ISSN 0023-1584, Kinetics and Catalysis, 2006, Vol. 47, No. 5, pp. 747–755. © MAIK "Nauka/Interperiodica" (Russia), 2006.
Original Russian Text © V.A. Matyshak, V.F. Tret'yakov, K.A. Chernyshev, T.N. Burdeinaya, V.N. Korchak, V.A. Sadykov, 2006, published in Kinetika i Kataliz, 2006, Vol. 47, No. 5, pp. 770–778.

Reaction Paths of the Formation and Consumption of Nitroorganic Complex Intermediates in the Selective Catalytic Reduction of Nitrogen Oxides with Propylene on Zirconia-Pillared Clays According to In Situ Spectroscopic Data

V. A. Matyshak[a], V. F. Tret'yakov[b], K. A. Chernyshev[a], T. N. Burdeinaya[b], V. N. Korchak[a], and V. A. Sadykov[c]

[a] *Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117977 Russia*
[b] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 117912 Russia*
[c] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

Received January 26, 2005

Abstract—It was found that the adsorption and catalytic properties of nanosized ZrO_2 particles as the pillar constituents of ZrO_2-pillared clay and bulk ZrO_2 are essentially different. The interaction of NO with the surface of bulk ZrO_2 resulted in the formation of three types of nitrate complexes. Only two nitrate species were formed on ZrO_2-pillared clay (the monodentate species was absent). Only an acetate complex was formed in the interaction of a mixture of propylene and oxygen with the surface of bulk ZrO_2, whereas an isopropoxide complex was the main propylene activation species on ZrO_2-pillared clay. On the surface of ZrO_2-pillared clay, isopropoxide and nitrate intermediates formed a complex structurally similar to adsorbed dinitropropane. On the surface of bulk ZrO_2, acetate and monodentate nitrate complexes formed a complex structurally similar to adsorbed nitromethane. The dinitropropane complex on ZrO_2-pillared clay was consumed in reactions with surface nitrates. The decomposition reaction of a dinitropropane compound with the formation of acetate complexes and ammonia predominated on the surface containing no nitrate complexes in the absence of NO + O_2 from a gas phase. The found differences in reactant activation species and their thermal stabilities explained differences in the activities of bulk ZrO_2 and nanosized ZrO_2 particles as pillars in pillared clay in the course of the selective catalytic reduction of nitrogen oxides with propylene in an excess of oxygen.

DOI: 10.1134/S0023158406050144

INTRODUCTION

Pillared clays containing nanosized zirconium dioxide particles (ZrO_2-pillared clays) are promising supports and catalysts for various petrochemical processes [1] and the selective catalytic reduction (SCR) of nitrogen oxides ($DENO_x$) with hydrocarbons in an excess of oxygen [2–6]. The activity of pillared clays depends on the size, shape, and structure of nanosized ZrO_2 pillars arranged between aluminosilicate layers.

Previously [7], we found that nitrate, acetate, and nitroorganic complexes are formed on the surface of bulk ZrO_2 under SCR $DENO_x$ reaction conditions. The nitroorganic complex is formed by the interaction of acetate and nitrate complexes because of the substitution of the nitro group for the carboxyl group in the acetate complex. Monodentate nitrate exhibits the highest reactivity in this process. The experimental results indicate that nitroorganic compounds are further consumed in the reaction with nitrate complexes; monodentate nitrate is also the most reactive species in this surface reaction.

Here, we report the results of a spectrokinetic study on the mechanism of the SCR of NO_x with propylene in an excess of oxygen on a ZrO_2-pillared clay catalyst. The main goal of this study was to find the reaction paths of formation and consumption of nitroorganic compounds, which are well-known key intermediates in this reaction [6]. The aim of this study was also to compare the adsorption and catalytic properties of bulk ZrO_2 and nanosized ZrO_2 pillars in pillared clay.

EXPERIMENTAL

The procedure used for the preparation of pillared clays was described in detail previously [4, 5]. The interactions of reaction components and their mixtures of various compositions with sample surfaces were studied in the course of reaching a steady state using transmission Fourier transform IR spectroscopy (a Spectrum RX I FT-IR System spectrometer from Perkin-Elmer). Before measuring the IR spectra, the samples (pellets of 10–20 mg/cm^2) were treated in a flow of N_2 at 450°C. The design of reactor cells, which

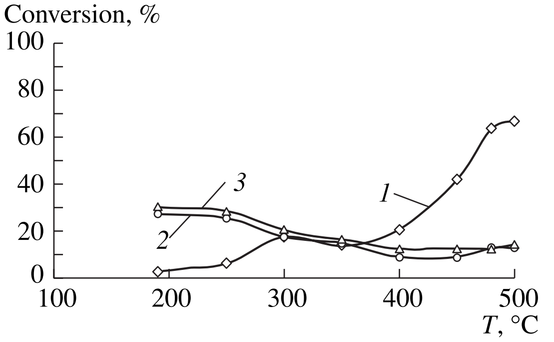

Fig. 1. The temperature dependence of the activity of ZrO_2-pillared clay in the course of the SCR of NO_x with propylene: (*1*) C_3H_6, (*2*) NO, and (*3*) NO_x. Gas mixture, 0.2 vol % NO + 0.2 vol % C_3H_6 + 2.5 vol % O_2/N_2; space velocity, 9000 h^{-1}.

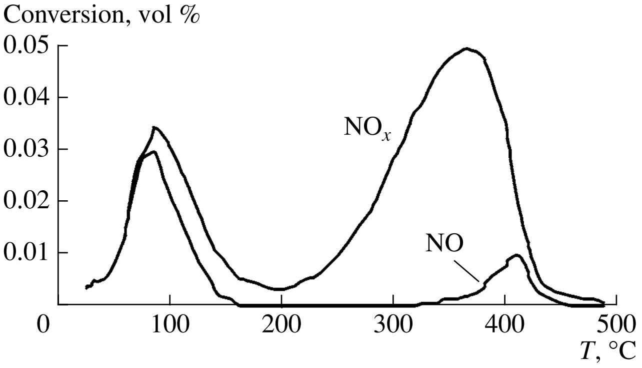

Fig. 2. TPD spectrum after the adsorption of NO on ZrO_2-pillared clay.

allowed us to measure the IR spectra at elevated temperatures, was described elsewhere [8]. The intensities of absorption bands in transmission spectra were measured in absorbance units (*A*). The interaction of nitrogen oxides with the surface of modified pillared clay was also studied using temperature-programmed desorption (TPD). The TPD under flow conditions in an IR-cell reactor was combined with the measurement of the IR spectra of surface complexes. Before performing a thermal-desorption experiment, the sample was treated in a flow of nitrogen at $T = 450°C$ immediately in the IR cell. Next, the sample was cooled to room temperature in the closed cell (without a flow of N_2); thereafter, the adsorption of NO(0.2%)/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 under conditions of continuous analysis for NO and NO_2 in a gas phase before and after the reactor using a Beckman 951A chemiluminescence NO/NO_x analyzer (nitrogen was a carrier gas; the rate of heating 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 composition upon heating the sample by 20°C.

