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The role of support in formation of the manganese–bismuth oxide catalyst for synthesis of nitrous oxide through oxidation of ammonia with oxygen

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Abstract

BET, XRD, XPS, and TPR by hydrogen were used for investigation of supported Mn–Bi oxide catalysts for ammonia oxidation into nitrous oxide. The catalysts were synthesized by impregnation of γ -, α -Al₂O₃ and SiO₂ with solutions of manganese and bismuth nitrates. The character of phase transformations, surface concentration, and state of the active component were shown to depend on the nature of the support. The sequence stabilization of active constituents of the Mn–Bi–O/ α -Al₂O₃ catalyst and types of the stabilized species were determined. The activity of the Mn–Bi–O supported catalysts calcined at 400 °C was established to equal 95–97% and to be practically independent of the support nature, while the activity decreased with elevation of the calcination temperature. The Mn–Bi–O/ α -Al₂O₃ catalysts exhibited the highest selectivity to N₂O (84.4%) under identical conditions. The correlation between the Mn³⁺/Mn^{δ +} (2 < δ < 3) ratio in the catalyst and the selectivity to N₂O was revealed.

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1. Introduction

The development of methods for the synthesis of nitrous oxide has received much attention in recent years because of its expanding application areas in industry. It is known [1,2] that oxidation of ammonia by oxygen can produce molecular nitrogen, nitrogen oxide, or nitrous oxide. The yield of each of the products depends both on the process conditions and on the nature of the catalyst used.

According to available literature and patent data [3–6], complex manganese dioxide-based catalysts for oxidation of ammonia by oxygen are the most active and selective with respect to N₂O. The binary composition of Mn–Bi–O is of particular interest among these systems. Since the active component is not effectively used in the bulk catalysts, the supported catalysts are most practiced [6].

The aim of the present work was to study the influence of the support nature on formation of the active state of the

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catalyst for oxidation of ammonia with oxygen to provide a high selectivity to nitrous oxide.

2. Experimental and methods

2.1. Catalysts

Mn–Bi–O-supported catalysts were synthesized using double 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.

Catalysts Mn-O/ α -Al₂O₃ and Bi–O/ α -Al₂O₃ were prepared by single incipient wetness impregnation with manganese (II) or bismuth (III) nitrate followed by drying at 80-130 °C.

Catalyst $Bi_2Mn_4O_{10}/\alpha$ - Al_2O_3 was prepared by precipitation on the support from a mixed solution of manganese (II) and bismuth (III) nitrates (taken in the required ratio) under

Table 1 Characterization of supports

| Nature | $S_{\text{specific}} (\text{m}^2/\text{g})$ | $V_{\Sigma} (\text{cm}^3/\text{g})$ | Bulk density (g/cm ³) |
|--|---|-------------------------------------|-----------------------------------|
| α -Al ₂ O ₃ | 10 | 0.40 | 1.09 |
| γ -Al ₂ O ₃ | 200 | 0.95 | 0.62 |
| SiO ₂ | 15 | 1.60 | 0.50 |

the action of ammonia solution at chosen values of pH and temperature. The resulting suspension was filtered out and washed with distilled water until nitrates were not detected in the filtrate. The precipitate was dried at room temperature until air-dry state and then in a drying oven at 110-120 °C.

All the synthesized samples were calcined at 400, 500, 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(NO₃)₃ · 5H₂O, Aldrich index 38,307-4.

Alumina in α - and γ -modifications and silica were used as the supports (see Table 1 for their parameters).

2.2. Methods

Atomic absorption spectroscopy [7] was used to measure the content of the basic components in the samples. XRD studies of the samples were carried out using a diffractometer HZG-4C with CuK_{α} monochromated radiation. High resolution electron microscopic (HREM) images were acquired using a JEM-2010 with lattice resolution 0.14 nm and accelerating potential 200 kV. Electron microdiffraction technique (selected area electron diffraction—SAED) was used for phase identification. Specific surface area was determined using heat desorption of argon [8] at an accuracy of $\pm 10\%$.

X-ray photoelectron spectroscopy (XPS) was applied for characterization of the surface concentrations and chemical states of manganese and bismuth. XP spectra were recorded with a VG ESCALAB HP spectrometer, which was precalibrated with respect to binding energies of Au $4f_{7/2}$ (84.0 eV) and Cu $2p_{3/2}$ (932.6 eV) measured using AlK_{α} radiation $(h\nu = 1486.6 \text{ eV})$. Catalyst samples were mounted on a sample holder using a nickel grid to allow their heating up to 400 °C. The charging effect induced by photoemission was taken into account using the internal reference method. The Al2p and Si2p lines from alumina and silica (the catalyst supports) at $E_{\rm b}({\rm Al}\,2{\rm p}) = 74.3 \,{\rm eV}$ and $E_{\rm b}({\rm Si}\,2{\rm p}) = 103.3 \,{\rm eV}$, respectively [9], were used as references. Accuracy of the charging corrections was also checked by binding energy of C1s line peak. The value of 284.8 ± 0.2 eV obtained after the corrections was typical of adsorbed hydrocarbons often used as internal reference for charge correction. Chemical composition expressed as atomic ratio to the basic element of the support, Al or Si, was calculated on the basis of areas of the corresponding XPS lines (I_i) corrected by atomic sensitivity factors (ASF),

$$n_x/n_{\rm Al,Si} = \frac{I_x/\rm ASF_x}{I_{\rm Al,Si}/\rm ASF_{\rm Al,Si}},$$

where n_x was the element concentration (at%) in the analysis zone. The values of ASF were taken from XPS handbook [10]: Al2p = 0.234; Si2p = 0.283; C1s = 0.29; O1s = 0.711; Bi4f = 9.14; Mn2p = 2.659. Relative accuracy of the atomic ratios is about 10%, but distribution of the absolute values can be much broader, for example, due to variation of ASF in different literature sources. Both freshly prepared and treated (after testing the catalytic properties) samples depending on the nature of the support and calcination temperature were studied by XPS. Furthermore, the fresh samples were treated in hydrogen at 400 °C and $P(H_2) = 50$ mbar in a preparation chamber of the electron spectrometer for an hour. Subsequent monitoring of the XP spectra was performed without contact of them with the atmosphere.

