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The ESR Study of O_2^- Radical Anion Formation during Adsorption of an NO + O_2 Mixture and O_2 on ZrO_2 and (0.1–2.0)% MoO_3/ZrO_2

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Abstract—The influence of conditions of the preliminary thermal treatment of ZrO_2, ammonia and methanol adsorption, and MoO_3 supporting on O_2^- formation during the adsorption of an NO + O_2 mixture was studied. The interaction of O_2^- with different molecules was studied. Adsorbed ammonia and methanol, as well as supported Mo^{6+} ions, were shown to inhibit this reaction. The involvement of the Zr^{4+} and O^{2-} Lewis sites in the reaction was concluded. The interaction of ammonia and methanol with the O_2^- radical anions changed the *g* tensor parameters and decreased the thermal stability of O_2^- in the case of methanol. O_2^- radical anions were formed on the reduced (0.1–2.0)% MoO_3/ZrO_2 samples during the interaction of O_2 with the Mo^{5+} ions in the octahedral configuration. As in the case of O_2^- formation during NO + O_2 adsorption on ZrO_2, the radical anions were localized in the coordination spheres of the coordinately unsaturated Zr^{4+} ions. A change in the MoO_3 content of the samples from 0.1 to 0.5% led to an increase in the amount of O_2^-, whereas a change from 0.5 to 2.0% led to a decrease in the O_2^- amount due to the screening of the Zr^{4+} ions by oxo complexes and polymolybdates.

INTRODUCTION

Catalytic systems based on zirconium oxide are an area of much current interest [1–3]. These systems are highly stable and active in the selective catalytic reduction of NO_x by hydrocarbons in excess oxygen. However, the mechanism of NO_x selective catalytic reduction is poorly studied. Assuming that redox processes during NO_x selective catalytic reduction occur due to electron exchange between the adsorbed reactants and zirconium oxide, we found by ESR that the O_2^- radical anions were formed at room temperature during the adsorption of NO + O_2 and NO_2 + O_2 mixtures on ZrO_2. However, these radical anions are not observed when oxygen is adsorbed without nitrogen oxides [4]. Based on the properties of the surface nitrite–nitrate complexes and O_2^- radical anions, we proposed a possible mechanism for radical anion formation [5].

In this work, we gave special attention to the study of active sites in O_2^- formation during NO + O_2 adsorption ($\mathbf{O_2^-(NO + O_2)}$) on ZrO_2. The influence of both preliminary thermal treatment of ZrO_2 in a vacuum and an atmosphere of different gases (O_2, CO, and H_2) in the temperature interval 400–700°C and different surface compositions, which were created by the adsorption of the O_2, CO, H_2, NH_3, and CH_3OH gases and MoO_3 supported on ZrO_2, was studied. The formation of O_2^- during oxygen adsorption on MoO_3/ZrO_2 depending on the state of the molybdenum ions and their concentration was studied to reveal the nature of sites of O_2^- (NO + O_2) stabilization on ZrO_2.

EXPERIMENTAL

Zirconium oxide was prepared from hydroxides using a known procedure [6]. Zirconium tetroxide was precipitated from a solution of $ZrO(NO_3)_2$ by the addition of NH_4OH. The precipitate was filtered off, dried at 100°C, and calcined in air at 500°C for 5 h. Zirconium oxide thus prepared had a specific surface area S_{sp} = 50 m^2/g. The subsequent calcination of the oxide at 600–700°C decreased its surface area to 20–30 m^2/g, respectively. The specific surface area was determined by the BET method from low-temperature argon adsorption.

MoO_3/ZrO_2 samples were prepared by the impregnation of ZrO_2 with solutions of ammonium paramolybdate with different concentrations (calculated from 0.1–2.0 mol % MoO_3 to be supported) followed by drying at 100°C and calcination at 350°C in an air flow for 5 h. When the Mo^{6+} ions are uniformly distributed over the oxide surface, their concentration (0.1×10^{18}–2.0×10^{18} m^{-2}) is lower than the concentration (~5.0×10^{18} m^{-2}) corresponding to a monolayer coverage of the ZrO_2 surface by the octahedral MoO_6 oxo complexes [7].

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The ZrO_2 sample under study (50 mg) was placed in an ESR tube, which was evacuated to 10^{-4} Pa at room temperature and heated in a vacuum at a chosen temperature for 1 h. After this thermal treatment, the gas under study was adsorbed on the sample at room temperature, and ESR spectra of adsorption complexes were recorded. The number of adsorbed molecules was determined from a change in the gas pressure during adsorption using a Pirani gage [8]. Similar studies were carried out for the oxidized and reduced (0.1–2.0 mol %) MoO_3/ZrO_2 samples. In this case, the samples were evacuated at T, heated in O_2 or H_2 ($P_{O_2} = 10^2$ and $P_{H_2} = 10^3$ Pa) at this temperature for 1 h, and evacuated at 20°C.

ESR studies were carried out on an EPR-V spectrometer (X range) at room temperature. The number of paramagnetic species was determined from ESR spectra after double integration and comparison of these values with that of $CuSO_4 \cdot 5H_2O$ was used as a reference. The measurement accuracy was 20%.

