The Mechanism of Selective NO$_x$ Reduction by Hydrocarbons in Excess Oxygen on Oxide Catalysts: VI. Spectroscopic and Kinetic Characteristics of Surface Complexes on a Ni–Cr Oxide Catalyst

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Received March 9, 2005

Abstract—The reaction mechanism of the selective catalytic reduction of NO$_x$ by propane in the presence of O$_2$ on a commercial Ni–Cr oxide catalyst was studied using in situ IR spectroscopy. It was found that nitrite, nitrate, and acetate surface complexes occurred under reaction conditions. Considerable amounts of hydrogen were formed in the interaction of NO + C$_3$H$_8$ + O$_2$ or C$_3$H$_8$ + O$_2$ reaction mixtures with the catalyst surface. The rates of conversion of the surface complexes detected under reaction conditions were measured. The resulting values were compared to the rate of the process. It was found that, at temperatures lower than 200°C, nitrate complexes reacted with the hydrocarbon to form acetate complexes; in this case, the formation of reaction products was not observed. In the temperature region above 250°C, two reaction paths took place. One of them consisted in the interaction of acetate and nitrate complexes with the formation of reaction products. The decomposition of NO on the reduced surface occurred in the second reaction path. Nitrogen atoms underwent recombination, and oxygen atoms reoxidized the catalyst surface and reacted with the activated hydrocarbon to form CO$_2$ and H$_2$O in a gas phase.

DOI: 10.1134/S0023158407010120

INTRODUCTION

The phenomenon of synergism found in the mechanical mixtures of catalysts used in the selective catalytic reduction of nitrogen oxides by hydrocarbons in the presence of O$_2$ (HC-SCR of NO$_x$) has been described in a series of publications [1–8]. A synergistic effect consists in a superadditive increase in the catalytic activity of a mechanical mixture as compared with the sum of the activities of the constituent catalysts. As a rule, the effective activation of a reactant on a catalyst of the mechanical mixture, diffusion, and interaction with other reactants on the second catalyst has been considered as the main reason for the phenomenon observed [9–12].

Previously [13], we studied the adsorption properties of a Ni–Cr oxide catalyst in order to explain the synergistic effect of a mechanical mixture of NTK-10-1 and Ni–Cr oxide catalysts. With the use of in situ IR spectroscopy, we found that nitrite, nitrate, and acetate surface complexes occurred under the reaction conditions of selective reduction of nitrogen oxides by propane in the presence of oxygen on a nickel–chromium catalyst. The nitrite complexes were converted into the nitrate complexes as the temperature was increased. The individual adsorption of oxygen was not observed;

however, oxygen-containing surface sites (Cr^{5+}=O) participated in the formation of reactant complexes.

The aim of this work was to determine the role of the detected surface complexes in the selective reduction of NO$_x$ by propane in the presence of oxygen on a commercial Ni–Cr oxide catalyst.

EXPERIMENTAL

In this work, we performed two types of spectrokinetic measurements (the simultaneous measurement of the activity of a catalyst and the spectra of surface compounds) [14].

(1) Steady-state experiments were performed using transmission and diffuse-reflectance IR spectroscopy [14, 15] to study the effects of temperature and the composition of a reaction mixture on the properties of surface complexes and on the catalytic activity. The spectra were measured on a Spectrum RX I FT-IR System spectrometer. The analysis of gases before and after a reactor cell was performed using a Beckman 951A chemiluminescence NO/NO$_x$ analyzer and a Beckman 590 HC/CO analyzer. The reactant concentrations in starting mixtures were varied over the ranges 0–0.22 vol % for NO, 0–0.76 vol % for C$_3$H$_8$, and

0–5 vol % for O$_2$. The main experiments were performed with a mixture of 0.1% NO + 0.5% C$_3$H$_8$ + 2.5% O$_2$/N$_2$. The flow rate of the reaction mixture was 150 ml/min (9000 h^{-1}). The rate of reactant conversion was calculated in accordance with an equation for an ideal mixing reactor.

(2) Non-steady-state experiments were performed in order to determine the role of the detected intermediate complexes in the test process. They were performed as follows: Adsorption complexes were formed on the catalyst surface, and the IR-cell reactor was closed. The gas-supply lines were blown with the reaction mixture (the interaction of which with these complexes was under study). After reaching a constant composition of gases in the gas lines, the reaction mixture was added to the sample. Experiments with an inert gas flow in place of the reaction mixture were also performed.

The intensities of absorption bands were determined from difference spectra, which were obtained by subtracting the spectra of a sample in the flows of a reaction mixture and nitrogen under the same conditions.

The reaction of propane oxidation was studied in a U-shaped quartz reactor using a flow setup. The weight of a catalyst sample was 1.0 or 1.2 g for a Ni–Cr oxide catalyst or a mechanical mixture (NTK-10-1 + Ni–Cr oxide catalyst in a ratio of 1 : 1), respectively. The experiments were performed at atmospheric pressure over the temperature range 250–500°C. Various mixtures were studied: 8 vol % C$_3$H$_8$/air/N$_2$, 4 vol % C$_3$H$_8$/air/N$_2$, and 0.7 vol % C$_3$H$_8$/air/N$_2$ with the ratio C$_3$H$_8$/O$_2$ = 1 : 2, as well as 0.5 vol % C$_3$H$_8$ + 2.5 vol % O$_2$/N$_2$ and 0.5 vol % C$_3$H$_8$ + 0.5 vol % O$_2$/N$_2$. The catalyst was pretreated at 500°C in a flow of nitrogen.