Temperature-programmed reduction (TPR) with hydrogen was conducted using a forced air circulation gradientless furnace. The heating rate was $10 \,^{\circ}$ C/min from room temperature to 900 $\,^{\circ}$ C. H₂O was frozen out at $-80 \,^{\circ}$ C in the course of the experiments. A thermal conductivity detector was used for measuring the concentration of hydrogen. Catalysts granules were 0.25–0.5 mm in size; the catalyst weighed 100 mg.

Catalytic properties of the samples were tested with respect to ammonia oxidation with oxygen using a plug flow reactor. They were estimated from the data on ammonia conversion and selectivity to N₂O, N₂, and NO. The reaction mixture comprising 8 vol% of NH₃ and 9 vol% of O₂ was passed through the catalyst bed (fraction 0.25–0.50 mm, contact time 0.7 s). The reaction temperature was varied in the range of 330 to 350 °C. A chromatographic technique was used for analyzing the inlet reaction mixture and the reaction products, ECOM-Omega (Austria) being installed for determination of NO and NO₂.

3. Results and discussion

Basic physicochemical properties of catalysts under study are summarized in Table 2. From the data of chemical analysis (Table 2), the contents of supported manganese and bismuth oxides are different but always $Mn/Bi \ge 1$. The surface concentration of the active components decreases depending on the support nature in the series,

$$Mn-Bi-O/\alpha-Al_2O_3 > Mn-Bi-O/SiO_2$$
$$> Mn-Bi-O/\gamma-Al_2O_3,$$

that is mainly accounted for by the specific surface area of the supports used (Table 1). Moreover, the specific surface area of the catalysts also is determined by the support nature. In particular, the specific surface area of catalysts Mn– O/α -Al₂O₃, Bi– O/α -Al₂O₃, Mn–Bi– O/α -Al₂O₃, and Mn– Bi– O/SiO_2 is close to that of the support (Tables 1 and 2). For catalysts Mn–Bi– O/γ -Al₂O₃, the specific surface area is approximately half of that of the support (Tables 1 and 2); this may result from a high concentration of the active com-

Table 2 Physicochemical properties Mn–Bi oxide catalysts

| Catalyst | Calcination temperature (°C), duration (h) | Active component | | | t | S _{specific} | Phase composition | |
|--|--|-----------------------------|---|-----------------|-------------------------------------|-----------------------|---|--|
| | | MnO ₂ (mass%) | Bi ₂ O ₃ (mass%) | Mn/Bi (mass) | $\frac{\sum(Mn + Bi)}{(atom/nm^2)}$ | (m ² /g) | | |
| Mn–Bi–O/ | 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 | |
| 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/ | 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 | |
| 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 | |
| Mn-Bi-O/ | 400, 2 | 15.6 | 9.7 | 1.13 | 58.5 | 17 | MnO ₂ , β -Bi ₂ O ₃ , amorphous phase | |
| SiO ₂ | 550, 2 | | | | | 16 | MnO ₂ , Bi ₂ SiO ₅ , amorphous phase | |
| | 550, 4 | | | | | 15 | MnO ₂ , Bi ₂ SiO ₅ , Mn ₇ SiO ₁₂ , amorphous phase | |
| | 750, 2 | | | | | 13 | Bi ₂ SiO ₅ , Mn ₇ SiO ₁₂ , Bi ₂ Mn ₄ O ₁₀ , amorphous phase | |
| $Mn-O/\alpha-Al_2O_3$ | 400, 2 | 11.3 | | | 78.1 | 10 | β -MnO ₂ , α -Al ₂ O ₃ | |
| $Bi-O/\alpha-Al_2O_3$ | 400, 2 | | 14.5 | | 37.4 | 10 | Bi_2O_3 , α -Al ₂ O ₃ | |
| $\frac{\text{Bi}_2\text{Mn}_4\text{O}_{10}}{\alpha\text{-Al}_2\text{O}_3\text{a}}$ | 750, 2 | 7.0 | 12.2 | | | 9.3 | $Bi_2Mn_4O_{10}$, α -Al ₂ O ₃ | |

^a Sample was prepared by precipitation of active components on the support.

ponent (Table 2), that causes a decrease in the catalyst surface area, or from formation of coarse phases. Elevation of the calcination temperature from 400 to 750 °C gives rise to a minor decrease in the surface area (Table 2).

According to XRD data (Table 2), synthesized Mn–Bi–O catalysts are multiphase. They contain, apart from the support phase, individual oxides of manganese, bismuth, and the products of interaction between the oxides. Fig. 1 shows typical diffraction patterns acquired with samples of Mn–Bi–O catalysts calcined at different temperatures.

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 formation of phases of β -Mn₂O₃, α -Bi₂O₃, and of their interaction product, Bi₂Mn₄O₁₀. The proportion of the latter increases as the temperature is elevated to



Fig. 1. Diffraction patterns of the Mn–Bi–O/ α -Al₂O₃ catalyst calcinated at different temperatures.

750 °C (Table 2), MnO_2 and Bi_2O_3 phases not being detected upon treating at 750 °C.

