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Chromia Supported on Titania

VI. Properties of Different Chromium Oxide Phases in the Catalytic Reduction of NO by NH_3 Studied by *in Situ* Diffuse Reflectance FTIR Spectroscopy

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Chromia on titania catalysts containing different chromium oxide phases, i.e., CrO_2, CrOOH, and Cr_2O_3, have been prepared and tested for the low-temperature selective catalytic reduction of nitric oxide by ammonia (SCR). The different chromium oxide phases (10 wt% total chromium oxide content) differ in their activity and selectivity to N_2. Supported CrOOH is oxidized to CrO_2 under SCR conditions above 570 K. The highest activity paired with a high selectivity to N_2 (>90%) is found for amorphous Cr_2O_3 supported on titania prepared by decomposition of $CrOOH/TiO_2$ under mild conditions. Crystallization of Cr_2O_3 induced at higher temperatures reduces the activity significantly. The surface adsorption sites for the components of the SCR feed gas were investigated using temperature-programmed desorption combined with *in situ* diffuse reflectance FTIR spectroscopy. NO, which is adsorbed as a nitrate species, is most abundant on CrO_2, and seems to be responsible for the formation of undesired N_2O at temperatures below 400 K over catalysis containing this chromium oxide. © 1995 Academic Press, Inc.

INTRODUCTION

Adsorption of Reactants on Chromia Catalysts

The activity of various Cr_2O_3 catalysts and the mechanism of the low-temperature selective catalytic reduction of nitric oxide by ammonia (SCR) over Cr_2O_3 and CrO_x-Al_2O_3 catalysts have been investigated by mass spectroscopy and isotopic labeling experiments by Niiyama *et al.* (1, 2). NO adsorption experiments on supported Cr(VI) oxide reported by Eley *et al.* (3) showed characteristic IR bands of NO bound to a chromia species with an oxidation state below +6. Upon exposure of silica-supported chromia to NO, Kugler *et al.* (4, 5) observed adsorbed N_2O_2 and NO, whereas on pure Cr_2O_3 NO was adsorbed as N_2O_2 and as NO_2 species. Belokopytov *et al.* (6) found from IR spectroscopy that ammonia binds to Lewis acidic sites of Cr_2O_3, whereas ammonia bound at Brønsted sites could not be observed on Cr_2O_3. TPD experiments on ammonia-loaded pure Cr_2O_3 (7) showed the existence of two different binding sites, as indicated by two desorption maxima.

On preoxidized Cr_2O_3 prepared from $Cr(NO_3)_3$, two types of Brønsted sites, as well as two kinds of Lewis sites, could be distinguished by IR spectroscopy. Crystalline and amorphous chromia prepared by this method showed significant differences in the distribution of acid sites (8). The oxidation of NH_3 adsorbed on these catalysts resulted in adsorbed N_2O_2 and adsorbed NO_2. For the same system, the interaction of NO with amorphous chromia was compared with that on the crystalline catalyst (9).

Selective Catalytic Reduction of NO

Bulk and supported chromium(III) oxide were shown to be active catalysts for the selective catalytic reduction of nitric oxide by ammonia in excess oxygen (10–14). Amorphous chromia clearly exhibits a higher activity and a better selectivity to N_2 than crystalline chromia (14).

Highly active chromia/titania catalysts could be prepared by impregnation of titania with chromium nitrate (15, 16). *In situ* FTIR and TPD experiments of these catalysts showed that Brønsted-bound ammonia is crucial for SCR (17). A clear assignment of the chromium oxide phase onto which NH_3 or NO are bound was difficult, however, in view of the presence of several, partly identified chromium oxide phases. Recently, we have succeeded in preparing pure and mixed phases of CrO_2, CrOOH, and Cr_2O_3 on titania with a total chromium content of ca. 7 wt% (18, 19). On these supported chromium oxide phases, a direct comparison of the catalytic behavior in SCR has been

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TABLE 1

Preparation and Phase Composition of Supported Chromium Oxide Catalysts

Sample	Preparation	Chromium oxide phases (at.%)
CrO_2-ST	Impregnation of TiO_2 by chromium nitrate, calcination in O_2 at 573 K, 3 h	95% CrO_2 5% Cr(VI, V, ...)
CrO_2-1 h	CrO_2-ST decomposed in Ar at 773 K, 1 h	27% CrO_2 73% Cr_2O_3
CrO_2-5 h	CrO_2-ST decomposed in Ar at 773 K, 5 h	22% CrO_2 78% Cr_2O_3
CrOOH-ST	CrO_2-ST reduced in H_2 at 523 K, 1 h	88% CrOOH 12% CrO_2
CrOOH-1 h	CrOOH-ST decomposed in Ar at 773 K, 1 h	73% Cr_2O_3 24% CrOOH 3% CrO_2
CrOOH-5 h	CrOOH-ST decomposed in Ar at 773 K, 5 h	83% Cr_2O_3 15% CrOOH 2% CrO_2
CrOOH-773	CrO_2-ST reduced in H_2 at 773 K, 0.25 h, decomposed in Ar at 773 K, 5 h	79% Cr_2O_3 19% CrOOH 2% CrO_2

performed. In the present paper we focus on the comparison of Cr_2O_3, CrOOH, and CrO_2 supported on titania. SCR feed gas and ammonia adsorption as well as TPD experiments are used to characterize the different acid/active sites of these catalysts.

