

The Mechanism of Selective NO_x Reduction by Hydrocarbons in Excess Oxygen on Oxide Catalysts: V. Adsorption Properties of a Commercial Ni–Cr Oxide Catalyst

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Abstract—According to X-ray diffraction analysis data, the test catalyst was a Ni–Cr spinel with an impurity of NiO. With the use of in situ IR spectroscopy, it was found that nitrite, nitrate, and acetate surface complexes occurred under the reaction conditions of the selective catalytic reduction of nitrogen oxides by propane in the presence of oxygen on the nickel–chromium catalyst. As the temperature was increased, the nitrite complexes were converted into nitrate species. The molar absorption coefficient of surface nitrate complexes was determined. According to IR-spectroscopic and TPD data, the nitrate complexes were bound relatively weakly to the surface. The temperature region of their existence was 50–200°C. The temperature region of existence of the surface acetate complexes was 200–400°C. The individual adsorption of oxygen was not observed; however, oxygen-containing surface sites ($\text{Cr}^{5+}=\text{O}$) participated in the formation of the surface complexes of reactants.

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INTRODUCTION

The results of studies on a synergistic effect in the selective catalytic reduction of NO_x by propane (HC-SCR of NO_x) on a mechanical mixture of commercial catalysts (NTK-10-1 + STK) were published previously [1–8]. The nature of the synergism was found by studying the process mechanism on each particular catalyst that constituted the mechanical mixture [5–8]. Because the synergistic effect in the HC-SCR reaction of NO_x on the mechanical mixture of catalysts was most clearly pronounced at a hydrocarbon/oxygen ratio close to the stoichiometry of the complete oxidation of the hydrocarbon, the mechanism of the process on catalysts that constituted the mechanical mixture was studied in a reaction atmosphere with the above hydrocarbon/oxygen ratio.

Under these process conditions of the HC-SCR of NO_x on Cu–Zn–Al oxide (NTK-10-1) and Fe–Cr oxide (STK) catalysts [5–8], nitrite and nitrate surface intermediates play a key role [9, 10]. Differences between the mechanisms on the NTK-10-1 and STK catalysts [6, 8] are due to the absence of a high-temperature NO adsorption species from STK and the greater ability of STK to undergo reduction in a reaction mixture. Another special feature of the STK catalyst is the ability to form propane mild oxidation and oxidative dehydrogenation products. These differences in the mechanisms explain the nature of the synergism.

The phenomenon of synergism was also observed in a mechanical mixture of NTK-10-1 and Ni–Cr oxide catalysts [3, 4]. To determine the reason for this synergism, the mechanism of the selective reduction of NO_x by propane in the presence of oxygen on a Ni–Cr oxide catalyst was studied. Here, we report the results of a study of surface compounds formed by the interaction of the catalyst with the components of a reaction mixture of $\text{NO} + \text{C}_3\text{H}_8 + \text{O}_2$.

EXPERIMENTAL

A Ni–Cr oxide catalyst (see *OST 06-03-314-86*) for hydrogenation processes from the Elektrokhimprom Production Association (Uzbekistan) was used in this study. The state of the sample was characterized using X-ray diffraction (XRD) analysis, temperature-programmed reduction (TPR), and specific surface area measurements. The TPR of the samples was performed in a U-shaped flow reactor in a flow of 6 vol % H_2/Ar (100 ml/min) with linear heating over the range 20–600°C at a rate of 10 K/min. The concentration of H_2 in the gas flow was continuously monitored using a thermal-conductivity detector. Before the TPR, a 0.4-g sample was treated in a flow of O_2 at 500°C for 1 h; thereafter, the sample was cooled in a flow of O_2 to room temperature and successively blown with Ar and a mixture of H_2/Ar .

Temperature-programmed desorption (TPD) under flow conditions in an IR-cell reactor was combined

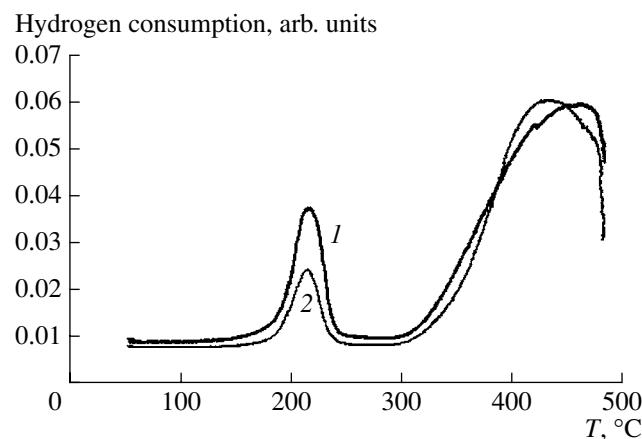


Fig. 1. TPR-H₂ reduction spectrum of the Ni-Cr oxide catalyst after the (1) first and (2) second oxidation-reduction cycles.

