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Effect of the Modification of ZrO_2-Containing Pillared Clay with Pt and Cu Atoms on the Properties of Inorganic Complex Intermediates in the Selective Catalytic Reduction of Nitrogen Oxides with Propylene According to In Situ IR-Spectroscopic Data

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Abstract—It was found that only bridging and bidentate nitrate complexes were formed on the surface of Pt,Cu/ZrO_2-pillared interlayered clay (ZrO_2-PILC) upon the interaction with a flow of the (0.2% NO + 2.5% O_2)/N_2 mixture, whereas monodentate and nitrosyl complexes were not detected. The concentration of nitrate complexes on Pt,Cu/ZrO_2-PILC was higher and the strength of their bond to the surface was weaker than those on unmodified ZrO_2-PILC. Isopropoxide and acetate complexes and coordinatively bound acetone were formed on the surface in the interaction of Pt,Cu/ZrO_2-PILC with a flow of the (0.2% C_3H_6 + 2.5% O_2)/N_2 mixture. The supporting of Pt and Cu onto zirconium dioxide pillars resulted in considerable changes in the concentration and the temperature region of the existence of hydrocarbon surface compounds, as compared with ZrO_2-PILC. Under reaction conditions at relatively low temperatures, isopropoxide and nitrate intermediates on the surface of Pt,Cu/ZrO_2-PILC formed a complex structurally similar to adsorbed dinitropropane. At elevated temperatures, a surface nitromethane complex was formed in the interaction of the acetate complex with nitrate species. The spectrokinetic measurements demonstrated that the apparent rate constants of consumption of nitrate and nitroorganic complexes considerably increased on going from ZrO_2-PILC to Pt,Cu/ZrO_2-PILC. Moreover, the constants of consumption of nitroorganic and nitrate complexes were similar for both of the catalysts. This fact suggests that, on the test catalysts, nitroorganic complexes were reaction intermediates in the selective catalytic reduction of NO_x (NO_x SCR) with hydrocarbons. The found differences in the activation species and thermal stabilities of reactants can explain different activities of ZrO_2-PILC and Pt,Cu/ZrO_2-PILC in the SCR reaction of NO_x with propylene in an excess of oxygen.

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INTRODUCTION

Systems containing ZrO_2 are promising supports and catalysts for the selective catalytic reduction (SCR) of nitrogen oxides with hydrocarbons in an excess of oxygen [1–6].

Previously [7, 8], we reported the results of spectrokinetic studies on the mechanism of the SCR of NO_x with propylene on bulk ZrO_2 and a pillared clay with nanosized ZrO_2 pillars (ZrO_2-PILC). The main goal was to find the reaction paths of formation and consumption of nitroorganic compounds, which are key intermediates in this reaction [6]. It was found that, in these systems, the structure of a nitroorganic complex depends on the forms of hydrocarbon activation. Propylene on the surface of ZrO_2 occurs as an acetate complex. The formation of a nitroorganic complex occurs by the replacement of the carboxyl group in the acetate complex by the nitro group of the nitrate complex. The structure of the nitroorganic complex is close to the structure of adsorbed nitromethane. Propylene forms an isopropoxide complex on the surface of nanosized ZrO_2 pillars in the pillared clay [8]. The nitroorganic complex is formed in the interaction of isopropoxide and nitrate complexes. In this case, the structure of the nitroorganic complex is similar to the structure of adsorbed dinitropropane.

In this work, we performed an analogous study with ZrO_2-PILC containing Cu and Pt (Pt,Cu/ZrO_2-PILC). The main goal was to study the effect of modification with Pt and Cu atoms on the properties and reactivity of nitroorganic complexes.

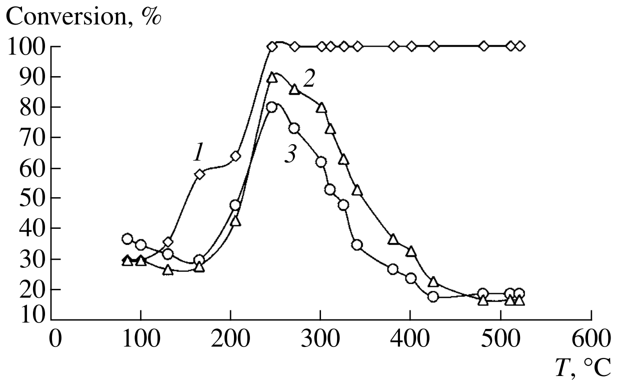

Fig. 1. The temperature dependence of the activity of Pt,Cu/ZrO_2-PILC in the SCR reaction of NO_x with propylene: (*1*) C_3H_6, (*2*) NO, and (*3*) NO_x. Gas mixture of (0.2% NO + 0.2% C_3H_6 + 2.5% O_2)/N_2; space velocity of 9000 h^{-1}.

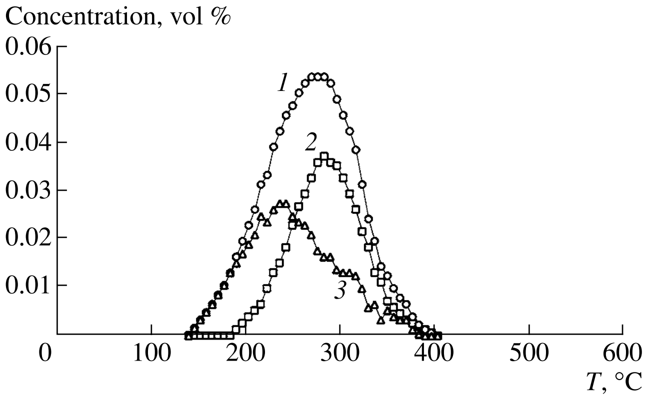

Fig. 2. TPD spectrum after the adsorption of NO on Pt,Cu/ZrO_2-PILC: (*1*) NO_x, (*2*) NO, and (*3*) NO_2.

EXPERIMENTAL

The procedure used for the preparation and modification of pillared clays was described previously [4, 5]. The sample studied in this work contained 1 wt % Cu and 0.2 wt % Pt.

The main investigation techniques were in situ IR spectroscopy [9], temperature-programmed desorption (TPD) combined with the measurement of IR spectra, and the measurement of catalytic activity in the SCR reaction of NO_x with propylene in an excess of oxygen. These techniques were described in detail elsewhere [7, 8].