The concentrations of starting reactants and reaction products were determined by chromatography (a Kristall 2000 chromatograph). The following phases were used: molecular sieves NaX and 5A, Porapak Q, Porapak S, and Durapak. The experimental procedures were described in detail elsewhere [13–17].

RESULTS

Previously [13], with the use of in situ IR spectroscopy, we found that the temperature ranges of the existence of nitrate and acetate surface complexes are 50–270 and 150–400°C, respectively.

Effect of the Composition of the Reaction Mixture on the Activity and Properties of Surface Compounds

The studies of the effect of reactant concentrations on the properties of surface compounds and on the catalytic activity in the HC-SCR reaction of NO$_x$ were performed at 250 and 300°C. At the specified temperatures, the conversion of NO$_x$ and the intensities of absorption bands in the spectra exhibited values that can be reliably measured simultaneously. At higher temperatures, the coverage with surface complexes
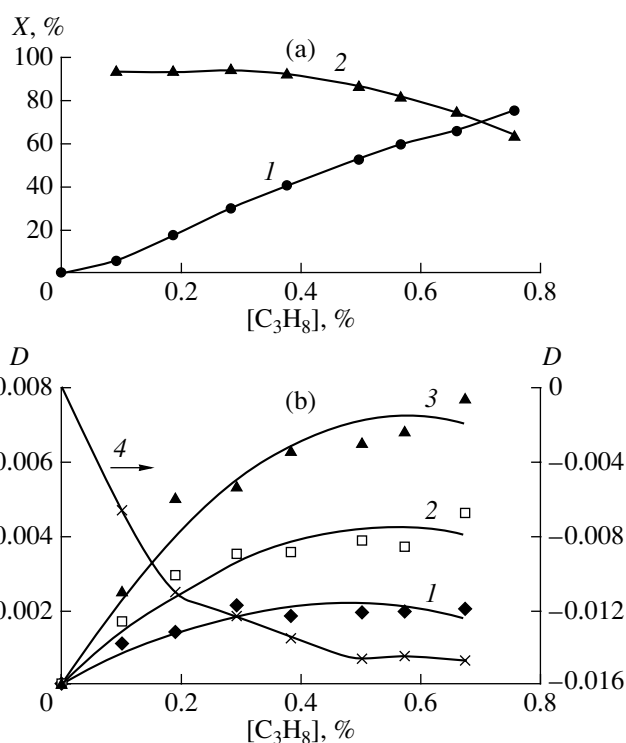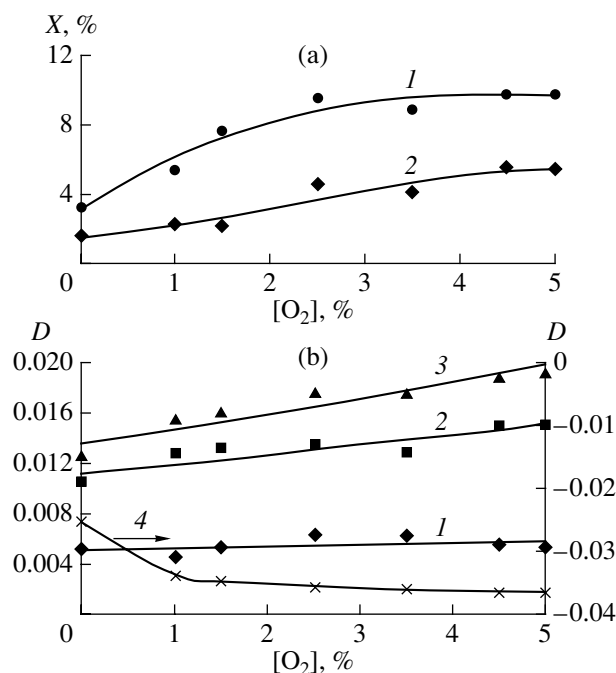

Fig. 1. Dependence of (a) the conversions of (*1*) NO$_x$ and (*2*) propane and (b) the intensities of absorption bands at (*1*) 1350, (*2*) 1425, (*3*) 1550, and (*4*) 1000 cm^{-1} in the spectra on the concentration of C$_3$H$_8$ in the reaction mixture. T_r = 300°C.

became negligibly small; at lower temperatures, the rate of the process was close to zero.

Acetate and oxygen complexes (Cr^{5+}=O) were observed on the catalyst surface over the test temperature range. Figures 1–3 show the concentration dependence of the conversion of reactants and the intensities of absorption bands due to the above surface complexes as functions of propane and oxygen concentrations in the NO + C$_3$H$_8$ + O$_2$ reaction mixture.

