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Chromia on Titania

IV. Nature of Active Sites for Selective Catalytic Reduction of NO by NH_3

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The surface sites on titania-supported chromia (CrO_x/TiO_2), which are relevant for the selective catalytic reduction (SCR) of NO by NH_3, and the undesired formation of N_2O have been investigated using temperature-programmed desorption (TPD) combined with *in situ* diffuse reflectance FTIR spectroscopy (DRIFT). The combined TPD and DRIFT measurements carried out on the differently pretreated (reduced, oxidised, exposed to SCR conditions) CrO_x/TiO_2 indicate that Brønsted-bound ammonia is crucial for the SCR reaction. N_2O is formed at temperatures above 450 K by direct oxidation of Lewis-bound NH_3 with oxygen present in the SCR feed gas.

TPD measurements carried out with CrO_x/TiO_2 previously loaded with NO and NH_3, respectively, showed that neither oxidised nor reduced CrO_x/TiO_2 convert NO *in the absence of NH_3* at the temperatures used for SCR. Adsorbed NO has been identified in various forms, including nitrate (1613 and 1517 cm^{-1}) and a Cr–ONO species (1458 cm^1). When adsorbed as a single reactant, *ammonia* desorbs molecularly from the prereduced catalyst and undergoes direct oxidation on a preoxidised catalyst leading to N_2O and H_2O at temperatures higher than about 350 K. At temperatures above 450 K, the direct oxidation of ammonia yielding N_2, becomes significant. In the absence of NO, direct oxidation of NH_3 to N_2 and N_2O occurs via Lewis-bound ammonia. In the presence of oxygen, ammonia is oxidised to NO above about 500 K.

TPD experiments with CrO_x/TiO_2, previously either reduced or oxidised and then exposed to the *SCR feed gas,* showed that the surface reduced with ammonia is inactive for the desired selective reaction between NO and NH_3, indicating that a partially oxidised state of the surface must be maintained for SCR; this observation confirms the crucial role of the oxygen in the SCR feed gas. The studies indicate that Brønsted-bound ammonia, characterised by bands at 1662 and 1425 cm^{-1}, enhances the adsorption of NO and is involved in the selective catalytic reduction of NO to N_2.

INTRODUCTION

Chromia belongs to the most active metal oxides for the selective catalytic reduction (SCR) of NO with ammonia, in the presence of an excess of oxygen (1–5). Amorphous chromia was found to be considerably more active and selective to N_2 formation than crystalline chromia (5). The activities of various Cr_2O_3 catalysts as well as the mechanism of the SCR reaction over Cr_2O_3 and Cr_2O_3–Al_2O_3 catalysts have been investigated by mass spectrometry and isotope labelling studies (6). In NO adsorption experiments on reduced supported chromium (VI) oxide, it has been reported that characteristic bands in the infrared spectrum are due to NO bound to chromium ions in oxidation states below +6 (7). The adsorbed species on silica-supported chromia catalysts following NO exposure have been assigned to N_2O_2 and NO (8), whereas on pure Cr_2O_3 catalysts NO adsorption has been suggested to lead to the two forms N_2O_2 and NO_2 (8). Infrared investigations have shown that ammonia is chemisorbed reversibly and irreversibly at Lewis site centres of Cr_2O_3, but NH_4^+ bound at Brønsted sites was not observed (9).

The thermal desorption curve of ammonia adsorbed on pure Cr_2O_3 contains two desorption maxima, indicating different binding sites (10). The rectangular pulse technique has yielded a number of active oxygen sites on the Cr_2O_3 surface of SCR catalysts (11). Two types of Brønsted sites as well as two types of Lewis sites have been deduced for preoxidised Cr_2O_3 from IR spectra, with significant differences in the distributions of the acid sites in crystalline and amorphous Cr_2O_3 species. The oxidation of NH_3 adsorbed on the catalyst leads to N_2O_2 and NO_2 species bound at the surface. The interaction of NO with amorphous Cr_2O_3 in comparison with crystalline Cr_2O_3 has been reported (12). Although the NO is adsorbed as nitrato and di-nitrosyl complexes on preoxidised catalysts, molecules of NO desorb without any decomposition during temperature-programmed desorption (TPD) (13).

Recently, we have extended our studies to titania-supported chromia catalysts and have reported the results as Parts I, II, and III of this series (14–16). The preparation, chemical, and structural properties, catalytic behaviour

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in SCR, and the oxidation state of the supported chromia have been addressed in these previous studies.

The aim of the present work was to gain information about the nature of the sites active in SCR of NO by NH_3 and the undesired reaction to N_2O. In the first section, TPD combined with *in situ* diffuse reflectance FTIR spectroscopy (DRIFT) is used to unravel the interaction of NH_3 and NO with differently pretreated CrO_x/TiO_2. In the second section transient experiments are used to determine the active sites for the formation of N_2 and N_2O, respectively.

EXPERIMENTAL

Catalysts were prepared by impregnation of TiO_2 (P25) with different amounts of $Cr(NO_3)_3 \cdot 9\ H_2O$, as described in detail in Part I (14) of this series. For the studies an FTIR instrument (Perkin–Elmer, model 1710) was connected to a mass spectrometer (Balzers, 6 × 125 mm-system quadrupole, Quadstar plus data reduction software). Diffuse reflectance FTIR measurements were carried out *in situ* with an environmental chamber (Starna, model HCV-D3) equipped with a temperature controller (Tecon 500). To simulate the conditions of a catalytic reactor, the sample holder was shaped as a small glass stew pan, with a sintered glass plate as the base. The mass spectrometer was used to monitor the concentrations of the different components in the product gas. Premixed gas mixtures (Carbagas, AG) consisting of 3600 ppm NH_3 in Ar, 3590 ppm NO in Ar, and 7.2% O_2 in Ar were used without further purification. Argon from cylinders (99.999) was first purified over Hydrosorb and Oxysorb (Messer–Griesheim). The gas flow was held constant at 50 ml/min (STP). SCR feed gas (900 ppm NH_3, 900 ppm NO, 18000 ppm O_2, in Ar) was mixed by mass flow controllers (Brooks).

The experimental procedure used is schematically represented in Fig. 1. The gas flow downstream of the sample was detected by mass spectroscopy (MS) during the whole experiments. The sample was calcined for 1 h in 7.2% O_2 in Ar; subsequently the temperature was reduced to 423 K, and an IR-background spectrum was recorded (200 scans, 8 cm^{-1}). The gas flow was changed to SCR feed gas at this temperature. After this period of stabilisation under reaction conditions, the sample was cooled to 373 K. Then the temperature was increased in steps of 50 K to 573 K, with each temperature value held constant for 30 min. *In situ* FTIR spectra were recorded (200 scans, 8 cm^{-1}) at each temperature plateau.

The gas flow was switched to pure Ar to start the temperature-programmed desorption (TPD) experiment on the SCR-feed-gas-loaded preoxidised catalyst (SCR-TPD) after cooling the sample to room temperature. In all TPD experiments a temperature ramp of 7.6 K/min was used.

