JOURNAL OF CATALYSIS **133,** 431–444 (1992)

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

III. Diffuse Reflectance FTIR Study of Ammonia Desorption from Brønsted and Lewis Acid Sites

M. Schraml-Marth,* A. Wokaun,[1],* H. E. Curry-Hyde,[2],† and A. Baiker†

Physical Chemistry II, University of Bayreuth, D-W-8580 Bayreuth, Germany; †Department of Chemical Engineering and Chemical Technology, Swiss Federal Institute of Technology, ETH Zentrum, CH-8092 Zürich, Switzerland

Received February 27, 1991; revised July 29, 1991

Ammonia has been adsorbed onto oxidized and reduced surfaces of crystalline α-Cr_2O_3 and of amorphous chromia, respectively. Temperature-dependent changes in the diffuse reflectance FTIR spectrum are monitored and are correlated with temperature-programmed reaction and desorption (TPRD) spectra reported in part I of this study (*1*). Two types of NH_3 molecules bound to Brønsted acidic sites on the surface of the chromia catalysts, as well as two species bound to Lewis sites, are identified from the IR spectra. The oxidized surface of α-Cr_2O_3 is characterized by a high surface coverage of strongly Lewis-bound ammonia molecules, which desorb at temperatures above 400 K. In contrast, weakly bound NH_3 prevails on the oxidized surface of amorphous chromia. The desorption of the latter species starts at 380 K and is completed around 480 K. A reductive pretreatment of the chromia surfaces by hydrogen (10% in Ar) decreases the number of surface hydroxyl groups and devoids the surface of adsorbed oxygen. As a consequence, the number of Brønsted acidic sites is reduced both on the crystalline and the amorphous catalyst. On the reduced surface of α-Cr_2O_3, strongly bound ammonia coordinated to Lewis acidic sites is observed to persist to temperatures beyond 560 K. In contrast, weakly Lewis-bound NH_3 prevails on reduced amorphous chromia, which is quantitatively desorbed at temperatures below 410 K. The formation of NH_3 oxidation products on α-Cr_2O_3 is manifested by the observation of two characteristic surface species, an N_2O_2 dimer and an NO_2 chelate surface complex. Corresponding signals are *not* observed on the surface of amorphous chromia. Apparently the removal of labile oxygen from the surface of α-Cr_2O_3 at moderate temperatures generates strongly Lewis acidic chromium sites, and the firm bonding of NH_3 to these sites is related to the undesired direct oxidation of ammonia.

1. INTRODUCTION

In part II of this study (*2*), differences in the surface structure of crystalline and amorphous chromia induced by thermal activation and oxygen adsorption have been investigated by FTIR and Raman spectroscopy. Amorphous and crystalline chromia catalysts exhibit remarkable differences in their activity for the selective catalytic reduction (SCR) of NO with NH_3 (*3*). This difference has been attributed to the fact that the labile oxygen on crystalline chromia is more weakly bound in comparison to amorphous chromia, and is therefore desorbed from the surface already at low temperatures. The high activity of amorphous chromia in SCR has therefore been ascribed to the higher labile oxygen density available on the surface under reaction conditions. In this study ammonia adsorption is used to

---

[1] To whom correspondence should be addressed.

[2] Present address: School of Chemical Engineering and Industrial Chemistry, University of New South Wales, PO Box 1, Kensington, 2033, Australia.

0021-9517/92 $3.00

investigate whether differences in the acidity of the respective catalyst surfaces have an influence on the observed activity and selectivity patterns. Besides being directly involved in the SCR reaction, ammonia has been established as a sensitive probe to characterize various types of acidic sites (*4, 5*), and to determine the nature of labile oxygen on the surface (*6*).

The chemisorption of ammonia to Lewis acid sites of Cr_2O_3 has been characterized by Filimonov *et al.* (*7*). Tret'yakov and Filimonov (*8*) and Eley *et al.* (*9*) identified two types of Lewis acid sites and reported hydrogen bonding of ammonia on hydroxylated chromia surfaces. In a comparative study of various transition metal oxides, Belokopytov *et al.* (*10*) established a correlation between the temperature of ammonia desorption and acrylic acid selectivity in the partial oxidation of acrolein. It was stated that a high temperature of NH_3 desorption correlates with strong acidity of the respective Lewis sites and poor partial oxidation selectivity. For NH_3 on α-Cr_2O_3, two temperature-programmed desorption (TPD) peaks were detected at 403 and 493 K.

The interaction of ammonia with chromia surfaces was further characterized by Belokopytov *et al.* (*11*) using IR spectroscopy. Prior to adsorption, bands at 880, 985, 998, and 1021 cm^{-1} were detected on the oxidized chromia surface. Upon NH_3 adsorption at room temperature, ammonia bound to Lewis acid sites was detected by two bands at 1225 and 1610 cm^{-1} (symmetric and asymmetric deformational modes). A decrease in the intensity of the 1021 cm^{-1} chromia band and the simultaneous appearance of a feature at 920 cm^{-1} were attributed to the filling of coordinatively unsaturated surface sites by ammonia. Further bands at 1650 and 1675 cm^{-1} disappeared upon evacuation and were interpreted as being due to NH_3 bound to Brønsted acid sites.

In 1982 Morishige *et al.* (*5*) investigated the acidic properties of Cr_2O_3 by ammonia adsorption and desorption. Following pretreatment of the chromia at 773 K and NH_3 adsorption at 473 K, four bands in the N-H stretching region, as well as the corresponding deformational motions, were observed. Bands at 3400 and 3330 cm^{-1} were assigned to NH_3 bound to strongly Lewis acidic sites; vibrations at 3220 and 3100 cm^{-1} were attributed to NH_3 involved in hydrogen bonds with lattice O^{2-} and adsorbed at weakly Lewis acidic sites. These species were characterized by desorption temperatures of 593 and 443 K, respectively. These and further relevant assignments are frequently referred to in the following sections, and are summarized in Table 1.

Recently, we have studied (*1*) the temperature-programmed reaction and desorption (TPRD) of ammonia from oxidized and reduced surfaces of crystalline α-Cr_2O_3, as well as from amorphous chromia. To obtain additional information on the surface state of the crystalline and amorphous chromia catalysts and to monitor potential transformations of the probe molecules, *in situ* FTIR studies of NH_3 adsorption/desorption are reported in the following sections from both oxidized and reduced chromia surfaces.