RESULTS AND DISCUSSION

According to Fig. 1, the conversion of NO_x on Pt,Cu/ZrO_2-PILC passed through a maximum, which was as high as 80%. The temperature region of activity was approximately the same as the region of thermal desorption of surface nitrogen–oxygen complexes (Fig. 2).

The TPD spectrum of NO_x was the superposition of two peaks corresponding to the release of NO and NO_2 molecules into the gas phase. In this case, the temperature maximums in the desorption spectra of NO and NO_2 did not coincide. From a comparison of changes in the intensities of absorption bands due to nitrate complexes in the course of desorption and data on the TPD of NO_x, as well as published data [10], it follows that the peak of NO_x release (T_{max} = 260–280°C) in the TPD spectrum corresponds to the decomposition of surface nitrate complexes.

The effect of modification manifested itself in the absence of a low-temperature desorption peak from the TPD spectrum of NO_x on Pt,Cu/ZrO_2-PILC and in a considerable decrease in the maximum temperature of the high-temperature peak (T_{max} = 260–280°C against 370–380°C for ZrO_2-PILC). Thus, the modification of ZrO_2-PILC with platinum and copper changed the composition of NO_x adsorption complexes and considerably decreased the strength of the bond of nitrate complexes to the catalyst surface.

STEADY-STATE SPECTROKINETIC MEASUREMENTS

Interaction of Binary Mixtures with the Surface of Pt,Cu/ZrO_2-PILC

(0.2% NO + 2.5% O_2)/N_2. As with unmodified pillared clay [8], the spectra exhibited absorption bands at 1617 (bridging nitrate) and 1591 cm^{-1} (bidentate nitrate) [11–16]. Absorption bands corresponding to monodentate nitrate, nitrite, and nitrosyl complexes were not detected. It is likely that the absence of monodentate nitrates was due to changes in the Zr–Zr and Zr–O distances in pillars, as compared with the corresponding distances in bulk ZrO_2 [5]. It is likely that the absence of nitrosyl complexes, which are formed by the interaction of NO molecules with Pt and Cu, can be explained by the fact that they are rapidly converted into nitrate species in the presence of oxygen. As a result, the concentration of nitrate complexes on Pt,Cu/ZrO_2-PILC was higher than that on ZrO_2-PILC, all other factors being the same (Fig. 3).

Previously [8], we observed a decrease in the intensities of absorption bands due to hydroxyl groups and a symbatic increase in the intensities of absorption bands over the range 3100–3400 cm^{-1} in the spectra obtained upon the interaction of (0.2% NO + 2.5% O_2)/N_2 with the surface of ZrO_2-PILC. This effect was explained by the fact 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 corresponded to vibrations in the range 3100–3400 cm^{-1}.

The same process also occurred on the surface of Pt,Cu/ZrO_2-PILC; however, the intensities of corresponding absorption bands were higher in the presence of Pt and Cu with a more rapid consumption of surface OH groups.

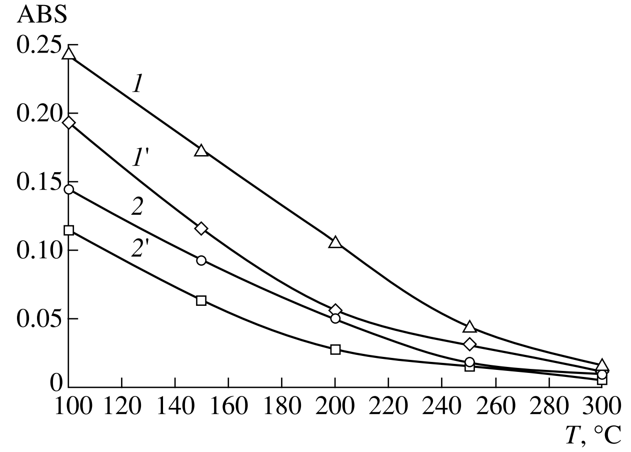

Fig. 3. The temperature dependence of the absorption band intensities of (*1*, *1*') bridging and (*2*, *2*') bidentate nitrate complexes in the spectra of (*1*, *2*) Pt,Cu/ZrO_2-PILC and (*1*', *2*') ZrO_2-PILC samples measured in a flow of NO_x.

The experimental data suggest that the number of sites capable of forming nitrate complexes increased because of the modification of ZrO_2-PILC with platinum and copper.

(0.2% C_3H_6 + 2.5% O_2)/N_2. The results of the IR-spectroscopic experiments and published data [11, 17–22] have led us to the conclusion that an isopropoxide complex (1394, 1383, 1464, and 1335 cm^{-1}), coordinatively bound acetone (1680, 1420, and 1371 cm^{-1}), and acetate (1555 and 1445 cm^{-1}) were formed on the surface of Pt,Cu/ZrO_2-PILC, as well as on the surface of ZrO_2-PILC [8], in the interaction with a flow of (0.2% C_3H_6 + 2.5% O_2)/N_2 (Fig. 4a). The absorption band at 1626 cm^{-1} belongs to the molecular vibrations of adsorbed water, which is a reaction product.

At the beginning of the interaction of the (0.2% C_3H_6 + 2.5% O_2)/N_2 mixture with the surface of Pt,Cu/ZrO_2-PILC at 100°C (Fig. 4a, spectrum *1*), the concentrations of coordinatively bound acetone and acetate were low: a spectrum characteristic of isopropoxide complexes was observed [11, 17–22]. Spectrum *2* was obtained as the reaction time of the (0.2% C_3H_6 + 2.5% O_2)/N_2 mixture with the catalyst was increased at the same temperature. For comparison, the spectrum of adsorbed acetone (spectrum *3*) is given. It can be seen that, under reaction conditions, the spectrum consisted of overlapping absorption bands that correspond to isopropoxide complexes and adsorbed acetone.

Figures 4b and 4c show the temperature dependence of the concentrations of various complexes (the intensities of corresponding absorption bands in the spectra) in the interaction of a flow of the (0.2% C_3H_6 + 2.5% O_2)/N_2 mixture with the surfaces of Pt,Cu/ZrO_2-PILC and ZrO_2-PILC, respectively. It can be seen that, on Pt,Cu/ZrO_2-PILC, the temperature at which isopropoxide was observed in the spectra (curves *3*) was lower and the concentration of acetate complexes (curves *2*) was much higher than those on ZrO_2-PILC. This result is consistent with data published by Schieber et al. [23], who noted that the supporting of platinum onto mesoporous Al_2O_3 considerably increased the adsorption of propylene. In other words, the formation of an acetate complex is activated in the presence of platinum.

