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On the Properties of Surface Complexes Formed upon the Adsorption of NO_x, C_3H_6, and Their Mixtures with Oxygen on ZrO_2 According to EPR, TPD, and Fourier Transform IR Spectroscopy Data

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Abstract—The adsorption of reactant mixtures is quantitatively and qualitatively different from the adsorption of the individual reactants. Thus, O_2 is almost not adsorbed on ZrO_2; however, a considerable concentration of molecular oxygen was detected among the products of desorption after the adsorption of a mixture of NO + O_2 and the total amount of desorbed molecules was greater by a factor of 10 than their total amount after the individual adsorption of NO and O_2. Among the qualitative differences is the formation of the O_2^- radical anion on the surface only upon the adsorption of the mixture of NO + O_2. Similarly, the number of desorbed molecules upon the simultaneous adsorption of C_3H_6, NO, and O_2 was much greater than that upon their individual adsorption; this is related to the formation of paramagnetic and nonparamagnetic NO_2—hydrocarbon complexes on the surface, which contained the NO_2 group and a hydrocarbon fragment.

Keywords: selective catalytic reduction of NO_x, zirconium dioxide catalysts, adsorption of NO_x, C_3H_6, and their mixtures with O_2, properties of surface complexes

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INTRODUCTION

Zirconium oxide and catalysts on its basis are used in a number of catalytic reactions, such as the synthesis of methyl formate [1], the hydrogenation and isomerization of alkanes [2, 3], the hydrogenation of CO_2 [4], and the reforming [5] and oxidation of methane [6].

A significant number of publications have been devoted to the use of zirconium dioxide in the synthesis of catalysts and catalyst supports for the selective catalytic reduction (SCR) of NO_x oxides by hydrocarbons [7–9]. Catalysts based on pillared clays stabilized by zirconium dioxide are examples of such systems.

Zirconium dioxide partially stabilized in a tetragonal or cubic modification is an analogue of structurally strained catalytic elements (pillars) in pillared clays. Therefore, a comparison of the SCR mechanisms of NO_x on massive ZrO_2 and on the pillars of ZrO_2 in the composition of clays becomes of primary importance when an effective catalyst for this process should be obtained. The first stage of this route is a study of the individual adsorption of reactants and the adsorption of their mixtures on ZrO_2. Earlier [10], with the use of Fourier transform IR spectroscopy, we found that nitrosyl and nitrate–nitrite N_xO_y complexes are formed upon the adsorption of NO_x (NO, NO + O_2) on the surface of ZrO_2. In this case, nitrates are the main final species of the adsorption of nitrogen oxides on the surface of zirconium dioxide; it is likely that they play a key role in the catalytic reduction of NO_x on oxide catalysts, and electron transfer from the adsorbed molecules of NO (NO_2) to oxygen facilitates their formation.

This work is a continuation of the study of the adsorption of reactants and their mixtures on ZrO_2 by temperature-programmed desorption, electron paramagnetic resonance (EPR) spectroscopy, and in situ Fourier transform spectroscopy.

EXPERIMENTAL

The preparation and characterization of the ZrO_2 samples were described earlier [10].

Temperature-programmed desorption (TPD) was performed in the batch mode in an ampoule for EPR spectroscopy and combined with the measurement of EPR spectra. Before the beginning of an experiment, a weighed portion of zirconium dioxide (50 mg) was subjected to standard treatment: evacuation at room

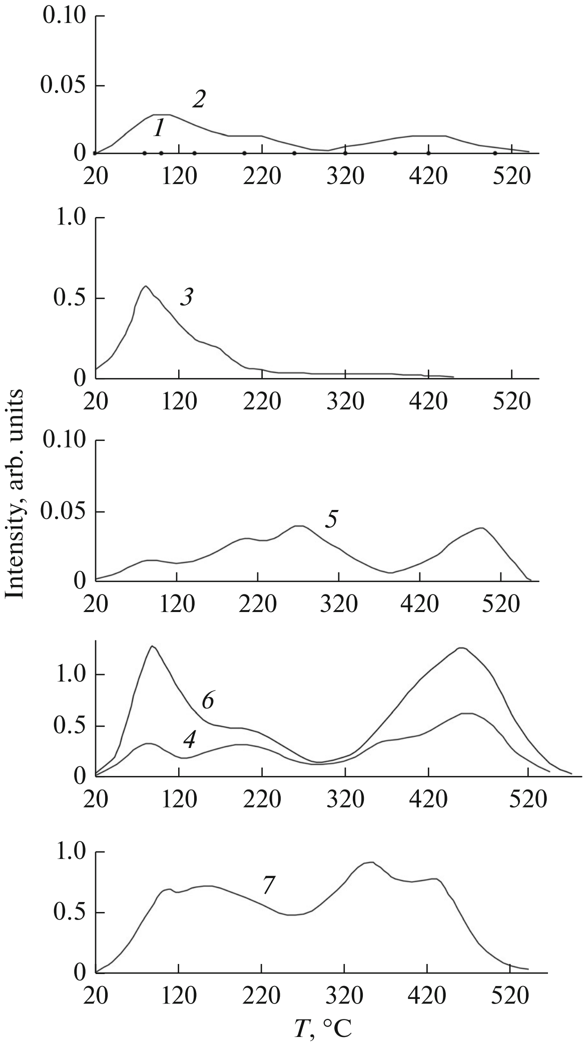


Fig. 1. TPD spectra of the ZrO_2 sample after the adsorption of (*1*) oxygen, (*2*) NO, (*3*) C_3H_6, (*4*) NO_2, (*5*) a mixture of NO + O_2, (*6*) a mixture of NO + O_2 for 40 min, and (*7*) C_3H_6 for 5 min and the subsequent adsorption of a mixture of NO + O_2.