2. EXPERIMENTAL

The preparation of the catalysts and the apparatus used have been described in detail in parts I and II of this study (*1, 2*). The oxidation or reduction treatment conditions and the NH_3 adsorption conditions were identical to those used in part I (*1*). An oxidized surface state was achieved by thermal pretreatment at 623 K for 1 h, followed by oxygen adsorption at 498 K for 1 h. Reduced surfaces were prepared by heating samples in a flow of 6% H_2/Ar to 623 K, where they were held for 1 h.

Prior to introduction of ammonia, background spectra have been accumulated at a resolution of 4 cm^{-1} for both the oxidized and the reduced states of the surface. The spectra in Figs. 1 to 8 are ratioed with respect to this background; therefore, they exhibit only bands due to adsorbed ammo-

TABLE 1

Reference Data for Deformational Vibrations of Adsorbed Ammonia (*14*)

Species	δ_{as} (cm^{-1})	δ_s (cm^{-1})
Lewis coordinated	1610–1650	1230–1280
Brønsted coordinated	1680–1695	1390–1490
Ammonium ion	1700	1450–1470
Hydrogen bonded (H_2N–H · · O^{2-})	1620–1630	1150
Amide ion	1510/1560	

nia, ammonia oxidation products, and changes in the background caused by ammonia adsorption and desorption.

In the TPRD experiments (*1*), the temperature was increased from 298 to 553 K at a rate of 2 K/min. As the desorption is a dynamic process that 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 256) were coadded while the temperature was being increased at the rate of 2 K/min. Therefore, a typical spectrum represents the state of the surface during TPRD as averaged over a 25 K temperature interval.

3. RESULTS

A. Experiments on Oxidized Chromia Surfaces

A.1. Adsorption of ammonia. Spectra of the oxidized surfaces of crystalline and amorphous chromia have been discussed in part II (*2*). Changes in the IR absorptions of the catalyst surfaces occurring upon ammonia adsorption at room temperature are visible from the difference spectra shown in Fig. 1. On crystalline α-Cr_2O_3 (lower trace), an increase of surface reflectance is observed as a narrow band at 1003–1014 cm^{-1}. New absorption bands appearing at 935/954 cm^{-1} are attributed to surface Cr=O groups with an electron-donating NH_3 molecule bound to a previously unoccupied coordination site. Bands developing above 1150 cm^{-1} are caused by adsorbed ammonia and its oxidation products. Two very intense features are centered at 1210 and 1440 cm^{-1}; weaker bands are observed at 1600, 1623, 1670, and 1720 cm^{-1}.

Upon ammonia adsorption onto amorphous chromia (upper trace in Fig. 1), the support reflectance again shows a marked increase above 1000 cm^{-1}, with a maximum now shifted toward 1031 cm^{-1}. Intense and broad ammonia-related bands are seen at 1260, 1445, and 1610 cm^{-1}, with a weak absorption at 1670 cm^{-1}. In this case no bands above 1700 cm^{-1} are present. In both spectra a broad band is observed around 1100 cm^{-1}, which is more intensive in the spectrum of amorphous chromia.

A.2. Desorption of ammonia from crystalline α-Cr_2O_3. The first spectrum was recorded after ammonia adsorption at room temperature while heating the sample from 298 to 323 K; the 900–1800 cm^{-1} region of this spectrum is reproduced at the bottom of Fig. 2. As mentioned in the experimental section, the spectra recorded during TPRD represent averages over a 25 K temperature interval: e.g., while recording the spectrum marked 311 K, the temperature was being ramped from 298 to 323 K at a rate of 2 K/min. There are no significant differences with the room-temperature spectrum, except for a very weak shoulder at 1180 cm^{-1}. In the 336 K spectrum, a decreased absorption around 1650 cm^{-1} and a sharpening of the most intensive band at 1437 cm^{-1} are observed. The dif-

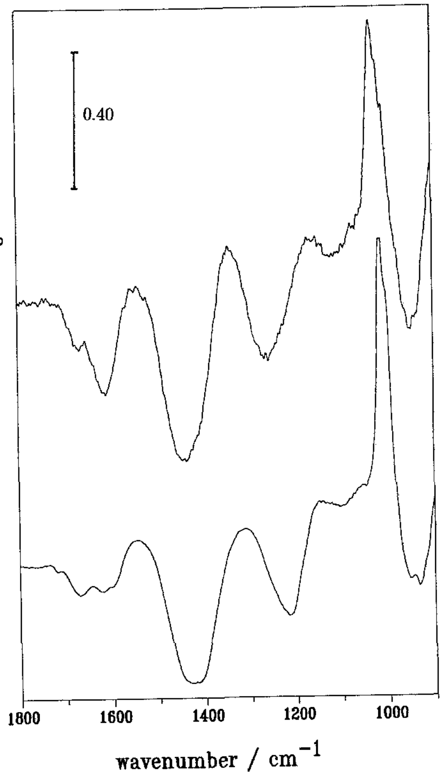


FIG. 1. Ammonia adsorption at room temperature onto the oxidized surfaces of crystalline (lower trace) and amorphous (upper trace) chromia. Catalyst surfaces were exposed to a flow of 10% NH_3 in argon for 1 h. Prior to recording of spectra, the environmental chamber was purged with argon. 500 scans were acquired at 4 cm^{-1} resolution.

ference spectrum (marked Δ_1) between this spectrum and the one recorded at 311 K, shows a set of decreasing absorptions at 1670 and 1458 cm^{-1}, weaker decreasing bands at 1625 and 1400 cm^{-1}, and a broad band centered at 1180 cm^{-1}.

In the spectrum recorded at 361 K, the band at 1420 cm^{-1} has lost intensity; a band at 1600 cm^{-1} and weaker absorptions at 1670 and 1720 cm^{-1} are visible. The difference spectrum (Δ_2) exhibits an increase in reflectance at 1420 cm^{-1} and a weaker one at 1670 cm^{-1}. Both these frequencies coincide with residual species seen in the 361 K spectrum and are assigned to ammonia molecules bound to Brønsted acidic sites. Further decreasing absorptions are observed at 1625 cm^{-1} {$\delta(H_2O)$} and 1180 cm^{-1} and a more pronounced decrease of absorption at 935 cm^{-1}.