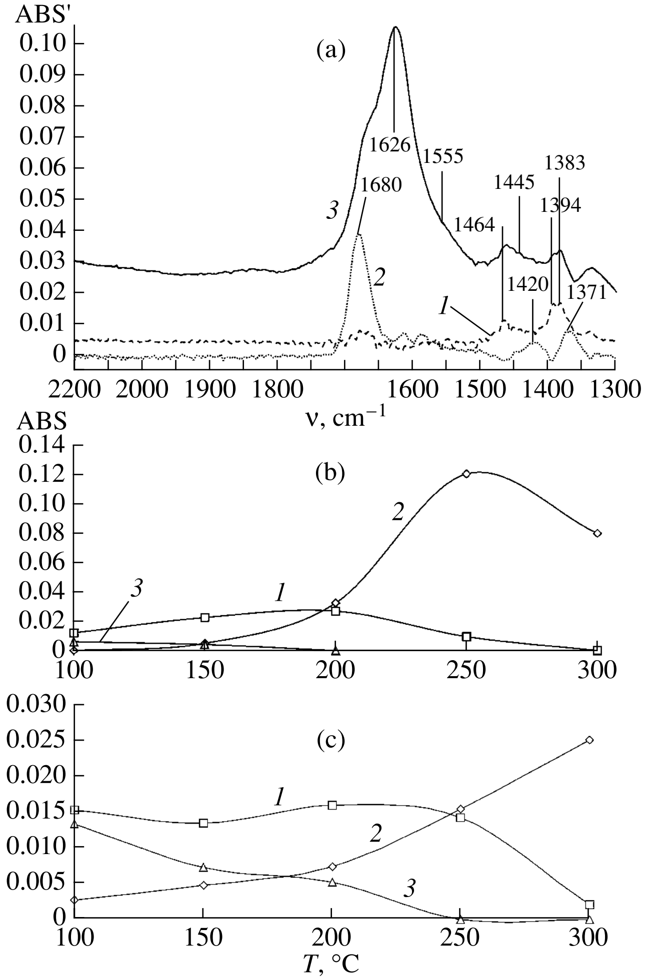

Fig. 4. (a) IR spectra obtained upon the interaction of Pt,Cu/ZrO_2-PILC with a mixture of (0.2% C_3H_6 + 2.5% O_2) (*1*) at the initial point of reaction progress at 100°C and (*2*) in the course of the experiment at the same temperature and (*3*) the spectrum of adsorbed acetone. (b) The temperature dependence of absorption band intensities due to (*1*) coordinatively bound acetone (1680 cm^{-1}), (*2*) an acetate complex (1560 cm^{-1}), and (*3*) an isopropoxide complex (1394 cm^{-1}) on the surface of Pt,Cu/ZrO_2-PILC in the spectra obtained upon the interaction of a flow of the (0.2% C_3H_6 + 2.5% O_2)/N_2 mixture with the surface of Pt,Cu/ZrO_2-PILC. (c) The above dependence for ZrO_2-PILC.

Previously [8], taking into consideration published data [5, 11, 20–25], we concluded that the isopropoxide complexes of propylene and coordinatively bound acetone are localized at the acid hydroxyl groups and Lewis acid sites of the ZrO_2-PILC surface. This conclusion was supported by the fact that the temperature of the occurrence of the isopropoxide complex decreased by 100°C after the supporting of Pt and/or Cu on ZrO_2 pillars, as compared with the unmodified pillared clay (Figs. 4b, 4c).

Note that the products of mild (coordinatively bound acroleine) or deeper propylene oxidation (acrylate) were not formed on Pt,Cu/ZrO_2-PILC because absorption bands over the range 3000–3100 cm^{-1} (=CH_2) were absent from the spectra. Because the mild oxidation of propylene on copper oxide clusters is possible [24], the absence of these absorption bands suggests that nitrate complexes are stabilized on the copper clusters of Pt,Cu/ZrO_2-PILC. In this case, the lower strength of the bond of nitrate complexes to the surface of Pt,Cu/ZrO_2-PILC, as compared with the bond strength to the surface of ZrO_2-PILC [8], becomes understandable (Fig. 2).

The above results demonstrate that the supporting of Pt and Co onto ZrO_2-PILC resulted in a considerable change in the concentrations and temperature regions of existence of surface compounds, as compared with these parameters for the unmodified pillared clay.

Interaction of the (0.2% NO + 0.2% C_3H_6 + 2.5% O_2)/N_2 Reaction Mixture with the Surface of Pt,Cu/ZrO_2-PILC

50–200°C. The spectra obtained in the interaction of the reaction mixture with the surface of Pt,Cu/ZrO_2-PILC (Fig. 5, spectra *1–4*) consist of overlapping absorption bands due to the isopropoxide complex of propylene, coordinatively bound acetone, and nitrates. They also contained absorption bands at 1386, 1435, 1576, 2993, 2942, 2920, and 2885 cm^{-1}, which can be attributed to symmetric and antisymmetric vibrations in the nitro group and to stretching and bending C–H vibrations in the nitroorganic surface complex (not shown in Fig. 5) [26–33]. 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 (Figs. 3, 4). Previously [8], based on the data of non-steady-state spectroscopic experiments, we demonstrated that the above absorption bands belong to vibrations in the same surface complex.