EXPERIMENTAL

Catalysts

The catalysts were prepared by impregnation of TiO_2 (P25, specific surface area 49 m^2/g, supplier Degussa) with chromium nitrate nonahydrate followed by thermal treatment, as described in the preceding paper (19). Starting from the catalyst calcined under oxygen for 3 h at 573 K, which contains mainly CrO_2, two series of catalysts were prepared, using two different routes starting from either CrO_2 or CrOOH. The thermal decomposition of these catalysts under argon yields mixtures of CrO_2 and Cr_2O_3 with an increasing fraction of Cr_2O_3 depending on conditions (18). The reduction of the initial catalyst under hydrogen produces CrOOH, which can be decomposed under argon between 673 and 773 K, providing mixtures of CrOOH and Cr_2O_3 (19). Table 1 lists the procedures used to transform the original CrO_2-containing catalysts to the specified chromium oxides. The mild conditions used prevent undesired crystallization of Cr_2O_3.

Apparatus and Experimental Procedures

The temperature-programmed desorption studies were carried out using an apparatus consisting of an FTIR instrument (Perkin–Elmer, Model 1710) equipped with a heatable environmental chamber (Starna, Model HCV-D3), which was connected to a mass spectrometer (Balzers OMG 420, 6 × 125 mm system, Quadstarplus software). The apparatus has been described in detail elsewhere (20). A stream of the reactant gas mixture was passed through the catalyst, which was placed on a sintered plate in a glass vessel. The temperature of the sample was measured to an accuracy of ±3 K using a Chromel–Alumel thermocouple.

Concentrations in the desorbing gas stream were monitored by mass spectrometry. The following gas mixtures (Carbagas, AG) were used directly as calibration gases and for the preparation of the SCR feed gas mixture: 3600 ppm NH_3 in Ar, 3590 ppm NO in Ar, 7.2% O_2 in Ar, 1980 ppm N_2O in Ar, and 3300 ppm N_2 in Ar.

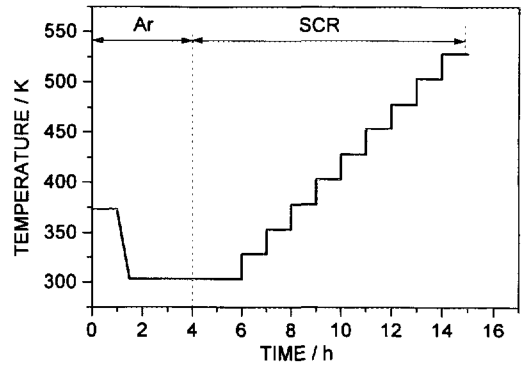

FIG. 1. Schematic presentation of the experimental procedure for change in temperature and feed composition as a function of time.

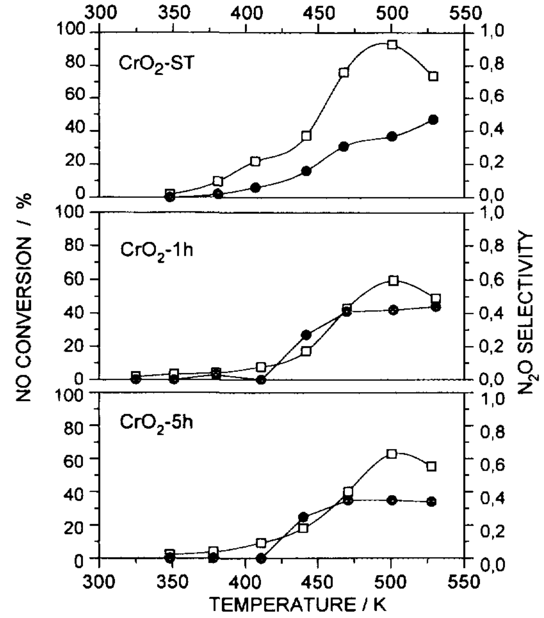

FIG. 2. Conversion of nitric oxide (open symbols) and selectivity to nitrous oxide (filled symbols) as a function of temperature for differently prepared (see Table 1) chromium oxide catalysts: CrO$_2$-ST: impregnation of TiO$_2$ by chromium nitrate followed by calcination in O$_2$ at 573 K for 3 h. CrO$_2$-1 h: sample CrO$_2$-ST decomposed in Ar at 773 K for 1 h. CrO$_2$-5 h: sample CrO$_2$-ST decomposed in Ar at 773 K for 5 h.

Ar (99.999%) was dried by passage through Hydrosorb and Oxysorb cartridges (Messer-Griesheim). The gas flow rate was adjusted to 50 ml (STP) min^{-1}. SCR-feedgas (900 ppm NH$_3$, 900 ppm NO, 1.8% O$_2$, balance Ar) was mixed by flow controllers (Brooks). For kinetic measurements the diffuse reflectance chamber was replaced by a heatable U-tube reactor with an i.d. of 3.6 mm, as described in Ref. (21). The measurements were carried out with the SCR feed gas at a gas hourly space velocity (GHSV) of 28,000 h^{-1}, and 0.062 g of catalyst, sieved to 300–500-μm-diameter grain size, corresponding to a catalyst bed volume of ca. 0.075 cm^3, were used. Selectivities to N$_2$ and N$_2$O are defined as $S_i = 2F_i/(F_{\mathrm{NO,in}} + F_{\mathrm{NH_3,in}} - F_{\mathrm{NO,out}} - F_{\mathrm{NH_3,out}})$, where F_i is the molar flow rate (mol s^{-1}) of species i (N$_2$ or N$_2$O) at the reactor outlet and the subscripts "in" and "out" indicate the flow rates of NO and NH$_3$ at the reactor inlet and outlet, respectively.

