The Mechanism of Selective NO_x Reduction by Hydrocarbons in Excess Oxygen on Oxide Catalysts: IV. Spectrokinetic Characteristics of Intermediate Complexes on the Commercial STK Catalyst

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Received September 2, 2003; in final form, January 14, 2005

Abstract—Surface nitrite–nitrate and acetate compounds were detected under conditions of the selective reduction of nitrogen oxides by propane on the STK iron–chromium oxide catalyst using spectrokinetic measurements. The rate of conversion of these complexes under reaction conditions was measured. The resulting values were compared to the rate of the process. The results of this comparison indicated that, at low temperatures (to ~250°C), the rate of reduction of nitrogen oxides was determined by the interaction of surface nitrite–nitrate complexes with the activated hydrocarbon. The amount of acetate complexes on the surface increased with temperature. A reduction of the surface was also observed as the temperature was increased. The reaction of NO decomposition began on the reduced surface. Nitrogen atoms recombined, and oxygen atoms reacted with the hydrocarbon to form CO_2 in a gas phase. A distinctive feature of the STK catalyst is its ability to form the products of propane mild oxidation and/or oxidative dehydrogenation. From a synergistic standpoint, the STK catalyst is an effective supplier of the activated hydrocarbon, whereas the NTK-10-1 catalyst well activates NO_x. This fact explains the nonadditivity effect observed in the catalytic properties of mechanical mixtures of these catalysts.

INTRODUCTION

In the preceding paper [1], in the context of a mechanistic study of the selective catalytic reduction of NO_x using hydrocarbons (propane) in an excess of oxygen (HC-SCR NO_x) on commercial oxide catalysts with the aim of explaining a synergistic effect in mechanical mixtures of these catalysts, we reported the adsorption and catalytic properties of the STK catalyst [2, 3]. We found that nitrite, nitrate, and acetate complexes occurred on the surface of this catalyst under reaction conditions.

In this work, we studied the reaction mechanism of HC-SCR NO_x with the use of a spectrokinetic method. The main goal was to examine the role of the detected complexes in the test process.

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) [4].

(1) In steady-state measurements we studied the effect of the composition of a reaction mixture on the properties of surface complexes and on the catalytic activity. In these experiments, the reactant concentrations in starting mixtures were varied over the ranges 0–0.22% for NO, 0–0.67% for C_3H_8, and 0–3.5% for O_2. Propane was used as a reducing agent; nitrogen was a carrier gas. The flow rate of the reaction mixture was 150 ml/min (9000 h^{-1}).

(2) Unsteady-state measurements were performed in order to determine the role of the detected intermediate complexes in the test process. The non-steady-state spectrokinetic experiments were performed as follows: Adsorption complexes were formed on the catalyst surface, and the IR-cell reactor was shut off. The gas-supply pipelines were purged with the test reaction mixture (the interaction of which with these complexes is of interest). After reaching a constant composition of gases in the gas pipelines, the reaction mixture was added to the sample. The experimental procedures were described in detail elsewhere [1–3].

RESULTS

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

The experiments were performed at 235 and 275°C with the use of diffuse-reflectance and transmission techniques. At the specified temperatures, the rate of
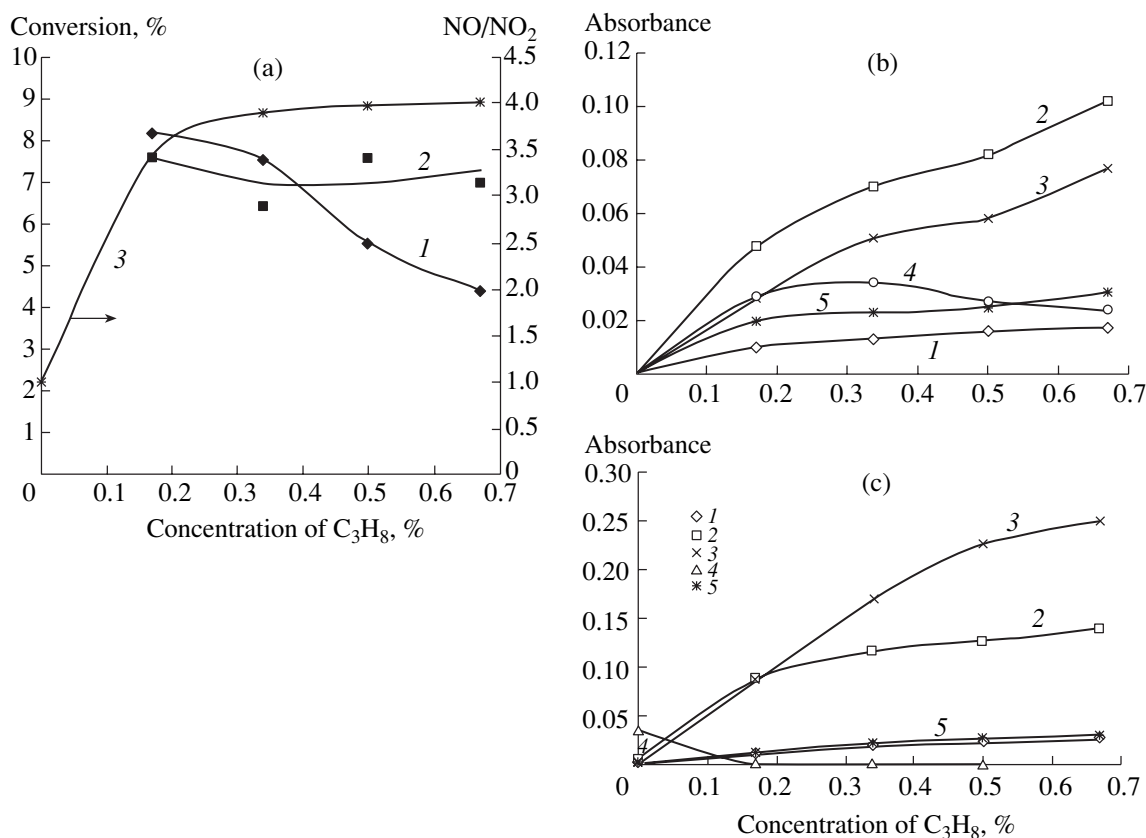
Fig. 1. Effect of the concentration of C_3H_8 on the interaction of (0.1% NO + 2.5% O_2 + x% C_3H_8)/N_2 mixtures ($x = 0$–0.67%) with the surface of the STK catalyst at 235°C: (a) conversion of (*1*) C_3H_8 or (*2*) NO_x and (*3*) NO/NO_2 ratio; (b) intensities of absorption bands at (*1*) 2870, (*2*) 1540, (*3*) 1430, (*4*) 1340, and (*5*) 1250 cm^{-1} in the diffuse-reflectance spectrum; and (c) intensities of absorption bands at (*1*) 2870, (*2*) 1540, (*3*) 1430, (*4*) 1290, and (*5*) 1250 cm^{-1} in the transmission spectrum.

the process and the spectra of surface compounds were measured simultaneously.