temperature to 10^{-4} Pa, heating to 700°C, and keeping at this temperature in a vacuum for 1 h. Thereafter, without changing the temperature, the sample was kept in an atmosphere of O_2 ($P = 2 \times 10^2$ Pa) for 1 h and finally evacuated and cooled to a specified temperature. The test gas was adsorbed for 5 min; thereafter, the sample was evacuated for 20 min and heated at a rate of 12 K/min with continuous evacuation.

The products of desorption were analyzed on an MKh-7303 mass spectrometer (NITI, Soviet Union) after sampling with a capillary. The sensor of the mass spectrometer was preliminarily calibrated with the test gases. The gases were detected based on the following peaks, *m/e*: NO, 30; NO_2, 46; C_3H_6, 42. The peaks of the fragments of these molecules were additionally analyzed for the identification of the desorption products of a mixture of gases.

The amount of molecules adsorbed on a sample was determined in thermal desorption experiments without the evacuation of a gas phase based on the pressure of desorbed gas. The desorption spectrum as the temperature dependence of the desorbed gas pressure $P = f(T)$ was recorded with the aid of a Pirani gauge [11]. The measurement error was no greater than 20%.

The diffuse reflectance IR spectra were measured on a Spectrum RX I FT-IR System spectrometer (Perkin Elmer, the United States). A weighed portion of ZrO_2 (340–400 mg) was preliminarily subjected to standard heat treatment in a flow of N_2 at 400–500°C. The spectra were recorded under the conditions of a gas flow in a temperature range from 25 to 500°C in a reactor cell in accordance with a procedure described earlier [12]. The intensities of absorption bands in the diffuse reflectance spectra were measured in Kubelka–Munk units.

EPR spectra were obtained on an EPR-V radiospectrometer (Semenov Institute of Chemical Physics, Russian Academy of Sciences, Russia) with a working wavelength of 3.2 cm equipped with a Diapazon temperature attachment. A weighed portion of zirconium dioxide (50 mg) was preliminarily subjected to standard treatment: evacuated at room temperature to 10^{-4} Pa, heated to 700°C, and kept at this temperature in a vacuum for 1 h and then in an atmosphere of O_2 ($P = 2 \times 10^2$ Pa) for 1 h without changing the temperature. In conclusion, the sample was evacuated and cooled to a specified temperature. The EPR spectra were recorded upon adsorbing the test gas onto the pretreated sample at a pressure of $(2–10) \times 10^2$ Pa. The amount of paramagnetic particles was determined from the EPR spectra after their double integration and comparison with the number of spins in a reference sample of $CuSO_4 \cdot 5H_2O$. The measurement error did not exceed 10%.

RESULTS

Adsorption of a Mixture of NO and O_2

Figure 1 shows the thermal desorption spectra obtained after the adsorption of NO, NO_2, O_2, C_3H_6, and their mixtures on ZrO_2 under vacuum conditions. It is evident (curve *1*) that oxygen is almost not adsorbed on ZrO_2: the number of O_2 molecules desorbed in the test temperature range (25–570°C) was lower than the sensitivity of measurements; that is, it was smaller than 10^{17} g^{-1}.

The spectrum of NO desorption (curve *2*) exhibits three peaks. The most intense peak maximum corresponds to 100°C. This peak has a shoulder (the second peak) at 220°C. The third peak in a high-temperature region has a maximum at 430°C. The total number of desorbed NO molecules is $N = 8 \times 10^{18}$ g^{-1}.

The consecutive adsorption of NO and O_2 significantly complicates the shape of the spectrum (curve *5*). In the test temperature range (25–570°C), it contains at least four peaks with maximums at 90, 200, 270, and 510°C. In this case, the total amount of desorbed molecules is 1.4×10^{19} g^{-1}, which is approximately twice as high as that upon the thermal desorption of NO after its individual adsorption. According to mass-spectrometric data, the molecules of two gases, NO and O_2, are released into a gas phase in the first low-temperature peak of desorption. In the other cases, the molecules of NO_2 occur in the gas phase together with NO.

We also studied the adsorptive properties of zirconium dioxide with respect to the molecules of NO_2 (curve *4*). The thermal desorption spectrum contained at least four peaks with maximums at 80, 200, 350, and 490°C. The most intense high-temperature peak was at 380–580°C, and the total quantity of desorbed molecules was 1.4×10^{20} g^{-1}.

Upon NO admission to a sample of ZrO_2 at −196°C, an EPR signal of a wide anisotropic line with $g_\perp = 1.94$ appeared. It was attributed to the NO–Zr^{4+} complexes formed upon the interaction of NO with the coordinatively unsaturated cations Zr^{4+} [13].

