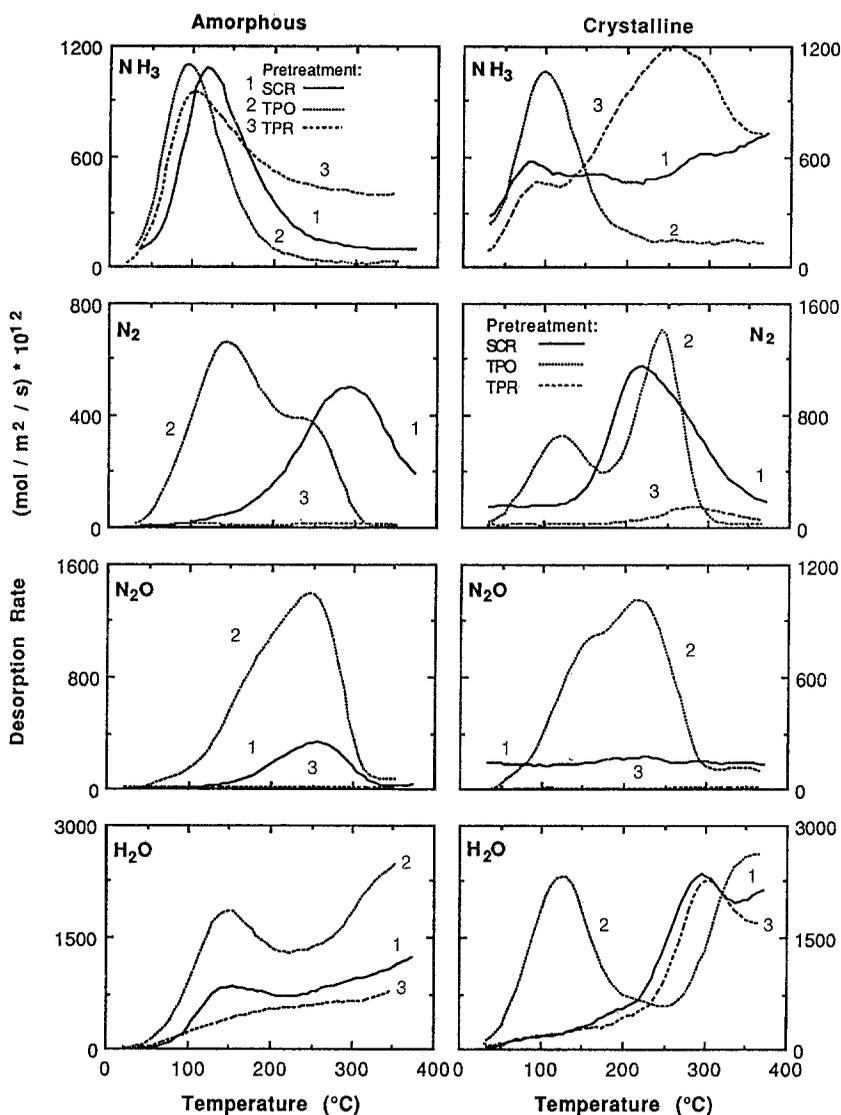


FIG. 2. The effect of pretreatment on the TPRD spectra after NH<sub>3</sub> had been adsorbed on amorphous chromia (left) and crystalline chromia (right). Samples were pretreated by TPR, TPO, and use as a catalyst for the reduction of NO by NH<sub>3</sub> in excess oxygen (SCR). Adsorption from carrier gas of 3500 ppm NH<sub>3</sub> in Ar at 1 atm, temperature program rate at 10°C/min with Ar carrier gas flow rate at 85 cm<sup>3</sup> (NTP)/min.

both morphologies desorb similar amounts of NH<sub>3</sub>. Reduction of both samples, however, increases the amount of NH<sub>3</sub> desorbed. It can be seen in Fig. 3e that this, however, does not represent an increase in the total amount of NH<sub>3</sub> adsorbed. The total

NH<sub>3</sub> adsorbed, calculated from the elemental balance over all nitrogen-containing species observed in the desorption studies, is in fact lowest for the reduced sample.

The amount of N<sub>2</sub> (Fig. 3b) produced is about 20% higher after oxidation and about

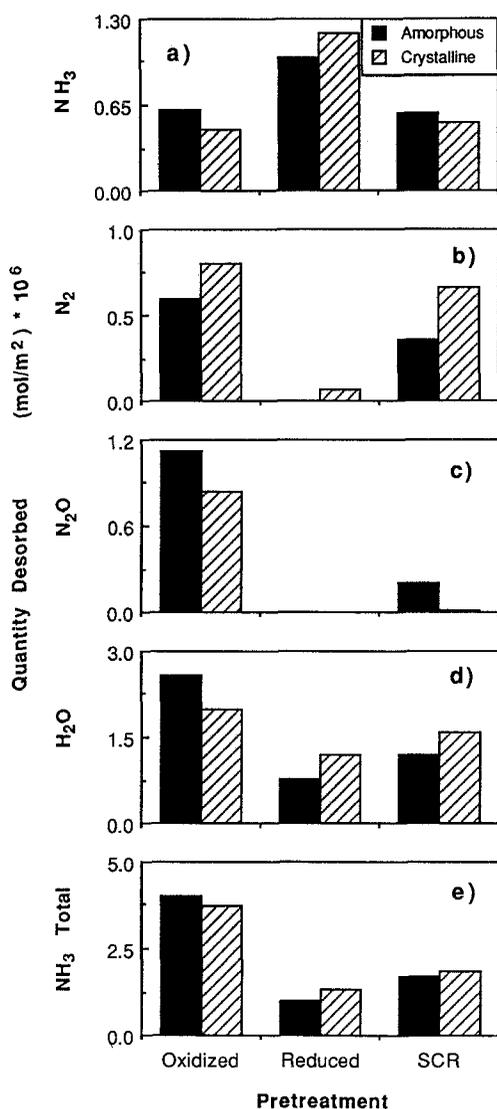


FIG. 3. Quantities of  $\text{NH}_3$  and decomposition components desorbed during TPRD period from crystalline and amorphous chromia. Quantities determined by integration of desorption spectra in Figs. 1 and 2 between 25 and 380°C.

40% higher after SCR pretreatment for the crystalline chromia compared to the amorphous chromia. The opposite is true for the production of  $\text{N}_2\text{O}$  (Fig. 3c), which is produced in greater amounts on the amorphous chromia after oxidation and SCR pretreat-

ment. The difference is most significant after SCR pretreatment when the crystalline chromia produces almost no  $\text{N}_2\text{O}$ .