The NO, CO, and O_2 gases were obtained under vacuum conditions using standard procedures [9]. Standard reagents (NH_3, anhydrous methanol, and propylene) were also used.

RESULTS

1. Formation of the O_2^- Radical Anions during NO + O_2 Adsorption on ZrO_2 and Their Interaction with Different Molecules

Adsorption of an NO + O_2 mixture ($P_{NO} = 10$ Pa, $P_{O_2} = 10^2$ Pa, and $T = 20$°C) on thermally activated ZrO_2 ($T = 500$°C) results in the appearance of an ESR signal with the parameters $g_1 = 2.033$, $g_2 = 2.008$, and $g_3 = 2.003$ (Fig. 1, curve *1*), which corresponds to the O_2^- radical anions localized in the coordination sphere of the Zr^{4+} cations [5]. The temperature of ZrO_2 vacuum treatment has no effect on the g tensor parameters but affects the O_2^- concentration. It can be seen from the data in the table that the concentration increases from 0.8×10^{16} to 4.5×10^{16} m^{-2} as the temperature changes from 350 to 700°C. Heating of the sample in dioxygen or carbon dioxide at $T = 350$–700°C and $P = 10^2$–10^3 Pa for 1 h followed by cooling and evacuation of ZrO_2 at 20°C practically does not change the O_2^- concentration. After ZrO_2 treatment in H_2 under similar conditions, the O_2^- concentration increases from 0.3×10^{16} to 2.6×10^{16} m^{-2} with an increase in the treatment temperature but remains lower than the O_2 concentration for ZrO_2 preheated in a vacuum (see table).

Thus, the concentration of the reaction sites increases with an increase in the temperature of the thermal vacuum treatment of ZrO_2. The sites do not perish upon thermal treatment of the sample in O_2 and CO but their number decreases after the sample was thermally treated in H_2.

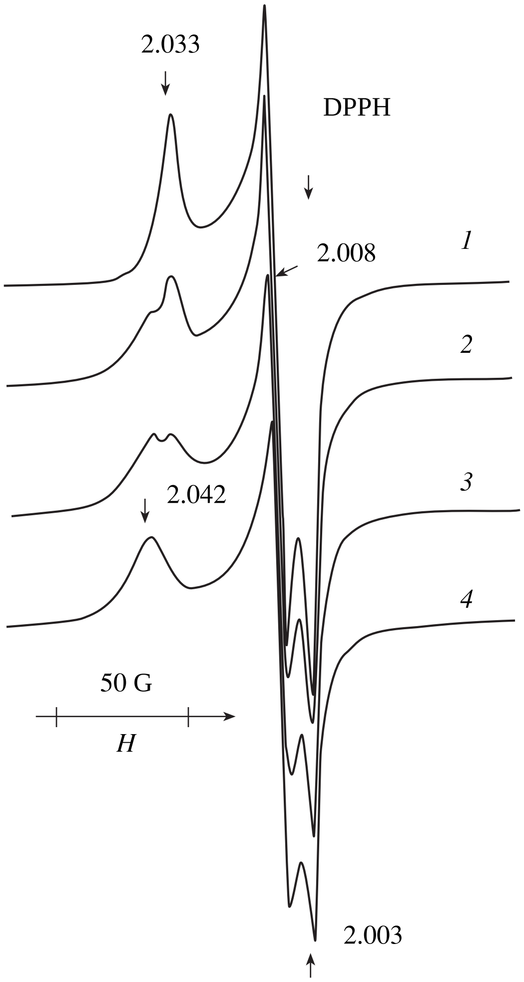

Fig. 1. ESR spectra of O_2^- on ZrO_2 ($T = 500$°C) in a vacuum after (*1*) adsorption of an NO + O_2 mixture at 20°C and subsequent adsorption of NH_3 in an amount of (*2*) 0.8×10^{18}, (*3*) 1.4×10^{18}, and (*4*) 2.0×10^{18} m^{-2}.

The O_2^- radical anions behave in differently when interacting with different gases. For example, for CO,

Concentrations of the O_2^- radical anions ($\times 10^{-16}$ m^{-2}) at different temperatures of ZrO_2 treatment in a vacuum and in different gases

Conditions of treatment	T, °C				
	350	400	500	600	700
Vacuum	0.8	1.6	2.8	4.3	4.5
O_2	0.7	1.2	2.5	4.0	4.0
CO	0.8	1.3	2.6	3.7	3.0
H_2	0.3	0.6	1.2	2.6	2.6

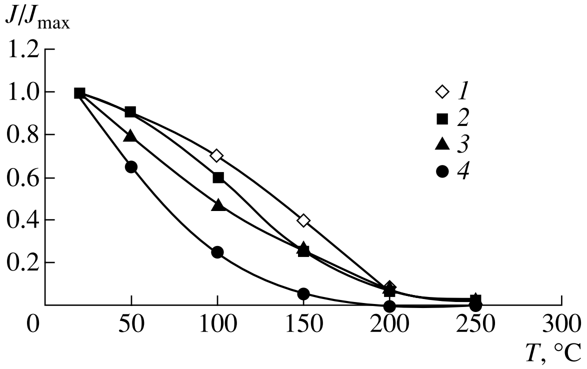

Fig. 2. Change in the intensity of the ESR spectrum of O_2^- with the temperature of ZrO_2 heating in (*1*) vacuum, (*2*) O_2, (*3*) H_2, and (*4*) C_3H_6 for 10 min.