Oxygen admission at a pressure of 1×10^3 Pa and a temperature of −196 or 25°C to ZrO_2 after its exposure at an evacuation temperature (T_e) from 400 to 700°C was not accompanied by the appearance of EPR signals. Signals did also not appear after the heating of a sample in oxygen at 700°C and the subsequent cooling in an atmosphere of O_2 to 25 or −196°C. On the other hand, an EPR signal ($g_1 = 2.033$, $g_2 = 2.007$, and $g_3 = 2.002$) appeared when NO (at pressures from 50 to 2×10^2 Pa) and then O_2 ($P = 10^3$ Pa) were admitted at 25°C to ZrO_2, which was heated both in a vacuum and in oxygen. It disappeared after the repeated admission of NO ($P = 2 \times 10^2$ Pa) and broadened in a atmosphere of oxygen ($P = 5 \times 10^2$ Pa). The evacuation of gases led to the complete restoration of the signal. Consequently, the test spectrum corresponds to a sufficiently stable complex formed upon the adsorption of a mixture of NO + O_2. It is likely that the reversible action of NO and O_2 molecules on the spectrum is related to their dipole–dipole interaction with the complex. The prolonged exposure of a sample in an atmosphere of this mixture led to the disappearance of the described signal. Curve *6* in Fig. 1 shows the corresponding TPD spectrum.

The parameters of the spectra recorded at −196 and 25°C are identical: $g_1 = 2.033$, $g_2 = 2.007$, and $g_3 = 2.003$. They coincide with the corresponding g-tensor values of the radical O_2^-, which is formed as a result of the photoadsorption of oxygen at 25°C on the irradiation of a sample with light from a DRSh-1000 lamp for 1 h. These observations and published data [14] make it possible to assume that the radical O_2^- is formed upon the adsorption of NO + O_2.

The same radical O_2^- as that formed upon the adsorption of a mixture of NO + O_2 was observed on oxygen admission to a sample of ZrO_2 (T_e = 700°C) with preliminarily adsorbed NO_2 (the adsorption was performed for 5 min at 25°C and $P = 2 \times 10^2$ Pa; then, evacuated was performed for 20 min). However, it disappeared after the removal of oxygen at room temperature [15, 16], whereas the signal of the radicals O_2^- obtained after the adsorption of NO + O_2 remained to 270°C.

Adsorption of NO and Hydrocarbons

After the adsorption of propylene on ZrO_2, the TPD spectrum (Fig. 1, spectrum *3*) contained two peaks at 80 and 190°C. The total amount of desorbed C_3H_6 molecules was 1.4×10^{18} g^{-1}.

A much more complicated spectrum was measured after the adsorption of propylene for 5 min and then a mixture of NO + O_2 for 40 min (spectrum *7*). It is not the result of the superposition of the thermal desorption spectra obtained after the adsorption of a mixture of NO + O_2 (spectrum *6*) and propylene (spectrum *3*). In a temperature range of 130–530°C, spectrum *7* is much more intense than spectra *1*–*3*, which were obtained after the separate adsorption of O_2, NO, and C_3H_6, and it is similar to spectra *4* and *5*, but it differs from them in terms of the presence of an additional peak at 380°C. The appearance of this peak can be related to the disintegration of the adsorption complex formed upon the interaction of the adsorbed hydrocarbon with NO_2. Note that this complex is nonparamagnetic.

According to the EPR spectroscopic data, paramagnetic complexes were not formed after the adsorption of propylene on ZrO_2 at room temperature. However, a paramagnetic complex was formed upon the subsequent adsorption of a mixture of NO + O_2 on the sample with preliminarily adsorbed propylene, and the signal of this complex appeared in the EPR spectrum after the evacuation of a gas phase (Fig. 2). This spectrum was not detected as a result of the adsorption of only NO or only O_2 on ZrO_2 with the preliminarily adsorbed hydrocarbon. Such a signal was also not detected upon the adsorption of NO, NO_2, or NO + O_2 in the absence of propylene. The replacement of C_3H_6 by C_3D_6 did not influence the shape of the spectrum. Consequently, it can be attributed to the complex of a molecule of NO_2 and the adsorbed hydrocarbon. This is also confirmed by the fact that the parameters of the spectrum ($g_\perp = 2.004$, $g_\parallel = 2.008$, $A_\perp =$