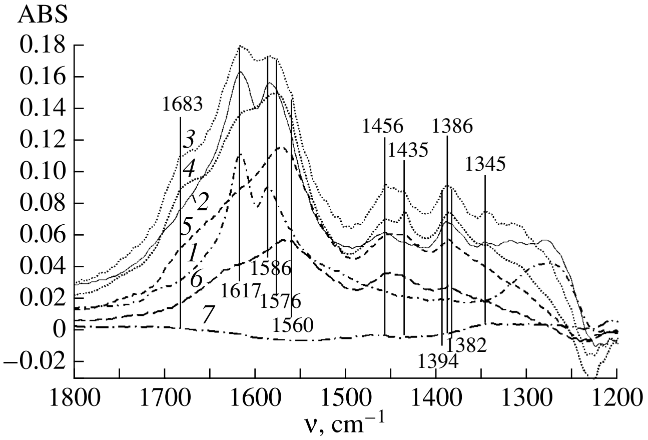

Fig. 5. IR spectra of surface compounds observed upon the interaction of the (0.2 vol % NO + 0.2 vol % C_3H_6 + 2.5 vol % O_2)/N_2 mixture with the surface of Pt,Cu/ZrO_2-PILC at (*1*) 50, (*2*) 100, (*3*) 150, (*4*) 200, (*5*) 250, (*6*) 300, and (*7*) 400°C.

To determine the structure of the nitroorganic complex, we studied the adsorption of various nitroorganic compounds (T = 150°C; the concentration of nitromethane, nitroethane, or 1-nitropropane in a flow of nitrogen was approximately equal to 3%) (Fig. 6). The spectra of the Pt,Cu/ZrO_2-PILC sample in a flow of these nitroorganic substances contained adsorption bands due to the vibrations of nitro groups and a set of absorption bands due to C–H vibrations. The spectrum of adsorbed 1-nitropropane (Fig. 6, spectrum *3*) is closest to the spectrum of the surface nitroorganic compound formed under the reaction conditions. The difference consists in the increased frequency of the antisymmetric vibration of the nitro group and a somewhat greater halfwidth of the symmetric vibration. As noted previously [8], an increased frequency of the antisymmetric vibration of the nitro group was observed in the case that two nitro groups were the constituents of a nitro compound, whereas an increased halfwidth of the symmetric vibration was related to the splitting of this absorption band. The above data, as well as published data [31, 34], allowed us to assume that the structure of the nitroorganic complex observed under the reaction conditions is close to the structure of adsorbed dinitropropane. The addition of two NO_2 groups to the propylene molecule in the course of the selective catalytic reduction of NO_x on zeolite catalysts was considered elsewhere [35, 36].

250–400°C. In this temperature range, the positions of the absorption bands of the nitroorganic compound changed with a general decrease in the intensities of all of the absorption bands (see also Fig. 7): the frequency of the antisymmetric vibration decreased, and the halfwidth of an absorption band due to the symmetric vibration of the nitro group increased so that this was absorption with poorly resolved maximums at 1394 and 1382 cm^{-1} (Fig. 5, spectra *5, 6*). For comparison, Fig. 6 (spectra *1*, *4*) shows the spectra of nitromethane adsorbed at 150 and 300°C, respectively. It can be seen that, as the interaction temperature was increased, the intensity and splitting of absorption bands at 1402 and 1379 cm^{-1} decreased so that at 300°C a poorly resolved doublet with maximums at 1394 and 1387 cm^{-1} was observed in the spectra. These results can be explained based on the assumption that acetate and nitrate complexes form a nitroorganic complex as the reaction temperature is increased and the surface becomes free of the isopropoxide complex. As on bulk ZrO_2, this nitro-

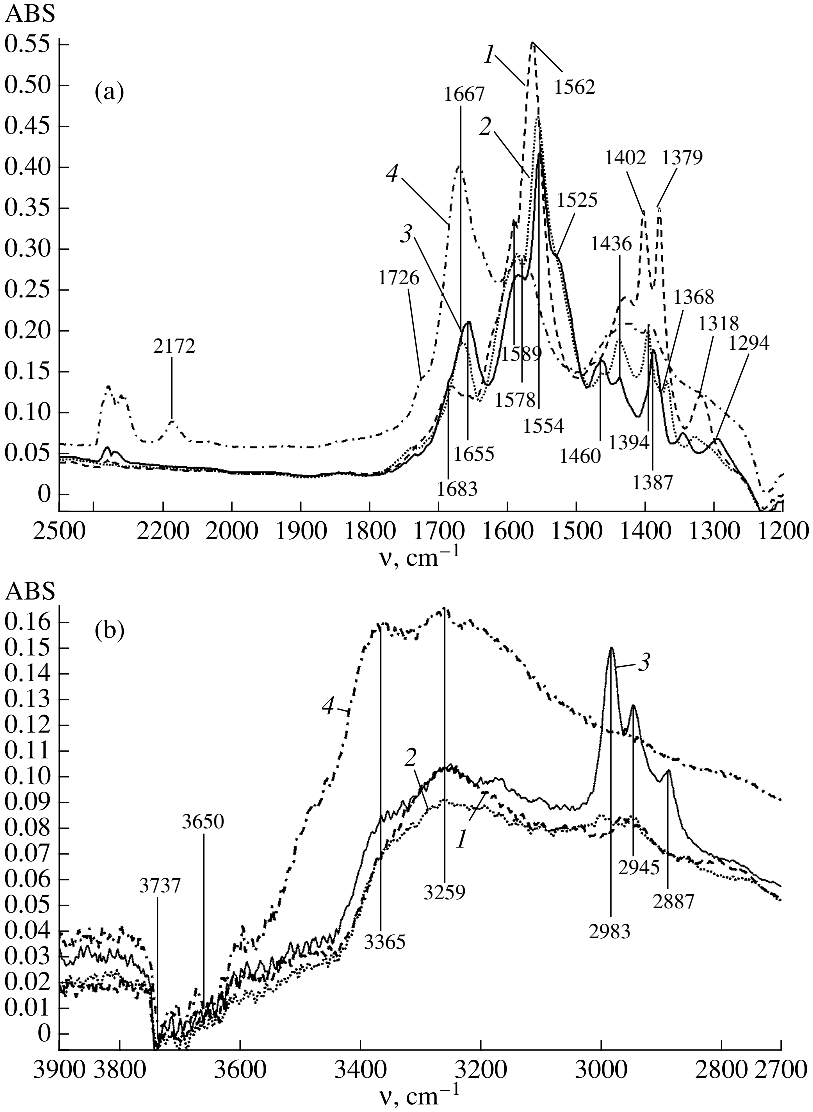

Fig. 6. IR spectra of surface compounds observed upon the interaction with the surface of Pt,Cu/ZrO_2-PILC at 150°C: (*1*) nitromethane, (*2*) nitroethane, (*3*) nitropropane, and (*4*) nitromethane adsorption at 300°C.

organic complex is structurally similar to adsorbed nitromethane.