with the measurement of the IR spectra of surface complexes. The transmission and diffuse-reflectance IR spectra were measured using a Spectrum RX I FT-IR System spectrometer. In the measurements of diffuse-reflectance spectra, the sample weight was 1200–1300 mg; in the measurements of transmission spectra, the pellet weight was 20–25 mg. In this work, difference spectra are given, which were obtained by subtracting the spectrum of a sample in a flow of nitrogen from the spectrum of a sample in a flow of the reaction mixture under the same conditions. The intensity of absorption bands in the spectra is expressed in absorbance units (D). To determine the composition of desorbed products, experiments were performed under vacuum conditions with mass-spectrometric analysis using a 150-mg catalyst sample. The analysis was performed using an MX 7303 mass spectrometer. Before experiments, the catalyst sample was subjected to a standard oxidizing or reducing treatment: it was evacuated to 10^{-4} Pa at room temperature, heated to 500°C, and kept at this temperature in a vacuum for 30 min; thereafter, the test sample was kept in an atmosphere of O₂ ($P = 2 \times 10^2$ Pa) or H₂ for 30 min without changing the temperature. Next, the sample was cooled to 20°C and then evacuated. Before TPD, the test gas (NO or C₃H₈) was adsorbed for 5 min and a gas mixture (NO + O₂, C₃H₈ + O₂, or NO + C₃H₈ + O₂) was adsorbed for 30 min; thereafter, the sample was evacuated (10 min) and heated at a rate of 10 K/min with continuous evacuation.

The experimental procedures were described in detail elsewhere [5, 6].

RESULTS

Characterization of the State of the Catalyst

According to XRD data, the initial catalyst was a Ni-Cr oxide spinel with an impurity of NiO; graphite

was a constituent of the catalyst. A nickel metal phase was detected in the sample after performing catalytic tests. The specific surface area (S_{sp}) of the Ni-Cr oxide catalyst was 150 m²/g.

Two peaks of hydrogen absorption with $T_{max} \approx 220$ and 475°C were observed in the TPR spectra of the Ni-Cr oxide catalyst (Fig. 1). If the oxidation-reduction cycle was repeated, the intensity of the low-temperature peak decreased (curve 2) at an almost unchanged intensity of the high-temperature peak of hydrogen absorption. The reduction of Cr³⁺ with hydrogen in the bulk of the catalyst at low temperature is improbable. The interaction of hydrogen with oxygen in the surface catalyst layer is more probable [11]. According to published data [12, 13], chromium ions in high oxidation states, namely, Cr⁵⁺ and (or) Cr⁶⁺ as the constituents of chromate groups, occurred on the surface of chromium oxide after performing an oxidation treatment at 400°C. Because these groups are stable at a temperature of no higher than 300°C, it is likely that the absorption of hydrogen at 220°C corresponds to the reduction Cr⁶⁺⁽⁵⁺⁾ → Cr³⁺. The high-temperature peak of hydrogen absorption corresponds to the reduction of Ni²⁺ cations to Ni⁰ [14]. The data obtained suggest that the Ni-Cr catalyst readily loses oxygen. By this is meant that the degree of surface reduction can increase under reaction conditions (in the presence of a reducing agent) as the temperature is increased.

Adsorption of Reaction Components

Adsorption species of NO and NO + O₂. To obtain detailed information, the adsorption species of nitrogen oxides were studied in thermal-desorption experiments combined with the measurement of the transmission spectra of the samples. The transmission spectra measured in the course of desorption exhibited broad absorption bands due to nitrite-nitrate complexes with maximums at 1540–1445, 1280–1330, and 1050–1000 cm⁻¹ (Fig. 2). Changes in the shapes and half-widths of the absorption bands with temperature indicate that each of them consists of several absorption bands. To find the temperature dependence of absorption band intensities, the total spectrum was deconvolved into components assuming Lorentzian and/or Gaussian shapes with the use of standard programs. As a result of the analysis of the total spectrum at various temperatures, we managed to separate reliably absorption bands at 1000, 1020, 1040, 1280, 1330, 1420, 1450, and 1540 cm⁻¹.

Figure 3 shows the temperature dependence of the intensities of absorption bands due to these surface complexes in the course of their desorption from the surface of the Ni-Cr oxide catalyst (Fig. 3a) and the TPD spectrum after NO adsorption at room temperature (Fig. 3b). It can be seen that absorption bands can be separated into a few groups with respect to intensity changes with temperature: (1) 1330 and 1420 cm⁻¹, (2)

