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Studies of the mechanism of ammonia oxidation into nitrous oxide over Mn–Bi–O/ α -Al₂O₃ catalyst

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Abstract

A complex of kinetic and physicochemical methods: temperature-programmed surface reaction (TPSR), pulsing NH₃ or NH₃/¹⁶O₂ (¹⁸O₂) reaction mixture, and infrared and photoelectron spectroscopies, was used for characterization of the highly selective supported manganese–bismuth oxide catalysts and for the study of the mechanism of the ammonia oxidation. Ammonia oxidation was demonstrated to proceed via alternating reduction and reoxidation of the catalyst surface with participation of the lattice oxygen. NH₃ interacts with weakly bonded oxygen species through hydrogen atom abstraction to form adsorbed [N] species, which are localized on Mn²⁺ and Mn^{δ +} (2 < δ < 3). Manganese ions with different oxidation degrees (Mn³⁺ (Mn⁴⁺) and Mn^{δ +}) serve as active sites of the catalyst surface. The correlation between the selectivity toward N₂O and the portion of manganese in the Mn³⁺ (Mn⁴⁺) state was established. Bismuth oxide plays an important role by increasing the quantity, mobility, and thermal stability of the subsurface oxygen. The reaction kinetic scheme is suggested based on the experimental results. Numerical simulation of TPSR data confirms the reliability of the proposed reaction mechanism. © 2003 Elsevier Inc. All rights reserved.

Keywords: Ammonia oxidation mechanism; Nitrous oxide; Supported manganese-bismuth oxide catalyst; TPSR; Pulse method

1. Introduction

Numerous papers are devoted to the mechanism of lowtemperature ammonia oxidation into nitrous oxide and nitrogen on heterogeneous catalysts. Experimental studies were carried out with metals [1–7] and oxides [8–14]. Ammonia oxidation was shown to occur by alternating reduction and oxidation of the catalyst, similar to the oxidation of hydrogen, CO, and general organic substances [1].

Numerous authors consider formation of NH_x species through oxydehydrogenation of ammonia as the first reaction stage. As to the next stages, there are several opinions:

 Successive abstraction of hydrogen atoms results in the formation of N_{ads} species. Interaction of N_{ads}, O_{ads}, and two N_{ads} produces NO and N₂, respectively, [2,4,5].

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- (2) NO, as the main intermediate, interacts with NH_x to form N₂ and with N_{ads} to form N₂O [6,7].
- (3) Formation of a dimmer (hydrazine) from NH₂ species results in the formation of N₂, and formation of nitroxyl (HNO) through interaction of NH_{ads} and O_{ads} leads to formation of N₂O [10,12,13].

A common feature of these stages is that the oxygen– catalyst bond is either formed or broken. The catalytic activity and selectivity are shown [8,15] to substantially depend on the oxygen bond energy measured by the heat of reaction: $0.5O_2 + [] \rightarrow [O]$. The higher the heat of reaction, the higher the selectivity to nitrogen. Nitrous oxide selectivity decreases in the transition metals series as follows: Pt > Pd > Ni > Fe > W > Ti.

Similarities between catalytic ammonia oxidation with gaseous oxygen and solid oxide reduction with ammonia [8] provide independent evidence for the participation of [O] species and the determination of the role of their surface concentration in the reaction kinetics. These similarities are as follows:

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- products of the same composition are formed during the catalytic reaction and the reduction;
- (2) longer reduction time results in an overall reduction of the rate of ammonia transformation;
- (3) the rate of the catalytic reaction equals the reduction rate at the same surface oxygen coverage;
- (4) selectivity to nitrogen increases while selectivity to nitrous oxide decreases when the reduction time is extended, i.e., when the surface oxygen coverage shrinks and, correspondingly, the surface bond energy increases.

Hence, interaction of ammonia with the surface is accompanied by electron transfer from ammonia molecules to the catalyst.

The mechanism of ammonia oxidation over complex oxide catalysts is not clearly understood. However, some analogies between the ammonia oxidation occurring on complex oxide catalysts, on metals, and on simple oxides are presented in the literature. These are similar temperature product formation relations [16] and the same product compositions formed by reduction and by catalytic oxidation reaction [8,17]. The same correlations between oxygen bond energy and the catalyst activity and selectivity are valid both for complex catalysts and for simple oxides. It should be noted that earlier investigations dealt with low-selectivity catalysts (less then 40%) with respect to nitrous oxide. Supported manganese-bismuth oxide systems have been proposed [18] as selective catalysts for the oxidation of ammonia into nitrous oxide. The present study aims at understanding the mechanism of ammonia oxidation over Mn-Bi oxides/a-Al₂O₃ (noted as Mn–Bi–O/ α -Al₂O₃) particularly in the 85– 90% selectivity range toward nitrous oxide.

2. Experimental and methods

2.1. Catalysts/gases

Supported manganese–bismuth oxide catalysts were prepared according to the procedure described elsewhere [19]. Mn–Bi–O-supported catalysts were synthesized using dou-

Table 1		
Physicochemical	properties Mn-Bi	oxide catalysts

ble impregnation of the support: incipient wetness impregnation of a weighed support sample with a solution of mixed manganese (II) and bismuth (III) nitrates taken in a certain volume was followed by drying at 80-130 °C. The dried sample was impregnated once again with a solution of the said nitrates and dried at 80-130 °C.

All the synthesized samples were calcined at 400, 550, and 750 °C for 2 or 4 h. The salts were manganese nitrate, $Mn(NO_3)_2 \cdot 6H_2O$, Aldrich index 28,864-0, and bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$, Aldrich index 38,307-4. Alumina in α - and γ -modifications were used as the supports.

These manganese–bismuth oxide catalysts contain multiple phases [19]. Apart from the support, they comprise individual manganese oxides (MnO₂, Mn₂O₃), bismuth oxide (Bi₂O₃), and their interaction products.

Catalysts Mn–Bi–O/ α -Al₂O₃ calcined at 400 °C comprise MnO₂, traces of undecomposed Bi(NO₃)₃, and α -Al₂O₃. A higher temperature or longer time of the thermal treatment favors the formation of phases of β -Mn₂O₃, α -Bi₂O₃, and their interaction product, Bi₂Mn₄O₁₀. The proportion of the latter increases as the temperature is elevated to 750 °C, MnO₂ and Bi₂O₃ phases not being detected upon treating at 750 °C (Table 1).

Approximately the same phase composition is established for catalysts Mn–Bi–O/ γ -Al₂O₃ calcined at 400 °C. Elevation of the calcination temperature or a longer calcination gives rise to formation of the following phases: Mn₂O₃, α -, β -Bi₂O₃, Bi₂Mn₄O₁₀; bismuth aluminate Bi₂Al₄O₉ also being formed. The proportion of the two latter phases increases with the calcination temperature. The lattice constant equal to 7.906 Å is characteristic of the support phase (γ -Al₂O₃) that is lower than the constant of the pure oxide. These data indicate formation of a γ -Al₂O₃-based solid solution.