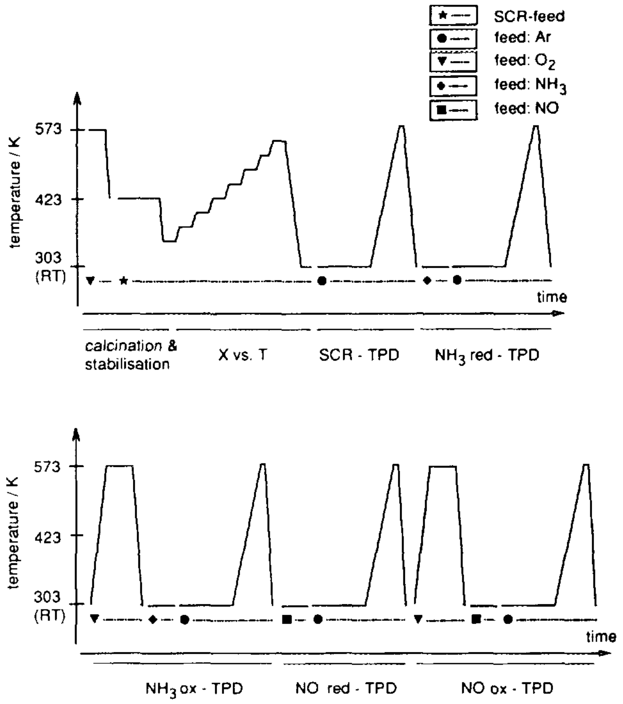

FIG. 1. Schematic representation of experimental procedure. Changes of temperature and composition of gas flow as a function of time are illustrated.

FTIR spectra were accumulated during successive intervals of 25 K each, while the temperature was increased from 298 to 573 K. These spectra represent an average of the surface state over each 25-K temperature interval, and are labelled with the initial temperature. For example, a spectrum labelled 323 K represents the spectra accumulated as the temperature was ramped from 323 to 348 K. To check the influence of the experiment on the state of the catalyst, a reference spectrum was recorded by FTIR after cooling the sample to room temperature every time.

The catalysts were exposed to NH_3 for 30 min at 298 K following the SCR-TPD (Fig. 1). This experiment, in which a prereduced surface is loaded with ammonia and then subjected to a temperature ramp, is henceforth referred to as "NH_3-(red)-TPD."

After the NH_3-(red)-TPD the sample was reoxidised at 573 K for 1 h in 7.2% O_2 in Ar (Fig. 1). Then the samples were again loaded with NH_3 for 30 min at 298 K. The TPD of a NH_3-loaded preoxidised catalyst is termed "NH_3-(ox)-TPD."

The last two experiments were repeated with the NO replacing NH_3 as the adsorbate gas, the resulting TPD spectra being referred to as "NO-(red)-TPD" and "NO-(ox)-TPD."

In the transient experiments background spectra were recorded as in the experiments above. The temperature was kept constant at 373 K in the first and at 423 K in the second series during these experiments. The SCR feed gas composition and the concentrations of the product gases were analysed by MS. Specific conditions are described under Results. The spectrum of the unloaded catalyst was used as background to obtain only the spectra of the adsorbed species in all FTIR spectra. The spectra are presented in the form of Kubelka–Munk $f(R/R_0)$ plots. The temperature of the sample was measured by a chromel–alumel thermoelement with an accuracy of ±3 K.

RESULTS

The TPD experiments were performed in the time sequence shown in Fig. 1, as described under Experimental. However, for presenting the assignments of the bands observed, we find it convenient to start with the description of the spectra exhibiting the smallest number of vibrational features, i.e., those recorded during NO-TPD. Subsequently, the FTIR and mass spectra observed during NH_3-TPD will be presented. The most complicated spectra, i.e., those observed during SCR-TPD, are discussed thereafter. After addressing the influence of the chromia content, FTIR spectra recorded *in situ* under reaction conditions and transient experiments will be described.

NO-TPD from a Pre-oxidised Surface

The spectrum recorded at 298 K (Fig. 2, left panel) exhibits two peaks at 1613 and 1562 cm^{-1}. The intense band at 1613 cm^{-1} was assigned by Schraml-Marth *et al.* (13) to bridging nitrate, and the 1562 cm^{-1} vibration to a bidentate nitrate species on chromia (both "type II" in the terminology of Ref. (13); higher frequency component of split ν_3 vibration in adsorbed nitrate ions). The corresponding lower wavenumber components (13) are detected as weak bands at 1215 and 1285 cm^{-1}. Similar bands due to adsorbed nitrate have been observed on oxidised and reduced titania by Dines *et al.* (17), Takagi-Kawai *et al.* (18), and Ramis *et al.* (19). It should be mentioned that all these groups worked with higher partial pressures of NO. In our study we found no evidence for adsorbed NO species on pure titania (P25). The broad band in the region 3750–3000 cm^{-1} is due to a small amount of physisorbed water, which was removed upon heating the sample to 398 K (Fig. 2, left panel). The intensity of both peaks at 1613 and 1562 cm^{-1} decreases with temperature, and no NO is observed to remain on the surface at 498 K.

The mass spectra recorded during TPD (Fig. 2, right panel) only show a desorption of NO, with maximum rate at 360 K. Formation of N_2, NH_3, H_2O, or N_2O is not observed. Note that the quantity of water physisorbed on the catalyst was below the detection limit of the mass spectrometer.

NO-TPD from a Pre-reduced Surface

Prominent new features in the FTIR spectra shown in Fig. 3 (left panel) are the intense band at 3630 cm^{-1} and

