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Formation Mechanism of O_2^- Radical Anions in the Adsorption of NO + O_2 and NO_2 + O_2 Mixtures on ZrO_2 According to EPR and TPD Data

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Abstract—The effects of various factors on the formation of O_2^- radical anions in the adsorption of an NO + O_2 or $NO_2 + O_2$ mixture on ZrO_2 were studied. It was found that the thermal stability of the O_2^- species depends on the composition of the adsorbed gas. It was suggested that nitrogen oxide complexes on ZrO_2 centers are responsible for the formation of O_2^-. These centers are formed upon the treatment of the oxide in a vacuum; however, they are different from both coordinatively unsaturated Zr^{4+} cations (NO adsorption centers at 77 K) and Zr^{4+}–O^-–O^-–Zr^{4+} centers, at which O_2^- are formed because of the adsorption of $H_2 + O_2$. Based on the experimental data, the mechanism of O_2^- formation in the adsorption of an NO + O_2 mixture is discussed.

INTRODUCTION

Presently, a search for efficient catalysts for the selective catalytic reduction of NO_x by hydrocarbons in an excess of oxygen is of paramount importance. It was found [1–3] that catalysts prepared from zirconia are highly active and stable in this reaction. Previously [4], we studied the adsorption of NO + O_2 and $NO_2 + O_2$ mixtures on ZrO_2 assuming that the activity of catalysts can be due to the activation of reactants on ZrO_2. We found that O_2^- radical anions were formed in the adsorption of these mixtures, unlike the adsorption of individual oxygen, on zirconia.

The formation of O_2^- was observed previously in the adsorption of $H_2 + O_2$, $CH_4 + O_2$, and HX + O_2 (HX is a weak acid) on MgO [5–8] and of $C_3H_6 + O_2$ on Mo/MgO and V/MgO catalysts [9]. In the cited publications, it was believed that an (H^-, CH_4^-, X^-)–electron donor complex is formed on the Lewis acid–base pairs of the oxide at the first step of the reaction as a result of the dissociative adsorption of a reactant. At the second step, the O_2^- radical anion is formed because of electron transfer from this complex to an adsorbed oxygen molecule.

The mechanism of O_2^- formation in the adsorption of NO + O_2 has hardly been studied at all. Note that only Martinez-Arias *et al.* [10] detected O_2^- in the adsorption of oxygen on CeO_2 with preadsorbed NO. They suggested that, in this process, electrons appeared as a result of the reaction of NO molecules with oxide anions $NO + O^{2-} \longrightarrow NO_2^- + e$.

Various complexes are formed in the adsorption of NO on zirconia. Thus, NO adsorbed on coordinatively unsaturated Zr^{4+} ions at 77 K was observed by EPR spectroscopy [11]. Nitrosyl ($NO^{\delta+}$–$Zr^{(4-\delta)+}$), nitrite (NO_2^-), and nitrate (NO_3^-) complexes of different stability were detected at 293 K by IR spectroscopy [12, 13]. However, it is unclear which of these complexes participate in the formation of O_2^- radical anions.

In this work, using EPR spectroscopy and temperature-programmed desorption (TPD), we studied in detail conditions under which O_2^- radical anions are formed in the adsorption of NO + O_2 and $NO_2 + O_2$ mixtures on ZrO_2 and the properties of O_2^-. We also attempted to identify the adsorbed NO species that participate in the formation of O_2^- and the nature of the active centers of ZrO_2.

EXPERIMENTAL

Zirconium dioxide was synthesized according to the published procedure [14], which allowed us to prepare the $ZrO(NO_3)_2$ oxide stabilized in tetragonal (t) and monoclinic (m) modifications and characterized by a high specific surface area ($S_{sp} \approx 140$ m^2/g) from parent

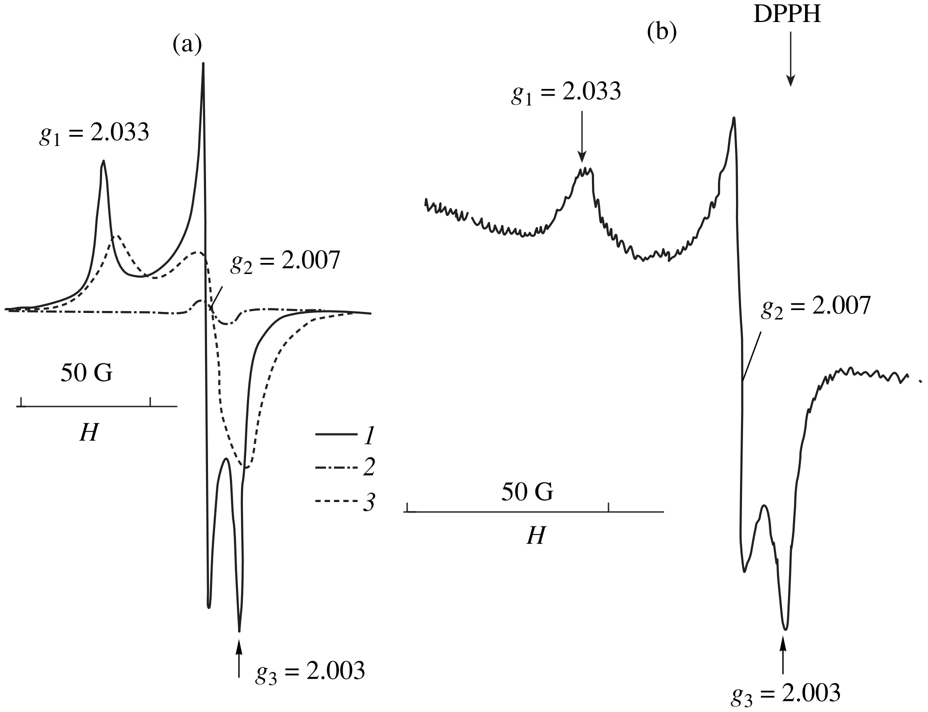

Fig. 1. EPR spectra of ZrO_2 samples (T_v = 970 K) (a) (*1*) after the adsorption of NO + O_2 at 293 K for 5 min followed by evacuation of the sample and after the subsequent admission of (*2*) NO or (*3*) O_2 onto the sample and (b) after the photoadsorption of O_2 for 1 h.