Based on flowthrough reactor data, Mn–Bi–O/ α -Al₂O₃ is more selective toward nitrous oxide compared with Mn–Bi–O/ γ -Al₂O₃ with respective selectivities between 80 and 85% versus between 43 and 59%; such selectivity provided by Mn–Bi–O/ α -Al₂O₃ further increases at higher calcination temperatures.

Catalyst	Calcination temperature (°C) (duration, h)	Active component			t	Sspecific	Phase composition
		MnO ₂ , mass (%)	Bi ₂ O ₃ , mass (%)	Mn/Bi, mass	$\frac{\Sigma(Mn + Bi)}{(atom/nm^2)}$	(m ² /g)	
Mn-Bi-O/ α -Al ₂ O ₃	400(2)	13.0	9.0	1.01	75.1	10	MnO ₂ , Bi(NO ₃) ₃ (traces), amorphous phase, α -Al ₂ O ₃
	550(2)					8.7	β - MnO ₂ , β -Mn ₂ O ₃ , α -Bi ₂ O ₃ , α -Al ₂ O ₃
	550(4)					8.0	β -MnO ₂ , β -Mn ₂ O ₃ , α -Bi ₂ O ₃ , Bi ₂ Mn ₄ O ₁₀ , α -Al ₂ O ₃
	750(2)					7.5	β -Mn ₂ O ₃ , Bi ₂ Mn ₄ O ₁₀ , α -Al ₂ O ₃
Mn–Bi– O/γ -Al ₂ O ₃	400(2)	21.1	12.0	1.23	5.8	100	β - MnO ₂ , Bi ₂ O ₃ , Bi(NO ₃) ₃ (traces), γ -Al ₂ O ₃
	550(2)					101	β - MnO ₂ , β -, α -Bi ₂ O ₃ , γ -Al ₂ O ₃
	550(4)					103	β -MnO ₂ , Mn ₂ O ₃ , β -, α -Bi ₂ O ₃ , Bi ₂ Mn ₄ O ₁₀ , Bi ₂ Al ₄ O ₉ ,
							γ -Al ₂ O ₃
	750(2)					97	β -Mn ₂ O ₃ , Bi ₂ Mn ₄ O ₁₀ , Bi ₂ Al ₄ O ₉ , γ -Al ₂ O ₃

All gases used in this study are high purity (about 99.999%). Isotech provided ${}^{18}O_2$ with an isotopic purity of about 99%.

2.2. Methods

Catalytic properties were studied by two methods using the RXM-100, catalyst testing/characterization equipment (ASDI, USA), installed at Solutia Inc (Pensacola, USA), equipped with multigas pulsing and on-line mass spectrometry. Mass axes were calibrated and corrected digital output numbers used for each mass were followed up during the experiments. Signals were deconvoluted using breakdown patterns determined under the same conditions prior to the experiments.

2.2.1. Pulsing of ammonia or ammonia/ ${}^{16}O_2$ (${}^{18}O_2$) on the catalyst

Typically 0.1 to 0.4 g of fresh catalyst is placed in a flowthrough quartz reactor connected to the RXM-100. The catalyst is heated to 350 °C and pretreated with 11 pulses of 0.25 cc of oxygen spaced at 120 s each. Helium at 40 cc/min was used as a carrier gas resulting in an oxygen pulse length of 0.375 s. Pulses of ammonia or reaction mixture (53% ammonia/47% $^{16}O_2$ ($^{18}O_2$)) are also passed through the pretreated catalyst.

2.2.2. Temperature-programmed surface reaction (TPSR)

TPSR of chemisorbed ammonia with catalyst oxygen was conducted over Mn–Bi–O/ α -Al₂O₃ calcined at 400, 550, and 750 °C and over Mn–Bi–O/ γ -Al₂O₃ calcined at 400 °C. The catalysts were pretreated in helium at 450 °C and evacuated at room temperature. Catalysts were pretreated with ammonia at room temperature and further treated at room temperature with helium to remove excess and labile ammonia. Temperature-programmed reaction was conducted by heating such catalyst from room temperature to 650 °C at a rate of 15 °C/min.

2.2.3. In situ IRS studies

In situ IR studies were carried out in a Fourier IR spectrometer BOMEM MB-102 using a high-temperature flow quartz IR cell reactor with CaF₂ optic windows. A catalyst pellet (1 \times 3 cm, 50 mg) was mounted in the cell (V = 1.5 cm^3). Before each run the tablet was pretreated directly in the IR cell in flowing air at 250°C for an hour. The cell was cooled to the required temperature and flowing ammonia was substituted for air. Ammonia was passed through the cell during the period of time needed to reach some stationary ammonia concentration in the gas phase inside the cell and then stopped and the cell was sealed. In several minutes the ammonia gas concentration decreased practically to below the detectable level. The procedure was repeated again. IR spectra were acquired, for 1.5 min (30 scans) each, in the course of the experiment. The spectra looked like a superposition of spectra of the catalyst and compounds adsorbed thereon. Spectra of the surface compounds were identified by subtracting the background spectrum of the catalyst recorded before flowing ammonia from the acquired spectra.

2.2.4. XPS studies of Mn–Bi– O/α - Al_2O_3 , Mn– O/α - Al_2O_3 , and Bi– O/α - Al_2O_3 samples

An X-ray photoelectron spectroscopy (XPS) technique was used to study states of oxygen and the surface species formed during the catalyst treatment with ammonia, to determine surface concentrations and chemical states of these compounds. XPS spectra were acquired in a VG ESCALAB spectrometer, which was calibrated with respect to the binding energies of the reference levels Au4 $f_{7/2}$ ($E_b = 84.0 \text{ eV}$) and Cu2p_{3/2} ($E_b = 932.7 \text{ eV}$) [20] using AlK_{α} radiation $(h\nu = 1486.6 \text{ eV})$. Catalyst samples were fixed on a holder either by rubbing into a fine-mesh nickel grid or by supporting from their alcohol suspension. The charging effect during photoemission was taken into account using an internal reference (line Al2p of the α -alumina support with $E_{b} = 73.8 \text{ eV}$), and the C1s line ($E_{b}(C1s) = 284.8 \text{ eV}$) of the surface carbon contaminations [20,21]. The concentration of surface species was calculated based on the measurements of the intensity (I) of certain XPS lines by the following formula:

$$n_x/n_{\rm Al} = \frac{I_x/(\rm ASF)_x}{I_{\rm Al}/(\rm ASF)_{\rm Al}}$$

where n_x is the element concentration (at%) in the analysis zone, (ASF)_i are atomic sensitivity factors of elements. According to the available data [21], the following atomic sensitivity factors were used: Al2p = 0.193, N1s = 0.477, O1s = 0.711, and Mn2p = 2.420.

The package of proprietary CALC programs was used for detailed spectra processing. The CALC programs allow carrying out the curve fitting analysis using Gaussian– Lorenzian (GL) with a variable Gaussian proportion.

A sample of Mn–Bi–O/ α -Al₂O₃ catalyst calcined at 550 °C was pretreated in helium at 473 K for an hour, treated with ammonia at room temperature for another hour, and blown by air for 30 min.