The space velocity of gas flows 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.

RESULTS AND DISCUSSION

According to Fig. 1, the conversion of NO_x in the SCR reaction with propylene on ZrO_2-pillared clay was no higher than 30% and it decreased with temperature; this is an essential difference between pillared clay and bulk ZrO_2 [7].

The TPD spectrum after the adsorption of NO on ZrO_2-pillared clay at room temperature (Fig. 2) consisted of low-temperature (~100°C) and high-temperature (~370°C) peaks. The superposition of desorption peaks corresponding to the release of NO and NO_2 molecules into a gas phase was observed in either of the temperature regions. In this case, the thermal desorption maximums that characterize the desorption of these oxides did not coincide. An analysis of the TPD spectra of NO_x and the simultaneously measured IR spectra of surface compounds, as well as published data [9], indicated that the decomposition of surface nitrite and nitrosyl complexes in the course of desorption corresponded to the low-temperature peak of NO_x release ($T_{max} \approx 100°C$), whereas the decomposition of nitrate complexes corresponded to the high-temperature peak ($T_{max} \approx 370°C$). Note that the TPD spectra of NO on bulk ZrO_2 [7, 9] and ZrO_2-pillared clay (Fig. 2) are qualitatively coincident.

Steady-State Spectrokinetic Measurements

1. Interaction of Binary Mixtures with the Surface of ZrO_2-Pillared Clay

1.1. (0.2%NO + 2.5%O_2)/N_2. Figure 3 shows a typical spectrum obtained by the interaction of a flow of a mixture of 0.2%NO + 2.5%O_2 with the surface of ZrO_2-pillared clay (spectrum *1*). The spectrum contained absorption bands due to bridging (1617 cm^{-1}) and bidentate (1591 cm^{-1}) nitrate complexes. An absorption band related to the spectroscopic splitting of twice-degenerate (ν_3) oscillation occurred in the region 1250–1300 cm^{-1}. The assignment was performed based on well-known published data [10–15].

Because the amount of NO_x molecules adsorbed on bulk ZrO_2 [7] was greater than that on pillared clay (Fig. 2) by a factor of about 5 and the ZrO_2-pillar content of clay was 20 wt %, we can state that the zirconia pillars are the localization sites of nitrate complexes. This conclusion was also supported by the fact that NO_x was not adsorbed as nitrates on aluminosilicates.

Note that, unlike bulk ZrO_2 [7], monodentate nitrate was not formed in detectable amounts on pillared clay. This was likely due to changes in the Zr–Zr and Zr–O distances in pillars, as compared with these distances in bulk ZrO_2 [5].

Data in Fig. 3b also show that the interaction of 0.2%NO + 2.5%O_2 with the surface resulted in a decrease in the intensity of absorption bands due to the hydroxyl groups of ZrO_2 (3740 and 3643 cm^{-1}) [5] and in a symbatic increase in the intensity of absorption bands at 3100–3300 cm^{-1}. It is likely that the interaction of a portion of NO molecules with surface hydroxyls resulted in the formation of NH_x groups, in which N–H vibrations manifested themselves in the range 3100–3300 cm^{-1}. The bands due to N–H vibrations disappeared from the spectra upon heating the sample to 250°C.

The experimental data suggest that the interactions of 0.2%NO + 2.5%O_2 with the surfaces of bulk ZrO_2 and ZrO_2 pillars as the constituents of pillared clay exhibited considerable qualitative differences with the retention of quantitative characteristics: monodentate nitrate was not formed on ZrO_2 as pillars.

1.2. (0.2%C_3H_6 + 2.5%O_2)N_2. Figure 3 shows the spectra obtained upon the interaction of a flow of a mixture of 0.2%C_3H_6 + 2.5%O_2 with the surface of ZrO_2-pillared clay at 100 and 200°C (spectra *2* and *3*, respectively). An analysis of changes in absorption band intensities with increasing time of reaction of the flow with the surface at different temperatures together with published data [10, 16–23] indicated that three types of complexes mainly occurred on the sample surface: an isopropoxide propylene complex, coordinatively bound acetone, and acetate. The formation of isopropoxide complexes was also supported by a decrease in the intensity of absorption bands due to hydroxyl groups at 3740 and 3643 cm^{-1} (Fig. 3b, spectra *2*, *3*). To confirm the assignment, Fig. 3 (spectrum *4*) shows the spectrum of acetone adsorbed on the sample at 150°C. Under these conditions (100–300°C), absorption bands due to carbonate structures were not observed.

Acidic hydroxyl groups and Lewis acid sites on the surface of zirconia pillars are the localization sites of the isopropoxide complex of propylene and coordinatively bound acetone. This statement is based on the fact that the intensities of absorption bands at 3740 and 3643 cm^{-1} (Fig. 3b) due to vibrations in two- and three-coordinated hydroxyl groups localized at ZrO_2 pillars decreased upon the interaction of propylene or its mixture with oxygen with the surface of ZrO_2-pillared clay [5].

The isopropoxide complex was observed on heating the sample to 250°C. The absorption bands of adsorbed acetone and an acetate complex appeared in the spectra at temperatures higher than 150 and 250°C, respectively.