A scheme illustrating the experimental procedure is shown in Fig. 1. In each phase of the experiments, the gas mixture was monitored by mass spectrometry. Background spectra (500 scans, resolution 4 cm^{-1}) were recorded after samples had been heated at 373 K under Ar for 1 h in order to remove residual physisorbed water (Fig. 1). Subsequently, the system was cooled to room temperature, and the gas flow was switched to SCR feed. The temperature was raised in steps of 25 K at a rate of 7 K min^{-1}; after each step, the temperature was held constant for 30 min to attain steady-state conversion (Fig. 1). DRIFTs-studies were performed during each step with 500 scans and a resolution of 4 cm^{-1}. The spectra are presented in the form of Kubelka-Munk $f(R/R_0)$ plots. After reaching 523 K, the sample was cooled to room temperature again.

NH$_3$—TPD

After dehydration at 373 K under Ar for 1 h, the catalysts were exposed to ammonia. Subsequently the gas was switched to argon again, which was passed over the catalyst for 1 h at room temperature in order to remove physisorbed species. In the TPD experiment the temperature was increased from 298 to 573 K at a rate of 7 K min^{-1}. Fifty FTIR scans were recorded at room temperature before this TPD experiment.

RESULTS

Catalytic Behavior

The results for the selective catalytic reduction of NO carried out with the different titania-supported chromium oxide phases derived from the standard CrO$_2$ and CrOOH samples are summarized in Figs. 2 and 3. The activities of the samples may be compared on the basis of the temperatures required for 50% conversion of NO ($T_{\mathrm{NO=50\%}}$), which are listed in Table 2. The temperature dependence of the NO conversion over supported chromium oxides derived from CrO$_2$-ST (series I) is presented in Fig. 2. The catalyst CrO$_2$-ST made up of 95% CrO$_2$ shows a high activity for NO conversion, which is reflected by the low value of $T_{\mathrm{NO=50}}$ = 453 K and a maximum conversion of 92% at 500 K. Oxidation of NH$_3$ at higher temperatures is indicated by a decrease in the NO conversion at 550 K, i.e., above the maximum conversion at 500 K. The selectivity to N$_2$O increases to 48% with increasing temperature.

As mentioned previously, the catalysts CrO$_2$-1h and CrO$_2$-5h contained Cr$_2$O$_3$ (73 and 78%) in addition to CrO$_2$ (27 and 22%) (19). These samples were found to be less active for SCR compared to CrO$_2$-ST; the $T_{\mathrm{NO=50}}$ shifts to higher values.

As can be deduced from the conditions of pretreatment, CrO$_2$-1h contains somewhat less Cr$_2$O$_3$ (73%) than does CrO$_2$-5h (78%) (19). This is in line with the result presented in Ref. (19), which indicated that supported CrO$_2$ decomposes very slowly under Ar at 773 K, and consequently the relative amount of Cr$_2$O$_3$ in CrO$_2$-5h is only a little higher than in CrO$_2$-1h and the catalytic behavior of these samples is very similar.

The catalytic behavior of the catalysts prepared by CrOOH decomposition is summarized in Fig. 3. CrOOH-ST, containing more than 88% CrOOH, showed 50% conversion ($T_{\mathrm{NO=50}}$) at 436 K (Table 2) and a maximum conversion of 82% at 475 K. The selectivity to N$_2$O is compara-

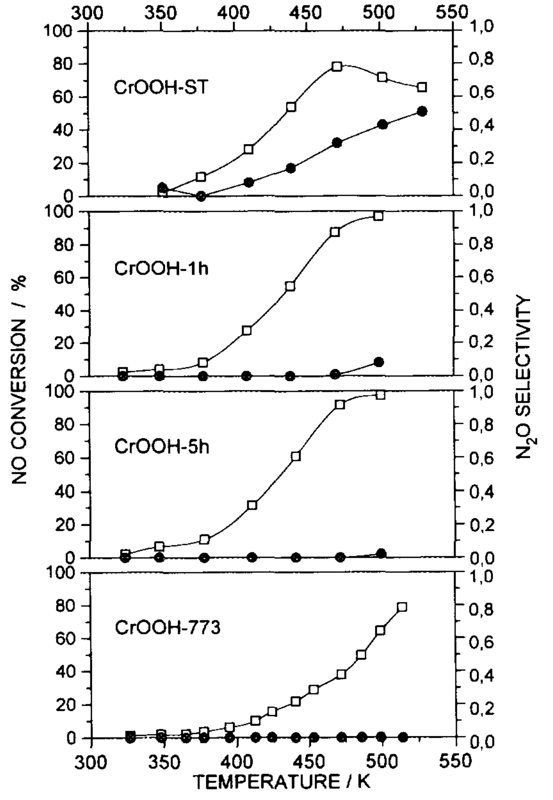

FIG. 3. Conversion of nitric oxide (open symbols) and selectivity to nitrous oxide (filled symbols) as a function of temperature for differently prepared (see Table 1) supported chromium oxide catalysts: CrOOH-ST: sample CrO_2-ST reduced in hydrogen at 523 K for 1 h. CrOOH-1 h: sample CrOOH-ST decomposed in Ar at 773 K for 1 h. CrOOH-5 h: sample CrOOH-ST decomposed in Ar at 773 K for 5 h. CrOOH-773: sample CrO_2-ST reduced in hydrogen at 773 K for 0.25 h and decomposed in Ar at 773 K for 5 h.