Effect of the concentration of C_3H_8. The conversion of NO at 235°C was almost independent of the amount of propane in the reaction mixture, and the conversion of propane decreased (Fig. 1a, curves *1*, *2*). The NO/NO_2 ratio in the flow at the outlet of the cell reactor reached a stationary value as the concentration of propane was increased (Fig. 1a, curve *3*).

As the concentration of propane in the reaction mixture was increased, the intensity of an absorption band due to adsorbed propane (2870 cm^{-1}), as well as the intensities of absorption bands at 1540, 1430, and 1250 cm^{-1}, increased (Fig. 1b, curves *1*–*3*, *5*). The intensity of an absorption band at 1340 cm^{-1} passed through a maximum and then decreased (Fig. 1b, curve *4*). Experiments with the use of transmission spectroscopy gave analogous results and additional information on a decrease in the intensity of absorption bands due to nitrite–nitrate complexes (at 235°C, only the most intense absorption band of these complexes was observed at 1290 cm^{-1}) with increasing concentration of propane (Fig. 1c).

Effect of the concentration of O_2. At 235°C, the conversion of propane was almost independent of the amount of oxygen; the conversion of nitrogen oxide passed through a maximum as the concentration of oxygen was increased. The NO/NO_2 ratio in a flow at the outlet of the cell reactor was also almost independent of the amount of oxygen (Fig. 2a).

The intensity of an absorption band at 2870 cm^{-1} (Fig. 2b, curve *1*) was almost independent of the concentration of oxygen. The intensities of absorption bands at 1540, 1430, and 1250 cm^{-1}, as well as the intensity of an absorption band at 1340 cm^{-1}, increased with oxygen concentration. The same results were obtained experimentally with the use of transmission spectroscopy.

Effect of the concentration of NO. The conversions of propane and NO at 235°C were almost independent of the concentration of nitrogen oxide in the flow of a reaction mixture (Fig. 3a, curves *1*, *2*). The NO/NO_2 ratio in the flow at the outlet of the cell reactor was close to 4 and was independent of the concentration of NO in the reaction mixture (Fig. 3a, curve *3*).
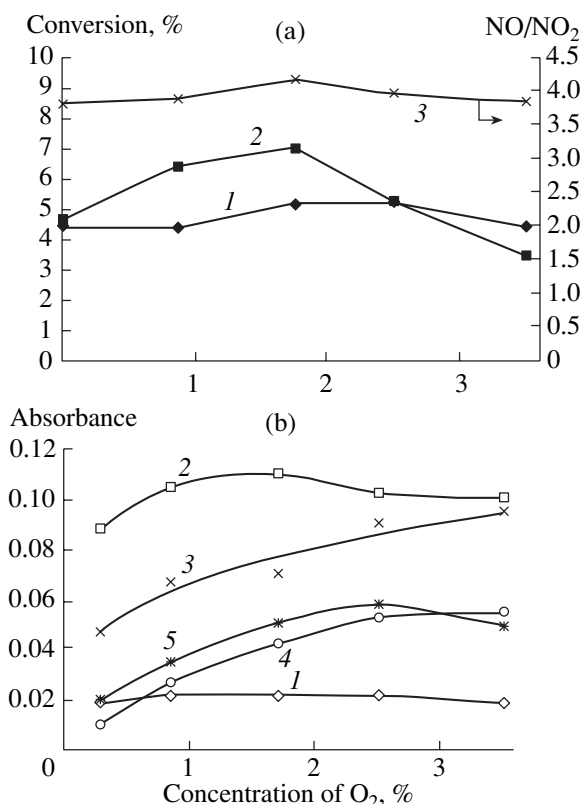
Fig. 2. Effect of the concentration of O$_2$ on the interaction of (0.1% NO + 0.5% C$_3$H$_8$ + x% O$_2$)/N$_2$ mixtures (x = 0–3.5%) with the surface of the STK catalyst at 235°C: (a) conversion of (*1*) C$_3$H$_8$ or (*2*) NO$_x$ and (*3*) NO/NO$_2$ ratio; (b) intensities of absorption bands at (*1*) 2870, (*2*) 1540, (*3*) 1430, (*4*) 1340, and (*5*) 1250 cm^{-1} in the diffuse-reflectance spectrum.

Fig. 3. Effect of the concentration of NO on the interaction of (0.5% C$_3$H$_8$ + 2.5% O$_2$ + x% NO)/N$_2$ mixtures (x = 0–0.22%) with the surface of the STK catalyst at 235°C: (a) conversion of (*1*) C$_3$H$_8$ or (*2*) NO$_x$ and (*3*) NO/NO$_2$ ratio; (b) intensities of absorption bands at (*1*) 2870, (*2*) 1540, (*3*) 1430, (*4*) 1340, and (*5*) 1250 cm^{-1} in the diffuse-reflectance spectrum.

An increase in the concentration of NO in the flow resulted in a small increase in the intensities of absorption bands at 1540, 1430, 1250, and 1340 cm^{-1}. The intensity of an absorption band at 2780 cm^{-1} remained unchanged (Fig. 3b).

Figure 4 demonstrates the results of analogous measurements with the use of transmission spectroscopy at 275°C. It can be seen that the dependence of the concentrations of surface complexes on the composition of the reaction mixture remained almost unaffected at the elevated temperature. At the same time, the measurements performed at this temperature are indicative of the direct participation of surface oxygen (absorption band at 1000 cm^{-1}) in the reaction. The concentration of surface oxygen decreased most rapidly as the concentration of propane in the reaction mixture was increased (Fig. 4a, curve *6*).