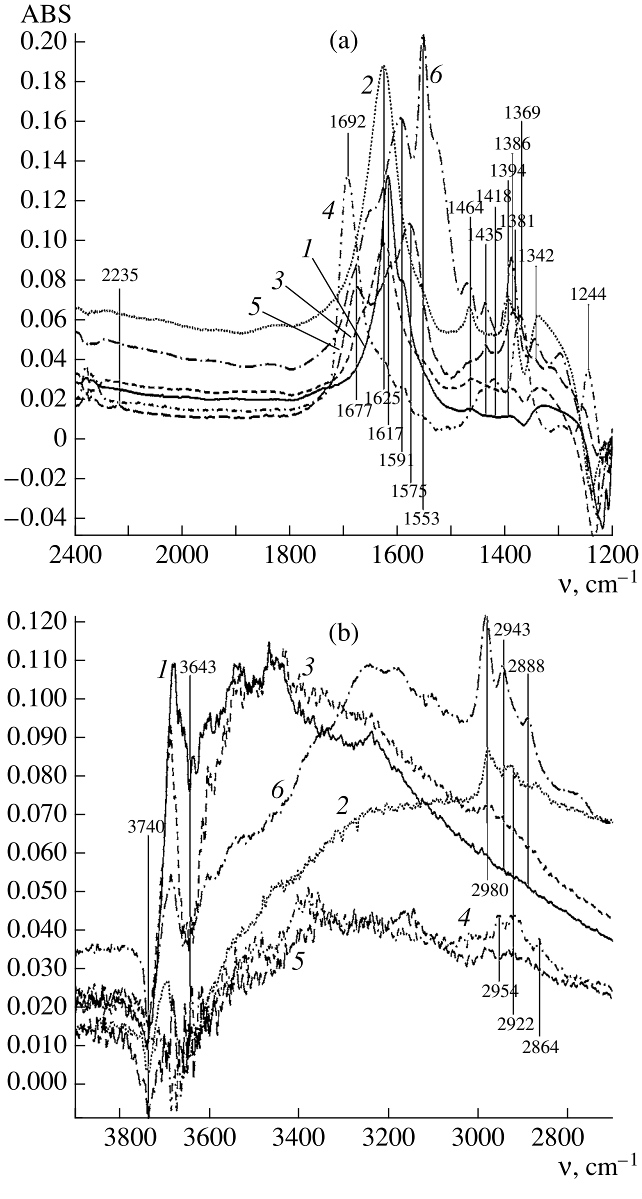

Fig. 3. IR spectra of surface compounds observed in the course of the interaction of the following mixtures with the surface of ZrO_2-pillared clay: (*1*) 0.2 vol % NO + 2.5 vol % O_2/N_2 (T = 150°C), (*2*) 0.2 vol % C_3H_6 + 2.5 vol % O_2/N_2 (T = 100°C), (*3*) 0.2 vol % C_3H_6 + 2.5 vol % O_2/N_2 (T = 200°C), and (*5*) 0.2 vol % NO + 0.2 vol % C_3H_6/N_2 (T = 150°C); (*4*) adsorbed acetone (T = 150°C); (*6*) adsorbed nitropropane (T = 150°C). Frequency ranges: (a) 1200–2400 and (b) 2700–3900 cm^{-1}.

The spectrum of the initial sample exhibited an absorption band due to the molecular vibrations of adsorbed water at 1625 cm^{-1}. Note that ZrO_2-pillared clay strongly retained adsorbed water molecules: the corresponding absorption band also remained in the spectrum on heating the sample to 250°C in an inert gas flow. Table 1 summarizes the assignment of the observed absorption bands [10, 16–24].

These data indicate a fundamental difference in the reactions of 0.2%C_3H_6 + 2.5%O_2 with the surfaces of

Table 1. Assignment of absorption bands in IR spectra after the interaction of $0.2\%C_3H_6$ + $2.5\%O_2$ with the surface of pillared clay

ν, cm^{-1}	Complex	Assignment
1677	Coordinatively bound acetone	$\nu(C{=}O)$
1418		$\delta_{as}(CH_3)$
1369		$\delta_s(CH_3)$
1244		$\nu(C–C)$
1394	Isopropoxide	$\delta(CH_3)$
1381		$\delta_{as}(CH_3)$
1464		$\delta_s(CH_3)$
1342		$\nu(CH)$
2980		
2943		
2888		
1553	Acetate	$\nu_{as}(COO^-)$
1435		$\nu_s(COO^-)$
1625	H_2O_{ads}	$\delta(O–H)$

Table 2. Assignment of absorption bands in IR spectra after the interaction of $(0.2\%NO + 0.2\%C_3H_6)/N_2$ with the surface of ZrO_2-pillared clay at 150°C

ν, cm^{-1}	Complex	Assignment
1677	Coordinatively bound acetone	$\nu(C{=}O)$
1418		$\delta_{as}(CH_3)$
1369		$\delta_s(CH_3)$
1244		$\nu(C–C)$
2235	Isocyanate	$\nu(N–C–O)$
1617	Bridging nitrate	–
1257		
1591	Bidentate nitrate	–
1248		$\nu(NOO)$
1575	Nitroorganic complex	$\nu(NOO)$
1386		$\delta(C–H)$
1342		$\delta(C–H)$
1435		$\nu(C–H)$
2888		
2943		
2980		

bulk ZrO_2 and ZrO_2 as pillars that constitute pillared clay. The isopropoxide complex and coordinatively bound acetone were formed on the ZrO_2 pillars; it is likely that this fact suggests an increase in the Brønsted and Lewis acidities of pillars, as compared with that of the bulk analog.

1.3. $(0.2\%NO + 0.2\%C_3H_7)/N_2$. The spectrum obtained in experiments with a mixture of NO and C_3H_6 was the superposition of absorption bands due to coordinatively bound acetone and nitrates; it also contained absorption bands at 1386 and 1575 cm^{-1}, which can be attributed to symmetric and antisymmetric vibrations of the nitro group in accordance with published data [4, 25–31]. Absorption bands at 1435 and 1342 cm^{-1} can be attributed to deformation vibrations, and absorption bands at 2888, 2943, and 2980 cm^{-1} can be attributed to stretching C–H vibrations in the 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 the gas phase (Fig. 3).

To determine the structure of the nitroorganic complex, we studied the adsorption of various nitroorganic compounds under analogous conditions (T = 150°C; nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane concentrations of ~3% in a flow of nitrogen). Figure 4 shows the spectra obtained by the interaction of a sample with a flow of nitroorganic substances. They contain absorption bands due to the vibrations of nitro groups and a set of absorption bands due to C–H vibrations. The results suggest that the spectrum of adsorbed 1-nitropropane (spectrum *4*) is closest to the spectrum of the surface nitroorganic compound. The difference consists in an increased frequency of the antisymmetric vibration of the nitro group and a somewhat greater halfwidth of the symmetric vibration. In accordance with published data [29, 32], the increased frequency of the antisymmetric vibration of the nitro group is observed when two nitro groups are the constituents of the nitro compound, whereas the increased halfwidth of the symmetric vibration is due to the splitting of this absorption band. Consequently, it is believed that the structure of the nitroorganic complex observed under conditions of the SCR DE NO_x reaction is similar to the structure of adsorbed dinitropropane [29, 32]. The addition of two NO_2 groups to an olefin molecule in the course of the SCR of nitrogen oxides on zeolite catalysts was considered previously [33, 34].

