In situ IR Spectroscopic and XPS Study of Surface Complexes and Their Transformations during Ammonia Oxidation to Nitrous Oxide over an Mn–Bi–O/α-Al₂O₃ Catalyst

E. M. Slavinskaya, Yu. A. Chesalov, A. I. Boronin, I. A. Polukhina, and A. S. Noskov

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia Received September 10, 2003; in final form December 21, 2004

Abstract—Surface complexes resulting from the interaction between ammonia and a manganese–bismuth oxide catalyst were studied by IR spectroscopy and XPS. At the first stage, ammonia reacts with the catalyst to form the surface complexes [NH] and [NH₂] via abstraction of hydrogen atoms even at room temperature. Bringing the catalyst into contact with flowing air at room temperature or with helium under heating results in further hydrogen abstraction and simultaneous formation of [N] from [NH₂] and [NH]. The nitrogen atoms are localized on both reduced (Mn²⁺) and oxidized (Mn^{δ +}, 2 < δ < 3) sites. Atomic nitrogen is highly mobile and reacts readily with the weakly bound oxygen of the oxidized (Mn^{δ +}–N) active site. The nitrogen atoms localized on oxidized sites play the key role in N₂O formation. Nitrous oxide is readily formed through the interaction between two Mn^{δ +}–N species. N₂ molecules result from the recombination of nitrogen atoms localized on reduced (Mn²⁺–N) sites.

The mechanism of low-temperature ammonia oxidation has been the subject of numerous publications. Highly selective catalysts producing nitrogen have mainly been studied since this process has been successfully used to reduce ammonia emission. The majority of works have been devoted to platinum catalysts. Three main schemes for the reaction mechanism were suggested in earlier studies. In Andrussov's mechanism [1], it is assumed that nitroxyl species [HNO] form and then react to yield N₂, N₂O, and NO. According to Bodenstein's hypothesis [2], the first step is the formation of hydroxylamine [NH₂OH], which then transforms to [HNO]. Raschig [3] and Zavadzki [4] proposed an imide mechanism in which the first step is assumed to be the formation of an imide [NH]. It was deduced from secondary ion mass spectrometry data that such intermediates as [HNO], [NH₂OH], [HNO₂], and [N₂O] do not appear during ammonia oxidation at partial pressures of about 10⁻⁴ Torr and that [NO] is the only intermediate and dinitrogen is formed via the reaction between [NO] and ammonia [5]. Autoion mass spectrometry data [6] showed that ammonia interacts with the surface covered with adsorbed atomic oxygen to form species of the imide ([NH]) type, which transform to nitroxyls [HNO]. Nitrogen results from the interaction between [NH] and [HNO], whereas nitrous oxide is formed by the recombination of two nitroxyls.

The schemes proposed in the above-cited works were not strongly supported by experimental data, and this fact explains their multiplicity. A new impetus to the study of the ammonia oxidation mechanism was given by the development of modern techniques for surface characterization, which provided a much deeper insight into the nature of catalysts and into the mechanism of catalysis.

Study of ammonia oxidation over metals [7–13] showed that [N] and [NO] form on the surface and their recombination or desorption results in N₂, N₂O, and NO. [N] species can both result from successive hydrogen abstraction yielding amide–imide species [NH₂–NH] and form from [HNO] species produced by the interaction between NH₃ and O₂ adsorbed molecularly at the early stages.

Study of the surface complexes forming upon NH_3 adsorption on metal oxides showed that ammonia successively loses a number of hydrogen atoms, depending on the acidity of the oxide [14]. The formation of $[NH_2]$ and its dimer, hydrazine, eventually yielding N_2 was observed by IR spectroscopy [15–18]. The species [NH] and [HNO], yielding N_2O and NO, were also found [15, 16]. It was shown that ammonia is oxidized via the selective reduction of NO (key intermediate) with ammonia (SCR mechanism) [19]. The activation of ammonia, that is, its oxidation to [NO], is the rate-determining step.

Intermediate surface complexes forming during ammonia oxidation were studied in [20]. The authors simultaneously measured the rate of surface species transformation by *in situ* IR spectroscopy and the rate of formation of reaction products. [NH₂], [NH], and [NO] species were detected. The interaction of [NO] with ammonia was shown to occur more rapidly than NO desorption. It was suggested that N_2O forms by the interaction between [NH] and [NO] and N_2 forms by the interaction between [NH₂] and [NO].