Reactivity of Surface Complexes

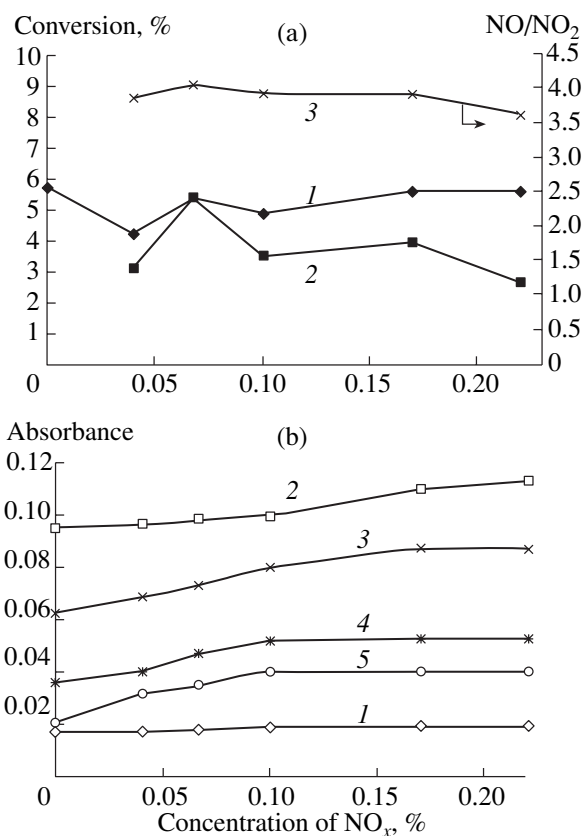The above results indicate that adsorbed propane complexes and surface nitrate compounds occurred on the catalyst surface under reaction conditions. The interaction of nitrite–nitrate complexes with propane was studied using transmission spectroscopy. The intensity of absorption bands was measured in difference spectra obtained by subtracting the spectrum of a sample in a flow of nitrogen from the spectrum of the sample in a flow of the reaction mixture under the same conditions.

Reactivity of nitrite–nitrate complexes. The formation of nitrite–nitrate complexes on the surface was performed in a flow of 0.1% NO/N$_2$ initially at room temperature for 15 min and then on heating to 70, 100, and 140°C. The time dependence of the intensities of absorption bands due to nitrite and nitrate complexes was obtained at each temperature upon blowing the cell with the sample with gas flows of N$_2$, 0.5% C$_3$H$_8$/N$_2$, and (0.5% C$_3$H$_8$ + 2.5% O$_2$)/N$_2$.

Figure 5 demonstrates the results of this experiment at 70°C. Changes in the intensities of absorption bands in a flow of (C$_3$H$_8$ + O$_2$)/N$_2$ were somewhat greater than those in the case of nitrogen. The absorption bands of adsorbed propane were not detected.
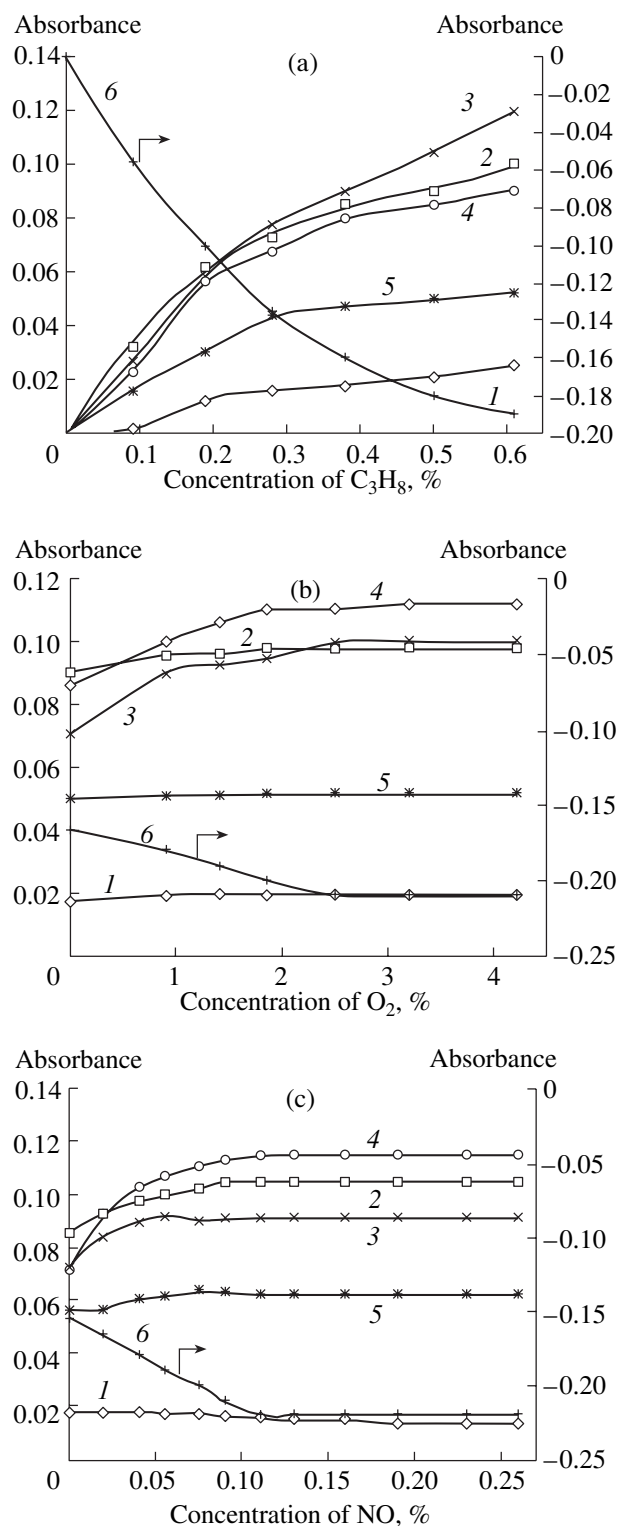
Fig. 4. Dependence of the intensities of absorption bands at (*1*) 2870, (*2*) 1540, (*3*) 1430, (*4*) 1340, (*5*) 1250, and (*6*) 1000 cm^{-1} in the transmission spectrum of the STK catalyst at 275°C on the concentration of (a) C_3H_8, (b) O_2, or (c) NO in the interaction with the following mixtures: (a) (0.1% NO + 2.5% O_2 + *x*% C_3H_8)/N_2 (*x* = 0–0.67%), (b) (0.1% NO + 0.5% C_3H_8 + *x*% O_2)/N_2 (*x* = 0–3.5%), and (c) (0.5% C_3H_8 + 2.5% O_2 + *x*% NO)/N_2 (*x* = 0–0.22%).
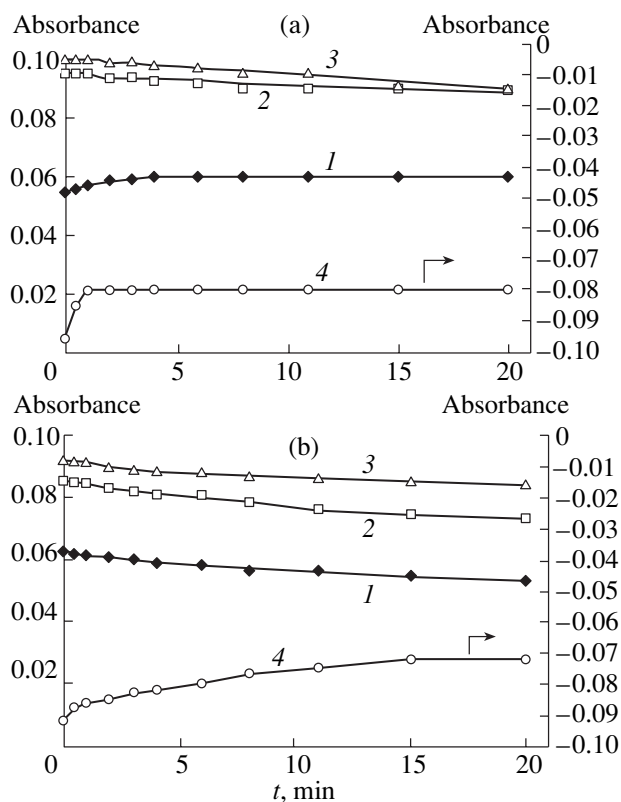

