# The Mechanism of Low-Temperature Ammonia Oxidation on Metal Oxides According to the Data of Spectrokinetic Measurements

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**Abstract**—Low temperature ammonia oxidation on MoO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, and ZnO is studied by the spectrokinetic method. It is shown that the following adsorbed species are intermediates in this reaction: NH<sub>3</sub> and N<sub>2</sub>O on Fe<sub>2</sub>O<sub>3</sub> and ZnO; NH<sub>3</sub>, N<sub>2</sub>O, and NO on Cr<sub>2</sub>O<sub>3</sub>. All of the detected intermediates are used to construct the mechanism of the process. In the framework of the proposed mechanism, stationary and nonstationary spectral and kinetic data are quantitatively processed. The dependence of the rate constants of the same steps on different oxides on their physicochemical properties is discussed.

### **INTRODUCTION**

The selective catalytic low-temperature oxidation of ammonia to nitrogen is one of the main processes that make it possible to decrease the concentration of ammonia in exhaust gases in industry. Note that the selectivity of this process is decreased because of the parallel formation of NO and N<sub>2</sub>O. Therefore, the mechanistic study of ammonia oxidation is of both theoretical and substantial practical interest from the standpoint of increasing catalytic activity and process selectivity in low-temperature oxidation.

Substantial information is currently available on the surface species formed in  $NH_3$  and  $O_2$  adsorption on the catalyst surfaces [1–3] and on the mechanism of this process [4–6].

Specifically, it is known that ammonia adsorbs in the form of  $NH_4^+$  on Brønsted acid sites (I) and in the form of coordinated ammonia  $NH_{3 ads}$  on Lewis acid sites (II).



The presence of coordinated ammonia was found on almost all metal oxide surfaces from which admixtures are removed studied to date [1].

It is also known that [1, 6, 7] oxygen adsorbs on transition metal oxides both in molecular and atomic forms:

$$O_{2 \text{ gas}} \longrightarrow O_{2 \text{ ads}}^{-} \longrightarrow O_{ads}^{-} \longrightarrow O_{ads}^{2-}$$

The ratio between different forms of adsorbed oxygen depends on the nature of the oxides.

Less information is available on the nature of complexes formed under reaction conditions.

Table 1 shows data from the literature on surface species formed in the reaction of ammonia oxidation. Note that information on intermediates was obtained in many studies using spectral measurements before and after the reaction. Therefore, it has not been proven that complexes found in the reaction participate in it. We rated the reliability of such information as low. The reliability of data obtained using measurements under conditions of a catalytic reaction is estimated as medium. When the reaction rate was compared with the rates of transformations of compounds observed *in situ*, the reliability was high. Analysis of data presented in Table 1 shows that highly reliable data are virtually absent.

The specific features of pathways to  $N_2$  and  $N_2O$  are also discussed in the literature. Specifically, the authors of [18–20] assumed that the NH<sub>2</sub> species participate in the formation of nitrogen, whereas HNO participates in the formation of N<sub>2</sub>O. On the other hand, Pery and Siebers [21] argued that N<sub>2</sub>O is formed via the NH species.

We have studied ammonia oxidation on MoO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, and ZnO [14–17] using the spectrokinetic method, which consists in simultaneous measurements of the rates of surface species transformations using *in situ* IR spectroscopy and the rate of product formation (see Table 1). Information on actual intermediates in low-temperature ammonia oxidation is also summarized in Table 1. Based on these data, the multiple-step mechanism of the process was proposed [16–17]. Earlier, the hypothesis was advanced [22] that the reaction mechanism is the same over different catalysts if the adsorbed reactants are the same. Unfortunately, for

Catalyst	Surface complex	Reliability*	Reference
MgO	NH <sub>2</sub>	L	[8]
Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	Si–NH <sub>2</sub> , Fe–NH <sub>2</sub>	L	[9]
V <sub>2</sub> O <sub>5</sub> , V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> , (V <sub>2</sub> O <sub>5</sub> -WO <sub>3</sub> /TiO <sub>2</sub> )	$\rm NH_2, \rm N_2H_4, \rm NH, \rm HNO, \rm NH_4^+$	L	[10]
CuO/TiO <sub>2</sub>	$NH_2, N_2H_4, NH, HNO, N_2^-, N_3^-$	М	[11]
CoO–MgO	$NO_2^-, NO_3^-$	М	[12]
$MnO_x/Al_2O_3$	$\rm NH_3, \rm NH_4^+, \rm NH_2$	L	[13]
MoO <sub>3</sub>	$\mathrm{NH}_4^+$	Н	[14]
ZnO, $Fe_2O_3$	NH <sub>3</sub> , H <sub>2</sub> O	Н	[15, 16]
Cr <sub>2</sub> O <sub>3</sub>	NH <sub>3</sub> , NH <sub>2</sub> , NO	Н	[17]