The same positions of absorption bands due to the nitro group of the nitroorganic compound obtained upon the adsorption of the reaction mixture and the dinitropropane molecule, a decrease in the intensity of absorption bands due to surface hydroxyl groups, and the appearance of a broad absorption peak due to bound hydroxyl groups (Figs. 3b, 4b) suggest that the nitroorganic complex is bound to the catalyst through surface hydroxyl groups.

Table 3 summarizes the detailed assignment of absorption bands in spectra measured after the interaction of a mixture of $0.2\%NO + 0.2\%C_3H_6$ with the surface of ZrO_2-pillared clay. In addition, this assignment was supported experimentally by measuring the intensities of absorption bands under steady-state and nonsteady-state conditions (see below).

The interaction of nitroorganic substances with the surface of ZrO_2 pillars resulted in not only adsorption but also conversion, as evidenced by the appearance of absorption bands at 1600–1700 cm^{-1} in the spectra. Absorption in this region is attributed to vibrations in the nitroorganic complex [4, 25–27, 35–40]. On the other hand, Satsuma et al. [41] reported that the surface compounds (absorption band at 1662 cm^{-1}) of triazine, melamine, and/or their derivatives were formed in the decomposition of nitromethane on CoZSM-5. It is believed that the occurrence of these complexes on the surface resulted in the blocking of zeolite channels and, consequently, in a loss of catalytic activity. In contrast to this, Haneda et al. [42] attributed the absorption band at 1655 cm^{-1} to vibrations in an acrylamide complex based on the fact that the intensity of this absorption band changed in the same manner as the intensity of an absorption band at 3370 cm^{-1}. Thus, the published data indicate that the assignment of absorption bands in the region 1600–1700 cm^{-1} to vibrations in the nitroorganic complex should be considered with caution.

Note that absorption bands due to the isocyanate complex occurred in the spectra (Fig. 3a, spectrum *5*). Two reasons may be responsible for the formation of this complex. One of them is related to the fact that CO molecules, which are formed in the oxidation of propylene, react with NO molecules to form surface isocyanate. The other consists in the possibility of a further transformation of the nitroorganic complex.

Note that the spectra of the nitroorganic compound on bulk zirconia and ZrO_2-pillared clay were essentially different. The reason consists in a fundamental difference between the forms of propylene activation on these catalysts at relatively low temperatures. It is believed that the above complexes are structurally similar at elevated temperatures when the forms of propylene activation are identical (acetate).

2. Interaction of a Reaction Mixture of $(0.2\%NO + 0.2\%C_3H_6 + 2.5\%O_2)/N_2$ with the Surface of ZrO_2-Pillared Clay

The spectra obtained in experiments with a reaction mixture of $0.2\%NO + 0.2\%C_3H_6 + 2.5\%O_2$ were qualitatively identical to the spectra of a mixture of $0.2\%NO + 0.2\%C_3H_6$. Bands due to different surface complexes occurred close together. Therefore, to determine the temperature dependence of the absorption band intensity of a particular complex, we decomposed complex spectra into components with the use of standard programs on the assumption of Lorentzian or Gaussian band shapes. The dependence of the concentration (absorption band intensity) of corresponding surface complexes on reaction parameters, which was obtained as a result of decomposing complex spectra into components, is considered below.

According to Fig. 5, the concentration of surface compounds decreased or passed through a maximum as the temperature was increased (curves *2* and *5* for acetates and the nitroorganic complex, respectively). It can also be seen that the decrease in activity with temperature in the course of NO_x reduction (Fig. 1) correlates with the decrease in the intensity of absorption bands due to surface isopropoxide compounds. Note that the absorption band intensity of the acetate complex on the surface of ZrO_2-pillared clay was much lower than that on the surface of bulk ZrO_2, all other factors being the same [7].

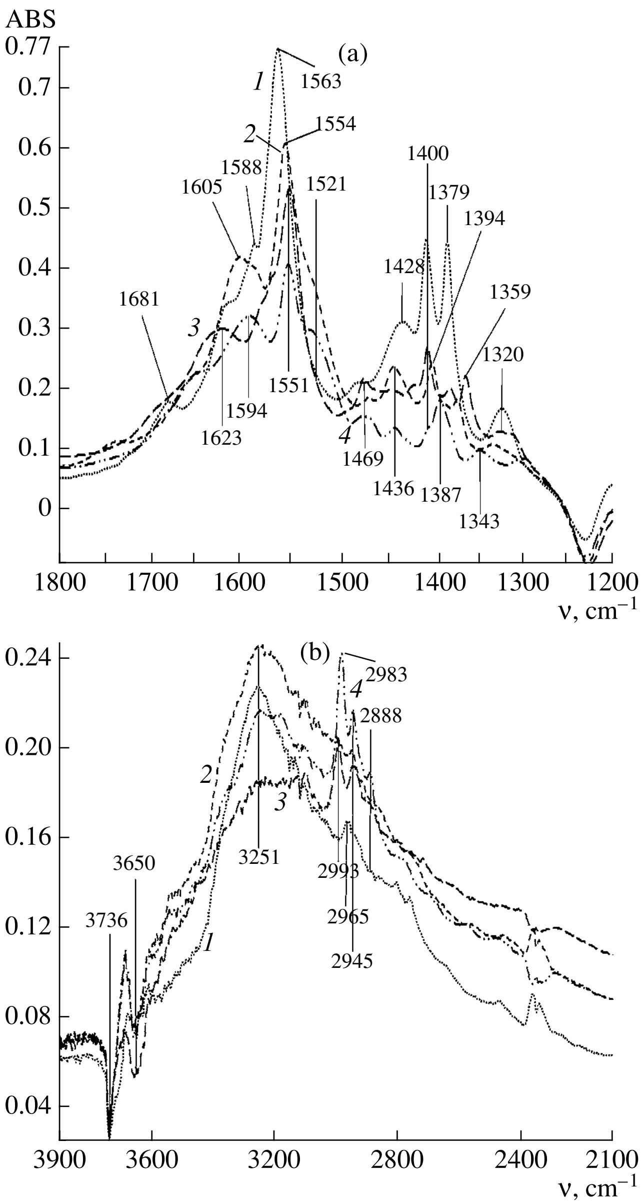

Fig. 4. IR spectra of surface compounds observed in the course of the interaction of (*1*) nitromethane, (*2*) nitroethane, (*3*) 2-nitropropane, and (*4*) 1-nitropropane with the surface of ZrO_2-pillared clay (150°C). Frequency ranges: (a) 1200–1800 and (b) 2100–3900 cm^{-1}.