Fig. 5. Dependence of the intensities of absorption bands at (*1*) 1610, (*2*) 1540, (*3*) 1290, and (*4*) 1000 cm^{-1} on the time of catalyst treatment with (a) nitrogen or (b) a (0.5% C_3H_8 + 2.5% O_2)/N_2 mixture at 70°C.

Figure 6 demonstrates the results of an analogous experiment at 100°C. It can be seen (Fig. 6a) that the amount of surface nitrate complexes (absorption bands at 1610, 1540, and 1290 cm^{-1}) remained almost unaffected upon the treatment of the catalyst with nitrogen. The intensities of the absorption bands at 1610, 1540, and 1290 cm^{-1} dramatically decreased upon the addition of (C_3H_8 + O_2)/N_2 (Fig. 6b). Note that the rate of decrease in the intensity of these absorption bands reached a maximum in the first minutes, whereas the intensities of absorption bands at 1540 and 1290 cm^{-1} did not decrease to zero at the end of the experiment. In the course of the reaction of (C_3H_8 + O_2)/N_2 with the surface, an absorption band at 1250 cm^{-1} appeared, and its intensity increased with experiment time.

Figure 7 demonstrates the results of an analogous experiment at 140°C. The amount of surface nitrite–nitrate complexes (absorption bands at 1610, 1540, and 1290 cm^{-1}) decreased upon blowing the cell with nitrogen (Fig. 7a).

Upon the addition of (C_3H_8 + O_2)/N_2 (Fig. 7b), the rate of decrease in the intensity of the above absorption bands was higher than that in a flow of nitrogen. Moreover, absorption bands at 1430 and 1250 cm^{-1} appeared in the spectra, and the intensities of these bands
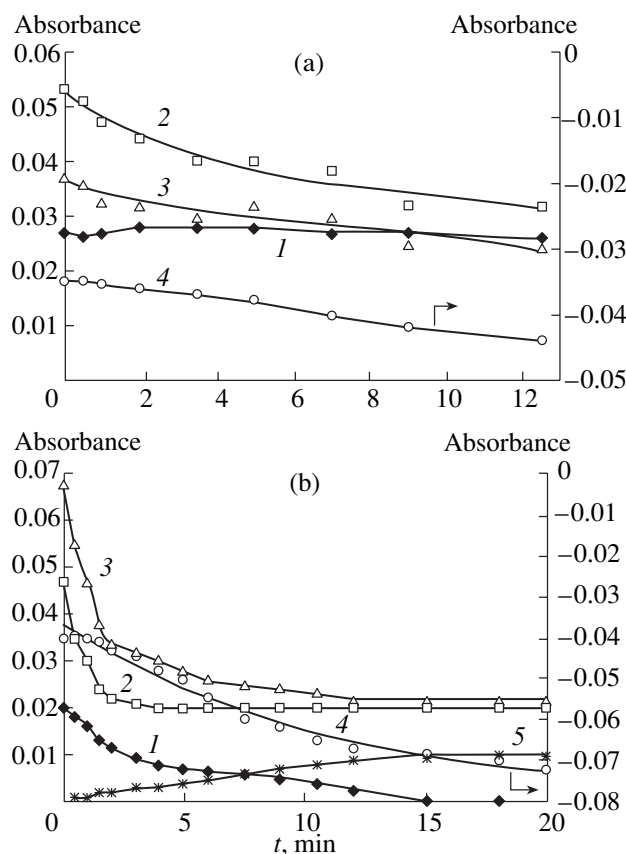
Fig. 6. Dependence of the intensities of absorption bands at (*1*) 1610, (*2*) 1540, (*3*) 1290, (*4*) 1000, and (*5*) 1250 cm^{-1} on the time of catalyst treatment with (a) nitrogen or (b) a (0.5%C$_3$H$_8$ + 2.5%O$_2$)/N$_2$ mixture at 100°C.

Fig. 7. Dependence of the intensities of absorption bands at (*1*) 1610, (*2*) 1540, (*3*), 1430, (*4*) 1000, and (*5*) 1290 cm^{-1} on the time of catalyst treatment with (a) nitrogen or (b) a (0.5%C$_3$H$_8$ + 2.5%O$_2$)/N$_2$ mixture at 140°C.

increased with time, whereas the intensities of absorption bands at 1610 and 1290 cm^{-1} decreased. The intensity of an absorption band at 1540 cm^{-1} passed through a minimum because an absorption band due to a nitrate complex is observed at this frequency in addition to the absorption band of an acetate complex.

The dependence of the intensities of absorption bands due to adsorption complexes on reaction time obtained using *in situ* IR spectroscopy was applied to calculate the apparent rate constants of corresponding reactions. Thus, we calculated the apparent rate constants of consumption of nitrite–nitrate complexes in N$_2$ and (0.5% C$_3$H$_8$ + 2.5% O$_2$)/N$_2$ gas flows. In this case, the initial portions of the intensities of IR absorption bands as functions of time were approximated by first-order rate equations with respect to the concentration of NO$_2^-$, and the degree of approximation (R$_2$) was no lower than 0.9. As an example, Fig. 8 shows the results of the treatment of experimental data obtained at 100°C.