Selective ammonia oxidation has recently been proposed as an efficient method for the production of nitrous oxide. Nitrous oxide attracts attention due to the fact that it is widely used as a mild oxidizing agent for benzene and other organic compounds [21]. To produce N₂O on a commercial scale, a supported Mn–Bi oxide catalyst affording N₂O with 90% selectivity was developed [22]. We studied the structure and surface composition of this catalyst as well as kinetics of the reaction $NH_3 + O_2$ [23, 24]. According to XRD data, the catalyst Mn–Bi–O/ α -Al₂O₃ contains manganese and bismuth oxides and a Mn-Bi-O mixed phase [23]. Transmission electron microscopy showed that structurally disordered layers of the manganese-bismuth oxide phase are localized on the surface of α -Al₂O₃ and replicate the shape of its particles, and the microcrystals of manganese oxide, 10 nm in size, are bound to the Mn–Bi–O phase. The high defectiveness of this phase is believed to be responsible for the presence of highly mobile active oxygen in the catalyst [24]. This inference is confirmed by data obtained by the pulse method for the reduction of the catalyst with ammonia and for NH₃ oxidation. In the course of the reduction process, approximately 4 oxygen monolayers are removed from the catalyst, and this amount is half the total oxygen of the active component. Replacing ${}^{16}O_2$ with ${}^{18}O_2$ in the gas phase demonstrated that the products of the catalytic reaction contain unlabeled oxygen. It became clear from the consumption of ${}^{16}O_2$ and ${}^{18}O_2$ in the course of the reaction that 1/3 of the oxygen in the catalyst is removed with the reaction products. This confirms that subsurface oxygen, that is, the lattice oxygen of the Mn-Bi-O phase is involved in the reaction and is highly mobile. The above data give evidence that ammonia oxidation involves lattice oxygen via an alternating reduction and reoxidation of the catalyst surface.

In this work, we studied, by *in situ* IR spectroscopy, XPS, and by the temperature-programmed surface reaction (TPSR) method, the surface complexes that result from the interaction between ammonia and the catalyst and their transformation into reaction products during ammonia oxidation to nitrous oxide in order to elucidate the reaction mechanism.

EXPERIMENTAL

Catalyst Preparation

The catalyst Mn–Bi–O/ α -Al₂O₃ was prepared by double impregnation of the support. At the first stage, a weighed portion of the support was impregnated to incipient wetness with a certain volume of a mixed solution containing appropriate proportions of Mn(II) and Bi(III) nitrates, and the resulting material was dried at 353–403 K [23]. The product was again impregnated with an appropriate volume of the mixed solution, dried at 353–403 K and calcined at 833 K for 2 h. Manganese nitrate Mn(NO₃)₂ · 6H₂O (Aldrich, No. 28.864-0) and

bismuth nitrate $Bi(NO_3)_3 \cdot 5H_2O$ (Aldrich, No. 38.307-4) were used as starting chemicals.

Methods

In situ IR spectroscopy. In our in situ IR spectroscopic studies, we used a BOMEM MB-102 Fourier transform spectrophotometer equipped with a flowthrough high-temperature reactor cell with CaF₂ optical windows. A 50-mg catalyst pellet 1×3 cm in size was placed in a 1.5-cm³ cell. Before each experiment, the pellet was conditioned in flowing air at 523 K for 1 h in the cell. Next, it was cooled to a preset temperature and the air flow was replaced with an ammonia flow. While 100% ammonia was passed, the spectra of surface compounds overlapped and intense absorption in the frequency range 1800–1300 cm⁻¹ due to gaseous NH₃ was observed. To monitor the evolution of the IR spectra of surface compounds, the experiment was conducted as follows. Ammonia was passed through the cell for 2 min, and then the flow was stopped and the cell was sealed. After several minutes, over which the concentration of gaseous ammonia decreased below the determination limit, a spectrum was recorded and the procedure was repeated. The concentration of surface complexes no longer changed after the third ammonia admission. The observed spectra were the superposition of the spectra of the catalyst and adsorbed compounds. The data acquisition time was 1.5 min (30 scans). To separate out the spectrum of the surface compounds, the background spectrum of the catalyst, recorded before ammonia admission into the reactor cell, was subtracted from the observed spectrum.

XPS. To study the surface compounds formed upon the treatment of the catalyst with ammonia and to determine their surface concentrations and chemical states, X-ray photoelectron spectroscopy was used. XPS spectra were recorded on a VG ESCALAB spectrometer (Al K_{α} radiation, hv = 1486.6 eV). The spectrometer was calibrated against the Au $4f_{7/2}$ ($E_b = 84.0 \text{ eV}$) and Cu $2p_{3/2}$ ($E_b = 932.7 \text{ eV}$) lines [25]. The catalyst, rubbed into a fine-meshed nickel gauze, was fixed in a holder. To take into account the charging effect arising from photoemission, both the internal standard (the Al2p line in the spectrum of the α -Al₂O₃ support, $E_b = 73.8$ eV) and the C1s line ($E_{\rm b} = 284.8$ eV) from carbonaceous surface impurities [25, 26] were used. The relative concentrations of the elements in the catalyst were derived from the observed integral intensities of XPS lines $(I_{\rm X}, I_{\rm Al})$ using the formula

$$n_{\rm X}/n_{\rm Al} = \frac{I_{\rm X}/(\rm ASF)_{\rm X}}{I_{\rm Al}/(\rm ASF)_{\rm Al}},$$

1

where n_X is the concentration of the element X (at. %) and (ASF)_i are the atomic sensitivity factors of the elements. The following ASF values were used [26]: Al2*p*, 0,193; N1*s*, 0.477; O1*s*, 0.711; Mn2*p*, 2.420, and Bi4*f*, 7.632. The line Al2*p* from the support was chosen as the

KINETICS AND CATALYSIS Vol. 46 No. 4 2005



Fig. 1. IR spectra of surface compounds resulting from the interaction between NH_3 and the catalyst $Mn-Bi-O/\alpha$ - Al_2O_3 at 300 K after (1) one and (2) two ammonia admissions. Spectrum 3 was recorded after N_2H_4 admission at 300 K.

reference, and the other lines of the photoelectron spectrum were normalized to its intensity.