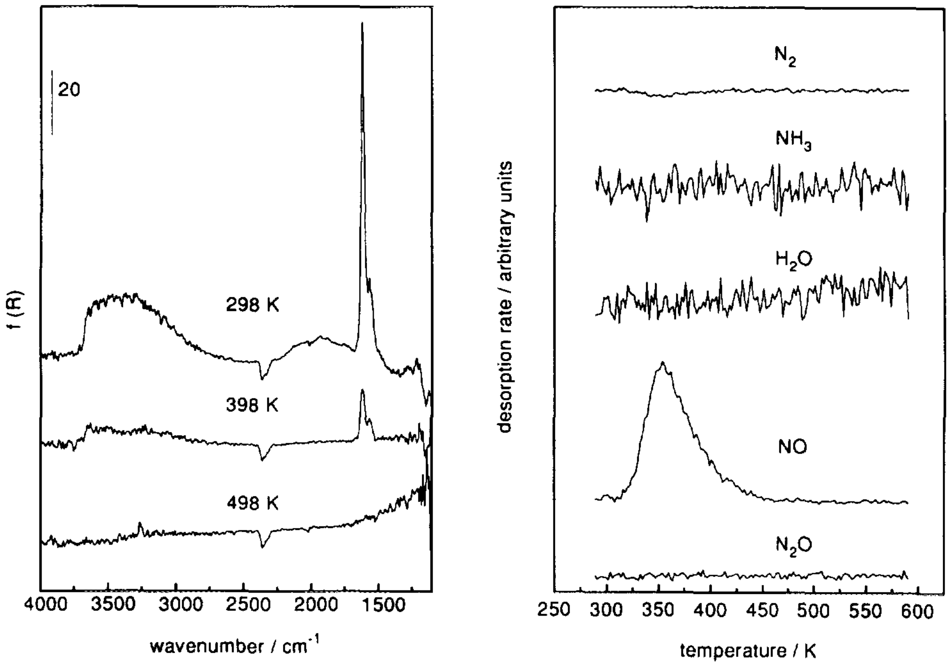

FIG. 2. NO desorption from 5 wt.% chromia/titania after *oxidative pretreatment* {NO-(ox)-TPD}. Left panel: DRIFT spectra at different temperatures; right panel: TPD recorded by mass spectroscopy.

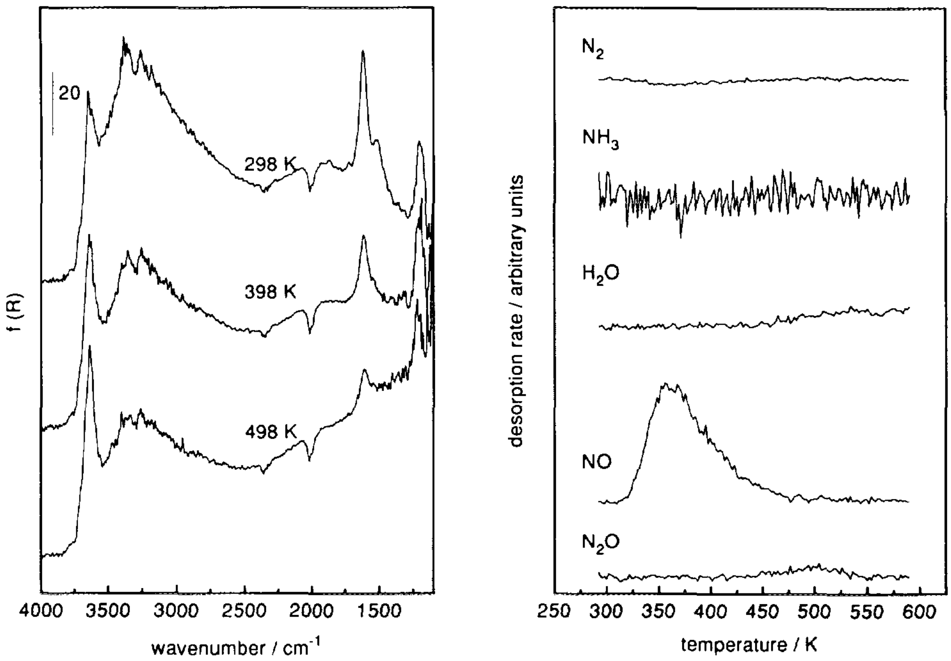

FIG. 3. NO desorption from 5 wt.% chromia/titania after *reductive pretreatment* {NO-(red)-TPD}. Left panel: DRIFT spectra at different temperatures; right panel: TPD.

the broad feature extending from 3500 to 3000 cm^{-1} at a temperature of 298 K. The latter band was assigned (16) to hydroxyl groups bound to surface chromium atoms in an oxidation state of +3, whereas the much narrower peak at 3630 cm^{-1} is due to the hydroxyl groups of TiO_2 (anatase). Further bands due to bridging nitrate (1613 cm^{-1}) (13) and bidentate nitrate at 1517 cm^{-1} ("type III," which is less strongly bound to the surface and desorbs at lower temperatures, as compared to the "type II" species mentioned above) are observed. The matching lower frequency vibrations of nitrate surface species appear as a broad band around 1200 cm^{-1}. The 1613 and 1517 cm^{-1} features decrease in intensity with increasing temperature; with the 1200 cm^{-1} band this tendency is less clear as a result of the smaller signal-to-noise ratio. All bands below 3500 cm^{-1} have become weaker at 498 K, whereas the anatase hydroxyl vibration at 3630 cm^{-1} has become better resolved.

With regard to NO, the TPD spectrum of Fig. 3 (right panel) shows the same pattern as described above with Fig. 2 (right panel). In addition, a small amount of water desorption is observed above 500 K.

NH_3-TPD from a Pre-oxidised Surface

Upon heating the catalyst subsequent to room temperature adsorption of ammonia, a complex band is observed in the 2500–3500 cm^{-1} range, as exemplified by the 323-K spectrum in Fig. 4 (left panel). The band was represented by a superposition of five vibrations; literature values (7, 20, 21) of the relevant frequencies were used as an input for the fit. The observed spectral envelope is well represented by the five components, shown as an inset. Bands at 3349 and 3227 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of Lewis-bound ammonia (7, 20, 21); the broad and intense band at 3162 cm^{-1} is thought to be due to the overtone of the asymmetric deformation mode enhanced by its Fermi resonance with the symmetric stretching mode. A peak at 2963 cm^{-1} and a shoulder at 2742 cm^{-1} have been attributed to the corresponding vibrations of Brønsted-bound ammonia by Busca (21).

Matching deformational motions are detected in the spectral region between 1200 and 1700 cm^{-1}. The peaks at 1603 and 1238 cm^{-1} are due to the asymmetric and symmetric deformational vibrations of Lewis-bound ammonia (12, 20, 22). The corresponding bands of the Brønsted-bound species are found at 1425 and 1662 cm^{-1}. We note that the symmetric deformation $\{\nu_2(E)\}$ of a free NH_4^+ ion at 1662 cm^{-1} is not IR active (23), but is commonly observed in the spectra of adsorbed ammonium ions.