Effect of the concentration of C$_3$H$_8$. To a flow containing 0.1% NO + 2.5% O$_2$/N$_2$ was added 0.8% C$_3$H$_8$. At 300°C, the conversion (*X*) of NO increased almost linearly with increasing propane concentration in the flow (Fig. 1a, curve *1*), and the conversion of propane decreased (Fig. 1a, curve *2*). The intensity of absorption bands due to an acetate complex (1550, 1425, and 1350 cm^{-1}) in the spectra measured simultaneously with the conversion of reactants increased (Fig. 1b, curves *1–3*).

As noted above, the spectrum of the initial sample exhibited absorption due to Cr^{5+}=O surface groups [13]. The concentration of these complexes decreased in the course of reaction of the catalyst with the reactants. This manifested itself in the appearance of negative absorption in difference spectra (the spectrum of the sample in an inert gas flow was subtracted from the spectrum of the sample under reaction conditions).
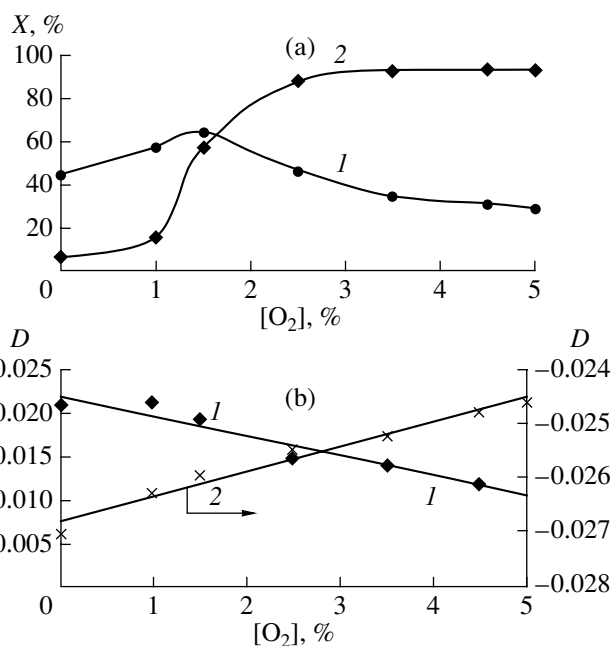
Fig. 2. Dependence of (a) the conversions of (*1*) NO and (*2*) C_3H_8 and (b) the intensities of absorption bands at (*1*) 1350, (*2*) 1425, (*3*) 1550, and (*4*) 1000 cm^{-1} in the spectra on the concentration of O_2 in the reaction mixture. $T_r = 250°C$.

Fig. 3. Dependence of (a) the conversions of (*1*) NO and (*2*) C_3H_8 and (b) the intensities of absorption bands at (*1*) 1350 and (*2*) 1000 cm^{-1} in the spectra on the concentration of O_2 in the reaction mixture. $T_r = 300°C$.

Curve *4* in Fig. 1b reflects a decrease in the concentration of $Cr^{5+}=O$ surface groups with increasing C_3H_8 content of the reaction mixture. It can be seen that the concentration of oxygen complexes ($Cr^{5+}=O$) changed antibatically with the concentration of acetate complexes as the C_3H_8 content of the reaction mixture was increased.

Effect of the concentration of O_2. To 5.0% O_2 was added a gas mixture containing 0.5% C_3H_8 + 0.1% NO/N_2. At 250°C, an increase in the concentration of O_2 resulted in an increase in the conversion of reactants (Fig. 2a) and in the intensity of absorption bands due to the acetate complex (Fig. 2b). The increase in the intensity of absorption bands due to the acetate complex was accompanied by a decrease in the concentration of surface oxygen complexes.

At 300°C, an increase in the O_2 content of the reaction flow resulted in an increase in the conversion of C_3H_8 to 100% at $[O_2] \geq 2.5\%$; a corresponding curve for the conversion of nitrogen oxide passed through a maximum (Fig. 3a). The concentration of the acetate complex (Fig. 3b, curve *1*) decreased. The concentration of the oxygen complex (Fig. 3b, curve *2*) changed antibatically with the concentration of the acetate complex over the entire range of O_2 concentrations studied.

Effect of the concentration of NO. To a flow containing 0.5% C_3H_8 + 2.5% O_2/N_2 was added 0.2% NO. At 250°C, the conversions of C_3H_8 and nitrogen oxide were independent of the NO content of the reaction mixture; the degree of conversion was no higher than

20%. At 300°C, the concentration of nitrogen oxide in the reaction mixture flow had almost no effect on the conversion of propane, which was equal to ~85%. The conversion of NO decreased from 70 to 45% as the concentration of nitrogen oxides was increased from 0.04 to 0.2 vol %. An increase in the concentration of NO resulted in an insignificant decrease in the intensity of absorption bands due to the acetate complex.

Reactivity of Surface Complexes

Data on the reactivity of nitrate and acetate surface complexes are given below, as found by transmission spectroscopy.

The non-steady-state spectrokinetic experiments were performed in accordance with procedure 2 (see the Experimental section) in order to determine the apparent rate constants of conversion of the surface complexes.