Table 1. Surface species in ammonia oxidation according to IR spectroscopic data

\* L = low, M = medium, and H = high.

any specific sample, it is not possible to obtain data for all intermediate species observed on different catalysts, but the possibility of unobserved species formation and participation in the reaction cannot be excluded. Indeed, in a stationary multiple-step process, the concentration of the most reactive intermediate species can be below the sensitivity threshold of a spectral method. Therefore, it was interesting to consider the multiplestep mechanism of the process, including the steps of formation and consumption of all adsorbed species identified in the process of ammonia oxidation on the cited catalysts, and compare the model calculations of the process behavior based on the quantitative analysis of this mechanism with experimental data.

#### EXPERIMENTAL

The setup for spectrokinetic measurements consisted of an IR spectrometer (UR-20 modified for hightemperature spectral measurements, Bruker IFS 45), a flow-type heated cell/reactor, and a unit for chromatographic analysis. The cell for registering the transmission spectra was described in [23]. The cell for registering the diffuse-reflectance IR spectra was a quartz disk with a rectangular slot  $(25 \times 8 \times 3 \text{ mm})$ . The open side was covered with a polished window made of zinc sulfide. A heating element, the cell, and the window were clamped up with springs in a special holder. The reaction mixture entered and left through the outlet and inlet on a side wall of the cell. The cell was mounted in the cell compartment of the spectrometer. The outflow gas was analyzed to determine the concentrations of reactants and products of the reaction. The concentrations of reactants and products of the reaction were measured in volume fractions (vol. fr.). The overall flow rate vwas 55 cm<sup>3</sup>/min. The concentration of NH<sub>3</sub> was varied from 0 to 30 vol %, and the concentration of  $O_2$  was varied from 0 to 70 vol %. Experiments were carried out at temperatures ranging from 150 to 350°C in stationary and nonstationary regimes.

The intensities of absorption bands were measured in units of extinction (D) in the transmittance spectra and in Kubelka–Munk units in diffuse-reflectance spectra [24],

$$f(R, R_0) = F(R_0) - F(R) = 2\varepsilon C/s,$$

where  $F(R_0) = (1 - R_0)^2/2R_0$ ;  $F(R) = (1 - R)^2/2R$ ;  $R_0$  and R are the reflectance coefficients (albedo) of the sample at a given frequency before and after molecule adsorption, respectively;  $\varepsilon$  is the extinction coefficient of the vibration; C is the concentration of adsorbed molecules; and s is the scattering ability of a unit volume.

Intermediate species of ammonia oxidation were studied on the  $Cr_2O_3$ ,  $Fe_2O_3$ , and ZnO catalysts (Table 2).

#### RESULTS

The following absorption bands are observed in the IR spectra obtained in the transmittance and diffuse-reflectance regimes under the reaction conditions: 2200 cm<sup>-1</sup> (ZnO and Fe<sub>2</sub>O<sub>3</sub>) and 2080 cm<sup>-1</sup> (Cr<sub>2</sub>O<sub>3</sub>). These bands were assigned to the v(N=N) and v(N–O) vibrations in surface N<sub>2</sub>O<sup> $\delta$ -</sup> and NO<sup> $\delta$ +</sup> compounds, respectively. In addition to these bands, we observed a band at 1560 cm<sup>-1</sup> on Cr<sub>2</sub>O<sub>3</sub> assigned to the  $\delta_{as}$  vibrations in the surface NH<sub>2</sub> complex. Also, a band at 1620 cm<sup>-1</sup> was observed on all catalysts and assigned to the  $\delta_{as}$  vibrations in NH<sub>3</sub> coordinatively bound to the metal cation. In the latter case, the reaction products contained N<sub>2</sub>O and N<sub>2</sub>.