The intensities of the peaks assigned to NH_3 bound to Brønsted sites have significantly decreased in the spectrum recorded at 398 K, whereas those attributed to Lewis-bound ammonia exhibit only a slight change. All

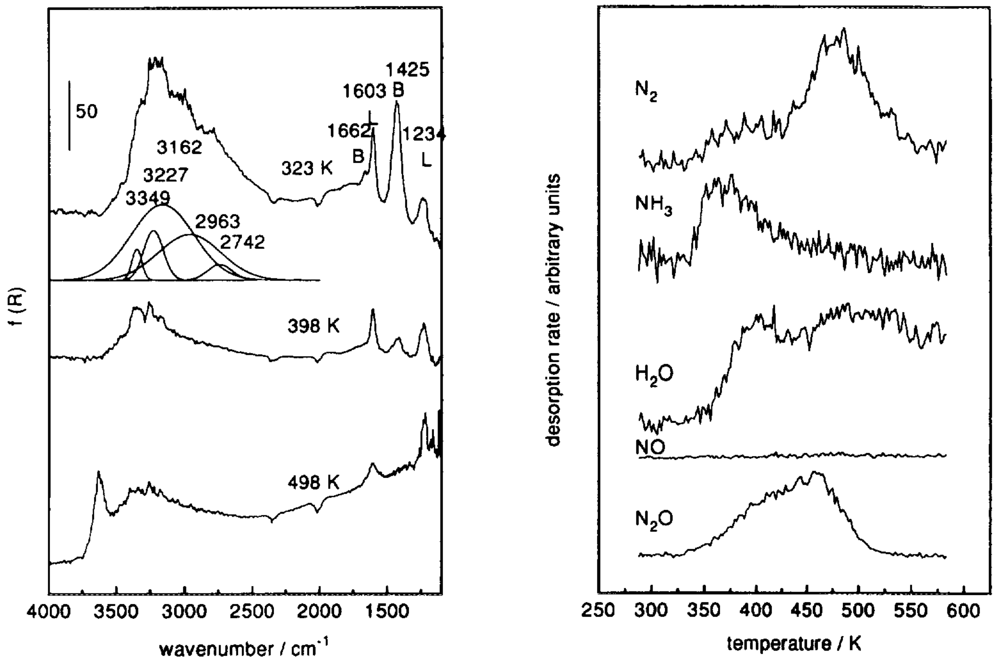

FIG. 4. NH_3 desorption from 5 wt.% chromia/titania after *oxidative pretreatment* {NH_3-(ox)-TPD}. Left panel: DRIFT spectra at different temperatures (bands due to Brønsted-bound and Lewis-bound ammonia are labelled by B and L, respectively); right panel: TPD.

mentioned bands have decreased in intensity at 498 K, whereas the 3630 cm^{-1} peak due to Ti–OH stretching vibrations has reappeared.

The mass spectra (Fig. 4, right panel) show, first, the expected signal due to molecular desorption of ammonia, peaking at 360 K. A weak nitrogen desorption around 380 K and a stronger one at 475 K suggest that N_2 has been produced by the oxidation of NH_3. Water evolution appears to be delayed with respect to the first nitrogen desorption event: for H_2O, a maximum at 390 K is followed by an almost constant desorption rate above 450 K. NO desorption is not observed during the entire TPD run. The N_2O mass signal shows a broad desorption band extending from 350 to 500 K, indicating that there are at least two types of differently bound species (12).

NH_3-TPD from a Prereduced Surface

The assignment of the 3350 and 3200 cm^{-1} vibrations in the NH-stretching region of the spectrum (Fig. 5, left panel), as well as that of the Ti–OH stretching band at 3630 cm^{-1} formed as a consequence of the reductive pretreatment, is the same as indicated above with Fig. 4. Similarly, the peak at 1603 cm^{-1} is attributed to the deformational vibration of Lewis-bound ammonia.

In the spectral region from 1220 to 1150 cm^{-1}, Busca *et al.* (21, 24) and Dines *et al.* (17) have reported bands from ammonia bound to different Ti^{4+} sites on pure titania. Following these authors, the 1210-cm^{-1} feature observed in our spectra is attributed to NH_3 bound to twofold coordinatively unsaturated Ti^{4+} centers, whereas the 1171 cm^{-1} vibration corresponds to ammonia at singly unsaturated Ti^{4+} sites. The 1135 cm^{-1} band is due to the symmetric deformational motion of hydrogen-bonded NH_3 on chromia (17, 21, 24, 25). From the observation of these three frequencies in our spectrum it is evident that the titania carrier is not completely covered by the deposited chromia in our catalyst.

In the corresponding TPD curves, ammonia desorption is found to first increase with temperature, reaching a maximum rate at 390 K; thereafter, the rate decreases again towards higher temperatures. Furthermore, water desorption starting at 350 K has been observed.

TPD from an SCR-Pretreated Surface

Besides the familiar NH stretching bands at 3350 and 3200 cm^{-1}, the FTIR spectrum recorded at 323 K (Fig. 6, left panel) shows a broad band extending from 3200 to 2700 cm^{-1}, assigned (7, 20, 21) to ammonium ions. The symmetric deformational vibration {ν_2 (E)} of surface-bound ammonium ions is observed as a small shoulder at 1663 cm^{-1}. The corresponding asymmetric deformation {ν_4 (F2)} at 1425 cm^{-1} overlaps with a band at 1458 cm^{-1} assigned to a surface nitrito species by Schraml-Marth *et al.* (13). The frequency position of the strongest peak, at 1608 cm^{-1}, corresponds to a value between those reported for Lewis-bound ammonia (1603 cm^{-1}) and for bridging

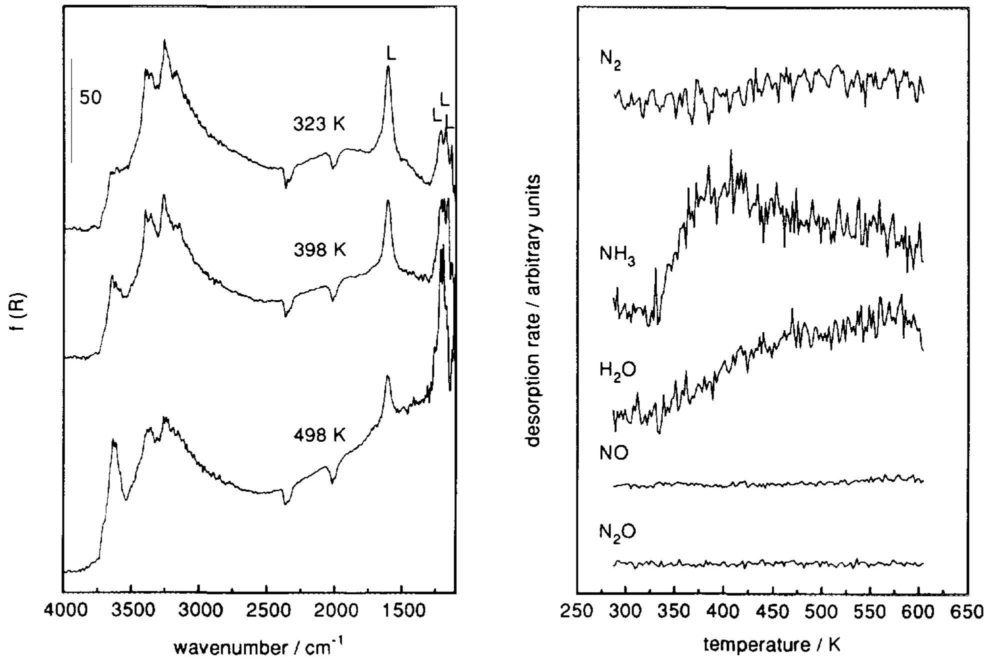

FIG. 5. NH_3 desorption from 5 wt.% chromia/titania after *reductive pretreatment* {NH_3-(red)-TPD}. Left panel: DRIFT spectra at different temperatures (labels as in Fig. 4); right panel: TPD.

nitrate (1613 cm^{-1}); hence the band is probably due to a superposition of these two species. Finally, the peak at 1238 cm^{-1} is assigned to the symmetric deformation vibration of Lewis-bound ammonia on chromia (7, 12, 20).