H_2, and C_3H_6 ($P = 10^2$ Pa, $T = 20$°C), the ESR spectrum of O_2^- remains unchanged compared to the spectrum of the sample in a vacuum and, hence, O_2^- does not react with these gases. In the case of NO, as it was shown by us previously [5], the ESR spectrum of O_2^- disappears, whereas it is broadened in an O_2 atmosphere. The evacuation of gases recovers the ESR spectrum of O_2^- to the initial shape. Such reversible changes in the spectrum are attributed to the dipole–dipole interaction of the NO and O_2 paramagnetic molecules with the O_2^- radical anions.

It can be seen from data in Fig. 1 (curves *2–4*) that the interaction of ammonium with O_2^- changes the parameters of the ESR spectrum of the radical anion. When the amount of adsorbed NH_3 increases from 0.8×10^{18} to 2.0×10^{18} molecule/m^2, a line appears at $g = 2.042$ and that at $g_1 = 2.033$ disappears. The ESR lines at g factors equal to 2.008 and 2.003 do not shift. The O_2^- concentration determined from the spectra before and after ammonia adsorption are 2.8×10^{16} and 2.0×10^{16} m^{-2}, respectively. Spectra *2–4* in Fig. 1 contain no HFS lines caused by the interaction of unpaired electrons with the nitrogen nuclei in NH_3 molecules ($I = 1$) indicating, most probably, the absence of an exchange interaction between the adsorbed NH_3 and O_2^- molecules. Methanol adsorption (2.0×10^{18} molecule/m^2) decreases tenfold the intensity of the ESR spectrum of O_2^-. In this case, the g tensor parameters were $g_1 = 2.040$, $g_2 = 2.008$, and $g_3 = 2.003$.

According to the ion model [10], a change in g_1 of the O_2^- radical anions from 2.033 to 2.040–2.042 can be the result of a decrease in the effective charge of the Zr^{4+} cations in the (O_2^-–Zr^{4+}) complexes due to their interaction with the polar NH_3 and CH_3OH molecules.

The O_2^- radical anions on ZrO_2 are stable at 20°C and decompose on heating of the sample. A plot of the relative intensity of the ESR spectrum of O_2^- (J/J_{max}) vs. temperature of sample heating in a vacuum and the atmospheres of H_2, O_2, and C_3H_6 ($P = 10^2$–10^3 Pa) for 10 min is presented in Fig. 2. The rate of O_2^- disappearance in H_2 and O_2 does not exceed the rate of its decomposition in a vacuum. The radical anion disappears completely at 250°C. In propylene, O_2^- is observed only below 200°C, and the rate of its disappearance is higher than that in a vacuum. This can be due to the reaction of the O_2^- radical anions with propylene at $T > 50$°C [11].

The O_2^- radical anions interacting with adsorbed NH_3 and CH_3OH exhibit close g tensor parameters but different thermal stabilities. Their ESR spectra remain unchanged after ammonia and methanol evacuation at 20°C for 30 min, and their intensities decrease on heating of the sample in a vacuum. In the case of NH_3, the O_2^- radical anions are decomposed in the 50–250°C interval with the same rate as O_2^- on ZrO_2 without ammonia, and O_2^- disappears at 50°C in the case of CH_3OH. These data confirm the conclusion [12] that methanol adsorption weakens the bond of the O_2^- radical anions with the Zr^{4+} cations, displacing them from the coordination sphere of the cations and decreasing the signal of O_2^-.

2. On the Role of the ZrO_2 Acid–Base Sites in the Formation of the O_2^-(NO + O_2) Radical Anions

Ammonia and methanol on ZrO_2 are known to be adsorbed on acid and base sites, respectively, and the MoO_3 supporting changes the number of both acid and base sites [13]. Assuming that the sites formed upon the thermal vacuum treatment of ZrO_2 are important for O_2^- radical anion formation, we studied the influence of adsorbed ammonia and methanol and supported MoO_3 on O_2^- formation during NO + O_2 adsorption.