$ZrO(NO_3)_2$ (of analytical grade). The surface areas of the samples were measured by the BET method using argon adsorption in a helium flow at 77 K. Monoclinic and tetragonal phases in ZrO_2 samples were determined by XRD analysis on a Dron-3 diffractometer. Changes in the phase composition of samples after heating at different temperatures for 1 h were monitored by measuring intensity ratios (J_m^{XRD}/J_m^{XRD}) between the characteristic XRD lines of these phases.

The EPR and TPD measurements were performed using a weighed sample (50 mg) in an EPR ampule under vacuum conditions. The test sample was evacuated to 10^{-4} Pa at room temperature and then heated at a specified temperature (T_v) for 1 h in a vacuum. After the thermal activation of ZrO_2, a test gas was adsorbed on it at a given temperature, and the EPR spectra of the resulting complexes were recorded.

The EPR experiments were performed on an EPR-V spectrometer with a Diapazon temperature-controlled attachment, which made it possible to record spectra at 77–600 K. The amount of paramagnetic species was determined by the double integration of EPR spectra with the use of $CuSO_4 \cdot 5H_2O$ as a reference sample. In this case, the accuracy of measurements was no worse than 20%.

In the TPD experiments, a test gas was adsorbed on the thermally activated oxide at room temperature for 5 min; next, the sample was evacuated for 20 min and heated at a rate of 12 K/min under continuous evacuation. The desorption spectrum (the pressure of a desorbed gas as a function of temperature) was measured using a Pirani manometer [15]. The products of desorption were also analyzed on an MX-7303 mass spectrometer with sampling through a capillary. The detector of the mass spectrometer was precalibrated with the test gases. Thus, NO, O_2, and NO_2^- were detected by measuring peaks at 30, 32, and 46 amu, respectively.

The amount of adsorbed molecules in a sample was determined from the pressure of the gas desorbed from the oxide in thermal desorption experiments without evacuating the gas phase. In the case of separate gas adsorption, the accuracy of these measurements was no worse than 20%.

RESULTS

Formation of O_2^- in the Adsorption of NO + O_2 and NO_2 + O_2 on ZrO_2

After admitting oxygen ($P = 1 \times 10^3$ Pa and T = 77 or 293 K) onto ZrO_2 (T_v = 400–970 K), as well as after heating a sample in oxygen at 970 K followed by cooling to 293 or 77 K in O_2, the EPR spectra exhibited no signals. On the other hand, after heating a sample either in a vacuum or in oxygen, the admission of initially NO (P = 1–100 Pa) and then O_2 ($P = 10^2$ Pa) to ZrO_2 at 293 K resulted in the appearance of an EPR signal (Fig. 1a, spectrum *1*). Spectrum *1* was measured after evacuating a gas mixture at 293 K. Upon subsequently admitting NO ($P = 2 \times 10^2$ Pa), the signal disappeared

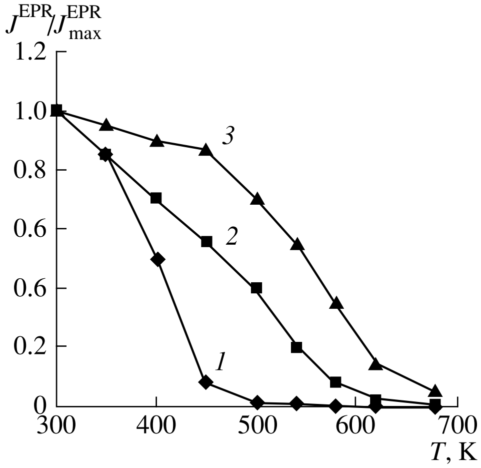

Fig. 2. Intensities of the EPR spectra of O_2^- on ZrO_2 (*1*) after the adsorption of NO + O_2, (*2*) after the photoadsorption of O_2, and (*3*) after the adsorption of H_2 + O_2 as functions of the temperature of heating the samples in a vacuum for 10 min.

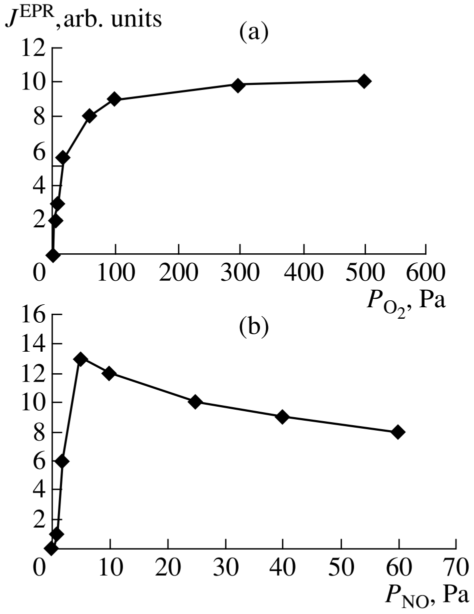

Fig. 3. Intensities of the EPR spectra of O_2^- formed after the adsorption of NO + O_2 on ZrO_2 (T_v = 970 K) at room temperature as functions of (a) O_2 pressure at P_{NO} = 10 Pa and (b) NO pressure at P_{O_2} = 3 × 10^2 Pa.

