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The Mechanism of Selective NO_x Reduction by Hydrocarbons in Excess Oxygen on Oxide Catalysts: III. Adsorption Properties of the Commercial STK Catalyst

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Abstract—According to X-ray diffraction data, the STK catalyst is a mixture of Fe_2O_3 and Cr_2O_3. The temperature-programmed reduction spectrum exhibited two reduction peaks: one, with T_{max} = 250°C, corresponds to the reduction process $Cr_2O_3 \longrightarrow CrO$ and the other, with T_{max} = 360°C, corresponds to the reduction $Fe_2O_3 \longrightarrow Fe_3O_4$. The results of thermal desorption measurements suggest that the individual adsorption of oxygen on the surface of the STK catalyst is low; in this case (according to IR-spectroscopic data), an atomic form is the main species. Surface nitrite–nitrate complexes are formed upon the adsorption of NO. Nitrite and nitrate complexes desorbed at maximum rates at 105 and 160°C, respectively. Unlike the NTK-10-1 catalyst, the NO species, which desorbed at high temperatures (250–400°C), was absent from the surface of STK. Propane adsorbed at room temperature to form surface compounds containing an acetate group. The interaction of propane with the surface of the STK catalyst at reaction temperatures resulted in strong surface reduction.

INTRODUCTION

Previously [1–8], a certain phenomenon of synergism, found in studies of the catalytic activity of a mechanical mixture of catalysts, was described. This phenomenon consists in a superadditive increase in the catalytic activity of a mechanical mixture of catalysts as compared with the activities of the individual constituents of the catalyst mixture.

In the preceding papers [7, 8], we reported the selective reduction of NO by methane and propane on the commercial oxide catalysts STK, Ni–Cr oxide, and NTK-10-1, which do not contain noble metals. Mechanical binary mixtures of these commercial catalysts exhibited a synergistic effect. It is likely that this synergism is rather common [9, 10], although the mechanism of this phenomenon is poorly understood.

Previously [1, 2], based on kinetic and thermal desorption measurements, we found experimental conditions under which synergism was observed and hypothesized its mechanism. We found that detailed mechanisms of the processes on each of the particular catalysts that constitute a mechanical mixture should be known in order to reveal the nature of the synergism. A detailed mechanistic study on a Cu–Zn–Al catalyst (NTK-10-1) [11, 12] demonstrated that surface nitrite and nitrate complexes play an important role in the reaction. It follows from the results of spectroscopic and kinetic measurements that the nitrate complex is a reaction intermediate at temperatures higher than 150°C. The next step of the process is the reaction of this complex with adsorbed propane to form a nitro organic compound, which not only can afford reaction products in an oxidizing atmosphere but also can undergo oxidation with the release of nitrogen oxides into a gas phase.

Below 150°C, the reaction occurs via the formation and consumption of the nitrite complex. This process explains the unexpectedly high activity of the catalyst at low temperatures. In this work, we performed an analogous mechanistic study of the selective catalytic reduction of NO_x using hydrocarbons (HC–SCR) on a Fe–Cr–O catalyst (STK). The main goal of this study was to examine the interaction of process reagents and their mixtures with the catalyst surface.

EXPERIMENTAL

The physicochemical properties of the catalyst were studied using X-ray spectrum analysis, X-ray diffraction (XRD), temperature-programmed reduction (TPR), and specific surface area measurements.

The composition and properties of surface compounds were studied using temperature-programmed desorption (TPD) combined with the measurement of the IR spectra of surface complexes in transmission and diffuse-reflectance modes. In the measurement of diffuse-reflectance spectra, the weight of the catalyst sample placed in the IR-cell reactor was 1200–1300 mg; in the measurement of transmission spectra, the weight of

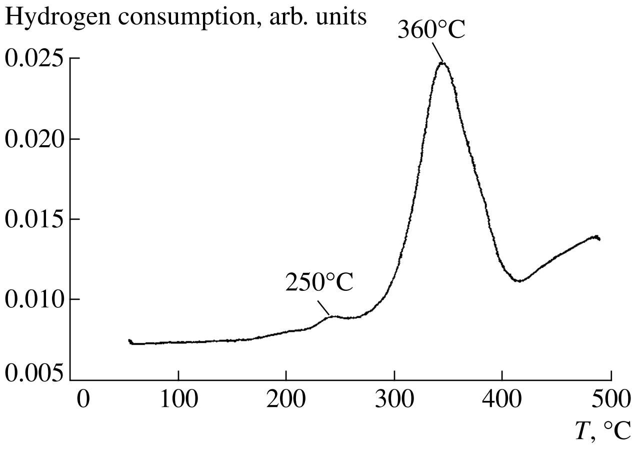

Fig. 1. TPR spectrum of the STK catalyst.

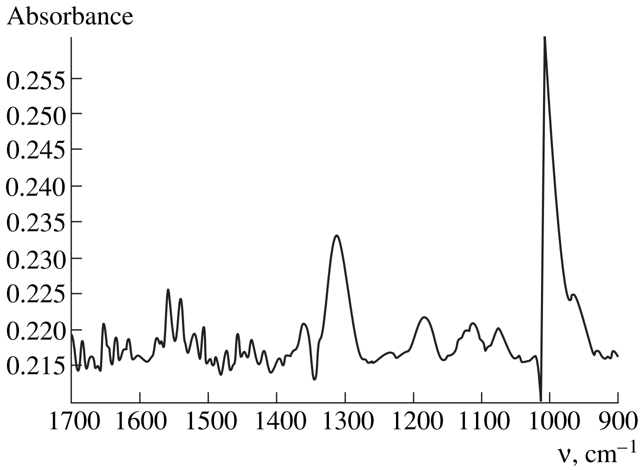

Fig. 2. IR spectrum of oxygen adsorbed on the surface of the STK catalyst.

the pellet was 54–76 mg. The IR spectra were measured on a Perkin-Elmer FTIR RXI spectrometer.