Approximately the same phase composition is established for catalysts Mn-Bi-O/y-Al₂O₃ calcined at 400 °C (Table 2). The difference is that, first, crystallization of individual (Bi2O3) phases is accelerated due to a higher concentration of the active component and, second, the lattice constant equal to 0.7906 nm is characteristic of the support phase (γ -Al₂O₃), that is, lower than that of the pure oxide [11]. This observation argues the formation of a γ -Al₂O₃-based solid solution. One can suppose based on comparative ion radii of aluminum (0.057 nm), bismuth ($r_{\text{Bi}^{3+}} = 0.120 \text{ nm}$), and manganese ($r_{\text{Mn}^{4+}} = 0.052$, $r_{Mn^{3+}} = 0.070, r_{Mn^{2+}} = 0.091$ nm) that alumina is promoted by manganese cations. Again, elevation of the calcination temperature or a longer calcination gives rise to formation of the following phases: Mn_2O_3 , α -, β -Bi₂O₃, Bi₂Mn₄O₁₀; bismuth aluminate Bi₂Al₄O₉ also being formed (Table 2). The proportion of two latter phases increases with the calcination temperature.

Three phases are detected in catalysts Mn–Bi–O/SiO₂ calcined at 400 °C. These are MnO₂, β -Bi₂O₃, and an amorphous phase. Calcination at an elevated temperature (up to 550 °C) produces bismuth silicate Bi₂SiO₅, while an increase in the time or treatment temperature leads to formation of phases of Mn₇SiO₁₂ and Bi₂Mn₄O₁₀ (Table 2).

XRD data reveal that catalysts $Mn-O/\alpha$ -Al₂O₃ and Bi-O/ α -Al₂O₃ are two-phase systems comprising the phases of MnO₂ (Bi₂O₃) and α -Al₂O₃ (Table 2). A phase mixture (Bi₂Mn₄O₁₀ (JCPDS 27-0048) and α -Al₂O₃) is detected in the Mn–Bi–O/ α -Al₂O₃ sample calcined at 750 °C (Fig. 2).

Thus, the obtained results on the phase composition allow the conclusion that supporting of the active component on α -Al₂O₃ is accompanied by interaction between con-



Fig. 2. Diffraction patterns of the Bi₂Mn₄O₁₀/ α -Al₂O₃ catalyst.

stituents of the active component to produce $Bi_2Mn_4O_{10}$. With γ -Al₂O₃ and SiO₂ used as supports, the interaction is observed not only between constituents of the active component but also between the active component and the support. Correspondingly, $Bi_2Al_4O_9$ or Bi_2SiO_5 and Mn_7SiO_{12} are observed along with $Bi_2Mn_4O_{10}$.

Typical survey XP spectra measured for granulated and ground Mn-Bi-O/a-Al2O3 catalysts calcined at 750 °C are shown in Fig. 3. One can see that both lines of the support-Al2p, Al2s, O1s, OKLL-and those of the supported oxides (both photo and Auger lines) in the spectra. Furthermore, lines from carbon-containing impurities-C1s and CKLLare observed in the spectra, with their intensities being much higher for the ground sample compared to the granulated one. Similar behavior is exhibited by the lines from the support: grinding of the sample increases considerably the line intensities (Fig. 3). This result allows us to suggest that carbon is a most probable impurity in the support, but is not introduced at the stage of supporting the active component. Another conclusion following from these data is a crustlike distribution of the active component through the catalyst granules. Namely, surface location of the active component



Fig. 3. Typical survey X-ray photoelectron spectra of granulated and ground catalyst Mn–Bi–O/ α -Al₂O₃ calcined at 750 °C.

particles will mask XP lines of the support. For these reasons further XRS studies are only focused on the ground samples. This makes it possible, first, to compare quantitative data for the samples supported on different materials and, second, to press the fine powders of the catalysts into a stainless-steel mesh mounted on a sample holder. The pressing provides a good contact between the sample and the holder and, hence, homogeneous heating of the sample during the reduction in H₂ inside the spectrometer.

Table 3 presents quantitative XPS data expressed as atomic ratios of the elements. One can see that the total concentration of the active component $(I_{(Mn+Bi)}/I_{Al})$ is varied depending on the nature of support and, to a lesser extent, on the calcinations temperature. The (Mn + Bi)/Al atomic ratio is higher than 1 for α -Al₂O₃ and equals 0.09–0.16 (i.e., is lower by an order of magnitude) for the γ -Al₂O₃ and the SiO₂ (Table 3). Contrary to the XPS data, weight contents of the active component constituents are similar (~22– 24 mass%) for the α -Al₂O₃- and SiO₂-supported samples, which is lower (ca. two thirds) than that for the γ -Al₂O₃ ones (Table 2). This disagreement can be explained by the smaller surface area of α -Al₂O₃ compared to γ -Al₂O₃. As shown earlier [12] the XPS intensity ratio of dispersed phase

Table 3

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Dependence of the surface chemical composition of Mn-Bi oxide catalysts on the nature of the support
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| Sample | Calcination | I(Al) | I(C)/I(Al) | I(O)/I(Al) | I(Mn)/I(Al) | I(Bi)/I(Al) | I(Mn)/I(Bi) | $\sum I(Mn) + I(Bi)/I(Al)$ |
|---|------------------|-------|------------|------------|-------------|-------------|-------------|----------------------------|
| | temperature (°C) | | | | | | | |
| Mn–Bi–O/ α -Al ₂ O ₃ | 400 | 1.0 | 1.08 | 4.57 | 0.76 | 0.31 | 2.45 | 1.07 |
| | 550 | 1.0 | 1.40 | 5.12 | 0.96 | 0.39 | 2.46 | 1.35 |
| | 750 | 1.0 | 1.70 | 4.04 | 0.51 | 0.20 | 2.55 | 0.71 |
| | 750 (gran.) | 1.0 | 0.55 | 9.22 | 2.97 | 1.43 | 2.08 | 4.40 |
| Mn-Bi-O/γ-Al ₂ O ₃ | 400 | 1.0 | 0.28 | 3.31 | 0.10 | 0.06 | 1.67 | 0.16 |
| | 550 | 1.0 | 0.21 | 3.30 | 0.09 | 0.05 | 1.80 | 0.14 |
| | | I(Si) | I(C)/I(Si) | I(O)/I(Si) | I(Mn)/I(Si) | I(Bi)/I(Si) | I(Mn)/I(Bi) | $\sum I(Mn) + I(Bi)/I(Si)$ |
| Mn-Bi-O/SiO2 | 400 | 1.0 | 0.57 | 2.90 | 0.09 | 0.02 | 3.85 | 0.11 |
| | 550 | 1.0 | 0.42 | 3.31 | 0.12 | 0.03 | 3.51 | 0.15 |
| | 750 | 1.0 | 0.36 | 2.97 | 0.14 | 0.04 | 3.80 | 0.18 |