Reactivity of nitrate complexes. The formation of nitrate complexes on the surface was performed by adding a mixture of 0.1 vol % NO + 2.5 vol % O_2/N_2 to a sample for 60 min at room temperature; then, the sample was heated to a specified temperature in the range 70–200°C in a flow of the above mixture. Three experiments were performed at each particular temperature to determine the rates of consumption of the nitrate complexes in reactions with the gas flows of N_2, 0.5% C_3H_8/N_2, and 0.5% C_3H_8 + 2.5% O_2/N_2.
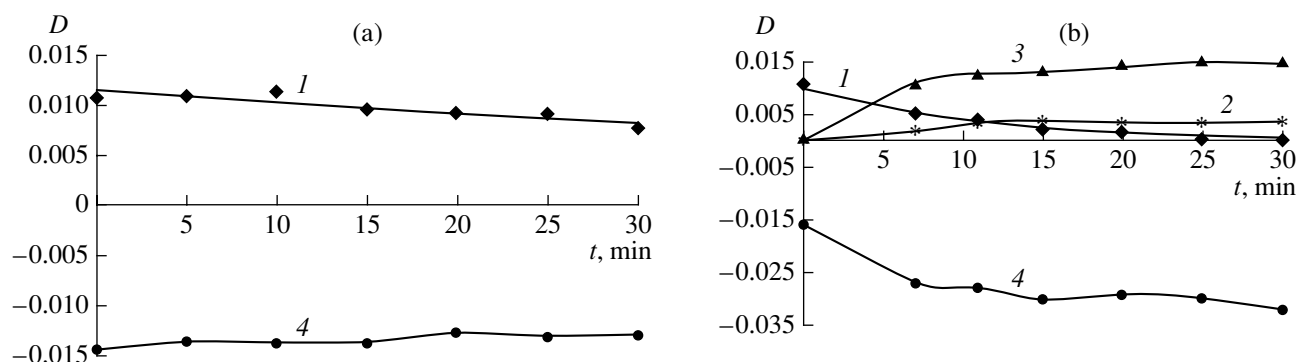
Fig. 4. The time dependence of the intensities of absorption bands at (*1*) 1280, (*2*) 1425, (*3*) 1550, and (*4*) 1000 cm^{-1} in the spectra obtained upon blowing the sample with preformed nitrite–nitrate complexes with a flow of (a) nitrogen or (b) a mixture of 0.5% C$_3$H$_8$ + 2.5% O$_2$ at 150°C.

Figure 4 shows the results of a typical experiment on the interaction of the nitrate complexes with the gas flows of N$_2$ and 0.5% C$_3$H$_8$ + 2.5% O$_2$/N$_2$ at 150°C. The decrease in the intensities of absorption bands due to nitrate structures in a flow of C$_3$H$_8$ + O$_2$/N$_2$ (Fig. 4b) was much greater than that in a flow of N$_2$ (Fig. 4a); this suggests the interaction of nitrate complexes with propane. Note that the absorption bands of acetate complexes grew in the course of consumption of the nitrate complexes (Fig. 4b, curves *2*, *3*).

The apparent rate constants of the reaction were calculated based on the kinetic dependence of the intensities of absorption bands due to adsorption complexes obtained in the course of non-steady-state measure-ments. This dependence was approximated using first-order equations with respect to the concentration of NO$_3^-$; the degree of approximation R^2 was no lower than 0.9. Table 1 summarizes the apparent rate constants of consumption (k_{app}) of nitrate complexes in the reaction of these complexes with a flow of 0.5% C$_3$H$_8$ + 2.5% O$_2$/N$_2$, which were calculated from an absorption band at 1280 cm^{-1}. Note that the k_{app} of nitrate complexes in the reaction with a flow of 0.5% C$_3$H$_8$/N$_2$ were equal to the values obtained in a flow of 0.5% C$_3$H$_8$ + 2.5% O$_2$/N$_2$ to within the measurement error (±8%) (Table 1).

For example:

$$T = 125°C, \quad k_{0.5C_3H_8 + 2.5O_2/N_2} = 0.019 \text{ min}^{-1}, \quad k_{0.5C_3H_8/N_2} = 0.014 \text{ min}^{-1};$$

$$T = 175°C, \quad k_{0.5C_3H_8 + 2.5O_2/N_2} = 0.226 \text{ min}^{-1}, \quad k_{0.5C_3H_8/N_2} = 0.264 \text{ min}^{-1}.$$

Reactivity of acetate complexes. The formation of surface acetate complexes was performed by passing a mixture of 0.5% C$_3$H$_8$ + 2.5% O$_2$/N$_2$ over a sample at an appropriate temperature (in the range 200–300°C) for 30 min. The apparent rate constants of consumption of adsorbed propane complexes were measured in gas flows of the following composition: N$_2$, 0.1% NO/N$_2$, 2.5% O$_2$/N$_2$, and 0.1% NO +2.5% O$_2$/N$_2$.