To determine the composition of desorbed products, vacuum experiments with mass spectrometric analysis were performed with the use of a 113-mg catalyst sample.

The concentrations of reactants in starting mixtures were varied in the ranges 0–0.22% NO, 0–0.67% C_3H_8, and 0–3.5% O_2. Propane was used as a reducing agent. Nitrogen was a carrier gas. The flow rate of a reaction mixture was 150 ml/min (9000 h^{-1}). All of the gases were dried in accordance with standard procedures using traps containing anhydrone and ascarite. Gas analysis at the inlet and outlet of the reactor cell was performed using a Beckman 951A chemiluminescence NO/NO_x analyzer and a Beckman 590 HC/CO analyzer.

The reaction temperature was controlled with a Miniterm 300.31 programmed temperature regulator; in this case, temperature deviations from specified values were no greater than 5 K. The experimental procedures were described in detail elsewhere [11, 12].

RESULTS

Catalyst Characterization

According to XRD data, the catalyst was a mixture of Fe_2O_3 and Cr_2O_3. The specific surface area of the sample was equal to 16 m^2/g.

We found by the X-ray spectrum analysis of a fresh catalyst and a catalyst used in the SCR reaction of nitrogen oxides with propane that the main constituent elements of the catalysts are iron (~60–70%), chromium (~6%), and oxygen.

According to TPR data (Fig. 1), the initial STK catalyst exhibited a reduction peak with T_{max} = 250°C, which corresponds to the reduction of chromium oxide. It is well known that the reduction of Cr^{3+} with hydrogen in the bulk is improbable at low temperatures. The interaction of hydrogen with oxygen in the surface layer of a catalyst is more probable [13]. According to published data [14, 15], chromium ions in high oxidation states, namely, Cr^{5+} and (or) Cr^{6+}, occur on the surface of chromium oxide after an oxidative treatment in oxygen at 400°C. Because CrO_3 is stable at temperatures no higher than 300°C, it is likely that the absorption of hydrogen at 250°C (Fig. 1) implies the reduction $Cr^{5+} \longrightarrow Cr^{3+}$. The degree of reduction of Cr_2O_3 decreased from 14.1 to 7.6% within three redox cycles. The reduction peak with T_{max} = 360°C corresponds to the reduction of Fe_2O_3. The reduction of Fe_2O_3 with hydrogen occurs stepwise: $Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow FeO \longrightarrow Fe$. The low-temperature ($T < 300$°C) peak is characteristic of the reduction $Fe_2O_3 \longrightarrow Fe_3O_4$ [16]. The high-temperature ($T > 400$°C) absorption of hydrogen (Fig. 1) is related to the subsequent reduction $Fe_3O_4 \longrightarrow FeO \longrightarrow Fe$. The degree of reduction of Fe_2O_3 changed from 7.5 to 7.0% upon repeating redox cycles.

Adsorption of Reaction Components

Adsorption of oxygen. The formation of adsorption oxygen complexes on the surface of STK was studied at room temperature in the course of adding oxygen to a sample preconditioned in N_2 at 400°C. Figure 2 shows the difference spectrum of the sample obtained by subtracting the spectrum of the sample in a flow of nitrogen from the spectrum of the sample in a flow of oxygen. It can be seen that the adsorption of oxygen resulted in an increase in the intensities of absorption bands at 1340 and 1000 cm^{-1}. The intensities and positions of these absorption bands depend on the temperature and treatment (oxidative or reductive) of the catalyst.

Adsorption of NO and NO + O_2. The thermal desorption experiments were performed in a cell for the measurement of diffuse-reflectance spectra after the

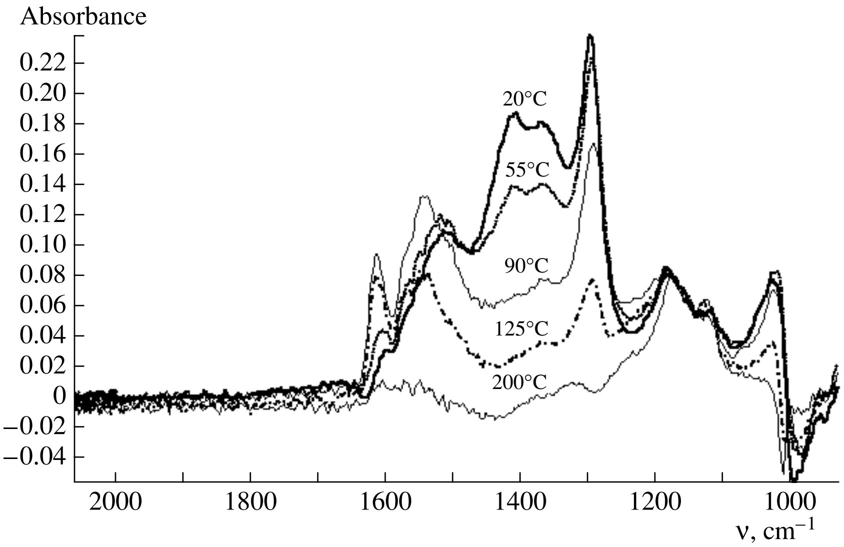

Fig. 3. IR spectra of the STK catalyst in the course of the TPD of NO_x after NO adsorption at room temperature.

adsorption of 0.1% NO/N_2. The TPD spectrum was characterized by the presence of a broad unresolved peak with T_{max} = 120°C. In accordance with gas-phase analysis data, NO_2 was the main product of desorption.