Fig. 4. XPS spectra of catalyst Mn-Bi-O/a-Al2O3: Bi (a), Mn (b).

to the support, R_d , can be expressed indeed by

$$R_{\rm d} = k \frac{W}{D \times S \times d},$$

where *k* is the proportional constant, *W* is the weight of the dispersed phase per gram of catalyst, *D* is the density of the dispersed phase, and *S* is the surface area of the support per gram of catalyst. Since the surface area of the support is in the denominator of the equation, it is clear that the lower the *S*, the higher the R_d . Therefore, the catalyst supported on α -Al₂O₃ with the lowest surface area will have the highest ratio of XPS intensities of the active component to that of alumina.

It should be also noted that the Mn/Bi intensity ratio varies with the nature of the support. It is 2.45 for the Mn–Bi–O/ α -Al₂O₃, 1.67 for the Mn–Bi–O/ γ -Al₂O₃, and 3.85 for the Mn–Bi–O/SiO₂ samples calcined at 400 °C (Table 3). Elevation of the calcination temperature results in an increase in this ratio for samples supported on α -Al₂O₃ and γ -Al₂O₃. This ratio is not altered for the silica-supported catalysts.

The chemical states of the observed elements are determined by analyzing narrow regions of the XP spectra. For example, Fig. 4 shows Bi4f and Mn2p core level spectra of the freshly prepared Mn–Bi–O/ α -Al₂O₃ samples calcined at various temperatures, which are acquired before (solid curves) and after (dashed curves) reduction inside the spectrometer. The spectra of the spent Mn–Bi–O/ α -Al₂O₃ sample calcined at 550 °C and those from the individual phases of Bi₂O₃ and MnO₂ supported on the α -Al₂O₃ are also shown for comparison. One can see that the Mn–Bi–O/ α -Al₂O₃ catalysts calcined at 400 and 550 °C are characterized by a Bi4f_{7/2} feature at 158.7 eV and a Mn2p_{3/2} feature at 642.2 eV which can be assigned to Bi(III) ions in Bi₂O₃ and Mn(IV) ions in MnO₂, respectively. This assignment is evident from coincidence of these spectra with the corresponding spectra of the individual Bi₂O₃ and MnO₂. Catalytic testing and, especially, reduction in hydrogen modify the shape of the spectra due to the appearance of additional signals at low binding energies. Contrary to the active component, the support constituents give XP spectra (are not shown) similar for all the samples. They are not changed after reduction.

Thorough analysis of the variations of the spectra, or chemical states of bismuth and manganese, is hardly possible without their deconvolution on separate components. For example, deconvolution of the Bi4f7/2 spectrum recorded for the reduced catalysts precalcined at 400 °C (Fig. 5a) reveals the occurrence of two components with $E_b = 157.0$ and 158.7 eV. The binding energies can be assigned to metallic bismuth and bismuth (III), respectively. Deconvolution of the corresponding $Mn2p_{3/2}$ spectra is more convincing due to their broadening and unstructured shape. To tackle this problem the data of other methods and literature data should be taken into account. First of all, XRD data should be noted which demonstrate that the treatment of the Mn-Bi–O/ α -Al₂O₃ catalyst calcined at 400 °C with ammonia results in reduction of the active components to form phases of β -Mn₃O₄, MnO, and bismuth metal. Another argument based on TPR data (see below) is that the original MnO₂ phase is transformed into Mn₂O₃ and Mn₃O₄ upon reduction with hydrogen at the temperature as low as 348 °C, whereas heating up to 400 °C (temperature of the reduction inside the spectrometer, see Experimental and methods)



Fig. 5. XPS spectra of catalyst Mn–Bi– O/α -Al₂O₃ calcined and reduced at 400 °C and the spectra deconvolution: Bi (a), Mn (b).

Table 4 XPS binding energies (eV) of Mn2p_{3/2} line

| Phase | Binding energy | Reference |
|--------------------------------|----------------|-----------|
| Mn | 639.2 | [13] |
| Mn | 639.0 | [14] |
| MnO | 641.0 | [13] |
| MnO | 640.7 | [16] |
| MnO | 640.6 | [17] |
| MnO | 640.9 | [19] |
| Mn ₃ O ₄ | 641.5 | [13] |
| Mn ₃ O ₄ | 641.4 | [18] |
| Mn ₃ O ₄ | 641.4 | [16] |
| Mn ₃ O ₄ | 641.4 | [17] |
| Mn ₂ O ₃ | 641.9 | [13] |
| Mn_2O_3 | 641.8 | [15] |
| Mn_2O_3 | 641.9 | [16] |
| Mn_2O_3 | 641.9 | [17] |
| Mn_2O_3 | 641.9 | [18] |
| Mn_2O_3 | 641.8 | [19] |
| MnO ₂ | 642.6 | [13] |
| MnO ₂ | 642.4 | [15] |
| MnO ₂ | 642.2 | [17] |
| MnO_2 | 642.6 | [18] |
| MnO ₂ | 642.5 | [19] |

results in the transformation into MnO. These observations and literature data for Mn2p_{3/2} binding energies in various manganese oxides (Table 4) are used for deconvolution of the Mn2p_{3/2} spectra, see Fig. 5b for an example. One can see at least four components with $E_b = 639.6$, 641.4, 641.9, and 644.2 eV. According to literature data (Table 4) features at 641.4 and 641.9 eV can be assigned to Mn₃O₄ and Mn₂O₃, respectively. This is more complex situation with the lowest and highest binding energies of the components. The lowest binding energy is close to the corresponding value of manganese metal, the formation of which is thermodynamically unfavored under the conditions used. Therefore, we assign this line to the phase of MnO to explain the lowering of E_b by the differential charging. This effect is often observed in the case of inhomogeneous samples containing phases with different conductivities [20,21]. The existence of bismuth metal makes appearance of this effect quite possible in our reduced samples. This explanation is also confirmed by some asymmetry with the low binding energy side of both Al2p and C1s spectra-the lines used as the internal reference for the charging correction. Assignment of the $Mn2p_{3/2}$ features at 644.2 can be made if we cite the paper of DiCastro and Polzonetti [13] who identify this line as a shake-up satellite from MnO. Thus, we can conclude that the reduction of Mn–Bi–O/ α -Al₂O₃ with hydrogen results in the formation of the MnO, Mn₃O₄, and Mn₂O₃ phases.