(spectrum *2*), and it became widened in an oxygen (P = 5 × 10^2 Pa) atmosphere (spectrum *3*). After evacuating the gases, the spectrum was fully restored.

Consequently, the above spectrum corresponds to a sufficiently stable complex formed upon the adsorption of NO + O_2. It is likely that the reversible effect of NO and O_2 molecules on the complexes is indicative of dipole–dipole interactions.

The parameters of the spectra of the complex recorded at 77 and 293 K were equal: g_1 = 2.033, g_2 = 2.007, and g_3 = 2.003. They are consistent with the corresponding g-tensor values of O_2^-, the EPR spectrum of which is shown in Fig. 1b. The spectrum was recorded after the photoadsorption of oxygen (UV + O_2) on ZrO_2 (T_v = 970 K) at 293 K and $P = 2 \times 10^3$ Pa. The photoadsorption was performed under irradiation of the sample with light from a DRSh-1000 lamp for 1 h.

The agreement between the shapes and parameters of spectra in Figs. 1a and 1b and published data [16, 17] allowed us to believe that O_2^- radical anions are formed in the adsorption of NO + O_2.

Upon admitting oxygen onto ZrO_2 (T_v = 970 K) with preadsorbed NO_2 (NO_2 was adsorbed at 293 K and 2 × 10^2 Pa for 5 min and then evacuated for 20 min), the same O_2^- radical anions were detected as in the case of the adsorption of NO + O_2. However, they disappeared after evacuating oxygen; this fact is indicative of their instability under these conditions.

The thermal stability of the O_2^-(NO + O_2) and O_2^- (UV + O_2) radical anions on ZrO_2 (T_v = 970 K) was studied. Figure 2 demonstrates the relative intensities (J^{EPR}/J^{EPR}_{max}) of the spectra of O_2^- radical anions as functions of the temperature of sample heating in a vacuum for 10 min. It can be seen in Fig. 2 that the signal intensity decreased with heating temperature regardless of the O_2^- preparation procedure. Thus, O_2^-(NO + O_2) were detected up to 540 K (curve *1*). After the disappearance of the spectrum of O_2^- as a result of heating the sample at 540 K, the subsequent adsorption of an NO + O_2 mixture at 293 K repeatedly produced the above species. This fact indicates that active centers remained upon the degradation of O_2^-. The O_2^- (UV + O_2) radical anions were detected up to 600 K (curve *2*). They were found more stable than the O_2^-(NO + O_2) radical anions.

The concentration of O_2^-(NO + O_2) depends on the pressure of admitted gases. This dependence was studied with ZrO_2 (T_v = 970 K) at room temperature. The O_2^- radical anions were generated by adding initially NO and then O_2 at specified pressures. Next, the sample was exposed to a gas atmosphere for 3 min and then evacuated to 10^{-4} Pa for 15 min. The spectrum was recorded after evacuating the sample. Next, the sample was repeatedly treated with the gases at a changed pressure of one of the components. It can be seen (Fig. 3a) that the concentration of radicals monotonically increased as the pressure of O_2 was increased from 1 to 3 × 10^2 Pa at a constant pressure of NO (10 Pa). At a

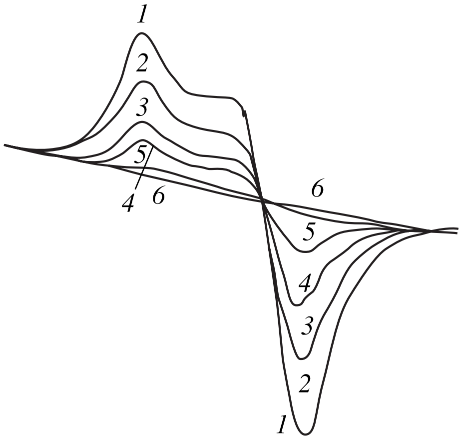

Fig. 4. EPR spectra of O_2^- on ZrO_2 upon the adsorption of NO + O_2 ($P_{NO} = 3 \times 10^2$ Pa, $P_{O_2} = 1 \times 10^3$ Pa, and T = 293 K) recorded after (*1*) 3, (*2*) 7, (*3*) 10, (*4*) 12, and (*5*) 15 min and (*6*) after the evacuation of the mixture for 60 min.

constant pressure of O_2 (3×10^2 Pa) and a pressure change of NO from 2 to 60 Pa, the concentration of O_2^- passed through a maximum at a nitrogen monoxide pressure equal to 5 Pa (Fig. 3b). It is likely that the concentration of O_2^- decreased because of the reaction of O_2^- with NO_2, which is formed in an NO + O_2 gas mixture. Indeed, on standing ZrO_2 in an NO + O_2 mixture ($P_{NO} = 3 \times 10^2$ Pa, $P_{O_2} = 1 \times 10^3$ Pa, and T = 293 K) for longer than 3 min, the intensity of the O_2^- spectrum decreased, and the signal completely disappeared after 15 min (Fig. 4). The evacuation for 1 h did not restore the EPR signal of O_2^-.