Reactivity of adsorbed propane complexes. The apparent rate constants of consumption of adsorbed propane complexes were measured in gas flows
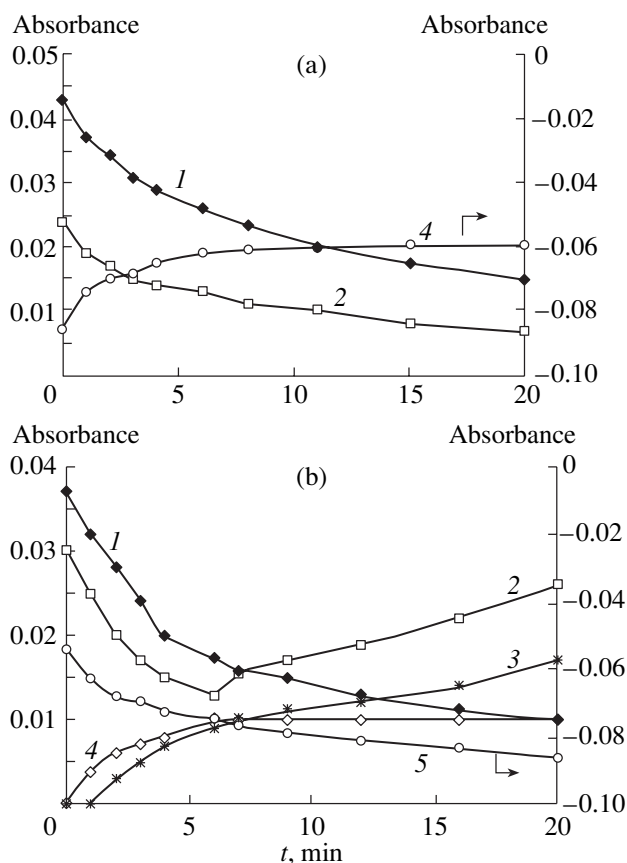
of the following composition: N$_2$, 0.1% NO/N$_2$, and (0.1% NO + 2.5% O$_2$)/N$_2$.

The formation of surface complexes was performed by passing a mixture of (0.5% C$_3$H$_8$ + 2.5% O$_2$)/N$_2$ over a sample initially at room temperature for 15 min and then on heating to 220 and 275°C. To determine the time dependence of the intensities of absorption bands due to adsorbed propane complexes on blowing a cell with the sample with the above gas flows, three experiments were performed at each of the specified temperatures.

Figure 9 demonstrates the results of this experiment at 275°C. It can be seen that the amount of adsorbed propane complexes on the surface decreased (absorption bands at 1540 and 1430 cm^{-1}) on blowing the cell with nitrogen (Fig. 9a). The rate of decrease in the intensity of the absorption bands at 1540 and 1430 cm^{-1} (Fig. 9b, curves *1*, *2*) increased upon the addition of (NO + O$_2$)/N$_2$, and the intensity of these bands decreased to zero after ~25 min. Figure 10 demonstrates the resulting kinetic curves linearized in the coordinates of a first-order rate equation. The same data were obtained in an analogous experiment at 220°C. At 350°C, we
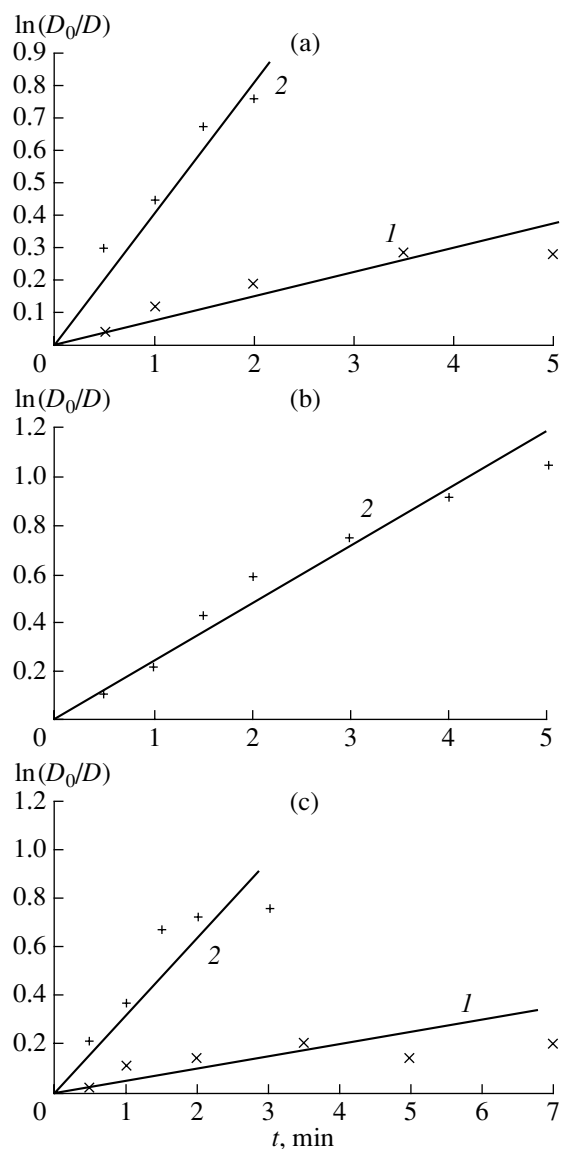
Fig. 8. Time dependence of the logarithms of the apparent constants of consumption of nitrite–nitrate complexes in a flow of (*1*) N_2 or (*2*) $(C_3H_8 + O_2)/N_2$ at 100°C for absorption bands at (a) 1540, (b) 1610, and (c) 1290 cm^{-1}.
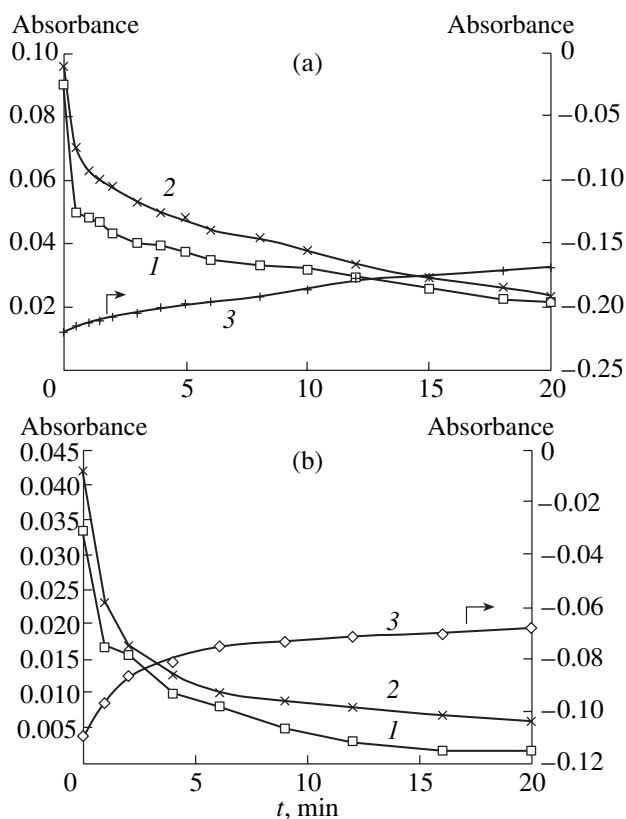

Fig. 9. Dependence of the intensities of absorption bands at (*1*) 1540, (*2*) 1430, and (*3*) 1000 cm^{-1} on the time of catalyst treatment with (a) nitrogen or (b) a mixture of $NO_x + O_2$ at 275°C.

failed to perform kinetic experiments because of a low surface concentration of adsorbed propane complexes.