In the 323-K spectrum, this last feature appears to be split, with a second peak at 1210 cm^{-1}. This band is assigned as described above to NH_3 bound to Lewis acidic sites on titania. The broad band between 3200 and 2700

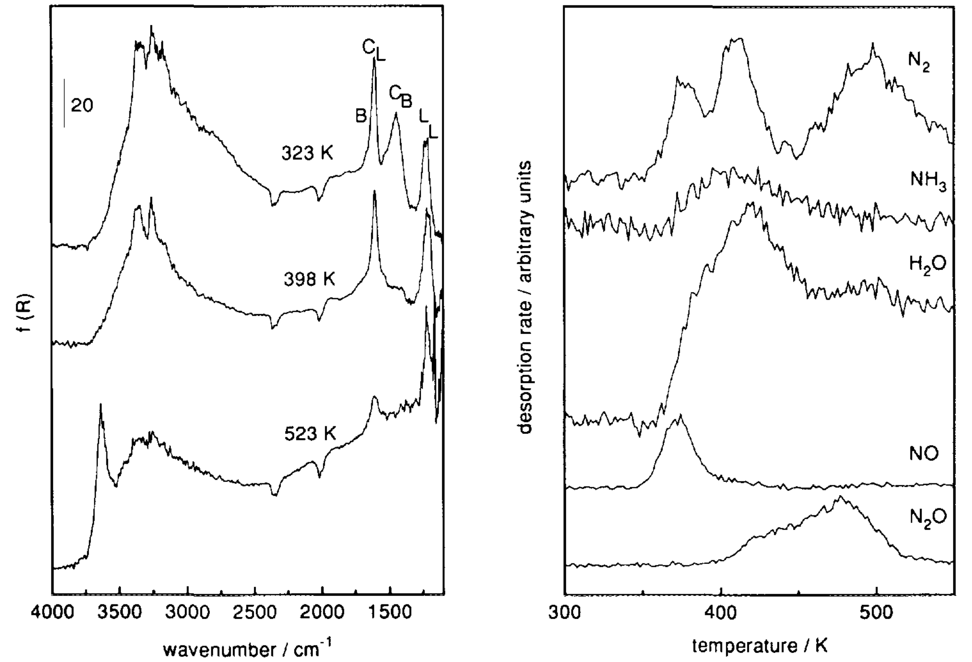

FIG. 6. Desorption experiment after *SCR pretreatment* (SCR-TPD) of 5 wt.% chromia on titania. Left panel: DRIFT spectra at different temperatures (C: surface-bound nitrites; other labels as in Fig. 4); right panel: TPD.

cm^{-1}, as well as the peaks at 1458, 1425, and 1214 cm^{-1}, has disappeared in the spectrum recorded at 398 K. A new band at 1415 cm^{-1} has appeared, which is assigned to $Cr-NO_2$ (13). From the ammonia, only two weak signals at 1603 and 1210 cm^{-1} are detected in the final spectrum taken at 523 K; the 3630 cm^{-1} band due to Ti–OH groups generated on the surface during the SCR reaction appears in addition.

In the SCR-TPD curves (Fig. 6, right panel), molecular desorption of NH_3 is seen to start at 360 K, reaching a maximum desorption rate at 390 K; NO shows maximum desorption at 370 K. Nitrogen desorption maxima are observed at 360, 400, and 490 K. From the comparison of these three curves, and those shown in Fig. 4, it is evident that nitrogen production at 360 K is due to the desired selective reaction between adsorbed NH_3 and coadsorbed NO (26). The nitrogen peak at 400 K is predominantly due to the same reaction, but here it seems that the NO is bound in a different position or with another kind of binding on the surface (cf. Fig. 4). According to the results of Topsøe (20) and Ramis *et al.* (19) NO binding on titania is different in the presence of ammonia. For the nitrogen desorption maximum at 490 K, a significant contribution of the direct oxidation process must be expected (cf. Fig. 4). N_2O exhibits a broad desorption band extending from 400 to 500 K, which according to its shape is apparently due to two different processes of N_2O formation.

Influence of the Chromia Loading

For chromia contents varying between 1 and 10 wt.%, FTIR spectra are shown in Fig. 7 (left panel) for catalysts that had been subjected to an oxidative pretreatment, and then loaded with SCR feed gas during the cooling process between 573 and 298 K (Fig. 1). The spectral features are qualitatively similar for all catalysts. However, with increasing chromia content the intensities of the NH stretching vibrations are drastically decreased relative to the lower frequency vibrations.

In the nitrogen TPD spectra (Fig. 7, right panel), the catalyst loaded with 1 wt.% of chromia features a single desorption event at 340 K. With increasing chromia loading new N_2-desorption peaks are seen to develop at 380 and 475 K.

Observation of the Catalyst Surface under Reaction Conditions

Catalysts containing different amounts of supported chromia have been exposed to SCR reaction conditions at 423 K *in situ* in the FTIR spectrometer, and are compared with respect to adsorbed surface species in Fig. 8. As indicated above with Fig. 7, the decrease in the NH stretching absorptions above 2500 cm^{-1} with increasing chromia content is remarkable. This is partly due to the fact that hydroxyl groups are no longer available for the binding of ammonia. We note, however, that the re-

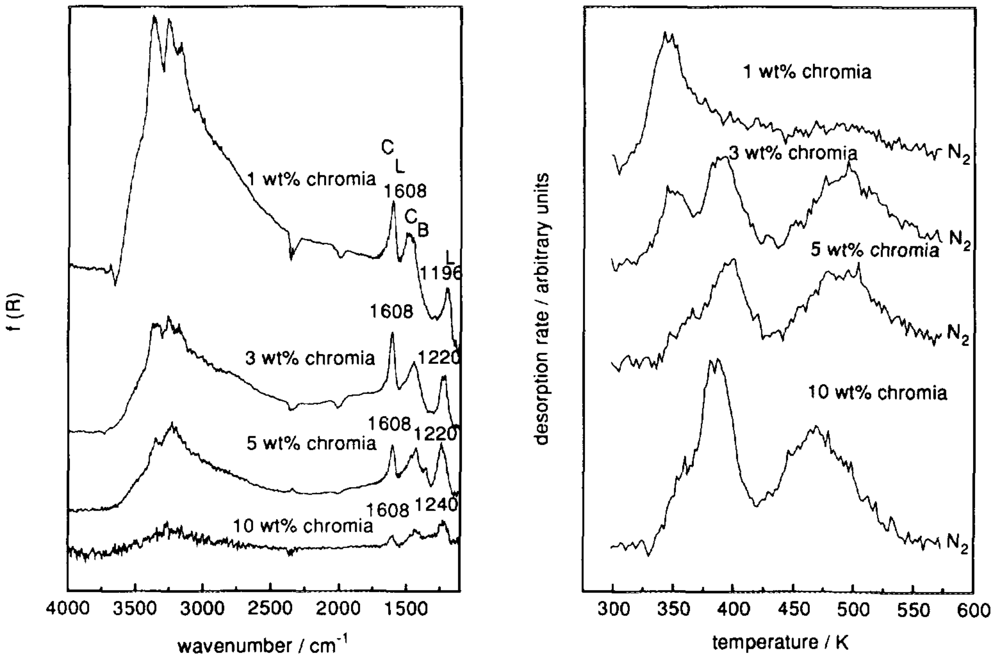

FIG. 7. Desorption after *SCR pretreatment* (SCR-TPD) of chromia/titania catalysts with different chromia loadings. Left panel: DRIFT spectra (labels as in Fig. 6); right panel: TPD.