To obtain detailed information on the adsorption species of nitrogen oxides, we performed thermal desorption experiments with smaller catalyst amounts using transmission IR spectroscopy. In this case, absorption bands at 1610, 1540, 1410, and 1290 cm^{-1} were observed in the course of desorption (Fig. 3). Figure 4a shows the TPD spectrum after NO adsorption at room temperature, and Fig. 4b demonstrates changes in the absorption band intensities of surface complexes in the course of desorption. The TPD spectra exhibited two desorption peaks with T_{max} = 105 and 160°C. Table 1 compares data on the amounts of desorbed NO molecules for STK and NTK-10-1 catalysts as the constituents of a mechanical binary mixture.

In the course of thermal desorption (Fig. 4b), absorption bands at 1410 and 1290 cm^{-1} symbatically decrease with temperature, whereas the intensities of absorption bands at 1610 and 1540 cm^{-1} pass through a maximum at 90°C.

Table 1. Numbers (*N*) of NO molecules desorbed from the surfaces of STK and NTK-10-1 catalysts*

Catalyst	T_{max}, °C	$N \times 10^{-18}$
STK	105	2.0
	160	1.8
NTK-10-1	90	0.5
	150	2.4
	380	0.3

* The adsorption of NO at 20°C.

To determine which surface complexes are desorbed at the temperatures of TPD peaks, we performed an experiment in which thermal desorption was initiated at 100°C. In this case, we assumed that a low-temperature peak should be absent from the TPD spectrum and the corresponding absorption bands should be absent from the IR spectra. Indeed, the TPD spectrum (Fig. 5a) exhibited a peak at 160°C and the IR spectra (Fig. 5b) exhibited absorption bands at 1610 and 1540 cm^{-1}.

These facts allowed us to relate the low-temperature peak in the TPD spectrum (Fig. 4a) to a decrease in the intensities of absorption bands at 1410 and 1290 cm^{-1} and the high-temperature peak to absorption bands at 1610 and 1540 cm^{-1}.

It is of importance that the NO species, which is desorbed in the temperature range 250–400°C, is absent from the test STK catalyst. This species is predominant on the NTK-10-1 Cu–Zn–Al oxide catalyst (Table 1) [11].

Figure 6 shows the results of an experiment on the interaction of a flow of 0.1% NO/N_2 with the surface of the STK catalyst; these results were obtained using diffuse-reflectance spectroscopy. As in the above thermal-desorption experiment, the spectra exhibited absorption bands at 1610 and 1540 cm^{-1}, as well as an absorption band at 1290 cm^{-1} (Fig. 6a). The intensity of these absorption bands decreased with temperature and became equal to zero at 200–250°C. A decrease in the intensity of the absorption band at 1290 cm^{-1} was accompanied by the appearance and growth of an absorption band at 1340 cm^{-1}. In other words, the absorption band at 1340 cm^{-1} increased its intensity as the surface coverage with other complexes decreased. Figure 6b demonstrates the temperature dependence of the conversion of NO_x and the NO/NO_2 ratio in a gas flow at the outlet of the reactor cell, which were measured simultaneously. It can be seen that both of these

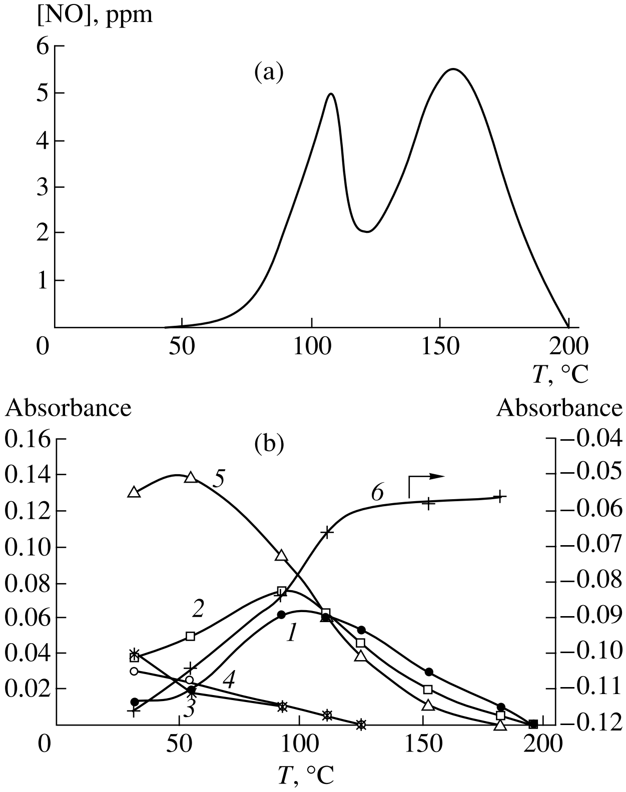

Fig. 4. (a) Spectrum of the TPD of NO_x after NO adsorption on the surface of the STK catalyst at room temperature; (b) changes in the intensities of the following absorption bands in the course of thermal desorption: (*1*) 1610, (*2*) 1540, (*3*) 1410, (*4*) 1360, (*5*) 1290, and (*6*) 1000 cm^{-1}.

functions have the shapes of curves with a minimum. Note that the apparent conversion at low temperatures (in the absence of a reducing agent) was related to the adsorption of NO_x (under conditions of our experiments, a steady-state surface coverage was not reached in 20 min when measurements were performed at each temperature). An increase in the NO/NO_2 ratio in the course of adsorption, as compared to this value for a gas at the inlet of the reactor cell, indicates that the rate of NO_2 adsorption is higher than the rate of NO adsorption. It is likely that the conversion of NO_x at high temperatures was associated with the decomposition of NO_x on a reduced portion of the catalyst.