DISCUSSION

Comparison of the Rates of Conversion of Surface Compounds with the Rate of Reaction

The surface concentration of a complex and the rate constant of its conversion should be known in order to compare the rate of conversion of surface compounds with the rate of reaction [5, 6].

The concentration of nitrates on the catalyst surface under conditions of HC-SCR was determined using the molar absorption coefficient ε (transmission IR spectroscopy), which relates the concentration of surface compounds (N/S) to the absorbance (D) of an absorption band:

$$N/S = D/\varepsilon, \qquad (1)$$

where N is the number of particles on the surface, and S is the surface area of a pellet.

The molar absorption coefficients were obtained using a combination of *in situ* IR spectroscopy and the temperature-programmed desorption (TPD) of NO_x. The thermal desorption data indicate that the first and second peaks in the TPD spectrum are due to the desorption of a nitrite complex (absorption bands at 1290 and 1410 cm^{-1}) and nitrate complexes (absorption bands at 1610 and 1540 cm^{-1}), respectively. This conclusion is based on the coincidence of the maximum temperatures of the desorption peaks and the maximum rates of decrease in the intensities of corresponding absorption bands. The number of NO_x molecules desorbed at each peak was reported elsewhere [1]. The calculated molar absorption coefficients of stretching vibrations in surface nitrite and nitrate complexes are as follows:

$\varepsilon_{1290} = 1.20 \times 10^{-19}$ cm^2/molecule;

$\varepsilon_{1610} = 0.25 \times 10^{-19}$ cm^2/molecule;

$\varepsilon_{1540} = 0.20 \times 10^{-19}$ cm^2/molecule.

An upper bound was obtained for ε_{1290} (a nitrite complex) because a portion of nitrites can be converted into nitrate complexes. The values of ε_{1610} and ε_{1540} were calculated on the assumption that the two nitrate complexes (bridging and bidentate) provided equal contributions to the desorption of NO$_x$ at the second peak. Note that the above experiments were repeatedly performed in order to improve the reliability.

The following molar absorption coefficients in an acetate complex were taken from [7]:

$\varepsilon_{1430} = 3.3 \times 10^{-19}$ cm^2/molecule;

$\varepsilon_{1540} = 7.0 \times 10^{-19}$ cm^2/molecule.

With the use of these values and the absorbance at the absorption bands of nitrite, nitrate, and acetate complexes under reaction conditions, we can determine the steady-state amounts of corresponding complexes on the surface. To determine the concentration of complexes on the catalyst surface under conditions of HC-SCR, we used the same samples as in the determination of ε.

The rate constants of conversion of the above surface complexes were determined in non-steady-state spectrokinetic experiments (Figs. 5–10). These data allowed us to calculate the rate of conversion of nitrate complexes (w_{calcd}) and to compare it with the rate of the HC-SCR reaction of NO$_x$ (w_{expt}).

The rate of conversion (w_{calcd}) of nitrate complexes on a sample was determined from the equation

$$w_{calcd} = kN, \qquad (2)$$

where k is the rate constant of conversion of a nitrate complex, and N is the number of surface atoms on the sample.

Tables 1 and 2 summarize the results of a comparison between the rates of reaction at various temperatures. Data given in Table 1 allowed us to estimate the activation energies (E_a) of the conversion of nitrite–nitrate structures in the reaction of nitrogen oxide reduction with propane and the activation energies of desorption (E_{des}) (Table 3).

Role of Surface Complexes in the SCR Reaction of NO$_x$

Oxygen-containing complexes. Changes in the intensities of the absorption bands of adsorbed oxygen (1000 cm^{-1}) and a complex with an absorption band at 1330–1360 cm^{-1} are indicative of the participation of these complexes both in the activation of NO (formation of nitrite–nitrate complexes) and in the activation of propane (formation of acetate structures).

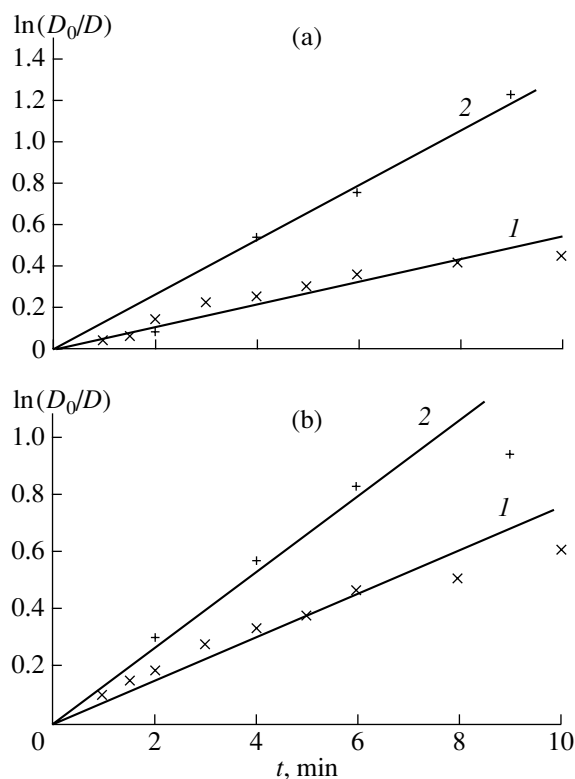**Nitrite–nitrate complexes.** In accordance with published data (for example, see the review [8]), sur-

Fig. 10. Time dependence of the logarithms of the apparent constants of consumption of adsorbed propane complexes in a gas flow of (*1*) N$_2$ or (*2*) (0.1%NO + 2.5%O$_2$)/N$_2$ at 275°C for absorption bands at (a) 1540 and (b) 1430 cm^{-1}.

face nitrite–nitrate complexes are intermediates in the HC-SCR reaction of NO$_x$. In the reaction with an activated hydrocarbon, these complexes formed a nitro organic complex, which was further converted into reaction products or oxidized to NO$_x$ and CO$_2$. We obtained the same result in a detailed study of the mechanism of this process on the NTK-10-1 Cu–Zn–Al oxide catalyst [2, 3]. From this standpoint, let us consider the results of this work.