In experiments with ammonia or methanol, the sample was first heated in a vacuum at 500°C for 1 h, and then a portion of NH_3 (CH_3OH) was adsorbed at 100°C to exclude physically adsorbed molecules on the surface [13]. After the whole portion of the gas was adsorbed, the sample was cooled to 20°C, an NO + O_2 mixture was adsorbed, and the ESR spectrum of the O_2^- radical anions was recorded. Then the sample was heated in a vacuum at 500°C, and adsorption was carried out under the same conditions, changing the amount of adsorbed NH_3 (CH_3OH). For this sequence of gas adsorption, the ESR spectrum exhibited a signal

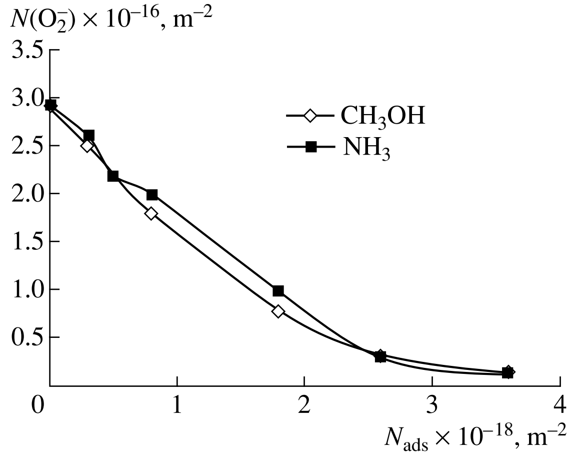

Fig. 3. Plot of the concentration of the O_2^- (NO + O_2) radical anions vs. concentration of preadsorbed ammonia and methanol on ZrO_2.

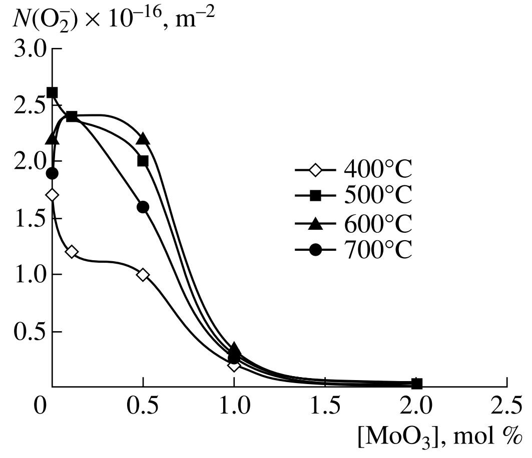

Fig. 4. Plot of the O_2^- (NO + O_2) concentration vs. MoO_3 content of the MoO_3/ZrO_2 samples preoxidized at 400–700°C.

only from the O_2^- radical anions with the parameters $g_1 = 2.033$, $g_2 = 2.008$, and $g_3 = 2.003$. As can be seen from Fig. 3, when the amount of adsorbed NH_3 or CH_3OH increases to 2.6×10^{18} m^{-2}, the amount of O_2^- decreases from 2.8×10^{16} to 0.3×10^{16} m^{-2}.

The oxidized (0.1–2.0) mol % MoO_3/ZrO_2 samples (O_2, T = 400–700°C) do not give ESR signals. Only after an NO + O_2 mixture was adsorbed on the samples at 20°C, a signal corresponding to O_2^- on the Zr^{4+} ions appears. The plots of the O_2^- concentration vs. MoO_3 content of the samples and temperature of oxidation are presented in Fig. 4. It is seen that the O_2^- concentration decreases with an increase in the MoO_3 concentration regardless of the oxidation temperature. The O_2^- radical anions are absent from the 2.0 mol % MoO_3/ZrO_2 sample.

Thus, adsorbed ammonia and methanol and supported MoO_3 inhibit O_2^- formation during NO + O_2 adsorption on ZrO_2.

3. The Formation of Mo^{5+} Cations during Reduction of the (0.1–2.0)% MoO_3/ZrO_2 Samples with Hydrogen and Their Interaction with NO and O_2

The ESR spectra of the reduced 0.1 and 2.0% MoO_3/ZrO_2 samples (H_2, T = 400–700°C) are presented in Fig. 5. It can be seen that they consist of a broad complicated anisotropic line in an g tensor region of 1.952–1.872 characteristic of the octahedral or tetrahedral Mo^{5+} oxo complexes on the surface of the molybdenum-containing catalysts [14, 15]. The low-intensity lines in spectrum (a) can be attributed to the HFS caused by splitting of nuclei of the ^{95}Mo and ^{97}Mo isotopes (I = 5/2) [16]. When the MoO_3 concentration in the samples increases, the intensity of the ESR spectra of Mo^{5+} increases (Figs. 5a and 5b), the lines are broadened, and the HFS lines disappear (Figs. 5b and 5c) due to the dipole–dipole interaction between the Mo^{5+} ions. The plots of the Mo^{5+} concentration vs. MoO_3 concentration and temperature of reduction of the samples are presented in Fig. 6. It can be seen that the Mo^{5+} concentration increases with an increase in both the reduction temperature from 400 to 700°C and the MoO_3 concentration from 0.1 to 2.0% and reaches 30–60% of the amount of supported Mo^{6+} ions.

In an NO atmosphere (P = 50 Pa, T = 20°C), the ESR spectra of Mo^{5+} disappear but are completely recovered upon gas evacuation. The reversible change in the spectra indicates the dipole–dipole interaction of the NO molecules with the Mo^{5+} cations and localization of the Mo^{5+} cations on the oxide surface.