The concentration of O_2^- depends on the temperature of ZrO_2 heating in a vacuum. Figure 5 demonstrates that the concentrations of both O_2^-(NO + O_2) and O_2^- (UV + O_2) increased with T_v (curves *1* and *2*). The concentration of O_2^- (UV + O_2) was lower than that of O_2^-(NO + O_2) by a factor of ~10, and it was no higher than 3.0×10^{17} g^{-1} even after an increase in the photoadsorption time from 1 to 2 h. These data indicate that O_2^- radical anions are formed in the adsorption of NO + O_2 much more efficiently than in the photoadsorption of O_2.

An increase in the concentration of O_2^-(NO + O_2) with increasing temperature of the vacuum pretreatment of the oxide is indicative of an increase in the number of active sites, which is likely due to the surface dehydroxylation of ZrO_2.

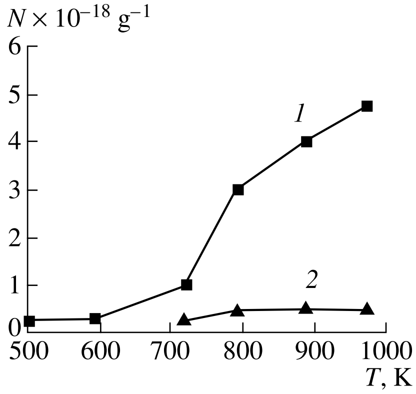

Fig. 5. Concentrations of O_2^- on ZrO_2 as functions of the temperature of sample pretreatment in a vacuum (*1*) after the adsorption of NO + O_2 for 5 min and (*2*) after the photoadsorption of oxygen for 1 h.

Adsorption of NO on ZrO_2 and the Interaction of Adsorbed NO with O_2 at 77 K According to EPR Data

An EPR signal appeared upon admitting NO (in an amount of 1.2×10^{21} molecule/g) onto ZrO_2 preheated at T_v = 800 K in a vacuum and then cooled to 77 K (Fig. 6). It was characterized by a broad anisotropic line with $g_{\|} = 1.94$ and by an amount of paramagnetic species equal to 6.0×10^{19} g^{-1}. The EPR spectrum remained unchanged upon evacuating the sample; however, it disappeared in the course of heating the sample from 77 to 293 K. In this case, NO was desorbed into a gas phase. The repeated adsorption of NO on the sample at 77 K resulted in the complete restoration of the EPR spectrum presented in Fig. 6.

An increase in the adsorbed gas dose from 1.2×10^{21} to 3.0×10^{21} molecule/g had no effect on the intensity of the spectrum, whereas a change in the dose to 1.0×10^{20} molecule/g decreased the intensity of the spectrum by a factor of ~10.

As well as published data [11], the above data suggest that the EPR signal that appears in the low-temperature adsorption of NO is due to NO molecules adsorbed on the surface of ZrO_2. The spectrum of adsorbed NO exhibits almost no HFS lines due to the interaction of an unpaired electron with the nuclear spin of nitrogen $I = 1$ in the NO molecule.

The g-tensor values of adsorbed molecules are close to the value of g_e. In this case, the levels of $2p\pi$ orbitals in a molecule of adsorbed NO are crystal-field split by the value of $\Delta E = 2\lambda(g_e - g_{\|})$, which is equal to 0.48 eV for the spin–orbital coupling constant in the NO molecule $\lambda = 0.015$ eV and $g_{\|} = 1.94$. This value of ΔE is indicative of strong perturbations of NO molecules upon adsorption. It is likely that surface hydroxyl groups cannot be adsorption sites in this case because their interaction with NO molecules is characterized by a smaller splitting of $\Delta E = 0.23$ eV [18].

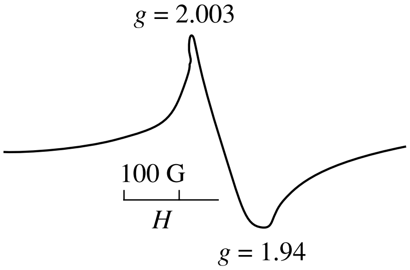

Fig. 6. EPR spectrum of a ZrO_2 sample (T_v = 800 K) after the adsorption of NO (1.2×10^{21} molecule/g) at T = 77 K.

The dependence of the amount of paramagnetic species and of the total amount of adsorbed NO molecules on the temperature of heating samples in a vacuum was studied. In these experiments, a sample of ZrO_2 was heated at T_v in a vacuum for 1 h; then, it was cooled to 77 K, and NO was added (1.2×10^{21} molecule/g). The sample was exposed to an NO atmosphere for 3 min and then evacuated. Next, the EPR spectrum of adsorbed NO molecules was recorded at 77 K, and the amount of these molecules was found. The total amount of adsorbed NO molecules was evaluated by a change in the pressure of a desorbed gas upon heating the sample from 77 to 293 K. Thereafter, the sample was heated in a vacuum at a higher temperature, and the experiment on NO adsorption was repeated under analogous conditions.

Figure 7 (curve *1*) indicates that the concentration of paramagnetic species on ZrO_2 increased from 1.3×10^{18} to 5.0×10^{19} g^{-1} as T_v was increased from 400 to 800 K. A further increase in the temperature up to 970 K decreased the concentration of paramagnetic species down to 1.0×10^{19} g^{-1}. The amount of desorbed NO (curve *2*) was symbatic with the concentration of paramagnetic species over a range from 400 to 970 K; however, the concentration of desorbed NO was higher than the concentration of NO observed by EPR spectroscopy.