XPS spectra were recorded at different temperatures (300 to 769 K) for samples of Mn–Bi–O/ α -Al₂O₃ catalyst calcined at 400, 550, and 750 °C, samples of Mn–O/ α -Al₂O₃ and Bi–O/ α -Al₂O₃ calcined at 400 °C.

3. Results

3.1. Reduction of Mn–Bi– O/α - Al_2O_3 —500 °C catalyst with ammonia

A reduced catalyst sample was prepared by exposing an oxygen-treated catalyst to a series of fifty 0.25 cc ammonia pulses.

Mass spectrometry data show that ammonia is oxidized by catalyst oxygen to produce N_2O , N_2 , and NO. Fig. 1



Fig. 1. Rate constants of catalyst reduction with ammonia as a function of the degree of surface reduction.



Fig. 2. Selectivity to reaction products (N₂O, N₂, and NO) during catalyst reduction with ammonia vs the degree of surface reduction.

presents the rate constant of ammonia oxidation versus the degree of reduction of the catalyst surface. The rate constant of ammonia oxidation is calculated by the flow reactor equation $k = -(\ln(1-x))/\tau$, where x is ammonia conversion, $\tau = 2.24 \times 10^{-15}$ cm² s/molecules is the contact time.

The degree of catalyst reduction is calculated as the ratio of the amount of oxygen eliminated from the catalyst to the total amount of surface oxygen species from the catalyst monolayer. It is assumed that the monolayer coverage corresponds to the amount of 0.238 cm³ O_2/m^2 of the catalyst surface [22]. The catalyst activity is seen to decrease with an increased degree of reduction. The amount of oxygen eliminated from the catalyst during the whole reduction period is 3.805 cm³; this is almost half of the total amount of oxygen in the catalyst's active components. This shows the rather high mobility of bulk oxygen. Elimination of half of the catalyst oxygen species can cause changes in the phase composition. XRD data [19] show that phases of Mn₃O₄, MnO, and bismuth metal are present in the ammonia-reduced catalyst at 400 °C.

Correspondingly, selectivity to the reaction products changes with the increased catalyst surface reduction (Fig. 2): the selectivity to nitrogen increases while the selectivity to nitrous oxide decreases; selectivity to nitrogen oxide is unchanged and remains low.



Fig. 3. Selectivity to reaction products $(N_2O, N_2, and NO)$ during ammonia oxidation vs the degree of surface reduction.



Fig. 4. Selectivity of the oxidized and reduced catalysts to reaction products (N_2O, N_2) versus the number of reaction mixture pulses.

3.2. Interaction of the reaction mixture $(NH_3 + O_2)$ with oxidized and reduced catalysts

Pulses of the reaction mixture containing ammonia and oxygen were fed to reduced and oxidized catalyst samples.

Figs. 3 and 4 demonstrate that the oxidized catalyst is more selective to nitrous oxide and less selective to nitrogen compared with the reduced catalyst. Variations in selectivity to N_2O and N_2 are observed with increasing time of catalyst treatment with the reaction mixture (Fig. 4). Selectivity to N_2O decreases by using the oxidized catalyst and increases with the reduced catalyst, while selectivity to nitrogen decreases with the reduced catalyst and increases with the oxidized form.

The degree of surface reduction of a stationary operating catalyst can be determined from comparative rate constants of the reduction and of the catalytic reaction over the oxidized and reduced catalysts [22]. It is 24.6% for the oxidized catalyst (point 1 in Fig. 1) and 77% for the reduced catalyst (point 2 in Fig. 1). The further extension of the treatment time may lead to equal activities and selectivities with



Fig. 5. Total oxygen consumption for the formation of the reaction products, oxygen consumption for formation of products from gas phase, and oxygen consumption for formation of products from the catalyst vs the number of reaction mixture pulses.

respect to N₂O and N₂ unless irreversible phase transformations occur during reduction.

Thus, the reaction of ammonia oxidation is probably proceeding through alternate reduction and reoxidation of the catalyst surface.

In order to verify if the catalyst oxygen species are involved in the reaction, the total oxygen consumption for the formation of the reaction products was compared to the oxygen consumption for the formation of the products from the gas phase. In addition, the composition of the reaction products was studied by substitution of ${}^{18}O_2$ for ${}^{16}O_2$ in the reaction mixture containing ammonia and oxygen.

3.3. Comparison of oxygen consumption for the formation of the reaction products

Fig. 5 shows the dependence of the total oxygen consumption for the formation of the reaction products ($\Sigma[O]$) and of the oxygen consumption for the formation of the products from the gas phase $(q_{[O]}^0 - q_{[O]}^{\text{current}})$ (where $q_{[O]}^0$ is the oxygen amount in a pulse and $q_{[O]}^{\text{current}}$ is the oxygen amount in gas phase) versus the number of pulses of the reaction mixture. The difference between the total oxygen amount consumed for the formation of the reaction products and the oxygen amount consumed for the formation of the reaction products from the gas phase equals the amount of oxygen consumed from the catalyst for the formation of the products. The amount of oxygen eliminated from the catalyst decreases with the increasing number of pulses. As soon as the stationary state is reached, the amount of oxygen consumed from the gas phase becomes equal to the amount quantified in the oxidation products. The amount of oxygen eliminated from the catalyst during the catalytic reaction can be calculated based on these data. It is 21.5% of the monolayer. That agrees well with the above estimated degree of surface reduction (24.6%) for the stationary operating catalyst.



Fig. 6. Amount of ammonia converted into $N_2^{16}O$, $N_2^{18}O$, N_2 (a) and into $N^{16}O$, $N^{18}O$ (b) vs the duration of the catalyst treatment with the reaction mixture containing NH_3 and $^{18}O_2$.

3.4. Reaction with labeled oxygen $^{18}O_2$

Fig. 6 shows the amount of ammonia converted to $N_2^{16}O$, $N_2^{18}O$, $N^{16}O$, $N^{18}O$, and N_2 versus the number of pulses of the reaction mixture. Since the stationary selectivity to nitrogen does not change, the amount of nitrogen formed through ammonia oxidation by ${}^{16}O_2$ and by ${}^{18}O_2$ can be separately calculated. Results show that the amount of products formed by ammonia oxidation with ¹⁶O₂ gradually decreases while it increases for ¹⁸O₂. Data on the consumption of ¹⁶O₂ and ¹⁸O₂ during the course of the reaction are shown in Fig. 7. During the experiment, an equivalent amount of 2.47 cm³ of ${}^{16}O_2$ is transferred from the catalyst in the reaction products; this corresponds to 2.3 oxygen monolayers. This corresponds to one-third of the total oxygen of the catalyst (7.8 monolayers) as assessed by hydrogen reduction in a temperature-programmed reduction [19]. These data support the assumption of a high mobility for the bulk oxygen species.

Therefore, it is reasonable to conclude that catalyst oxygen is involved in the reaction of ammonia oxidation through alternate reduction and reoxidation of the catalyst surface.



