Reaction Paths of the Formation and Consumption of Nitroorganic Complex Intermediates in the Selective Catalytic Reduction of Nitrogen Oxides with Propylene on Zirconium Dioxide According to In Situ Fourier Transform IR Spectroscopic Data

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Abstract—Nitrate, acetate, and nitroorganic complexes were detected on the surface of ZrO_2 under the reaction conditions of nitrogen oxide reduction with propylene using Fourier transform IR spectroscopy. The nitroorganic complex was formed in the reaction between acetate and nitrate complexes by the replacement of the carboxyl group in the acetate complex by the nitro group. Monodentate nitrate was the most reactive species in this process. The adsorption of various nitroorganic substances was studied. It was found that the nitroorganic complex was structurally analogous to the nitromethane molecule bound to the surface through the nitro group. The experimental data led us to a conclusion that nitroorganic compounds were subsequently consumed in reactions with nitrate complexes. In this surface reaction, monodentate nitrate was also the most reactive species. The presence of oxygen had no effect on the consumption of the nitroorganic complex.

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INTRODUCTION

The selective catalytic reduction (SCR) of nitrogen oxides with hydrocarbons in an excess of oxygen is a promising method for the removal of NO_x from industrial waste gases and automotive exhaust emissions [1]. A great number of publications were devoted to the mechanistic studies of this process [2–18].

Currently, it is well established that nitrate complexes participate in the reaction. As a result of many studies on the role of nitrite–nitrate structures in SCR, the concept of the interaction of nitrate complexes and/or NO_2 (their degradation product) with hydrocarbons and/or their partial oxidation products has been most widely developed. This interaction causes the formation of nitrogen-containing substances, primarily, nitroorganic compounds $O_2N–C_mH_n$ and organic nitrites $ONO–C_mH_n$ [19–28].

At elevated temperatures, these compounds react with $NO + O_2/NO_2$ to form molecular nitrogen. At an insufficient amount of an oxidizing agent and at temperatures higher than 200–300°C, nitrogen-containing organic compounds can decompose to form OCN^- [26, 28] and NC^- anions [28, 29], organic nitriles [21], cyanogen [30], hydrocyanic acid [30, 31], or even ammonia

[21, 24]. Surface isocyanates are the most stable and, consequently, most often detectable decomposition products of N-containing compounds.

Isocyanates, as well as surface cyanides, readily react with a mixture of $NO + O_2$ and/or NO_2 even at room temperature to be converted into molecular nitrogen and N_2O [26, 28, 29, 31–33].

Thus, the reduction of surface nitrates with hydrocarbons primarily results in the appearance of nitrogen-containing organic compounds, which either directly interact with $NO_x + O_2$ to form SCR products or decompose to substances containing NC^- and OCN^- anions. In an excess of oxygen, the undesirable oxidation of nitrogen-containing organic compounds can occur to result in the formation of a superequilibrium concentration of NO_2 [24]:

$$C_mH_nNO_2 + O_2 \longrightarrow NO_2 + CO_2 + H_2O.$$
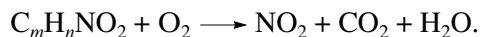
As follows from the published data cited above, common properties of surface nitroorganic compounds have been determined to date. At the same time, there is no information on the steps of the formation of these complexes, on the structure of organic moieties, on the mechanism of conversion of a nitrate complex into

molecular nitrogen, and on the roles of oxygen and nitrogen oxides in this process. Information on the role of the nature of the catalyst in the above surface reactions is of paramount importance from the standpoint of SCR process activity and selectivity control.

In this context, the aim of this study was to determine the reaction paths of formation and consumption of nitroorganic complex intermediates in the SCR of nitrogen oxides with propylene in the presence of catalysts based on zirconium dioxide with the use of in situ Fourier transform IR spectroscopy. The ZrO_2-containing systems are promising low-temperature catalysts for the SCR of NO_x with hydrocarbons in an excess of oxygen; they exhibit good hydrothermal properties and resistance to sulfur poisoning [34, 35]. Here, we report the results of a study of the properties of nitroorganic compounds on the surface of zirconium dioxide.

EXPERIMENTAL

ZrO_2 was synthesized in accordance with a published procedure [36]. A freshly prepared 1.5 M aqueous solution of $ZrO(NO_3)_2$ was aged for 15 h and then hydrolyzed in excess aqueous ammonia with intense stirring; pH ~ 9.5 was adjusted. The resulting zirconium hydroxide in the mother liquor was hydrothermally treated in an autoclave at 90°C for 24 h and at 110°C for 8 h.

$$ZrO^{2-} + OH^- \longrightarrow ZrO_c(OH)_d \longrightarrow ZrO_2 \cdot nH_2O.$$
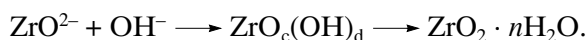
The resulting $ZrO_2 \cdot nH_2O$ was filtered off, washed with 0.1 M NH_4OH, dried at 110°C, and then calcined at 500°C for 2 h (the sample designated as $ZrO_2(500)$).

The X-ray diffraction (XRD) analysis of samples was performed on a DRON-3 diffractometer (CuK_α (λ = 1.54178 Å), 2θ step of 0.1°, and exposure time of 2 s). All of the calculations, including the evaluation of interplanar distances, were performed in accordance with standard procedures. The phase composition analysis was performed by comparing with data in the JCPDS File.