As an example, Fig. 5 shows the time dependence of the intensities of absorption bands due to acetate com-

Table 1. Comparison between the rates of conversion of nitrate surface complexes in the HC-SCR reaction of NO$_x$

T, °C	k_{app}, min^{-1}		D_{st}	w_c (calculated)	w_r (experimental)
	N$_2$	C$_3$H$_8$ + O$_2$/N$_2$		×10^{-17}, molecule/min	
70	0.0033	0.0032	0.0137	0.015	0
100	0.0066	0.0100	0.0146	0.049	"
125	0.0090	0.0190	0.0135	0.086	"
150	0.0084	0.0923	0.0116	0.360	"
175	0.0127	0.2260	0.0076	0.570	"
200	0.0381	0.5596	0.0035	0.640	"

Note: Mixture: 0.1% NO + 0.5% C$_3$H$_8$ + 2.5% O$_2$/N$_2$. Sample weight: 25 mg. $\varepsilon = (0.3 \pm 0.1) \times 10^{-19}$ cm^2/molecule. w_c is the rate of conversion of the complexes; w_r is the reaction rate of reduction of nitrogen oxides.
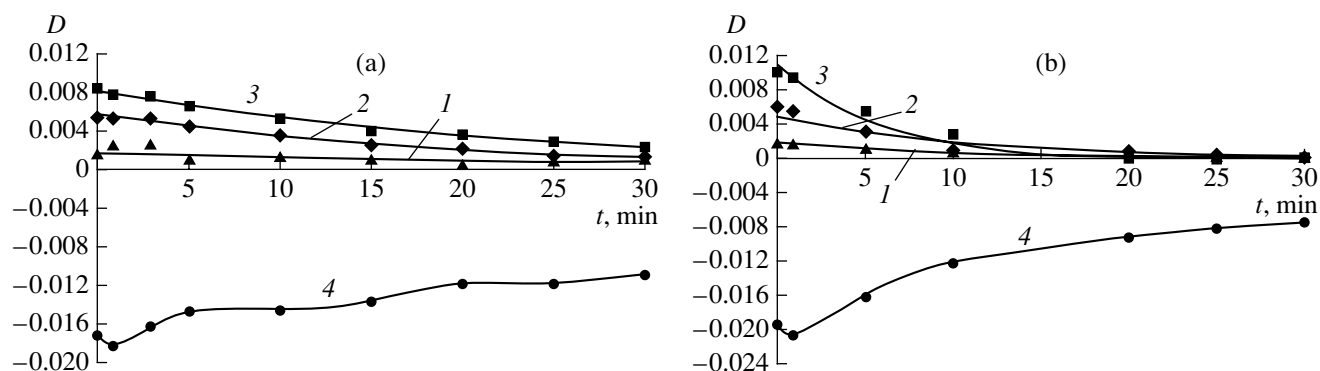
Fig. 5. The time dependence of the intensities of absorption bands at (*1*) 1350, (*2*) 1425, (*3*) 1550, and (*4*) 1000 cm^{-1} in the spectra obtained upon blowing the sample with preformed acetate complexes with a flow of (a) nitrogen or (b) a mixture of NO + O$_2$ at 300°C.

plexes (1550, 1425, and 1350 cm^{-1}) in the spectra obtained upon the interaction of a sample with the flows of N$_2$ (Fig. 5a) and 0.1% NO + 2.5% O$_2$/N$_2$ (Fig. 5b) at 300°C. It can be seen that the amount of acetate complexes on the surface decreased after purging the cell with N$_2$ (Fig. 5a). This decrease was due to the degradation of a portion of acetate complexes with the release of CO and CO$_2$ into the gas phase. The release of CO and CO$_2$ into a gas phase after propane adsorption was detected in TPD experiments [13]. Note that the rate of decrease of the above absorption band intensities in the spectra obtained in a mixture of NO + O$_2$/N$_2$ (Fig. 5b) was much higher than that in the spectra obtained in an atmosphere of N$_2$.

The time dependences of the absorption band intensities were linearized in the coordinates of a first-order equation. Thus, the values of k_{app} were found for all of the absorption bands (1550, 1425, and 1350 cm^{-1}) due to acetate complexes. Table 2 summarizes the values of k_{app} averaged over the three absorption bands. In these experiments, the concentration of an oxygen complex changed antibatically with the surface coverage of acetate complexes (Fig. 5). Therefore, the structure of surface oxygen sites was restored as the acetates were consumed.

DISCUSSION

Burdeinaya [18] noted that a synergistic effect in the HC-SCR reaction of NO$_x$ on a mechanical mixture of NTK-10-1 and Ni–Cr oxide catalysts was most pronounced at a hydrocarbon/oxygen ratio close to the stoichiometry of the complete oxidation of the hydrocarbon. On this basis, the following mixture was chosen as a reference in the spectrokinetic study of the process mechanism on the catalysts (mechanical mixture components): 0.1 vol % NO + 0.5 vol % C$_3$H$_8$ + 2.5 vol % O$_2$/N$_2$. To expand the concepts of the process mechanism, we studied the effect of the concentrations of reaction mixture components on the catalytic activity of catalysts and the properties of surface complexes.