Consequently, only a portion of adsorbed NO manifests itself in the EPR spectrum. Both the dimerization of NO molecules and the presence of adsorbed NO molecules subjected to an insignificant crystal-field gradient on the surface can be responsible for the inconsistency between the concentrations of adsorbed NO and NO detected by EPR [19].

A decrease in the concentration of adsorbed NO as T_v was changed from 800 to 970 K is due to a decrease in the sample surface area. As can be seen in Table 1, the surface area changed from 90 to 30 m^2/g in this temperature range. Indeed, the concentrations of adsorbed NO recalculated per unit surface area in the range $800 \le T_v \le 970$ K demonstrated that the total concentration of adsorbed NO increased from 1.3×10^{18} to 2.0×10^{18} molecule/m^2. However, the concentration of paramagnetic species changed only slightly, and it was equal to 4.5×10^{17} or 3.3×10^{17} m^{-2} at 800 or 970 K, respectively.

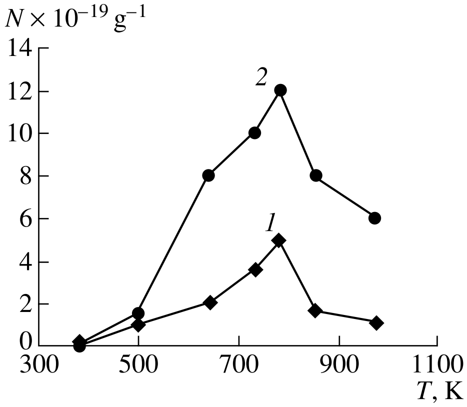

Fig. 7. (*1*) Concentration of adsorbed NO detected by EPR spectroscopy and (*2*) the amount of adsorbed NO molecules as functions of the temperature of sample preheating in a vacuum.

An increase in both the total amount of adsorbed NO and the amount of NO detected by EPR is indicative of the appearance of new NO adsorption centers upon the dehydroxylation of the samples in a temperature range of 400–970 K. Lunina *et al.* [11] believed that the adsorbed NO molecules detected by EPR are localized at isolated coordinatively unsaturated Zr^{4+} ions. If this is the case, a change in the temperature of the thermal vacuum treatment of a sample from 400 to 970 K increases the number of coordinatively unsaturated Zr^{4+} ions in the sample. The NO molecules undergo strong perturbations due to the interaction with coordinatively unsaturated Zr^{4+} ions. However, no strong bond between NO and a coordinatively unsaturated Zr^{4+} ion is formed because the EPR spectrum of NO adsorbed on ZrO_2 fully disappeared at $T \ge 180$ K.

The EPR spectrum of NO adsorbed on ZrO_2 ($T_v <$ 800 K) at 77 K disappeared upon admitting oxygen (in an amount of 6.0×10^{20} molecule/g) onto the sample. In this case, new EPR signals did not appear. The evacuation of the sample at 77 K did not restore the initial EPR spectrum; however, the EPR spectrum was completely restored upon the subsequent adsorption of NO. On the other hand, after the disappearance of the spectrum of adsorbed NO in the presence of O_2 and the evacuation of the sample, the amount of desorbed gas upon heating the sample from 77 to 293 K was lower than that upon the thermal desorption of NO without oxygen treatment by a factor of ~20. Consequently, the interaction of adsorbed NO molecules with oxygen is accompanied by either the displacement of NO from the surface or, less probably, the formation of nonparamagnetic complexes, which are more tightly bound to the surface and removed from it at $T > 293$ K.

In addition to the disappearance of the EPR spectrum of NO adsorbed on ZrO_2 samples (T_v = 800–

973 K) in an oxygen atmosphere, the appearance of an EPR signal due to O_2^- radical anions was observed. The concentration of these radical anions was ~10 times lower than the concentration of O_2^- attained by the adsorption of an NO + O_2 mixture on this sample at 293 K. This fact is indicative of an activation character of the reaction of O_2^- radical anion formation.

Thus, the adsorption of NO on ZrO_2 at 77 K is physisorption, and this type of NO adsorption takes no part in the formation of O_2^-.

Adsorption of O_2, NO, NO_2, and an NO + O_2 Mixture on ZrO_2 at 293 K According to TPD Data

As O_2^- is efficiently formed in the combined adsorption of NO and O_2 and the adsorption of NO, O_2, or NO_2 on ZrO_2 did not result in the appearance of EPR signals at room temperature, the adsorption was studied by TPD.

Figure 8 demonstrates the TPD spectra after the adsorption of gaseous O_2, NO, NO_2, and an NO + O_2 mixture on ZrO_2 (T_v = 970 K) at room temperature for 5 min. It can be seen in Fig. 8 that, after the oxygen treatment of a sample, O_2 was hardly desorbed at all in a temperature range from 300 to 850 K (curve *1*). In the case of NO, two peaks were present in the TPD spectrum (curve *2*). The first most intense peak had a maximum at 400 K and a shoulder at 500 K. The second peak was located in the high-temperature region at 700 K. The total concentration of desorbed NO molecules was 8.0×10^{18} g^{-1}. The intensity of these peaks increased by a factor of 10 after the adsorption of NO_2 (curve *3*), and the amount of desorbed molecules increased to 1.4×10^{20} g^{-1}. In accordance with data on the thermal stability of complexes observed after the adsorption of both NO and NO_2 on ZrO_2 [12, 13], the desorption of NO at the first peak is likely due to the decomposition of nitrosyls and nitrites, whereas the desorption at the second peak is due to the decomposition of nitrates.