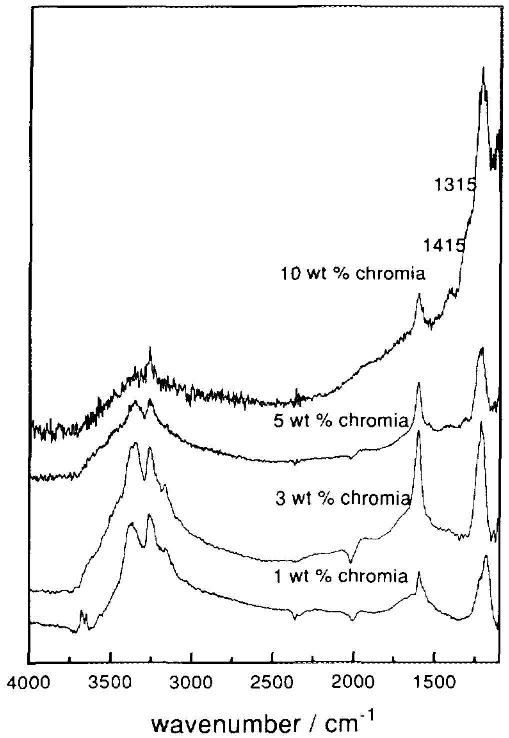

FIG. 8. *In situ* DRIFT spectra recorded *during SCR reaction* at 473 K over chromia/titania catalysts with different chromia loadings.

flectivity of the unloaded catalyst decreases with increasing chromia content, as a consequence of a broad electronic absorption band extending from the visible to the near infrared region. Recently, the presence of Cr(IV) on the catalyst surface has been established under reaction conditions. The presence of this additional oxidation state gives rise to the visible black colour of the catalyst, and to a structureless broad absorption which is characteristic for a material with delocalized electrons. Consequently, it is difficult to compare the absolute intensities of the peaks in the spectra recorded for different chromia contents.

The spectrum of the 1 wt.% chromia catalyst (Fig. 8) exhibits two prominent features at 1190 and 1596 cm^{-1} in the lower frequency region. With 3 wt.% loading of CrO_x, the peak positions have shifted to 1214 and 1603 cm^{-1}, respectively. Bands at 1190 and 1214 cm^{-1} are assigned to NH_3 bound to differently coordinated Ti^{4+} sites (17, 19, 21, 24). Frequencies of 1596 and 1603 cm^{-1} are due to the asymmetric deformational motion of Lewis-bound NH_3. The slight frequency differences observed point to a slightly different type of binding depending on the chromia loading.

The spectrum of the catalyst containing 5 wt.% chromia shows the corresponding NH_3 features at the further shifted frequencies of 1223 and 1603 cm^{-1}. In addition, two small shoulders at 1315 and 1415 cm^{-1} have been assigned (22) to stretching motions of NO_2 bound to chromia ($Cr-NO_2$). The spectrum of the catalyst with the highest chromia content shows only three bands at 1220, 1311 (shoulder), and 1603 cm^{-1}, which are assigned as above.

The influence of the reaction temperature on the concentrations of surface species observed *in situ* under SCR reaction conditions is displayed in Fig. 9. At the lowest temperature, 373 K, a signal at 1425 cm^{-1} is detected, which is not observed at higher temperatures. Upon raising the temperature from 373 to 473 K, the peak at 1603 cm^{-1} due to Lewis-bound ammonia loses intensity as compared to the band at 1215 cm^{-1}. At 523 K the peak position appears shifted to 1611 cm^{-1}, indicating the presence of surface-bound nitrate. Between the above-mentioned major bands, two smaller signals at 1311 and 1415 cm^{-1} are observed to grow upon increasing the temperature from 423 to 473 K.

Transient Experiments

In the transient experiments performed at 373 and 423 K, the ammonia component in the feed was momentarily switched to argon after the catalyst had been exposed to SCR reaction conditions for 30 min. At the lower temperature, rapid disappearance (Fig. 10) of the peak at 1425 cm^{-1} due to Brønsted-bound ammonia during the first

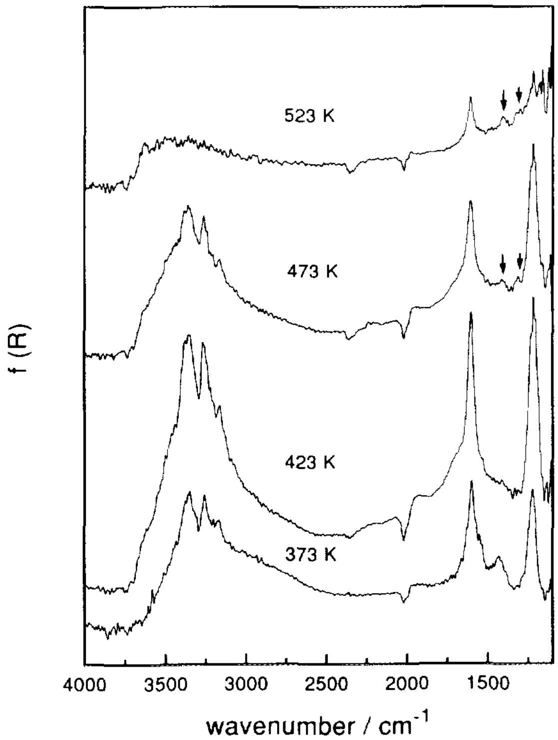

FIG. 9. *In situ* DRIFT spectra recorded *during SCR reaction* over 5 wt.% chromia/titania at different reaction temperatures.