Role of surface complexes in the SCR reaction of NO$_x$. To determine the role of the detected surface complexes in the reaction, we compared the rates of their conversion with the rate of the reaction. The computational procedure for the concentrations of surface complexes and the rates of reactions was described in detail elsewhere [14, 15]. The molar absorption coefficients of nitrate complexes were determined from spectroscopic and thermal-desorption experimental data [13]. Note that the values of these coefficients for nitrate structures are close to the values obtained previously for an STK Fe–Cr oxide catalyst [19]. The molar absorption coefficients of an acetate complex at the

Table 2. Comparison between the rate of conversion of the surface acetate complex and the rate of the HC-SCR reaction of NO$_x$

T, °C	k_{app}, min^{-1}		D_{st}	w_c (calculated)	w_r (experimental)
	N$_2$	0.1NO + 2.5O$_2$/N$_2$		×10^{-17}, molecule/min	
225	~0	0.017	0.0057	0.0320	0.128
250	0.0080	0.110	0.0066	0.0194	0.256
275	0.0170	0.160	0.0075	0.0410	0.297
300	0.0557	0.310	0.0069	0.0690	0.400

Note: Mixture: 0.1% NO + 0.5% C$_3$H$_8$ + 2.5% O$_2$/N$_2$. Sample weight: 25 mg. $\varepsilon = 7.0 \times 10^{-19}$ cm^2/molecule.

absorption bands of 1425 and 1550 cm^{-1} were taken from [20]:

$$\varepsilon_{1425} = 3.3 \times 10^{-19} \text{ cm}^2/\text{molecule},$$

$$\varepsilon_{1550} = 7.0 \times 10^{-19} \text{ cm}^2/\text{molecule}.$$

Nitrate complexes. Table 1 summarizes the results of a comparison between the rate of conversion of nitrate surface complexes and the rate of the HC-SCR reaction of NO$_x$.

According to published data (e.g., see reviews [21, 22]), nitrite–nitrate surface complexes are intermediates in the HC-SCR reaction of NO$_x$. These complexes react with an activated hydrocarbon to form a nitroorganic complex, which is subsequently converted into reaction products or oxidized to NO$_x$ and CO$_2$. These conclusions were supported by the results of a detailed study of the process mechanism on copper–zinc–aluminum (NTK-10-1) and iron–chromium (STK) catalysts [17, 19]. From this standpoint, let us consider the results of this work.

Data given in Table 1 indicate that nitrate surface structures are converted at a noticeable rate by the interaction with propane at 100–200°C. At the same time, because the conversion of nitrogen oxides was not observed in the specified temperature range, the rate of reduction of nitrogen oxides was almost equal to zero. To test this fact, we also measured the conversion with a sample of weight higher than that specified in Table 1 by a factor of 50 (1250 mg) [13]. The conversion of nitrogen oxides was not observed over this temperature range. Simple estimations based on the constants of conversion of nitrate complexes (Table 1) demonstrate that the conversion of nitrogen oxides on the 1250-mg sample at 100 or 200°C is ~5 or ~60%.

The set of the above data suggests that the nitrate complexes participate in the process that does not lead to the formation of reaction products. For example, the displacement of nitrates stabilized at Cu^{2+} ions as the constituents of pillared clay by propylene in the interaction with a flow of C$_3$H$_6$ + O$_2$ was considered [23, 24]. In our case, this process was accompanied by the formation and accumulation of acetate complexes on the surface, evidently, with the release of NO$_x$ into the gas phase. Indeed, the accumulation of acetate complexes on the surface in the course of consumption of nitrate complexes by the interaction with a mixture of C$_3$H$_8$ + O$_2$ on a Ni–Cr oxide catalyst was observed (Fig. 4b, curves 2, 3). Recall that acetate complexes were also formed in the interaction of a mixture of C$_3$H$_8$ + O$_2$ with the initial surface of the Ni–Cr oxide catalyst. Figure 6 shows the temperature dependence of the concentration of acetate complexes formed in the interaction of a mixture of C$_3$H$_8$ + O$_2$ with the initial surface (curve 2) and the surface covered with nitrate complexes (curve 1). It can be seen that the temperature region of the existence of acetate complexes in the presence of nitrate complexes (curve 1) is much lower with the retention of the same intensity, as compared with the region of exist-
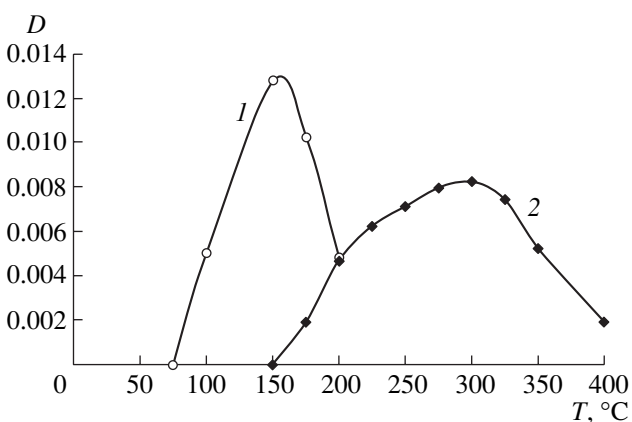
Fig. 6. The temperature dependence of the intensity of an absorption band at 1550 cm^{-1} in the spectra obtained upon the interaction of a mixture of 0.5% C$_3$H$_8$ + 2.5% O$_2$ with (2) the initial catalyst surface or (1) the surface with preformed nitrate complexes.

ence of acetate complexes in the reaction of propane oxidation (curve 2). In other words, the surface nitrate complexes facilitate the activation of propane without the formation of reaction products. The presence of oxygen in a mixture with propane had almost no effect on this process because the values of k_{app} for the consumption of nitrate complexes by the interaction with a flow of 0.5% C$_3$H$_8$/N$_2$ are equal to the values obtained in a flow of 0.5% C$_3$H$_8$ + 2.5% O$_2$/N$_2$ to within the measurement error.