The interaction of reaction components and their mixtures with sample surfaces was studied in the course of reaching a steady state using transmission Fourier transform IR spectroscopy (Spectrum RX I FT-IR System spectrometer from Perkin-Elmer). Before measuring the IR spectra, ZrO_2 pellets (10–20 mg/cm²) were treated in a flow of N_2 at 400°C. The design of IR reactor cells, which allowed us to measure the spectra at elevated temperatures, was described elsewhere [37]. The intensities of absorption bands in transmission spectra were measured in absorbance units (A).

The IR spectra were obtained by subtracting the spectra of a sample in a flow of nitrogen from the spectra of sample $ZrO_2(500)$ in a flow of a reaction mixture under the same conditions.

The interaction of NO_x with the surface of ZrO_2 was also studied using temperature-programmed desorption (TPD). The TPD under flow conditions in a reactor cell was combined with the measurement of the IR spectra of surface complexes. Before performing a thermal-desorption experiment, the sample of ZrO_2 was treated with nitrogen at 400–500°C immediately in the IR cell. Unless otherwise specified, the samples were cooled to room temperature in a closed cell (without a flow of N_2); thereafter, the adsorption of 0.2% NO/N_2 was performed for 20 min. An excess amount of NO was displaced with a flow of nitrogen for 25 min. Thermal desorption was performed with continuous analysis for NO and NO_x in a gas phase before and after the reactor using a Beckman 951A chemiluminescence NO/NO_x analyzer (nitrogen was a carrier gas; the heating rate was 5 K/min). In the course of thermal desorption, the spectra of surface compounds were measured. Each particular spectrum provided information on changes in the surface state upon heating by 20°C.

The gas flow rate was 9000 h^{-1} in all of the experiments. All of the gases were purified with the use of traps containing anhydrone and Ascarite. The base composition of the mixture was 0.2% NO + 0.2% C_3H_6 + 2.5% O_2/N_2. In a study of the effect of the composition of the mixture on the properties of surface compounds, the concentrations of NO, C_3H_6, and O_2 were varied from 0 to 0.5, 1.0, and 4.0%, respectively. The analysis of gases before and after the reactor cell was performed using a Beckman 951A NO/NO_x chemiluminescence analyzer and a Beckman 590 HC/CO infrared analyzer.

RESULTS AND DISCUSSION

According to XRD data, the resulting samples of zirconium dioxide were a mixture of two phases, monoclinic (m-ZrO_2) and tetragonal (t-ZrO_2); the latter was predominant. The average size of the coherent-scattering region (CSR) was evaluated from the half-width of a reflection corresponding to the (111) face of m-ZrO_2.

The TPD spectra of NO_x after the adsorption of NO on the surface of $ZrO_2(500)$, which mainly contained a tetragonal phase, consisted of two broad peaks with T_{max} = 240 and 490°C (Fig. 1). Both of the peaks corresponded to the release of NO and NO_2 molecules into a gas phase; as a rule, the thermal-desorption maximums of these oxides did not coincide. The thermal-desorption curves shown in Fig. 1 suggest that low-temperature desorption was primarily related to the release of NO, whereas the amount of NO_2 molecules formed in the high-temperature region predominated over the release of NO.

The IR spectra measured in the course of the above thermal-desorption experiments mainly exhibited absorption bands due to nitrate (~1610, 1587, and 1568 cm^{-1}) and nitrite (~1505 and 1291 cm^{-1}) com-

Concentration, vol %
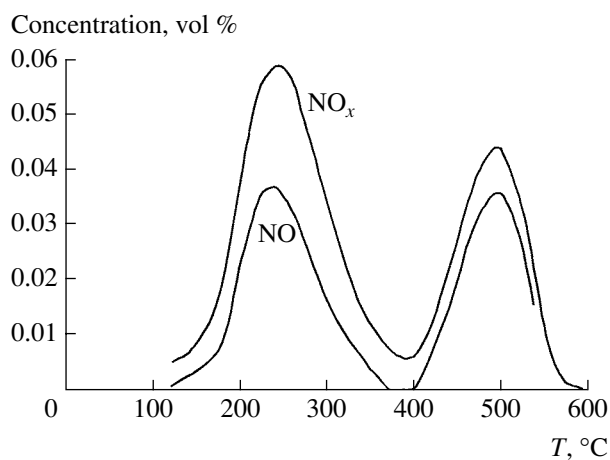
Fig. 1. TPD spectrum of NO_x after the adsorption of NO on the surface of $ZrO_2(500)$.

plexes. Matyshak et al. [38] found that the intensity of absorption bands due to nitrate complexes decreased upon desorption over the range 400–500°C, whereas the intensity of absorption bands due to bridging nitrite complexes (1505 and 1291 cm^{-1}) decreased over the range 200–300°C. A comparison between spectroscopic and TPD data showed that the decrease in the intensity of absorption bands due to nitrate complexes in the course of desorption corresponds to the high-temperature peak of NO_x release (T_{max} = 430–480°C) in

the TPD spectrum. The decrease in the intensity of absorption bands due to bridging nitrite complexes (1530 and 1180 cm^{-1}) in the course of desorption corresponds to the peak with T_{max} = 230–240°C (Fig. 1).

Steady-Sate Spectrokinetic Data

Figure 2 shows the IR spectra obtained upon the interaction of binary mixtures with the surface of ZrO_2 and the spectrum of a mixture of NO + C_3H_6 + O_2. Spectrum *1* (a mixture of 0.2% NO + 2.5% O_2/N_2) consists of absorption bands due to nitrate and nitrite complexes. Bands corresponding to nitrosyl complexes were not observed under these conditions. The assignment of absorption bands was performed based on well-known published data [39–44] (Table 2).