When O_2 is adsorbed (P = 50 Pa, T = 20°C, t = 5 min) on the reduced (0.1–2.0)% MoO_3/ZrO_2 samples, the intensity of the Mo^{5+} signal first decreases, and a new complicated signal appears. Its spectrum is presented in Fig. 7 (curve *1*) for the 0.1% MoO_3/ZrO_2 sample (H_2, T = 700°C). Spectrum *1* consists of intense lines with the parameters $g_1 = 2.033$, $g_2 = 2.008$, and $g_3 = 2.003$ (signal A) and a low-intensity line at g = 2.060 (signal B). Signal A disappears after heating of the sample in a vacuum at 250°C, whereas signal B disappears at 50°C. The g tensor parameters and thermal stability of signal A correspond to those of the O_2^- radical anions observed during adsorption of an NO + O_2 mixture on pure ZrO_2 (see Fig. 7, curve *2*). The nature of signal B is unclear. Perhaps, it is related to a minor amount of the O_2^- radical anions for which the first component of the g tensor is $g_1 = 2.060$, whereas g_2 and g_3 are close to 2.008 and 2.003, respectively. According

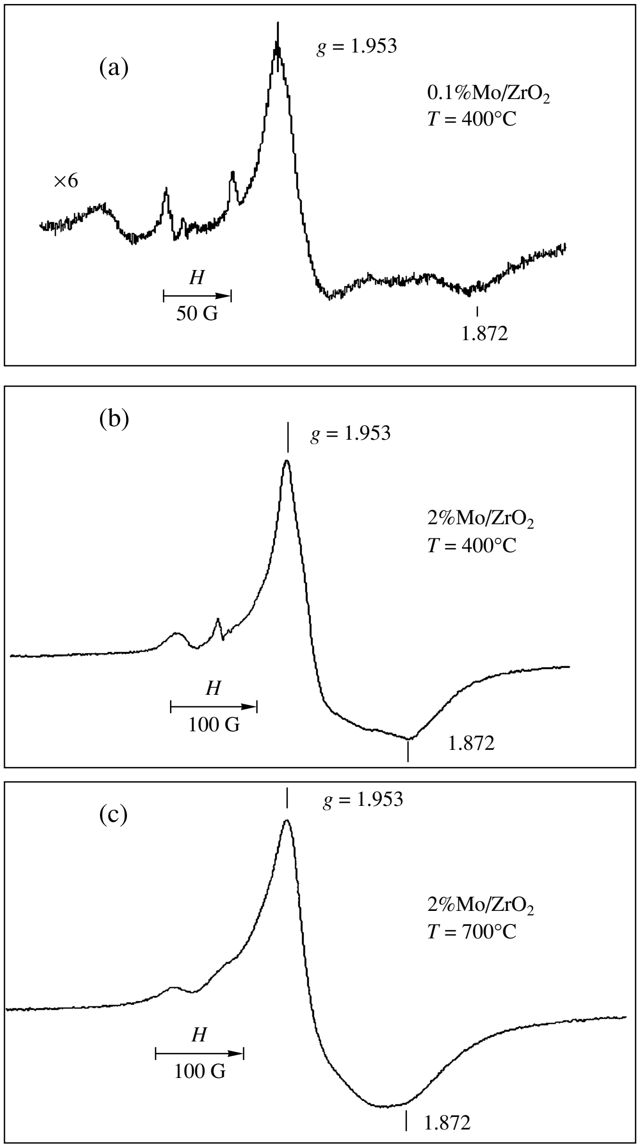

Fig. 5. ESR spectra of the samples containing (a) 0.1 and (b, c) 2.0% MoO_3 after they were reduced at temperatures: (a, b) 400 and (c) 700°C.

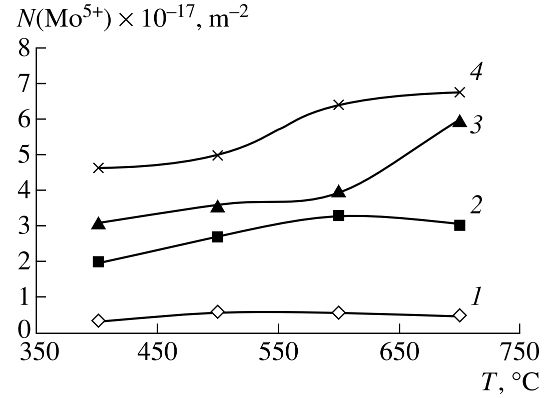

Fig. 6. Plots of the Mo^{5+} ion concentration vs. temperature of reduction in H_2 of the MoO_3/ZrO_2 samples containing (*1*) 0.1, (*2*) 0.5, (*3*) 1.0, and (*4*) 2.0% MoO_3.

to the ion model [10], such O_2^- radical anions are stabilized in the coordination sphere of cations with a charge of (2+)–(3+).