3. Non-Steady-State Measurements

In order to determine the nature of surface reactions that lead to the formation of nitroorganic complexes,

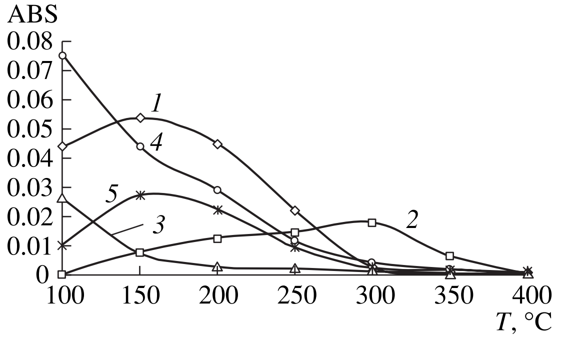

Fig. 5. The temperature dependence of the absorption band intensities of (*1*) acetone (1677 cm^{-1}), (*2*) acetate (1445 cm^{-1}), (*3*) isopropoxide (1394 cm^{-1}), (*4*) nitrate (1617 cm^{-1}), and (*5*) nitroorganic (1386 cm^{-1}) complexes in the spectra obtained upon the interaction of a mixture of 0.2 vol % NO + 0.2 vol % C_3H_6 + 2.5 vol % O_2/N_2 with the surface of ZrO_2-pillared clay.

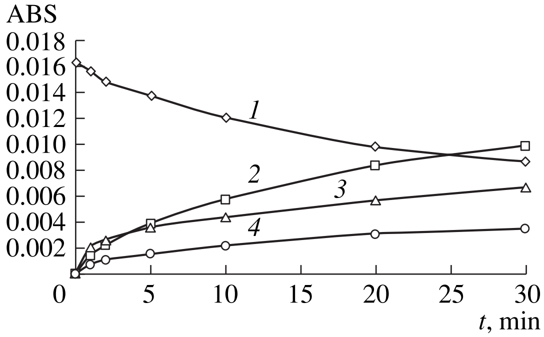

Fig. 6. The time dependence of the absorption band intensities of (*1*) bridging nitrate (1617 cm^{-1}), (*2*) acetate (1553 cm^{-1}), (*3*) acetone (1677 cm^{-1}), and (*4*) nitroorganic (1575 cm^{-1}) complexes in the spectra obtained upon the interaction of the previously formed nitrate complexes with a reaction mixture of 0.2 vol % C_3H_6 + 2.5 vol % O_2/N_2 on the surface of ZrO_2-pillared clay at $T = 250$°C.

we performed a series of non-steady-state experiments. The experiments were performed over a wide temperature range (100–300°C), in which both the catalytic activity and the spectra of surface compounds could be measured.

3.1. Reactivity of surface nitrate complexes. The surface nitrate complexes were formed by the interaction of a flow of NO + O_2 with the sample surface. Next, the cell with the sample was successively purged with a flow of an inert gas and a flow of a mixture of C_3H_6 +O_2. In this case, the intensity of absorption bands due to surface compounds was monitored.

At 100°C, nitrate complexes were not removed from the catalyst surface upon purging with an inert gas flow; this is consistent with data on the thermal desorption of NO (Fig. 1).

Nitrate complexes were also not consumed on the addition of a mixture of propylene and oxygen at 100°C. In this case, coordinatively bound acetone and isopropoxide were accumulated on the surface, whereas nitroorganic and acetate complexes were not detected. Note that an amount of the nitroorganic complex was formed in an analogous experiment at 150°C. This process became intense at 250°C (Fig. 6). It can be seen that nitrate complexes were consumed on the addition of a mixture of propylene and oxygen at this temperature (curve *1*), whereas the concentrations of acetate (curve *2*), coordinatively bound acetone (curve *3*), and the nitroorganic compound (curve *4*) increased. By this is meant that bridging nitrate is mainly the source of the formation of the nitroorganic compound. The same qualitative result was also obtained in experiments at 200 and 300°C.

Kinetic curves for the formation of the nitroorganic compound were treated in the coordinates of a first-order equation: the rate constants of formation of intermediates with absorption bands at 1575, 1386, and 2954 cm^{-1} were almost equal; this fact additionally demonstrated that they belong to the same surface complex.

At low temperatures, isopropoxide was the main form of propylene activation (Fig. 5). Its interaction with surface nitrates (primarily bridging nitrate) resulted in the formation of surface complexes analogous to adsorbed dinitropropane (Fig. 6). Both the concentration of isopropoxide and the catalytic activity decreased with temperature (Figs. 1, 5).

At a high temperature (>250°C), the oxidation of propylene to acetate complexes occurred on the surface (Fig. 5, curve *2*). According to Finocchio et al. [17], these complexes are reaction intermediates in the deep oxidation of propylene. Previously [7], we noted that the interaction of acetate and nitrate complexes on the surface of ZrO_2 resulted in the formation of an intermediate nitromethane complex. Under conditions of our experiments, a relatively low concentration of the acetate complex and the absence of the most active (monodentate) nitrate species did not allow us to detect the nitromethane complex.

3.2. Reactivity of surface hydrocarbon complexes. Figure 7 shows the results of a study of the reactivity of surface isopropoxide and acetate complexes.

Hydrocarbon complexes on the surface were obtained by the interaction of a flow of C_3H_6 + O_2 with the sample surface at various temperatures. Then, the cell with the sample was successively purged with a flow of an inert gas and a flow of a mixture of NO +O_2; in this case, the intensity of absorption bands due to surface compounds was measured.