Upon further raising the temperature to 386 K (Fig. 3), ammonia molecules bound to Brønsted sites have been largely desorbed, and bands at 1220 and 1600 cm^{-1} due to NH_3 adsorbed at Lewis acid sites are clearly visible. Further absorptions are observed at 935–960, 1420 (broad), 1670, and 1720 cm^{-1}. A reflectivity increase is observed at 1030 cm^{-1}. When the temperature is increased to 403 K, the absorption around 1420 cm^{-1} (due to Brønsted-bound NH_3) has disappeared, and the absorption at 1225 cm^{-1} has become narrower as compared to the 386 K spectrum. The difference spectrum (Δ_1) clearly shows a decrease in absorption at

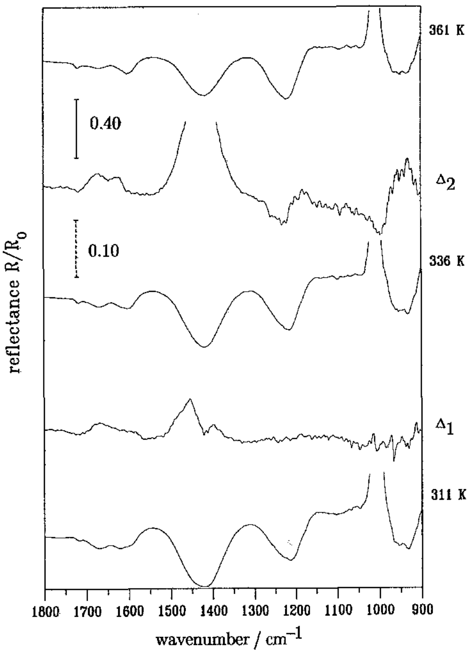


FIG. 2. Diffuse reflectance FTIR spectra recorded during the thermal desorption of ammonia from the oxidized surface of α-Cr_2O_3 (accumulated over a 25 K interval, with mean temperature indicated in the plot). The scale of the reflectivity changes R/R$_0$ (cf. Experimental) is defined by the full vertical bar. Traces labeled Δ represent differences of the spectra plotted immediately above and below. In this, as well as in subsequent figures, the difference spectra are reproduced on a four times expanded vertical scale (dashed bar).

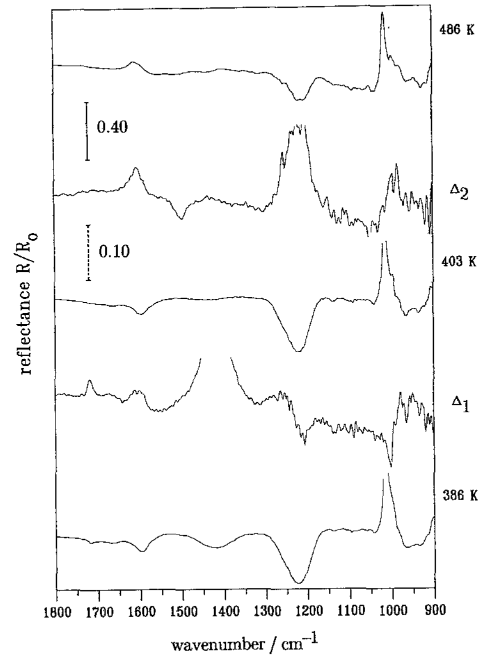


FIG. 3. Thermal desorption of ammonia from the oxidized surface of α-Cr_2O_3. The temperature program of Fig. 2 is continued to higher temperatures.

1260 cm^{-1}, i.e., at the high-frequency edge of the band under discussion. Further desorbing species are observed at 1420 (dominant), 1670, and 1615 cm^{-1}. A band at 1720 cm^{-1} indicates the desorption of a reaction product that gave rise to a band at the same position in the 386 K spectrum. At the same time the reflectance is decreased at 1030 cm^{-1}, indicating that coordinatively unsaturated sites are being restored as ammonia is desorbed.

In the spectrum recorded at 486 K, only one residual band is observed at 1220 cm^{-1}. The difference spectrum (Δ_2) shows an asymmetric decreasing band at 1210 cm^{-1}, as well as decreasing absorption at 1605 and 990 cm^{-1}. In contrast, there is an increase in absorption at 1030 and around 1500 cm^{-1}.

A.3. Desorption of ammonia from amorphous Cr_2O_3. Spectra recorded during a TPRD run subsequent to ammonia adsorption at room temperature are presented in Figs. 4 and 5. The spectrum (at 311 K) is essentially unchanged compared to the room-temperature spectrum, except for a slight decrease in the high-frequency shoulder of the 1440 cm^{-1} band. The 336 K spectrum shows a further shift in the maximum of the most intense absorption to 1425 cm^{-1}. In the difference spectrum (Δ_1), loss of absorption at 1470 cm^{-1} is clearly visible, which demonstrates that the broad room-temperature band centered around 1440 cm^{-1} represents a superposition of contributions from two species. Further disappearing features are recognized as a double hump at 1630/1670 cm^{-1} and a broad band at 1125 cm^{-1}.

At 386 K (top trace in Fig. 4), the intensity of the 1425 cm^{-1} absorption is strongly decreased (see also difference spectrum Δ_2). As the desorption of NH_3 from Brønsted sites is nearly complete at this temperature, the pair of bands at 1610 and 1250 cm^{-1},

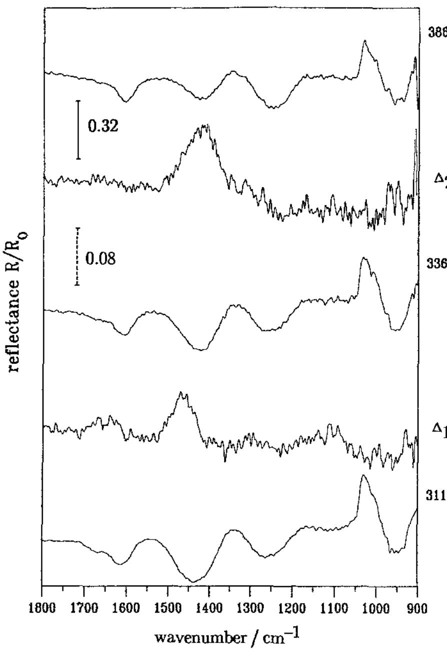


FIG. 4. Thermal desorption of ammonia from the oxidized surface of an amorphous chromia catalyst (see text). Experimental conditions and notations are the same as those in Fig. 2.

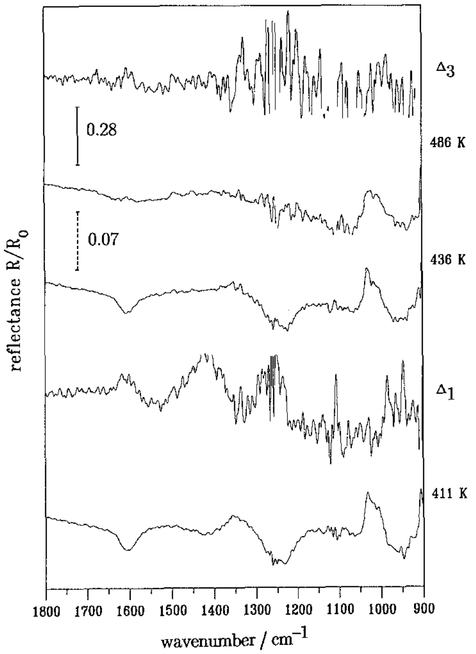


FIG. 5. Thermal desorption of ammonia from the oxidized surface of amorphous chromia. The temperature program of Fig. 4 is continued to higher temperatures.

which is characteristic for Lewis site bound ammonia, becomes prominent.