Fig. 7. Consumption of ${}^{16}O_2$ and ${}^{18}O_2$ for the formation of the reaction products vs the duration of the catalyst treatment with the reaction mixture containing NH₃ and ${}^{18}O_2$.



Fig. 8. Temperature-programmed surface reaction of ammonia over Mn–Bi– O/α -Al₂O₃ calcined at 400 °C.



Fig. 9. Temperature-programmed surface reaction of ammonia over Mn–Bi–O/ α -Al_2O_3 calcined at 550 $^{\circ}C.$

3.5. Temperature-programmed surface reaction of chemisorbed ammonia

Figs. 8–11 show that no ammonia is formed during the temperature-programmed surface reactions.



Fig. 10. Temperature-programmed surface reaction of ammonia over Mn–Bi– O/α -Al₂O₃ calcined at 750 °C.



Fig. 11. Temperature-programmed surface reaction of ammonia over Mn–Bi– O/γ -Al₂O₃ calcined at 400 °C.

Evolution of nitrous oxide from Mn–Bi– O/α -Al₂O₃ calcined at 400 °C occurs over a broad range of temperatures with maximum at 176, 305, and 496 °C, while nitrogen evolution shows two sharp peaks with maximum at 300 and 598 °C. Nitrogen oxide evolved at a much higher temperature compared with nitrous oxide with a maximum at 533 °C. Catalyst calcination at 550 °C leads to very similar results whereby calcination at 750 °C results in considerable changes. Indeed, the low-temperature maximum for nitrogen evolution is shifted toward higher temperatures (377 °C) but the high-temperature peak (at 598 °C) disappears. Two peaks appearing at 458 and 516 °C characterize the NO evolution. Formation of nitrous oxide is proportionally reduced and characterized by three peaks with maximum at 183, 233, and 350 °C.

Fig. 11 shows the TPSR observed for $Mn-Bi-O/\gamma-Al_2O_3$ calcined at 400 °C. Nitrous oxide appears as three poorly separated peaks with maximum at 205, 318, and 605 °C. Three maximum at 187, 336, and 605 °C are observed for nitrogen formation and two peaks with maximum at 505 and 605 °C for nitrogen oxide.



Fig. 12. IR spectra of surface compounds acquired after adsorption of ammonia by the Mn–Bi–O/ α -Al₂O₃ catalyst calcined at 550 °C. The spectra are recorded during desorption in helium at different temperatures.

3.5.1. In situ IR studies

Fig. 12 shows spectra of surface species (SS) formed upon interaction of NH_3 with the surface at room temperature (20 °C) at single and double feeding. In the IR spectra absorption bands at 1610, 1545, and 1411 cm⁻¹ are observed. A low intense band at 1610 cm⁻¹ relates to adsorbed molecular ammonia. The bands at 1545 and 1411 cm⁻¹, in accordance with available data [10], are assigned to NH_2 and NH adsorbed species, respectively. The repeated feeding of ammonia results in an increase in the concentration of SS.

The SS concentrations do not practically change after blowing with helium at room temperature. Elevation of the temperature during blowing with helium results in a progressive decrease in the SS concentration; the bands of SS disappear from the IR spectra upon blowing at 120 °C. Also SS concentration decreases if blowing with air at room temperature for 2 min occurs. Note that the reaction products or NH₃ are not detected in the gas phase while the SS concentrations decrease in the course of these experiments. Hence, the decrease is accounted for not by desorption of the compounds to the gas phase but by their further transformation to form SS which are not detected in the measured frequency range of the IR spectra (4000–1300 cm⁻¹).

3.5.2. XPS studies of Mn–Bi– O/α - Al_2O_3 , Mn– O/α - Al_2O_3 , and Bi– O/α - Al_2O_3

XPS studies were used to identify surface species formed on adsorption of ammonia. The survey XPS spectra demonstrate that a N1s line, which is not seen before treatment, becomes observable after adsorption of ammonia and blowing with air. The chemical state of the element is established by the high-resolution inspection of the spectra N1s region (see Fig. 13). Curve fitting shows that the resulting spectrum is composed of two components with $E_b = 397.0 \text{ eV}$ and 399.3 eV. The analysis of the literature XPS data of nitrogen-containing materials and nitrogen-containing molecules on the oxide surfaces has been done [20,21,23]. Comparison with the experimental results shows that the peak at



Fig. 13. N1s spectrum acquired with the Mn–Bi–O/ α -Al₂O₃ catalyst (calcined at 550 °C) after treatment with ammonia followed by blowing with oxygen. The spectra are recorded at 300 K.

 $E_{\rm b} = 397.0$ eV is within the region, which is characteristic of metal nitrides or nitrogen adsorbed on the surface of metals and oxides. The value $E_b = 399.3$ eV is in the end of the spectral N1s region, which is typical both for the nitrogen constituent of oxynitrides [24–26] and for the nitrogen constituent of adsorbed NO, N-H, NHOH, or nitrosyl complexes [20,21,23]. Therefore, XPS data alone are insufficient for unambiguous conclusions about the nature of nitrogen with $E_b = 399.3$ eV. At the same time, the above discussed IRS data indicate the absence of bands related to N-O and N-H bonds in the samples treated with ammonia and blown by air at room temperature or by helium at 393 K. Consequently, it seems reasonable to assign the lines at $E_{\rm b} = 397.9$ and 399.3 eV to nitrogen species localized on Mn²⁺ and $Mn^{\delta+}$ (2 < δ < 3) ions, respectively. It is shown in the previous paper [19] that species of manganese in different oxidation states are formed upon treatment of the catalysts with the reaction mixture or ammonia.

The surface nitrogen concentration expressed as the N/Mn ratio is calculated from N1s and Mn2p intensity ratio; it equals ca. 0.5. The study of the thermal stability of these nitrogen species reveals that the line N1s decreases in intensity on heating the sample immediately in the analyzer chamber of an electron spectrometer that makes nitrogen undetectable in the XPS spectra at 700 K.

4. Discussion

4.1. Studies of surface intermediates

In situ IRS studies of the surface species formed through interaction of ammonia with Mn–Bi–O/ α -Al₂O₃—550 °C reveal that NH₃ abstracts hydrogen atom during the interaction to form NH and NH₂. Blowing with helium at a temperature elevation up to 120 °C or blowing with air at room temperature results in the disappearance of SS bands from IR spectra. Evolution of either NH₃ or the reaction products is not observed in this case but XPS data indicate that nitrogen remains on the surface. Therefore, it is reasonable to conclude that the further abstracting of hydrogen atoms occurs to produce nitrogen atoms by the parallel pathway:

$$NH_2 \rightarrow N$$
, $NH \rightarrow N$.

XPS data are evidence of the localization of nitrogen atoms on Mn^{2+} and $Mn^{\delta+}$ (2 < δ < 3) ions.