In the interaction of nitroorganic compounds with the surface of Pt,Cu/ZrO_2-PILC, they undergo not only adsorption but also transformations, as evidenced by the appearance of absorption bands due to the vibrations of surface carbonate–carboxylate complexes at 1667, 1589, 1525, and 1460 cm^{-1} in the spectra. The absorption band at 1667 cm^{-1} may belong to vibrations in a nitroorganic complex [26–29, 37–42]. Moreover, according to Satsuma et al. [43], it can belong to vibrations in 1,3,5-triazine, melamine, or their derivatives. Note that, in this case, the spectra did not exhibit absorption bands due to adsorbed CO and NO molecules and isocyanate complexes (Fig. 6).

An analysis of data given in Fig. 7 shows that the temperature dependence of the concentration of a nitroorganic complex (curve *2*) or coordinatively bound acetone (curve *1*) exhibited a maximum (T_{max} = 200 or 150°C, respectively) under the reaction conditions, whereas the concentrations of acetate (curve *4*), isopropoxide (curve *3*), and nitrate complexes (curves *5*, *6*) decreased with temperature. Note that, as the temperature was increased in the course of NO_x reduction, the activity (Fig. 1) decreased symbatically with the decrease of the intensities of absorption bands due to surface acetate and nitrate complexes (Fig. 7).

From the above results, it follows that, unlike ZrO_2-PILC, two propylene activation species occurred in detectable amounts on the surface of Pt,Cu/ZrO_2-PILC: isopropoxide (low-temperature species) and acetate

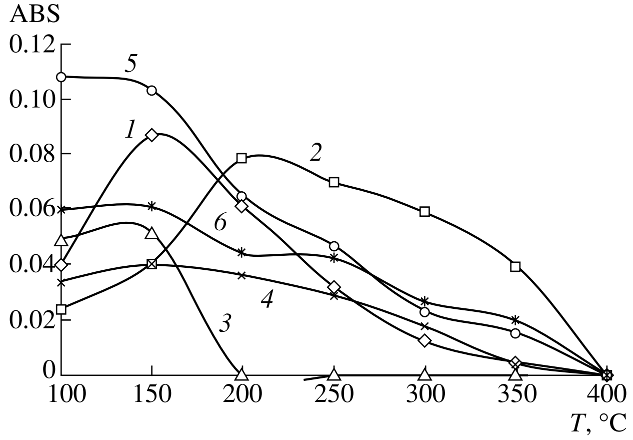

Fig. 7. The temperature dependence of the absorption band intensities of (*1*) acetone (1683 cm^{-1}), (*2*) nitroorganic (1435 cm^{-1}), (*3*) isopropoxide (1394 cm^{-1}), and (*4*) acetate (1560 cm^{-1}) complexes and (*5*) bridging (1617 cm^{-1}) or (*6*) bidentate (1588 cm^{-1}) nitrate in the spectra obtained upon the interaction of the (0.2% NO + 0.2% C_3H_6 + 2.5% O_2)/N_2 mixture with the surface of Pt,Cu/ZrO_2-PILC.

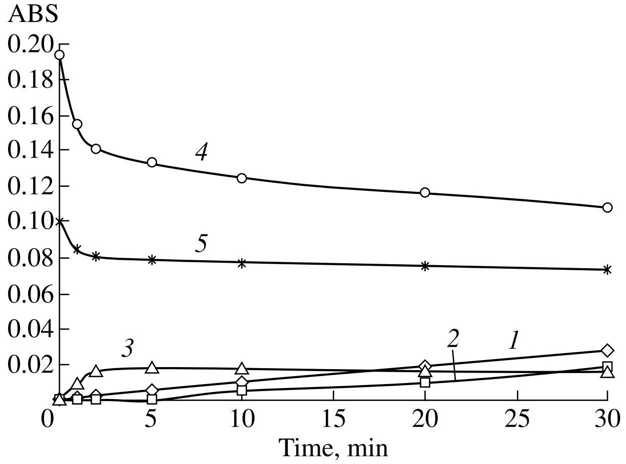

Fig. 8. The time dependence of the absorption band intensities of (*1*) acetone (1680 cm^{-1}), (*2*) nitroorganic (1386 cm^{-1}), and (*3*) isopropoxide (1394 cm^{-1}) complexes and (*4*) bridging (1617 cm^{-1}) or (*5*) bidentate (1588 cm^{-1}) nitrate in the spectra obtained upon the supply of the (0.2% C_3H_6 + 2.5% O_2)/N_2 mixture onto the previously formed nitrate complexes at 150°C.

(high-temperature species). It is likely that the presence of these species is responsible for the occurrence of structurally different nitroorganic compounds in different reaction temperature regions: a dinitropropane complex at low temperatures and a nitromethane complex at high temperatures.

In order to study the roles of nitrate and hydrocarbon complexes in the formation of nitroorganic intermediates, we performed a series of non-steady-state experiments.

Non-Steady-State Measurements

The experiments were performed over the temperature range 100–300°C with the simultaneous measurements of the catalytic activity and the IR spectra of surface compounds.

Reactivity of Surface Nitrate Complexes

The surface nitrate complexes were formed by the interaction of a flow of (0.2% NO + 2.5% O_2)/N_2 with the sample surface. Next, the cell with the sample was purged with a flow of an inert gas (N_2), and a mixture of (0.2% C_3H_6 + 2.5% O_2)/N_2 was introduced. In this case, the intensity changes of absorption bands due to surface compounds were monitored.

At 150°C, nitrate complexes were retained on the surface upon purging the catalyst with an inert gas flow. Upon the addition of the mixture of propylene and oxygen, nitrate complexes were consumed (Fig. 8, curves *4*, *5*) and the concentrations of isopropoxide (curve *3*), coordinatively bound acetone (curve *1*), and the nitroorganic compound (curve *2*) increased. Experiments at higher temperatures gave an analogous result: a decrease in the intensity of absorption bands due to nitrate complexes was accompanied by an increase in the intensity of absorption bands due to coordinatively bound acetone and the nitroorganic compound. We failed to monitor isopropoxide concentration changes at an elevated temperature because the concentration of this species was low.