In the spectrum observed at 411 K (Fig. 5), these trends continue. An increase in transmission at 900 cm^{-1} is observed, compared to 386 K. At 436 K the band at 1425 cm^{-1} has completely disappeared, but the intensity of the Lewis site-related features at 1610 and 1235 cm^{-1} has decreased as well. In the difference spectrum (Δ_1) one observes, in addition, a weak reflectivity increase around 940 cm^{-1}.

At 486 K significant changes in the reflectivity of the substrate occur. Reflectance increases at 950 cm^{-1} and decreases at 1010–1025 cm^{-1}, which points again to the regeneration of coordinately unsaturated sites after ammonia desorption. When increasing the temperature beyond 500 K, no further spectral changes are observed, as demonstrated by the difference spectrum shown in the top trace of Fig. 5 (Δ_3).

B. Experiments on Reduced Chromia Surfaces

B.1. Adsorption of ammonia. Diffuse reflectance spectra recorded after ammonia adsorption at room temperature for 1 h (Fig. 6) exhibit the characteristic modes of adsorbed ammonia species. For crystalline chromia (lower trace) two strong bands at 1195 and 1620 cm^{-1} due to Lewis-bound ammonia are observed. The 1420 cm^{-1} band, which was dominant for the oxidized surface (Fig. 1), is replaced by a broad and weak absorption extending from 1325 to 1520 cm^{-1}. As before, a decrease in absorption at 1000 cm^{-1} and an increase at 950 cm^{-1} are noted.

With amorphous chromia (Fig. 6, upper

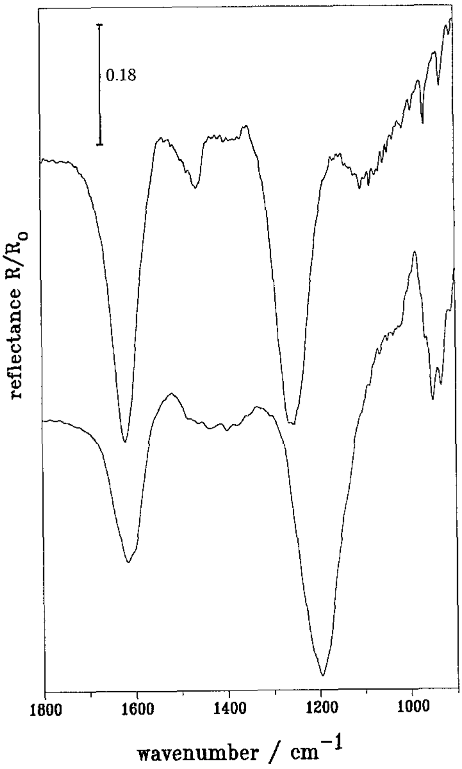


FIG. 6. Ammonia adsorption at room temperature onto the reduced surfaces of crystalline (lower trace) and amorphous (upper trace) chromia. The same procedure as that in Fig. 1 has been used. For experimental details, see text.

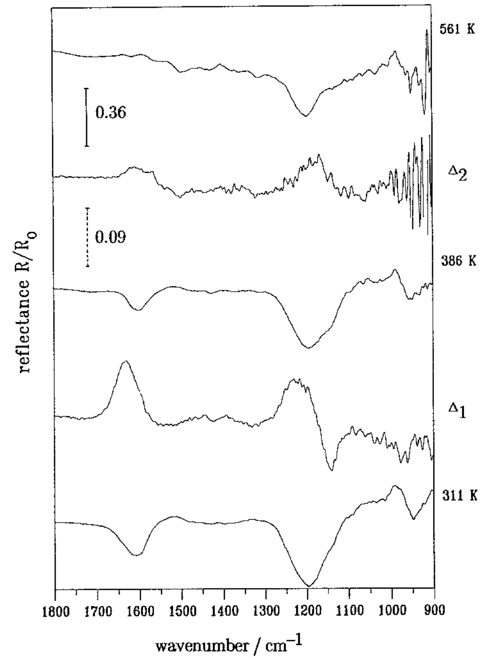


FIG. 7. Thermal desorption of ammonia from the reduced surface of an α-Cr_2O_3 catalyst (see text). Experimental conditions and notations are the same as those in Fig. 2.

trace) the dominant peak at 1260 cm^{-1} appears shifted in frequency by +65 cm^{-1}, and the 1620 cm^{-1} peak is much more intense as compared to the spectrum of the crystalline sample. A peak at 1460 cm^{-1} and a broad feature around 1100 cm^{-1} are detected.

B.2. Desorption of ammonia from reduced crystalline α-Cr_2O_3. In the range between 298 and 323 K (Fig. 7, lowest trace), no substantial changes are recorded. In the spectrum recorded at 386 K, a pronounced shoulder at 1140 cm^{-1} develops at the low-frequency edge of the 1195 cm^{-1} band. The presence of two Lewis-bound ammonia species is clearly inferred from a comparison of the spectra recorded at 386 and 311 K, respectively, and their difference spectrum (marked Δ_1 in Fig. 7). The wavenumbers of the disappearing peaks in the difference spectrum (1625 and 1220 cm^{-1}) are both higher than the absorption maxima in the 311 K spectrum. In addition, a weak decrease in absorption is seen at 1460 and 1400 cm^{-1}, corresponding to the desorption of Brønsted-bound ammonia.

Upon increasing the temperature above 400 K a continuous decrease of the bands at 1620 and 1200 cm^{-1} is observed. At 561 K the 1620 cm^{-1} absorption is no longer observed, and the intensity of the 1200 cm^{-1} band is reduced to a half of its value at 311 K. The latter band persists up to 623 K, in agreement with the TPRD spectrum (*1*).

B.3. Desorption of ammonia from reduced amorphous Cr_2O_3. Features of the 311 K spectrum shown in Fig. 8 agree with those discussed in Section B.1. When the temperature is raised to 386 K, the bands at 1460 and 1100 cm^{-1} disappear. Further, the difference spectrum (Δ_1) shows a decrease of Lewis-coordinated ammonia at 1620 and 1270 cm^{-1}. In contrast to crystalline chromia, no significant absorptions are detected in the spectrum recorded at 561 K. This observation correlates well with the fact that ammonia desorbs from amorphous chromia at comparatively low temperatures, as deduced from the TPRD spectrum (*1*). The desorption of ammonia bound to Lewis acid sites is confirmed by positive bands at 1240 and 1600 cm^{-1} in the difference spectrum (Δ_2 in Fig. 8).