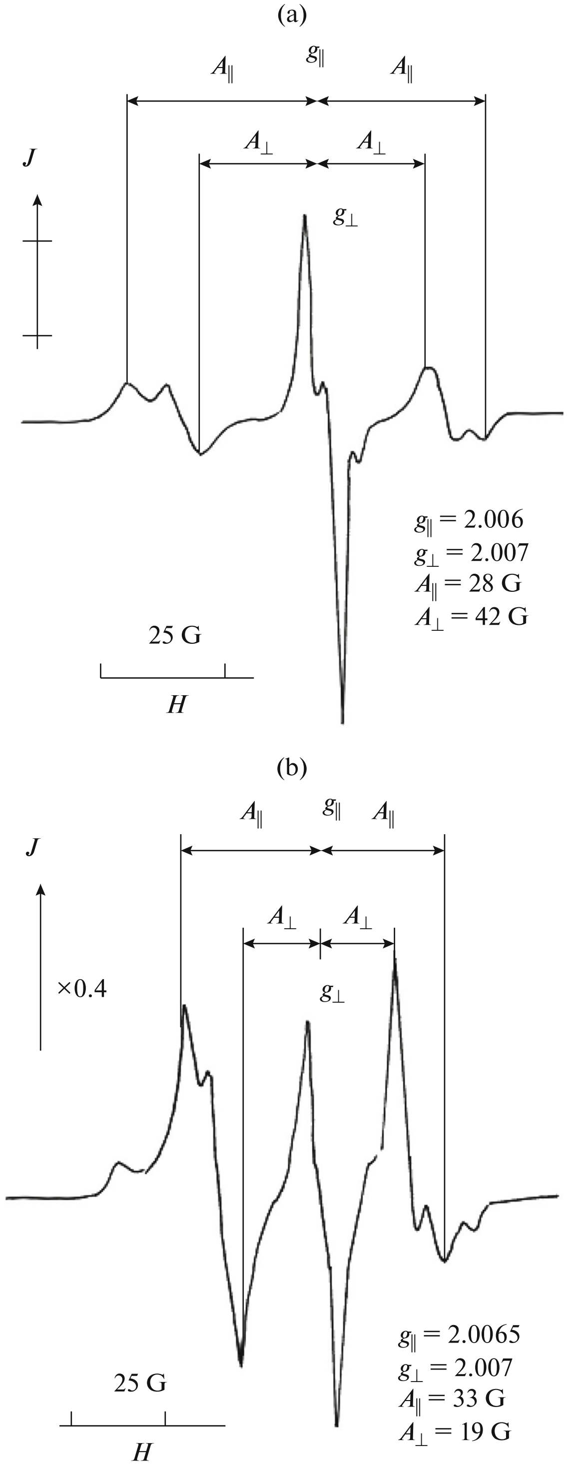


Fig. 2. EPR spectra of the ZrO_2 sample (T_e = 700°C) after the adsorption of C_3H_6 at 25°C for 5 min and then a mixture of NO + O_2 for 40 min and the subsequent evacuation: (a) with the participation of ^{14}NO and (b) with the participation of ^{15}NO.

28 G, and $A_{\parallel} = 50$ G) are close to the parameters of the EPR spectra of nitroxyl radicals [17]. The concentration of this complex was 5×10^{17} g^{-1}. Similar complexes were observed earlier upon the adsorption of a mixture of C_3H_6 + NO + O_2 on H-ZSM-5 and the oxide Al_2O_3 [18].

This complex easily interacts with nitrogen monoxide. The EPR signal of this complex disappeared after NO admission, but it was restored after evacuation. On the thermovacuum treatment of the sample, this signal remained to 230°C. An increase in the sample treatment temperature to $T > 230$°C led to not only the disappearance of the EPR signal but also the appearance of a singlet line with $g_{av} = 2$, whose intensity increased as the complex was decomposed. The signal was not observed in the course of the thermal desorption of propylene from ZrO_2.

The above data show that complexes of two types were formed on the surface of ZrO_2. These complexes contained the NO_2 group and a hydrocarbon fragment, but they differed in terms of electronic states and the strengths of bonds with the surface: a paramagnetic complex, which occurred on the surface to 230°C, and a nonparamagnetic complex, whose decomposition products were desorbed at 380°C. In the subsequent discussion, we will designate these complexes by the general formula NO_2–HC.

We failed to observe the destruction of the paramagnetic complex in the TPD spectra because intense desorption in a range of 30–230°C (Fig. 1, spectrum *7*) was caused by the decomposition of the adsorption complexes formed upon the adsorption of NO_2 and a mixture of NO + O_2.

IR spectrum *4* in Fig. 3 was measured in the course of the addition of a reaction mixture flow of NO + C_3H_6 + O_2/N_2 to the sample at 340°C. It contains an absorption band at 1565 cm^{-1}, which is absent from the spectra of the same sample obtained upon the adsorption of both propylene together with O_2 (spectrum *1*, the peaks of acetate complexes at 1544 and 1440 cm^{-1}) and a mixture of NO + O_2 (spectrum *2*, nitrate complexes). Therefore, the band at 1565 cm^{-1} should be attributed to the vibrations of the adsorption complex formed upon the interaction of NO_x with propylene and/or its partial oxidation products. Its intensity decreased as the sample was heated in the flow of the reaction mixture to temperatures higher than 500°C (spectrum *3*). It is likely that this band, which corresponds to the symmetrical vibration of the NO_2 group, is related to the formation of surface complexes including the NO_2 group and a fragment of the hydrocarbon (in this case, of propylene) activated as a result of adsorption (NO_2–HC complexes). The corresponding antisymmetric vibration of this group was noted at 1380 cm^{-1} (Fig. 3). This spectral pattern was