Principally different behavior of the active component is observed in catalysts Mn–Bi–O/ γ -Al₂O₃ and Mn–Bi– O/SiO₂. The related Bi4f and Mn2p spectra are shown in Figs. 6 and 7. Neither catalytic testing nor reduction in hydrogen are seen to cause a considerable variation in the spectra. All Bi4f_{7/2} spectra are characterized by the feature at ~ 158.7 eV that indicates the presence of bismuth (III). Minor variation of the spectra can be accounted for by incorporation of Bi(III) ions into different surface compounds and their transformations during the treatment.

Reduction of Mn–Bi– O/γ -Al₂O₃ with hydrogen results in the appearance of another line at lower E_b , which is precisely determined from the differential spectrum as equal to 640 eV typical of MnO (Table 4). The fact that this value is close to literature data for MnO oxide suggests the absence of the differential charging effect in this case. Formation of



Fig. 6. XPS spectra of catalyst Mn-Bi-O/γ-Al₂O₃: Bi (a), Mn (b).



Fig. 7. XPS spectra of catalyst Mn-Bi-O/SiO₂: Bi (a), Mn (b).

no bismuth metal and observation of no asymmetry of the Al2p lines also are in accordance with this fact.

It should be noted that thermal treatment of Mn–Bi– O/SiO₂ at 750 °C changes the recorded spectra (Fig. 7) to make binding energies somewhat higher for both lines of the supported oxides. Thus, surface compounds are more stable when supported on γ -Al₂O₃ and SiO₂ than on α -Al₂O₃. Similar to Bi4f_{7/2}, only small variations are observed in the Mn2p_{3/2} spectra testifying to a higher stability of the Mn–Bi surface compounds on γ -Al₂O₃ and on SiO₂ compared with α -Al₂O₃-supported samples.

Thus, the obtained XPS data indicate that there is no interaction between the active component and the support in the case of α -Al₂O₃. As a consequence, the active component is readily reduced under the action of not only hydrogen but also the reaction mixture.

Temperature-programmed reduction with hydrogen was used for establishing the sequence of reduction of active



Fig. 8. TPR spectra recorded for catalyst Mn–Bi–O/ α -Al₂O₃ calcined at 400 °C (1), 550 °C (2), 750 °C (3).

components in the Mn–Bi–O/ α -Al₂O₃ catalyst depending on the calcination temperature. The recorded TPR spectra (Fig. 8) are complex in shape; elevation of the calcination temperature is seen to cause intensity variations of the corresponding peaks, which are shifted to the range of higher temperatures. If the XRD data is taken into account indicating no interaction between the active component and the support, then the observed surface species can be thought to be oxide modifications of the corresponding components. Therefore, the next stage was to reduce α -Al₂O₃-supported oxides with hydrogen. Hydrogen TPR spectra are shown in Fig. 9 for the model systems under study. $Mn-O/\alpha$ - Al_2O_3 calcined at 400 °C is reduced in two stages that is seen from the presence of two peaks (maxima at 313 and 403 °C, Fig. 9a) in the curve; a small peak at the temperature region of 200–220 °C can relate to reduction of the surface [22]. The results obtained agree with the data reported elsewhere [23,24] which demonstrate that MnO_2 and Mn_2O_3 are reduced according to the following scheme:



Phase Mn₃O₄ is detected at 320 °C and phase MnO at 400 °C [23] that is in good agreement with the results obtained. However, bear in mind that MnO₂ and Mn₂O₃ may be reduced at different temperatures because reducibility of the oxides depends equally on the modification (γ -, β -, α -), particle size, and nature of the precursor salt. It is seen elsewhere [22] that peaks at 350 and 515 °C are characteristic of the reduction of β -MnO₂, peaks at 320 and 400 °C of the reduction of γ -MnO₂ + α -Mn₂O₃.

The experimental ratio $H_2/Mn = 0.92$ is close to the calculated $H_2/Mn = 1$; hence, MnO_2 is reduced into MnO. Since $H_2/Mn = 0.59$ (against calculated 0.67) for the first and second peaks, the first stage is reduction of MnO_2 into



Fig. 9. TPR spectra of Mn–O/ α -Al₂O₃ calcined at 400 °C (a), Mn–O/ α -Al₂O₃ calcined at 750 °C (b), Bi–O/ α -Al₂O₃ (c), and Bi₂Mn₄O₁₀/ α -Al₂O₃ (d).

 Mn_3O_4 . $H_2/Mn = 0.33$ for the third peak equal to the calculated ratio (0.33) that argues for reduction of Mn_3O_4 into MnO during the third stage.

The reduction profile does not change considerably upon thermal treatment of Mn–O/ α -Al₂O₃ at 550 °C but does upon treatment at 750 °C (Fig. 9b): there are two not very pronounced peaks with maxima at 172 and 274 °C and peaks at 389 and 447 °C. The correct deconvolution of the spectrum is hardly possible because of very broadened peaks. The results obtained may be accounted for by the fact that Mn₂O₃ is formed at the said temperature as differently sized particles that are reduced at different temperatures. For example, Mn₃O₄ with S_{sp} = 8 m²/g is shown [25] to be reduced at a lower temperature that Mn₃O₄ with S_{sp} = 1 m²/g.