4.2. Studies of temperature-programmed surface reaction of chemisorbed ammonia

As ammonia is not desorbed during the TPSR, the reaction rate constant (K_r) is much higher than the desorption rate constant (K_d) in the process:

$$\mathrm{NH}_3(\mathbf{g}) \stackrel{K_{\mathrm{d}}}{\longrightarrow} \mathrm{NH}_3(\mathbf{a}) \stackrel{K_{\mathrm{r}}}{\longrightarrow} \mathrm{N}_2\mathrm{O}(\mathbf{g}) + \mathrm{N}_2(\mathbf{g}) + \mathrm{NO}(\mathbf{g}).$$

Therefore, the surface ammonia concentration during heating is completely determined by the rate of the surface reaction. Reaction activation energy (E_r) can be calculated by Eq. (1) with the assumption that $A = 10^{13} \text{ s}^{-1}$ [27],

$$E_{\rm r} = \frac{A}{\beta} R T_{\rm p}^2 \exp\left(-\frac{E_{\rm r}}{R T_{\rm p}}\right),\tag{1}$$

 $T_{\rm p}$ is the peak maximum temperature; β is the heating rate (15°/min).

The quantity of the reaction products formed during the TPSR is used to calculate the amount of oxygen removed from the catalyst. It is 21.8% of monolayer.

The appearance of several peaks of the same reaction product in the course of TPSR may indicate nonuniformity of the active surface with respect to the given reaction, i.e., the occurrence of various types of active sites. This is valid when there is no influence of the processes of diffusion, desorption, and reaction kinetics on the characteristics of the spectrum.

From TPSR data, nitrous oxide starts releasing into the gas phase at temperatures above 120 °C. Therefore, one can conclude on the basis of IRS and XPS data that there are only species of one type, namely [N], before the evolution of gaseous products. Then, stages of NH₂ and NH transformations into the N species are very fast, so the hydrogen abstraction reactions do not determine the shape of TPSR spectrum.

Formation of nitrous oxide during TPSR needs to break the oxygen–catalyst bond. Hence, the existence of several temperature peaks of nitrous oxide evolution may argue for the presence of surface sites with different energies of the oxygen–catalyst bonds.

Table 2 presents the TPSR results and more particularly the calculated activation energies, the amounts of products released, and the fractional quantity of ammonia adsorption sites. Poorly resolved peaks of nitrous oxide were geometrically divided in order to evaluate the respective amounts of N_2O produced from the different sites.



Fig. 14. Temperature dependence of TPSR rate of formation of nitrogen in linearized coordinates.

One can see for Mn–Bi–O/α-Al₂O₃ calcined at 400 °C that the amount of sites responsible for the formation of nitrous oxide and nitrogen is approximately half of the total number of ammonia adsorption sites at the temperature range used for the catalytic reaction (315 to 350 °C). Among them, 70% are sites responsible for the formation of nitrous oxide. The proportion of the sites responsible for the formation of nitrous oxide at low activation energy (27 kcal/mol) is ca. 0.6% of the total number of ammonia adsorption sites. Higher catalyst calcination temperatures result in a proportional increase of these sites: 1.7% after calcination at 550 °C and 2.6% after calcination at 750 °C. Also calcination at 750 °C creates sites with higher activation energy (30 kcal/mol) at about 7.3%. In this case, increasing activation energy for nitrogen formation is observed in agreement with an increase in the selectivity to N₂O.

In the Mn–Bi–O/ γ -Al₂O₃ calcined at 400 °C, the proportion of the sites responsible for the formation of nitrous oxide is lower than that of the sites responsible for the formation of nitrogen. At the same time, the proportion of sites that produce nitrogen, with low metal–oxygen bond energy (activation energy of about 27.6 kcal/mol), is much higher than the proportion of the sites responsible for the formation of nitrous oxide.

The reaction order was determined for the formation of nitrogen by TPSR. A linear correlation is obtained for the nitrogen formation expressed as $\ln(W/N^2)$ versus 1/T(Fig. 14), where W is the reaction rate and N the concentration of the adsorbate. This leads to a probable second order for the nitrogen formation [28]. It is difficult to provide for a correct determination of the orders for the formation of nitrous oxide and nitrogen oxide because of the poorly resolved peaks. Nevertheless, by analogy with nitrogen, the former reaction order is probably 2.

4.3. Studies of catalyst reduction by ammonia

Studies of the catalyst reduction with ammonia reveal that the reduction rate constant decreases with an increased degree of surface reduction (Fig. 1), the reduction being higher

Table 2 Comparative kinetic TPSR parameters of chemisorbed ammonia over various catalysts

Catalyst/calcination temperature (°C)	Peak	<i>T</i> (°C)	$E_{\rm r}$ (kcal/mol)	Amount of product $(\mu mol/m_{cat}^2)$	Fractional quantity of NH ₃ adsorption sites (%)
Mn–Bi–O/α-Al ₂ O ₃ —400 °C	N ₂	300	34.6	0.148	13.1
	N ₂ O	176	26.9	0.007	0.6
	-	305	34.9	0.290	25.8
		496	46.8	0.063	5.6
	NO	533	49.2	0.893	39.7
	N_2	598	53.3	0.173	15.3
Mn–Bi–O/α-Al ₂ O ₃ —550 °C	N_2	301	34.6	0.138	13.7
	N ₂ O	176	26.9	0.017	1.7
		306	34.9	0.238	23.6
		496	46.8	0.080	7.9
	NO	500	47.1	0.703	34.8
		544	49.9		
	N ₂	601	53.5	0.187	18.5
Mn–Bi–O/ α -Al ₂ O ₃ –750 °C	N ₂	377	39.4	0.690	46.4
	N ₂ O	183	27.3	0.038	2.55
		233	30.4	0.108	7.26
		350	37.7	0.167	11.2
	NO	458	44.5	0.970	32.6
		516	48.1		
Mn–Bi–O/γ-Al ₂ O ₃ —400 °C	N2	187	27.6	0.635	38.5
		336	36.8		
		605	53.7		
	N ₂ O	205	28.7	0.48	29.0
		318	35.7		
		605	53.7		
	NO	505	47.4	0.535	32.5
		605	53.7		



Fig. 15. Rate constant of ammonia oxidation into reaction products (N_2O , N_2 , and NO) versus the degree of reduction of the catalyst surface.

for the oxidation of ammonia into nitrous oxide compared with oxidation to nitrogen (Fig. 15). These observations may be explained by a low mobility of the bulk oxygen, by the locking of the active surface with strongly bonded ammonia species, or by a different oxygen state at the catalyst surface. This study shows that the mobility of the bulk oxygen is significant; therefore, the lower reduction rate constant can be attributed to the latter two factors. The different states of oxygen at the catalyst surface are indeed observed from the TPSR data (Fig. 9) obtained with the Mn–Bi–O/ α -Al₂O₃ catalyst calcined at 550 °C. This is reflected by the presence of surface sites of different natures: there are three types of such sites responsible, respectively, for the formation of N₂O, N₂, and NO. In addition, each type may be energetically inhomogeneous. For example, three types of sites (activation energies equal to 27, 35, and 47 kcal/mol) are responsible for the formation of nitrous oxide, two types of sites (activation energies equal to 35 and 53.5 kcal/mol) for the formation of nitrogen, and two types of sites (activation energies equal to 47 and 50 kcal/mol) for the formation of nitrogen oxide. A significant reduction in the rate constant observed during ammonia oxidation into nitrous oxide is explained by the fact that N₂O formation requires that a larger number of oxygen-catalyst bonds are broken compared with the formation of N₂ [5]. Elimination of weakly bonded oxygen results in a reduction of the overall rate constant of ammonia consumption and in a significant reduction in the rate constant for ammonia oxidation into N2O compared to the rate constant of ammonia oxidation into N₂. As a consequence, the selectivity to N₂ increases with the oxygen-catalyst bond energy [5,29-32]. On the other hand, the lower reduction rate constant may result from the locking of the active surface with strongly adsorbed species. The related TPSR data show that approximately half of the sites are occupied by strongly bonded species eliminated at considerably higher temperature than the normal reaction temperature.