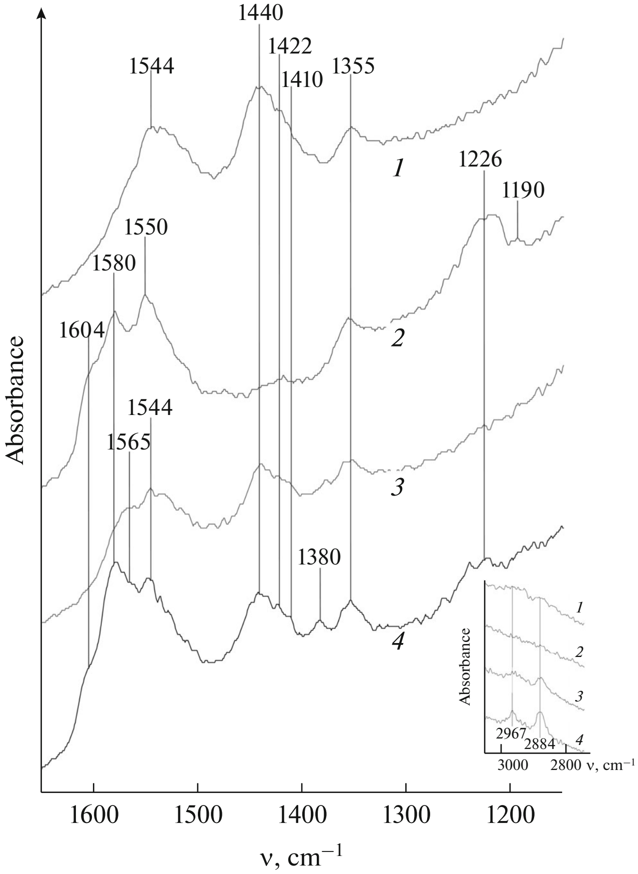


Fig. 3. Diffuse reflectance IR spectra measured after the interaction of ZrO_2 with the flows of the mixtures of (*1*) 0.2% C_3H_6 + 2.5% O2, (*2*) 0.2% NO + 2.5% O_2, and (*3, 4*) 0.2% NO + 0.2% C_3H_6 + 2.5% O_2. Spectra *1–3* were obtained at 500°C, and spectrum *4* was obtained at 340°C.

observed under the conditions of reaction at 150–500°C.

DISCUSSION

The use of EPR spectroscopy and in situ IR spectroscopy made it possible to establish that the formation of a large number of adsorption complexes can occur on the interaction of zirconium dioxide with NO_x, C_3H_6, and their mixtures with oxygen. Under the conditions of the selective catalytic reduction (SCR) of NO_x, paramagnetic complexes on the surface of ZrO_2 can be formed only with the participation of nitrogen oxides (NO or NO_2).

It is well known [13] that the formation of paramagnetic nitrosyls occurs at Lewis acid sites—the coordinatively unsaturated sites (CUSs) of the surface. Therefore, the number of CUSs can be judged from the intensity of the corresponding EPR signal. In particular, with an increase in the catalyst pretreatment temperature, the dependence of the amount of NO–Zr^{4+} complexes on T_e exhibited an extremum (Fig. 4). This result is consistent with well-known published data [19]. Strongly coordinatively unsaturated ions at an interface are usually formed in the course of a structural rearrangement of oxide surfaces [20]. In this case, an initial increase in the concentration of CUSs with T_e is caused by an increase in the degree of surface cleaning. After reaching a maximum, the concentration of strongly coordinatively unsaturated ion sites decreases because of a change in the ratio between the tetragonal and monoclinic phases in the sample. Because the specific surface area of the monoclinic phase is smaller, the data given in Fig. 4 make it possible to estimate the temperature at which the tetragonal phase transoforms into the monoclinic phase. It is 510–550°C.

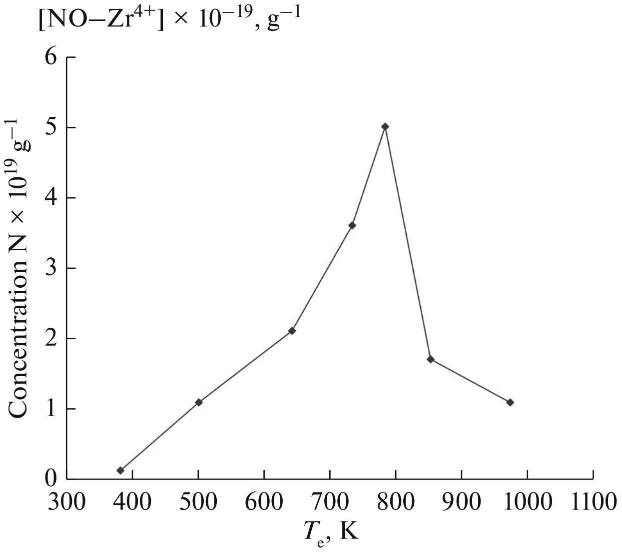


Fig. 4. Dependence of the concentration of the NO–Zr^{4+} complexes formed as a result of NO adsorption at –196°C on the ZrO_2 sample upon the temperature of its thermo-vacuum treatment for 1 h.