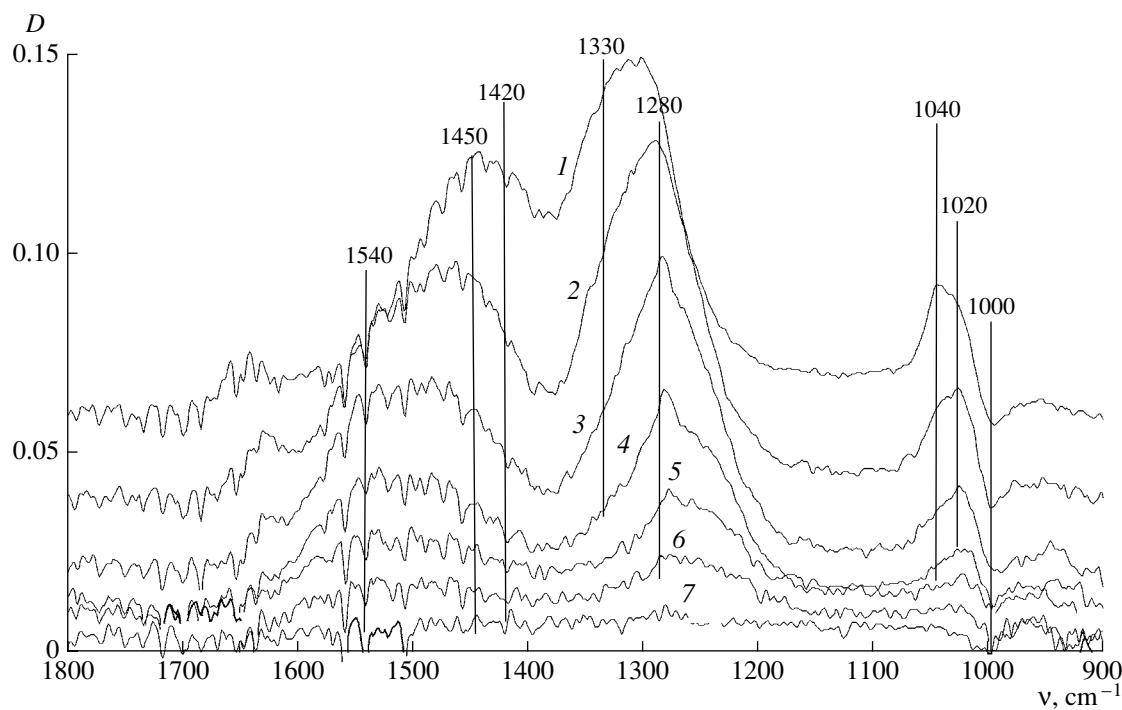


Fig. 2. IR spectra measured in the course of the TPD of NO from the surface of the Ni–Cr oxide catalyst at T , °C: (1) 30, (2) 70, (3) 110, (4) 155, (5) 190, (6) 210, and (7) 250°C.

1280 and 1540 cm⁻¹, and (3) 1450 cm⁻¹ (Fig. 3a). The IR spectra obtained upon the interaction of a mixture of NO + O₂ with the surface of the Ni–Cr oxide catalyst also exhibited a negative peak at 1000 cm⁻¹. Its negative value decreased as the surface complexes were desorbed (Fig. 3a, curve 6). The nature of the surface complex corresponding to this absorption band will be discussed below.

The TPD spectrum (Fig. 3b) exhibited a broad desorption peak with a maximum in the range 100–170°C. The total amount of NO_x molecules desorbed from this sample was 8.7×10^{19} molecule/g (0.6×10^{18} molecule/m²).

The known amount of desorbed NO_x molecules allowed us to evaluate a coefficient that relates the intensity of an absorption band at 1280–1330 cm⁻¹ and the concentration of nitrite–nitrate complexes on the surface. This coefficient was equal to $(0.3 \pm 0.1) \times 10^{-19}$ cm²/molecule, as determined from the results of three experiments. The integrated absorption coefficient for this band was equal to $(1.7 \pm 0.3) \times 10^{-18}$ cm/molecule. In the same manner, we evaluated the coefficient that relates the absorption band intensity at 1450 cm⁻¹ to the surface concentration of nitrite–nitrate complexes. This coefficient was equal to 0.13×10^{-19} cm²/molecule.

Thermal-desorption experiments with the mass-spectrometric analysis of products were performed in order to refine the composition of desorption products. Figure 4 shows the results of these experiments in oxi-