We studied the dependences of intensities of absorption bands at 1620, 2080, and 2200 cm<sup>-1</sup> and the rates of  $N_2$  and  $N_2O$  formation on the concentrations of oxygen and ammonia and on temperature in stationary measurements. Typical results of spectrokinetic mea-

surements are shown in Figs. 1 and 2. It is seen that the rates of product (N<sub>2</sub> and N<sub>2</sub>O) formation on all the catalysts studied grow with an increase in the ammonia concentration in the reaction mixture from 0.20 to 0.25 vol. fr. (Fig. 1a) at a constant concentration of oxygen (0.40 vol. fr.). With a further increase in the concentration of ammonia in the mixture, the rates of product formation stop changing. The rate of N<sub>2</sub>O formation changes in a similar way depending on the concentration of oxygen in the mixture (Fig. 2a). The concentration of ammonium in these experiments was constant and equal to 0.30 vol. fr. On the Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> catalysts, the rate of nitrogen formation passed through a maximum at an oxygen concentration of 0.20-0.25 vol. fr. and steadily increased on ZnO over the whole range of measurements.

The band intensities at 1620 and 2200 cm<sup>-1</sup> (on ZnO and Fe<sub>2</sub>O<sub>3</sub>) and at 2080 cm<sup>-1</sup> (Cr<sub>2</sub>O<sub>3</sub>) decrease with an increase in the concentration of oxygen in the reaction mixture and increase with an increase in the concentration of ammonia (Figs. 1b and 2b).

In the surface ammonia oxidation, the authors of [10, 11] found bands characteristic of adsorbed hydrazine N<sub>2</sub>H<sub>4</sub>. To elucidate the nature of possible intermediates in the low-temperature oxidation of ammonia, we carried out experiments on hydrazine oxidation on  $Cr_2O_3$ , and the results are shown in Fig. 3. It is seen that, during hydrazine oxidation, absorption bands at 2200 and 2080 cm<sup>-1</sup> appear in the spectra. These are analogous to those observed under conditions of ammonia oxidation on the catalysts studied. Our data show that hydrazine N<sub>2</sub>H<sub>4 ads</sub> can be the precursor of compounds characterized by bands at 2200 and 2080 cm<sup>-1</sup>.

In nonstationary measurements, we studied the consumption of surface species absorbing at 2080 and 2200 cm<sup>-1</sup> (Fig. 4). The spectrometer was set to the desired frequency and at the moment t = 0, ammonia was excluded from the flow of the reaction mixture. As a result of this experiment, we obtained the dependence of the surface species concentration on time. Experiments carried out at different temperatures make it possible to determine the dependence of the rate of surface species transformation on temperature and the activation energy of this process. The resulting values of the activation energies are listed in Table 3.

It was shown using quantitative spectrokinetic measurements that the surface compound with a band at 2200 cm<sup>-1</sup> is an intermediate product in the reaction of



**Fig. 1.** Dependences of the concentrations of products ( $C_{\rm pr}$ ) and surface species on the concentration of ammonium in the reaction mixture at  $C_{\rm O_2} = 0.40$  vol. fr.,  $T = 240^{\circ}$ C (Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>) and 340°C (ZnO): (a) Experimental values of the concentrations (*1*–3) N<sub>2</sub> and (4–6) N<sub>2</sub>O for (*1*, 4) ZnO, (2, 5) Fe<sub>2</sub>O<sub>3</sub>, and (3, 6) Cr<sub>2</sub>O<sub>3</sub>; (b) (*1*) experimental values of the intensity of the absorption band at 2200 cm<sup>-1</sup>  $D_{2200}$  and (2) the calculated values of N<sub>2</sub>O<sub>ads</sub> coverage on the Fe<sub>2</sub>O<sub>3</sub> surface ( $\Theta_{\rm N_2O}$ ).

ammonia oxidation on ZnO and Fe<sub>2</sub>O<sub>3</sub> [15, 16], and the surface complexes with bands at 2080 and 1620 cm<sup>-1</sup> are intermediates in the reaction on Cr<sub>2</sub>O<sub>3</sub> [17]. Taking into account that surface complexes with bands at 2200 and 2080 cm<sup>-1</sup> are formed in hydrazine oxidation, we conjecture that a hydrazine-like structure participates in ammonia oxidation.