### 3.2. TPRD AFTER NITRIC OXIDE ADSORPTION

#### *Morphology Comparison*

*After reduction.* TPRD after NO adsorption is compared for previously reduced amorphous and crystalline chromia in Fig. 4 (left). The desorption of NO occurs from two adsorption states on the crystalline chromia resulting in a desorption peak at 105°C and a broad shoulder on the peak at 180°C. The dominant adsorption state is indicated by the desorption peak at lower temperature. On the amorphous chromia, NO is also adsorbed in more than one state as evidenced by the broad desorption rate maximum at 100°C and the tailing off in desorption rate on the high-temperature side of the peak maximum.

Decomposition of NO results in the desorption of  $\text{N}_2$  and  $\text{N}_2\text{O}$ . Decomposition to  $\text{N}_2$  occurs with maximum rate at 205°C for the amorphous chromia and at 250°C for the crystalline chromia. No simultaneous  $\text{O}_2$  desorption is observed. The formation of  $\text{N}_2\text{O}$ , on the crystalline chromia, takes place on two distinct sites with rate maxima at 105 and 195°C. On the amorphous chromia the decomposition of NO to  $\text{N}_2\text{O}$  occurs over a broad range of temperatures on the low-temperature side of the rate maximum, which appears at 160°C.  $\text{H}_2\text{O}$  desorption appears to be independent of morphology except at high temperature where the increase in desorption rate from crystalline chromia is greater than that for amorphous chromia.

*After oxidation.* Figure 4 (right) depicts, the TPRD after NO adsorption on previously oxidized chromia samples. NO desorption takes place at low temperature on both morphologies of chromia. Significantly more NO desorbs from the crystalline chromia than from the amorphous chromia. Insignificant amounts of  $\text{N}_2$  and  $\text{N}_2\text{O}$  are desorbed from either of the two morpholog-

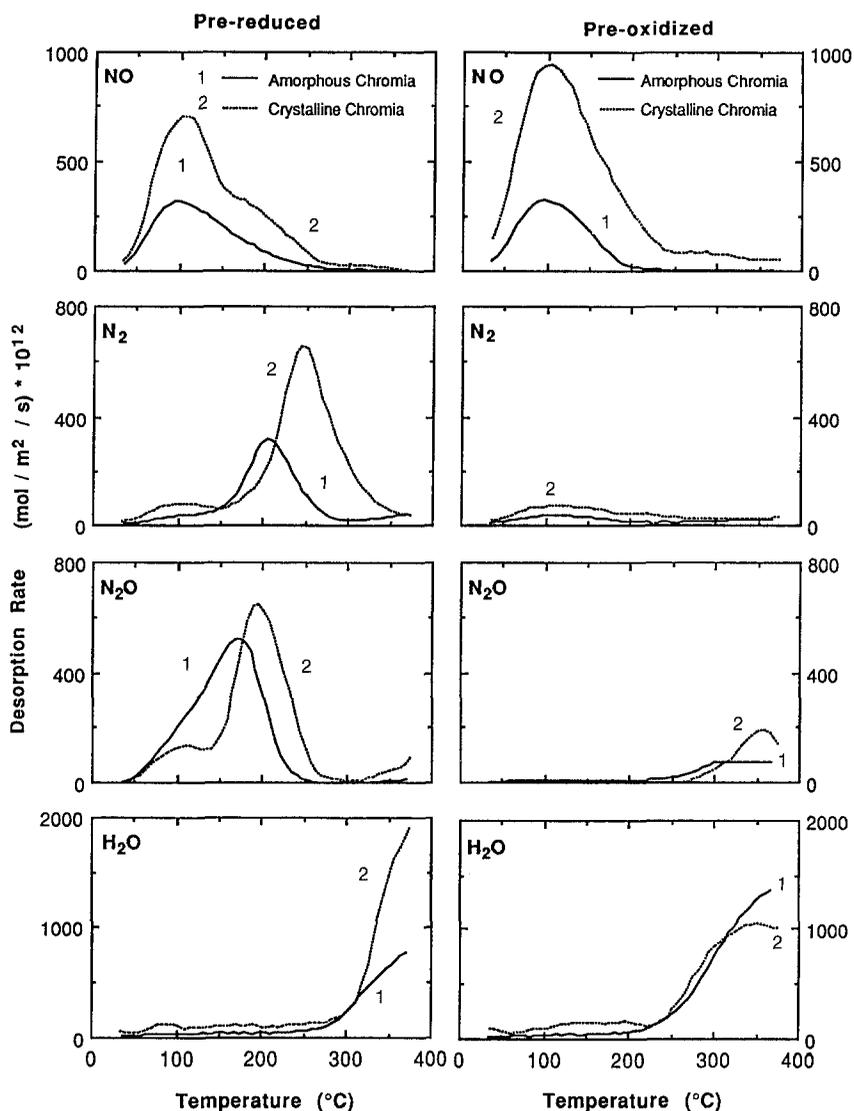


FIG. 4. The effect of morphology on the TPRD spectra after nitric oxide had been adsorbed on preoxidized (right) and prerduced (left) crystalline and amorphous chromia. Adsorption from carrier gas of 3500 ppm  $\text{NH}_3$  in Ar at 1 atm, temperature program rate at  $10^\circ\text{C}/\text{min}$  with Ar carrier gas flow rate at  $85 \text{ cm}^3$  (NTP)/min.

ies of chromia. No low-temperature  $\text{H}_2\text{O}$  desorption results from the oxidized samples until high temperatures and the effect of morphology appear to be insignificant.