Reduction of Bi_2O_3/α -Al₂O₃ is a one-stage process characterized by a single peak with a maximum at 432 °C (Fig. 9c). The ratio H₂/Bi = 1.35 is close to the calculated ratio (1.5) that indicates reduction of Bi_2O_3 into bismuth metal.

Reduction of Bi₂Mn₄O₁₀/ α -Al₂O₃ is a one-stage process with the maximum at 460 °C (Fig. 9d). The peaks with maxima at \approx 300 and 360 °C may relate to the two-stage reduction of excess Mn₂O₃ which have not reacted with Bi₂O₃ and have been formed at the said treatment temperature (Table 2). The calculated data argue in favor of this assumption: Among the components introduced into the catalyst, $2.62 \times$ 10^{-4} mol/g_{cat} of Bi₂O₃ reacts with 8.13 × 10^{-4} mol/g_{cat} of MnO_2 to form $2.62 \times 10^{-4} \text{ mol/g}_{cat}$ of $Bi_2Mn_4O_{10}$, the rest being $6.9 \times 10^{-4} \text{ mol/g}_{cat}$ of MnO_2 or $6.3 \times 10^{-4} \text{ mol/g}_{cat}$ of Mn₂O₃. The calculated amount of hydrogen consumed for reduction of 1 mol of Bi₂Mn₄O₁₀ into Bi and MnO is 6 mol; therefore reduction of $Bi_2Mn_4O_{10}$ and Mn_2O_3 in the catalyst needs $2.2 \times 10^{-3} \text{ mol/g}_{cat}$ of H₂ that is close to the experimental amount equal to $2.5 \times 10^{-3} \text{ mol/g}_{cat}$ of H₂. Hence, the case under consideration is reduction of Bi₂Mn₄O₁₀ into MnO and bismuth metal, and Mn₂O₃ into MnO.

The TPR spectra acquired with the Mn–Bi–O/ α -Al₂O₃ catalyst calcined at 400, 550, and 750 °C are deconvoluted based on above speculations (Fig. 10). It is seen that all the spectra can be described using sets of two or three peaks related to the stabilized species of the active components at the surface support.

Comparison of the results obtained with Mn–Bi–O/ α -Al₂O₃ calcined at 400 °C and the available literature data leads to the suggestion that there occurs reduction of manganese oxides and, probably, Bi₂O₃ (the latter is not detected by XRD). Since Mn₃O₄ and Bi₂O₃ are reduced at close temperatures (402 and 432 °C, respectively), it is hardly possible to distinguish them correctly. The spectrum is decomposed into two peaks (Fig. 10a) with maxima at 348 and 406 °C. The H₂/Mn ratio is 0.69 for the first peak; it is practically coinciding with the calculated value (0.67) corresponding to reduction of MnO₂ into Mn₃O₄. The calculated total amount of hydrogen to be used for reduction of Mn₃O₄ and Bi₂O₃ into MnO and Bi⁰, respectively, equals 1.07 × 10⁻³ mol Fig. 10. TPR spectra of catalyst Mn–Bi–O/ α -Al₂O₃ calcined at 400 °C (a), 550 °C (b), 750 °C (c) and the spectra deconvolution.

 H_2/g_{cat} that is close to the experimental result equal to $1.13 \times 10^{-3} \text{ mol/g}_{cat}$ (Fig. 10a). Therefore, the second stage is the reduction of Mn_3O_4 and Bi_2O_3 into MnO and Bi^0 , respectively. Note that the first peak is at a temperature of 348 °C, that is, higher than the temperature observed with $Mn-O/\alpha$ -Al₂O₃ (313 °C).

The spectrum of Mn–Bi–O/ α -Al₂O₃ calcined at 550 °C comprises three peaks with maxima at 348, 411, and 434 °C (Fig. 10b) which can be assigned to reduction of the MnO₂+Mn₂O₃ mixture into Mn₃O₄ (I peak), Mn₃O₄ and Bi₂O₃ into MnO and Bi, respectively (II peak), and Bi₂Mn₄O₁₀ into MnO and Bi (III peak). Validity of the assignment is



10

0

Mn-Bi-O/a-Al_O_-400°C

(a)

2.17E-3 mol H,/g cat

1.04E-3 mol H₂/g cat

1.13E-3 mol H,/g cat

Original

Regression peak1 - 348°C

peak2 - 406°C

supported by the comparable calculated and experimental amounts of hydrogen used for the reduction.

One can see from the data in Fig. 10b that reduction of $Bi_2Mn_4O_{10}$ (peak III) needs 4.66×10^{-4} mol H_2/g_{cat} to produce 7.65×10^{-5} mol $Bi_2Mn_4O_{10}/g_{cat}$ that means consumption of 7.65×10^{-5} mol Bi₂O₃/g_{cat} and $3.06 \times$ 10^{-4} mol MnO₂/g_{cat}. When it is considered that the initial catalyst comprises MnO2 and Bi2O3 in the amounts of 1.5×10^{-4} and 1.9×10^{-4} mol/g_{cat}, respectively, then the individual oxides remain in the amounts of 1.14×10^{-4} mol Bi_2O_3/g_{cat} and 1.19×10^{-3} mol MnO₂/ g_{cat} after formation of Bi₂Mn₄O₁₀. At stage II, reduction of 1.14×10^{-4} mol Bi_2O_3/g_{cat} and 3.98×10^{-4} mol Mn_3O_4/g_{cat} needs $3.40 \times$ 10^{-4} and 3.98×10^{-4} mol H₂/g_{cat}, respectively, i.e., in total 7.38×10^{-4} mol H₂/g_{cat} that practically coincides with the experimental data (7.44 \times 10⁻⁴ mol H₂/g_{cat}, see Fig. 10b). It is seen in Fig. 10b that reduction of the $MnO_2 + Mn_2O_3$ phase mixture takes 6.69×10^{-4} mol H₂/g_{cat} (peak I). With the known content of the rest amount of manganese oxide in the catalyst and the known amount of hydrogen consumed for the reduction, one can establish the ratio of MnO₂ to Mn_2O_3 . In accordance with the calculation, the approximate composition of the catalyst is determined as produced at this calcination temperature; it consists of 8.2 wt% of MnO₂, 2.0 wt% of Mn₂O₃, 5.3 wt% of Bi₂O₃, 6.1 wt% of $Bi_2Mn_4O_{10}$.