Catalyst	Preparation procedure	Phase composition	Surface area, m <sup>2</sup> /g
Cr <sub>2</sub> O <sub>3</sub>	Decomposition of (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>3</sub>	$\alpha$ -Cr <sub>2</sub> O <sub>3</sub>	40
Fe <sub>2</sub> O <sub>3</sub>	Decomposition of FeO(OH) obtained by the reaction between $NH_4OH$ and $Fe_2(C_2O_4)_3$	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	37
ZnO	Extra purity great reagent	ZnO	9

 Table 2. Characteristics of the samples

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**Fig. 2.** Dependences of the concentrations of products  $(C_{pr})$  and surface species on the concentration of oxygen in the reaction mixture at  $C_{\rm NH_3} = 0.30$  vol. fr.,  $T = 240^{\circ}$ C (Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>) and 340°C (ZnO): (a) Experimental values of the concentrations (1-3) N<sub>2</sub> and (4-6) N<sub>2</sub>O for (1, 4) ZnO, (2, 5) Fe<sub>2</sub>O<sub>3</sub>, and (3, 6) Cr<sub>2</sub>O<sub>3</sub>; (b) (1) experimental values of the intensity of the absorption band at 2200 cm<sup>-1</sup> D<sub>2200</sub> and (2) the calculated values of N<sub>2</sub>O<sub>ads</sub> coverage on the Fe<sub>2</sub>O<sub>3</sub> surface ( $\Theta_{\rm N,O}$ ).

Assuming that all the intermediates found participate in the reaction on the oxides studied, we propose the following scheme to describe the process of lowtemperature ammonia oxidation on metal oxides:

(1)  $NH_{3(gas)} + Z \longrightarrow NH_3Z$ (ZnO,  $Cr_2O_3$ ,  $Fe_2O_3-1620 \text{ cm}^{-1}$ ) (2)  $NH_3Z \longrightarrow NH_{3(gas)} + Z$ (3)  $O_2 + Z \longrightarrow O_2Z$ (4)  $O_2Z \longrightarrow O_2 + Z$ (5)  $O_2Z + Z \longrightarrow 2OZ (Cr_2O_3-1010 \text{ and } 990 \text{ cm}^{-1})$ (6)  $NH_3Z + OZ \longrightarrow NH_2Z + OHZ (Cr_2O_3-1560 \text{ cm}^{-1})$ (7)  $2NH_2Z \longrightarrow N_2H_4Z + Z$ (8)  $N_2H_4Z + O_2Z \longrightarrow N_{2(gas)} + 2H_2O + 2Z$ (9) $NH_2Z + O_2Z \longrightarrow NOZ + H_2O + Z$ (C $r_2O_3-2080 \text{ cm}^{-1}$ ) (10)  $NOZ + OZ \longrightarrow NO_{2b}Z + Z$ (11)  $NH_2Z + NO_2Z \longrightarrow N_2OZ + Z$ (ZnO,  $Fe_2O_3-2200 \text{ cm}^{-1}$ ) (12)  $N_2OZ \longrightarrow N_2O_{(gas)} + Z$ 

(13) OHZ + OHZ 
$$\longrightarrow$$
 H<sub>2</sub>O + OZ + Z

Here, Z is the free site on the oxide surface. Oxides on which the surface species were observed experimentally are presented in parentheses. The absorption bands of water were only observed in the spectra at temperatures below 100°C. The spectra obtained at the reaction temperature did not contain these bands. Therefore, the step of water adsorption was not included in the reaction scheme.

Based on the above scheme, we calculated the concentrations of products and surface coverages depending on the composition of the reaction mixture. The set of differential equations for the changes in the concentrations of species in the gas phase corresponding to this scheme was solved using a standard program in the approximation of a well-stirred reactor. Estimates of the rate constants obtained from nonstationary spectrokinetic measurements were used as reference values. We obtained effective values for  $k_{12}$  (0.012 s<sup>-1</sup> on ZnO and 0.020 s<sup>-1</sup> on Fe<sub>2</sub>O<sub>3</sub>). The effective values of  $k_6$ (1 × 10<sup>-3</sup> s<sup>-1</sup>) and  $k_{10}$  (2 × 10<sup>-3</sup> s<sup>-1</sup>) were estimated for Cr<sub>2</sub>O<sub>3</sub> in [17].