Adsorption of C_3H_8 and C_3H_8 + O_2. The interaction of propane with the catalyst surface at reaction temperatures resulted in the strong reduction of this surface and, as a consequence, in a dramatic increase in the intrinsic absorption of the catalyst, which interfered with spectroscopic measurements. For this reason, the subsequent spectroscopic and kinetic studies were performed with the use of a propane + oxygen mixture.

Upon the interaction of a (0.5% C_3H_8 + 2.5% O_2)/N_2 gas mixture with the catalyst surface (the experiment was performed with decreasing sample temperature), the diffuse-reflectance spectra exhibited absorption bands at 2870, 1540, 1430, 1340, and 1250 cm^{-1} (Fig. 7). The intensities of the absorption bands at 1540, 1430, and 1250 cm^{-1} changed symbatically and passed through a maximum at 100–150°C. The intensity of the absorption band at 2870 cm^{-1} decreased with increasing temperature. The above absorption bands were not detected at 300–350°C.

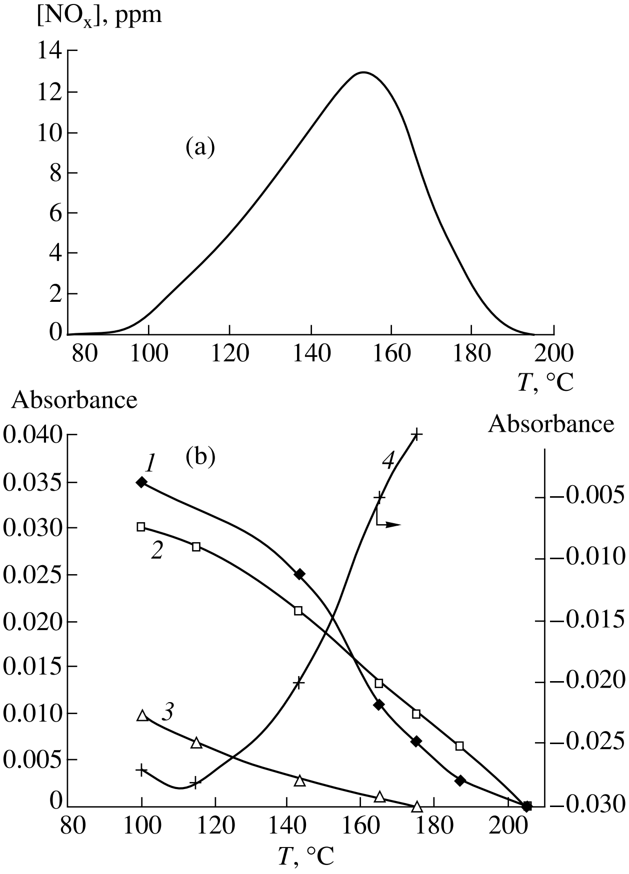

Fig. 5. (a) Spectrum of the TPD of NO_x after NO adsorption on the surface of the STK catalyst at 100°C; (b) changes in the intensities of the following absorption bands in the course of thermal desorption: (*1*) 1610, (*2*) 1540, (*3*) 1290, and (*4*) 1000 cm^{-1}.

The absorption band at 1340 cm^{-1} was detected at a temperature higher than 150°C. The intensity of this band increased with temperature, and this increase occurred with a simultaneous decrease in the intensities of the other absorption bands.

The catalyst exhibited a high activity in the reaction of propane oxidation: a conversion of propane equal to 80% was reached at 370°C (Fig. 7a, curve *6*).

To obtain detailed information on surface complexes, we performed spectroscopic and kinetic studies with the use of transmission spectroscopy in the low-frequency region (the experiments were performed with increasing sample temperature).

Upon heating a sample in a flow of (0.5% C_3H_8 + 2.5% O_2)/N_2, the spectra exhibited absorption bands at