The spectrum of Mn–Bi–O/ α -Al₂O₃ calcined at 750 °C is decomposed into two peaks with maxima at 425 and 468 °C (Fig. 10c) because the peaks related to reduction of manganese oxides calcined at 750 °C are so broadened as to be hardly distinguished (see Fig. 9b). Therefore, one can suppose that the first peak in the spectrum under consideration relates to reduction of a mixture of oxides (MnO2 and Mn₂O₃ into MnO and Bi₂O₃ into Bi⁰) and the second peak to reduction of Bi₂Mn₄O₁₀. The phase composition in the initial catalyst is determined in the same way as that in the catalyst calcined at 550 °C; viz. the amount of hydrogen used for reduction of Bi2Mn4O10 is used for calculation of the amount of this phase $(1.23 \times 10^{-4} \text{ mol/g}_{cat})$. The amount of oxides taken for formation of this compound is subtracted from the amount of oxides in the catalyst. Reduction of the rest of manganese and bismuth oxides consumes 9.06×10^{-4} mol H_2/g_{cat} (peak I), 2.01×10^{-4} mol H_2/g_{cat} of which is consumed for reduction of 6.7×10^{-5} mol Bi_2O_3/g_{cat} . The rest of hydrogen $(7.05 \times 10^{-4} \text{ mol/g_{cat}})$ is used for reduction of MnO2 and Mn2O3 into MnO. The calculations give the following composition of the catalyst calcined at 750 °C: 2.6 wt% of MnO₂, 6.3 wt% of Mn₂O₃, 3.1 wt% of Bi₂O₃, 9.8 wt% of Bi₂Mn₄O₁₀.

Comparison of the results obtained allows the conclusion that manganese oxide is easier reduced in the absence than in the presence of bismuth oxide. Hence, manganese is in a more oxidized state in the presence of bismuth oxide. As the temperature of treatment of Mn–Bi–O/ α -Al₂O₃ increases, the reduction temperature also increases, for example, for reduction Mn₃O₄ into MnO it is 406 \rightarrow 411 \rightarrow 425 °C,

Table 5 Catalytic properties of Mn–Bi oxide catalysts in ammonia oxidation at 350 °C

| Sample | T_{calc} (°C), duration (h) | X _{NH3} (%) | S _{N2O} (%) | S _{N2} (%) | S _{NO} (%) | | | | |
|---|---|-------------------------|-------------------------|------------------------|------------------------|--|--|--|--|
| Mn–Bi–O/α-Al ₂ O ₃ | 400, 2 h | 96.5 | 79.4 | 19.8 | 0.8 | | | | |
| Mn-Bi-O/ γ -Al ₂ O ₃ | 400, 2 h | 97.0 | 54.0 | 45.9 | 0.1 | | | | |
| Mn-Bi-O/SiO2 | 400, 2 h | 95.3 | 72.1 | 27.8 | 0.1 | | | | |
| Mn-O/ α -Al ₂ O ₃ | 400, 2 h | 99.0 | 75.0 | 24.4 | 0.6 | | | | |
| $Bi-O/\alpha$ - Al_2O_3 | 400, 2 h | ~ 0 | ~ 0 | ~ 0 | ~ 0 | | | | |
| $Bi_2Mn_4O_{10}/\alpha$ - Al_2O_3 | 750, 2 h | 43.5 | 63.6 | 31.9 | 4.5 | | | | |

probably due to a lower dispersion of the active component (accordingly, the surface area also decreases, see Table 2).

Variations in the activity and selectivity of the catalysts under consideration for ammonia oxidation are shown in Table 5. The main reaction products are nitrous oxide, nitrogen, and nitrogen oxide. It is seen in Table 5 that the conversion of ammonia is 95.3–99.0% at 350 °C irrespective of the nature of the support, except samples of Bi₂O₃/ α -Al₂O₃ and Bi₂Mn₄O₁₀/ α -Al₂O₃ (X_{NH3} for them is 0 and 43.5, respectively).

The most selective among the catalysts calcined at 400 °C is Mn–Bi–O/ α -Al₂O₃ and the least selective Mn–Bi–O/ γ -Al₂O₃. In view of the fact that these samples are not considerably different in phase composition (Table 2), the observed differences may be accounted for by the following factors: first, the active component concentrations of the surface of these supports differ by more than an order of magnitude (Tables 2 and 3). For Mn–Bi–O/ γ -Al₂O₃ the surface concentration is 5.8 atoms/nm², which is insufficient for formation of the monolayer and may result in lowering the selectivity to N₂O. Second, XPS studies reveal different surface species of the active components.

Most of the catalysts under consideration are close in the selectivity for nitrogen oxide except $Bi_2Mn_4O_{10}/\alpha$ - Al_2O_3 (almost 4-fold higher, see Table 5). The catalyst Bi_2O_3/α - Al_2O_3 is inactive to this reaction.