The reverse problem was solved using the experimental values of the rate constants  $k_{12} = 0.012 \text{ s}^{-1}$  for ZnO,  $k_{12} = 0.02 \text{ s}^{-1}$  for Fe<sub>2</sub>O<sub>3</sub>, and  $k_{10} = 2 \times 10^{-3} \text{ s}^{-1}$  for Cr<sub>2</sub>O<sub>3</sub> by optimizing the values of other constants so that the difference between the calculated and experimentally measured values of the rates of product formation was at most 20%. Note that we failed to adequately describe the results with any other combinations of the rate constants when we used the experimental value of  $k_6$  for Cr<sub>2</sub>O<sub>3</sub>. It is likely that the reason for this is that the experimental value of  $k_6$  is underestimated because of ammonia readsorption. The presence of readsorption is associated with the high adsorption ability of ammonia (the characteristic time during which the stationary value of ammonia absorption band is settled is several seconds), the low flow rate of feed supply (50 ml/min), and the relatively small amount of the catalyst used (in the diffuse-reflectance method,  $\sim 1 \text{ cm}^3$  of the catalyst is used). Under these conditions, the measurements of the rate constant of adsorbed ammonia consumption results in the underestimation of the values (for  $Cr_2O_3$ , the measured value is  $k_6 = 3.5 \times 10^{-3} \text{ s}^{-1}$ , the calculated value,  $k_6 = 0.2 \text{ s}^{-1}$ ).

For the convenience of calculations, the rate constants were expressed in reciprocal seconds. For that, the surface coverages were expressed in monolayer fractions, and the concentrations of reactants and products in the gas phase were expressed in volume fractions. That is, these values were dimensionless. In this case, the equation for concentration changes of, for instance, nitrogen takes the following form:

$$d[N_2]/dt = B_1 w_{N_2} - B_2[N_2].$$



Fig. 3. IR spectra obtained in the process of hydrazine oxidation on  $Cr_2O_3$  at T, °C: (1) 80, (2) 120, (3) 240, and (4) 310.

Here,  $w_{N_2}$  is the rate of nitrogen formation,  $w_{N_2} = k_8 \Theta_{N_2H_4} \Theta_{O_2}$ ; N<sub>2</sub> is the concentration of nitrogen in volume fractions;  $B_1 = GSC_L/V_RC_N$ ,  $B_2 = v/V_R$ , and  $B_1$  and  $B_2$  are dimensionless values; G is the catalyst loading (g); S is the catalyst specific surface area (m<sup>2</sup>/g),  $C_N = 0.446 \times 10^{-4}$  mol/cm<sup>3</sup> =  $1/V_M$ , where  $V_M = 22.4 \times 10^3$  cm<sup>3</sup>/mol is the molar volume;  $C_L = 1.66 \times 10^{-5}$  mol/m<sup>2</sup> is the number of active sites per unit surface area; v is the flow rate (cm<sup>3</sup>/s); and  $V_R$  is the reactor volume (cm<sup>3</sup>).

It is easy to show that, if the rates of surface steps are expressed in units of molecule cm<sup>-2</sup> s<sup>-1</sup>, then the dimensionality of the rate constant can be converted to the dimensionality corresponding to the second-order reaction (cm<sup>2</sup> molecule<sup>-1</sup> s<sup>-1</sup>): the value of the rate constant should be divided by the value of  $C_L$  expressed in molecule cm<sup>2</sup> (10<sup>15</sup> molecule cm<sup>2</sup>).

Figure 5 shows the concentrations of products and surface coverages measured experimentally and calculated on the basis of the proposed scheme for Fe<sub>2</sub>O<sub>3</sub>. The coincidence of the calculated and experimental dependences is rather good considering the assumption made. Acceptable agreement was also obtained in the framework of the same mechanism for ZnO and Cr<sub>2</sub>O<sub>3</sub>. Figure 6 shows the experimental and calculated values of the surface coverage by N<sub>2</sub>O in the course of the settling of the stationary reaction regime on ZnO. It is seen that the general S-like shape of the kinetic curve is acceptably described. The differences are probably due to the fact that the mathematical description of the results assumed well-stirred reactor conditions, although the well-stirred reactor model does not accurately describe the cell/reactor for the registration of diffuse-reflectance spectra. Data presented in Fig. 6 were obtained in this cell/reactor. The values of the rate constants of steps at which the coincidence is observed are shown in Table 4.