The absence of any complexes formed as a result of the further conversion of nitrates is indirect evidence for the occurrence of propane activation without the formation of reaction products. Note that a nitroorganic complex was formed on oxide catalysts based on ZrO$_2$ in the interaction of nitrate and acetate structures [25].

Acetate complexes. In a study of the process of the SCR of NO$_x$ by propylene on Al$_2$O$_3$ and Cu/Al$_2$O$_3$, it was found that the interaction of acetate complexes with nitrate complexes is a rate-determining step in the formation of reaction products [21, 22, 26]. In our case, the acetate complexes were consumed at a noticeable rate by the interaction with a mixture of 0.1% NO + 2.5% O$_2$/N$_2$ (Table 2). To reveal the details of the process of conversion of acetate complexes, we measured the values of k_{app} in the reactions with flows of N$_2$, 0.1% NO/N$_2$, 0.1% NO + 2.5% O$_2$/N$_2$, and 2.5% O$_2$/N$_2$. At 250°C, the resulting values can be arranged in the following order:

$$k_{N_2} = 0.008, \quad k_{2.5\% \text{ O}_2/\text{N}_2} = 0.0363,$$

$$k_{0.1\% \text{ NO/N}_2} = 0.0733, \quad k_{0.1\% \text{ NO} + 2.5\% \text{ O}_2/\text{N}_2} = 0.110 \text{ min}^{-1}.$$

It can be seen that the interaction with nitrogen oxide made the main contribution to the consumption of acetate complexes. At the same time, the interaction with oxygen is a noticeable reaction path in the con-

X_{NO_x}, %
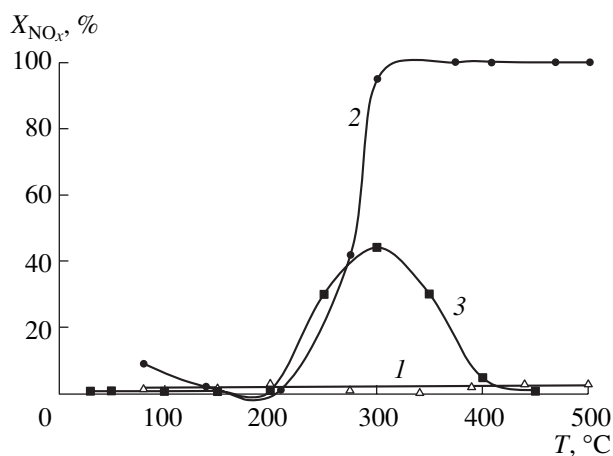
Fig. 7. The temperature dependence of the conversion of NO_x in the reduction of nitrogen oxides in the mixtures of (*1*) 0.1% NO + 3.0% H_2 + 2.5% O_2/N_2, (*2*) 0.1% NO + 10.0% H_2 + 2.5% O_2/N_2, and (*3*) 0.1% NO + 0.5% C_3H_8 + 2.5% O_2/N_2 on the Ni–Cr oxide catalyst.

sumption of acetate complexes. It is believed that this surface reaction terminated the process of deep propane oxidation, whereas the interaction of acetate complexes with nitrogen oxide is a part of the process of nitrogen oxide reduction.

An analysis of data in Table 2 demonstrated that the rate of the HC-SCR reaction of NO_x at temperatures higher than 200°C was much higher than the rate of conversion of the acetate complex by the interaction with a mixture of 0.1% NO + 2.5% O_2/N_2. This suggests that the interaction of acetate with NO_x is only a reaction path of the process.

Let us consider the nature of possible reaction paths at elevated temperatures. The test catalyst is characterized by the ability to undergo partial reduction as the temperature is increased in the presence of a reaction mixture. Experimental evidence for this consists in an impairment of transmission in the IR spectra upon heating the sample in a reaction mixture and in a decrease in the concentration of surface oxygen complexes with temperature. Moreover, according to XRD data, a nickel metal phase was detected as a sample constituent after performing the reaction [13]. On the reduced surface, molecular nitrogen was the main constituent of NO desorption products (according to data on the TPD of NO with mass-spectrometric analysis [13]). This suggested the occurrence of the reaction of NO decomposition. Nitrogen atoms underwent recombination, and oxygen atoms reoxidized the surface to form oxygen-containing sites on it. Activated hydrocarbon species can react with these sites to regenerate the reduced surface.

To reveal the nature of activated hydrocarbon species at high temperatures (above 300°C), we studied the composition of C_3H_8 + O_2 reaction products on the Ni–Cr oxide catalyst. We found that oxygen-containing

organic compounds (acrolein and acrylic acid), oxidative dehydrogenation products (such as propylene), and cracking products (C_1 and C_2 hydrocarbons) were absent from the products. At the same time, considerable amounts of hydrogen and CO_2 and an amount of CO were detected in the products. In particular, 0.65% H_2, 1.52% CO_2, and 0.05% CO were formed at 400°C (the mixture of 0.5% C_3H_8 + 2.5% O_2/N_2) and 100% propane conversion. The formation of hydrogen in the catalytic oxidation of saturated hydrocarbons was detected and explained previously [28, 29].