For detailed processing of the spectra, we used the original program package, which allows the deconvolution of a complex spectrum into individual components each having a mixed, Gaussian–Lorentzian shape with a variable fraction of the Gaussian.

The catalyst Mn–Bi–O/ α -Al₂O₃ calcined at 833 K was preliminarily conditioned in helium at 473 K for 1 h. Next, it was treated with ammonia at room temperature for 1 h and purged with air for 30 min. XPS spectra were recorded between 300 and 769 K.

TPSR technique. A catalyst sample was loaded into the reactor, conditioned in flowing helium at 723 K, and pumped at room temperature. After ammonia adsorption at room temperature and removal of reversibly adsorbed ammonia with flowing helium, a temperatureprogrammed surface reaction was carried out by heating the reactor from room temperature to 923 K at a rate of 15 K/min. Substances that were desorbed into the gas phase during TPSR were analyzed with a quadrupole mass spectrometer.

RESULTS

In situ IR Spectroscopic Studies

Figure 1 presents the spectra of surface compounds resulting from the interaction between NH_3 and the catalyst surface at room temperature (300 K) after a single (spectrum 1) and two (spectrum 2) admissions of ammonia to the IR cuvette. Absorption bands at 1655 (shoulder), 1610, 1547, 1460, and 1410 cm⁻¹ are observed in the spectra. This large number of absorp-



Fig. 2. IR spectra of surface compounds resulting from the interaction between NH_3 and the catalyst Mn–Bi–O/ α -Al₂O₃ at 300 K after ammonia admission: (1) oxidized catalyst and (2) catalyst reduced with NH_3 at 673 K. The deconvolution of these spectra is shown.

tion bands indicates the formation of several types of surface compounds under the above conditions. The absorption bands at 1655 and 1460 cm⁻¹ are due to the symmetrical and asymmetrical bending vibrations of NH_4^+ ion, respectively. The weak band at 1610 cm⁻¹ is likely due to the symmetrical bending vibration of the molecularly adsorbed ammonia. The band due to the asymmetrical bending vibration of this surface complex likely occurs at a frequency below 1300 cm⁻¹ and, therefore, cannot be observed in the IR spectrum. The bands at 1547 and 1410 cm⁻¹ are likely to be assignable to the products of ammonia oxidation. During adsorption, the ratio between the intensities of these bands remains nearly unchanged. These bands can be considered to be induced by the same surface complex. However, in a study of ammonia adsorption on MgFe₂O₄ [27], bands near 1550 and 1410 cm⁻¹ were assigned to two different surface compounds, namely, coordinated [NH₂] and [NH], respectively. To verify the assignment of these bands, ammonia adsorption was studied on the catalyst Mn-Bi-O/α-Al₂O₃ preliminarily reduced at 673 K in an NH₃ atmosphere. As can be seen in Fig. 2, this pair of bands is also observed in the IR spectra of the reduced sample. However, the ratio of the integral intensities of the bands at 1547 and 1410 cm⁻¹ in the spectrum of the oxidized sample is ~1.5 times higher. Taking into account this fact, we suggest that the bands at 1547 and 1410 cm⁻¹ are due in fact to different surface complexes, namely, the [NH₂] and [NH] species, respectively. Another admission of ammonia resulted in an increase in the concentration of the above surface compounds. Their surface concentrations decreased



Fig. 3. IR spectra of surface compounds resulting from the interaction between NH₃ and the catalyst Mn–Bi–O/ α -Al₂O₃ recorded as the temperature rose during purging of the sample with helium. *T* = (*1*) 300, (*2*) 333, (*3*) 363, (*4*) 393, and (*5*) 413 K.

with an increase in adsorption temperature from 300 to 353 K and were below the sensitivity limit at 393 K.

Purging the catalyst with helium at room temperature changed the concentration of surface compounds only slightly. The increase in temperature during purging resulted in a gradual decrease in the intensity of the absorption bands due to the surface compounds. These bands disappeared completely at 393 K (Fig. 3). Purging with air for 5 min was sufficient to decrease the intensities of the absorption bands due to the surface compounds below the sensitivity limit of the IR technique (Fig. 4). During purging with air, the concentration of surface compounds decreases but the intensity ratio of the absorption bands of [NH₂] and [NH] remains nearly unchanged. Note that the decrease in the concentration of surface compounds in this experiment was not accompanied by the appearance of reaction products or NH₃ in the gas phase. Hence, the decrease in the concentration of the above surface compounds is due not to their desorption to the gas phase but to their further transformation into surface compounds that do not give rise to any absorption bands in the IR region available for measurements $(4000-1300 \text{ cm}^{-1})$.

Figure 1 shows the spectrum recorded after the interaction of N_2H_4 with the catalyst surface at room temperature (spectrum 3). The absorption bands at 1600 and 1560 cm⁻¹ are due to the symmetrical vibrations, whereas the absorption bands at 1386 and 1362 cm⁻¹ are due to the asymmetrical vibrations of the hydrazine NH₂ group [28, 29].