4. DISCUSSION

Experiments on Oxidized Chromia Surfaces

The spectroscopic results are correlated with the TPRD experiments reported in part I (*1*), which may be summarized as follows. On crystalline Cr_2O_3, the ammonia desorption is characterized by a peak at 373 K followed by a long tail extending to higher temperatures. The desorption of nitrogen produced from ammonia decomposition is double-peaked, with a smaller maximum at 388 K and a major peak at 518 K. N_2O desorption also exhibits two maxima at 423 and 493 K. In contrast, on the amorphous chromia the long tail of the ammonia desorp-

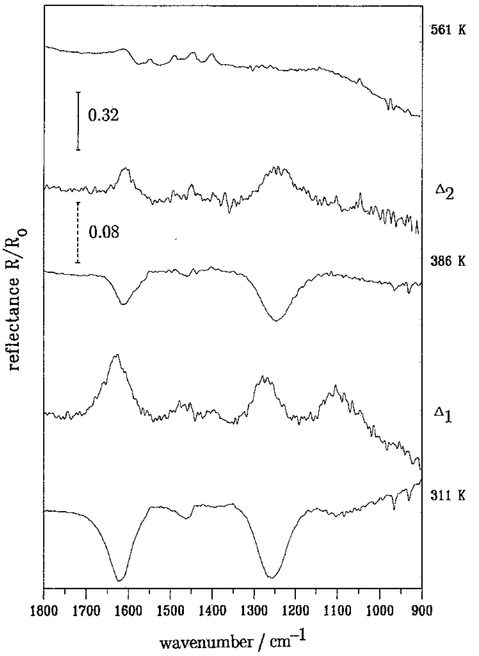
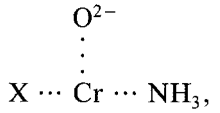


FIG. 8. Thermal desorption of ammonia from the reduced surface of an amorphous chromia catalyst (see text). Experimental conditions and notations are the same as those in Fig. 2.

tion is absent: the curve practically drops to zero above 473 K. As a consequence, nitrogen is now predominantly desorbed at 418 K, with a less intense second maximum at 523 K. N_2O desorption occurs mainly at 523 K.

Assignment of Spectral Features

The ammonia adsorption experiment on oxidized chromia surfaces (Fig. 1) provides evidence for the existence of several adsorbed ammonia species as well as the formation of adsorbed ammonia-oxidation products. An increase in reflectance at $\nu \geq 1000\ \mathrm{cm}^{-1}$ is accompanied by a decrease in reflectance (growing absorption) at 950 cm^{-1}. The areas of the two features are equal within the accuracy of the measurement. In agreement with Zecchina *et al.* (*12*), this change is attributed to ammonia adsorption onto coordinatively unsaturated sites on the oxidized chromia surface, e.g.,



$$\mathrm{X} \cdots \overset{\mathrm{O}^{2-}\atop \vdots}{\mathrm{Cr}} \cdots \mathrm{NH}_3,$$

where $X = O^{2-}$ or OH^-.

It has been shown in part II of this study (*2*), that one- and twofold coordinatively unsaturated chromium ions are generated during thermal treatment of α-Cr_2O_3; the concentration of the latter species is reduced upon dissociative adsorption of oxygen. These coordinatively unsaturated Lewis acid centers provide favorable adsorption sites for Lewis bases like ammonia, pyridine, ethanol, or water. Upon binding of the adsorbent, the coordinative unsaturation is reduced, and the Cr═O stretching frequency is decreased. For example, Zecchina *et al.* (*13*) have observed a decrease of $\nu_{\mathrm{Cr=O}}$ from 1024–1016 cm^{-1} to 980–960 cm^{-1} upon pyridine adsorption. It is expected that this change depends on the electron-donating properties of the ligand, but this correlation has not yet been quantified.

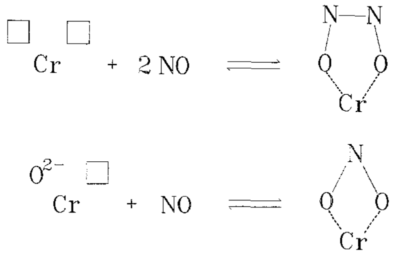
The assignment of the ammonia-related bands, which is based on a large body of literature data (*11, 14*) on ammonia adsorption onto various metal oxides, has been summarized in Table 1. The observation of Lewis-bound species confirms the interpretation of the chromia-related spectral changes discussed in the preceding paragraph. The band center on amorphous chromia (1260 cm^{-1}) corresponds to the high-frequency shoulder on α-Cr_2O_3, but is shifted in frequency by +40 cm^{-1} as compared to the main peak in the α-Cr_2O_3 spectrum. Morishige *et al.* (*5*) have pointed out that a stronger nitrogen–metal bond, and hence a lower electron density on the nitrogen atom, result in a lower NH_3 deformational frequency. In this light, the above observation points to the existence of two Lewis-bound ammonia species on crystalline chromia, an abundant strongly bound species (1210 cm^{-1}) and a weakly bound minor species (1260 cm^{-1}). In contrast, weakly bound species appear to be prevailing on the surface of the amorphous chromia.

Further evidence for this fact is obtained when analyzing temperature-dependent changes in the adsorbate spectra (Figs. 2–5), which complement the TPRD results in Ref. (*1*). With crystalline chromia, the spectra recorded at 311, 336, and 361 K (Fig. 2) show a dominant peak with an average frequency shifting from 1440 to 1420 cm^{-1}. The difference spectra clearly reveal the presence of two Brønsted bound species. The one desorbing at lower temperatures is characterized by absorptions at 1460 and 1670 cm^{-1}, while the one desorbing at 336–361 K gives rise to bands at 1420 and 1625 cm^{-1}.

The changes described for Brønsted sites are accompanied by a slight shift of the δ_{sym} vibrational band maximum of Lewis-bound ammonia from 1210 to 1220 cm^{-1}, as indicated by increased absorption at 1240 cm^{-1} in the difference spectrum Δ_2. Such a shift would correspond to a weaker bonding of the ammonia molecule to the surface.