#### Pretreatment Comparison

*On amorphous chromia.* Figure 5 (left) compares the TPRD spectra after NO ad-

sorption for amorphous chromia after SCR, reduction, and oxidation pretreatments. The desorption of NO from the amorphous chromia appears not to be influenced by the pretreatment of the sample. All samples display a single desorption peak between  $95$  and  $100^\circ\text{C}$ , and only the SCR-pretreated amorphous chromia displays a high-temper-

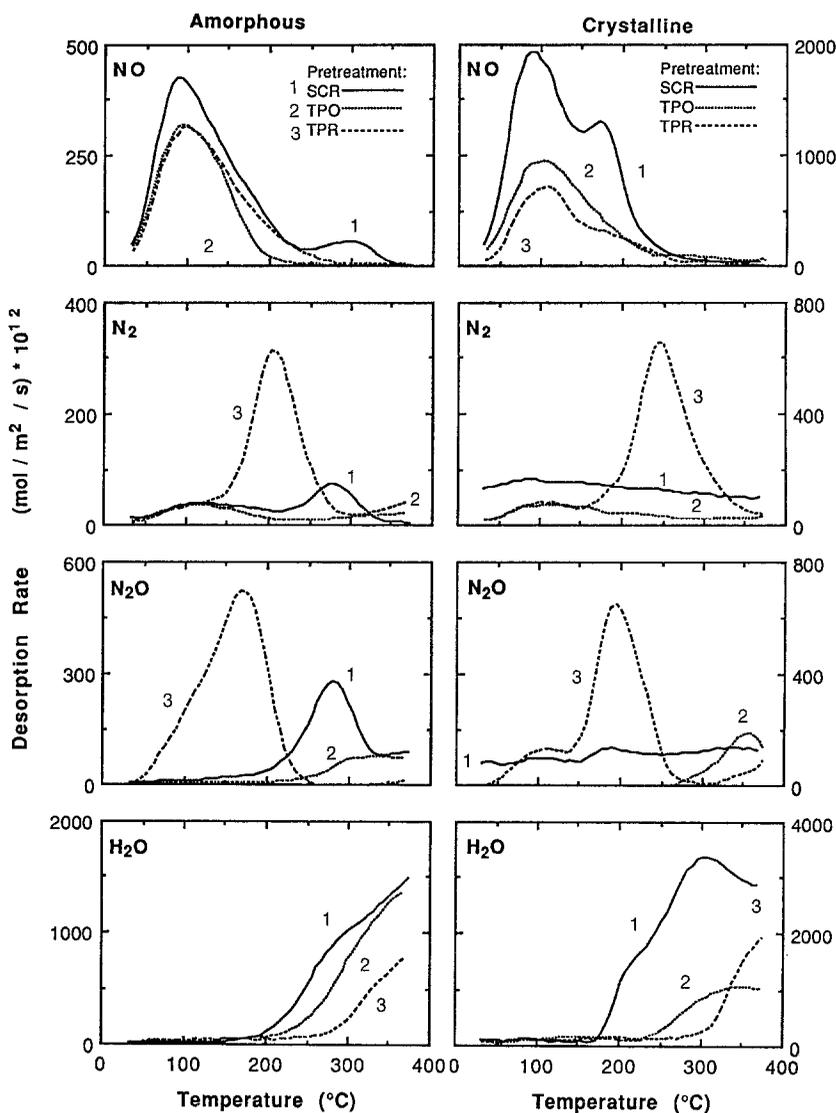


FIG. 5. The effect of pretreatment on the TPRD spectra after NO had been adsorbed on amorphous chromia (left) and crystalline chromia (right). Samples were pretreated by TPR, TPO, and use as a catalyst for the reduction of NO by  $\text{NH}_3$  in excess oxygen (SCR). Adsorption from carrier gas of 3500 ppm NO in Ar at 1 atm, temperature program rate at  $10^\circ\text{C}/\text{min}$  with Ar carrier gas flow rate at  $85\text{ cm}^3$  (NTP)/min.

ature desorption state at  $300^\circ\text{C}$ . The decomposition of NO to  $\text{N}_2$  on the SCR-pretreated chromia occurs to a limited extent with maximum rate at  $290^\circ\text{C}$ . In comparison, on the reduced chromia decomposition occurs to a greater extent and with maximum rate at  $200^\circ\text{C}$ , and on the oxidized chromia, no decomposition occurs.

A similar result to that described above is found for the decomposition of NO to  $\text{N}_2\text{O}$ . The decomposition takes place at a much higher temperature ( $T_{\text{max}}$  at  $290^\circ\text{C}$ ) and to a lesser extent on the SCR-pretreated sample compared to the reduced sample ( $T_{\text{max}}$  at  $170^\circ\text{C}$ ).

*On crystalline chromia.* TPRD after NO

adsorption on crystalline chromia is compared in Fig. 5 (right) after SCR, reduction, and oxidation pretreatments. The desorption of NO occurs at maximum rate at 100°C for each pretreatment of the crystalline chromia. Desorption from the SCR-pretreated chromia occurs at a rate significantly higher than that from the reduced crystalline chromia. Both the reduced and SCR-pretreated samples show an additional desorption from a strongly bound state at 170°C. Decomposition of NO to N<sub>2</sub>O and N<sub>2</sub> occurs only on the reduced crystalline chromia.

Figure 6 shows the integral values of the desorbed components from the NO TPRD for the amorphous and crystalline chromia. The amount of NO desorbed from the crystalline chromia (Fig. 6a) is between 50 and 60% greater than from the amorphous chromia after oxidation and reduction pretreatment. After SCR pretreatment the NO desorption from the crystalline chromia is more than four times greater than that from the amorphous chromia.

The decomposition of NO to N<sub>2</sub> on the prerduced crystalline chromia is again 50% greater than that found for the prerduced amorphous chromia. The amount of NO decomposition to N<sub>2</sub>O (Fig. 6c) is approximately the same for both morphologies of prerduced chromia, but is larger for the amorphous chromia after SCR pretreatment.

In Fig. 6e the total amount of NO desorbed either in molecular form or as decomposition products is between 40 and 60% larger for the crystalline chromia after all pretreatments. Note that the total amount of NO desorbed from the SCR-pretreated crystalline chromia is only 10% lower than that desorbed from the reduced crystalline chromia.

#### 4. DISCUSSION

##### 4.1. TPRD AFTER AMMONIA ADSORPTION *Morphological Comparison*

Burwell *et al.* (6) described the chemisorption of NH<sub>3</sub> on chromia as a "hetero-