TABLE 2

Catalytic Behavior of Catalysts in SCR of NO by NH_3

Sample	$T_{NO=50}$[a] (K)	$S_{N_2O,T=50}$[b] (K)	$S_{N_2O,500K}$[c] (%)
CrO_2-ST	453	20	38
CrO_2-1 h	480	40	42
CrO_2-5 h	485	37	36
CrOOH-ST	436	15	52
CrOOH-1 h	432	0	10
CrOOH-5 h	430	0	4
CrOOH-773	487	0	0

[a] Temperature at which 50% NO conversion was attained.

[b] Selectivity to N_2O at temperature at which 50% NO conversion was attained.

[c] Selectivity to N_2O at 500 K.

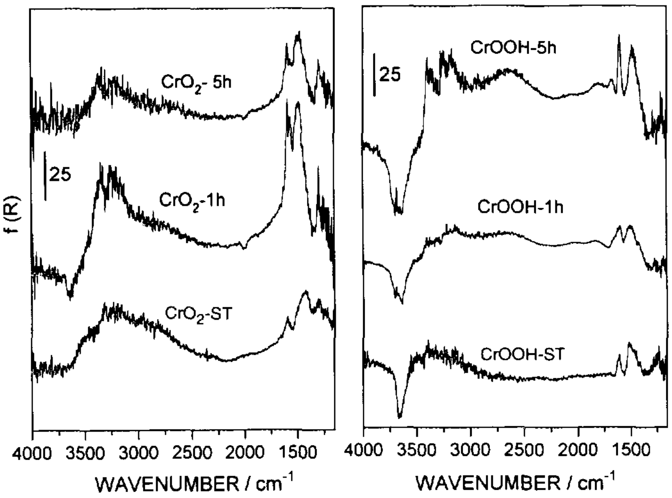

FIG. 4. DRIFT spectra recorded *in situ* during SCR at 348 K over supported chromium oxide catalysts. For preparation and designation of catalysts, see legends of Figs. 2 and 3.

ble to that of CrO_2-ST. As has been shown for the bulk oxyhydroxide in Ref. (19), CrOOH is oxidized under SCR conditions at $T > 450$ K. Therefore it is not surprising that the catalytic behavior is very similar to that of CrO_2-ST. The smaller activity of CrOOH-ST compared with that of CrO_2-ST must be discussed along the same lines as mentioned above for CrO_2-1h and CrO_2-5h.

CrOOH-1h consists of 73% Cr_2O_3, 24% CrOOH, and 3% CrO_2 supported on titania (19). The sample shows a high activity for SCR, reflected in the low $T_{NO=50} = 432$ K and in a maximum conversion of 100% at 500 K. No N_2O was formed at $T_{NO=50}$, whereas at 500 K the N_2O production amounted to 10%.

The Cr_2O_3 fraction of CrOOH-5h (83%) is only slightly larger than that of CrOOH-1h (73%), and consequently the SCR activity is very similar: $T_{NO=50}$ is reached at 430 K, and a maximum in NO conversion of 100% occurred at 500 K. Again no N_2O was observed at $T_{NO=50}$, and at 500 K the N_2O production amounted to 4%. The difference in Cr_2O_3 content is only reflected in the selectivity to N_2O.

XRD measurements indicated the growth of the crystallites of Cr_2O_3 occurring during synthesis under hydrogen at a temperature of 773 K (sample CrOOH-773). The catalytic behavior is characterized by $T_{NO=50} = 487$ K and a maximum NO conversion (74%) at 523 K. Note that no N_2O was formed over the whole temperature range.

In Situ Diffuse Reflectance FTIR Spectroscopy

The catalysts containing different amounts of supported Cr_2O_3, CrOOH, and CrO_2 were exposed to SCR conditions at different temperatures in the FTIR spectrometer. The reflectivity of the catalysts containing various chromia species is different, as a consequence of a broad electronic absorption band extending from the visible to the near-infrared region (17). The presence of Cr(IV) on the catalyst surface gives rise to the black color 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 contents of the various chromium oxide phases. The spectra recorded under reaction conditions are presented for one temperature (T = 348 K) in Fig. 4.

Spectra measured with the samples prepared by decomposition of CrO_2 (left) are compared with spectra of the samples prepared by decomposition of CrOOH (right). Positive bands in the spectra are indicative of the ammonia species adsorbed on the surface, whereas the negative bands show the disappearance of some surface hydroxyl groups upon NH_3 adsorption (22).