Oxidation Products of Ammonia

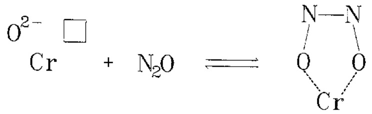
Several features in the spectra of Fig. 1 can be assigned to oxidation products of adsorbed ammonia. This observation is important in view of the earlier TPRD results (*1*), where N_2O and N_2 formation on oxidized chromia was observed already at low temperatures. Kugler *et al.* (*15*) have studied NO adsorption onto a reduced surface of crystalline chromia. It was suggested that two different adsorption sites are involved. Bands at 1865 cm^{-1} (weak) and 1735 cm^{-1} (strong) have been assigned to a *cis*-N_2O_2 dimer surface complex, whereas IR bands at 1285 cm^{-1} (weak) and 1180 cm^{-1} (strong) have been ascribed to a NO_2 chelate complex. Oxygen adsorption prior to NO introduction prevented the formation of the N_2O_2 dimer, but not of the NO_2 chelate. It was concluded that the dimer adsorbs on surface chromium sites with two vacancies, whereas onefold coordinative unsaturation is sufficient for NO_2 chelate formation:



In the 311 K and 336 K spectra of Fig. 2 we observe a weak shoulder at 1180 cm^{-1} on the low-frequency side of the 1210 cm^{-1} band. At 361 K this shoulder has disappeared, as evidenced by a band at 1180 cm^{-1} in spectrum Δ_2. Although the counterpart of the 1180 cm^{-1} peak at 1285 cm^{-1} cannot be observed due to the strong absorption of Lewis-bound ammonia in this region, we assign the 1180 cm^{-1} band to the NO_2 surface chelate complex formed by the oxidation of adsorbed NH_3. The chelate appears to have low stability and is readily decomposed below 373 K (cf. Δ_2). This species could therefore be connected with the *low-temperature* formation of N_2O and N_2 detected in the TPRD spectra of Ref. (*1*).

Another indication of the transformation of adsorbed ammonia on the oxidized surface of α-Cr_2O_3 is the small peak at 1720 cm^{-1}, which is already observed in the room-temperature spectrum of Fig. 1. Close inspection reveals that there is also a weaker peak at 1835 cm^{-1} (not shown). We can therefore conclude that adsorbed ammonia molecules are oxidized at room temperature to yield the N_2O_2 dimer surface complex. The characteristic peak at 1720 cm^{-1} disappears at a temperature of 403 K (Fig. 3). It could therefore be argued that the desorption of the *cis*-N_2O_2 dimer in the 386–403 K temperature interval is associated with the high-temperature N_2O and N_2 desorption detected in the TPRD spectra (*1*).

The assignment of the 1180 and 1720 cm^{-1} bands to oxidation products of adsorbed ammonia is supported by the detection of a disappearing band at 950 cm^{-1} in the difference spectrum Δ_2 (Fig. 2), which is associated with the consumption of adsorbed oxygen during N_2O/N_2 formation. Further support for the existence of surface-bound N_2O_2 comes from the observation (*12, 16*) that N_2O can be adsorbed onto crystalline chromia in a nondissociative and reversible manner. Active sites for N_2O adsorption (*12, 16*) are surface chromium ions, which are not fully coordinated with oxygen ligands. In light of our observations, an equilibrium between desorbing N_2O and surface-bound N_2O_2 may be formulated as follows:



Correlation with the TPRD Spectra

In the temperature interval between 386 and 403 K (difference spectrum Δ_1 in Fig. 3), desorption of Brønsted-bound ammonia molecules proceeds to completion. Incipient desorption from Lewis acid sites is observed. Clear evidence for the presence of two types of Lewis-bound NH_3 is obtained. First, a weakly bound species characterized by $\delta_{sym} = 1260\ cm^{-1}$ is desorbing (spectrum Δ_1); the residual band in the spectrum recorded at 403 K is narrowed and shifted to 1210 cm^{-1}. At higher temperatures, the latter, more strongly bound species starts to desorb (strong disappearing band in spectrum Δ_2). The TPRD spectra indicate (*1*) that NH_3 desorption continues beyond 573 K. The weak new absorption appearing at 1510 cm^{-1} might be associated (*14*) with the breaking of N–H bonds and the appearance of NH_2 species on the surface, as observed by Morishige *et al.* (*5*) (cf. Table 1).

The corresponding ammonia desorption experiment from an oxidized surface of *amorphous* chromia is discussed with reference to Figs. 4 and 5. In the interval from 311 to 386 K, the desorption of Brønsted-bound NH_3 is observed (Fig. 4). As with crystalline Cr_2O_3, two species characterized by different bond strengths can be identified. The 311 K spectrum (Fig. 4) shows a broad band centered at 1440 cm^{-1}, which represents a superposition of the absorptions from both types of species. In the difference spectrum Δ_1, desorption of the less strongly bound species is recognized from a decrease in absorption at 1470 cm^{-1}, i.e., on the high-frequency side of the above-mentioned band. The band due to hydrogen-bound ammonia, detected at 1100 cm^{-1} in the room-temperature spectrum of amorphous chromia, is strongly reduced already at 311 K. Several interpretations have been proposed in the literature for IR absorptions in this frequency range. Filimonov *et al.* (*7*) have assigned bands between 1050 and 1120 cm^{-1} to NH_3 bound to lattice O^{2-} by bridges $H_2N\text{–}H \cdots O^{2-}$, with the lattice oxygen exposed during water desorption. Belokopytov *et al.* (*11*) have attributed a band at 1140 cm^{-1}, observed subsequent to NH_3 adsorption onto oxidized Cr_2O_3, to weakly bound surface NO. At higher temperatures (difference spectrum Δ_2), desorption is observed at 1420 cm^{-1}, which coincides with the frequency of the residual absorption at 386 K.

The spectrum recorded at 411 K (Fig. 5) is dominated by bands of Lewis coordinated ammonia molecules (δ_{sym} at 1260 cm^{-1}, δ_{as} at 1610 cm^{-1}). When the temperature is raised to 436 K, these species start to desorb (vanishing band at 1270 cm^{-1} in spectrum Δ_1). Further features in this spectrum are due to completed desorption from Brønsted sites and to surface oxygen consumption, as discussed above. Again, the maximum of the symmetric deformational vibration shifts from 1260 (411 K) to 1230 cm^{-1} (436 K). The desorption of Lewis-coordinated NH_3 is completed at 486 K. Upon raising the temperature to 523 K, no further desorption is observed (difference spectrum Δ_3 in Fig. 5). Note that in Figs. 4 and 5 we observe neither the band at 1180 cm^{-1} nor a peak at 1720 cm^{-1} that would be indicative of NH_3 oxidation products.