It was noted [27, 30] that the formation of hydrocarbon radicals at elevated temperatures can be a form of the activation of hydrocarbons. The interaction of these radicals or hydrogen with oxygen-containing surface sites can close the catalytic cycle of nitrogen oxide reduction. Note that an increase in the activity of catalysts in the SCR of NO_x by hydrocarbons in the presence of hydrogen was described previously [31–34]. It is believed that the surface was reduced even with a large excess of oxygen in the presence of hydrogen. The NO and O_2 molecules dissociated at the surface. The resulting surface oxygen atoms were activation sites for both NO and the hydrocarbon.

To test these concepts, we performed an experiment on the SCR of NO_x by hydrogen on the Ni–Cr catalyst. Figure 7 shows the results of this experiment. We found that the reduction of NO_x did almost not occur in the presence of 3% hydrogen in the reaction mixture (curve *1*). This fact allowed us to assume that, under the conditions of our experiments, hydrogen formed on the Ni–Cr catalyst under reaction conditions cannot provide the observed conversion of nitrogen oxides.

The set of the above data allowed us to propose the following description for the mechanism of the SCR of NO_x by propane on the Ni–Cr catalyst: At low temperatures (to ~200°C), the interaction of surface nitrate complexes with the hydrocarbon resulted in the formation of surface acetate complexes. The reaction did not proceed beyond this step at these temperatures.

As the temperature was further increased, the reaction occurred with the participation of acetate complexes. In addition to this reaction, the reaction of NO decomposition began on the reduced surface. Finally, nitrogen atoms recombined with the formation of molecular nitrogen and oxygen atoms formed water and CO_2 in the reaction with the activated hydrocarbon (likely in a radical form). As a result, the active site of the surface was regenerated. The deep oxidation of propane was another reaction whose contribution to the overall process increased with temperature. The increase in the reaction rate of the deep oxidation of propane with temperature was responsible for the volcano-shaped dependence of the conversion of NO_x upon temperature (Fig. 7, curve *3*).

The formulated concepts of the mechanism of the HC-SCR reaction of NO_x were supported by data on the

concentration dependence of the conversions of reactants and surface complexes (Figs. 1–3).

At 300°C, acetate complexes predominated on the surface. An increase in the concentration of propane (Fig. 1b) resulted in an initial increase and flattening out of the concentration of the acetate complex. By this is meant that the contribution of a reaction path through acetate complexes to the overall process was constant at a propane concentration higher than 0.2 vol %. In this case, the increase in the conversion of NO$_x$ (Fig. 1a, curve *1*) was related to an increase in the contribution of the reaction path on the reduced surface.

The concentration of acetate structures somewhat increased as the oxygen content of the reaction mixture was increased at 250°C (Fig. 2b, curves *1–3*); this resulted in an increase in the conversions of NO and C$_3$H$_8$ (Fig. 2a). The reaction path through acetate complexes made the main contribution to the overall process at this temperature.

At 300°C, the concentration of the acetate complex decreased as the concentration of oxygen in the reaction flow was increased (Fig. 3b). This character of the dependence was related to an increase in the conversion of propane as the oxygen content of the mixture was increased. Finally, the contribution of the reaction path through acetate complexes to the overall process decreased, and the shape of the concentration dependence of NO$_x$ conversion (Fig. 3a, curve *1*) was determined by the degree of reduction of the catalyst surface and the reaction rate of the deep oxidation of propane, which depends on the C$_3$H$_8$/O$_2$ ratio.

In a study of the properties of surface oxygen groups (Cr^{5+}=O), it was found that their concentration depended only slightly on temperature and the oxygen content of the reaction mixture [13] (in an atmosphere of 100% O$_2$, an increase in the temperature from 200 to 300°C had almost no effect on the concentration of these groups). At the same time, the interaction of the surface with reactants considerably decreased the concentration of oxygen groups. Therefore, the concentrations of acetates and surface oxygen changed antibatically in all of the experiments.

CONCLUSIONS

Under conditions of the selective reduction of NO$_x$ by propane in the presence of O$_2$, we measured the rates of conversion of nitrate and acetate surface complexes using a spectrokinetic technique. We compared the resulting values with the rate of the process. We found that nitrate complexes reacted with the hydrocarbon to form acetate complexes at a temperature lower than 200°C (over the entire region of existence of nitrates). In this case, the formation of reaction products did not occur.

At temperatures higher than 250°C, two reaction paths occurred in the reduction of nitrogen oxides by the hydrocarbon. One of them consisted in the interaction of acetate complexes with nitrate complexes with the formation of reaction products. The second was related to the fact that the surface was reduced as the temperature was increased. The reaction of NO decomposition began on the reduced surface. Nitrogen atoms recombined, whereas oxygen atoms reacted with the activated hydrocarbon to form H$_2$O and CO$_2$ in a gas phase. The higher the temperature, the greater the contribution of the second mechanism to the overall process.

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