XPS Study of the Mn–Bi– O/α -Al₂O₃ Catalyst

To identify the surface compounds formed upon ammonia adsorption, the catalyst was studied by XPS.



Fig. 4. IR spectra of surface compounds resulting from the interaction between NH_3 and the catalyst Mn–Bi–O/ α -Al₂O₃ recorded while purging the sample with air at 300 K: (1) initial spectrum and (2–4) spectra recorded after the sample is purged for (2) 1, (3) 2, and (4) 5 min.

Examination of the wide-range photoelectron spectra showed that, after ammonia adsorption and purging with air, an intense N1s line appeared, which was virtually absent before the ammonia treatment. To estimate the nitrogen concentration and elucidate the chemical state of nitrogen, the highly resolved spectrum in the N1s region was analyzed. Figure 5 presents a series of N1s spectra obtained directly in the chamber of the spectrometer analyzer during stepwise heating of the sample. Spectrum 1 corresponds to the initial state of the catalyst before the ammonia treatment. A broad, low-intensity line near 398 eV is observed, which is most probably due to the strongly bound species of residual nitrogen that are localized on the lattice defects of the active component after catalyst calcination at 833 K. After ammonia adsorption followed by purging the sample with air, a broad asymmetrical line at $E_{\rm b}({\rm N1}s) \approx 399$ eV appeared. When the sample was heated above 400 K, the N1s line changed its shape and its intensity decreased (Fig. 5, curves 2–9). The intensity of the nitrogen line observed at the rather high temperature of ~800 K (Fig. 5, curve 9) is higher than the background intensity, indicating that part of the nitrogen stays on the surface under the above conditions.

The N/Mn surface concentration ratio calculated from the intensity ratio of the N1s and Mn2p lines is ~0.5. While the sample was heated from room temperature to 800 K, the relative nitrogen concentration decreased by a factor of 3.5.

As mentioned above, the N1s line has a complicated shape, suggesting that nitrogen is in different states. To identify these states, we used a stepwise procedure to deconvolve the spectra. At the first stage, the spectra were normalized to the background of the spectrum of the starting sample (Fig. 5, curve 1). Then the spectrum



Fig. 5. N1s XPS spectra of the catalyst Mn–Bi–O/ α -Al₂O₃ (*1*) before and (2–9) after ammonia treatment followed by purging with oxygen, recorded at *T* = (1, 2) 298, (3) 335, (4) 365, (5) 398, (6) 460, (7) 529, (8) 627, and (9) 769 K.

of the starting sample (Fig. 6a, curve 1) was subtracted from the spectrum recorded at a certain specified temperature after treatment of the catalyst with ammonia (Fig. 6a, curve 2). The difference spectrum is represented by curve 3 in Fig. 6a. Next, this spectrum was smoothed and deconvolved into components of the Gaussian–Lorentzian type (Fig. 6b). This deconvolution procedure allowed us to reveal two main elementary components. A third component, at a lower binding energy, is considered for more exact description of the spectrum. However, this component is extremely weak and can therefore be neglected.

All N1s spectra were processed similarly, and some of them are presented in Fig. 7a. As can be seen, the resulting spectra recorded at 300-400 K contain two components at $E_{\rm b} \approx 398.0$ and 399.5 eV. Comparison of these data with XPS data reported previously for nitrogen-containing materials and molecules on the surface of metal oxides [25, 26, 30] shows that the peak at $E_{\rm h} \approx$ 398.0 eV is within the range typical of metal nitrides and nitrogen adsorbed on the surface of metals and oxides. The peak at $E_{\rm b}$ = 399.5 eV corresponds to the boundary between the binding energy ranges typical of nitrogen in oxynitrides [31-33] and nitrogen in adsorbed NO, N-H, NHOH and nitrosyl complexes [25, 26, 30]. Lines at 403–406 eV must be observed for nitrite structures [34-36]; lines at 406-407 eV, for nitrate structures [34, 35]. Even E_b for nitrosyl complexes is reported to lie in the range 400-402 eV. In our experiments performed at room temperature, no lines in this range were observed, but lines at substantially lower binding energies of 398-399.5 eV were found. Therefore, it is difficult to conclude unambiguously on the nature of nitrogen with $E_{\rm b}$ = 399.5 eV. However, taking into account the above IR spectroscopic data indicating the absence of the bands typical of the N-O and N-H bonds on the catalyst surface after ammonia treatment and purging with helium at 393 K, one can assign the lines at $E_{\rm b} \approx 398.0$ and 399.5 eV to nitrogen species localized on the Mn²⁺ and Mn^{δ +} ions (2 < δ < 3), respectively. As was shown earlier [23], manganese ions in various oxidation states appear upon treatment of the catalysts with the reaction mixture or ammonia.

Fig. 6. (a) N1s XPS spectra of the catalyst Mn–Bi–O/ α -Al₂O₃ after its treatment with ammonia followed by purging with oxygen: (1) initial spectrum, (2) spectrum recorded after treatment, and (3) difference spectrum. (b) Deconvolution of the N1s spectrum of the catalyst Mn–Bi–O/ α -Al₂O₃ (Fig. 5a, curve 3) to individual components.