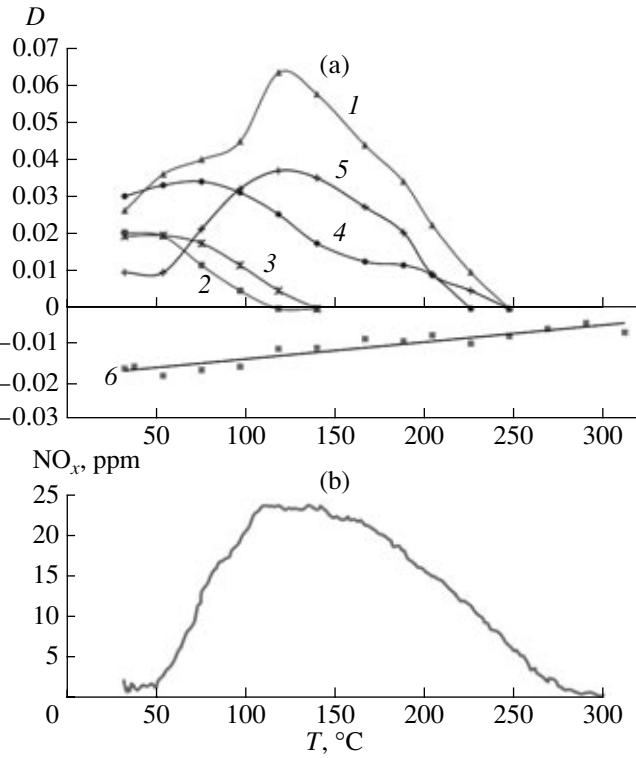


Fig. 3. (a) The temperature dependence of the intensities of absorption bands at (1) 1280, (2) 1330, (3) 1420, (4) 1450, (5) 1540, and (6) 1000 cm⁻¹ in the IR spectra in the course of the TPD of NO. (b) The TPD spectrum after the adsorption of NO on the surface of the Ni–Cr oxide catalyst.

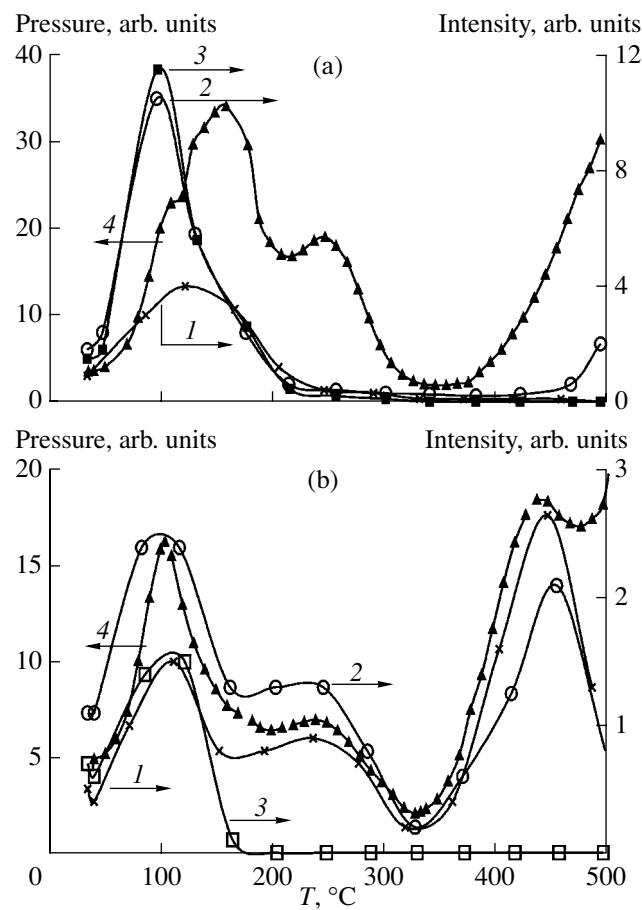


Fig. 4. TPD spectra after the adsorption of NO on the (a) oxidized and (b) reduced surfaces of the Ni–Cr oxide catalyst and the results of the mass-spectrometric analysis of products with $m/z = (1) 14$, (2) 28, and (3) 30; (4) pressure changes in the mass-spectrometer chamber in the course of NO desorption.

dized (Fig. 4a) and reduced (Fig. 4b) samples. As the constituents of desorption products, NO (curve 3) and N_2 molecules (curve 2), as well as nitrogen (curve 1) and oxygen atoms as the fragments of these molecules, were detected. It can be seen that neither NO nor N_2 were the constituents of products in the oxidized sample at temperatures higher than 250°C (Fig. 4a). In contrast to this, the release of N_2 into a gas phase was observed in the reduced sample over this temperature range (above 250°C) (Fig. 4b). The total change in the pressure in the course of TPD (Fig. 4a, curve 4) corresponds to the release of NO_x in the TPD spectrum under flow conditions (Fig. 3b) up to 300°C. An increase in the pressure at higher temperatures was related to the desorption of CO and CO_2 (carbon was present in noticeable amounts as a catalyst constituent).