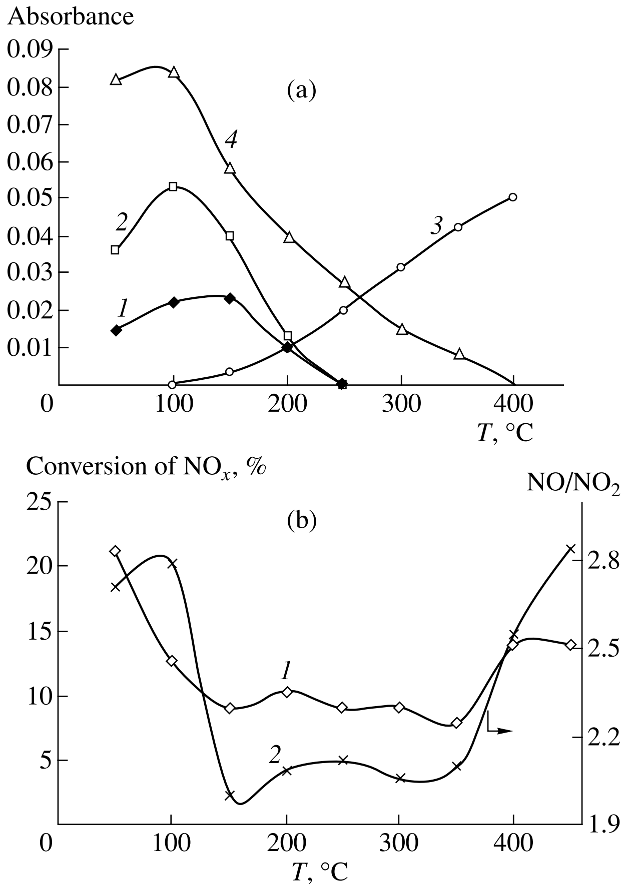

Fig. 6. Temperature dependence of (a) the intensities of absorption bands at (*1*) 1610, (*2*) 1540, (*3*) 1340, and (*4*) 1290 cm^{-1} in the diffuse-reflectance spectrum in the interaction of a 0.1% NO/N_2 mixture with the surface of the STK catalyst, (b) (*1*) the conversion of NO_x, and (*2*) the NO/NO_2 ratio.

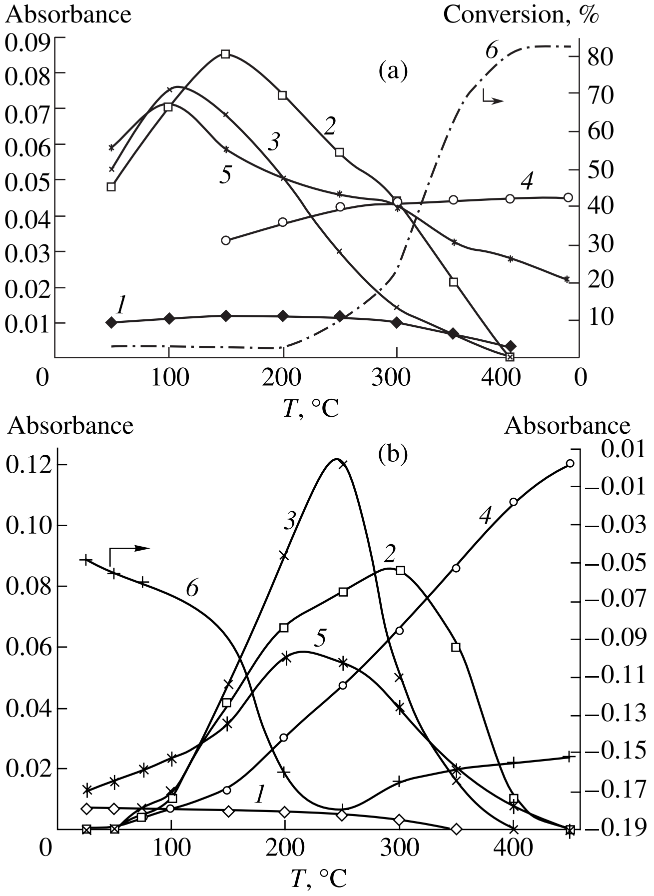

Fig. 7. Temperature dependence of (a) the intensities of absorption bands at (*1*) 2870, (*2*) 1540, (*3*) 1430, (*4*) 1340, and (*5*) 1250 cm^{-1} in the diffuse-reflectance IR spectra and (*6*) the conversion of propane in the interaction of a (0.5% C_3H_8 + 2.5% O_2)/N_2 mixture with the surface of the STK catalyst and (b) the intensities of absorption bands at (*1*) 2870, (*2*) 1540, (*3*) 1430, (*4*) 1340, (*5*) 1250, and (*6*) 1000 cm^{-1} in the transmission IR spectra.

2870, 1540, 1430, 1340, 1250, and 1000 cm^{-1} (Fig. 7b). The absorption bands at 1540, 1430, and 1250 cm^{-1} were observed at temperatures higher than 75°C, and their intensity passed through a maximum at 220–300°C. The intensity of the absorption band at 1340 cm^{-1} increased with temperature, and this increase was most pronounced at temperatures such that the intensities of the other absorption bands decreased. With the use of transmission spectroscopy, we managed to observe changes in the intensity of an absorption band due to another oxygen-containing surface complex (1000 cm^{-1}). The concentration of this complex decreased as the mixture was added and the temperature was increased to 250°C. A further increase in the temperature resulted in an increase in the intensity of the absorption band at 1000 cm^{-1}.

The intensity of the absorption band at 2870 cm^{-1} decreased with temperature and became equal to zero at 300–350°C.

Note that data obtained by various spectroscopic techniques are in qualitative agreement. It is likely that quantitative differences between measurements performed on cooling or heating the sample were due to different states of the catalyst surface in the interaction with the reaction mixture at high and low temperatures.

Thermal desorption measurements with mass-spectrometric analysis demonstrated that propane was adsorbed at room temperature. The products were desorbed at temperatures higher than 200°C (Fig. 8). Products with m/z = 28 (CO), 29 (C_2H_5), 44 (C_3H_8, CO_2), and 42 (C_3H_6) were mainly desorbed.