At a higher temperature or longer calcination of the samples, the ammonia conversion decreases but the factor differs (Fig. 11a). Among the catalysts calcined at 750°C the highest activity (84.1%) is characteristic of Mn-Bi-O/ γ -Al₂O₃, and the lowest activity (8.8%) of Mn–Bi–O/SiO₂ (Fig. 11a). As the calcination temperature increases, the selectivity to N₂O increases over Mn–Bi–O/ α -Al₂O₃, goes through a maximum over Mn–Bi–O/ γ -Al₂O₃, and decreases over Mn-Bi-O/SiO₂ (Fig. 11b). However, the highest selectivity by absolute value is reached with Mn–Bi–O/ α -Al₂O₃ under otherwise identical conditions. Probably, the selectivities also vary due to phase transformations (Table 2) including, among others, formation of compounds of Bi₂Mn₄O₁₀, Bi₂Al₄O₉, Bi₂SiO₅, and Mn₇SiO₁₂, as well as due to changes in the active component states on the catalyst surface (Table 3, Figs. 4-7) depending on the support nature and calcination temperature of the catalyst.



Fig. 11. Influence of temperature and time of calcination on activity (a) and selectivity to N₂O (b) of Mn–Bi–O/ α -Al₂O₃, Mn–Bi–O/ γ -Al₂O₃, Mn–Bi–O/SiO₂ catalysts.

Therefore, Mn–Bi–O/ α -Al₂O₃ is the most effective among the catalysts under study. Comparative activities and selectivities of Mn–O/ α -Al₂O₃, Bi–O/ α -Al₂O₃, and Mn– Bi–O/ α -Al₂O₃ show (Table 5) that manganese oxides play a key role in the activity and selectivity of manganese–bismuth oxide catalysts.

The presence of the bismuth oxide component in the catalysts is necessary because it prevents manganese oxide particles from aggregation. This is supported by EM studies of Mn–O/ α -Al₂O₃ and Mn–Bi–O/ α -Al₂O₃ samples calcined at 400 and 550 °C (Figs. 12–14).

In the Mn–O/ α -Al₂O₃ catalyst calcined at 400 °C, threedimensional MnO₂ particles of 10 to 30 nm in size are seen (Fig. 12) as arranged on the surface of α -Al₂O₃ particles (50–100 nm). In the Mn–Bi–O/ α -Al₂O₃ catalyst calcined at 400 °C (Figs. 13 and 14), 20–50 nm particles of Bi₂O₃ and differently crystallized Bi₂Mn₄O₁₀ particles also are observed along with MnO₂ particles of ca. 10 nm in size (smaller than the particles in the Mn–O/ α -Al₂O₃ catalyst). EM images show the indefinitely shaped particles of wellcrystallized Bi₂Mn₄O₁₀ (10 to 100 nm in size). The particles are not bonded to the support surface. In addition, there are particles shaped as two-dimensional islands of 20–100 nm in size on the support surface; they replicate the shape of the α -Al₂O₃ particles and shield a part of the surface (Fig. 13). The finest of these particles are not thicker than 3–5 nm. These



Fig. 12. Catalyst Mn–O/ α -Al₂O₃. Microcrystals of MnO₂ on the surface of α -Al₂O₃.



Fig. 13. Catalyst Mn–Bi–O/ α -Al₂O₃ (400 °C). 2D particles of bismuth–manganese oxide on the surface of α -Al₂O₃.



Fig. 14. Catalyst Mn–Bi–O/ α -Al₂O₃ (400 °C). A microcrystal of MnO₂ (A) and a particle of bismuth–manganese oxide in the form of structurally disordered layer attached to the surface of α -Al₂O₃ (B).

fragments are combinations of bismuth and manganese oxides. EM data demonstrate that the finest islands are amorphous but they undergo crystallization, as the thickness increases, to produce the phase of $Bi_2Mn_4O_{10}$. An increase in



Fig. 15. Ratio of oxidized to reduced manganese species (a) in catalyst Mn–Bi–O/ α -Al₂O₃ and selectivity to N₂O (b) as a function of calcination temperature.

the time of calcination and temperature to 550 °C results in accumulation of the phase and separation from the support surface.

On the other hand, if there is the bismuth oxide in the Mn–Bi–O/ α -Al₂O₃ catalyst calcined at 400 °C, the temperature of the catalyst reduction by hydrogen increases, as it is supported by TPR data. For example, the temperatures of reduction of MnO₂ into Mn₃O₄ under the action of hydrogen are 348 and 313 °C in the Mn–Bi–O/ α -Al₂O₃ and Mn–O/ α -Al₂O₃ catalysts, respectively, calcined at 400 °C (Figs. 9a and 10a).

The data obtained suggest that the selectivity to N₂O in the reaction of ammonia oxidation over Mn–Bi–O/ α -Al₂O₃ varies mainly due to the redox properties of manganese oxide. In order to support this suggestion, the ratio of the oxidized manganese species to the reduced ones for all calcination temperatures is determined by deconvolution of XPS spectra of the reduced samples and the sample of Mn– Bi–O/ α -Al₂O₃–550 °C treated with the reaction mixture. Fig. 15a show variations in these ratios for the Mn–Bi–O/ α -Al₂O₃ catalyst as a function of calcination temperature. One can see that Mn³⁺/Mn^{δ +} (2 < δ < 3), Mn³⁺/Mn²⁺, and Mn³⁺/ \sum (Mn^{δ +} + Mn²⁺) ratios increase with calcination temperature. Therefore, elevation of the calcination temperature makes the degree of the catalyst reduction decreased after treatment with hydrogen, probably due to formation of the phase of $Bi_2Mn_4O_{10}$ (Table 2). However, the observed dependencies differ in nature (Fig. 15a). Figures 15a and 15b show that the selectivity of Mn–Bi–O/ α -Al₂O₃ to N₂O varies along with changes in the Mn³⁺/Mn^{δ +} ratio (both in the samples reduced with hydrogen and in the ones treated with the reaction mixture) as the temperature of catalyst calcination increases. It can be therefore assumed that oxidation of ammonia proceeds through the stage of activation of Adsorbed ammonia that is accompanied by reduction of Mn⁴⁺ (Mn³⁺) into Mn²⁺ followed by its reoxidation with oxygen. Hence, nitrous oxide can be supposed to form over oxidized manganese sites Mn⁴⁺(Mn³⁺) and nitrogen over Mn^{δ +} sites.

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