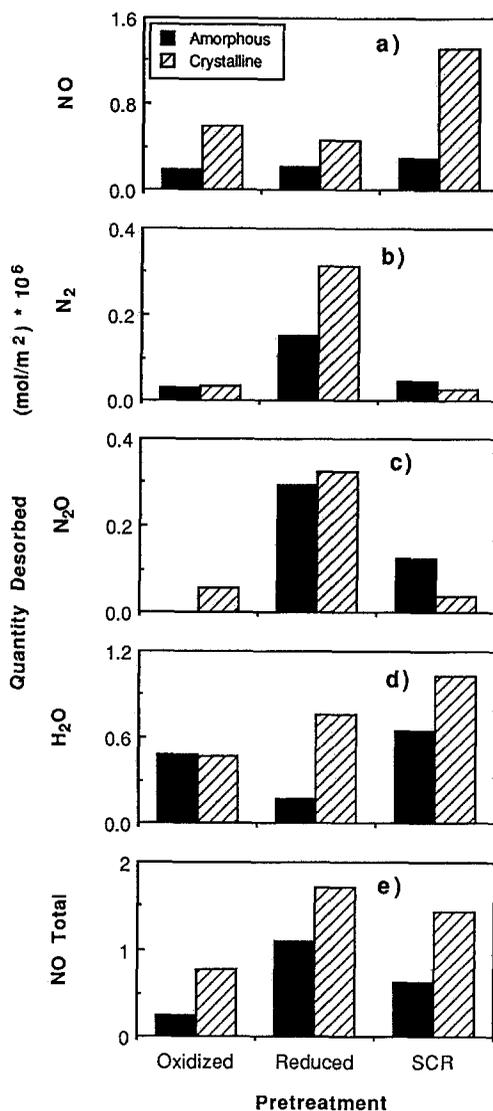


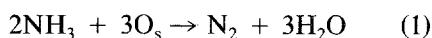
FIG. 6. Quantities of NO and decomposition components desorbed during TPRD period from crystalline and amorphous chromia. Quantities determined by integration of desorption spectra in Figs. 4 and 5 between 25 and 380°C.

lytic ligand displacement adsorption," which involves the rearrangement of cation-anion pairs when the anions are displaced. This, they suggested, could occur more readily on amorphous chromia than on crystalline chromia. More recent infrared studies of the chemisorption of NH<sub>3</sub> on well-

dehydroxylated chromia have shown that this occurs on the Lewis acid sites (21–24), and at room temperature the adsorption is by coordination to the  $\text{Cr}^{3+}$  site (10). The infrared spectra at room temperature indicated the existence of two coordinatively bound species. These have been assigned to two  $\text{Cr}^{3+}$  sites of weak and strong acidity. The weakly bound species disappeared above  $100^\circ\text{C}$  and only the  $\text{NH}_3$  coordinated to the strongly acidic sites remained at  $200^\circ\text{C}$ . At  $300^\circ\text{C}$  all coordination species were removed.

The above results serve well to explain some of the features in the TPRD spectra of  $\text{NH}_3$  in Fig. 1. Ammonia desorbs intact from the surfaces of both oxidized and reduced chromia of both morphologies. On the reduced chromia there is clear evidence for the existence of two molecularly adsorbed species. These most likely correspond to the two species observed by Morishige *et al.* (10) adsorbed on a weak Lewis acid site and a strong Lewis acid site. The reduced  $\alpha\text{-Cr}_2\text{O}_3$  shows a predominance of strong Lewis acid sites compared to the amorphous chromia, which exposes predominantly weak Lewis acid sites.

The  $\text{N}_2$  and  $\text{N}_2\text{O}$  desorption occurs only from the preoxidized chromia (Fig. 1, left) and not from the prerduced chromia (Fig. 1, right). Low-temperature  $\text{H}_2\text{O}$  desorption also only occurs on preoxidized chromia. The  $\text{N}_2$  is formed by reaction of  $\text{NH}_3$  and labile oxygen according to the reaction



while the  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$  are formed by the reaction of  $\text{NH}_3$  with the oxygen species according to



The lack of reaction on the reduced chromia indicates that the labile oxygen is removed by reduction at  $380^\circ\text{C}$ . Further experiments show that heating the sample to  $200^\circ\text{C}$  in He after the reduction does not reactivate the  $\text{NH}_3$  oxidation sites. First, this suggests that the oxygen involved in the  $\text{NH}_3$  oxidation is

supplied by a reversible chemisorption of  $\text{O}_2$  from the gas phase, such as during the oxidation pretreatment, and does not come from the bulk. Second, thermal treatment does not appear to activate oxygen transfer of the bulk to the surface.

The existence of two  $\text{N}_2$  and two  $\text{N}_2\text{O}$  desorption peaks for both morphologies of preoxidized chromia indicates the presence of labile oxygen in a number of reactivity states. Kobayashi and Kanno (16) showed similar results, finding that labile oxygen on the surface could be divided into two groups, one with high oxidizing power ( $\text{O}_s^h$ ) and the other with low oxidizing power ( $\text{O}_s^l$ ). The difference in oxidizing power is most likely related to the acidity of the Lewis acid site with which the labile oxygen is associated.

The low-temperature desorption of  $\text{N}_2$  would correspond to oxygen with high oxidizing power ( $\text{O}_s^h(\text{N}_2)$ ) associated with weak Lewis acid sites. The second  $\text{N}_2$  desorption corresponds to oxygen species of low oxidizing power ( $\text{O}_s^l(\text{N}_2)$ ), which are associated with strong Lewis acid sites. The  $\text{H}_2\text{O}$  formed from this reaction does not appear to desorb until higher temperatures are reached indicating that it is strongly held by the Lewis acid sites. The comparison in Fig. 1 (left) of the amorphous and crystalline chromia, after oxidation, shows that there is more of the  $\text{O}_s^l(\text{N}_2)$  species on the crystalline chromia than on the amorphous chromia. This suggests that the crystalline chromia has a higher proportion of strong Lewis acid sites on which adsorbed labile oxygen have low oxidizing strength. These results also confirm the earlier observation for  $\text{NH}_3$  adsorption on the reduced chromia, that crystalline chromia has a higher proportion of strong Lewis acid sites.

Reaction (2) producing  $\text{N}_2\text{O}$  represents a deeper oxidation of ammonia than reaction (1) and is favored at higher temperatures. The two oxygen species that produce  $\text{N}_2\text{O}$  appear to be present on both morphologies (Fig. 1, left). These species are not likely to be the same as those involved in the reaction

producing  $N_2$ . First, one labile oxygen species leads to  $NH_3$  to produce  $N_2O$ , while the other species produces  $N_2$ . Second, the proportions of oxygen species producing  $N_2O$  are similar on both morphologies of chromia. This is not true for the oxygen species that react with  $NH_3$  oxidation to  $N_2$ . These labile oxygen species can then be labeled as two distinct species,  $O_s^h(N_2O)$  for the high-oxidizing-strength oxygen, which leads to low-temperature formation of  $N_2O$ , and  $O_s^l(N_2O)$  for the low-oxidizing-strength oxygen, which reacts at higher temperature to give  $N_2O$ .