The experimental data indicated that nitrogen oxide adsorption species on the Ni–Cr oxide catalyst depend on temperature and the degree of surface reduction. To 250°C, nitrate–nitrite structures were the main NO_x surface species. At temperatures higher than 300°C, the

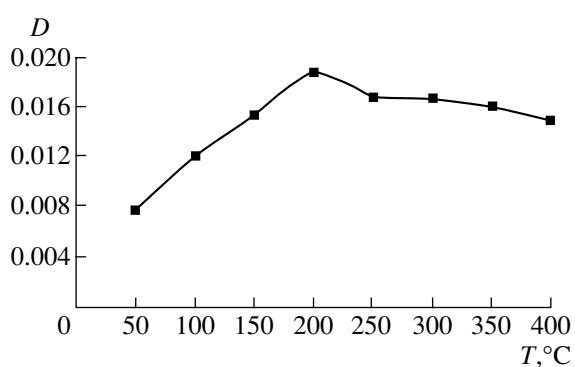


Fig. 5. The temperature dependence of the intensity of an absorption band at 1000 cm^{-1} in the IR spectra obtained upon the interaction of O_2 with the catalyst surface.

interaction of nitrogen oxides with the reduced surface of the catalyst resulted in the dissociation of NO molecules (Fig. 4b). Nitrogen atoms recombined with the liberation of molecular nitrogen into a gas phase, and oxygen atoms reoxidized the surface.

Adsorption species of O_2 . The results of thermal-desorption studies with mass-spectrometric analysis showed that oxygen was almost not adsorbed on the surface of the Ni–Cr oxide catalyst. At the same time, the IR spectrum of the sample treated in an inert gas exhibited an absorption band at 1000 cm^{-1} . Absorption in this region can be due to the vibrations of M–O bonds. To confirm this assumption, we studied the effect of oxygen adsorption on the spectrum of the sample in this region. Figure 5 shows the temperature dependence of the absorption band intensity at 1000 cm^{-1} in the spectra obtained upon the interaction of oxygen with the catalyst surface. Difference spectra (the spectrum of a sample in an atmosphere of nitrogen subtracted from the spectrum of the sample in the presence of oxygen, all other factors being the same) showed that oxygen adsorption resulted in an increase in the absorption band intensity at 1000 cm^{-1} over the temperature range 50–200°C and flattening out as the temperature was further increased. The intensity of this absorption band depended on the character of catalyst treatment (oxidative or reductive). The absorption band intensity in the spectrum of a reduced sample was lower than that in the spectrum of an oxidized sample.

The concentration of a surface complex (the intensity of an absorption band at 1000 cm^{-1}) significantly decreased upon the interaction of the catalyst with reactants: NO (Fig. 2) and $C_3H_8 + O_2$ (Fig. 6) (a decrease in the concentration of an oxygen complex manifested itself as a negative peak in difference spectra). This fact suggests the participation of the oxygen complex in the adsorption of reactants.

Adsorption species of C_3H_8 and $C_3H_8 + O_2$. The interaction of propane with the catalyst surface at reaction temperatures resulted in strong surface reduction and, as a consequence, a dramatic increase in the intrin-

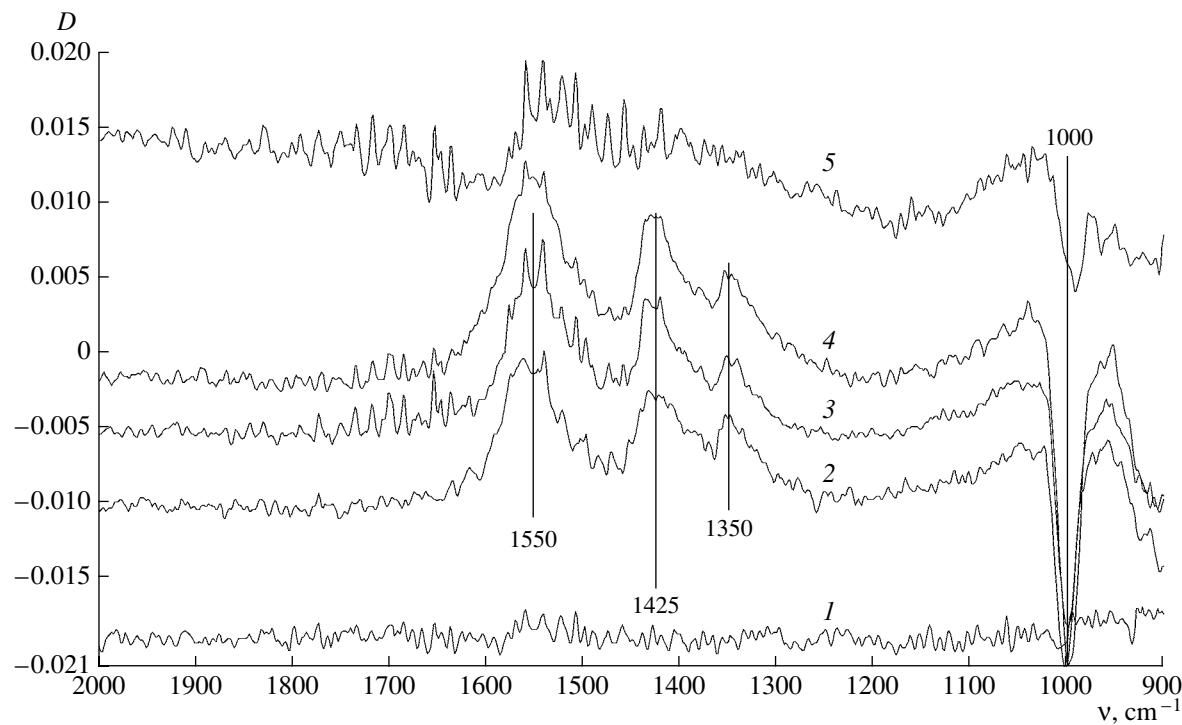


Fig. 6. IR spectra of surface compounds observed in the course of the interaction of a flow of 0.5% C₃H₈ + 2.5% O₂/N₂ with the catalyst at (1) 100, (2) 200, (3) 250, (4) 300, and (5) 400°C.