The results of the non-steady-state measurements demonstrated that, in this case, bridging nitrate was the main source of the formation of the nitroorganic compound. Note that we managed to detect the consumption of nitrate complexes on unmodified pillared clay in analogous experiments performed only at 250°C [8].

Table 1 summarizes the quantitative characteristics of the conversion of nitrate complexes under conditions of the SCR of NO_x on Pt,Cu/ZrO_2-PILC and ZrO_2-PILC. The rate of conversion of surface complexes on a sample weight basis was determined from the equation

$$W = k_1N,$$

where k_1 is the apparent rate constant of conversion of the nitrate complex, and N is the amount of surface complexes in a sample of a certain weight. The procedure used for the determination of rate constants and the surface concentrations of nitrate complexes was described in detail elsewhere [9, 10]. For Pt,Cu/ZrO_2-PILC, the apparent rate constant of conversion of nitrate complexes was determined from the initial portion of curve *4* in Fig. 8.

Data given in Table 1 allowed us to make two conclusions:

Table 1. Characteristics of the conversion of surface nitrate complexes

Catalyst	T, °C	Apparent rate constant of the conversion of nitrate complexes k_1, min^{-1}	Rate of the conversion of nitrate complexes W, mol/min	Reaction rate, mol/min	References
ZrO_2	400	0.038	5.0×10^{18}	5.6×10^{18}	[7]
ZrO_2-PILC	250	0.035	2.0×10^{18}	1.8×10^{18}	[8]
Pt,Cu/ZrO_2-PILC	150	0.070	2.7×10^{18}	3.0×10^{18}	This work

(1) The rate of conversion of nitrate complexes is close to the reaction rate of the SCR of NO_x. This fact demonstrates the participation of nitrate complexes as intermediates in the reaction.

(2) The reactivity of nitrate complexes considerably increases on going from bulk ZrO_2 to ZrO_2-PILC and further to the modified pillared clay Pt,Cu/ZrO_2-PILC.

Reactivity of Surface Hydrocarbon Complexes

Figures 9 and 10 show the results of a study on the reactivity of surface isopropoxide and acetate complexes.

Hydrocarbon complexes on the surface were formed by the interaction of a flow of (0.2% C_3H_6 + 2.5% O_2)/N_2 with the sample surface at various temperatures. Then, the cell with the sample was purged with a flow of an inert gas and a flow of a mixture of (0.2% NO + 2.5% O_2)/N_2. In this case, changes in the intensities of absorption bands due to surface compounds in the flows of an inert gas and (0.2% NO + 2.5% O_2)/N_2 were monitored.

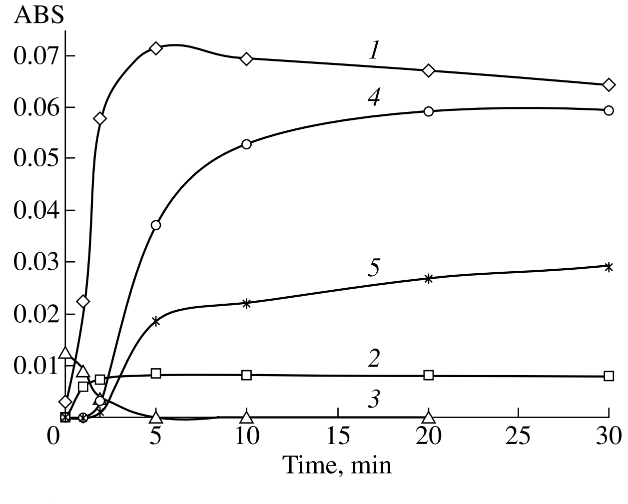

Fig. 9. The time dependence of the absorption band intensities of (*1*) acetone (1680 cm^{-1}), (*2*) nitroorganic (1386 cm^{-1}), and (*3*) isopropoxide (1394 cm^{-1}) complexes and (*4*) bridging (1615 cm^{-1}) or (*5*) bidentate (1588 cm^{-1}) nitrate in the spectra obtained upon the supply of the (0.2% NO + 2.5% O_2)/N_2 mixture onto the previously formed isopropoxide complexes at 100°C.

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 a mixture of (0.2% NO + 2.5% O_2)/N_2, isopropoxide complexes were rapidly consumed (Fig. 9, curve *3*) with a simultaneous increase in the concentrations of acetone and nitroorganic compounds (Fig. 9, curves *1* and *2*, respectively). 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, as the experiment temperature was increased, the initial isopropoxide concentration decreased and became negligibly small at 200°C.

Figure 10 shows changes in the spectra in the course of the reaction of acetate complexes with a flow of N_2 (spectrum *1*) or (0.2% NO + 2.5% O_2)/N_2 (spectrum *2*) at 300°C. Upon the interaction of acetates with (0.2% NO + 2.5% O_2)/N_2, the spectra exhibited a low-intensity broad absorption band at 1390–1380 cm^{-1}. A comparison with data on nitromethane adsorption (Fig. 6) indicated that the above absorption was analogous to the absorption of nitromethane adsorbed at 300°C. The same absorption but with a greater intensity was detected in the spectra obtained upon the interaction of the (0.2% NO + 0.2% C_3H_6 + 2.5% O_2)/N_2 reaction mixture with the sample surface (Fig. 5, spectrum *6*).

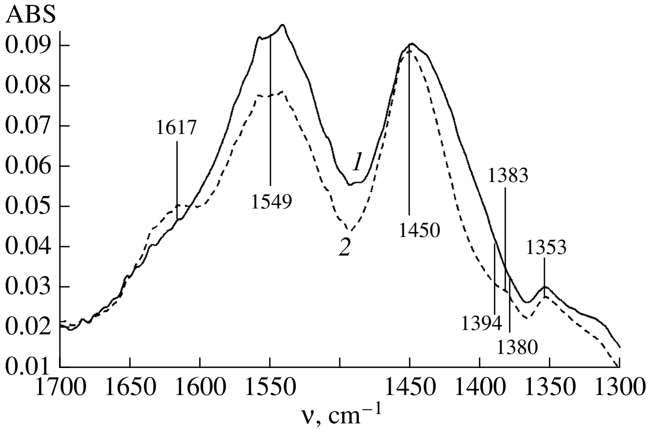

Fig. 10. IR spectra obtained upon the supply of (*1*) N_2 and (*2*) (0.2% NO + 2.5% O_2)/N_2 onto the previously formed acetate complex on the surface of Pt,Cu/ZrO_2-PILC.