The disappearance of an EPR signal due to the NO–Zr^{4+} complex upon oxygen admission is indicative of its high reactivity with respect to $O_{2(gas)}$. It is likely that, because of the presence of unpaired electrons in paramagnetic nitrosyls, diamagnetic nitrogen–oxygen complexes are formed upon their interaction with oxygen; these complexes may block the strongly coordinatively unsaturated ion sites of adsorption as a result of the formation of strong nitrate complexes. This assumption was confirmed by a 100-fold decrease in the amount of gas desorbed upon the heating of the system from –196 to 25°C, as compared with an experiment in which only NO was desorbed. Furthermore, after the interaction of $NO_{(ads)}$ with oxygen, the EPR signal from NO–Zr^{4+} can be restored only by the high-temperature (530°C) evacuation of the surface with the subsequent adsorption of NO at −196°C. In the absence of oxygen from the gas phase, the EPR signal of NO–Zr^{4+} disappeared after heating the system to 25°C.

The formation of the radical anion of oxygen as a result of electron transfer from an adsorption site to the molecule of O_2 can occur only in the presence of an excess electron density at the surface of a metal ion. This is possible in the presence of adsorbed molecules. Previously, the formation of O_2^- radicals was observed on the adsorption of the mixtures of $H_2 + O_2$, $CH_4 + O_2$, and weak acids $HX + O_2$ [14, 21–23] on MgO or a mixture of $C_3H_6 + O_2$ on Mo/MgO and V/MgO catalysts [24]. It was assumed that, at the first stage of the reaction, the (H^-, CH_4^-, X^-)–electron donor complex is formed as a result of the dissociative adsorption of a reactant on the Lewis acid pairs of the oxide. At the second stage, the O_2^- radical appears as a result of electron transfer from this complex to the adsorbed molecule of oxygen.

In our case, the adsorbed molecules of nitrogen oxides (NO or NO_2) served as the donors of electrons [15, 16]. According to the EPR and IR spectroscopic data [10], paramagnetic nitrosyl, nitrite–nitrate, N_xO_y, and nitroorganic complexes are formed on the adsorption of these molecules. Let us consider in more detail the participation of these complexes in the reaction.

Paramagnetic NO–Zr^{4+} complexes. The interaction of NO–Zr^{4+} with oxygen at 77 K was accompanied by the disappearance of the spectrum of this complex and by the formation of nitrate complexes on the surface. The subsequent adsorption of NO at −196°C led to the complete restoration of the spectrum of the paramagnetic complex. Note that the paramagnetic complex of NO did not exist at temperatures higher than room temperature, whereas O_2^- was efficiently formed.

The dependences of the concentrations of the paramagnetic complexes of NO and O_2^- radicals on the temperature of sample heating in a vacuum have different shapes. In the former case, the dependence passes through a maximum at 530°C, and it monotonically increases with temperature in the second case. This fact allowed us to assume that the paramagnetic complex of NO does not participate in the formation of O_2^-.

Nitrate complexes. The temperature range of existence of nitrates (25–500°C) is considerably wider than the region of existence of the O_2^- radicals (25–270°C). The O_2^- radical is decomposed in a vacuum at 270°C. At the same time, according to the TPD (Fig. 1) and IR-spectroscopic data [10], nitrates remained on the surface at this temperature. The subsequent adsorption of oxygen at 25°C on the sample containing nitrates that were not decomposed at 270°C was not accompanied by the formation of O_2^-. Consequently, nitrates are also not electron donors in the reaction $NO + O_2 \rightarrow O_2^-$.

Nitrosyl complexes. According to published data [10, 25], the $NO^{\delta+}$ and NO^+ nitrosyl complexes are formed on the adsorption of NO on the surface of ZrO_2 as a result of electron transfer from the adsorbed molecules of NO to the zirconium oxide. The temperature range of existence of these complexes coincides with the region of existence of the O_2^- radical (from 25 to 200°C); this fact suggests that nitrosyl complexes are the most probable participant of the formation of O_2^-. According to IR spectroscopic data [10], the absorption bands of the complexes of $NO^{\delta+}$ and NO^+ upon the adsorption of oxygen are not shifted into the high-frequency region. By this is meant that complexes with the complete charge transfer from NO to ZrO_2 are the most probable electron source in the formation of O_2^-. Otherwise, if the complex of $NO^{\delta+}$ was an electron donor, a high-frequency shift of the absorption band of $NO^{\delta+}$ would be observed.

An increase in the concentration of radicals in the reaction $NO + O2 \rightarrow O_2^-$ with an increase in the temperature of sample heating in a vacuum indicates that active sites on the surface of ZrO_2 are formed in the course of heat treatment. Previously [16], we hypothesized that these sites can be the Lewis acid pairs Zr^{4+}–O^-–O^-–Zr^{4+}. To test this hypothesis, we used the test reaction $H_2 + O_2 \rightarrow O_2^-$, which occurs on the Lewis acid sites of magnesium oxide [14].

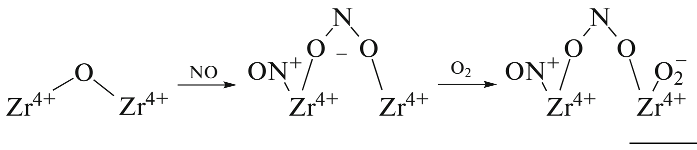
Indeed, upon the adsorption of a mixture of $H_2 + O_2$ ($P_{H_2} = 1 \times 10^3$, $P_{O_2} = 2 \times 10^2$ Pa, and $T = 25$°C) on ZrO_2 ($T_e = 700$°C), the O_2^-, radical is formed, whose parameters ($g_1 = 2.038$, $g_2 = 2.011$, and $g_3 = 2.004$) are close to the parameters of the O_2^- radical ($NO + O_2$). By this is meant that Lewis acid pairs occur on the surface of ZrO_2.