Adsorption of the NO + C_3H_8 + O_2 mixture. The spectrum of surface compounds measured upon the interaction of a (0.1% NO + 0.5% C_3H_8 + 2.5% O_2)/N_2 reaction mixture with the catalyst surface is very similar to the spectrum measured in a flow of the (0.5% C_3H_8 + 2.5% O_2)/N_2 mixture (cf. Figs. 7 and 9). The *in situ* diffuse-reflectance spectra exhibited absorption bands at

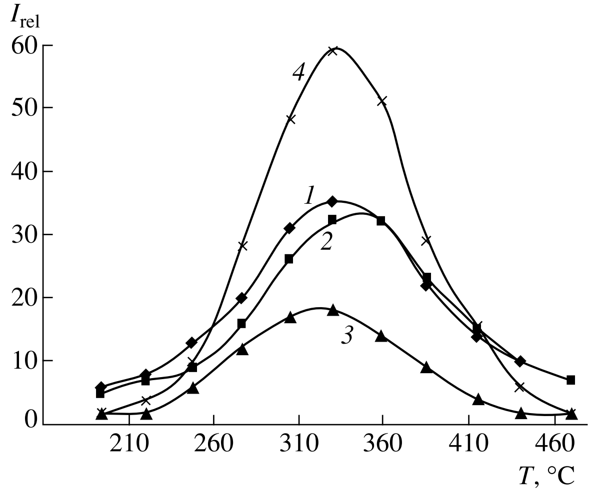

Fig. 8. Mass-spectrometric analysis of TPD products in a vacuum after the adsorption of $C_3H_8 + O_2$ at room temperature on the surface of the STK catalyst: (*1*) CO, (*2*) C_2H_5, (*3*) C_3H_6, and (*4*) CO_2 and C_3H_8.

2870, 1540, 1430, 1340, and 1250 cm^{-1} (Fig. 9a). The absorption band intensity at 1340 cm^{-1} increased, whereas the absorption band intensity at 2870 cm^{-1} decreased with temperature. The intensities of the absorption bands at 1540, 1430, and 1250 cm^{-1} symbatically changed with temperature and exhibited no maximums at ~150°C. Figure 9b shows the temperature dependence of the conversion of propane and NO_x. Note that a decrease in the intensities of absorption bands (except that at 1340 cm^{-1}) corresponds to the onset of propane oxidation. Analogous experimental results were obtained using transmission spectroscopy.

DISCUSSION

Identification of Surface Complexes

Adsorption of oxygen. The formation of oxygen adsorption complexes by the interaction of molecular oxygen with the surface of α-Fe_2O_3 corresponds to the appearance of absorption bands in the range 900–1360 cm^{-1} in the absorption spectra [17].

In accordance with published data [18], the absorption bands of adsorbed molecular oxygen lie between the frequencies of stretching ($\nu_{(O-O)}$) vibration of the adsorbed molecular oxygen species O_2 (1460–1700 cm^{-1}) and O_2 (1015–1180 cm^{-1}).

Various dissociatively adsorbed oxygen species can be formed on the surface of α-Fe_2O_3 depending on the duration and temperature of a reaction between the catalyst and oxygen. It was reported [17–19] that the use of a mixture of $^{16}O_2$ and $^{18}O_2$ isotopes allowed one to distinguish between the molecular and dissociative species of adsorbed oxygen. As a result of these experiments, it was found that absorption bands in the range 1100–900 cm^{-1} belong to oxygen adsorbed in an atomic form. The occurrence of several bands was related to various degrees of the coordinative saturation of surface Fe^{3+} cations.

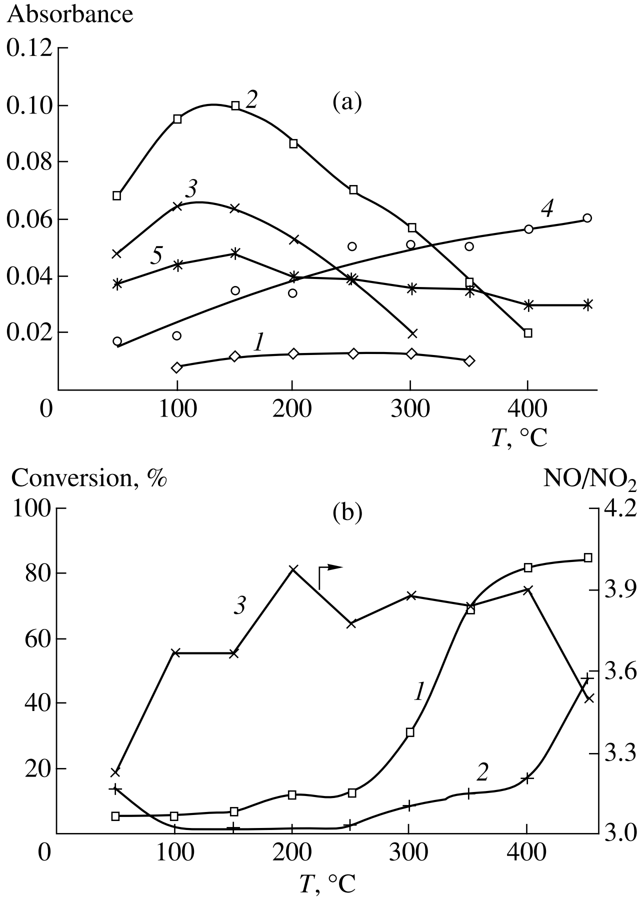

Fig. 9. Temperature dependence of (a) the intensities of absorption bands at (*1*) 2870, (*2*) 1540, (*3*) 1430, (*4*) 1340, and (*5*) 1250 cm^{-1} in the diffuse-reflectance spectrum in the interaction of a (0.1% NO + 0.5% C_3H_8 + 2.5% O_2)/N_2 mixture with the surface of the STK catalyst, (b) the conversions of (*1*) propane and (*2*) NO_x, and (*3*) the NO/NO_2 ratio.