At 100°C, only isopropoxide complexes were formed on the surface; these complexes were not removed from the surface upon purging the catalyst with a flow of an inert gas. On the addition of NO + O_2, isopropoxide complexes were consumed (Fig. 7, curve *1*);

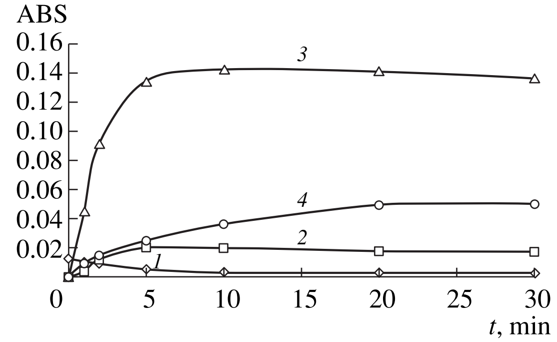

Fig. 7. The time dependence of the absorption band intensities of (*1*) isopropoxide (2980 cm^{-1}), (*2*) nitroorganic (1386 cm^{-1}), and (*3*) acetone (1677 cm^{-1}) complexes and (*4*) bidentate nitrate (1588 cm^{-1}) in the spectra obtained upon the interaction of isopropoxide complexes with a mixture of 0.2 vol % NO + 2.5 vol % O_2/N_2 on the surface of ZrO_2-pillared clay at $T = 100$°C.

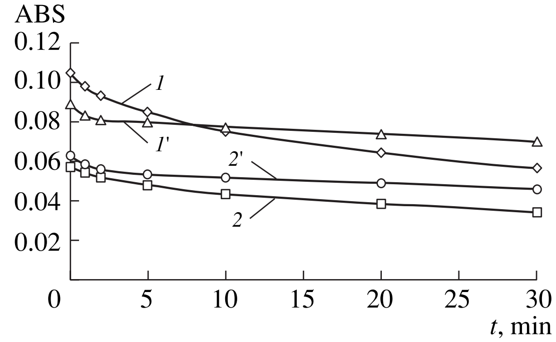

Fig. 8. The time dependence of the absorption band intensities of (*1*) nitroorganic (1575 cm^{-1}) and (*2*) acetone (1677 cm^{-1}) complexes in the spectra obtained upon the interaction of the nitroorganic compound with a mixture of 0.2 vol % NO + 2.5 vol % O_2/N_2 (*1'* and *2'*, respectively, in a flow of nitrogen) on the surface of ZrO_2-pillared clay at $T = 250$°C.

in this case, the concentrations of nitroorganic compounds (curve *2*) and acetone (curve *3*) increased. By this is meant that the isopropoxide complex was the source of the formation of the nitroorganic compound, as well as acetone. The same result was also obtained in experiments at higher temperatures. The difference is that the initial isopropoxide concentration decreased with temperature and became negligibly small at 300°C. Remember that the catalyst activity in the reaction also decreased.

The intensity of absorption bands due to the isopropoxide complex did not decrease to zero upon the interaction with a flow of NO + O_2 (Fig. 7). This can be explained by the fact that closely spaced absorption bands due to nitroorganic compounds, acetone, and acetate appeared at the position of the absorption band of the isopropoxide complex. This was supported by the fact that, when changes in the isopropoxide concentration were terminated, the concentrations of all of the other surface compounds reached a plateau.

The decrease in the isopropoxide concentration, a relatively low concentration of the acetate complex, and the absence of the most active form of the nitrate complex (monodentate species) explain the decrease in the activity of ZrO_2-pillared clay at $T > 250$°C (Fig. 1). Because of the low concentration of the acetate complex, we failed to detect its conversion under reaction conditions.

3.3. Reactivity of surface nitroorganic complexes. Nitroorganic compounds were formed by the interaction of a reaction mixture with the catalyst surface. Gas flows of N_2, O_2, NO, or a mixture of NO + O_2 were supplied to the complex formed. Figure 8 shows the time dependence of the intensities of absorption bands due to adsorbed acetone (curve *1*) and the nitroorganic complex (curve *2*) in the spectra obtained in the course of interaction with a flow of NO + O_2 and, for comparison, with a flow of nitrogen (curves *1*' and *2*', respectively). It can be seen that the rate of decrease in the concentrations (absorption band intensities in the spectra) of the above complexes in the reaction mixture was much higher than that in the inert gas flow. Note that the rate of decrease in absorption band intensities in the spectra obtained in a flow of oxygen and in a flow of NO was consistent with the rate of decrease in the absorption band intensities in the spectra obtained in the inert gas flow. By this is meant that the consumption of the nitroorganic compound was due to the occurrence of NO_2 complexes under reaction conditions. Because the equilibrium concentration of NO_2 complexes is low at elevated temperatures, the occurrence of these complexes on the surface is related to the formation and degradation of surface nitrates. Note that the interaction of nitroorganic complexes with NO_2 complexes came into play at $T > 200$°C.

We also studied possible reaction paths in the conversion of nitroorganic complexes in non-steady-state experiments performed in a closed reactor. After attaining steady-state reaction conditions, the inlet and outlet of the cell reactor were closed and changes in the spectra of surface compounds were monitored. The experiments were performed at 150–300°C. Figure 9 shows the spectra obtained in the course of an experiment at 250°C. It can be seen that a decrease in the intensity of an absorption band due to the nitroorganic complex was accompanied by an increase in the absorption of the acetate complex (1570 and 1455 cm^{-1}) and adsorbed ammonia (1622 and 3200–3400 cm^{-1}). In other words, in the absence of NO + O_2 from a gas phase, an intramolecular rearrangement reaction was predominant on the surface free of nitrate complexes; this reaction resulted in the formation of acetate complexes and ammonia. The rate of this process became noticeable at $T > 200$°C.