Infrared spectroscopy studies of  $O_2$  chemisorption on crystalline chromia show the existence of as many as five species of oxygen chemisorbed on Lewis acid sites (25, 26). The chemisorbed species was suggested to be  $Cr=O$ , produced by dissociation of  $O_2$  at room temperature and the formation of covalent bonds with a chromium ion. The five species of  $Cr=O$  are said to arise from the chromium ion being in either four- or fivefold coordination states and being surrounded by different combinations of  $OH^-$  and  $O_2^-$  ligands. A recent study (27) also suggest that after oxygen pretreatment at  $400^\circ C$  the surface exposes  $4+$  and  $5+$  c.u.s. This will obviously add to the heterogeneity of adsorption and reaction sites for the  $NH_3$ .

In conclusion it can be said that the presence of at least four species of labile oxygen  $\{O_s^l(N_2), O_s^h(N_2), O_s^l(N_2O), O_s^h(N_2O)\}$  is indicated by the TPRD spectra after  $NH_3$  adsorption on the amorphous and crystalline chromia. Further support for this result emerges from vibrational spectroscopy, as shown in parts II and III (18, 19) of this series. The differences between each species are related to the acidity of the Lewis acid site on which the labile oxygen is adsorbed. From the stoichiometry of the surface reactions (1) and (2) we may infer that the sites from which  $N_2$  is desorbed must be surrounded by at least three labile oxygens and the sites from which  $N_2O$  desorbs must have at least four neighboring labile oxygen species.

### *Pretreatment Comparison*

The TPRD spectra after  $NH_3$  adsorption (Fig. 2) shows significant differences in the characteristics of the Lewis acid sites when amorphous and crystalline chromia are treated by SCR, reduction, or oxidation. On the amorphous chromia the weakly acidic Lewis acid sites appear to adsorb  $NH_3$  more strongly after SCR pretreatment than after reduction or oxidation pretreatments.  $NH_3$  desorption from high acidity Lewis acid sites, indicated by the desorption tail for the reduced amorphous chromia, is not present on the SCR-pretreated amorphous chromia. The  $NH_3$  associated with these sites appears to react with labile oxygen still present on the high acidity sites after the SCR treatment. This results in the singular, high-temperature desorptions of  $N_2$  and  $N_2O$  and indicates that only the  $O_s^l(N_2)$  and  $O_s^l(N_2O)$  species of labile oxygen are still present on the amorphous chromia after SCR treatment.

On the crystalline chromia the state of the weakly acidic sites after the SCR treatment appears to be similar to that after reduction treatment. The highly acidic sites show some desorption of  $NH_3$  (Fig. 2, right) in contrast to the amorphous chromia, which showed none. There is, however, a simultaneous oxidation of ammonia that takes place at high temperature to give a singular desorption of  $N_2$ . This indicates that, in contrast to the amorphous chromia, on the crystalline chromia highly acidic sites exist both with and without labile oxygen associated with them after SCR treatment. An additional difference is that of the four possible labile oxygen species only the  $O_s^l(N_2)$  species of labile oxygen is present on the crystalline chromia after SCR. This species has higher oxidizing strength than on the amorphous chromia indicated by the lower temperature of  $N_2$  desorption (Fig. 2).

In conclusion it appears that SCR treatment removes from both morphologies of chromia, the high oxidizing power labile oxygen ( $O_s^h(N_2)$  and  $O_s^h(N_2O)$ ) associated with weak Lewis acid sites. Both of the low oxi-

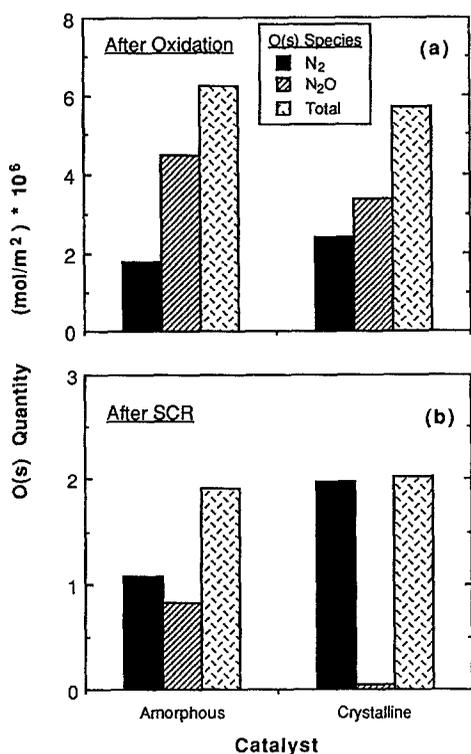


Fig. 7. Quantities of labile oxygen,  $O_s$ , present on amorphous and crystalline chromia after oxidation (a) and after use as a catalyst for SCR (b). Quantities determined from the desorbed amounts of the  $NH_3$  oxidation products,  $N_2$  and  $N_2O$  in Fig. 3.

dizing power labile oxygen species ( $O_s(N_2)$  and  $O_s(N_2O)$ ) exist on the amorphous chromia while only one ( $O_s(N_2O)$ ) exists on the crystalline chromia.

#### Distribution of Oxygen Species

It is possible to determine the quantities of the two main groups of labile oxygen species,  $O_s(N_2)$  and  $O_s(N_2O)$ , using the stoichiometries given in reactions 1) and 2), and the integral amounts of desorbed  $N_2$  and  $N_2O$  (Fig. 3). The results presented in Fig. 7 for the SCR- and oxidation-pretreated samples show that the total amounts of labile oxygen reacting with  $NH_3$  on the two morphologies are similar. The distributions between  $N_2$  and  $N_2O$  producing oxygen species are, however, markedly different.

On the preoxidized amorphous chromia

the amount  $O_s(N_2O)$  is 150% larger than the amount of  $O_s(N_2)$ , while on the crystalline chromia it is only 40% larger. The TPRD spectra in Fig. 2 shows that most of the oxygen on the amorphous chromia has high oxidation strength while most of the oxygen on the crystalline chromia has low oxidizing strength.

After SCR treatment the amorphous chromia shows similar amounts of  $O_s(N_2)$  and  $O_s(N_2O)$ . In contrast to this, all the labile oxygen on the crystalline chromia is present in the  $O_s(N_2)$  form and no  $O_s(N_2O)$  is present after SCR treatment. Comparison of the amounts of  $O_s(N_2)$  present after SCR treatment and oxidation treatment shows a 50% decrease on the amorphous chromia after SCR, whereas on the crystalline chromia there appears to be no change after SCR. The  $O_s(N_2O)$  species decreases by 80% on the amorphous chromia and by almost 100% on the crystalline chromia after SCR treatment.