After the formation of O_2^- radical anions on the surface of ZrO_2 as a result of the adsorption of NO + O_2 for 5 min, the desorption spectrum (Fig. 8, curve *4*) consisted of four peaks with T_{max} = 380, 480, 550, and 750 K. The mass-spectrometric data (Fig. 9) indicate that O_2 (32 amu) and NO (30 amu) were desorbed at the first low-temperature peak at T_{max} = 380 K; NO was desorbed in a temperature range from 400 to 700 K, and the desorption of NO, O_2, and NO_2 (46 amu) was observed at the peak at 750 K. The total amount of desorbed molecules was equal to 2.0×10^{19} g^{-1}. In this case, the desorption of NO in a temperature range of 320–480 K can be ascribed to the decomposition of nitrosyls, and the peaks of NO, NO_2, and O_2 desorption at 750 K can be attributed to the decomposition of nitrates. The peak at T_{max} = 550 K corresponds to the desorption of NO formed in the decomposition of nitrites [20].

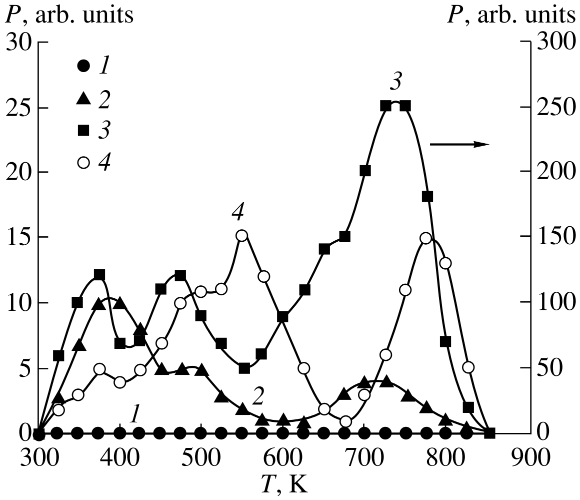

Fig. 8. TPD spectra after the adsorption of (*1*) O_2, (*2*) NO, and (*3*) NO_2 on ZrO_2 (T_v = 970 K) and (*4*) after the formation of the O_2^- radical anion by the adsorption of NO + O_2 at room temperature.

Oxygen was not desorbed after the treatment of a sample with oxygen, whereas oxygen desorption was observed after the formation of the O_2^- radical anion (Fig. 9). In this case, the temperature range of O_2 desorption coincided with the temperature range of decomposition of O_2^- radicals (Fig. 2). These facts allowed us to state that in this case oxygen desorption is associated with the decomposition of O_2^-.

The temperature range 293–700 K of the existence of nitrates (Fig. 8) is much wider than the region of existence of O_2^- radical anions (293–540 K, Fig. 2). The O_2^- radical anions decomposed in a vacuum at 540 K; however, thereafter, the sample retained the ability to form radical anions at 293 K. At the same time, according to TPD data (Figs. 8 and 9) and IR spectroscopy [13], nitrates were retained at the surface at 540 K. The adsorption of oxygen at 293 K on a sample containing undecomposed nitrates at 540 K did not

Table 1. Specific surface areas and phase compositions of ZrO_2 after heating at different temperatures in a helium flow for 1 h

Parameter	Treatment temperature, K		
	573	800	970
S_{sp}, m^2/g	140	90	30
J_m^{XRD} / J_t^{XRD}	1 : 1	2 : 1	3 : 1

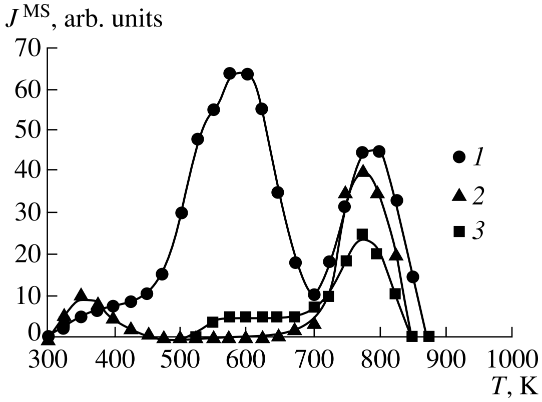

Fig. 9. Changes in the mass-spectrometric peak intensities (J^{MS}) at (*1*) 30, (*2*) 32, and (*3*) 46 amu in the course of TPD after the formation of the O_2^- radical by the adsorption of $NO + O_2$.

result in the formation of O_2^-. Consequently, nitrates do not serve as electron donors in the formation of O_2^- radical anions.

DISCUSSION

Let us consider the conceivable mechanisms of O_2^- formation in the adsorption of $NO + O_2$ and $NO_2 + O_2$.

The adsorption of O_2 on ZrO_2 (T_v = 500–970 K) at 293 K does not produce O_2^-; however, under these conditions, O_2^- is formed in the adsorption of an $NO + O_2$ mixture (see Fig. 2). Thus, nitrogen oxide compounds that are electron donors for the formation of O_2^- occur at the surface of ZrO_2.

Facts such as an increase in the amount of O_2^- as the ZrO_2 pretreatment temperature was increased from 500 to 970 K (Fig. 5) and equal amounts of O_2^- on samples preheated in oxygen, hydrogen, or a vacuum at 970 K for 1 h suggest that the dehydroxylation of ZrO_2 likely produces centers for O_2^- formation. We believe that these can be coordinatively unsaturated Zr^{4+} ions and O^{2-} and that electron donors are formed in the adsorption of NO at these centers.