Experiments on Reduced Chromia Surfaces

In the TPRD spectra of ammonia from the reduced surfaces of crystalline α-Cr_2O_3 and of amorphous chromia reported in Ref. (*1*), the influence of crystallinity on the TPD spectra is much more pronounced than that found for the oxidized surfaces. With crystalline chromia, a small maximum of ammonia desorption at 353 K is followed by a dominant maximum rate of desorption at 548 K. Desorption continues beyond 573 K at a fairly high rate. For amorphous chromia, a single prominent desorption maximum at 388 K is observed. At higher temperatures the desorption rate decreases to reach a plateau value of 400 pmol m^{-2} s^{-1} at 673 K. While neither N_2O nor N_2 desorption is detected on amorphous chromia, some N_2 desorption is observed from the surface of crystalline chromia above 473 K.

An absorption increase at 950 cm^{-1} with a concomitant decrease at 1000 cm^{-1} (lower trace in Fig. 6) is due to the occupation of coordinatively unsaturated sites by ammonia, as discussed above. The fact that this double feature persists, although weakly, up to 561 K (Fig. 7) is a first indication of the fact that part of the ammonia remains bound at crystalline chromia even at 561 K.

For both crystalline and amorphous chromia, the absence of strong bands around 1420 cm^{-1} points to a thorough dehydroxylation of the surface; as a consequence, only few Brønsted-bound ammonia molecules are detected. Weak bands at 1460 and 1400 cm^{-1} seen in the difference spectrum (Δ_1) in Fig. 7 indicate that structural inhomogeneity with respect to Brønsted-bound ammonia is present on the reduced α-Cr_2O_3 surface as well, in spite of the substantial dehydroxylation of the surface occurring during reduction. Desorption of weakly bound Lewis-coordinated ammonia is indicated by a disappearing band at 1220 cm^{-1}. The strong decrease in absorption observed at 1625 cm^{-1} most likely contains a contribution from residual surface water.

In view of these results, the smaller TPRD maximum at 373 K (cf. Ref. (*1*)) is attributed to ammonia desorption from Brønsted acid sites. Ammonia desorption was found to go through a minimum at 393 K, but does not drop to zero at this temperature. Then the desorption rate increases again to reach a maximum at 423 K. This temperature dependence indicates that desorption of weakly Lewis bound ammonia species starts at temperatures around 383 K, in agreement with the IR evidence mentioned above.

The appearance of an absorption at 1140 cm^{-1} (spectrum recorded at 386 K and difference spectrum Δ_1 in Fig. 7) points to the formation of an NH_3 oxidation product. A band at 1180 cm^{-1} has been assigned to the NO_2 chelate on the oxidized surface of crystalline chromia. The reduced surface of α-Cr_2O_3 is characterized by a shift to lower frequencies of vibrations for all species bound to Lewis acid sites. This effect is ascribed below to strengthening of the interaction between the adsorbed molecules and the coordinatively unsaturated chromium sites. This stronger interaction might also account for a downshift of the 1180 cm^{-1} band for the NO_2 chelate surface complex. The shoulder at 1140 cm^{-1} is strongest in the 386 K spectrum but is no longer seen at 403 K, which indicates desorption of the NO_2 chelate at temperatures above 400 K. Note that on the oxidized surface, the 1180 cm^{-1} absorption already disappears below 361 K. This comparison again points to a stronger fixation of the NO_2 chelate on the reduced chromia surface. Interestingly no N_2O desorption is observed for the reduced α-Cr_2O_3 surface in the TPRD spectra (*1*); rather, a weak N_2 desorption is detected above 473 K.

When the temperature is increased beyond 386 K, a continued desorption of ammonia bound to Lewis acid sites is observed. This correlates with the TPRD experiment where the desorption rate increases up to 523 K. The strength of the Lewis-type interaction between NH_3 and the coordinatively unsaturated surface chromia sites is reflected (5) by the frequency of the symmetric deformational mode (Fig. 7). The band center continuously shifts downward to 1195 (561 K) and 1190 cm^{-1} (573 K), in agreement with the fact that the most strongly bound species are desorbing last.

Weak interactions prevail on the reduced surface of amorphous chromia (Fig. 8). The double peak at 1460 and 1410 cm^{-1} due to desorbing Brønsted-bound NH_3 molecules is very weak, indicating that their contribution is small. The leaving species characterized by a broad band around 1100 cm^{-1} might again be due to $H_2N{-}H \cdots O^{2-}$ or to weakly bound surface NO.

Desorption from Lewis sites starts at low temperatures, in agreement with the TPRD spectra. The prominent disappearing band at 1625 cm^{-1} contains contributions from water desorption. This implies that even subsequent to reduction at 598 K, the structure of the amorphous chromia is comparatively loose and contains abundant Cr–OH groups from which water can be liberated by condensation reactions forming Cr–O–Cr bridges. At 386 K, the intensity of the bands due to Lewis-bound ammonia appears already significantly decreased. The remaining molecules desorb quickly upon a further increase in temperature (spectrum Δ_2 in Fig. 8). For a direct comparison with the crystalline sample (Fig. 7), the spectrum recorded at 561 K is reproduced in the top trace. In agreement with the TPRD results, all NH_3 molecules have been desorbed, which confirms that only weak Lewis acidic centers are present on amorphous chromia.

SUMMARY AND CONCLUSIONS

In light of the FTIR results, the TPRD experiments performed on oxidized chromia surfaces (*1*) are interpreted as follows. The desorption maximum observed at 373 K for both crystalline and amorphous chromia is mainly due to ammonia bound to Brønsted acid sites. With both chromia modifications, two types of NH_3 species adsorbed to Brønsted acidic sites are distinguished. The desorption of the more strongly bound species is completed at ≈400 K on α-Cr_2O_3 and at ≈420 K on amorphous chromia. Desorption from Lewis acid sites starts around 380 K. The existence of two types of Lewis-bound species, which was proposed previously (*5, 9*), has been clearly established by the results of this study. Ammonia molecules that are weakly bound to Lewis acid sites desorb between 373 and 403 K and are characterized by a symmetric deformational mode of 1260 cm^{-1}. More strongly bound ammonia starts to desorb from Lewis sites at temperatures above 403 K, and is identified by a deformational mode of 1210 cm^{-1}.

Crystalline and amorphous chromia exhibit different surface concentrations of the two types of ammonia species. While strongly Lewis-bound NH_3 molecules prevail on the oxidized surface of α-Cr_2O_3, a dominant contribution of the weakly bound species is observed on the surface of amorphous chromia pretreated in the same manner. With crystalline chromia, a significant NH_3 coverage persists at temperatures above 486 K, whereas with amorphous chromia, NH_3 desorption is complete at this temperature.