It can be concluded that under SCR conditions a loss of labile oxygen occurs from different sites on the two morphologies of chromia. As a result the oxygen species,  $O_s(N_2)$ , is present in significantly higher amounts on the crystalline chromia than on the amorphous chromia after SCR treatment. On both morphologies the  $O_s(N_2)$  species is mainly in a weakly oxidizing form and on the amorphous chromia it is weaker than on the crystalline chromia. In contrast to this the  $N_2O$  producing oxygen species,  $O_s(N_2O)$ , is evident only on the SCR-treated amorphous chromia, suggesting that this oxygen species is more stable on the amorphous chromia than on the crystalline chromia.

#### 4.2 TPRD AFTER NITRIC OXIDE ADSORPTION

##### Morphological Comparison

The adsorption of NO on chromia takes place at the Lewis acid sites on the surface (7–9). Infrared studies indicate that at least two adsorbed species are formed on unsupported crystalline chromia (9) and up to four

adsorption forms are found on supported crystalline chromia (7, 8). The desorption of NO from both the reduced and oxidized chromia (Fig. 4) indicates that on some Lewis acid sites the NO is coordinatively adsorbed. The high-temperature NO desorption from reduced chromia (Fig. 4, left) indicates a bimodal acidity distribution in the Lewis acid sites. This bimodal character in the acid strength of the Lewis acid sites was also observed in the NH<sub>3</sub> desorption spectrum. The largest proportion of NO is coordinated to weakly acidic sites from which desorption occurs at low temperature. The distribution of NO between the two adsorption states is the same for both morphologies of chromia and is not significantly affected by reduction or oxidation.

The TPRD after NO adsorption shows no O<sub>2</sub> desorption between 25 and 390°C from amorphous chromia. The desorption of N<sub>2</sub> and N<sub>2</sub>O must, therefore, result from decomposition of NO and oxidation of the surface chromium ions or the filling of unsaturated Cr<sup>3+</sup> sites according to two reactions:



It appears that both reactions occur more readily on the amorphous chromia than on the crystalline chromia, but to a lesser extent. The most significant difference is seen for the reaction producing N<sub>2</sub>, which reaches maximum rate on the amorphous chromia 50°C lower than on the crystalline chromia. This suggests that after reduction the Lewis acid sites that promote the decomposition of NO to N<sub>2</sub> will more readily accept oxygen on the amorphous chromia than those on the crystalline chromia.

On both morphologies of chromia the sites resulting in the decomposition of NO to N<sub>2</sub>O are activated at temperatures 40–50°C lower than the sites producing N<sub>2</sub>. This is most likely due to the fact that only one oxygen must be accepted by the site when NO decomposes to N<sub>2</sub>O, whereas two must be accepted when NO decomposes to N<sub>2</sub>. The decomposition to N<sub>2</sub>O will then be the

more favorable reaction. The reaction stoichiometry with the Lewis acid sites also indicates that the sites on which decomposition to N<sub>2</sub>O occurs are most likely of lower acidic strength than those promoting the decomposition to N<sub>2</sub>. These results confirm that the Lewis acid sites that adsorb NO have higher acidity on amorphous chromia than on crystalline chromia. This provides further evidence of the heterogeneous nature of the Lewis acid sites.

A degree of disagreement between Ghiotti *et al.* (8) and Kugler *et al.* (9) on the form of the NO adsorption complex on 2 c.u.s. was highlighted in Section 1. The desorptions of N<sub>2</sub>O and N<sub>2</sub> observed in this study indicate that at higher temperatures a dimer complex such as the *cis*-N<sub>2</sub>O<sub>2</sub> dimer described by Kugler *et al.* (9) must form on the 2 c.u.s. from two adsorbed NO molecules. The desorption of N<sub>2</sub> results in two oxygens being left on the surface and the N<sub>2</sub>O desorption results in one oxygen being left on the surface. The desorption of NO could therefore take place from the 1 c.u.s.

The lack of N<sub>2</sub> and N<sub>2</sub>O desorption from either morphology of preoxidized chromia indicates that the oxidation pretreatment of the chromia selectively deactivates the sites on which NO decomposition of N<sub>2</sub> and N<sub>2</sub>O can occur. The oxidation pretreatment does not, however, affect the sites from which NO will desorb. This observation confirms the postulation that only the 2 c.u.s. are affected by oxygen chemisorption (9).

#### Pretreatment Comparison

The effect of SCR, oxidation, and reduction pretreatments on the amorphous chromia in Fig. 5 (left) shows that the 2 c.u.s. responsible for decomposition of NO to N<sub>2</sub> are almost all deactivated after SCR use. Only a small number of sites that react at high temperature are still exposed. The same is true for those sites producing N<sub>2</sub>O from NO decomposition.

The most striking feature of the pretreatment comparison for crystalline chromia (Fig. 5, right) is the large desorption of NO

from the SCR pretreated crystalline chromia and the complete lack of  $N_2$  and  $N_2O$  desorptions from this sample. The latter indicates that all 2 c.u.s. that produced  $N_2$  and  $N_2O$  on the reduced crystalline chromia are poisoned on the SCR-pretreated crystalline chromia and the 1 c.u.s. that chemisorb NO have been promoted on the surface.

#### Distributions of Coordinatively Unsaturated Sites

The distributions of coordinatively unsaturated sites as detected by NO decomposition and desorption can be estimated using the assignments discussed above and the integral amounts of each desorbed component reported in Fig. 6. These results are reported in Figs. 8 and 9. Figure 8 compares the effects of morphology of the chromia on the c.u.s. distribution after reduction, oxidation, and SCR pretreatments. Figure 9 compares the effects of pretreatment on the c.u.s. distribution on crystalline chromia and on amorphous chromia.

After reduction, both the 1 c.u.s. and 2 c.u.s. are more abundant on the crystalline chromia than on the amorphous chromia (Fig. 8, top), the 1 c.u.s. being more than twice as abundant. Comparison of the oxidation pretreatment to reduction pretreatment shows that the oxidative treatment (Fig. 8, middle) causes almost complete loss of 2 c.u.s. on both morphologies of chromia; insignificant change in the density of 1 c.u.s. on amorphous chromia; and a slight increase in density of 1 c.u.s. on the crystalline chromia. From these results it is clear that  $O_2$  chemisorbs on the 2 c.u.s. thereby preventing NO from using these sites for dissociation. This also confirms the observations made by Kugler *et al.* (9) that the chemisorption of  $O_2$  prevents the formation of some of the adsorption complexes of NO.