The rate of formation of O_2^- radicals on the adsorption of a mixture of $H_2 + O_2$ is considerably lower than that on the adsorption of $NO + O_2$. In the former case, the concentration of O_2^- reached a maximum value of 6×10^{18} g^{-1} after the treatment of the oxide with the mixture for 3–5 min, and it slowly increased in the course of adsorption in the latter case; after the treatment of the sample with the mixture for 1 h, it did not exceed 1×10^{18} g^{-1}.

Furthermore, after the adsorption of $NO + O_2$ and then $H_2 + O_2$, the concentration of O_2^- was equal to the sum of the concentrations of these radicals after the separate adsorption of the above mixtures. An analogous result was obtained upon the adsorption of initially $H_2 + O_2$ and then $NO + O_2$. Hence, it follows that the formation of the O_2^- radicals upon the adsorption of the mixtures of $NO + O_2$ and $H_2 + O_2$ occurs independently of each other at different sites.

According to published data [25], the complex of NO^+ is formed in the reaction $2NO + O_{(surface)} \to NO^+ + NO_2^-$ with the participation of surface oxygen. Furthermore, NO^+ is stabilized on the extralattice ions (ELIs) of Zr^{4+} [13]. The Zr^{4+} extralattice ions and regular structure Zr^{4+} ions are connected by bridging oxygen [19, 26, 27]. We assume that the most probable sites of the process in question are the surface bridging structures $Zr^{4+}(ELI)–O–Zr^{4+}$, and the $NO^+–NO_2^-$ complex formed on them is an electron donor for the formation of the O_2^- radical.

Taking into account these facts, we can schematically represent the reaction $NO + O_2 \to O_2^-$ on the bridging structures $Zr^{4+}(ELI)–O–Zr^{4+}$ by the following diagram:



Here, we assume that, at the first stage of the adsorption of NO on the bridges, a complex is formed in which one molecule of NO is stabilized on the cation to form nitrosonium NO^+ and the second molecule is inserted at the stressed bond to form the $–O–N^-– O$ compound. This complex containing two NO molecules does not possess paramagnetic properties. It should be more stable than the uncharged forms of NO adsorption on the cations [25]. At the second stage, on the adsorption of oxygen, the electron is transferred from the complex to the adsorbed O_2 molecule, which is further stabilized as O_2^- at the bridge cation or at the Zr^{4+} cations adjacent to the bridge on the oxide surface. The reaction $NO_2 + O_2 \to O_2^-$ can occur in accordance with an analogous scheme; one should only replace NO by NO_2. In this case, the donor complex consists of NO_2^- and the $–O–NO^-–O–$ compound. Note that these forms of NO adsorption on ZrO_2 were observed earlier [10].

The same concentration of the O_2^- ions (2.5×10^{15} g^{-1}) regardless of the electron donor molecule (NO or NO_2) indicates that the amount of the radical anions of oxygen on the surface of ZrO_2 depends on the concentration of corresponding adsorption sites, whereas the conditions of O_2^- formation affect the stability of the resulting radical anions. Apparently, the O_2^- ions cannot exist in the absence of corresponding nitrogen–oxygen complexes; it is most likely that the conditions of the occurrence of the radical forms of O_2 adsorption depend on the stability of these complexes.

The interaction of O_2^- with NO and a mixture of $NO + O_2$ leads to the formation of new diamagnetic nitrogen–oxygen complexes, which are different in terms of stability. Thus, NO admission can cause (depending on the interaction time) both reversible and irreversible disappearance of O_2^-. At the same time, even short interaction with NO_2 or a mixture of $NO + O_2$ leads to irreversible changes in the nitrogen–oxygen complexes containing the radical anions of oxygen. In this case, according to in situ IR-spectroscopic data [10], both of the described processes are accompanied by the formation of the nitrite–nitrate structures—the most stable forms of NO_x adsorption on the surface of ZrO_2:

$$\mathrm{NO} + \mathrm{O}_2 \to \underset{2240\ \mathrm{cm}^{-1}}{([\mathrm{NO}]^+, \mathrm{O}_2)} \to \underset{2480,\ 2614\ \mathrm{cm}^{-1}}{(\mathrm{N}_x\mathrm{O}_y)_z} \to \underset{1190\ \mathrm{cm}^{-1}}{\text{nitrites,}}\ \underset{1540–1620\ \mathrm{cm}^{-1}}{\text{nitrates.}}$$

Quantitative and qualitative differences in the adsorption of mixtures and individual reactants should be noted. Thus, O_2 is almost not adsorbed on ZrO_2 (Fig. 1); however, a considerable concentration of molecular oxygen was detected among the products of desorption after the addition of a mixture of $NO + O_2$, and the total amount of desorbed molecules was 10 times higher than their total amount after the individual adsorption of NO and O_2. The formation of O_2^- radical anions on the surface only upon the adsorption of a mixture of $NO + O_2$ is among the qualitative differences.