sic absorption of the catalyst, which hindered spectroscopic measurements. In this connection, the subsequent studies were performed with the use of a mixture of C₃H₈ + O₂/N₂.

The transmission spectra measured upon the interaction of a mixture of 0.5% C₃H₈ + 2.5% O₂/N₂ with the catalyst surface (Fig. 6) exhibited absorption bands at 2965, 1550, 1425, and 1350 cm⁻¹. It can be seen that the intensity of the above absorption bands passed through a maximum as the reaction temperature was increased. The value of a negative peak at 1000 cm⁻¹ changed with temperature symbatically with the intensity of absorption bands at 1550, 1425, and 1350 cm⁻¹.

Thermal-desorption measurements with mass-spectrometric analysis demonstrated that propane was adsorbed at room temperature. The products were desorbed at temperatures higher than 150°C (Fig. 7, curve 1). Products with *m/z* = 28 (CO) and 44 (CO₂), as well as water, were mainly desorbed.

Surface Compounds under the Reaction Conditions of NO_x Reduction by Propane in the Presence of Oxygen

The spectra of surface compounds measured upon the interaction of a reaction mixture of 0.1% NO + 0.5% C₃H₈ + 2.5% O₂/N₂ with the catalyst surface are similar in many respects to the sum of the spectra measured in a flow of a mixture of 0.1% NO + 2.5% O₂/N₂ and in a flow of a mixture of 0.5% C₃H₈ + 2.5% O₂/N₂

(Figs. 2, 6). The only difference consists in a somewhat lower intensity of absorption bands due to nitrite-nitrate complexes. Figure 8a shows the temperature dependence of the intensities of absorption bands observed in the spectra. The temperature regions of existence of complexes formed upon the adsorption of 0.1% NO + 2.5% O₂/N₂ (curves 1–3) almost did not overlap with the region of existence of complexes formed upon the adsorption of 0.5% C₃H₈ + 2.5% O₂/N₂ (Fig. 8, curves 4, 5). Note that the intensity of an

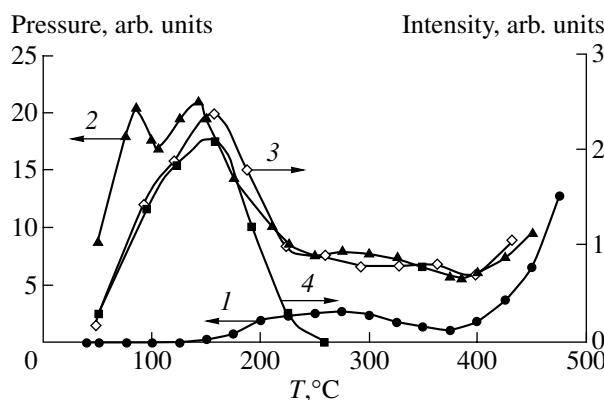


Fig. 7. TPD spectra after the adsorption of (1) 0.5% C₃H₈/N₂ and (2) 0.1% NO + 0.5% C₃H₈ + 2.5% O₂/N₂ on the surface of the Ni-Cr oxide catalysts and the results of the mass-spectrometric analysis of products: (3) *m/z* = 28 (CO) and (4) *m/z* = 30 (NO).