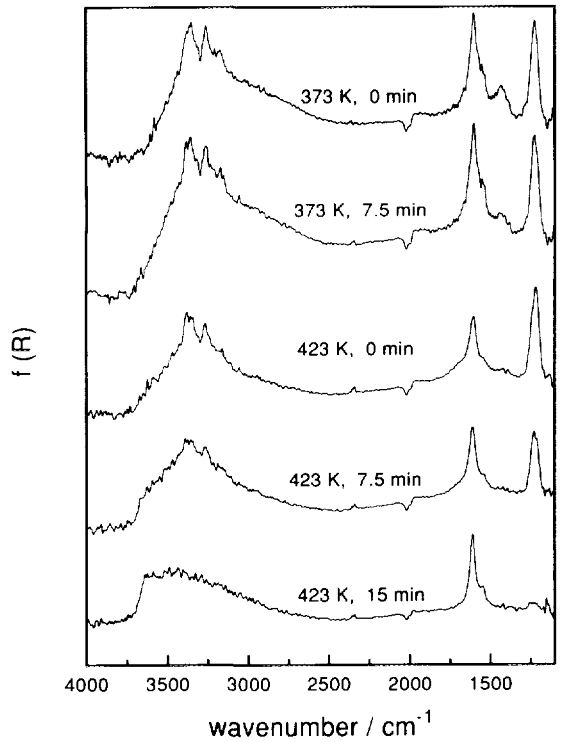

FIG. 10. Transient DRIFT experiments, in which the NH$_3$ component of the SCR feed gas was substituted by Ar at t = 0 min. Catalyst: 5 wt.% chromia/titania; temperature: 373 K and 423 K, as labelled.

few minutes is accompanied by termination of the N$_2$ production, as monitored in the mass spectrometer.

When the same substitution of NH$_3$ by argon is carried out at 423 K (lower traces in Fig. 10), all peaks except those due to surface-bound NO are observed to decrease in intensity during the first 7.5 min. After 15 min., the signals due to adsorbed NO are the only ones that remain observable; N$_2$ production stopped simultaneously.

In an analogous experiment at 423 K (spectra not shown), the NO component in the SCR feed was suddenly replaced by argon, other conditions being the same as in Fig. 10. No changes in the intensities of the peaks assigned to Lewis-bound ammonia were observed subsequent to this switch. A gradual decrease in the formation of N$_2$ and H$_2$O was observed in the mass spectrometer after 30 min. From the continuation of N$_2$ production after termination of the NO feed, we conclude that nitrogen and water must be produced by the direct oxidation of ammonia, in a catalytic reaction with the oxygen contained in the feed.

DISCUSSION

TPD of Ammonia

On a prereduced chromia surface, as resulting, e.g., from SCR-TPD, adsorption of ammonia exclusively results in binding to Lewis sites, as shown in Fig. 5. In the corresponding TPD experiment, NH$_3$ is observed to desorb molecularly, and no other nitrogen-containing species are observed. Water desorption persisting up to higher temperatures is observed simultaneously. Thus it appears that coordinatively bound ammonia does not react with a prereduced surface. As the possibility exists that the pretreatment of the sample in the DRIFT cell under the flow of the various feeds may not lead to complete removal of adsorbed water, the proportions of Brønsted-bound and Lewis-bound ammonia could not be determined absolutely.

Adsorption of ammonia on a preoxidised surface (Fig. 4) gives rise to a significantly different behaviour. In this case, both Lewis-bound and Brønsted-bound ammonia are detected. Upon increasing the temperature to 398 K, a decrease in the intensity of the bands related to the Brønsted-bound species (1662 and 1425 cm^{-1}) is observed; the mass spectra show that this is mainly due to molecular desorption of NH$_3$. Development of N$_2$ and water in the same temperature region (Fig. 4, right panel) demonstrates that a minor fraction of the adsorbed NH$_3$ reacts with surface oxygen.

Referring again to Fig. 4, desorption of NH$_3$ from Lewis sites (bands at 3370, 3200, and 1603 cm^{-1}) sets in at higher temperatures. Ammonia molecules bound through their lone pairs to surface chromium ions do react with surface oxygen, thereby reducing the surface. This is observed by the formation of a Ti–OH peak at 3630 cm^{-1} above 498 K, and is confirmed in the TPD spectra (Fig. 4, right panel). Above 425 K nitrogen formation becomes significant; N$_2$O and water are observed above 350 K. The appearance of a very broad N$_2$O desorption feature, which consists of at least two peaks, may be attributed to the existence of differently bound types of Lewis-bound ammonia molecules, in agreement with the results of Schraml-Marth *et al.* (12) on pure chromia samples.

SCR–TPD Experiments

When a catalyst which has been exposed to SCR reaction conditions up to 573 K is subsequently exposed to the SCR feed at ambient temperature, the DRIFT spectra (Fig. 6, left panel) show the presence of both Brønsted-bound and Lewis-bound ammonia, as well as of adsorbed NO. First, as mentioned under Results, the precise frequency position of the most intense 1608-cm^{-1} band indicates that the latter represents a superposition of Lewis-bound ammonia, and of NO adsorbed in the form of surface nitrates (1613 cm^{-1}). Second, the shoulder at 1445 cm^{-1} (on the high-frequency side of the 1425-cm^{-1} peak) points to a Cr–ONO vibrational mode (13). Third, the doublet around 1225 cm^{-1} is assigned to NH$_3$ Lewis-bound to the TiO$_2$ surface (17, 19, 21, 24).

When the temperature is increased to 398 K during a TPD run on this sample (Fig. 6, left panel), the NO-related features at 1613 and 1445 cm^{-1} disappear together with the description of Brønsted-bound ammonia. This observation strongly suggests that the adsorption of NO on chromia depends on the presence of ammonia on the surface. A similar change in the adsorptive properties of NO on V_2O_5/TiO_2 has been reported by Topsøe (20).

In the temperature range from 300 to 440 K, desorption of NH_3 and NO, as well as the formation of N_2 and H_2O is observed in the TPD spectra (Fig. 6, right panel). Comparing this result with the NH_3 desorption experiments discussed above, we conclude that during SCR-TPD, part of the adsorbed ammonia reacts with adsorbed NO, forming N_2 and H_2O. The two N_2 desorption peaks observed between 350 and 440 K suggest that two variants of the described reaction are proceeding on the surface. This correlates with the fact that NO is known to adsorb on the chromia surface in the form of two species bound with different strengths (8, 13): A chelate-bound NO_2- complex was found to desorb around 423 K, and a Cr-ONO complex around 473 K. In contrast, surface-bound nitrates of "type II" (13) are thermally much more stable, and reside on the surface up to 573 K.

In addition to the selective reaction with NO, Lewis-bound ammonia may react with surface oxygen directly at temperatures above 420 K, as was found in the case of the NH_3 (ox)-TPD experiment (Fig. 4, right panel). This behaviour is further supported by the kinetic measurements reported in Part II of this study (15), where the selectivity to N_2O was found to increase sharply above 420 K (Fig. 9 of Ref. (15)). Nitrogen and N_2O (peaking around 480–490 K), as well as H_2O, are produced by this reaction. The concomitant reduction of the surface is observed by the appearance of the 3630 cm^{-1} Ti–OH vibrational band.