Spectrum *2* (a mixture of 0.2% C_3H_6 + 2.5% O_2/N_2) includes low-intensity absorption bands due to carbonate–carboxylate structures. Table 3 summarizes the assignment of absorption bands [39]. Note that the intensity of these absorption bands passed through a maximum as the temperature was increased.

Spectrum *3* for a mixture of 0.2% NO + 0.2% C_3H_6/N_2 is similar to spectrum *2* in the occurrence of absorption bands due to nitrate and nitrite complexes. The difference consists in the presence of absorption bands at 1360–1380 and 1560–1570 cm^{-1} in spectrum *3*. In accordance with published data [25–28, 45, 46], these bands can be attributed to symmetric and anti-
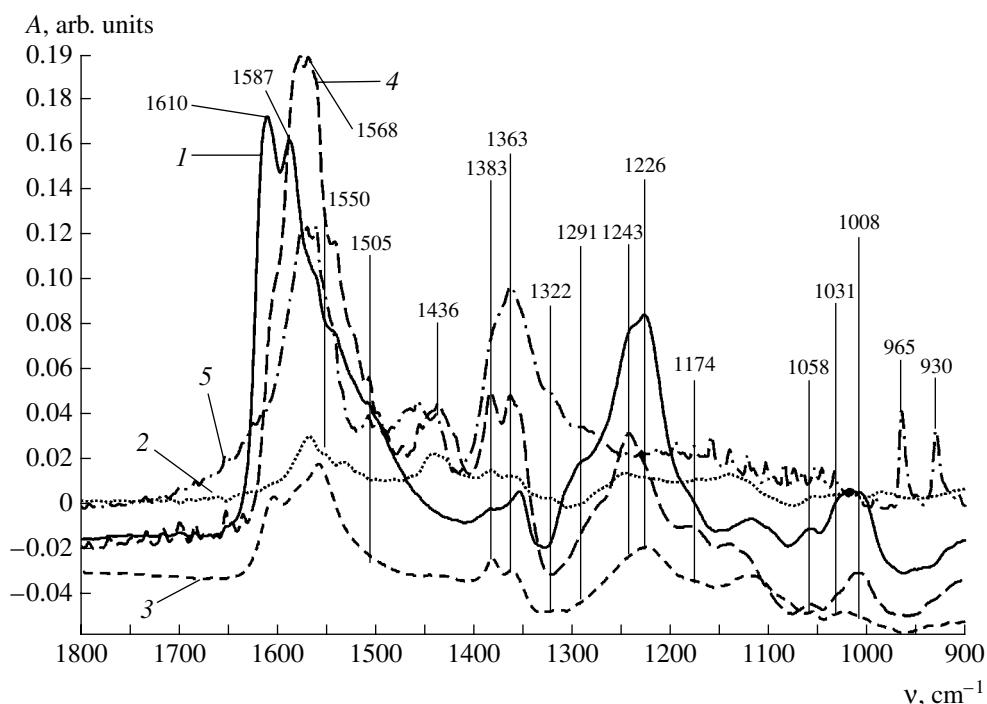
Fig. 2. IR spectra obtained upon the interaction of (*1*) 0.2 vol % NO + 2.5 vol % O_2/N_2 (T = 250°C), (*2*) 0.2 vol % C_3H_6 + 2.5 vol % O_2/N_2 (T = 250°C), (*3*) 0.2 vol % NO + 0.2 vol % C_3H_6/N_2 (T = 300°C), and (*4*) 0.2 vol % NO + 0.2 vol % C_3H_6 + 2.5 vol % O_2/N_2 (T = 300°C) mixtures or (*5*) nitromethane (T = 300°C) with the surface of ZrO_2.

Table 1. Characteristics of sample $ZrO_2(500)$

S_{sp}, m^2/g	CSR, Å	$I_t(111)/I_m(111)$, arb. units
116	195	1.4

Table 2. Assignment of absorption bands in spectra after the interaction of a 0.2 vol % NO + 2.5 vol % O_2/N_2 gas mixture with the surface of ZrO_2 at 150°C

Complex	Absorption bands, cm^{-1}
Bridging nitrate	1610
	1226
	1031
Bidentate nitrate	1587
	1243
	1058
Monodentate nitrate	1580
	1226
	1008
Monodentate nitrite	1505
	1291
Bidentate nitrite	1531
	1174

Table 3. Assignment of absorption bands in spectra after the interaction of a 0.2 vol % C_3H_6 + 2.5 vol % O_2/N_2 gas mixture with the surface of ZrO_2 at 250–350°C

Complex	Absorption bands, cm^{-1}	Complex	Absorption bands, cm^{-1}
Monodentate carbonate	1560	Acetate	1550
	1250		1445
	1133		

Table 4. Assignment of absorption bands in spectra after the interaction of a 0.2 vol % NO + 0.2 vol % C_3H_6/N_2 gas mixture with the surface of ZrO_2 at 250°C

| Complex	Absorption bands, cm^{-1}
Bridging nitrate	1610, 1226, 1031
Bidentate nitrate	1587, 1243, 1058
Monodentate nitrate	1568, 1228, 1008
Nitroorganic complex	1560, 1383, 1363
Monodentate nitrite	1505, 1291
Acetate	1550, 1445

symmetric vibrations of the nitro group in a nitroorganic surface complex. This assignment was also supported by the fact that these absorption bands were not observed in the absence of NO or C_3H_6 from a gas phase, as well as by special experiments on the adsorption of various nitroorganic compounds under analogous conditions (Fig. 3). For comparison, Figure 2 (spectrum *5*) shows the spectrum of nitromethane adsorbed under identical conditions. Konin [47] reported additional TPD and IR- and EPR-spectroscopic data on the formation of nitroorganic complexes in this system. The presence of absorption bands due to acetate complexes in the spectra is also possible. Table 4 summarizes the assignment of absorption bands [25–28, 45, 46].