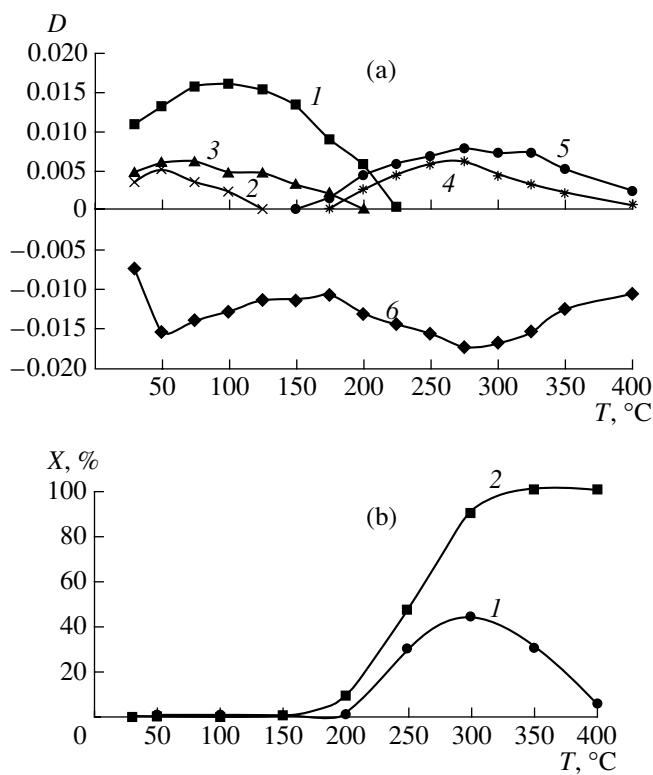


Fig. 8. (a) The temperature dependence of the intensities of absorption bands at (1) 1280, (2) 1320, (3) 1440, (4) 1425, (5) 1550, and (6) 1000 cm⁻¹ in the spectra after the adsorption of a mixture of 0.1 vol % NO + 0.5 vol % C₃H₈ + 2.5 vol % O₂/N₂ on the surface of the Ni-Cr oxide catalyst. (b) The temperature dependence of the conversions of (1) NO and (2) C₃H₈.

absorption band at 1000 cm⁻¹ increased as the concentration of surface complexes decreased.

The conversion of propane (Fig. 8b) reached ~100% at a temperature of about 300°C. The conversion of NO passed through a maximum at the same temperature.

The thermal-desorption measurements with mass-spectrometric analysis after the interaction of a reaction mixture with the catalyst surface demonstrated that the TPD spectrum (Fig. 7, curve 2) practically coincided with the sum of TPD spectra after the adsorption of NO (Figs. 3b, 4) and propane (Fig. 7, curve 1). At low temperatures, NO (*m/z* = 30) and CO (*m/z* = 28) were primarily desorbed (Fig. 7, curves 3, 4). At temperatures higher than 200°C, N₂, CO₂, and water were desorbed.

DISCUSSION

Properties of Surface Complexes

Adsorption of NO and NO + O₂. An analysis of the temperature dependence of absorption band intensities in the spectra showed that the absorption bands can be subdivided into a few groups with respect to the characters of intensity changes: (1) 1330 and 1420 cm⁻¹; (2) 1020, 1280, and 1540 cm⁻¹; and (3) 1040 and 1450 cm⁻¹.

These groups of absorption bands belong to three types of surface nitrate-nitrite complexes: 1540, 1280, and 1020 cm⁻¹ belong to a monodentate nitrate; 1420 and 1330 cm⁻¹ belong to a nitrite bound to the surface through the nitrogen atom; and 1450 and 1040 cm⁻¹ belong to a linear nitrite. The assignment was based on well-known data [6, 8, 15–20].

In the course of thermal desorption (Fig. 3a), the intensities of absorption bands at 1540 and 1280 cm⁻¹ passed through a maximum at 110°C; the absorption band intensity at 1450 cm⁻¹ passed through a maximum at 70°C; and the intensity of absorption bands at 1420 and 1330 cm⁻¹ monotonically decreased with temperature. The increase in the intensity of absorption bands due to the nitrate complex with temperature was related to the conversion of a portion of nitrite complexes into nitrate species. Nitrite complexes were desorbed at low temperatures (to 130°C), whereas nitrate complexes were desorbed at higher temperatures.

Adsorption of O₂. It was reported [15, 21–23] that studies with the use of an isotope mixture of ¹⁶O₂ and ¹⁸O₂ allowed one to separate the molecular and dissociative forms of oxygen adsorption. The results of these experiments showed that absorption bands in the range 1100–900 cm⁻¹ belong to oxygen adsorbed in an atomic form.

In our case, the IR spectrum of a sample treated in an inert gas exhibited an absorption band at 1000 cm⁻¹. It was observed even in the sample heated to 450°C. In an atmosphere of oxygen, the intensity of this absorption band increased over the temperature range 50–200°C and flattened out, as the temperature was further increased (Fig. 5). In an atmosphere of the reactants (Figs. 2, 6), the absorption band intensity at 1000 cm⁻¹ significantly decreased; this manifested itself as a negative peak in the spectra. Note that, in the spectra obtained upon the interaction of 0.5% C₃H₈ + 2.5% O₂/N₂ with the surface, the temperature dependence of the intensity of this peak had the shape of a curve with a maximum at 300°C. According to TPR data (Fig. 1), surface chromium ions in a high oxidation state underwent reduction in a close temperature region (*T*_{max} ≈ 220°C). The set of the above results shows that complexes characterized by a vibration at 1000 cm⁻¹ occurred on the catalyst surface. These complexes can be the surface chromate group and the Cr⁵⁺=O group [24, 25]. Because the chromate group is characterized by two (symmetrical and antisymmetrical) vibrations of Cr=O bonds and we detected one absorption band in our spectra, the assignment of an absorption band at 1000 cm⁻¹ to the vibrations of the Cr=O bond in surface Cr⁵⁺=O groups is most probable.