Data given in Table 1 indicate that the overall rate of conversion of nitrite–nitrate structures at 70°C corresponds to the rate of conversion of NO$_x$. By this is meant that these surface structures are intermediates in the SCR of NO$_x$ with propane in an excess of oxygen. It is likely that the same ratio between the rate of conversion of nitrite–nitrate structures and the rate of oxidation is also valid at higher temperatures (100–140°C). However, we failed to test this hypothesis for two reasons. One of them consists in a considerable decrease in the surface coverage with nitrite–nitrate structures (the activation energy of desorption on these complexes is sufficiently high, see Table 3) as the reaction temperature was increased. This fact is consistent with a decrease in the rate of reaction with temperature (Table 1). The other reason is that the absorption band of a bidentate nitrate complex (1540 cm^{-1}) practically

Table 1. Comparison between the rate of conversion of surface nitrite–nitrate complexes in reaction with a mixture of $(C_3H_8 + O_2)/N_2$ and the rate of the selective reduction of NO_x

T, °C	Surface complex	k_{eff}, min^{-1}	D_{st}	$w_{calcd} \times 10^{-17}$, molecule/min	$w_{expt} \times 10^{-17}$, molecule/min
70	Nitrite (1290 cm^{-1})	0.005	0.	0	4.5
	Bridging nitrate (1610 cm^{-1})	0.012	0.004	0.42	
	Bidentate nitrate (1540 cm^{-1})	0.008	0.035	3.50	
100	Nitrite (1290 cm^{-1})	0.19	0	0	1.3
	Bridging nitrate (1610 cm^{-1})	0.25	0.003	0	
	Bidentate nitrate (1540 cm^{-1}) + acetate	0.28	0.042	123	
140*	Nitrite (1290 cm^{-1})	–	0	0	1.5
	Bridging nitrate (1610 cm^{-1})	0.38	0.002	0	
	Bidentate nitrate (1540 cm^{-1}) + acetate	0.43	0.033	156	

* As follows from data in Fig. 7, the consumption of nitrate–nitrite structures was accompanied by the formation of surface acetate. The rate constant of this process was determined from an ascending portion of the curve of acetate formation (1540 cm^{-1}). The rate constants of nitrate consumption are given with consideration for the rate of acetate formation.

Table 2. Comparison between the rate of reaction (w_{calcd}) of a surface acetate complex with a reaction mixture of (0.1% NO + 2.5% O_2)/N_2 and the rate of the selective reduction of NO_x (w_{expt})

T, °C	ν, cm^{-1}	k, min^{-1}	D_{st}	$w_{calcd} \times 10^{-17}$, molecule/min	$w_{expt} \times 10^{-17}$, molecule/min
220	1540	0.036	0.024	0.27	1.5
	1430	0.033	0.032		
275	1540	0.080	0.018	0.45	3.6
	1430	0.075	0.022		

coincides with an absorption band due to the asymmetric vibrations of an acetate complex. Therefore, a steady-state concentration of the bidentate nitrate under reaction conditions cannot be determined.

Acetate complexes. Shimizu and coauthors [9–11] studied the SCR of NO_x with propylene on Al_2O_3 and Cu/Al_2O_3. They found that the interaction between acetate and nitrate complexes is a rate-determining step in the formation of reaction products. In our case (Table 2), a comparison of the rate of conversion of an acetate complex with the rate of reaction indicates that the reaction of acetate with $NO_{x, ads}$ is only one of the reaction paths. The fraction of this reaction path in the overall process decreases with temperature. This result is consistent with spectroscopic and TPD data, which

Table 3. Activation energies of the conversion of nitrite–nitrate structures in the reduction of nitrogen oxides with propane and the activation energies of desorption

Surface complex	ν, cm^{-1}	E_a, kJ/mol	E_{des}, kJ/mol
Nitrite	1290	62 ± 15	65 ± 15
Bidentate nitrate	1540	80 ± 20	85 ± 20
Bridging nitrate	1610	65 ± 15	–

indicate that the surface coverage with $NO_{x, ads}$ complexes rapidly decreased with temperature.

An increase in the reaction temperature resulted in the reduction of the surface. Upon the admission of NO to the reduced surface, this surface was reoxidized from N_2. This fact was supported by data on the TPD of NO with mass spectrometric analysis of desorption products (Fig. 11): molecular nitrogen was the main constituent of these products.

The set of the above data allowed us to propose the following mechanism for the SCR of NO_x with propane on the STK catalyst. At low temperatures (to ~250°C), the rate of reduction of nitrogen oxides is determined by the interaction of surface nitrite–nitrate complexes with the activated hydrocarbon, and the subsequent process occurs in accordance with the mechanism described previously [8]. The amount of nitrite–nitrate complexes rapidly decreased with temperature, and the rate of reaction decreased until the onset of NO decomposition on the reduced surface. Nitrogen atoms recombine to form molecular nitrogen in a gas phase. Oxygen atoms react with the hydrocarbon to form CO_2 in a gas phase.

These concepts were supported by data on the concentration dependence of the conversions of reactants and the surface coverages obtained at 235 and 275°C

(Figs. 1–3). At these temperatures, acetate complexes were predominant on the surface. The rate of the process primarily depended on the concentration of nitrate structures. Therefore, an increase in the concentration of propane did not change the conversion of NO and decreased the conversion of propane (i.e., the rate of propane conversion remained practically unchanged). An increase in the concentration of oxygen somewhat decreased the conversion of NO because of an increase in the concentration of acetate structures. An increase in the concentration of NO did not affect the conversion of NO (the rate of NO conversion linearly increased). In this case, the conversion of propane should increase, and this increase was observed experimentally.