The plots of the O_2^- concentration on the reduced MoO_3/ZrO_2 samples vs. MoO_3 concentration and temperature of catalyst reduction are shown in Fig. 8. The O_2^- concentration increases with an increase in the MoO_3 concentration from 0.1 to 0.5% and then decreases regardless of the temperature of catalyst reduction with a change in the MoO_3 concentration from 0.5 to 2.0%. The maximum O_2^- concentration (1.6×10^{17} m^{-2}) is observed for the 0.5% MoO_3/ZrO_2 sample (H_2, T = 600°C). In this case, for oxygen adsorption, the concentration of the Mo^{5+} cations changes from 3.0×10^{17} to 1.0×10^{17} m^{-2}. Their difference (2×10^{18} m^{-2}) corresponds to the amount of the oxidized Mo^{5+} cations and is comparable with the amount of the O_2^- radical anions formed. This suggests that the Mo^{5+} cations are electron donors in O_2^- formation during O_2 adsorption on the reduced (0.1–2.0)% MoO_3/ZrO_2 samples. A plot of the O_2^- concentration vs. the MoO_3 concentration with an extremum indicates that some Zr^{4+} cations are deactivated due to supporting of molybdenum oxide on ZrO_2.

DISCUSSION

1. Active Sites of O_2^- Formation during NO + O_2 Adsorption on ZrO_2 and Their Deactivation by Ammonia, Methanol, and Mo^{6+} Ions

Brønsted acid sites, Lewis acid sites, and base sites (Zr^{4+} and O^{2-} in a concentration of ~10^{18} m^{-2}) are known [17] to be formed on the surface of ZrO_2 samples obtained by hydroxide decomposition at 400 and 600°C in a vacuum. The influence of ammonia and methanol on the formation of O_2^- (NO + O_2) indicates that the acid–base sites are involved in the reaction. In this case, their concentration should increase with an increase in the temperature of preliminary treatment of the sample in a vacuum from 350 to 700°C because, as can be seen from the data in the table, the O_2^- concentration increases.

We believe that O_2^- formation during NO + O_2 adsorption occurs on the Zr^{4+} and O^{2-} Lewis sites. Let us consider their involvement in the reaction. The O_2^- radical anions (NO + O_2) on ZrO_2 and O_2^- radical anions (O_2) on the reduced (0.1–2.0)% MoO_3/ZrO_2 samples are characterized by the same *g* tensor param-

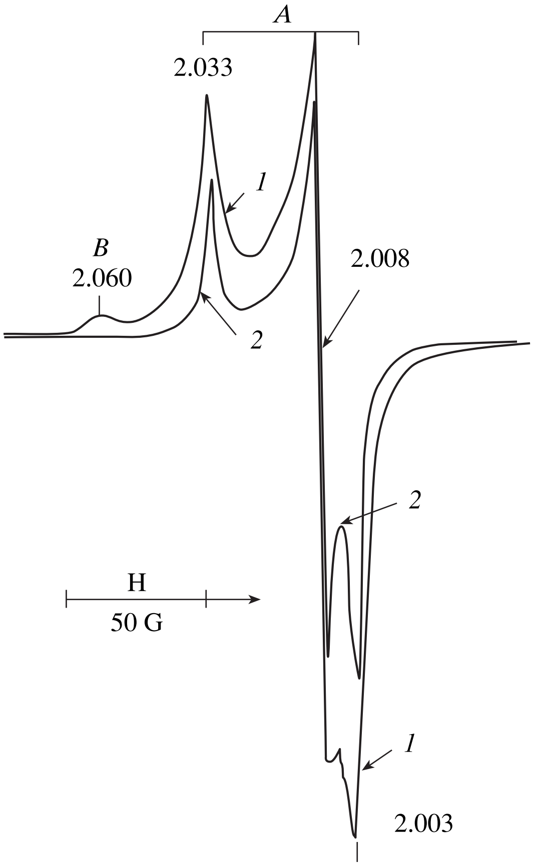

Fig. 7. ESR spectra of O_2^- on (*1*) 0.1% MoO_3/ZrO_2 (H_2, T = 700°C) after O_2 adsorption and (*2*) ZrO_2 (T = 600°C) after adsorption of an NO + O_2 mixture at 20°C.

eters (g_1 = 2.033, g_2 = 2.008, and g_3 = 2.003 (Fig. 7)) and the same stability. Therefore, they are localized on ZrO_2 cations of the same type, regardless of the type of O_2^- generation on the ZrO_2 and MoO_3/ZrO_2 samples. According to the ion model [10], a cation charge of 4+ corresponds to g_1 = 2.033. This implies that the Zr^{4+} ions are the centers of stabilization of the O_2^- radical anions.

According to the data presented in Fig. 3, for NH_3 adsorption on ZrO_2 in an amount of 3×10^{18} molecule/m^2 corresponding to a number of Zr^{4+} ions of 3.3×10^{18} m^{-2} on the surface, the amount of O_2^- (NO + O_2) decreases tenfold. In this case, ammonia is adsorbed on the ZrO_2 Brønsted and Lewis acid sites [13]. Therefore, the inhibition of O_2^- formation (NO + O_2) on ZrO_2 by ammonia is related to NH_3 adsorption on the Zr^{4+} sites.