4.4. Influence of calcination temperature on the proportion of various sites for ammonia adsorption

Based on the TPSR data, we observe an increase in the selectivity of Mn–Bi–O/ α -Al₂O₃ to nitrous oxide with higher calcination temperatures. This results from an increase in the number of ammonia adsorption sites having a lower manganese-oxide bond energy (low activation energy of the reaction) responsible for the formation of nitrous oxide. The oxygen-manganese bond energy is 62.2 kcal/gat O in MnO₂, 76.1 kcal/gat O in Mn₂O₃, and 82.8 kcal/gat O in Mn₃O₄ [33]. Hence, an increase in the proportion of the sites with lower bond energy means an increase in the proportion of the oxidized manganese state. This conclusion agrees with the data cited elsewhere [19] and indicates that the $Mn^{3+}/Mn^{\delta+}$ ratio increases with higher calcination temperature. The selectivity to N₂O varies with this ratio. Hence, it is reasonable to conclude that the reduced manganese species are responsible for the formation of nitrogen and the oxidized species for the formation of nitrous oxide. The selectivity of the catalyst on γ -alumina is low due to a higher proportion of low bond energy sites involved in the formation of nitrogen.

4.5. The role of bismuth oxide in the manganese–bismuth oxide catalyst

Comparative data on activity and selectivity toward N₂O obtained with samples of Mn–O/ α -Al₂O₃, Bi–O/ α -Al₂O₃, and Bi₂Mn₄O₁₀/ α -Al₂O₃ [19] demonstrate that the selectivity ity to N₂O is around 75% on the Mn–O/ α -Al₂O₃ catalyst, the selectivity is equal to 63.6% on the Bi₂Mn₄O₁₀/ α -Al₂O₃ catalyst, while the Bi–O/ α -Al₂O₃ is not active in ammonia oxidation. Thus, the manganese oxide phase is active in ammonia oxidation toward N₂O. A comparison of the selectivity toward N₂O of Mn–O/ α -Al₂O₃ and Mn–Bi–O/ α -Al₂O₃ catalysts shows that bismuth oxides play a key role in the selectivity toward nitrous oxide is higher over the manganese–bismuth oxide catalyst.

Nitrous oxide is known to form due to the presence of active oxygen species in the catalyst [34], which can produce NO from N_{ads} and lattice oxygen (O_{lat}) [35]. In accordance with earlier paper [7], the selectivity toward N_2 and N_2O is determined by the relative rates of reactions (I) and (II):

$$NH_x + NO \rightarrow N_2 + OH_x,$$
 (I)

$$N + NO \rightarrow N_2O.$$
 (II)

The reaction rates depend on the surface oxygen coverage. The more surface oxygen coverage, the faster the reactions of NO_{ads} and N_{ads} formation. As a result, the surface



Fig. 16. (a) Relative intensities of O1s/Al2p lines in XPS spectra of samples recorded at different temperatures: 1, α -Al₂O₃; 2, Bi–O/ α -Al₂O₃; 3, Mn–O/ α -Al₂O₃; 4, Mn–Bi–O/ α -Al₂O₃—750 °C; 5, Mn–Bi–O/ α -Al₂O₃—550 °C; 6, Mn–Bi–O/ α -Al₂O₃—400 °C. (b) Normalized relative concentration of oxygen in the samples.

concentration of NH_x species and, correspondingly, the reaction rate (I) decrease abruptly to cause an increase in the selectivity toward N_2O .

Addition of bismuth oxide to manganese oxide leads to improvement of the catalyst performance for three reasons. First, bismuth oxide makes manganese oxide more dispersed [19] which results in an increase in the amount of active oxygen. Second, bismuth oxide makes the active component surface more defective and, as a result, oxygen more labile. The third reason is the increased thermal stability of oxygen. XPS studies of the oxygen behavior during heating samples in the analyzer chamber in situ regime support this conclusion. XPS data are illustrated in Fig. 16. Fig. 16a shows the O1s/Al2p intensity ratio for the samples of α -Al₂O₃, Mn-Bi-O/α-Al₂O₃, Mn-O/α-Al₂O₃, and Bi-O/α-Al₂O₃. These comparative values for an individual support and catalyst characterize an increase in the oxygen loading in the catalysts due to supporting of the active component. It is seen in Fig. 16a that supporting the active component results in an increase in the O1s/Al2p ratio. The ratio increases considerably in the catalyst samples against that of the supported individual oxides Bi_2O_3 (curve 2) and MnO_2 (curve 3). Since manganese and bismuth are loaded in ap-

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proximately equal amounts in all the samples, the sharp increase of the O1s/Al2p ratio is accounted for by dispersion of manganese oxide under the action of bismuth oxide supported on α -Al₂O₃. The surface sensitivity in XPS measurements is determined by the mean free path of emitted electrons λ ($\lambda \sim 20-30$ Å); therefore, it is reasonable to suppose that the observed process of dispersing leads to formation of thin Mn–Bi–O film that coats the support particles.

Note that the highest O1s/Al2p ratio is observed with the catalyst calcined at 400 °C. Elevation of the calcination temperature results to some decrease in the ratio due to sintering processes detected by XRD and TEM [19].

Fig. 16a also shows some decrease in the O1s/Al2p ratio upon sample heating in vacuum that may happen due to desorption of the active oxygen. To know in more detail about the oxygen loss on heating, the curves in Fig. 16a are normalized (Fig. 16b). The changes in the temperaturedependent relative oxygen content in the active phase are seen to follow different ways in the one-component samples (Mn–O/ α -Al₂O₃, Bi–O/ α -Al₂O₃) and in the catalysts under study. For example, the relative oxygen loss is noticeably lower in the catalysts than in the individual oxides Mn–O/ α -Al₂O₃ and Bi–O/ α -Al₂O₃. A comparison reveals that the presence of bismuth oxide makes the thermal stability of the active oxygen much higher in the catalyst.