Influence of the Chromia Loading

The nitrogen desorption observed (Fig. 7, right panel) shows pronounced differences between the catalysts with varying chromia content. In particular, attention is drawn to the desorption events between 350 and 450 K. Correlating these observations with the results of the previous section, we can conclude that the catalyst exhibits different binding sites for NO, associated with different binding energies.

The catalyst containing 1 wt.% of chromia gives rise to a single N_2 desorption peak (Fig. 7); the low temperature of about 330 K matches the thermal stability of a chelating NO_2- species. As the chromia loading is increased to 3 wt.% this peak shifts to 340 K, and its strength is decreased. In addition, a second peak due to the specific reduction of ammonia appears at 390 K. The described changes continue as the loading is increased to 5 wt.%; for the catalyst containing 10 wt.% of CrO_x the 380 K desorption feature is dominant.

The changes in bonding strength inferred from the TPD spectra are also reflected in the DRIFT spectra of Fig. 7 (left panel), where the frequency of the peak assigned to the more weakly bound NO_2- chelate complex increases from 1196 to 1240 cm^{-1} with increasing chromia loading, paralleling the shift of the lowest N_2 desorption maximum from 330 to 340 K. At the same time, the relative intensity of the 1458-cm^{-1} feature assigned to Cr–ONO and Brønsted-bound ammonia is increasing, such that the latter species can be associated with the 380-K nitrogen production peak.

A further conclusion that may be drawn from the DRIFT spectra of Fig. 7 is that the relative amount of Brønsted-bound ammonia increases with the chromia loading. This finding correlates with the size of the low-temperature nitrogen desorption signals in Fig. 7, and with the turnover measurements (15) which showed the low-temperature nitrogen production to increase with the chromia loading.

A high-temperature nitrogen desorption event is seen between 475 and 500 K in Fig. 7 for the catalysts containing between 3 and 10 wt.% of chromia. From the SCR-TPD experiments discussed above and previous kinetic measurements (15), this process may be associated with the direct oxidation of Lewis-bound ammonia. The NH_3-(ox)-TPD and the SCR-TPD both show the same pattern of the N_2O desorption. Also, the N_2 desorptions in the temperature range above 450 K are comparable in both TPD experiments. As in the NH_3-(ox) experiments, N_2O and N_2 originate from bound NH_3. The existence of the same N_2O desorption curve, as well as the similarity of the N_2 desorption pattern in the region above 450 K, corroborates that N_2 originates from direct oxidation of NH_3 in the high-temperature region of the SCR experiments (Fig. 7).

Adsorbed Species under Reaction Conditions

The influence of temperature on the adsorbate concentrations, as evidenced in Fig. 9, supports the above conclusions on the reaction mechanism. At 373 K bands due to both Brønsted-bound and Lewis-bound ammonia, as well as the various forms of surface-bound NO, are detected. Under these conditions the desired reaction of adsorbed NH_3 and NO, to yield N_2 and H_2O, is observed; this temperature is not high enough to activate the production of N_2O.

At 423 K the peaks due to Lewis-bound ammonia are seen to dominate, whereas the band at 1425 cm^{-1}, due to Brønsted-bound ammonia, is hardly detectable. TPD spectra recorded under these conditions indicate that the effluent concentrations of NH_3 and NO are smaller than in the feed gas, and that N_2, N_2O, and H_2O are produced.

The two additional bands, observed at 1415 and 1315 cm^{-1} in the 473-K spectrum of Fig. 9, have been assigned (13) to a surface nitrite species. Here the TPD spectra show relative increases in the amounts of both N_2 and NO leaving the catalyst surface. The effluent concentration of NH_3 decreases, while that of water increases.

Upon increasing the temperature to 523 K, even larger concentration of NO, N_2O, and H_2O are detected in the mass spectra, whereas the concentrations of NH_3 and N_2 are decreasing. This indicates that, at higher temperatures, formation of N_2O is favored over nitrogen production. In addition, direct oxidation of NH_3 is occurring. Peaks at 1223, 1415, and 1612 cm^{-1} are observed in the top spectrum of Fig. 9. The relative increase in the intensity of the 1415-cm^{-1} peak may be correlated with the increase in the NO concentration in the effluent gas stream, and is in agreement with the production of NO from adsorbed nitrite reported by Curry-Hyde *et al.* (27).

The chromia content has a pronounced influence on the surface species present under reaction conditions at the higher temperature of 473 K, as seen in Fig. 8. Whereas only small peaks at 1596 and 1196 cm^{-1} assigned to Lewis-bound ammonia species on Ti^{4+} are seen in the spectrum of the 1 wt.% chromia catalyst, the intensity of the NH_3-related features increases for the catlayst containing 3 wt.% of CrO_x. For the catalysts loaded with 5 and 10 wt.% of chromia, weak peaks at 1315 and 1415 cm^{-1} due to adsorbed NO (Cr–NO) are detected. This may be correlated with the increasing turnover frequency (15) for higher chromia loading, as a consequence of which some adsorbed surface intermediates become observable.

Transient Experiments

When the ammonia component of the SCR feed is substituted by argon, the NO turnover gradually decreases to zero. Simultaneously, the peaks due to Brønsted-bound ammonia disappear in the FTIR spectra (Fig. 10) within 7.5 min at 373 K. After 15 min at 423 K, the only remaining bands detected are those due to NO adsorbates.

In the complementary experiment where the NO component of the feed is replaced by argon (spectra not shown), no changes in the signals due to Lewis-bound ammonia are observed. At sufficiently high temperatures, some nitrogen and water continue to be produced by the direct oxidation of ammonia.

CONCLUSIONS

TPD experiments performed on catalysts loaded with the individual reactants show that on CrO_x/TiO_2, in either the reduced or the oxidised surface states, NO is not transformed. In contrast, ammonia desorbs molecularly from the reduced catalysts, but undergoes direct oxidation on preoxidised catalyst surfaces. Thereby N_2O is produced at temperatures above 350 K, and nitrogen is released above 450 K.

TPD experiments with the SCR-feed-gas-loaded catalysts in comparison with SCR tests show that a reduced surface is inactive for the desired selective reaction between NO and NH_3: A partly oxidised state of the surface must be maintained by the presence of oxygen in the feed to balance the partial reduction by NH_3.

Adsorbed NO has been identified in various forms, including surface nitrite (Cr–ONO) and surface nitrate. The presence of Brønsted-bound ammonia promotes the adsorption of NO, and appears to be crucial for the selective reduction.

At temperatures above 420 K (15), the direct oxidation of ammonia yielding N_2, N_2O, and H_2O becomes significant. In this temperature range, only Lewis-bound ammonia is observed in the *absence* of NO. This ammonia species is oxidised to N_2 and N_2O. In the *presence* of NO, the reaction of the Lewis-bound NH_3 with NO, forming N_2O, occurs concomitantly with the ammonia oxidation described above. At still higher temperature, ammonia oxidation to NO is favoured.

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