Under reaction conditions at 323 K, the spectrum of CrO_2-ST exhibits a small broad band from 1300 to 1500 cm^{-1}, and a broad absorption from 2500 to 3500 cm^{-1}. A complex band is observed in the range 2500–3500 cm^{-1} in the spectrum of CrO_2-1h. The band may be represented by a superposition of five vibrations, which are interpreted as follows (17, 22–24). Bands at 3350 and 3225 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of Lewis-bound ammonia; the broad and intense band at 3160 cm^{-1} is attributed 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 the shoulder at 2742 cm^{-1} were attributed to the corresponding vibrations of Brønsted-bound ammonia (17, 22–24). Matching deformational motions are detected in the spectral region between 1200 and 1800 cm^{-1}. The peak at 1596 cm^{-1} is due to Lewis-bound ammonia. The dominant peak in this spectrum is observed at 1461 cm^{-1}, which is assigned to a deformation band of $NH_4^+\{\nu_4(F_2)\}$ at 1440 cm^{-1} which overlaps with a band at 1491 cm^{-1}, assigned to a surface nitrate species (9). For comparison the spectra of CrOOH-ST-derived catalysts are plotted in the right half of Fig. 4. The peak at 1596 cm^{-1} in the spectrum of CrOOH-ST is assigned to Lewis-bound ammonia on the surface of CrOOH. Compared with the intense broad peak at 1461 cm^{-1} in the spectrum of CrO_2-1h, the corresponding signal is shifted to higher frequencies for CrOOH-ST, and is observed at 1493 cm^{-1}. This peak is assigned to a surface nitrate species which overlaps with a deformation band of NH_4^+.

In the spectrum of CrOOH-1h a broad feature is seen in the NH-stretching mode region. Compared with the spectra of the samples prepared via the CrO_2 route, only bands assigned to Brønsted-bound ammonia are observed. In the region from 2250 to 1150 cm^{-1} four bands are seen. Signals at 2000 and 1825 cm^{-1} are assigned to N_2O_2 (4, 5); the band at 1637 cm^{-1} is probably due to an overlap of a deformational mode of Brønsted-bound ammonia (9, 17), a deformational mode of Lewis-bound ammonia at 1599 cm^{-1}, and a mode of bridging nitrate at 1613 cm^{-1} (9). Finally, the peak at 1467 cm^{-1} is assigned to a superposition of the band at 1425 cm^{-1} of Brønsted-bound ammonia and the surface nitrate species at 1491 cm^{-1} (9). In the spectra of CrOOH-5h the same peaks appear as in the spectra of CrOOH-1h but have become more clearly resolved. In region from 2500 to 3500 cm^{-1} the peaks assigned to Lewis-bound ammonia appear as above, and the bands at 1665 and 1599 cm^{-1} are seen as two single bands. However, the overlay of the band due to surface bound nitrite with the deformational band of Lewis-bound ammonia remains unresolved.

Spectra recorded at 348 K under reaction conditions are seen in Fig. 4. Because of the decreased adsorbate coverages at this higher temperature the peaks become more clearly resolved. Deformational motions due to Lewis- and Brønsted-bound ammonia are detected at 1600, 1460, and 1280 cm^{-1} in the spectrum of CrO_2-ST (left panel). In the spectrum of CrO_2-1h the broad band at 2500 to 2800 cm^{-1} becomes less intense compared to the spectrum at 323 K, indicating that the amount of Brønsted-bound ammonia is smaller. As a consequence, the corresponding deformational peak at 1465 cm^{-1} decreases and the peak at 1596 cm^{-1} splits into two peaks. A new band at 1569 cm^{-1} is recognizable, which is assigned to bidentate nitrate ("type II" in the terminology of Ref. (8)).

The spectra recorded at 348 K for the catalysts derived from CrOOH are assigned as above. The spectrum of CrOOH-ST at 348 K shows the same pattern as that at 323 K. In the spectrum of CrOOH-1h, a decrease of the modes due to Brønsted-bound ammonia is recognized. This results in a change in the relative band intensities. The pattern at 1610 and 1497 cm^{-1} is assigned as described above. As the modes in the spectrum of CrOOH-5h at 348 K are clearly resolved, this trace is best suited for discussing the assignment. First, a decrease in the broad band at 2500 to 2800 cm^{-1} indicates again a decrease in the amount of Brønsted-bound ammonia. The bands at 1780 and 1665 cm^{-1} remain observable. The frequency shift of the band from 1599 cm^{-1} at 323 K to 1590 cm^{-1} at 348 K results from a change in the relative concentrations of surface bound NO and of Lewis-bound ammonia. As a consequence of the desorption of NO from the surface, the peak contribution due to this species disappears, and an apparent frequency downshift of the band results. The band at 1590 cm^{-1} increased in intensity relative to the band at 1467 cm^{-1}.

In the spectrum of CrO_2-ST recorded at 398 K (not shown), the peak at 1467 cm^{-1} decreases and splits into two bands at 1498 and 1421 cm^{-1}. The bands assigned to Lewis-bound ammonia are still present.