Hence, manganese oxide looses oxygen more rapidly, i.e., is easier reduced, in the absence of bismuth oxide. The same conclusion follows from the TPR data [19] showing that the temperature of reduction of MnO₂ into Mn₃O₄ is lower for the Mn–O/ α -Al₂O₃ catalyst (the peak maximum is equal to 313 °C) than for the Mn–Bi–O/ α -Al₂O₃ catalyst (the peak maximum is equal to 348 °C). One can conclude based on these data that the reduction degree is considerably higher in the Mn–O/ α -Al₂O₃ catalyst under steady-state operation than in the Mn–Bi–O/ α -Al₂O₃ catalyst. As demonstrated above, the selectivity toward N₂ increases but the selectivity toward N₂O decreases as the surface reduction degree increases. Therefore, the manganese-bismuth oxide catalyst under steady-state operation in ammonia oxidation is more selective toward N₂O than the manganese catalyst. Note that the same was concluded for the Mn/La/SiO₂ system [36].

The manganese–bismuth oxide catalyst supported on γ -Al₂O₃ is considerably lower selective toward N₂O than the one supported on α -Al₂O₃. The observed distinctions may be accounted for by the following reasons. As shown elsewhere [19], in the catalyst based on γ -Al₂O₃ the active components interact with the support to produce the Bi₂Al₄O₉ phase and solid solutions of manganese ions in alumina that is indicated by a lower lattice constant than that of pure alumina. Since $r_{Mn^{4+}} = 0.52 < r_{Al^{3+}} = 0.57$ Å, then alumina may be promoted by Mn⁴⁺ ions. Moreover, the surface concentration of manganese and bismuth, in accordance with XPS data, is lower by an order of magnitude than those in the catalysts supported on α -Al₂O₃. As a result, the amount of active oxygen responsible for formation of N₂O is considerably lower than that in the Mn–Bi–O/ α -Al₂O₃ catalyst.

It is known that the reaction products are not formed in the absence of oxygen in the gas phase [37] on the Mn–O/ γ -Al₂O₃. NO interacts with NH₃ in the absence of oxygen to form nitrogen. Addition of oxygen to the NO/NH₃ mixture results in the acceleration of N₂ formation, no N₂O being formed. The catalyst pretreated with the NO/O₂ mixture interacts with ammonia to form N₂ and a small amount of N₂O. It is reasonable to assume based on these data that the lattice oxygen is not labile and inactive in the Mn–O/ γ -Al₂O₃ catalyst.

The presence of bismuth oxide in the catalyst supported on γ -Al₂O₃ causes an increase in the proportion of active oxygen but to a lesser extent than in the α -Al₂O₃-based catalyst. Hence, the presence of bismuth oxide makes the γ -Al₂O₃-based catalyst active to formation of nitrous oxide, but less active than the catalyst based on α -Al₂O₃.

4.6. Studies of behavior of the catalyst during treatment with the reaction mixture

The catalyst was tested with pulses of ammonia and the ammonia/oxygen reaction mixture. The same products, N₂O, N₂, and NO, were formed during both the reduction and the catalytic reaction with the rate constants being equal for the catalytic reaction and the reduction at the same degree of surface reduction (Fig. 1). As stated above (Fig. 5), comparison of the total oxygen consumption for the reaction products with the consumption of the gas-phase oxygen for the products demonstrates the participation of oxygen of the catalyst in the reaction. Our results lead to the conclusion that ammonia oxidation proceeds via alternate reduction and reoxidation of the catalyst surface. When the reaction mixture slightly affects the buried oxygen layers in the catalyst, the rate of the reduction stage equals the rate of the catalytic reaction. At higher reduction, the phase composition can be changed and the oxygen supply from the reaction mixture is not sufficient in restoring the initial activity (Fig. 1, point 2).

4.7. The reaction mechanism

It is shown in our previous work [19] that an increase in the $Mn^{3+}/Mn^{\delta+}$ ratio correlates with the increase in the selectivity toward N₂O that is supported again by the data reported here. The studies on the catalyst reduction under the action of ammonia pulses reveal that the selectivity toward N2 increases but toward N2O decreases with an increase of the reduction degree. Experimental studies including feeding of the reaction mixture in the pulse mode demonstrate that the selectivity toward N₂O is much higher over the oxidized catalyst than over the catalyst treated with ammonia. The selectivity into N₂O decreases with an increase of number of pulses over oxidized catalyst and increases over the reduced catalyst. The latter phenomenon indicates changes in the oxidation state: The oxidized sample is reduced under the action of the reaction mixture and the reduced sample is reoxidized.

The results obtained allow the reaction mechanism to be presented as follows: ammonia is adsorbed on active sites of the catalyst, which are manganese ions in different oxidation states, i.e., Mn^{3+} (Mn^{4+}) and $Mn^{\delta+}$. While ammonia is adsorbed, the manganese sites are partially reduced to form surface complexes [$Mn^{\delta+}-N$], if ammonia is adsorbed by Mn^{3+} and [$Mn^{2+}-N$], if ammonia is adsorbed by $Mn^{\delta+}$. That the complexes are formed is supported by IRS and XPS studies; [NH_2] and [NH] adsorbed complexes are identified in the spectra, which are then transformed into [N] species under the action of oxygen.

Interaction of the surface intermediates at a comparatively high oxidation state [Mn^{$\delta+-N$}] leads to formation of N₂O. N₂ is formed through the interaction of more reduced intermediates. In addition, TPSR data show that elevation of temperatures up to 200–250 °C gives rise to decomposition of the surface complexes to release NO. It seems like NO is formed, similar to N₂O, on the oxidized manganese sites.

The reaction pathways corresponding to the suggested mechanism are as follows:

$$\mathbf{NO} + [\mathbf{Mn}^{2+}] + (\mathbf{H}_2\mathbf{O}), \quad (I)$$

$$NH_{3}^{(M_{1})} = \frac{1}{M_{1}\delta^{\lambda_{+}}} N_{2}O + [Mn^{\delta^{+}}] + (H_{2}O), \quad (II)$$

$$M_{n^{2+}}N] \xrightarrow{[Mn^{2+}N]} N_2 + [Mn^{2+}] + (H_2O),$$
 (III)

$$[\mathbf{Mn}^{2^+}] \underbrace{\{\mathbf{0}_s, \mathbf{0}_2\}}_{[\mathbf{Mn}^{\delta_+}]} [\mathbf{Mn}^{\delta_+}] \underbrace{\{\mathbf{0}_s, \mathbf{0}_2\}}_{[\mathbf{Mn}^{3^+}]} [\mathbf{Mn}^{3^+}].$$
(IV)

Numerical modeling of TPSR was carried out in terms of the suggested mechanism. The process of evolution of the reaction products in the course of heating was described by a set of differential equations:

$$U\frac{\partial\theta_k}{\partial T} = -\sum_{i=1}^{N_k} k_i e^{-E_i/(RT)} \theta_k f_i(\bar{\theta}),$$
$$U\frac{\partial C_{\rm m}}{\partial T} = \tau b \sum_{j=1}^{N_m} k_j e^{-E_j/(RT)} \theta_j f_j(\bar{\theta}),$$

where θ_k (k = 1, 2) is the concentration of adsorbed [Mn^{x+} -N] complexes, C_m is the concentration of the reaction products (NO, N₂, N₂O), $k_{i(j)}$ are constants of stage rates, $E_{i(j)}$ are activation energies, τ is contact time, b is the ratio of the molecule concentrations in the reaction volume and on the catalyst surface, and $f(\bar{\theta})$ is the coverage function of power type.