The EPR data indicate that the molecules of NO adsorbed at the coordinatively unsaturated Zr^{4+} ions at 77 K do not form strong bonds with them. They are easily replaced by oxygen from the surface at 77 K, or they undergo desorption at $T \geq 180$ K. On the other hand, according to TPD data (Fig. 8) and IR spectroscopy [12, 13], the adsorption of NO, hypothetically, at O^{2-} at 293 K forms nitrates, which decompose at $T > 600$ K. Both weakly bound adsorbed NO species and nitrates were found to be inactive in the formation of O_2^-.

Nitrosyls and nitrites are formed along with nitrates in the adsorption of NO and $NO + O_2$ on ZrO_2. The decomposition of these compounds is accompanied by the desorption of NO at 380–550 K (Fig. 8). The temperature ranges of decomposition of these complexes overlap with the temperature range 300–540 K in which O_2^- radical anions undergo decomposition (Fig. 2). Moreover, quantitative TPD measurements indicated that after the adsorption of NO on ZrO_2 (T_v = 970 K) the amount of desorbed molecules (8.0×10^{18} g^{-1}) corresponds to the amount of O_2^- radical anions (6.0×10^{18} g^{-1}) formed by the adsorption of an $NO + O_2$ mixture on this sample. In the latter case, the total amount of desorbed molecules was 2.0×10^{19} g^{-1}. Approximately half of them were due to the decomposition of nitrates at $T > 600$ K, the other half, to the decomposition of nitrosyls and nitrites.

The overlapping of the temperature ranges of decomposition of nitrosyls, nitrites, and O_2^- radical anions; the correspondence of the concentration of O_2^- to the concentration of desorbed NO molecules after the decomposition of nitrosyls and nitrites; and the regeneration of the oxide activity upon O_2^- decomposition in a vacuum at 540 K allow us to consider the participation of these complexes in the formation of O_2^-.

In a number of publications [10, 12, 21–23] devoted to the adsorption of NO and NO_2 on various oxides, including ZrO_2, it was suggested that nitrites are formed by the interaction of NO molecules with O^{2-} ions at the M^{n+}–O^{2-} centers according to the reaction

$$M^{n+} - O^{2-} + NO \longrightarrow M^{(n-1)+} - NO_2^-. \qquad (I)$$

Reaction (I) demonstrates that in the formation of nitrite an unpaired electron is transferred from an NO molecule to an oxide cation (M^{n+}). This reaction can also be a source of electrons in the formation of O_2^- by the adsorption of $NO + O_2$ at Zr^{4+}–O^{2-} centers. The participation of nitrosyls in the formation of O_2^- is less probable. Nitrosyls are formed by the reaction of NO with Zr^{4+} cations. These complexes have the coordination bond $NO^{\delta+}$–$Zr^{(4-\delta)+}$, and electron density is partially transferred from the molecule to the cation, as distinct from the complete electron transfer in (I).

The interaction of "free" electrons formed in reaction (I) with oxygen molecules on the surface can produce O_2^- radical anions, which should be stabilized at oxide cations. The EPR spectra of O_2^- after the adsorption of $NO + O_2$ and $NO_2 + O_2$ mixtures and after the photoadsorption of O_2 exhibited the same parameters $g_1 = 2.033$, $g_2 = 2.007$, and $g_3 = 2.003$ (Figs. 1a and 1b). Thus, regardless of the procedure used for preparing O_2^-, these radical anions were trapped at surface centers of the same type. According to the ion model [16], the cationic charge 4+ corresponds to the tensor component $g_1 = 2.033$; that is, the O_2^- radical anions are localized at the Zr^{4+} cations.

As mentioned above, the $O_2^-(NO + O_2)$ radical anions are reasonably stable. They underwent complete degradation only at 540 K. We estimated the activation energy of oxygen desorption in the decomposition of $O_2^-(NO + O_2)$ using the equation $E = 35RT_{max}$, which was derived from a first-order rate equation for desorption with the rate constant $k = 10^{13}\exp(-E/RT)$ s^{-1} at the heating rate β = 12 K/min [24]. We found E = 102 kJ/mol for a maximum rate of oxygen desorption at T_{max} = 350 K (Fig. 9). This value is comparable with the heat of O_2^- formation (75–100 kJ/mol) measured by the adsorption of oxygen on MoO_3/MgO and MoO_3/Al_2O_3 [25, 26].

The reaction of O_2^- formation in the adsorption of $NO + O_2$ exhibits an activation character because it occurs at 293 K, whereas it was not observed at 77 K. This reaction consists of several steps such as the formation of free electrons in the adsorption of NO, electron transfer, and the trapping of electrons by adsorbed O_2 molecules. It is likely that the first step is responsible for the activation character. According to (I), new N–O bonds are formed at this step. The activation energy of this process should be higher than the activation energy of the reaction associated with electron transfer and the subsequent O_2^- formation at the Zr^{4+} cation.

According to Ramis [23], it is believed that, in the case of O_2^- formation in the adsorption of $NO_2 + O_2$, "free" electrons result from the formation of nitrates at the same centers Zr^{4+}–O^{2-} in accordance with the equation

$$M^{n+} - O^{2-} + NO_2 \longrightarrow M^{(n-1)+} - NO_3^-. \qquad (II)$$

Previously [4], we assumed that the Zr^{4+}–O^-–O^-–Zr^{4+} pairs can serve as active centers for the formation of $O_2^-(NO + O_2)$ because O_2^- is formed at this type of center in the adsorption of an $H_2 + O_2$ mixture, and the amount of these centers should increase as the temperature of the thermal vacuum treatment of oxides is increased because of surface dehydroxylation [5–8]. This assumption was tested in this study.