Compared with the spectrum recorded at 343 K, a de-

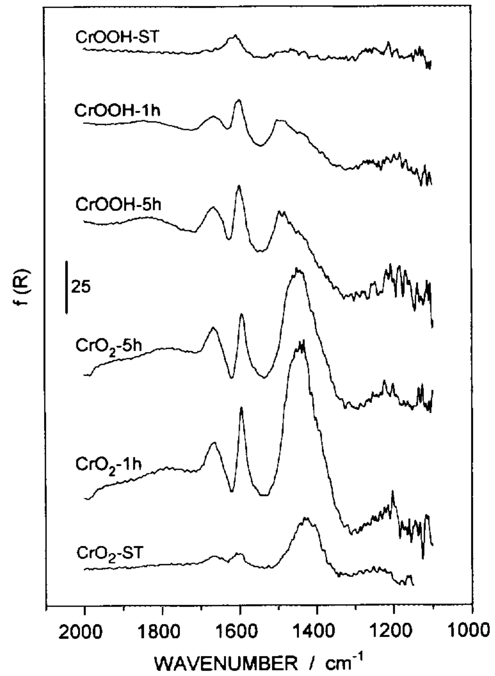

FIG. 5. DRIFT spectra recorded from supported chromium oxide catalysts after adsorption of NH_3 at room temperature. For preparation and designation of catalysts, see legends of Figs. 2 and 3.

crease in intensity of the band at 1495 cm^{-1}, as accompanied by a small shift to 1506 cm^{-1}, is observed in the spectrum of CrO_2-1h.

The spectra of the samples obtained via the CrOOH route recorded at 398 K under reaction conditions are shown in the right panel of Fig. 4. In the spectrum of CrOOH-ST only a small peak at 1611 cm^{-1} is observed at 398 K under reaction conditions. In the spectrum of CrOOH-1h only weak broad bands are observed. In the spectrum of CrOOH-5h the stretching modes at 2800 to 3500 cm^{-1}, as well the deformational mode of Lewis-bound ammonia at 1590 cm^{-1}, are still present. The band at 1467 cm^{-1} decreases in intensity, but remains observable.

Adsorption of Ammonia

The spectra recorded after preadsorption of NH_3 at room temperature are shown in Fig. 5. The peaks are readily assigned in agreement with the literature (17, 24). In the spectrum of the sample loaded with CrOOH (CrOOH-ST), only small amounts of Brønsted-bound ammonia are observed. The peak at 1610 cm^{-1} is assigned to ammonia bound to a Lewis site.

The spectra of CrO_2-1h and CrO_2-5h are characterized by three bands in the deformational region. The bands at 1660 and 1440 cm^{-1} result from the adsorption of NH_3 bound to Brønsted sites. The peak at 1592 cm^{-1} is assigned to Lewis-bound ammonia. In the spectra of CrOOH-1h and CrOOH-5h containing a large amount of Cr_2O_3 four peaks are observed. The bands at 1660, 1592, and 1440 cm^{-1} are assigned as above. The band at 1485 cm^{-1} was assigned by Schrami-Marth *et al.* (8) to an ammonia species bound to another kind of Brønsted site.

NH_3—TPD from the Surface Preloaded with Ammonia

In the TPD curves recorded after exposure of the samples to ammonia, different patterns are observed, depending on the composition of the supported chromium oxide. For representation, the TPD curves are shown for one sample only (CrO_2-ST) (Fig. 6). No detectable NH_3 desorption is observed in the case of CrOOH-ST. CrOOH-1h and CrOOH-5h show a continuous desorption of NH_3 starting at 350 K and ending at 550 K. The NH_3 desorption profiles of samples CrO_2-ST (Fig. 6), CrO_2-1h, and CrO_2-5h, which contain mixtures of different chromium oxide phases, exhibit a similar pattern, i.e., a molecular ammonia desorption starting at 350 K with a maximum at ca. 375 K.

Desorbing NO is only observed with CrOOH-ST in significant amounts starting from 400 K. Samples containing a mixture of chromium oxides show only small desorbing quantities of NO at higher temperatures (500 K). In the curves recorded with CrOOH-1h and CrOOH-5h, no NO desorption is observed.

Desorption of N_2O starting at 350 K and continously increasing with temperature is observed in the TPD curve of CrOOH-ST. In contrast, CrOOH-1h and CrOOH-5h do not show desorption of N_2O. A broad N_2O desorption starting at 400 K with a maximum at 475 K is observed for the samples derived from CrO_2 (Fig. 6), which contain different chromium oxides.

Desorption of N_2 is observed starting at 475 K only with CrO_2-derived samples (Fig. 6). The amount of evolving N_2 is largest for the catalyst CrO_2-ST. For the latter sample, a second broad desorption maximum (extending from 350 to 450 K) may be discerned. For CrO_2-ST, a continuously rising desorption of H_2O is observed starting at 350 K (Fig. 6). CrO_2-5h and CrO_2-1h show a small maximum at ca. 425 K. CrOOH-ST exhibits a small, continuously increasing desorption starting at 350 K. For CrOOH-1h and CrOOH-5h, no significant desorption of water is detectable.