KINETICS AND CATALYSIS Vol. 46 No. 4 2005

1100

1000

Nitrogen concentration, arb. units

(b)

900 800 700 600 500 400 300 200 100 0 390 398 402 406 300 400 500 600 700 800 900 T. K $E_{\rm b}, {\rm eV}$

Fig. 7. (a) N1*s* XPS spectra of the catalyst Mn–Bi– O/α -Al₂O₃ recorded at (*1*) 298, (*2*) 335, (*3*) 365, (*4*) 460, and (*5*) 627 K. (b) Nitrogen concentration on the catalyst surface as a function of temperature.

Figure 7b shows the temperature dependence of the integral intensity of the normalized N1s spectra. This intensity is proportional to the concentration of nitrogen atoms on the catalyst surface. The plot has an extremum: initially, the nitrogen concentration increases by a factor of ~2, achieving a maximum at 350-370 K; it then drops in the temperature range 370-550 K and remains almost unchanged at higher temperatures. The increase in the integral intensity with an increase in temperature from 300 to 370 K can be due to either the dispersion of the active component accompanied by an increase in the outer surface area or the outcrop of part of the nitrogen atoms from the subsurface layers to the surface. However, dispersion is unlikely to occur in the temperature range of 300-400 K because the Mn/Bi/Al intensity ratio remains entirely unchanged, indicating the stability of the chemical state and morphology of the active phase. Hence, one can conclude that the increase in the integral intensity of the N1s line is due to the outcrop of part of the nitrogen atoms from the subsurface layer of the catalyst to the surface. The initial nitrogen location both on the surface and inside subsurface layers is likely to be due to the defectiveness of the active Mn-Bi-O phase [23]. This allows nitrogen atoms to penetrate efficiently to the subsurface layers of the active component of the catalyst after the decomposition of the amide-imide complexes.

Comparison of XPS and TPRS Data

The decrease in the nitrogen concentration on the catalyst surface at T > 370 K is likely due to either the recombination of N atoms followed by N₂ desorption or their interaction with active oxygen yielding NO or N₂O. To find out what elementary reactions lead to the removal of nitrogen atoms from the surface, we compared the results obtained by XPS and TPSR of chemisorbed ammonia (for details, see [24]). Figure 8a shows the temperature variation of the surface coverage due to nitrogen species localized on both reduced and oxidized adsorption sites, and Fig. 8b presents the TPSR spectra.

As seen in Fig. 8b, the reaction products or ammonia are not evolved below ~400 K. According to the XPS data (Fig. 8a), nitrogen atoms appear on sites of both types in the temperature range 300–340 K, and the relative surface coverages due to nitrogen species are redistributed without nitrogen desorption from the surface. A further increase in temperature (above 340 K) results in the diffusion of part of the nitrogen atoms from the oxidized sites to the reduced sites Mn^{2+} , which are energetically more stable. This fact explains the increase in the nitrogen concentration on the reduced sites (Fig. 8a, curve 1) and its decrease on the oxidized sites (Fig. 8a, curve 2). This means that a thermodynamic equilibrium is established between different states (species) of nitrogen.

Fig. 8. (a) Concentration of nitrogen species localized on (1) Mn^{2+} and (2) $Mn^{\delta+}$ sites as a function of temperature. (b) TPSR spectrum of ammonia on the catalyst Mn–Bi– O/α -Al₂O₃.

Above 350 K, the amount of nitrogen on the oxidized sites ([$Mn^{\delta+}-N$] species) begins to decrease because of its interaction with weakly bound active oxygen, and this results in the N₂O evolution at T > 400 K (Fig. 8b). Obviously, the recombination of nitrogen atoms does not make any considerable contribution, since, as follows from the TPSR spectra, N₂ desorbs only above 520–530 K, whereas most of the nitrogen disappears from the surface at 370–520 K (Fig. 7b). The IR spectroscopic study showed that no absorption bands, including those due to nitrite–nitrate ($NO_2^2-NO_3^2$) complexes, are observed in the temperature range 300–500 K.

Figure 9 plots binding energy and intesity ratio as a function of temperature for the components of the N1s spectrum (see Figs. 7, 8). These plots show how the state of nitrogen on the reduced and oxidized sites changes during the surface reactions with oxygen and the recombination of nitrogen atoms. As seen in Fig. 9a,

KINETICS AND CATALYSIS Vol. 46 No. 4 2005

Fig. 9. (a) Temperature dependence of binding energy for the components of the N1*s* spectrum corresponding to the species (1) $[N-Mn^{2+}]$ and (2) $[N-Mn^{\delta+}]$. (b) Temperature dependence of the concentration ratio between nitrogen species localized on different sites.