It is likely that the reason for this phenomenon consists in the fact that the adsorption of one of the components leads to a change in the surface properties, and this facilitates the adsorption of another component. In this case, the adsorption of NO creates electron-donor sites, which facilitate the formation of the O_2^- radical anion, which, in turn, facilitates the oxidation of $NO_{(ads)}$ to nitrates to increase the concentration of nitrogen-containing complexes on the surface.

Nitro-organic complexes. According to the TPD data (Fig. 1, curve *3*), propylene is adsorbed on ZrO_2 in two forms, which can be formed at two different sites: coordinatively unsaturated Zr^{4+} ions and Bronsted acid sites. However, none of the adsorption forms of C_3H_6 gives a signal in the EPR spectrum. The fact that the interaction of $C_3H_{6(ads)}$ with NO_2 or a mixture of NO + O_2 leads to the appearance of an EPR signal, which corresponds to a complex with the nuclear spin $I = 1$ (Fig. 2), makes it possible to assume the formation of a paramagnetic nitroxyl hydrocarbon complex. It is likely that the EPR signal belongs to the NO_2 fragment of the NO_2–HC complex and three spectral lines are caused by the interaction of unpaired electrons with the atomic nucleus of nitrogen. The similarity of the g-tensor (2.006) to the value of $g_e = 2.0023$ is explained by the freezing of the orbital angular momentum of electron in the NO_2–HC complex. Similar EPR signals were observed earlier in the spectrum of NO_2 in a rigid polymeric matrix [11] and also on the formation of paramagnetic nitroxyl hydrocarbon complexes on the surfaces of H-ZSM-5 and γ-Al_2O_3 [18, 28]. Under the conditions of the thermovacuum treatment of a ZrO_2 sample, the EPR signal corresponding to NO_2–HC was retained to 500 K. In the course of decomposition of this complex at temperatures higher than 230°C, a signal with $g_{av} = 2$ appeared in the EPR spectrum and its intensity increased with the degree of decomposition. The circumstance that this signal was detected on the decomposition of nitroxyl hydrocarbon complexes makes it possible to believe that it was due to coke [29].

The study of the reactivity of the NO_2–HC complex showed that its interaction with NO leads to the formation of a diamagnetic complex with a rather low stability. However, its destruction under the conditions of evacuation at 25°C was accompanied by the restoration of the EPR signal due to NO_2–HC, whereas it is likely that the decomposition of a similar adduct of [NO] · [NO_2–HC] at an elevated temperature (230°C or higher) will lead to the formation of a nitrogen–nitrogen bond and the release of N_2 or N_2O into a gas phase.

The conclusion on the formation of a nitroxyl hydrocarbon complex of one additional type was made based on the data TPD. As a result of the interaction of $C_3H_{6(ads)}$ with nitrogen dioxide, new peaks appeared in the thermal desorption spectra (Fig. 1, curve *7*), which were absent after the individual adsorption of C_3H_6, NO, NO_2, O_2, and NO + O_2 (Fig. 1, curves *1*–*6*). We relate their appearance with the decomposition of the complex formed upon the interaction of NO_2 with the hydrocarbon activated on the coordinatively unsaturated Zr^{4+} ions.

The formation of the NO_2–HC complex was confirmed by the results of spectral measurements. Figure 3 (spectra *3* and *4*) shows the IR spectra obtained in the course of the admission of a flow of the reaction mixture of NO + C_3H_6 + O_2/N_2 to the sample. The appearance of a new absorption band at 1565 cm^{-1} in them can be noted. This band was absent from the IR spectra of a sample after the adsorption of both propylene and the mixtures of C_3H_6 + O_2 and NO + O_2. Therefore, it should be attributed to the vibrations of the adsorption complex formed upon the interaction of NO_x with propylene and/or its partial oxidation products. It is likely that the band at 1565 cm^{-1} is related to the formation of the NO_2–HC complexes on the catalyst surface.

The fact that the band at 1565 cm^{-1} is not related to the ν_{as} vibrations of carboxyl groups and it corresponds to the formation of a new complex of the NO_2–HC type was confirmed by the absence of a proportional change in the intensities of absorption bands at 1565 and 1440 cm^{-1} during the admission of a mixture of NO + C_3H_6 + O_2 to the catalyst surface. The intensities of these two bands were comparable in the first 3 min of adsorption; however, later (with an increase in the time of catalyst interaction with the reaction mixture), the absorption band intensity at 1565 cm^{-1} increased more rapidly. This band became the most intense 20 min after gas admission. The comparison of the intensities of different bands in the course of catalyst interaction with the mixture of NO + C_3H_6 + O_2 at 150°C allowed us to assume that the formation of the NO_2–HC complexes results from the interaction of NO_x with the acetate-like surface complexes.

The data obtained by TPD and EPR spectroscopy showed that the joint adsorption of reactants, as well as the adsorption of a mixture of NO + O_2, is qualitatively and quantitatively different from the adsorption of the individual reactants. The amount of desorbed molecules sharply increased (Fig. 1), and this was due to the formation of paramagnetic and nonparamagnetic surface complexes, which contained the NO_2 group and a hydrocarbon fragment.

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