DISCUSSION

All three observed chromium oxide phases, i.e., CrOOH, CrO_2, and Cr_2O_3 supported on titania, exhibit catalytic activity for the selective reduction of nitric oxide by ammonia. However, the differences in activity and selectivity to N_2O are significant. The investigation of defined supported chromium oxide phases offers the opportunity to characterize the catalytic properties of each individual phase. The present findings indicate that SCR of NO is very sensitive to structural changes of the oxide phase. In a sense, SCR

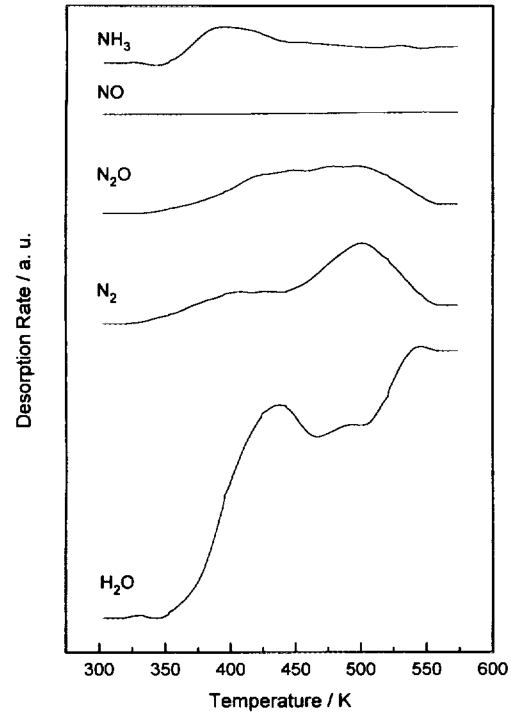

FIG. 6. Temperature-programmed desorption (TPD) of NH_3-preloaded CrO_2-ST. The evolution of NH_3, NO, N_2O, N_2, and H_2O was detected by mass spectrometry.

might be considered as a test reaction for fingerprinting supported and unsupported chromium oxide systems. The selective reduction of NO by NH_3 over CrO_2/titania (CrO_2-ST) is characterized by a high conversion of NO and a high selectivity to (undesired) N_2O. As shown in Fig. 2, a maximum conversion of 92% for a GHSV of 28,000 h^{-1} is achieved at 500 K. The selectivity to N_2O is 38% at this temperature. The catalysts containing both CrO_2 and Cr_2O_3, supported on titania, exhibit smaller activity, but also a comparable high selectivity to N_2O. This indicates that the total activity of the mixed phase system is not the sum of the activities of its pure components for the same total chromium content (see below for Cr_2O_3). In line with this argument, it is known from the literature that the SCR activity of chromia/titania catalysts depends on the chromium content (16). Obviously, both oxide phases, CrO_2 and Cr_2O_3, do not coexist as isolated and independent species on the surface of titania. They can simultaneously influence the catalytic reaction and change its mechanism. The small differences in the catalytic properties of CrO_2-1h and CrO_2-5h agree well with the small differences in their quantitative composition (19). This emphasizes the suitability of SCR for characterizing supported chromium oxides, even concerning their quantitative composition.

The CrOOH/titania catalyst, CrOOH-ST exhibits a catalytic behavior comparable to that observed for the CrO_2/titania system. This especially holds true for temperatures higher than 450 K. As known from earlier studies, unsupported as well as supported CrOOH is oxidized to CrO_2 by the oxygen contained in a typical SCR atmosphere at temperatures above 450 K (18, 19). Thus, the comparable catalytic activity and selectivity of both oxide phases for $T > 450$ K can be easily understood. The lower maximum conversion observed may be explained by the incomplete oxidation of CrOOH, which proceeds further during the comparatively short duration of the catalytic reaction. The pathway of the catalytic reaction may also be influenced by the oxidation of CrOOH proceeding in parallel.

The Cr_2O_3/titania catalyst prepared by decomposition of the CrOOH/TiO_2 system exhibits increasing activity and selectivity to N_2 with longer duration of the decomposition, i.e., with increasing relative content of Cr_2O_3. The highest activity ($T_{NO=50}$ = 430 K, conversion of 96% at T = 500 K) and selectivity to N_2 (96% N_2 at 500 K) is measured for CrOOH-5h, i.e., for the sample containing the largest amount of poorly crystalline Cr_2O_3. Even the maximum selectivity to N_2O at 500 K is small (4%).

The activity of the Cr_2O_3/titania catalysts is strongly influenced by the dispersion and size of the chromia agglomerates. Thus, CrOOH-773 containing crystalline Cr_2O_3, as proven by XRD and antiferromagnetic resonance (19), shows a maximum conversion of 78% only. This agrees well with the observation of Curry-Hyde and Baiker (14) that bulk amorphous Cr_2O_3 exhibits higher activity than bulk crystalline chromium(III) oxide. The higher selectivity to N_2 of the supported crystalline chromia, as compared to the bulk crystalline chromia, could be caused by the smaller crystallite size expected for the supported chromia (14).

On the surface of supported CrOOH, ammonia is adsorbed predominantly on Lewis sites (Fig. 5). The same spectral pattern was obtained for 5 wt% chromia/titania catalysts reduced by ammonia (17). It may therefore be argued that in both cases, a CrOOH-like phase is present. By the same argument, CrO_2 is expected to represent the main component prior to the reduction of supported chromia/titania catalysts prepared in Ref. (17). This is confirmed by the infrared spectra of NH_3 adsorbed on CrO_2. In complete accordance, both the CrO_2/titania sample investigated here and the oxidatively pretreated sample of the chromia/titania catalyst mentioned above (17) show bands due to ammonia bound to Lewis as well as to Brønsted sites. This finding provides further insight into the composition of the catalysts investigated in Ref. (17). It demonstrates that the catalysts characterized in the present paper can actually serve as model systems for real supported chromium oxide systems in general. The IR spectrum of NH_3 adsorbed on CrOOH-5h, which mainly consists of Cr_2O_3 on the surface of titania, shows the same adsorbate vibrations as pure bulk Cr_2O_3 (8). In addition to a deformation band ($\nu_4(F_2)$) at 1440 cm^{-1}, a band appears at 1485 cm^{-1}. This band indicates the presence of an additional Brønsted site on the surface of Cr_2O_3. This band is not observed for samples which do not contain Cr_2O_3, and could be the key to the explanation of a high SCR activity at low temperatures.