We believed [5] that complexes formed during NO adsorption on the O_2^- sites are electron donors in the formation of the O_2^- radical anions (NO + O_2) on ZrO_2. The inhibition of this reaction by methanol (Fig. 3) is likely due to the poisoning of the O^{2-} sites by the formation of stable compounds on these sites, such as dioxymethylene and carbonates, [13]. When the O^{2-} sites are deactivated by methanol, the rate of formation of electron-donating complexes decreases and, hence, the amount of O_2^- formed also decreases.

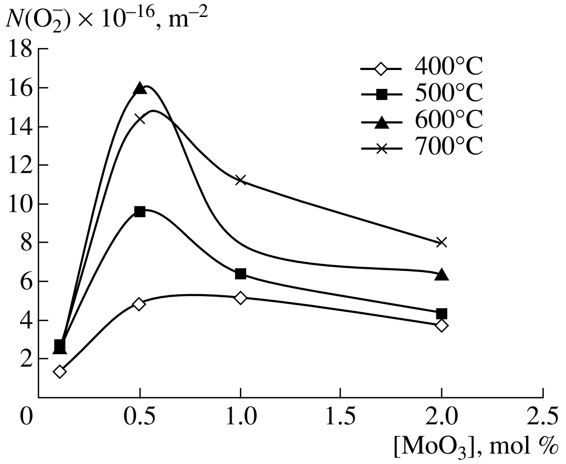

Fig. 8. Plots of the concentration of O_2^- formed during oxygen adsorption vs. MoO_3 content of the (0.1–2.0)% MoO_3/ZrO_2 samples and temperatures of their prereduction in H_2.

A decrease in the amount of O_2^- (NO + O_2) with an increase in the MoO_3 content of the (0.1–2.0)% MoO_3/ZrO_2 samples (Fig. 4) indicates the influence of supported molybdenum on the formation of reaction sites. It is known that the dehydroxylation of the samples containing 0.1–2.0% MoO_3 in an oxygen flow results in the formation of isolated molybdenum oxo complexes and dimeric polymolybdates on the ZrO_2 surface, where the Mo^{6+} cations are bound to the surface and outer-lattice O^{2-} ions, and the MoO_3 and $Zr(MoO_4)_2$ phases are not formed [7]. The immobilization of the Mo^{6+} cations on the O^{2-} ions of the surface decreases the probability of formation of the O^{2-} Lewis sites during thermal treatment of the samples. On the other hand, the oxo complexes and polymolybdates can shield some of the Zr^{4+} cations. In our case, the Zr^{4+} cations are not completely shielded on the (0.1–2.0)% MoO_3/ZrO_2 samples because the maximum concentration of the supported Mo^{6+} ions (2×10^{18} m^{-2}) is 1.5-fold lower than the Zr^{4+} concentration on the surface and 2.5-fold lower than the concentration corresponding to a monolayer coverage of MoO_6 octahedra. This is also indicated by the formation of the O_2^- radical anions during oxygen adsorption on the reduced (0.1–2.0)% MoO_3/ZrO_2 samples (Fig. 8). These data suggest that the Mo^{6+} ions inhibit O_2^-(NO + O_2) formation on

ZrO_2 due to a decrease in the O^{2-} sites rather than Zr^{4+} sites during the formation of the oxo complexes and polymolybdates on (0.1–2.0)%MoO_3/ZrO_2.

The Mo^{6+} ions inhibit $O_2^-(NO + O_2)$ formation more efficiently than the adsorbed methanol molecules, which follows from a comparison of the data presented in Figs. 3 and 4. For example, an increase in the concentration of the supported Mo^{6+} ions from 0.1×10^{18} to 2.0×10^{18} m^{-2} decreases the O_2^- concentration from 2.8×10^{16} m^{-2} to zero, while the O_2^- concentration only decreases ~8 times after methanol (~2×10^{18} m^{-2}) was adsorbed on ZrO_2. This fact can be explained as follows. When the concentrations of Mo^{6+} ions and adsorbed methanol molecules on the surface are equal, the Mo^{6+} ions are likely to bind more O^{2-} ions than the adsorbed methanol molecules and products of its transformation (dioxymethylene and carbonates).

The numbers of methanol molecules and Mo^{6+} ions deactivating the O^{2-} sites differ by two orders of magnitude from the number of $O_2^-(NO + O_2)$. Only some O^{2-} sites are likely to be active in $O_2^-(NO + O_2)$ formation. This is indicated by the published data [5] according to which the ZrO_2 surface contains oxygen sites involved in O_2^- formation during the adsorption of an $H_2 + O_2$ mixture and inactive in $O_2^-(NO + O_2)$ formation.

Although methanol and ammonia deactivate different reaction sites of $O_2^-(NO + O_2)$ formation on ZrO_2, the adsorption of these reactants in equal amounts results in the same decrease in the number of $O_2^-(NO + O_2)$ radical anions (see Fig. 3). Perhaps, the Zr^{4+}–O^{2-} pairs are the reaction sites on ZrO_2 instead of individual Zr^{4+} and O^{2-} ions.