Thus, based on published data [17–20], the absorption band at 1000 cm^{-1} observed in this work (Fig. 2) can be attributed to oxygen adsorbed in an atomic form. The intensity of this absorption band is low; this fact suggests a limited number of oxygen adsorption sites. This conclusion was supported by TPD data, which demonstrated that the individual adsorption of oxygen is small.

An absorption band the position of whose maximum can vary over the range 1340–1380 cm^{-1} deserves special attention. This absorption band is a consequence of surface dehydroxylation because the adsorption of water at room temperature (due to the presence of water vapor in the adsorbed NO/N_2 gas mixture) resulted initially in a decrease in the intensity and then in the complete disappearance of this absorption band. The intensity of the absorption band at 1340–1380 cm^{-1}

Table 2. Identification of surface compounds on STK and NTK-10-1 catalysts

ν, cm^{-1}	Attribution of observed absorption bands
	STK catalyst
O_2	
1340	ν(M–O), M is an extralattice Fe cation
1000	ν(M–O), M is a coordinatively unsaturated surface site
NO	
1610	ν_3, Bridging nitrate $(M–O)_2=NO$
1540	ν_3, Bidentate nitrate
1410	ν_3, Nitrite bound to the surface through the nitrogen atom
1290	ν_1, Nitrite bound to the surface through the nitrogen atom
$C_3H_8 + O_2$, $NO + C_3H_8 + O_2$	
2960*	$\nu_{as}(CH_3)$, Adsorbed propane
2870	$\nu_{sym}(CH_3)$, Adsorbed propane
1690	ν(C=O), Acrolein
1650	ν(C=C), Acrolein
1540	ν_{as}(COO), Acetate
1430	ν_{sym}(COO), Acetate
1250	ν(C–C), Acetate
	NTK-10-1 catalyst
NO	
1610	ν_3, Bridging nitrate $(M–O)_2=NO$
1280	ν_3, Bridging nitrate $(M–O)_2=NO$
1020	ν_1, Bridging nitrate $(M–O)_2=NO$
1215	ν_3, Bridging nitrite $(M–O)_2=N$
1200	ν_3, Bridging nitrite $(M–O)_2=N$
$C_3H_8 + O_2$, $NO + C_3H_8 + O_2$	
2960	$\nu_{as}(CH_3)$, Adsorbed propane
2870	$\nu_{sym}(CH_3)$, Adsorbed propane
1760	Nitro organic compound
1500	Adsorbed CO_2

* Absorption bands at 2960 and 2870 cm^{-1} in the IR spectra exhibited similar changes; therefore, for the sake of convenience only the absorption band at 2870 cm^{-1} is discussed in the text.

decreased upon the adsorption of reaction components and increased when the surface concentration of complexes decreased (Figs. 6, 7, 9). Hence, it follows that this absorption band corresponds to the vibrations of atoms that occur on the surface rather than in the bulk of the sample. A single narrow absorption band with a maximum in the region 1340–1360 cm^{-1} was observed previously upon the thermal oxidative treatment of γ-Al_2O_3 and Fe_2O_3; this absorption band was attributed to molecularly adsorbed oxygen with a weakened double bond [20, 21]. However, this assignment is unlikely because of the low sensitivity of this band to sample reduction in a flow of hydrogen at 465°C, as well as the high thermal stability of this band. On the other hand, an increase in the intensity of this absorption band in a flow of O_2 and a decrease in its intensity upon reduction in hydrogen suggest that the absorption band at 1340–1360 cm^{-1} belongs to an oxygen-containing complex. The insignificant change in the frequency of absorption found in the comparison of various metal oxides is indicative of an insignificant effect of the nature of the metal on the structure of the given surface complex.

Despite considerable differences between the properties of aluminum and iron, oxides in which an absorption band at 1340–1360 cm^{-1} was detected have a common feature: they form a metastable highly symmetrical phase that can be converted into a corresponding stable metal oxide species upon heating (γ-$Al_2O_3 \longrightarrow \alpha$-$Al_2O_3$; γ-$Fe_2O_3 \longrightarrow \alpha$-$Fe_2O_3$). In the course of phase transition, highly coordinatively unsaturated ions (extralattice ions) are formed on the surface. Being

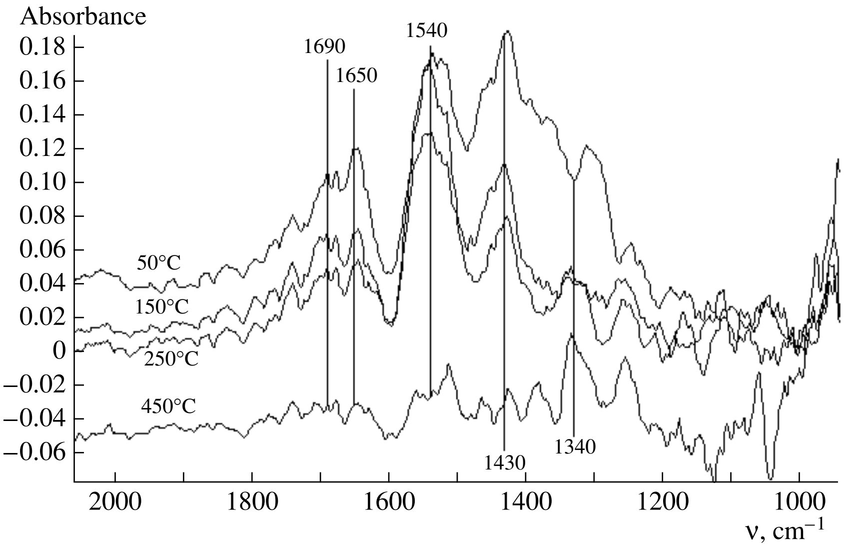

Fig. 10. IR spectra of surface compounds observed *in situ* in the interaction of a (0.1% NO + 0.5% C_3H_8 + 2.5% O_2)/N_2 mixture with the STK catalyst at various temperatures.