Thus, the O_2^- radical anions with the parameters g_1 = 2.038, g_2 = 2.011, and g_3 = 2.004, which are close to the parameters of $O_2^-(NO + O_2)$, are formed in the adsorption of $H_2 + O_2$ ($P_{H_2} = 1 \times 10^3$ Pa, $P_{O_2} = 2 \times 10^2$ Pa, and T = 293 K) on ZrO_2 (T_v = 970 K). However, as can be seen in Fig. 2, $O_2^-(H_2 + O_2)$ are more stable than $O_2^-(NO + O_2)$. The appearance of $O_2^-(H_2 + O_2)$ on the surface of ZrO_2 is indicative of the presence of the Zr^{4+}–O^-–O^-–Zr^{4+} centers on the surface.

The rate of formation of O_2^- radical anions in the adsorption of $H_2 + O_2$ is much lower than that in the adsorption of $NO + O_2$. Thus, in the case of $NO + O_2$, the concentration of O_2^- reached a maximum value of 6.0×10^{18} g^{-1} after the treatment of the oxide with the mixture for 3–5 min. In the case of $H_2 + O_2$, the concentration of O_2^- slowly increased with time during the adsorption of the mixture, and it was no higher than 1.0×10^{18} g^{-1} after the treatment of the sample with the mixture for 1 h.

Table 2 demonstrates the dependence of the concentrations of $O_2^-(NO + O_2)$ and $O_2^-(H_2 + O_2)$ radical anions on the temperature of the vacuum treatment of the samples and on the time (τ) of the adsorption of the mixtures. It can be seen that the amounts of O_2^- after the adsorption of $NO + O_2$ (τ = 5 min) or $H_2 + O_2$ (τ = 14 h) were approximately equal, and they varied by no more than 25% as T_v was increased from 970 to 1090 K or as the adsorption time of the $H_2 + O_2$ mixture was increased up to 34 h.

Moreover, after the adsorption of first $NO + O_2$ and then $H_2 + O_2$, the concentration of O_2^- was equal to the sum of O_2^- concentrations obtained after the separate adsorption of the mixtures. A similar result was observed upon the adsorption of first $H_2 + O_2$ and then $NO + O_2$. Consequently, the $O_2^-(NO + O_2)$ and $O_2^-(H_2 + O_2)$ radical anions are formed independently of one another at different centers.

It is likely that the rates of O_2^- formation in the adsorption of $NO + O_2$ and $H_2 + O_2$ (Table 2) are different because the rate of formation of an electron-donor complex in the adsorption of NO is higher than the rate of formation of this complex in the dissociative adsorption of H_2 molecules.

Table 2. Concentrations (N) O_2^- $(NO + O_2)$ and O_2^- $(H_2 + O_2)$ on ZrO_2 at different temperatures (T_v) of the sample treatment in a vacuum and at different adsorption times (τ) at 293 K

Mixture	τ	T_v, K	$N \times 10^{-18}$, g^{-1}
$NO + O_2$	3–5 min	970	6.0
$H_2 + O_2$	14 h	970	7.5
$H_2 + O_2$	38 h	970	7.5
$NO + O_2$	3–5 min	1090	6.0
$H_2 + O_2$	14 h	1090	7.8
$(H_2 + O_2) + (NO + O_2)$	14 h + 5 min	970	13.0
$(NO + O_2) + (H_2 + O_2)$	5 min + 14 h	970	13.5

Thus, the thermal vacuum treatment of ZrO_2 at 500–970 K results in the formation of two types of acid–base centers on the surface. We believe that O_2^- is formed at Zr^{4+}–O^{2-} or Zr^{4+}–O^-–O^-–Zr^{4+} centers in the adsorption of an NO + O_2 or H_2 + O_2 mixture, respectively. The concentrations of these centers evaluated from the amounts of O_2^- are similar and equal to ~(6–7) × 10^{18} g^{-1} (Table 1); however, they are lower than the concentration of coordinatively unsaturated Zr^{4+} ions, which is equal to (1–5) × 10^{19} g^{-1} (see Fig. 7). The differences in the concentrations of O_2^- and coordinatively unsaturated Zr^{4+} ions and in the behaviors of these concentrations as functions of the temperature of the vacuum treatment of ZrO_2 (Figs. 5 and 7) count in favor of the hypothesis that "free" electrons are produced in the reaction of NO with coordinatively unsaturated O^{2-} ions rather than Zr^{4+}.

Different stabilities of O_2^- radical anions prepared by the adsorption of NO + O_2, NO_2 + O_2, and H_2 + O_2 (Fig. 2) can be explained on the assumption that reversed electron transfer is a rate-limiting step in the decomposition of O_2^-. Indeed, before desorption, O_2^- should give an electron to NO_2^-, NO_3^-, or H^+ species or to the solid. As the above species exhibit different electron affinities, the thermal stabilities of the neighboring O_2^- radicals are also different. However, the different stabilities of O_2^- radical anions, which have equal *g*-tensor parameters, obtained at different compositions of adsorbed gases cannot be explained in terms of the ion model.

The results of this work demonstrate that O_2^- radical anions are formed in the adsorption of NO + O_2 and NO_2 + O_2 mixtures on ZrO_2. We believe that they can participate in the formation of surface nitrates and in the activation of hydrocarbons in the selective catalytic reduction of NO_x. The role of O_2^- in the selective catalytic reduction of NO_x with hydrocarbons in an excess of oxygen on zirconia-based catalysts will be examined in subsequent studies.

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