The results of the NH_3 TPD experiments confirm that the surface of (supported) Cr_2O_3 is stable against reduction by NH_3. Practically no N_2, N_2O, or NO desorbed during the TPD. This finding agrees well with the results of Curry-Hyde and Baiker for bulk Cr_2O_3 (14) and represents a crucial point in the explanation of their high SCR activity. Ammonia desorbs continuously with increasing tendency over the full temperature range investigated, which indicates its bonding to centers of different Lewis acidity. In contrast, ammonia desorbs from CrO_2/TiO_2 below 425 K, and from $CrOOH/TiO_2$ no ammonia desorption is observed in this temperature range. From the chromium-dioxide-containing catalysts, N_2 and N_2O are desorbed above 400 K. This oxidation of ammonia is, as expected, accompanied by the evolution of water. The oxidation of Lewis-bound ammonia is accompanied by the reduction of CrO_2. Chromium dioxide can be expected to be an active catalyst for the ammonia oxidation. The desorption of NO from CrOOH/titania can be explained by the incomplete reduction of CrO_2 to CrOOH during the preparation procedure. Residual CrO_2 on CrOOH-ST is reduced during the TPD.

Although no reaction mechanism can be deduced from our investigations, valuable statements can be made concerning the specific sites and their involvement in the reactions occurring at the surface, especially from the adsorption behavior under *in situ* conditions. Assuming that Brønsted-bound ammonia is crucial for the reduction of NO (17) and that ammonia is bound with different strengths on the various chromium oxide phases, all the experiments may be interpreted considering the following aspects.

First, an analogy with supported vanadia catalysts will be invoked, which are known to exhibit high activity and selectivity to N_2. Here, ammonia is bound to Brønsted sites even at higher temperatures. An analogous behavior was found for (amorphous) Cr_2O_3/TiO_2 catalysts. The surface of Cr_2O_3 is stable against reduction by Lewis-bound ammonia, which holds true for V_2O_5 below 500 K as well. N_2O is thought to be formed by oxidation of Lewis-bound ammonia with oxygen on the surface of the catalyst (17). Lewis- and Brønsted-bound ammonia and adsorbed nitric oxide are observed at 323 and 348 K for both CrO_2/titania and Cr_2O_3/titania; the bands due to Brønsted-bound ammonia are shifted to higher frequencies for the latter. However, the oxidation of ammonia to N_2O is connected with a feasibility of oxidation and reduction processes on the surface requiring reducible chromium surface sites. This condition is not fulfilled for Cr_2O_3, which is in the lowest oxidation state accessible under SCR conditions, but is met for CrO_2, which is readily reduced and reoxidized (18, 19, 25). Accordingly, chromium-dioxide-containing catalysts show high selectivities to N_2O. In contrast, on Cr_2O_3 the onset of N_2O formation is observed at higher temperatures only.

In contrast to Cr_2O_3 and V_2O_5, bands due to surface-bound NO (1491 and 1569 cm^{-1}) are found under reaction conditions for the CrO_2-containing samples. This binding capacity for NO and the specific interaction between CrO_2 Lewis-sites and NH_3 described above are suggested to be the reasons for the high selectivity toward N_2O at temperatures below 400 K.

During TPD experiments, Lewis-bound ammonia can react with the surface to produce N_2O at temperatures above 400 K (17). During SCR, N_2O is formed by oxidation of Lewis-bound ammonia with NO and/or oxygen present in the feed gas (17, 26). In the case of V_2O_5 (26) and Cr_2O_3, which do not exhibit the presence of bound NO, this oxidation of NH_3 to N_2O occurs at temperatures higher than 450 K. $CrOOH/TiO_2$, which does not "produce" N_2O itself, is oxidized to CrO_2 at higher temperatures under SCR conditions, and consequently exhibits the same high selectivity to N_2O as CrO_2. Note that the IR band at 1569 cm^{-1} is observed in these systems already at SCR reaction temperatures of 398 K.

CONCLUSIONS

From the present results obtained with defined supported chromium oxide phases, the activity for the desired selective reduction of NO yielding N_2 may, for the first time, be attributed to one particular chromium oxide phase. CrOOH, CrO_2, and Cr_2O_3 supported on titania show a clearly different catalytic activity and selectivity in the selective reduction of NO by NH_3. Each particular phase has its specific catalytic properties. Differences in the catalytic behavior of chromia/titania catalysts with mixed chromium oxide phases, originating from different pretreatment and conditions, can be traced back to the presence, absence, or mutual interconversion of these oxide phases. Amorphous Cr_2O_3 supported on titania exhibits very high activity and selectivity to N_2, which is strongly influenced by its dispersion on the surface. Mixtures of the particular phases generally show a reduced activity in comparison to the pure phases. Due to its structural sensitivity, the SCR reaction is thus a suitable test reaction for characterizing supported and unsupported chromium oxide systems.

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