energetically excessive surface sites, these ions, which do not belong to the crystallographic plane of the surface, exhibit the greatest electron-acceptor ability. Adsorption at these sites results in the greatest gain in energy. As a result of surface dehydroxylation, the coordination sphere of extralattice ions is completed by oxygen atoms. It is likely that these oxygen atoms can react with each other to form a peroxo complex. The absorption frequency of 1340–1380 cm^{-1} lies in the range of absorption due to O–O bond vibrations in peroxo complexes [22].

Adsorption of NO and NO + O_2. The spectra measured in the course of thermal desorption experiments (Fig. 4) and experiments on NO adsorption from a flow at various temperatures (Fig. 6) exhibited absorption bands at 1610, 1540, 1410, and 1290 cm^{-1}. The intensities of the absorption bands at 1410 and 1290 cm^{-1} changed symbatically; this fact allowed us to attribute these bands to vibrations in a surface complex. In accordance with published data [17, 23–25], the absorption bands at 1610 and 1540 cm^{-1} belong to ν_3 vibrations in monodentate and bridging surface nitrate complexes, respectively. The absorption bands at 1410 and 1290 cm^{-1} can be attributed to ν_3 and ν_1 vibrations in a nitrite complex bound to the surface through a nitrogen atom [17, 23–25].

Adsorption of C_3H_8 and C_3H_8 + O_2. The diffuse-reflectance and transmission spectra measured in the course of spectroscopic and kinetic experiments (Fig. 7) under the reaction conditions of propane oxidation exhibited absorption bands at 2870, 1540, 1430, 1340, and 1250 cm^{-1}. The absorption band at 2870 cm^{-1} belongs to vibrations in the CH_3 group of adsorbed propane. The presence of adsorbed propane on the surface was supported by the presence of peaks with m/z equal to 29 and 44 in the mass spectra of propane desorption products. Note that the intensities of these absorption bands were relatively low; therefore, we failed to determine reliably whether the changes in their intensities are symbatic to changes in the intensities of absorption bands at 1540, 1430, and 1250 cm^{-1}. However, the intensities of absorption bands at 1540, 1430, and 1250 cm^{-1} symbatically changed in all of the experiments. Moreover, the constants of consumption of surface complexes, which were determined from the intensities of these bands in spectroscopic non-steady-state kinetic experiments, were found to be equal. These facts, as well as published data [17], allowed us to attribute them to vibrations in a surface carboxylate (acetate) complex. Table 2 summarizes the assignment of absorption bands observed in STK and NTK-10-1 catalysts.

The absorption band at 1340–1360 cm^{-1} belongs to vibrations in an oxygen complex bound to a coordinatively unsaturated iron ion. This assignment is additionally supported by the fact that the intensity of this absorption increased as the intensities of the other absorption bands decreased (Figs. 6, 7, 9), that is, as the surface became free.

Surface Compounds under the Reaction Conditions of NO$_x$ Reduction by Propane in an Excess of Oxygen

Under reaction conditions, acetate and nitrite–nitrate (at a low temperature) complexes were mainly observed (Fig. 9). Absorption bands due to adsorbed propane and adsorbed oxygen complexes were detected. The spectra did not exhibit absorption bands due to complexes formed by the interaction of propane complexes and nitrite–nitrate structures. Complexes formed as a result of the mild oxidation of propane can occur on the surface. This is evident from the presence of absorption bands at 1650 and 1690 cm^{-1} due to the vibrations of C=C and C=O bonds in adsorbed acrolein in the *in situ* spectra [17].

In summary, we can draw the following conclusions: A comparison of complexes formed on the surface of a sample as a mechanical mixture of STK and NTK-10-1 catalysts by interaction with reaction mixture components under conditions of the selective reduction of nitrogen oxides by propane in an excess of oxygen allows us to explain differences in HC-SCR mechanisms based on observed differences in the adsorption properties of the test catalysts.

No individual adsorption of oxygen on the surface of the NTK-10-1 catalyst was observed. The individual adsorption of oxygen on the surface of the STK catalyst was small; oxygen was adsorbed in an atomic form as a complex with a coordinatively unsaturated Fe ion.

In the adsorption of NO on the surfaces of STK and NTK-10-1 catalysts, two surface complexes were formed, namely, nitrite and nitrate complexes. However, unlike the NTK-10-1 catalyst, a high-temperature adsorption NO species was absent from the surface of STK.

The adsorption of propane on the surface of the NTK-10-1 catalyst is an activated process, in which oxygen plays an important role to decrease the adsorption temperature. Upon the addition of NO, the concentration of adsorbed propane species increases. According to the data of thermal desorption measurements, propane is adsorbed on the surface of the STK catalyst at room temperature. The interaction of propane with the surface of the STK catalyst at reaction temperatures results in the strong reduction of this surface. An oxygen-containing carboxylate (acetate) surface complex is formed on the STK catalyst; in the case of the NTK-10-1 catalyst, this complex was not detected.

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