Using the values of the rate constant  $k_{10} = 0.5 \times 10^{-18} \text{ cm}^2$  molecule<sup>-1</sup> s<sup>-1</sup> (Table 4) and the activation energy  $E_a = 98 \text{ kJ/mol}$  for step 10 (Table 3) for Cr<sub>2</sub>O<sub>3</sub>, we can estimate the value of the preexponential factor. It is equal to  $5 \times 10^{-8} \text{ cm}^2$  molecule<sup>-1</sup> s<sup>-1</sup>. This value is within the range of the preexponential factors for the elementary heterogeneous reactions ( $10^{-1} - 10^{-8} \text{ cm}^2$  molecule<sup>-1</sup> s<sup>-1</sup>) [25].

#### DISCUSSION

As can be seen from the data shown in Table 1, the main information on intermediate compounds was obtained under conditions that are far from the real conditions of the low-temperature catalytic oxidation of ammonia. Obviously, this information is not very reliable. Unfortunately, it is this information that forms the basis for the proposed multiple-step mechanisms of the reaction. For instance, Bagnasco *et al.* [11] proposed the reaction mechanism based on changes in the spectra of adsorbed ammonia in the absence of oxygen during heating to 150°C. Changes in the activity in parallel experiments showed that the reaction products can be detected only at 250°C. Therefore, a reasonable ques-



**Fig. 4.** Dependences of experimental values of the intensities of adsorption bands (*D*) and the calculated values of the surface coverages by the corresponding species ( $\Theta$ ) on the time elapsed after excluding NH<sub>3</sub> from the flow of the reaction mixture on (a) ZnO, (b) Cr<sub>2</sub>O<sub>3</sub>, and (c) Fe<sub>2</sub>O<sub>3</sub>. *T* = 240°C (Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>) and 340°C (ZnO).

tion arises: Are the changes observed in the spectrum of adsorbed ammonia relevant to the reaction? It is clear that the proposed mechanism is unreliable. We studied the mechanism of this reaction using the spectrokinetic method [14–17] and simultaneously recorded the spectrum of surface species under the reaction conditions and the rates of product formation. The procedure of these measurements was described in detail in [23, 26]. This method makes it possible to determine whether or not the complex observed is an intermediate of the reaction by comparing the rates of surface compound transformation and the rate of product formation. If these rates coincide, then we have reasons to assume that the surface compounds observed are intermediates in the reaction [27]. Thus, we managed to determine the intermediate species of this reaction, NH3 ads and N2Oads, on



**Fig. 5.** Dependence of the (1, 3) experimental and (2, 4) calculated values of the concentrations of N<sub>2</sub> and N<sub>2</sub>O for Fe<sub>2</sub>O<sub>3</sub> at 240°C (a) on the concentration of ammonia in the reaction mixture at  $C_{O_2} = 0.40$  vol. fr. and (b) on the concentration of oxygen in the reaction mixture at  $C_{\rm NH_3} = 0.25$  vol. fr.

 $Fe_2O_3;$   $NH_3$   $_{ads},$   $N_2O_{ads},$  and  $NO_{ads}$  on  $Cr_2O_3;$  and  $NH_3$   $_{ads}$  and  $N_2O_{ads}$  on ZnO.

Results obtained in this work show that, in the framework of the proposed mechanism, it is possible to describe the experimental data for the oxides studied (Figs. 1b, 2b, and 4–6). In our case, we managed to describe quantitatively the dependences of the rate of nitrogen and N<sub>2</sub>O formation on the composition of the reaction mixture (Fig. 5). The composition of the reaction mixture varied over broad ranges. Moreover, the mechanism describes the experimental dependences of surface coverages by intermediate complexes on the same parameters under stationary conditions and the dependences of coverages on time when ammonia is excluded from feed flow (Fig. 4) and in the course of the settling of the stationary regime of the reaction (Fig. 6).