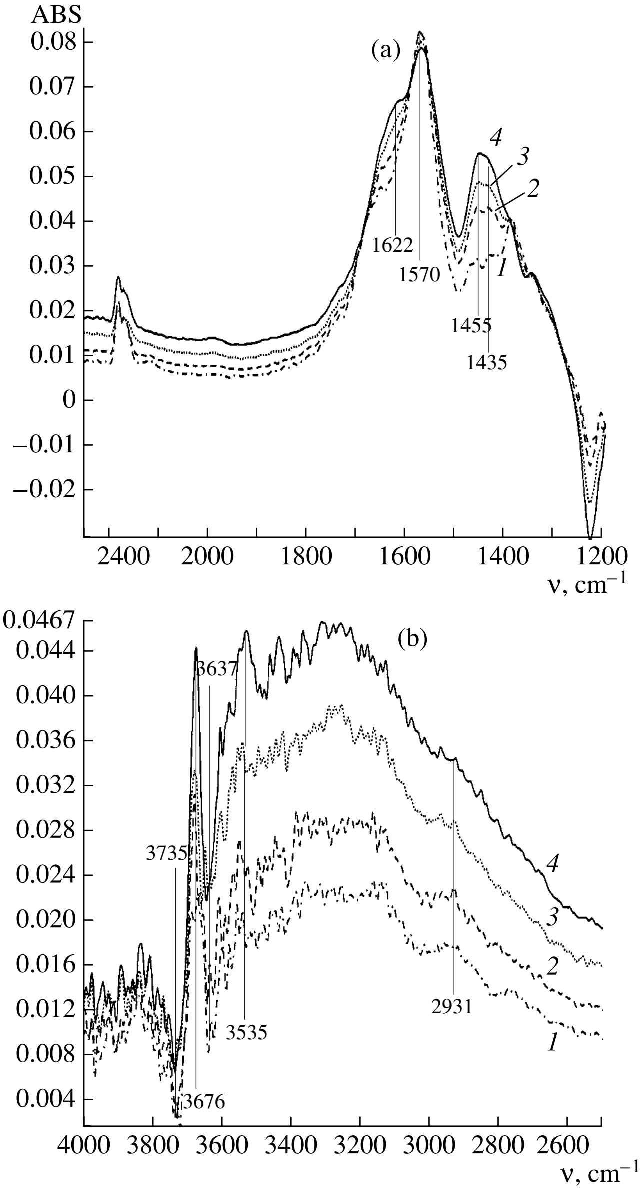

Fig. 9. IR spectra measured in a closed reactor upon the interaction of a mixture of 0.2 vol % NO + 0.2 vol % C_3H_6 + 2.5 vol % O_2/N_2 with the surface of ZrO_2-pillared clay for (*1*) 0, (*2*) 10, (*3*) 30, and (*4*) 60 min at 250°C.

CONCLUSIONS

The results of this work demonstrate that the adsorption and catalytic properties of bulk ZrO_2 and nanosized ZrO_2 particles as pillars in pillared clay are essentially different [7]. The interaction of NO with the surface of bulk ZrO_2 results in the formation of three types of nitrate complexes. Only two nitrate species are formed on ZrO_2-pillared clay: monodentate nitrate is absent. The interaction of a mixture of propylene and oxygen with the surface of bulk ZrO_2 results in the formation of only an acetate complex, whereas an isopropoxide complex is the main form of propylene activation on ZrO_2 as pillars; the acetate complex is formed only in a small amount at elevated temperatures. Changes in the Zr–Zr and Zr–O distances in the pillars, as compared with the corresponding distances in bulk ZrO_2, which were detected previously [5], may be responsible for this difference. It is likely that these changes are the reason for an increase in the Brønsted and Lewis acidity of ZrO_2 pillars, as compared with that of the bulk oxide.

Differences in the forms of reactant activation result in differences in the structure of nitroorganic complexes. On bulk ZrO_2, acetate and monodentate nitrate complexes form a surface complex that is structurally similar to adsorbed nitromethane [7]. On ZrO_2 as pillars, isopropoxide and nitrate (bidentate and bridging) complexes form a surface complex that is structurally similar to adsorbed dinitropropane. On ZrO_2 as pillars, the dinitropropane complex is consumed in the interaction with surface NO_2 complexes. The occurrence of these complexes is related to the decomposition of surface nitrates.

In the absence of NO + O_2 from a gas phase, the intramolecular rearrangement reaction that leads to the formation of acetate complexes and ammonia predominates on the surface containing no nitrate complexes.

The found differences in the forms of reactant activation and in their thermal stabilities also explain differences in the activities of bulk ZrO_2 and nanosized ZrO_2 particles as pillars in pillared clay in the course of the selective catalytic reduction of nitrogen oxides with propylene in an excess of oxygen. A considerable decrease in the concentration of the isopropoxide complex and nitrate complexes on the surface of pillars with temperature is the main reason for the decrease of the activity of ZrO_2-pillared clay with temperature (Fig. 1). The relatively high stability and concentration of acetate and nitrate complexes on the surface of bulk ZrO_2 and the presence of the most active monodentate nitrate explains the increase of the activity with temperature.

REFERENCES

1. Gil, A. and Gandia, L.M., *Catal. Rev—Sci. Eng.*, 2000, vol. 42, p. 289.
2. Yang, R.T., Trappiwattanannon, N., and Long, R.Q., *Appl. Catal., B*, 1998, vol. 19, p. 289.
3. Sadykov, V.A., Bunina, R.V., Alikina, G.M., Doronin, V.P., Sorokina, T.P., Kochubei, D.I., Novgorodov, B.N., Paukshtis, E.A., Fenelonov, V.B., Derevyankin, Yu., Ivanova, A.S., Zaikovskii, V.I., Kuznetsova, T.G., Beloshapkin, S.A., Kolomiichuk, V.N., Plyasova, L.M., Matyshak, V.A., Konin, G.A., Rozovskii, A.Ya., Tretyakov, V.F., Burdeynaya, T.N., Davydova, M.N., Ross, J.R.H., Breen, J.P., and Meunier, F.C., *Mater. Res. Soc. Symp. Proc.*, 2000, vol. 581, p. 435.
4. Konin, G.A., Il'ichev, A.N., Matyshak, V.A., Khomenko, T.I., Korchak, V.N., Sadykov, V.A., Doronin, V.P., Bunina, R.V., Alikina, G.M., Kuznetsova, T.G., Paukshtis, E.A., Fenelonov, V.B., Zaikovskii, V.I., Ivanova, A.S., Beloshapkin, S.A., Rozovskii, A.Ya.,

Tretyakov, V.F., Ross, J.R.H., and Breen, J.P., *Top. Catal.*, 2001, vol. 17, p. 193.