Spectrum *4* was obtained upon the interaction of a ternary reaction mixture of 0.2% NO + 0.2% C_3H_6 + 2.5% O_2/N_2 with the surface of ZrO_2. This spectrum consists of several closely spaced absorption bands due to nitrite, nitrate, acetate, and nitroorganic complexes. In order to find the temperature dependence of the intensity of an absorption band due to a particular complex, the total spectrum was decomposed into constituents with the use of standard programs assuming Lorentzian or Gaussian shapes of absorption bands.

Figure 4 shows how absorption band intensities (*1–9*) and the activity of ZrO_2 in the SCR of NO_x with propylene (*10, 11*) vary as the sample temperature in the flowing reaction mixture is increased. An analysis of these data provides support for the assignment of absorption bands observed under reaction conditions to vibrations in a nitroorganic complex, two nitrates (bridging and bidentate), nitrite, and acetate complexes. As the temperature was decreased, the surface concentration of these complexes either increased or passed through a maximum. Moreover, an increase in catalytic activity with temperature is accompanied by a decrease in the intensity of absorption bands due to surface compounds. Note that absorption bands due to a nitrite complex (curves *8, 9*) disappeared from the spectra at a lower temperature than the absorption bands of other surface compounds.

In order to study the effect of the composition of a reaction mixture, spectroscopic measurements were performed at 250, 300, and 350°C. Data obtained at 250°C are considered below. An increase in the O_2 content of the reaction mixture resulted in a monotonic increase in the concentrations (intensities of corresponding absorption bands in the spectra) of all of the above complexes with a plateau at 2–2.5% O_2. An increase in the concentration of NO in the reaction mixture to 0.4% was characterized by an increase in the concentrations of all of the complexes.
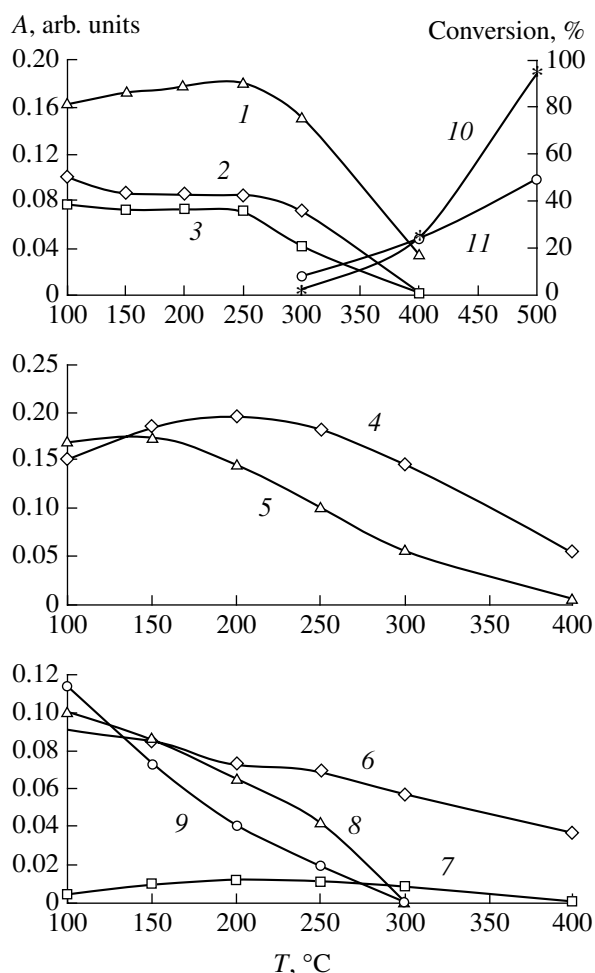
The most interesting results were obtained with increasing propylene concentration (0–0.4%) in the reaction mixture (Fig. 5). The addition of a small amount of propylene to the flow of a mixture of 0.2% NO + 2.5% O_2/N_2 resulted in a considerable increase in
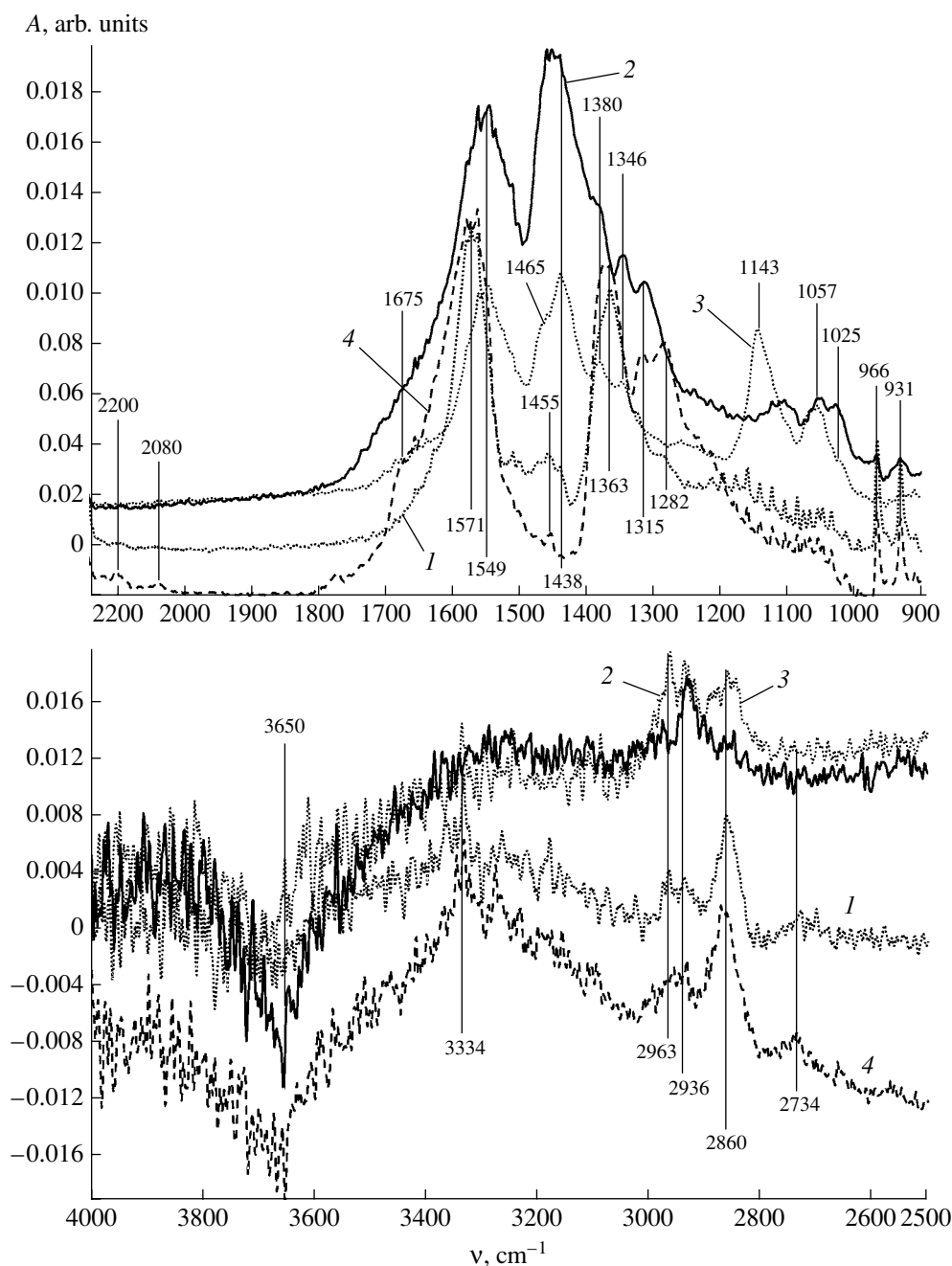
Fig. 3. IR spectra measured in the course of the interaction of (*1*) nitromethane, (*2*) nitroethane, and (*3*) nitropropane at 300°C or (*4*) nitromethane at 250°C with the surface of ZrO_2.