the behavior of nitrogen on these sites is different. An increase in $E_{\rm b}$ of nitrogen localized on both reduced (Mn^{2+}) and oxidized $(Mn^{\delta+})$ sites is found in the temperature range 300–350 K. This can be due to a change in the oxygen surrounding of nitrogen atoms upon their outcrop to the surface, that is, to an increase in the efficient oxidation number. An increase in binding energy from 399.5 to 400 eV upon heating the sample to 400 K can only be due to the fact that weakly bound oxygen increases the efficient oxidation number of both sites, $Mn^{\delta+}$ and Mn^{2+} . As the temperature is further increased, the nitrogen atoms localized on the oxidized manganese site, that is, on the sites including oxygen, interact rapidly with one another to form nitrous oxide (Fig. 8b). The sharp increase in the N1s binding energy from 400 to 402 eV above 400 K is due to the formation of more strongly bound nitrogen atoms, whose desorption at high temperatures, according to TPSR data, results in the formation of NO. The constancy of $E_{\rm b}({\rm N1}s)$ of the species [Mn²⁺–N] (Fig. 9a) in the range 350–700 K gives evidence that nitrogen on the reduced sites does not change its state and only the recombination of nitrogen atoms can occur on these sites. By contrast, the state of nitrogen in [Mn^{δ+}–N] changes dramatically at T > 400 K, as follows from the sharp increase in $E_{\rm b}$. The latter can be due to the increase in the efficient oxidation number of the manganese site on which the nitrogen atom is localized [25, 26, 30]. According to TPSR data (Fig. 8b), the nitrogen atoms interact with oxygen at higher temperatures (above 550 K) and are desorbed as NO.

Figure 9b shows the temperature dependence of the ratio between the nitrogen species localized on both Mn^{2+} and $Mn^{\delta+}$ sites. This ratio is constant in the range 300-350 K. A further increase in temperature from 350 to 400 K causes an increase in nitrogen mobility. A portion of the nitrogen atoms diffuses from the oxidized sites to the reduced sites, resulting in some increase in the ratio $[Mn^{2+}-N]/[Mn^{\delta+}-N]$. A particularly sharp increase is observed in the temperature range 400–450 K. As follows from the TPSR spectra, this is due to the evolution of N_2O to the gas phase, that is, to the decrease in the nitrogen concentration on the oxidized sites. The fact that this ratio is constant in the range 450–550 K is also consistent with the TPSR data. Simultaneous evolution of N₂O and N₂ is observed in this range; that is, the nitrogen concentration decreases on the sites of both types. A further increase in temperature is accompanied by NO evolution, and a decrease in the nitrogen concentration on the oxidized sites results in an increase in the ratio considered.

DISCUSSION

Thus, the *in situ* IR spectroscopic study of the surface compounds resulting from the interaction between ammonia and the catalyst Mn–Bi–O/ α -Al₂O₃ demonstrated that hydrogen atoms are abstracted from NH₃ to form [NH] and [NH₂] species. This conclusion is in agreement with the data of many authors [8–14, 20]. Ammonium ions and coordinated ammonia molecules are also formed. No [NO] species were found. The increase in temperature during the purging of the catalyst with helium led to the disappearance of the bands of the surface compounds from the IR spectra. Note that this is not accompanied by the evolution of ammonia or reaction products to the gas phase. According to TPSR data, the evolution of nitrous oxide begins above 393 K (Fig. 8b, [24]). According to IR spectroscopic, TPSR, and XPS data, atomic nitrogen remains on the surface, and, hence, it is quite likely that hydrogen atoms are further abstracted from [NH₂] and [NH] via a parallel scheme to form [N] species.

It is most probable that ammonium ions and coordinated ammonia molecules are oxidized via a similar mechanism to form nitrogen atoms. According to XPS data, the nitrogen atoms are localized on Mn^{2+} and $Mn^{\delta+}$ (2 < δ < 3) sites not only on the surface but also in the subsurface layers of the catalyst.

Comparison between the bands due to the surface compounds resulting from the adsorption of ammonia and hydrazine (Fig. 1) shows that ammonia adsorption on the catalyst does not produce the dimeric surface compound [NH₂–NH₂], that is, hydrazine. Thus, hydrazine is not an intermediate in the NH₃ conversion. This is due to the role that oxygen plays in this conversion. The active oxygen in the Mn-Bi oxide catalyst is weakly bound to the surface and is highly mobile [24]. As a consequence, the interaction of oxygen with ammonia, leading to the abstraction of hydrogen atoms, occurs more rapidly than the formation of dimeric species [NH₂–NH₂], unlike processes occurring on the catalysts with strongly bound oxygen, for example, Cr, Mn, Fe, Co, Ni, and Cu oxides supported on TiO₂ (anatase) [15, 16, 27]. The presence of weakly bound and mobile oxygen likely explains the absence of signals from [NO] in the IR spectra. These species form and interact to form N₂O so rapidly that the concentration of [NO] species becomes lower than the sensitivity limit of the spectrometer.

The surface species $[NH_2]$ and [NH] can be formed on active sites that are manganese ions in different oxidation states, namely, Mn^{3+} (Mn^{4+}) and $Mn^{\delta+}$ [24]. When ammonia is adsorbed on the oxidized sites Mn^{3+} (Mn^{4+}), the surface species [NH] appears, whereas the surface species $[NH_2]$ appears on the partially reduced sites $Mn^{\delta+}$:

$$\begin{split} & [O \cdots Mn^{3+} \cdots O] + NH_3 \longrightarrow [O \cdots Mn^{\delta +} - NH] + H_2O, \\ & [O \cdots Mn^{\delta +}] + NH_3 \longrightarrow [Mn^{2+} - NH_2] + [OH]. \end{split}$$

This assumption is confirmed by data for ammonia adsorption on the reduced catalyst. As the ratio between the reduced and oxidized sites, $Mn^{\delta+}/Mn^{3+}(Mn^{4+})$, is increased, the [NH₂]/[NH] intensity ratio increases.