Treatment under SCR conditions (Fig. 8, bottom) results in a large increase in the number of 1 c.u.s. on the crystalline chromia and a small increase on amorphous chromia. The increase in 1 c.u.s. is accompanied by a decrease in the number of 2 c.u.s. on both

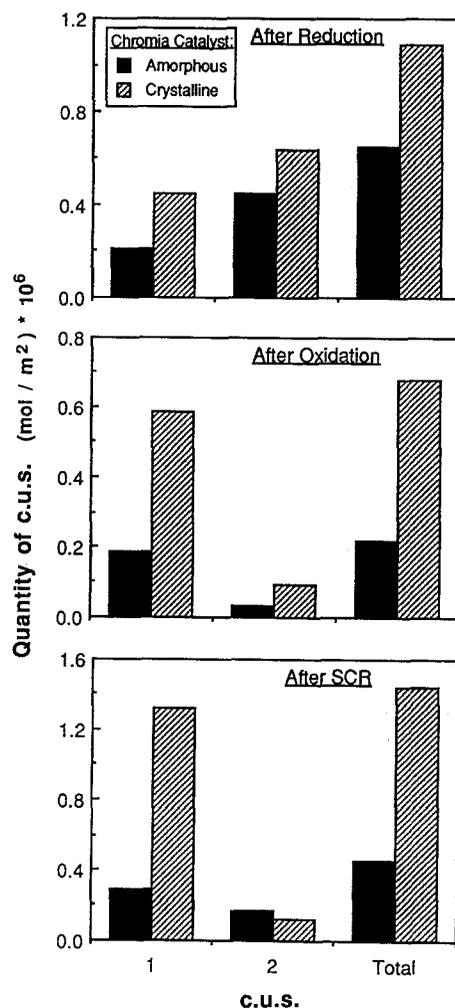


Fig. 8. The effect of morphology on the number of coordinatively unsaturated sites (c.u.s.) present on the chromia samples after reduction, oxidation, and use as a catalyst for SCR. The number of c.u.s. was determined from the quantities of desorbed NO and its decomposition products reported in Fig. 6.

morphologies of chromia. Figure 9 shows that the effect of SCR treatment compared to reduction treatment on the site distribution is to lower the total number of c.u.s. by 30% on the amorphous chromia (Fig. 9, top), and increase it by 30% on the crystalline chromia (Fig. 9, bottom). The number of 1 c.u.s. detected after SCR treatment shows a 36% increase on the amorphous chromia and a 300% increase on the crystalline

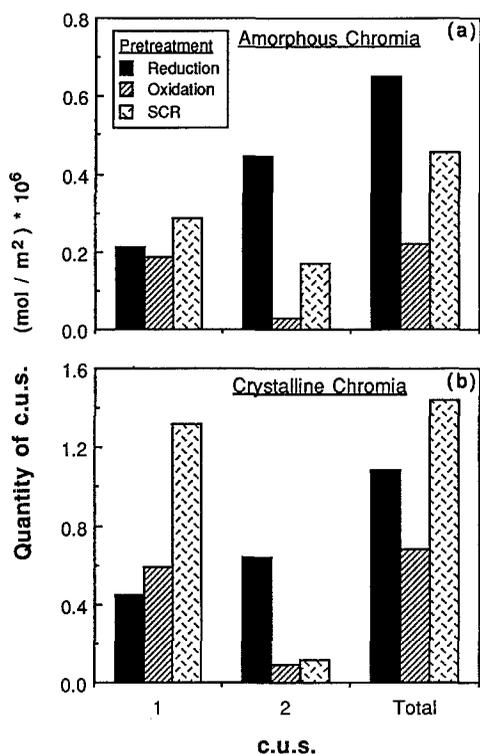


FIG. 9. The effect of pretreatment on the number of c.u.s. present on the amorphous and crystalline chromia samples. The number of c.u.s. were determined from the quantities of desorbed NO and its decomposition products reported in Fig. 6.

chromia compared to postreduction treatment.

The loss of 2 c.u.s. and gain in 1 c.u.s. that takes place during SCR treatment could result from the conversion of 2 c.u.s. to 1 c.u.s. It is unlikely that this site conversion could be due to  $O_2$  interaction with the 2 c.u.s. Results presented earlier showed that the chemisorption of  $O_2$  leads to the loss of 2 c.u.s. without an associated gain in 1 c.u.s. A conversion of 2 c.u.s. to 1 c.u.s. should take place through the abstraction of oxygen from NO by the 2 c.u.s. From Fig. 9 it would appear that the conversion process takes place more readily on crystalline chromia under SCR conditions than on amorphous chromia. The apparent loss of some 2 c.u.s.

by the amorphous chromia under SCR conditions suggests that it will take up oxygen from the gas phase as well as abstracting oxygen from NO.

The crystalline chromia also shows an increase in the total number of c.u.s. after SCR, compared to postreduction (Fig. 9, bottom), suggesting that there is almost complete conversion of 2 c.u.s. to 1 c.u.s. together with the generation of new 1 c.u.s. On the amorphous chromia conversion of 2 c.u.s. to 1 c.u.s. is only partial and is accompanied by a loss in the total number of c.u.s. as well. Comparison of the two morphologies shows that after SCR treatment, the number of 1 c.u.s. on the crystalline chromia is more than 4.6 times the number of 1 c.u.s. on the amorphous chromia (Fig. 8, bottom). Both morphologies have similar 2 c.u.s. densities after SCR pretreatment.

It can be concluded that on both morphologies of chromia, Lewis acid sites with up to four different acidities can be detected. Two of the weakest are 1 c.u.s. that chemisorb NO molecularly. The other two are 2 c.u.s. that will decompose NO; one site readily accepting two oxygen atoms and producing  $N_2$ , and the other accepting one oxygen atom and producing  $N_2O$ . It has been found that both the 2 c.u.s. Lewis acid sites on amorphous chromia are more acidic than those on the crystalline chromia. This is supported by the  $NH_3$  desorption study of labile oxygen which showed that the labile oxygen associated with these sites is more stable on the amorphous chromia. Comparison of the reduced chromia to the SCR-pretreated chromia shows that the SCR treatment causes the conversion of 2 c.u.s. to 1 c.u.s. On crystalline chromia complete conversion of all 2 c.u.s. to 1 c.u.s. occurs. On the amorphous chromia the conversion of 2 c.u.s. to 1 c.u.s. is only partial and there is evidence that some 2 c.u.s. are lost completely. The conversion of 2 c.u.s. to 1 c.u.s. was proposed to occur through the abstraction of oxygen from NO during SCR reac-

tion. The complete loss of 2 c.u.s., which occurs only on the amorphous chromia, results from O<sub>2</sub> chemisorption.