All these facts allow us to assume that the mechanism of the reaction is the same on the oxides studied. At the same time, we do not believe that the proposed mechanism completely described the process of lowtemperature ammonia oxidation on oxides, because not all the intermediates were detected experimentally. Similarly, not all of the rate constants were measured. However, it is clear from the above experimental data that the main features of the process are reflected in the scheme. This fact allows us to analyze changes in the rate constants of the same steps when changing the oxide nature. Analysis of data presented in Table 4 shows that, in the series ZnO,  $Fe_2O_3$ , and  $Cr_2O_3$ , the rate constants of steps change in two ways:  $k_7$  and  $k_{10}$  are described by a curve with a maximum, whereas the other constants change steadily in the same series. However, the rates of increase in these constants differ. When solving the reverse problem, it was found that the calculated values are most sensitive to changes in the values  $k_1 - k_4$  when the experimental data are described quantitatively. The value of the constant  $k_9$  determined the ratio between the rates of N<sub>2</sub> and N<sub>2</sub>O formation. A change in the adsorption constant of ammonia  $k_1$  correlates with a change in the rate of reaction product formation and with the heat of ammonia adsorption [28]. The corresponding data are presented in Table 5. The same table shows data from the literature on the activation energy of oxygen desorption [29].

Such a ratio of parameters (the reaction rate, the constant, and the heat of ammonia adsorption) can be explained using the Brønsted–Polanyi relationship

$$E_{\rm r} = E_0 - \alpha Q_{\rm NH_3},\tag{1}$$

where  $E_{\rm r}$  is the activation energy of the reaction,  $E_0$  is a constant term, and  $Q_{\rm NH_2}$  is the heat of the formation of a complex between the reactant and a Lewis site (in our case, the heat of ammonia adsorption). Similar relationships for reactions over Lewis sites were considered in detail in [30]. According to formula (1), an increase in the heat of ammonia adsorption should lead to a decrease in the activation energy of the reaction and, therefore, to an increase in the reaction rate. The experimental heats of ammonia adsorption [28] increase when switching from ZnO to  $Cr_2O_3$ . The reaction rate increases in the same series (Table 5). This fact confirms that formula (1) is correct for this reaction, that the proposed mechanism correctly describes ammonia oxidation on all the oxides studied, and that ammonia adsorption plays an important role in determining the rate of ammonia oxidation.

The acidic properties of Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> were compared in [30] using the adsorption band  $\delta_s$  of (NH<sub>3 ads</sub>) [31]. According to [32], the acidity of the oxides studied increases in the series ZnO, Fe<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub>. Because the constants  $k_1$  and  $k_3$  are the constants of reactant adsorption (for ammonia and oxygen) on coordinatively unsaturated surface sites (Lewis acid sites), the transfer of electrons from the reactant molecules of the surface sites requires a lower activation energy if an oxide is less acidic.



**Fig. 6.** Changes in (1)  $D_{2200}$  (experiment) and (2)  $\Theta_{N_2O}$  (calculation) in the process of settling the stationary regime of NH<sub>3</sub> oxidation on ZnO. The feed composition is 0.2% NH<sub>3</sub> + 0.4% O<sub>2</sub>.  $T = 240^{\circ}$ C.

The correctness of the calculated constants, specifically  $k_4$ , is supported by data from the literature on the values of the activation energies of oxygen desorption from the oxides studied (Table 5). This value decreases in the series ZnO, Fe<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub>. This corresponds to an increase in the respective constant (Table 4).

The constants  $k_7$  and  $k_{10}$  refer to the addition-type steps, and their values pass through a maximum in the series ZnO, Fe<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> (Table 4). According to [33], the distance between the metal atoms and the nonmetal atoms on the oxide surface passes through a minimum. In other words, there is a reverse dependence of the constant and the distance between metal and nonmetal atoms. Possibly, the distance between the stabilization sites of neighboring species is important for these steps: the shorter this distance, the higher the constant.

It is clear that the conclusions drawn here are tentative. For a more detailed determination of the nature of the steps, it is necessary to determine the preexponential factors of the rate constants and the activation energies. In this work, we failed to do that because the temperature interval where spectral and catalytic studies could be carried out simultaneously was short (~20°C).