With the reduced chromia surfaces, these general trends are confirmed. Surface hydroxyl concentrations are decreased by the reductive treatment, especially on *crystalline* chromia, and consequently the relative size of the Brønsted desorption peak at 373 K is reduced (*1*). Again, two types of both Brønsted- and Lewis-bound ammonia molecules are identified. With α-Cr_2O_3, desorption from Lewis sites starts around 383 K, and the desorption rate reaches a maximum at 523 K. Weakly Lewis-bound ammonia molecules desorb between 311 and 386 K; the desorption of the more strongly Lewis-bound NH_3 species is still incomplete at 561 K.

The reduced surface of *amorphous* chromia is characterized by a very small surface coverage of Brønsted-bound ammonia molecules. Water desorption is observed when temperature rises to 373 K (subsequent to reduction at 598 K), indicating that water is produced by condensation of Cr–OH groups and the formation of Cr–O–Cr bridges. On the Lewis acid sites, only weakly bound NH_3 is observed on this surface, which is completely desorbed at 411 K.

The differences between the two morphologies, both in the oxidized and reduced states, with respect to relative concentrations of weakly and strongly bound NH_3 species are understood in terms of the results obtained in parts I and II of this study. It has been established (*1, 2*) that on the surface of α-Cr_2O_3, labile oxygen is only weakly bound and is therefore desorbed at low temperatures. In this process, one- and twofold coordinatively unsaturated chromium ions that exhibit strong Lewis acidity are generated. The present adsorption experiments suggest that even after oxidative treatment at 473 K, coordinatively unsaturated chromium sites that are capable of forming strong coordinative bonds with adsorbed ammonia are still present. Lewis acidity is particularly strong for the reduced α-Cr_2O_3 surface, as demonstrated by the high NH_3 desorption temperature observed both in TPRD experiments (*1*) and in this study (Fig. 7).

For amorphous chromia the labile oxygen density is still considerably higher after thermal treatment at 473 K, and the coordinatively unsaturated chromium sites are generated to a much lesser extent (cf. (*2*)). A high-surface oxygen density will lower the Lewis acidity of the chromium cations. Even after reduction of amorphous chromia, weakly Lewis acidic cations are observed, which are not capable of forming strong coordinative bonds with NH_3 molecules.

The two chromia modifications differ in yet another aspect: bands at 1720/1835 cm^{-1} and 1180 cm^{-1} assigned to the N_2O_2 dimer and the NO_2 chelate complex, respectively, are *not* observed on the surface of amorphous chromia. On α-Cr_2O_3, these two species are formed by oxidation of adsorbed NH_3 molecules.

Finally, implications of the present results for SCR selectivities are discussed. In the desired reaction, NH_3 is consumed for the reduction of NO in a stoichiometric amount. Besides, NH_3 can be oxidized directly according to either of two reactions,

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

and

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O$$

It has been discussed that the *cis*-N_2O_2 dimer and the NO_2 chelate surface complex are intermediates on the reaction pathway to N_2O. An oxidized surface state of crystalline chromia is required for the observation of the N_2O_2 dimer formed from ammonia. This reaction appears to be structure sensitive, as it requires two adjacent vacancies. These are present only on α-Cr_2O_3 to a significant extent. Structure sensitivity has been observed for the N_2O formation in SCR investigations over MoO_3 (*17*). No conclusion with respect to the immediate surface precursor of the N_2 product can be drawn from the present results.

The adsorption and binding of NO is another important factor that is likely to influence the SCR behavior of chromia catalysts. Further work in our laboratories is directed toward characterization of the NO adsorption using spectroscopic techniques.

ACKNOWLEDGMENTS

M.S.-M. thanks the Verband der Chemischen Industrie for a graduate research fellowship. Financial support of this work by the Deutsche Forschungsgemeinschaft (SFB 213) and by the Schweizerische Nationalfons is gratefully acknowledged.

REFERENCES

1. Curry-Hyde, H. E., Musch, H., Baiker, A., Schraml-Marth, M., and Wokaun, A., *J. Catal.* **133**, 397 (1992).

2. Schraml-Marth, M., Wokaun, A., Curry-Hyde, H. E., and Baiker, A., *J. Catal.* **133** (1992).

3. Curry-Hyde, H. E., Musch, H., and Baiker, A., *Appl. Catal.* **65**, 211 (1990).

4. 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.

5. Morishige, K., Kittaka, S., and Katsuragi, S., *J. Chem. Soc. Faraday Trans. 1* **78,** 2947 (1982).
6. Miyamoto, A., Ui, T., and Murakami, Y., *J. Catal.* **80,** 106 (1983).
7. Filimonov, V. N., Lopatin, Y. N., and Sukhov, D. A., *Kinet. Katal.* **10,** 458 (1969). [In English]
8. Tret'yakov, N. E., and Filimonov, V. N., *Kinet. Katal.* **14,** 803 (1973). [In English]
9. Eley, D. D., Rochester, C. H., and Scurrell, M. S., *J. Chem. Soc. Faraday Trans. 1* **69,** 660 (1973).
10. Belokopytov, Y. V., Kholyavenko, K. M., and Rubanik, M. Y., *Kinet. Katal.* **14,** 1280 (1973). [In English]
11. Belokopytov, Y. V., Kuznetsov, V. A., Kholyavenko, K. M., and Gerei, S. V., *J. Catal.* **44,** 1 (1976).
12. Zecchina, A., Coluccia, S., Guglielminotti, E., and Ghiotti, G., *J. Phys. Chem.* **75,** 2774 (1971); Zecchina, A., Coluccia, S., Cerruti, L., and Borello, E., *J. Phys. Chem.* **75,** 2783 (1971).
13. Zecchina, A., Guglielminotti, E., Cerruti, L., and Coluccia, S., *J. Phys. Chem.* **76,** 571 (1972).
14. Dunken, H., and Fink, P., *Chem. Tech.* **18,** 490 (1966). For a selection of references on ammonia adsorption, see, e.g., Jobson, E., Baiker, A., and Wokaun, A., *J. Chem. Soc. Faraday Trans.* **86,** 1131 (1990).
15. Kugler, E. L., Kadet, A. B., and Gryder, J. W., *J. Catal.* **41,** 72 (1976).
16. Winter, E. R. S., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, and V. I. Komarewsky, Eds.), Vol. 10, p. 196. Academic Press, New York, 1958.
17. Baiker, A., Dollenmeier, P., and Reller, A., *J. Catal.* **103,** 394 (1987).