#### CONCLUSIONS

Temperature-programmed reaction and desorption studies, with NH<sub>3</sub> and NO as probe molecules, revealed that the earlier observed differences in the catalytic behavior for SCR (1, 2) are due to significantly different surface properties of crystalline and amorphous chromia. This is indicated by the distinct differences in the adsorption and surface reaction behavior of NH<sub>3</sub> and NO with crystalline and amorphous chromia.

Labile oxygen is less strongly bound on crystalline chromia than on amorphous chromia and has higher oxidizing strength. The density of low-coordinated chromium ions is higher on the surface of crystalline chromia than on the surface of amorphous chromia. The adsorption behavior and the surface reactions of the probe molecules used are not only influenced by the chromia structure, but also by the pretreatment conditions.

In the oxidized state of the surface, the ratio of total labile oxygen to total coordinatively unsaturated sites is more than three times larger on the amorphous chromia than on the crystalline chromia. This difference also applies for SCR-pretreated samples. The majority of the coordinatively unsaturated sites are singularly unsaturated (1 c.u.s.). Reduced chromia surfaces exhibit a significantly higher concentration of 2 c.u.s. and as a consequence of the removal of labile oxygen the direct oxidation of NH<sub>3</sub> is completely suppressed. Similarly NO does not undergo any observable surface reaction. The TPRD investigations reveal that under SCR conditions the chromia surface is in a partly oxidized state.

The differences in the SCR activity of the two morphologies of chromia must be related to these differences in site characteristics. Previous studies of the reaction mecha-

nism (28) have suggested that the active site is created by the formation of an adsorption complex between NH<sub>3</sub> and a chromyl oxygen. The stability of the NH<sub>3</sub>-O<sub>s</sub> complex seems to play a crucial role in determining whether oxidation of NH<sub>3</sub> or the reaction of this complex with NO is favored. Hence a detailed characterization of the structure of these sites is a necessary prerequisite to understanding the differences in the catalytic behavior of the crystalline and amorphous chromia. Further support for the findings derived from the TPRD investigations and a detailed characterization of the structure of the chromia sites interacting with NH<sub>3</sub>, NO, and O<sub>2</sub> are provided by the vibrational spectroscopy studies reported in parts II and III (18, 19) of this series.

#### ACKNOWLEDGMENTS

Financial support of this work by the Swiss National Science Foundation (NFP 24) and the Deutsche Forschungsgemeinschaft (SFB 213) is gratefully acknowledged.

#### REFERENCES

1. Curry-Hyde, H. E., and Baiker, A., *Ind. Eng. Chem. Res.* **29**, 1985 (1990).
2. Curry-Hyde, H. E., Musch, H., and Baiker, A., *Appl. Catal.* **65**, 211 (1990).
3. Kobylinski, T. P., and Taylor, B. W., *J. Catal.* **31**, 450 (1973).
4. Niiyama, H., Murata, K., Ebitani, A., and Echigo, E., *J. Catal.* **48**, 194 (1977).
5. Wong, W. C., and Nobe, K., *Ind. Eng. Chem. Prod. Res. Dev.* **25**, 179 (1986).
6. Burwell, R. L., Haller, G. L., Taylor, K. C., and Read, J. F., in "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 20, p. 1. Academic Press, New York, 1969.
7. Conway, P. J. M., Falconer, J. W., and Rochester, C. H., *J. Chem. Soc. Faraday Trans. 1*, **85**, 79 (1989).
8. Ghiotti, G., Garrone, E., Della Gatta, G., Fubini, B., and Giamello, E., *J. Catal.* **80**, 249 (1983).
9. Kugler, E. L., Kadet, A. B., and Gryder, J. W., *J. Catal.* **41**, 72 (1976).
10. Morishige, K., Kittaka, S., Katsuragi, S., and Morimoto, T., *J. Chem. Soc. Faraday Trans. 1*, **78**, 2947 (1982).
11. Miyamoto, A., Ui, T., and Murakami, Y., *J. Catal.* **80**, 106 (1983).
12. Merryfield, R., McDaniel, M., and Parks, G., *J. Catal.* **77**, 348 (1982).

13. Günert, W., Shipiro, E. S., Feldhaus R., Anders, K., Antoshin, G. V., and Minachev Kh.M., *J. Catal.* **100**, 138 (1986).
14. Allen, G. C., Curtis, M. T., Hooper, A. J., and Tucker, P. M., *J. Chem.Soc. Dalton Trans.*, 1675 (1973).
15. Allen, G. C., Tucker, P. M., and Wild, R. K., *J. Chem. Soc. Faraday Trans. 2* **74**, 1126 (1978).
16. Kobayashi, M., and Kanno, T., *J. Chem. Soc. Faraday Trans. 1* **85**, 579 (1989).
17. Kobayashi, M., and Kobayashi, H. B., *Chem. Soc. Jpn.* **49**, 3009 (1976).
18. Schraml-Marth, M., Wokaun, A., Curry-Hyde, H. E., and Baiker, A., *J. Catal.* **133** (1992).
19. Schraml-Marth, M., Wokaun, A., Curry-Hyde, H. E., and Baiker, A., *J. Catal.* **133** (1992).
20. Curry-Hyde, H. E., and Baiker, A., to be published.
21. Filimonov, V. N., Lopatin, Y. N., and Sukhov, D. A., *Kinet. Katal.* **10**, 458 (1969).
22. Tref'yakov, N. E., and Filimonov, V. N., *Kinet. Katal.* **14**, 803 (1973).
23. Eley, D. D., Rochester, C. H., and Scurrall, M. S., *J. Chem. Soc. Faraday Trans. 1* **69**, 660 (1973).
24. Belokopytov, Yu. V., Kuznetsov, V. A., Kholyavenko, K. M., and Gerei, S. V., *J. Catal.* **44**, 1 (1976).
25. Zecchina, A., Coluccia, S., Cerruti, L., and Borrello, E., *J. Phys. Chem.* **75**, 2783 (1971).
26. Carrott, P. J. M., Sheppard, N., *J. Chem. Soc. Faraday Trans. 1* **79**, 2425 (1983).
27. Zaki, M. I., and Knözinger, H., *J. Catal.* **119**, 311 (1989).
28. Niiyama, H., Murata, K., and Echigoya, E., *J. Catal.* **48**, 201 (1977).