**Table 3.** Activation energies of surface species consumption in the reaction of  $NH_3$  oxidation on the samples studied

Catalyst	Intermediate complex	Absorption band, cm <sup>-1</sup>	$E_{\rm a}$ , kJ/mol
ZnO	N <sub>2</sub> O <sub>ads</sub>	2200	54
Fe <sub>2</sub> O <sub>3</sub>	N <sub>2</sub> O <sub>ads</sub>	2200	104
Cr <sub>2</sub> O <sub>3</sub>	NO <sub>ads</sub>	2080	98
Cr <sub>2</sub> O <sub>3</sub>	NH <sub>3 ads</sub>	1620	25

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Constant	ZnO		Fe <sub>2</sub> O <sub>3</sub>		Cr <sub>2</sub> O <sub>3</sub>	
Constant	$s^{-1}$	cm <sup>2</sup> molecule <sup>-1</sup> s <sup>-1</sup>	s <sup>-1</sup>	cm <sup>2</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$s^{-1}$	cm <sup>2</sup> molecule <sup>-1</sup> s <sup>-1</sup>
<i>k</i> <sub>1</sub>	0.02	$2 \times 10^{-17}$	0.01	$1 \times 10^{-17}$	0.1	$1 \times 10^{-16}$
$k_2$	0.01	_	0.1	_	0.2	_
<i>k</i> <sub>3</sub>	0.01	$1 \times 10^{-17}$	0.1	$1 \times 10^{-16}$	0.1	$1 \times 10^{-16}$
$k_4$	0.1	_	0.2	_	1.5	_
$k_5$	0.02	$2 \times 10^{-17}$	0.003	$3 \times 10^{-18}$	0.2	$2 \times 10^{-16}$
$k_6$	0.2	$2 \times 10^{-16}$	0.2	$2 \times 10^{-16}$	2.0	$2 \times 10^{-15}$
<i>k</i> <sub>7</sub>	0.3	$3 \times 10^{-16}$	5.0	$5 \times 10^{-15}$	3.0	$3 \times 10^{-15}$
$k_8$	0.5	$5 \times 10^{-16}$	5.0	$5 \times 10^{-15}$	5.0	$5 \times 10^{-15}$
$k_9$	0.02	$2 \times 10^{-17}$	0.1	$1 \times 10^{-16}$	0.8	$8 \times 10^{-16}$
$k_{10}$	0.01	$1 \times 10^{-17}$	0.1	$1 \times 10^{-16}$	0.005*	$5 \times 10^{-18}$
<i>k</i> <sub>11</sub>	0.01	$1 \times 10^{-17}$	0.1	$1 \times 10^{-16}$	0.2	$2 \times 10^{-17}$
<i>k</i> <sub>12</sub>	0.012*	_	0.02*	_	0.1	_
k <sub>13</sub>	0.1	$1 \times 10^{-16}$	1.0	$1 \times 10^{-15}$	2.0	$2 \times 10^{-15}$

Table 4. The values of the rate constants for the steps of low-temperature ammonia oxidation at 240°C

\* Experimentally determined.

In this interval, we were unable to determine the above parameters with a high degree of accuracy.

Above, we considered the results of spectrokinetic measurements on oxides with pronounced Lewis acidity. At the same time, there are some data suggesting that the surface  $NH_4^+$  complex is formed on oxides with Brønsted acidity. Corresponding evidence was obtained for MoO<sub>3</sub> [14] and Cr<sub>2</sub>O<sub>3</sub> [17]. In the latter case, the formation of Brønsted sites was provided by the oxidative treatment of the sample. More detailed information on the steps associated with further trans-

**Table 5.** Some parameters of the reaction of ammonia oxidation on the studied catalysts (the values of  $w_{N_2}$ ,  $w_{N_2O}$ , and  $k_1$  correspond to 240°C)

Parameter	ZnO	Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>
$w_{\rm N_2}$ , molecule cm <sup>-2</sup> s <sup>-1</sup>	$2.7 \times 10^{14}$	$1.9 \times 10^{15}$	$1.5 \times 10^{16}$
$w_{\rm N_2O}$ , molecule $\rm cm^{-2}~s^{-1}$	$3.3 \times 10^{13}$	$3.6 \times 10^{14}$	$1.3 \times 10^{15}$
$k_1,  \mathrm{s}^{-1}$	0.02	0.01	0.1
$Q_{\mathrm{ads NH}_3}$ , J/mol [28]	160		230
$E_{\text{des O}_2}$ , kJ/mol [29]	226	143	109

formations of ammonium ions is currently unavailable. At the same time, another mechanism of ammonia oxidation is possible that involves the formation of an ammonium ion on the surface and its further transformation.

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