As the temperature is increased in the absence of oxygen in the gas phase, the surface species [NH] and $[NH_2]$ interact with oxygen of the catalyst:

$$[O \cdots Mn^{\delta_+} - NH] + [O] \longrightarrow [O \cdots Mn^{\delta_+} - N] + [OH],$$

$$[\mathrm{Mn^{2+}\!-\!NH_2}] + [\mathrm{O}] \longrightarrow [\mathrm{Mn^{2+}\!-\!N}] + \mathrm{H_2O}.$$

When oxygen is present in the gas phase, the surface species [NH] and $[NH_2]$ lose hydrogen to form [N] even at room temperature.

As follows from TPSR data, nitrous oxide evolution to the gas phase begins at 400 K. The XPS data indicate that it is preceded by a series of surface processes:

(1) Initially, nitrogen comes out from the subsurface layers to the catalyst surface. This was confirmed in an earlier study [24], in which not only the surface but also subsurface layers of the active phase of the catalyst were shown to interact with oxygen under steady-state conditions. This process occurs at T > 300 K.

(2) At T > 350 K, the oxidation number of the manganese sites increases significantly due to their interaction with weakly bound active oxygen.

(3) As the temperature is further increased, the nitrogen atoms localized on an oxidized (oxygen-containing) manganese site interact readily with oxygen to form nitrous oxide, which then desorbs. The remaining oxygen reoxidizes the active site.

The formation of N_2O at low temperatures is due to the localization of nitrogen atoms on the adjacent oxidized sites, as was suggested previously [24]. The first weak TPSR peak of nitrous oxide, with a maximum at 449 K (Fig. 8b), originates from this interaction.

The removal of part of the nitrogen atoms with an increase in temperature results in a decrease in the [N] coverage of the surface. At the same time, the mobility of these species also increases with increasing temperature. The interaction of a nitrogen atom on an oxidized (oxygen-containing) site with a mobile [N] species results in N₂O formation, whereas the interaction of two [N] species leads to N₂ formation:

$$\begin{split} & [O \cdots Mn^{\delta_{+}} - N] + [N] \longrightarrow N_{2}O + [Mn^{2+}], \\ & [Mn^{2+} - N] + [N] \longrightarrow N_{2} + [Mn^{2+}]. \end{split}$$

These processes can be responsible for N_2O and N_2 evolution in the same temperature range. The maximum of the second N_2O peak in the TPSR spectrum (Fig. 8b) is observed at 579 K, and the maximum of the N_2 peak occurs at 574 K. This is possible when nitrous oxide and dinitrogen are evolved from sites of the same type.

Many authors believe that N_2 is formed from two [N] species, but the mechanism of N_2O formation is not quite clear. Some authors [13] suggest that the reaction $N + NO \longrightarrow N_2O$ takes place. This reaction can be considered to take place in our experiments if NO is treated as a nitrogen atom localized on an oxidized manganese site. Furthermore, the reaction $NO + NO \longrightarrow N_2O + O$ occurs, which proceeds at lower temperatures and is, therefore, more efficient. The highly reactive species [NO], which forms only with the participation of mobile active oxygen weakly bound to an [Mn^{δ+}–N] active site, is necessary for both reactions.

When oxygen is absent from the gas phase, the reduced manganese sites are reoxidized with subsurface oxygen. The presence of oxygen favors the rapid recovery of oxygen vacancies, thereby accelerating the conversion $Mn^{2+} \longrightarrow Mn^{3+}$ at the surface.

Thus, it was found by IR spectroscopy and XPS that ammonia interacts with the catalyst to lose hydrogen atoms and to form [N] species via the parallel reactions $[NH_2] \longrightarrow [N]$ and $[NH] \longrightarrow [N]$. The nitrogen species are localized on Mn^{2+} and $Mn^{\delta+}$ ($2 < \delta < 3$) ions. The nitrogen atoms formed are highly mobile and react readily with weakly bound oxygen of the active sites $[Mn^{\delta+}-N]$. The [N] atoms play the key role in N₂O formation: nitrous oxide is readily formed upon the inter-

KINETICS AND CATALYSIS Vol. 46 No. 4 2005

action of these atoms localized on the oxidized sites. N_2 is formed by the recombination of the nitrogen atoms in $[Mn^{2+}-N]$.