5. Sadykov, V.A., Kuznetsova, T.G., Doronin, V.P., Sorokina, T.P., Alikina, G.M., Kochubei, D.I., Novgorodov, B.N., Paukshtis, E.A., Fenelonov, V.B., Zaikovskii, V.I., Rogov, V.A., Anufrienko, V.F., Vasenin, N.T., Matyshak, V.A., Konin, G.A., Rozovskii, A.Ya., Tretyakov, V.F., Burdeynaya, T.N., Ross, J.R.H., and Breen, J.P., *Chem. Sustainable Dev.*, 2003, vol. 11, p. 249.
6. Tanaka, T., Okuhara, T., and Misono, M., *Appl. Catal., B*, 1994, vol. 4, p. L1.
7. Matyshak, V.A., Tret'yakov, V.F., Chernyshov, K.A., Burdeinaya, T.N., Korchak, V.N., and Sadykov, V.A., *Kinet. Katal.*, 2006 (in press).
8. Matyshak, V.A. and Krylov, O.V., *Catal. Today*, 1995, vol. 25, no. 1, p. 1.
9. Konin, G.A., *Cand. Sci. (Chem.) Dissertation*, Moscow: Semenov Inst. of Chemical Physics, 2001.
10. Davydov, A.A., *Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides*, New York: Wiley, 1990.
11. Pozdnyakov, D.V. and Filimonov, V.N., *Kinet. Katal.*, 1973, vol. 14, p. 760.
12. Beutel, T., Sarkany, J., Lei, G.-D., Yan, J.Y., and Sachtler, W.M.H., *J. Phys. Chem.*, 1996, vol. 100, p. 845.
13. Sadykov, V.A., Baron, S.L., Matyshak, V.A., et al., *Catal. Lett.*, 1996, vol. 37, p. 157.
14. Shimizu, K., Kawabata, H., Satsuma, A., and Hattori, T., *J. Phys. Chem. B*, 1999, vol. 103, p. 5240.
15. Weingand, T., Kuba, S., Hadjiivanov, K., and Knozinger, H., *J. Catal.*, 2002, vol. 209, p. 539.
16. Efremov, A.A. and Davydov, A.A., *React. Kinet. Catal. Lett.*, 1981, vol. 18, nos. 3–4, p. 353.
17. Finocchio, E., Busca, G., Lorenzelli, V., and Willey, R.J., *J. Chem. Soc., Faraday Trans.*, 1994, vol. 90, no. 21, p. 3347.
18. Finocchio, E., Busca, G., Lorenzelli, V., and Escribano, V.S., *J. Chem. Soc., Faraday Trans.*, 1996, vol. 92, no. 9, p. 1587.
19. Liengme, B.V. and Hall, W.K., *Trans. Faraday Soc.*, 1966, vol. 62, no. 11, p. 3229.
20. Eberly, P.E., *J. Phys. Chem*, 1967, vol. 71, p. 1717.
21. Gordymova, T.A. and Davydov, A.A., *Geterogennyi kataliz: Trudy 4 Mezhdunarodnogo simpoziuma po geterogennomu katalizu* (Proc. 4th Int. Symp. on Heterogeneous Catalysis), Sophia, 1979.
22. Bellami, L.J., *Infra-Red Spectra of Complex Molecules*, London: Methuen, 1958.
23. Sadykov, V.A., Kuznetsova, T.G., Doronin, V.P., Moroz, E.M., Ziuzin, D.A., Kochubei, D.I., Novgorodov, B.N., Kolomiichuk, V.N., Alikina, G.M., Bunina, R.V., Paukshtis, E.A., Fenelonov, V.B., Lapina, O.B., Yudaev, I.V., Mezentseva, N.V., Volodin, A.M., Matyshak, V.A., Lunin, V.V., Rozovskii, A.Ya., Tretyakov, V.F., Burdeynaya, T.N., and Ross, J.R.H., *Top. Catal.*, 2005, vol. 32, nos. 1–2, p. 29.
24. Krylov, O.V. and Matyshak, V.A., *Promezhutochnye soedineniya v geterogennom katalize* (Intermediates in Heterogeneous Catalysis), Moscow: Nauka, 1996.
25. Sumiya, S., He, H., Abe, A., et al., *J. Chem. Soc., Faraday Trans.*, 1998, vol. 94, no. 15, p. 2217.
26. Maunula, T., Ahola, J., and Hamada, H., *Appl. Catal., B*, 2000, vol. 26, p. 173.
27. Chi, Y. and Chuang, S.S.C., *J. Catal.*, 2000, vol. 190, p. 75.
28. Sadykov, V.A., Paukshtis, E.A., Beloshapkin, S.A., Ucharskii, A.A., Il`ichev, A.N., Lunin, V.V., Matyshak, V.A., and Rozovskii, A.Ya., *React. Kinet. Catal. Lett.*, 1999, vol. 66, no. 2, p. 297.
29. Paperno, T.Ya. and Perkalin, V.V., *Infrakrasnye spektry nitrosoedinenii* (Infrared Spectra of Nitro Compounds), Leningrad: Leningr. Gos. Univ., 1974.
30. Lobree, L.J., Hwang In-Chul, Reimer, J.A., and Bell, A.T., *Catal. Lett.*, 1999, vol. 63, p. 233.
31. Hadjiivanov, K., Knozinger, H., Tsyntarski, B., and Dimitrov, L., *Catal. Lett.*, 1999, vol. 62, p. 35.
32. Noble, P., Borgardt, F.G., and Reed, W.L., *Chem. Rev.*, 1964, vol. 64, p. 19.
33. Yokoyama, C. and Misono, M., *J. Catal.*, 1994, vol. 150, p. 9.
34. Martens, J.A., Cauvel, A., Francis, A., Hermans, C., Jayat, F., Remy, M., Keung, M., Lievens, J., and Jacobs, P., *Angew. Chem., Int. Ed. Engl.*, 1998, vol. 37, no. 13/14, p. 1901.
35. Haneda, M., Kintaichi, Y., Inaba, M., and Hamada, H., *Catal. Today*, 1998, vol. 42, p. 127.
36. Yokoyama, C. and Misono, M., *Catal. Today*, 1994, vol. 22, p. 59.
37. Gerlach, T. and Baerns, M., *Chem. Eng. Sci.*, 1999, vol. 54, p. 4379.
38. Hadjiivanov, K.I., *Catal. Rev.—Sci. Eng.*, 2000, vol. 42, no. 1, p. 71.
39. Adelman, B., Beutel, T., Lei, G., and Sachtler, W.M.H., *J. Catal.*, 1996, vol. 158, p. 327.
40. Meunier, F.C., Breen, J.P., Zuzniuk, V., et al., *J. Catal.*, 1999, vol. 187, p. 493.
41. Satsuma, A., Cowan, A.D., Cant, N.C., and Trimm, D.L., *J. Catal.*, 1999, vol. 181, p. 165.
42. Haneda, M., Joubert, E., Menezo, J.-Ch., Duprez, D., Barbier, J., Bion, N., Daturi, M., Saussey, J., Lavalley, J.-C., and Hamada, H., *J. Mol. Catal. A: Chem.*, 2001, vol. 175, p. 179.