It is of interest that the combined adsorption of dioxygen with ammonia or methanol produces O_2^- on MgO [11]. However, this type of reaction was not found for ZrO_2, which is possibly due to different reactivities of the ammonia and methanol adsorption sites on ZrO_2 and MgO. For example, dioxymethylene and carbonates are formed by the reaction of methanol with O^{2-} (ZrO_2) [13], whereas the reaction of methanol with O^{2-} (MgO) leads to the formation of OH^- and CH_3O^- involved in O_2^- formation [11].

2. Formation of O_2^- during Interaction of Dioxygen with Mo^{5+} Cations on Reduced (0.1–2.0)% MoO_3/ZrO_2 Samples

The O_2^- radical anions are formed by oxygen adsorption only on the (0.1–2.0)% MoO_3/ZrO_2 samples preliminarily reduced in hydrogen. As shown previously, they are stabilized mainly in the coordination sphere of the Zr^{4+} ions. In this case, the Mo^{5+} cations are electron donors. This is indicated by such facts as a simultaneous increase in the concentrations of O_2^- and Mo^{5+} ions in the (0.1–0.5)%MoO_3/ZrO_2 samples (see Figs. 5 and 7) and close concentrations of the O_2^- radical anions formed (1.6×10^{17} m^{-2}) and oxidized Mo^{5+} cations (2.0×10^{17} m^{-2}) during O_2 adsorption on the 0.5%MoO_3/ZrO_2 sample. Based on these data and the results in [18], we propose that O_2^- are formed in Zr^{4+} due to the electron transfer from either the Mo^{5+} cation or (Mo^{6+}–O_2^-) complex to the (O_2–Zr^{4+}) adsorption complex, which is localized near the Mo^{5+} cation.

The samples containing the MoO_3 amount greater than 0.5% exhibit the reverse correlation between the amounts of the O_2^- radical anions and Mo^{5+} cations. In this case, the concentration of the Mo^{5+} ions increases with an increase in the MoO_3 concentration (Fig. 6), and the O_2^- concentration decreases (Fig. 8). This can be assigned to a decrease in the concentration of the Zr^{4+} ions due to their screening by the oxo complexes and polymolybdates.

The coordination of the Mo^{5+} ions on a ZrO_2 surface is of interest. The authors of [15] showed that in the molybdenum-containing catalysts the Mo^{5+} ions in the octahedral or tetrahedral coordination were characterized by $g_\perp$ and $g_\parallel$ values in the 1.92–1.95 and 1.87–1.94 intervals, respectively. The Mo^{5+} ions on the ZrO_2 surface are characterized by the following g tensor values: $g_\perp = 1.953$ and $g_\parallel = 1.872$. However, these facts do not unambiguously suggest the coordination of the Mo^{5+} ions.

According to Raman spectroscopic data, after the dehydroxylation of the MoO_x/ZrO_2 catalysts at different temperatures, the surface contains the tetrahedral MoO_4 (393–973 K), octahedral MoO_6 (673 K), and pyramidal O–MoO_4 (973 K) oxo complexes [7]. They are reduced by hydrogen at different temperatures. Temperature-programmed reduction data show that the reduction temperature of the Mo^{6+} ions in the octahedral coordination (400°C) is much lower than that of reduction of the Mo^{6+} ions in the tetrahedral coordination (700°C) [19]. These complexes should also differ in the parameters of the g tensor anisotropy [20]. For example, for the tetrahedral coordination of ions in the d^1 configuration, a theoretical calculation of the g tensor anisotropy ($\Delta g = g_\perp - g_\parallel$) gives a value much higher than the experimental one $\Delta g = 0.08$, which was obtained for $g_\perp = 1.952$ and $g_\parallel = 1.872$ taken from the ESR spectra in Fig. 5.

Coincidence of the temperature of hydrogen reduction of the (0.1–2.0)%MoO_3/ZrO_2 samples (at which a signal from the Mo^{5+} cations appears in the ESR spectrum (see Fig. 6)), according to the temperature-programmed reduction data, with the reduction temperature of the Mo^{6+} ions in the octahedral coordination and analysis of the g tensor anisotropy values suggest that the ESR signal at $g = 1.952–1.872$ in the spectra of the reduced (0.1–2.0)%MoO_3/ZrO_2 samples corresponds to the Mo^{5+} cations in a strongly distorted octahedral coordination. It is noteworthy that it cannot be attributed to the O–MoO_4 oxo complexes because they are formed at 700°C due to the decomposition of the dimeric polymolybdates, and their appearance on the surface after polymolybdate reduction by hydrogen at 400°C is improbable.

According to the ESR data, the number of the Mo^{5+} cations on the surface of the reduced (0.1–2.0)% MoO_3/ZrO_2 samples is 30–60% of the supported Mo^{6+} ions (Fig. 6). The remaining part of supported ions can exist as isolated Mo^{5+} ions in the tetrahedral coordination and dimeric ($–Mo^{5+}–O^{2–}–Mo^{5+}–$) polymolybdates in which the molybdenum cations are linked by oxygen bridges. These forms are not detected by ESR at 20°C because of the short time of spin-lattice relaxation or the high symmetry of the oxo complexes [21], or due to the exchange interaction between the ions in the $Mo^{5+}–O^{2–}–Mo^{5+}$ pairs [22].

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