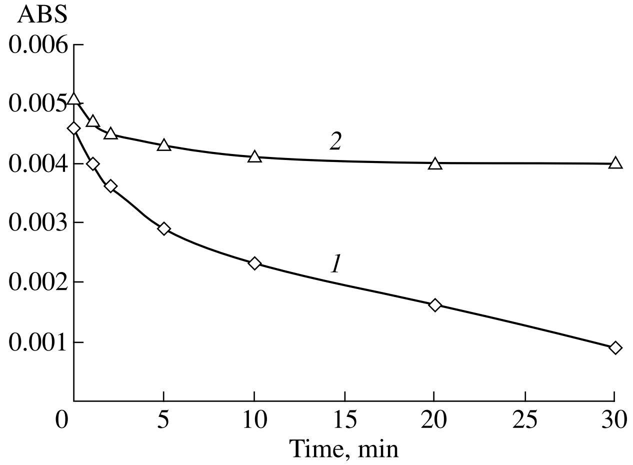

Fig. 11. The time dependence of the absorption band intensities of the nitroorganic complex (1386 cm^{-1}) in the spectra obtained upon the supply of (*1*) (0.2% NO + 2.5% O_2)/N_2 and (*2*) N_2 onto the previously formed nitroorganic complex on the surface of Pt,Cu/ZrO_2-PILC.

The experimental results suggest that, at relatively high temperatures, acetate complexes can be a source of the formation of a nitroorganic complex structurally similar to adsorbed nitromethane. At a temperature higher than 300°C, the surface concentrations of acetate and nitrate complexes decreased (Figs. 3, 4, 7). This circumstance can explain the observed decrease in the catalyst activity as the temperature was increased (Fig. 1).

Reactivity of Surface Nitroorganic Complexes

The nitroorganic complex was formed by the interaction of a flow of (0.2% NO + 0.2% C_3H_6 + 2.5% O_2)/N_2 with the surface of Pt,Cu/ZrO_2-PILC. Curves *1* and *2* in Fig. 11 reflect the time dependence of the intensity of an absorption band due to the nitroorganic complex in flows of (0.2% NO + 2.5% O_2)/N_2 and N_2, respectively. It can be seen that the intensity of this absorption band due to the nitroorganic complex in the reaction mixture decreased more rapidly than in the inert gas flow. Table 2 summarizes the quantitative characteristics of the conversion of nitroorganic complexes under the reaction conditions of the SCR of NO_x on Pt,Cu/ZrO_2-PILC, ZrO_2, and ZrO_2-PILC.

Table 2. Characteristics of the conversion of surface nitroorganic complexes

Catalyst	T, °C	Apparent rate constant of the conversion of nitroorganic complexes k_2, min^{-1}
ZrO_2	350	0.032
ZrO_2-PILC	250	0.040
Pt,Cu/ZrO_2-PILC	150	0.070

It can be seen that the value of k_2 increased on going from bulk ZrO_2 to ZrO_2-PILC and further to Pt,Cu/ZrO_2-PILC. Moreover, the apparent rate constant of consumption of nitroorganic complexes for each particular catalyst was close to the apparent rate constant of consumption of nitrate complexes (Tables 1, 2). This fact suggests that nitroorganic complexes are real reaction intermediates in the SCR of NO_x with propylene on the test catalysts.

We also performed experiments in which the gas flows of 2.5% O_2/N_2 and 0.2% NO/N_2 were supplied onto the surface nitroorganic complexes. The rate of decrease in the concentration of the nitroorganic complexes in a flow of either 2.5% O_2/N_2 or 0.2% NO/N_2 was equal to that observed in a flow of N_2. 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 is low at elevated temperatures, the formation of these complexes on the surface can be related to the degradation of surface nitrates.

This assumption was supported by the above experiments performed over a wide range of temperatures (100–300°C). The interaction of nitroorganic complexes with NO_2 complexes came into play at ~200°C. In accordance with thermal desorption data, the degradation of surface nitrate complexes (Fig. 2) with the formation of activated NO_2 complexes begins in this temperature region.

CONCLUSIONS

The IR-spectroscopic and TPD studies of the interaction of a mixture of (0.2% NO + 2.5% O_2)/N_2 with the surface of Pt,Cu/ZrO_2-PILC demonstrated that the modification of pillars caused a change in the composition of NO adsorption complexes (only bridging and bidentate nitrate complexes were present on the surface) and a considerable decrease in the strength of the bonds of nitrate complexes to the catalyst surface. Moreover, the modification facilitated an increase in the number of sites capable of forming nitrate complexes, as compared with unmodified pillars.

The following three types of complexes were present on the surface of Pt,CU/ZrO_2-PILC, as well as on the surface of unmodified pillared clay, upon the interaction with a flow of the (0.2% C_3H_6 + 2.5% O_2)N_2 mixture: an isopropoxide complex, coordinatively bound acetone, and acetate. The supporting of Pt and Cu onto the pillars of zirconia resulted in a considerable change in the concentration and the temperature region of existence of surface hydrocarbon compounds, as compared with the corresponding values for unmodified clay.

Under the reaction conditions on both modified and unmodified ZrO_2-PILC samples, isopropoxide and nitrate (bidentate and bridging) complexes formed a surface complex that was structurally similar to adsorbed dinitropropane. The dinitropropane complex on ZrO_2-PILC was consumed in the interaction with surface nitrates. In the absence of $(NO + O_2)$ from a gas phase and nitrate complexes from the surface, the decomposition reaction of the dinitropropane complex with the formation of surface acetate complexes and ammonia was predominant. At elevated temperatures, the surface nitromethane complex was formed by the interaction between acetate and nitrate complexes on modified ZrO_2 pillars (unlike unmodified pillars on which the concentration of acetate complexes was small). This surface nitromethane complex reacted with surface nitrates to be converted into molecular nitrogen and CO_2.

The spectrokinetic measurements demonstrated that nitroorganic complexes were reaction intermediates in the SCR of NO_x on the test catalysts.