Based on the experimental data and taking into account the difference between the spectroscopic and adsorption properties of STK and NTK-10-1 catalysts, we can propose the following mechanism of synergism:

The oxidation of propane on the STK catalyst occurs with the participation of lattice oxygen. This is evidenced by the reduction of a sample in the SCR reaction of nitrogen oxide with propane and the appearance of nitrogen among the products of thermal desorption from the surface of this catalyst. Propane can undergo oxidation due to oxygen from the catalyst, as evidenced by the fact that propane conversion was observed for a time upon the admission of only C_3H_8 to the surface of STK. The products of propane oxidative dehydrogenation and/or partial oxidation (propylene and acrolein) are formed on the surface of the STK catalyst. These products are effective reducing agents for NO. To support this reaction scheme, we performed special experiments for detecting these products on the STK catalyst. Thus, absorption bands at 1650 and 1690 cm^{-1} were observed in the *in situ* IR spectra measured in the interaction of a reaction mixture of (0.1% NO + 0.5% C_3H_8 + 2.5% O_2)/N_2. These absorption bands were attributed to the vibrations of C=C and C=O bonds in a surface complex of acrolein that resulted from the mild oxidation of propane. A compound with $m/z = 42$, which was attributed to propylene, was detected in thermal desorption experiments with the mass-spectrometric analysis of desorption products performed after the adsorption of propane at room temperature. Propylene was experimentally detected in the oxidation of propane with atmospheric oxygen using the analysis of reaction products on a chromatograph with a flame-ionization detector.

Next, the adsorbed NO molecule and the product of C_3H_8 partial oxidation and/or oxidative dehydrogenation can react to form N_2 and CO_2. Because the amount of NO$_{ads}$ on STK is small at reaction temperatures, an excess amount of the product of C_3H_8 conversion is desorbed from the STK surface. At the next step, it can be adsorbed on the surface of NTK-10-1. The concentration of NO$_{ads}$ on this catalyst is high. The reduction of NO to molecular nitrogen results from the reaction of NO with the product of propane conversion.
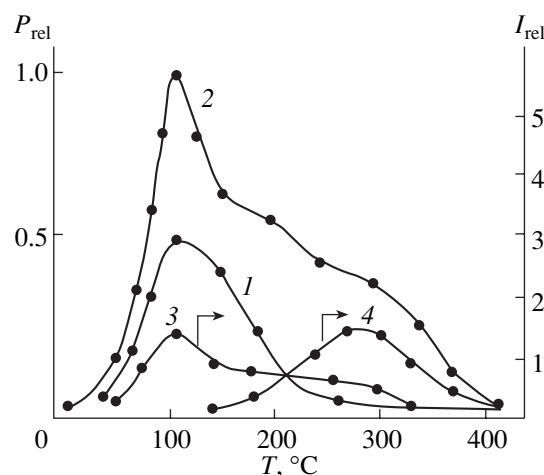

Fig. 11. Total TPD spectra of NO from the (*1*) oxidized and (*2*) reduced surfaces of the STK catalyst and the TPD spectra of (*3*) NO and (*4*) N_2 according to mass-spectrometric analysis data.

In addition to the above reactions, the product of propane partial oxidation can be further oxidized in the test system with oxygen on both of the components of a binary catalytic system (STK and NTK-10-1). The occurrence of synergism depends on the ratio between the rates of oxidation of the product of propane partial oxidation on STK and NTK-10-1, interfacial diffusion, and the interaction of the resulting product with NO$_{ads}$ on NTK-10-1.

CONCLUSIONS

Thus, quantitative spectrokinetic *in situ* measurements demonstrated that the rate of reduction of nitrogen oxides on the STK catalyst at temperatures to 250°C depends on the interaction of surface nitrite–nitrate complexes with an activated hydrocarbon, whereas the reaction on NTK-10-1 occurs via the formation and consumption of a nitrite complex at temperatures lower than 150°C. The amount of nitrite–nitrate complexes on the STK catalyst rapidly decreases with temperature, and the rate of reaction decreases until the onset of NO decomposition on the reduced surface to cause reoxidation of the catalyst surface. Nitrogen atoms undergo recombination to form molecular nitrogen in a gas phase. Oxygen atoms react with the hydrocarbon to form CO_2 in a gas phase. The nitrate complex is an intermediate in the selective reduction of nitrogen oxides with propane on the NTK-10-1 catalyst at temperatures higher than 150°C. The next step of the process is the formation of a nitro organic compound, which not only can yield deep oxidation products in an oxidizing atmosphere but also can undergo further oxidation with the release of nitrogen oxides into a gas phase.

In conclusion, note that differences between the mechanisms of the HC-SCR reaction of NO$_x$ on STK

and NTK-10-1 catalysts are due to the absence of high-temperature NO adsorption species from STK and a greater ability of STK to undergo reduction in the reaction mixture. Another special feature of the STK catalyst consists in the ability to form mild oxidation products of propane. These circumstances may explain a synergistic effect on the mechanical mixtures of the STK and NTK-10-1 catalysts.

REFERENCES

1. Tret'yakov, V.F., Burdeinaya, T.N., Zakorchevnaya, Yu.P., Matyshak, V.A., and Korchak, V.N., *Kinet. Katal.*, 2005, vol. 46, p. 556 [*Kinet. Catal.* (Engl. Transl.), 2005, vol. 46, p. 516].
2. Matyshak, V.A., Tret'yakov, V.F., Burdeinaya, T.N., and Zakorchevnaya, Yu.P., *Kinet. Katal.*, 2003, vol. 44, no. 6, p. 921.
3. Tret'yakov, V.F., Matyshak, V.A., Burdeinaya, T.N., and Zakorchevnaya, Yu.P., *Kinet. Katal.*, 2003, vol. 44, no. 6, p. 915.
4. Matyshak, V.A., *Kinet. Katal.*, 1997, vol. 38, no. 3, p. 432.
5. Matyshak, V.A. and Krylov, O.V., *Catal. Today*, 1995, vol. 25, no. 1, p. 1.
6. Matyshak, V.A., *Kinet. Katal.*, 1997, vol. 38, no. 3, p. 432.
7. Matyshak, V.A. and Krylov, O.V., *Kinet. Katal.*, 2002, vol. 43, no. 3, p. 422.
8. Sadykov, V.A., Lunin, V.V., Matyshak, V.A., Paukshtis, E.A., Rozovskii, A.Ya., and Bulgakov, N.N., and Ross, Dzh., *Kinet. Katal.*, 2003, vol. 44, no. 3, p. 412.
9. Shimizu, K., Kawabata, H., Satsuma, A., and Hattori, T., *J. Phys. Chem. B*, 1999, vol. 103, p. 5240.
10. Shimizu, K., Kawabata, H., Maeshima, H., Satsuma, A., and Hattori, T., *J. Phys. Chem. B*, 2000, vol. 104, p. 2885.
11. Shimizu, K., Kawabata, H., Satsuma, A., and Hattori, T., *Appl. Catal., B*, 1998, vol. 19, p. L87.