REFERENCES

- 1. Andrussov, L., Angew. Chem., 1926, vol. 39, p. 321.
- 2. Bodenstein, M., Z. Electrochem., 1935, vol. 41, p. 466.
- 3. Raschig, F., Angew. Chem., 1927, vol. 40, p. 1183.
- 4. Zavadzki, I., Disc. Faraday Soc., 1950, no. 8, p. 140.
- Fogel, Ya.M., Nadykto, B.T., Rybalko, V.F., Shvachko, V.I., and Korobchanskaya, I.E., *Kinet. Catal.*, 1964, vol. 8, p. 431.
- Il'chenko, N.I. and Golodets, G.J., J. Catal., 1975, vol. 39, no. 11, p. 57.
- Gorodetskii, V.V., Smirnov, M.Yu., and Cholach, A.R., *Proc. X Int. Cong. on Catalysis*, Budapest: Akad. Kiado, 1993, vol. B, p. 1587.
- 8. Mieher, W.D. and Ho, W., Surf. Sci., 1995, vol. 322, p. 151.
- 9. Selwyn, G.S., Fujimoto, G.T., and Lin, M.C., J. Phys. Chem., 1982, vol. 86, p. 760.
- 10. Guo, X.-C. and Madix, R.J., Faraday Disc., 1996, vol. 105, p. 139.
- 11. Carley, A.F., Davies, P.R., and Roberts, M.W., *Chem. Commun.*, 1998, p. 1793.
- 12. Boronin, A.I., Pashusky, A., and Roberts, M.W., *Catal. Lett.*, 1992, vol. 16, p. 345.
- 13. Lu, Gang., Anderson, B.G., van Grondelle, J., and van Santen, R.A., *J. Catal.*, 2001, vol. 199, p. 107.
- De Boer, M., Huisman, H.M., Mos, R.J.M., Leiveld, R.G., van Dillen, A.J., and Geus, J.W., *Catal. Today*, 1993, vol. 17, p. 189.
- Bagnasco, G., Peluso, G., Russo, G., Turco, M., Busca, G., and Ramis, G., 3rd World Cong. on Oxidation Catalysis, 1997, p. 643.
- Amores, J.M.G., Escribano, V.S., Ramis, G., and Busca, G., *Appl. Catal.*, *B*, 1997, vol. 13, p. 45.
- 17. Trombetta, M., Ramis, G., Busca, G., Montanari, B., and Vaccari, A., *Langmuir*, 1997, vol. 13, p. 4628.
- Ramis, G., Yi, L., and Busca, G., *Catal. Today*, 1996, vol. 28, p. 373.
- 19. Amblard, M., Burch, R., and Southward, B.W.L., *Catal. Today*, 2000, vol. 59, p. 365.
- Sil'chenkova, O.N., Matyshak, V.A., and Korchak, V.N., *Kinet. Katal.*, 1999, vol. 40, no. 4, p. 583.
- Kharitonov, A.S., Sheveleva, G.A., Panov, G.I., Sobolev, V.I., Paukshtis, E.A., and Romannikov, V.N., *Appl. Catal.*, *A*, 1993, vol. 98, p. 33.
- 22. Mokrinskii, V.V., Slavinskaya, E.M., Noskov, A.S., and Zolotarsky, I.A., PCT Int. Appl. WO 9825698, 1998.
- Ivanova, A.S., Slavinskaya, E.M., Mokrinskii, V.V., Polukhina, I.A., Tsybulya, S.V., Prosvirin, I.P., Bukhtiyarov, V.I., Rogov, V.A., Zaikovskii, V.I., and Noskov, A.S., *J. Catal.*, 2004, pp. 213, 221.
- 24. Slavinskaya, E.M., Veniaminov, S.A., Notte, P., Ivanova, A.S., Boronin, A.I., Chesalov, Yu.A., Polukhina, I.A., and Noskov, A.S., *J. Catal.*, 2004, vol. 222, p. 129.

- 25. Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, Briggs, D. and Seah, M.P., Eds., Chichester: Wiley, 1983.
- 26. Handbook of X-ray Photoelectron Spectroscopy, Moulder, J.F., Stickle, W.F., Sobol, P.E., et al., Eds., Eden Prairie: Perkin-Elmer, 1992.
- Ramis, G., Yi, L., Busca, G., Turco, M., Kotur, E., and Willey, R.J., J. Catal., 1995, vol. 157, p. 523.
- Sverdlov, L.M., Kovner, M.A., and Krainov, E.P., *Kolebatel'nye spektry molekul* (Vibrational Spectra of Molecules), Moscow: Nauka, 1970.
- 29. Sathyanarayana, D.N. and Nicholls, D., *Spectrochim. Acta*, 1978, vol. 34, p. 263.
- Wagner, C.D., Naumkin, A.V., Kraut-Vass, A., Allison, J.W., Powell, C.J., and Rumble, J.R., Jr., *NIST X-ray Photoelectron Spectroscopy Database. NIST Standard Reference Database 20*, version 3.3 (Web Version).

- 31. Biwer, B.M. and Bernasek, S.L., J. Electron Spectrosc. Relat. Phenom., 1986, vol. 40, p. 339.
- 32. Marchand, R., Agliz, D., Boukbir, L., and Quemerais, A., *J. Non-Cryst. Solids*, 1988, vol. 103, p. 35.
- Guimon, C., Gonbeau, D., Guillouzo, G.P., Dugne, O., Guette, A., Naslain, R., and Lahaye, M., *Surf. Interface Anal.*, 1990, vol. 16, p. 440.
- Handbook of X-ray Photoelectron Spectroscopy, Wagner, C.D., Riggs, W.M., Davis, L.E., Moulder, J.F., and Muilenberg, G.E., Eds., Eden Prairie: Perkin-Elmer, 1979.
- 35. Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, Briggs, D. and Seah, M., Eds., Chichester: Wiley, 1983.
- 36. Latha, G., Rajendran, N., and Rajeswari, S., J. Mater. Eng. Perform., 1997, vol. 6, no. 6, p. 743.