Adsorption of C₃H₈ + O₂. In all of the experiments, the intensities of absorption bands at 2965, 1550, 1425, and 1350 cm⁻¹ observed in the IR spectra obtained upon the interaction of 0.1% NO + 0.5% C₃H₈ + 2.5% O₂/N₂ and 0.5% C₃H₈ + 2.5% O₂/N₂ mixtures with the surface of the Ni-Cr oxide catalyst (Figs. 6, 8) changed sym-

batically. Based on published data [15, 26–31], this fact allowed us to attribute them to vibrations in a single surface complex, the acetate complex. The intensity of these absorption bands passed through a maximum at 250–300°C. We failed to detect other hydrocarbon complexes on the surface.

Surface Compounds under the Reaction Conditions of NO_x Reduction by Propane in the Presence of Oxygen

Nitrite and nitrate surface complexes were observed on the Ni–Cr oxide catalyst under reaction conditions at low temperatures, whereas acetate complexes were detected at high temperatures (Fig. 8a). Absorption bands due to Cr=O vibrations in the surface Cr⁵⁺=O groups were also detected.

We failed to detect absorption bands due to surface compounds formed by the interaction of acetate and nitrite–nitrate structures. The absorption band intensities of nitrate and acetate complexes changed antibiatically with the intensity of the absorption band of the oxygen complex (the Cr⁵⁺=O group) (Fig. 8a). By this is meant that the surface oxygen sites of the Ni–Cr oxide catalyst participated in the formation of both nitrate and acetate complexes.

The experimental results indicated that nitrite–nitrate, acetate, and oxygen complexes were formed and consumed on the surface of the Ni–Cr oxide catalyst. The table summarizes the assignment of absorption bands observed in the Ni–Cr oxide catalyst.

Figure 8b shows the temperature dependence of the conversions of reactants in the HC-SCR reaction of NO_x. At 300°C, 100% C₃H₈ conversion was achieved. The maximum degree of NO conversion was 40% at the specified temperature. A comparison between data in Figs. 8a and 8b demonstrated that the temperature regions of the appearance of catalyst activity in the reduction of nitrogen oxides by propane and the existence of acetates on the surface coincided.

A synergistic effect in a mechanical mixture of NTK-10-1 and STK catalysts in the process of the HC-SCR of NO_x was found and explained previously [1–8]. In this work, in order to determine the nature of the synergism observed in a mixture of NTK-10-1 and Ni–Cr oxide catalysts, we studied the properties of surface compounds formed by the interaction of the Ni–Cr oxide catalyst with the components of a reaction mixture of NO + C₃H₈ + O₂. It was of interest to compare the adsorption properties of STK and Ni–Cr oxide catalysts. The results of this work and previous data [7] indicate that the properties of these catalysts are similar with respect to the adsorption of nitrogen oxides. Both of the catalysts form nitrite–nitrate complexes, which are characterized by the low bond strength of the complexes to the surface. The NO species, which was desorbed in the temperature range 250–400°C, was absent from both of the catalysts. This was the main species on the Cu–Zn–Al oxide catalyst (NTK-10-1) [5, 6].

Surface compounds identified on the Ni–Cr oxide catalyst upon the adsorption of a mixture of 0.1% NO + 0.5% C₃H₈ + 2.5% O₂/N₂

Band, cm ⁻¹	Assignment of observed absorption bands	Structure
NO		
1540, 1280, 1020	Monodentate nitrate	$M^*-\text{O}-\text{N}=\text{O}$
1420, 1330	Nitrate bound to the surface through the nitrogen atom	$M-\text{NO}_2$
1450, 1040	Linear nitrite	$M-\text{O}-\text{N}=\text{O}$
	$\text{C}_3\text{H}_8 + \text{O}_2$	
2965	$\nu_{\text{as}}(\text{CH}_3)$ in acetate	$\text{CH}_3\text{COO}-\text{M}$
1550, 1425, 1350	$\nu_{\text{as}}(\text{COO})$, $\nu_{\text{s}}(\text{COO})$, $\nu(\text{C}-\text{C})$ in acetate	
	O_2	
1000	$\nu(\text{Cr}-\text{O})$ in Cr ⁵⁺ =O groups	
	$\text{NO} + \text{C}_3\text{H}_8 + \text{O}_2$	
Nitrite–nitrate complexes, $\text{CH}_3\text{COO}-\text{M}$		

* M is the adsorption site.

According to thermal-desorption measurements, propane was adsorbed on the surface of either of the catalysts at room temperature. The interaction of propane with the surface of test catalysts resulted in strong surface reduction. An oxygen-containing carboxylate (acetate) surface complex was formed upon the interaction of a mixture of C₃H₈ + O₂ with the catalyst surface. It is likely that the ability of catalysts to activate propane forms the basis of the synergistic effect.

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