The found differences in the forms of reactant activation and in their thermal stabilities can also explain differences in the activities of unmodified and modified ZrO_2-PILC in the SCR reaction of nitrogen oxides with propylene in an excess of oxygen. A considerable decrease in the concentration of the isopropoxide and nitrate complexes on the surface of unmodified samples with temperature is the main reason for the decrease of the activity of pillared clay as the temperature was increased [8]. On modified ZrO_2-PILC, the initial increase in the reaction rate with temperature was due to the transformation of the dinitropropane complex. The decrease in the reaction rate as the temperature was further increased depended on the decrease of the concentration of surface nitrate and acetate complexes.

REFERENCES

1. Gil, A. and Gandia, L. M., *Catal. Rev. Sci. Eng.*, 2000, vol. 42, p. 146.
2. Yang, R.T., Trappiwattananon, 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, Y., 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.
7. Matyshak, V.A., Tret'yakov, V.F., Chernyshev, K.A., Burdeinaya, T.N., Korchak, V.N., and Sadykov, V.A., *Kinet. Katal.*, 2006, vol. 47, no. 4, p. 610 [*Kinet. Catal.* (Engl. Transl.), vol. 47, no. 4, p. 593].
8. Matyshak, V.A., Tret'yakov, V.F., Chernyshov, K.A., Burdeinaya, T.N., Korchak, V.N., and Sadykov, V.A., *Kinet. Katal.*, 2006, vol. 47, no. 5, p. 770.
9. Matyshak, V.A. and Krylov, O.V., *Catal. Today*, 1995, vol. 25, no. 1, p. 1.
10. Konin, G.A., *Cand. Sci. (Chem.) Dissertation*, Moscow: Semenov Inst. of Chemical Physics, 2001.
11. Davydov, A.A., *Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides*, New York: Wiley, 1990.
12. Pozdnyakov, V.N. and Filimonov, V.N., *Kinet. Katal.*, 1973, vol. 14, p. 760.
13. Beutel, T., Sarkany, J., Lei, G.-D., Yan, J.Y., and Sachtler, W.M.H., *J. Phys. Chem.*, 1996, vol. 100, p. 845.
14. Sadykov, V.A., Baron, S.L., Matyshak, V.A., et al., *Catal. Lett.* 1996, vol. 37, p. 157.
15. Shimizu, K., Kawabata, H., Satsuma, A., and Hattori, T., *J. Phys. Chem. B*, 1999, vol. 103, p. 5240.
16. Weingand, T., Kuba, S., Hadjiivanov, K., and Knozinger, H., *J. Catal.*, 2002, vol. 209, p. 539.
17. Efremov, A.A. and Davydov, A.A., *React. Kinet. Catal. Lett.*, 1981, vol. 18, nos. 3–4, p. 353.
18. Finocchio, E., Busca, G., Lorenzelli, V., and Willey, R.J., *J. Chem. Soc., Faraday Trans.*, 1994, vol. 90, no. 21, p. 3347.
19. Finocchio, E., Busca, G., Lorenzelli, V., and Escribano, V.S., *J. Chem. Soc., Faraday Trans.*, 1996, vol. 92, no. 9, p. 1587.
20. Liengme, B.V. and Hall, W.K., *Trans. Faraday Soc.*, 1966, vol. 62, no. 11, p. 3229.
21. Eberly, P.E., *J. Phys. Chem.*, 1967, vol. 71, p. 1717.
22. Gordymova, T.A. and Davydov, A.A., *Trudy 4 Mezhdunarodnogo simpoziuma po geterogennomu katalizu* (Proc. 4th Int. Symp. on Heterogeneous Catalysis), Sofia, 1979, p. 157.
23. Schieber, W., Vinek, H., and Jentys, A., *Appl. Catal., B*, 2001, vol. 33, p. 263.
24. Margolis, L.Ya., *Okislenie uglevodorodov na geterogennykh katalizatorakh* (Oxidation of Hydrocarbons on Heterogeneous Catalysts), Moscow: Khimiya, 1977.
25. 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.
26. Tanaka, T., Okuhara, T., and Misono, M., *Appl. Catal., B*, 1994, vol. 4. p. L1.
27. Sumiya, S., He, H., Abe, A., et al., *J. Chem. Soc., Faraday Trans.,* 1998, vol. 94, no. 15, p. 2217.

28. Maunula, T., Ahola, J., and Hamada, H., *Appl. Catal., B*, 2000, vol. 26, p. 173.
29. Chi, Y. and Chuang, S.S.C., *J. Catal.*, 2000, vol. 190, p. 75.
30. 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.
31. Paperno, T.Ya. and Perkalin, V.V., *Infrakrasnye spektry nitrosoedinenii* (IR Spectra of Nitro Compounds), Leningrad: Leningr. Gos. Univ., 1974.
32. Lobree, L.J., Hwang I.-Ch., Reimer, J.A., and Bell, A.T., *Catal. Lett.*, 1999, vol. 63, p. 233.
33. Hadjiivanov, K., Knozinger, H., Tsyntarski, B., and Dimitrov, L., *Catal. Lett.*, 1999, vol. 62, p. 35.
34. Noble, P., Borgardt, F.G., and Reed, W.L., *Chem. Rev.*, 1964, vol. 64, p. 19.
35. Yokoyama, C. and Misono, M., *J. Catal.*, 1994, vol. 150, p. 9.
36. 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, nos. 13–14, p. 1901.
37. Haneda, M., Kintaichi, Y., Inaba, M., and Hamada, H., *Catal. Today*, 1998, vol. 42, p. 127.
38. Yokoyama, C. and Misono, M., *Catal. Today*, 1994, vol. 22, p. 59.
39. Gerlach, T. and Baerns, M., *Chem. Eng. Sci.*, 1999, vol. 54, p. 4379.
40. Hadjiivanov, K.I., *Catal. Rev.-Sci. Eng.*, 2000, vol. 42, no. 1, p. 71.
41. Adelman, B., Beutel, T., Lei, G., and Sachtler, W.M.H., *J. Catal.*, 1996, vol. 158, p. 327.
42. Meunier, F.C., Breen, J.P., Zuzniuk, V., et al., *J. Catal.*, 1999, vol. 187, p. 493.
43. Satsuma, A., Cowan, A.D., Cant, N.C., and Trimm, D.L., *J. Catal.*, 1999, vol. 181, p. 165.