the intensities of absorption bands due to bridging and bidentate nitrates (curves *1* and *2*) and a decrease in the intensities of absorption bands due to monodentate nitrates up to the disappearance of these bands (curve *3*). As the concentration of propylene in the mixture was increased, the concentration of bridging nitrates decreased, whereas the concentration of bidentate nitrates remained unchanged. Simultaneously, an increase in the surface concentrations of nitroorganic (curve *4*) and acetate (curve *5*) complexes was
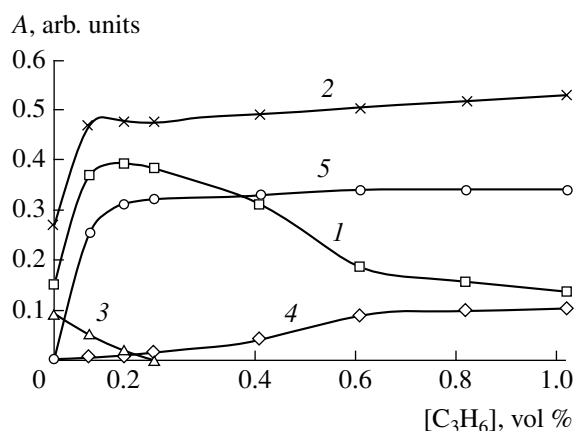
observed. The observed changes can be explained based on the assumption that monodentate nitrates most efficiently react with propylene to form nitroorganic complexes. This assumption was also supported by the fact that the absorption bands of monodentate complexes were not observed under reaction conditions (Fig. 3). In this case, a portion of oxygen sites on the surface became free. An additional amount of bridging and bidentate nitrates was formed at these sites. It is likely that surface nitrite complexes were a source for

Fig. 5. Changes in the intensities of absorption bands as functions of propylene concentration in the reaction mixture: (*1*) bridging nitrate (1610 cm^{-1}), (*2*) bidentate nitrate (1587 cm^{-1}), (*3*) monodentate nitrate (1568 cm^{-1}), (*4*) nitroorganic complex (1383 cm^{-1}), and (*5*) acetate complex (1550 cm^{-1}); $T = 250°C$.