The results obtained are illustrated in Fig. 17. One can see that the peak of N_2 evolution and main peaks of N_2O and NO evolution are described well enough. The calculated activation energies are 35.8 kcal/mol for the stage of N_2 formation (III), and 14.3 kcal/mol for the stages of N_2O and NO formation. It is important to note that the rates of N_2O and N_2 formation depend rather strongly on the coverage, namely, of the fourth order with respect to the intermediate species. That is most likely to result from strong bonds between the adsorbed complexes and the manganese sites. The



Fig. 17. Comparative experimental and calculated TPSR spectra of the Mn–Bi–O/ α -Al₂O₃ catalyst calcined at 550 °C.

low rate of the nitrogen atoms diffusion over the catalyst surface causes a sharp decrease in the probability of the surface species interactions as the coverage decreases. It is noteworthy that exactly the different dependencies of the stage rates of N_2O and N_2 formation on coverage result in the shift of the NO peak (the dependence of first order is in the case of NO) in comparison to N_2O peak position in the TPSR spectra.

The presence of less pronounced peaks of N₂O (peaks at $T_p = 176$ and 496 °C) and NO (peak at $T_p = 544$ °C) evolution may be explained as follows.

The surface coverage by intermediates is no more than 0.1; therefore, the proportion of intermediates occupying neighboring sites is not high. If so, the occurrence of three peaks of nitrous oxide evolution may be determined from several reasons. First, the intermediates [N] can interact both with the same intermediates localized on the neighboring sites and with the labile [N] species diffusing over the surface. The labile [N] species can be formed on the sites of all types as the temperature increases. At the same time, upon temperature elevation the [Mn^{$\delta+-N$}] intermediates can be reoxidized by oxygen supplied from the subsurface layers to produce the [Mn³⁺–N] intermediate. Due to different Mn–O bond energies, the interaction of $[Mn^{\delta+}-N]$ and $[Mn^{3+}-N]$ intermediates may also be responsible for appearance of the extra N₂O peak in the TPSR spectrum. The presence of the extra NO peak may be attributed to the formation of the $[Mn^{3+}-N]$ intermediate.

The second peak of nitrogen evolution ($T_p = 601 \,^{\circ}$ C) is observed in the high-temperature range over Mn–Bi–O/ α -Al₂O₃ catalysts calcined at 400 and 550 $^{\circ}$ C but not over the catalyst calcined at 750 $^{\circ}$ C. The peak may be assigned to the adsorption of ammonia and the formation of a [N] species adsorbed on bismuth oxide. This assumption agrees with the fact that the catalyst calcined at 750 $^{\circ}$ C does not contain the phase of bismuth oxide; for this reason the high-temperature peak of nitrogen evolution does not exist.

The process of the catalyst reduction by ammonia also can be considered in terms of the suggested scheme.

The first ammonia pulse produces $[Mn^{\delta+}-N]$ due to the presence of weakly bonded and labile oxygen. A part of Mn^{3+} sites are reduced to $Mn^{\delta+}$. Ammonia is adsorbed by the Mn^{δ +} sites to form [Mn²⁺–N] species. [Mn^{δ +}–N] and labile N species interact to form N_2O , while $[Mn^{2+}-$ N] forms N₂. Since $[Mn^{\delta+}-N]$ is formed over the oxidized catalyst in a much larger amount than $[Mn^{2+}-N]$, then N₂O also is formed in a larger amount during the first pulse. More than four oxygen monolayers are removed during reduction by ammonia which makes it reasonable to assume that the reduced Mn²⁺ sites are reoxidized by subsurface oxygen (O_{ss}) as the surface oxygen (O_s) is consumed. The reoxidation degree depends on the strength of oxygen/manganese bonds and on the rate of oxygen diffusion to the surface. The stronger the bonds, the lower the reoxidation rate. As a result, $[Mn^{2+}-N]$ species formed on $Mn^{\delta+}$ increase in number but $[Mn^{\delta+}-N]$ formed on Mn^{3+} decrease. Therefore, the concentration of [Mn²⁺-N] increases with an increase in the number of pulses and, correspondingly, the selectivity to nitrogen increases. This is just what is experimentally observed.

5. Conclusions

The pulse kinetic method and methods of temperatureprogrammed surface reaction, IRS, and XPS were used for characterization of the highly selective supported manganese–bismuth oxide catalyst. The studies revealed that:

- (1) Manganese ions at different oxidation states, viz Mn^{3+} (Mn^{4+}) and $Mn^{\delta+}$, behave as active sites of the catalyst. Formation of the reaction products: N₂O, N₂, and NO, was revealed. The reaction pathways are determined by the energetically nonuniform state of the surface oxygen involved in the manganese oxide. Relatively reduced sites $Mn^{\delta+}$ bear the responsibility for the formation of N₂ but more oxidized Mn^{3+} sites for the formation of N₂O.
- (2) N₂O selectivity correlates with a proportional increase of active sites with low manganese–oxygen bond energy. A relative portion of these active sites is increased with the catalyst calcination temperature.
- (3) Bismuth oxide plays an important role for the following reasons: First, it disperses manganese oxide on the support surface and prevents the manganese oxide particles from aggregation during calcination and the reaction mixture action. Second, it increases the defect extent of the supported active Mn–Bi–O phase, resulting in high mobility of subsurface oxygen. Finally, it increases the thermal stability of the active oxygen.
- (4) Studies of the mechanism of ammonia oxidation showed that:
 - (4.1) Ammonia oxidation proceeds via alternating reduction and reoxidation of the catalyst surface of manganese oxide particles.

- (4.2) NH₃ interacts with weakly bonded oxygen species through hydrogen atom abstraction, giving rise to key intermediate [N] localized on Mn^{2+} and $Mn^{\delta+}$ (2 < δ < 3).
- (4.3) The reaction mechanism is proposed. The main features are as follow: ammonia is adsorbed by manganese ions of different oxidation states Mn^{3+} (Mn^{4+}) and $Mn^{\delta+}$. The surface complexes $[Mn^{\delta+}-N]$ are formed on Mn^{3+} sites, while the $[Mn^{2+}-N]$ species are formed on $Mn^{\delta+}$. The $[Mn^{\delta+}-N]$ species are responsible for N₂O formation and $[Mn^{2+}-N]$ species are intermediates of N₂ formation. Formation of NO, similar to N₂O, is most likely to proceed on oxidized manganese sites.
- (4.4) The reaction kinetic scheme is proposed based on the experimental results. Numerical simulation of TPSR data confirms the reliability of the reaction mechanism. Activation energies were estimated for the stages of formation of the reaction products.

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