Fig. 4. Changes in the activity of ZrO$_2$ and in the intensities of absorption bands due to nitroorganic ((*1*) 1560, (*2*) 1383, and (*3*) 1363 cm^{-1}), nitrate ((*4*) 1610 and (*5*) 1587 cm^{-1}), acetate ((*6*) 1550 and (*7*) 1445 cm^{-1}), and nitrite ((*8*) 1505 and (*9*) 1291 cm^{-1}) complexes as a function of reaction temperature: (*10*) C$_3$H$_6$ conversion and (*11*) NO$_x$ conversion (a mixture of 0.2 vol % NO + 0.2 vol % C$_3$H$_6$ + 2.5 vol % O$_2$/N$_2$).

the formation of nitrates. A decrease in the concentration of bridging nitrates as the concentration of propylene in the mixture was increased can also be explained by their interaction with propylene to form nitroorganic complexes.

The experimental data suggest that nitrates are among the surface reagents yielding nitroorganic complexes; the rates of their reactions with propylene decreased in the following order: monodentate, bridging, and bidentate. We failed to identify the surface propylene species that participate in the formation of nitroorganic compounds based on the experimental data. The only propylene species on the surface is an acetate complex. If it participates in the formation of nitroorganic complexes, their structure should be close to the structure of nitromethane. Analogous conclusions were

drawn based on analogous experiments at 300 and 350°C.

In order to refine the structure of the nitroorganic complex, we performed the adsorption of various nitroorganic compounds on ZrO$_2$ ($T = 250$ and 300°C; nitromethane, nitroethane, and nitropropane concentrations in a flow of nitrogen were 3%). Figure 3 shows the results of such experiments. The spectra obtained upon the interaction of a sample with a flow of nitropropane and nitroethane were similar, and they were characterized by the presence of intense absorption bands at 1440 and 1550 cm^{-1} (spectra *2* and *3*). In contrast to this, absorption bands at 1560–1570 cm^{-1} and a doublet at 1380 and 1363 cm^{-1} were the main components of the spectra of adsorbed nitromethane (spectra *1* and *4*). An analogous spectrum obtained upon nitromethane adsorption on Pt/SiO$_2$ [25] is consistent with spectrum *5*, which was observed under reaction conditions, in Fig. 2. This similarity allowed us to state that the structure of the nitroorganic complex observed under reaction conditions is close to the structure of adsorbed nitromethane. A comparison of the position of absorption bands due to adsorbed nitromethane with the position of absorption bands due to nitromethane molecules in a gas phase demonstrates that the symmetric vibrations of the NO$_2$ group underwent the greatest low-frequency shift (~40 cm^{-1}). By this is meant that NO bonds of the nitro group participated in the formation of a bond between the complex and the surface.

The interaction of nitromethane with the surface of ZrO$_2$ resulted not only in its adsorption but also in its conversion, as evidenced by the appearance of an absorption band at 1675 cm^{-1} (Fig. 3, spectrum *4*) in the spectra; this band was due to vibrations in a nitritoorganic complex [19–28]. Moreover, the spectra exhib-

ited absorption bands due to CH$_2$ groups (2936 and 2860 cm^{-1}), NO$_{ads}$ (2080 and 2200 cm^{-1}), and NH$_3$ (931 and 966 cm^{-1}); this is indicative of deeper degradation of the nitromethane molecule.

Note that nitritoorganic complexes are thermally less stable than nitroorganic surface compounds (Fig. 3, spectra *1* and *4*). By this is meant that the participation of nitritoorganic complexes in reaction would be expected at lower temperatures, as compared with nitroorganic surface compounds.

The experimental data suggest that the surface complex of nitromethane is formed by the interaction of surface acetate and nitrate complexes via the replacement of the COO group of acetate by the NOO group of the nitrate complex.

The above data exhibit an additional interesting property of the test system. Upon the combined adsorption of C$_3$H$_6$, NO, and O$_2$ or upon the addition of a third component to a flow of two reagents, the amount of surface complexes dramatically increased, as compared with the individual adsorption of the reagents. In particular, the concentration of surface nitrates increased upon the addition of propylene to a flow of NO + O$_2$ (Fig. 4); the concentration of surface acetates increased upon the addition of NO to a flow of C$_3$H$_6$ + O$_2$. It is likely that surface properties were changed upon the adsorption of a reagent; this facilitated the adsorption of other reagents.

Non-Steady-State Measurements

Figures 6–8 illustrate the results of non-steady-state measurements. Strongly bound acetate (Fig. 6, curve *4*) and nitrate complexes (Fig. 6, curves *1–3*) were formed upon the interaction of C$_3$H$_6$ + O$_2$/N$_2$ or NO + O$_2$/N$_2$ mixtures with the surface of ZrO$_2$. At 350°C, these complexes were not removed from the surface after blowing the catalyst with an inert gas flow. This result is consistent with data on the thermal desorption of NO (Fig. 1).

The study of the reactivity of surface acetate complexes demonstrated that earlier formed acetate complexes were consumed upon the addition of a flow containing NO (Fig. 7, curve *3*), whereas the concentration of nitroorganic compounds and nitrate complexes passed through a maximum (Fig. 7, curves *1* and *2*). Simple evaluations demonstrated that the intensity of absorption bands due to a nitroorganic compound was approximately proportional to the product of the absorption band intensities of nitrate and acetate compounds. Consequently, the nitroorganic compound was formed by the interaction of nitrate and acetate surface complexes. The additional decrease in the absorption band intensity of nitroorganic compounds can be explained by the subsequent consumption of these
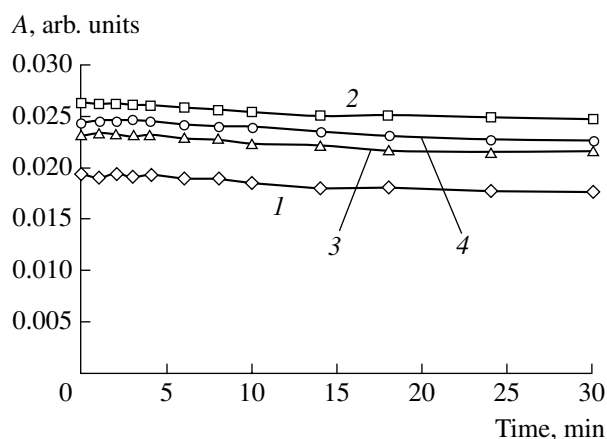
Fig. 6. Changes in the intensities of absorption bands in the spectra obtained with increasing time of purging the reactor cell with a flow of nitrogen: (*1*) bridging nitrate (1610 cm^{-1}), (*2*) bidentate nitrate (1587 cm^{-1}), (3) monodentate nitrate (1568 cm^{-1}), and (*4*) acetate complex (1550 cm^{-1}); $T = 350$°C.
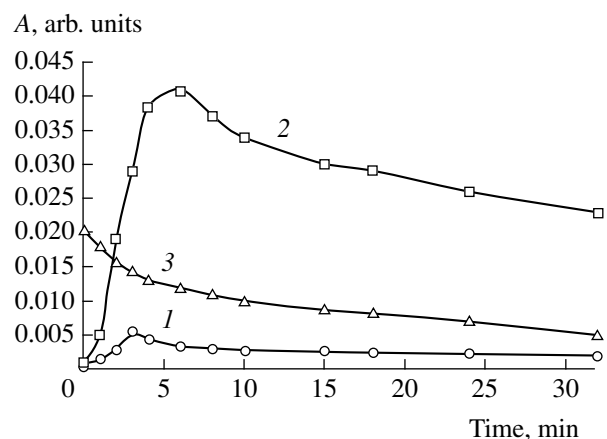
Fig. 7. Changes in the intensities of absorption bands in the spectra obtained with increasing time of purging the reactor cell with a flow of a 0.2 vol % NO/N$_2$ mixture: (*1*) nitroorganic complex (1383 cm^{-1}), (*2*) bridging nitrate (1610 cm^{-1}), and (*3*) acetate complex (1445 cm^{-1}); $T = 350$°C.

compounds in reactions with NO or NO$_2$, which were released in the degradation of surface nitrates, with the formation of reaction products.

Table 5. Rate constants of consumption of nitroorganic (k(I)) and nitrate (k(II)) complexes on the surface of ZrO$_2$

T, °C	k(I), min^{-1}	k(II), min^{-1}		
	1383 cm^{-1}	1568 cm^{-1}	1587 cm^{-1}	1610 cm^{-1}
250	0	0	0	0
300	0.021	0.019	0	0
350	0.042	0.045	0.012	0.010

A, arb. units

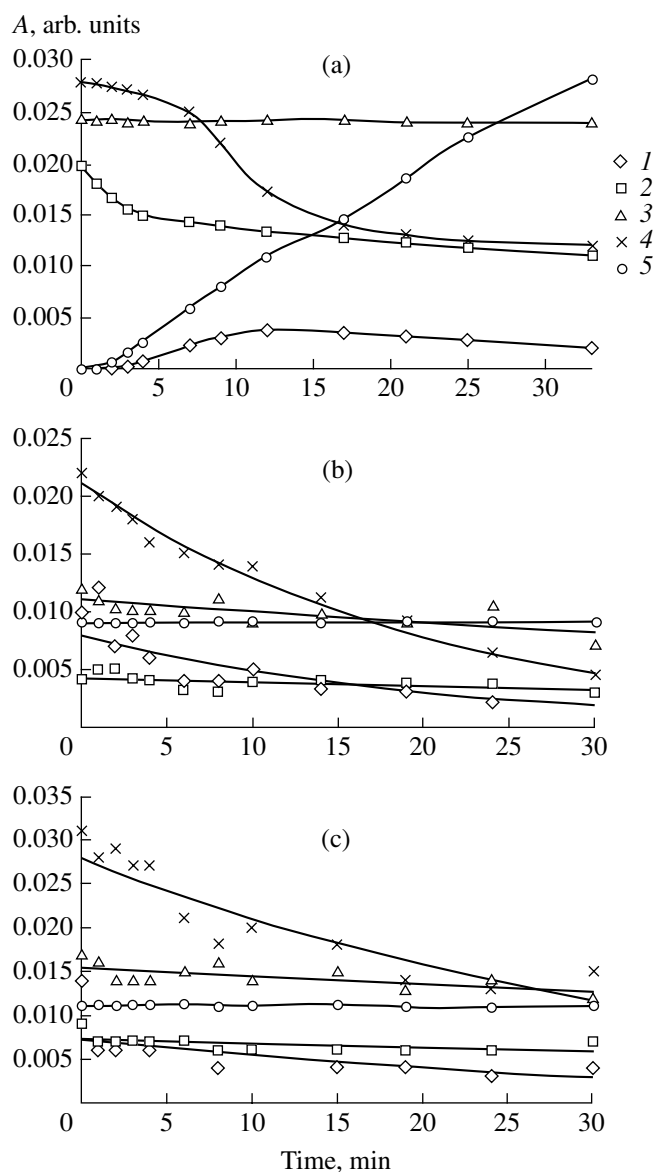

Fig. 8. Changes in the intensities of absorption bands in the spectra obtained with increasing time of purging the reactor cell with a flow of (a) a 0.2 vol % C_3H_6 + 2.5 vol % O_2/N_2 mixture, (b) nitrogen, or (c) a 2.5 vol % O_2/N_2 mixture: (*1*) nitroorganic complex (1383 cm^{-1}), (*2*) bridging nitrate (1610 cm^{-1}), (*3*) bidentate nitrate (1587 cm^{-1}), (*4*) monodentate nitrate (1568 cm^{-1}), and (*5*) acetate complex (1445 cm^{-1}); $T = 350°C$.

Figure 8a shows the results of an analogous study of the reactivity of surface nitrate complexes. It can be seen that, upon the addition of a mixture of propylene and oxygen, previously formed nitrate complexes were consumed (Fig. 8a, curves *2–4*), whereas the concentration of nitroorganic compounds passed through a maximum (curve *1*). Note that monodentate nitrate exhibited the highest reactivity (curve *3*). The intensities of absorption bands due to acetate complexes increased (curve *5*). In this case, as estimated, the intensity of

absorption bands due to a nitroorganic compound was also approximately proportional to the product of the concentrations of nitrate and acetate compounds.

Figures 8b and 8c show plots that characterize the consumption of nitroorganic compounds. These compounds were formed on the surface by the interaction of a mixture of propylene, NO, and oxygen with the catalyst surface. In this case, nitrate and acetate complexes were formed on the surface in addition to the nitroorganic complex. As the duration of purging the cell with a flow of nitrogen was increased (Fig. 8), a decrease in the concentration of the nitroorganic compound (curve *1*) and nitrate complexes (curves *2–4*) was observed at a constant concentration of surface acetate complexes (curve *5*). Because the nitrate and acetate complexes individually occurring on the surface were not desorbed in a flow of nitrogen (Fig. 6), this fact unambiguously indicates that nitroorganic compounds were consumed in the interaction with nitrate complexes. In this case, monodentate nitrate was the most reactive species (curve *4*).

Figure 8c shows changes in the intensities of adsorption bands due to surface compounds with increasing duration of purging the cell with a flow of a mixture of oxygen and nitrogen. It can be seen that the rate of decrease of the concentration of a nitroorganic compound (curve *1*) and nitrate complexes with time does not depend on the presence of oxygen in a gas phase (cf. Figs. 8b and 8c). Therefore, the nitroorganic complex on the surface of ZrO_2 almost does not react with oxygen.

Analogous experiments were also performed at 300 and 250°C. The results of these experiments allowed us to evaluate the rate constants and activation energy of the interaction of a nitroorganic compound and a monodentate nitrate complex on the surface of ZrO_2 (Table 5).

Data given in Figs. 3 and 4 and Table 5 indicate that, at 250°C, nitroorganic complexes were formed but almost not consumed. This fact is consistent with the fact that ZrO_2 did not exhibit detectable activity at 250°C (Fig. 3, curves *10*, *11*).

The equality of the rate constants of consumption of nitroorganic and monodentate nitrate complexes supports the fact that the interaction between them is the main surface reaction that leads to the formation of SCR products. This conclusion is supported by the estimated activation energies of the consumption of nitroorganic and monodentate nitrate complexes. The estimated values were found approximately equal to 60 kJ/mol and close to the activation energy of the overall SCR of NO_x found previously [47].

CONCLUSIONS

Under the reaction conditions examined, nitrate, acetate, and nitroorganic complexes occurred on the surface of ZrO_2. Surface reaction between nitrate and

acetate complexes resulted in the formation of a nitro-organic compound. A monodentate nitrate complex was most reactive in this process; this was likely because its structure was most capable of forming an NOO group upon activation. Based on the experimental results obtained in this work, we can state that the replacement of the carboxyl group in an acetate complex by this group is the main surface reaction of the formation of a nitroorganic complex. The participation of an acetate surface complex in the formation of a nitroorganic compound was also reported by Shimizu et al. [12].

Nitroorganic compounds are usually identified by the occurrence of vibrations of the nitro group. The structural identification of the organic moiety of a nitro-organic complex is very difficult to perform. For example, Chi and Chuang [28] assumed the structure of a nitroorganic complex to be identical to that of adsorbed nitropropane without experimental justification. Haneda et al. [17] interpreted the fact that the sets of reaction products were identical with the use of propylene and nitropropane as reducing agents in favor of a structural similarity between the nitroorganic complex and nitropropane.

In this study, we attempted to determine the structure of the nitroorganic complex based on a spectroscopic study of the interaction of various nitroorganic substances with the surface of ZrO_2 under analogous reaction conditions. The results of this study (Figs. 2, 3) indicate that the spectrum of the nitroorganic complex measured under reaction conditions is similar to the spectrum obtained upon the interaction of a sample with nitromethane. It is believed that the nitroorganic complex is a nitromethane molecule bound to the surface through the nitro group.

Data obtained in this work (Figs. 8b, 8c) suggest that nitroorganic compounds are further consumed in reactions with nitrate complexes; a monodentate nitrate complex is also most reactive in this process.

Note that the rate of decrease of the concentration of a nitroorganic compound with time does not depend on the presence of oxygen in a gas phase (Figs. 8b, 8c). By this is meant that the nitroorganic complex on the surface of ZrO_2 almost does not react with oxygen; that is, a side reaction of the additional oxidation of the nitro-organic complex with the release of NO_x into a gas phase does not occur on the surface of ZrO_2. The stable structure of the nitroorganic complex explains the fact that we failed to detect complexes formed by surface transformations of the nitroorganic complex (isocyanate, nitrile, ammonia, etc.) under reaction conditions (at 250–350°C).

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