The Mechanism of Selective NO$_x$ Reduction by Hydrocarbons in Excess Oxygen on Oxide Catalysts: I. Adsorption Properties of the Commercial NTK-10-1 Catalyst

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Abstract—According to X-ray phase and spectral analyses, the NTK-10-1 catalyst is a mixture of ZnO, CuO, NiO, ZnAl$_2$O$_4$, CuAl$_2$O$_4$, and CaCO$_3$. Under conditions of selective reduction of nitrogen oxides by propane, nitrite and nitrate complexes are formed on the surface of the NTK-10-1 catalyst. With an increase in temperature, nitrite complexes transform to nitrate complexes at a rate that decreases in the presence of propane in the gas phase. Propane adsorption is an activated process in which oxygen plays an important role. The results of temperature-programmed reduction showed that oxygen readily desorbs from the catalyst surface even under oxidative conditions.

INTRODUCTION

Considerable recent attention has been given to the development of catalysts for selective catalytic reduction of nitrogen oxides by hydrocarbons in excess oxygen. Copper-containing zeolites showed a high activity in this reaction [1, 2]. It was found in the study of the mechanism of this process [3–7] that the activity is due to the presence of isolated copper cations. These centers are characterized by weak molecular, rather than dissociative, adsorption of oxygen, because paired centers are not available and there is no competition of nitrogen oxide and oxygen molecules for the sites on the surface. Somewhat more recently, it was found [8–11] that oxide systems catalyze the reaction. In this case oxygen favors and does not prevent nitrogen oxide activation and the formation of surface nitrate complexes [12–16], which play the key role in the process over such catalysts. The decomposition of nitrates at the reaction temperatures leads to the formation of NO$_2$ (which is very active in the reaction with hydrocarbons [17–20]) right in the reaction zone.

Recently, considerable attention has been given to catalytic systems with a synergistic effect. Mechanical mixtures belong to such systems [21–25]. In previous papers [26, 27], we presented the results of the study of the selective NO reduction by methane and propane over commercial catalysts (STK, Ni–Cr oxide, and NTK-10-1) that do not contain noble metals in their compositions. Mechanical binary mixtures of such catalyst show a synergistic effect, which is a higher activity of the combined system than the sum of activities of catalyst components. To elucidate the nature of synergism, it is necessary to know the mechanism of the process for each of the components of a mechanical mixture. In connection with this, the goal of this work was to study the mechanism of selective reduction of nitrogen oxides by hydrocarbons on the NTK-10-1 catalyst.

EXPERIMENTAL

Physicochemical properties of the catalyst were characterized by X-ray phase analysis, temperature-programmed reduction (TPR), X-ray spectral analysis, and specific surface area measurements.

X-ray phase analysis was carried out on a Dron-3 diffractometer (CuK_α radiation). The phase composition was determined by comparing the results with JCPDS data.

For X-ray spectroscopic analysis of the catalyst, the Camebax MBX-1 analyzer was used. The elemental composition was determined using a crystal-diffraction spectrometer with the following crystals: OdPb, TAP, PET, and LiF. The averaged composition was determined using an area of 100×100 μm.

TPR of the samples was carried out in a flow-type U-shaped reactor in a flow of 10% H$_2$/Ar (40 ml/min) at a temperature ramp of 10°C/min in the range 20–600°C. The concentration of hydrogen in the flow was analyzed continuously using a thermal conductivity detector. Before the TPR experiments, a sample (40 mg) was treated with O$_2$ at 500°C for 1 h, cooled in a flow of O$_2$ to room temperature, and purged with argon and a mixture of 10% H$_2$ in Ar. The amount of hydrogen consumed for reduction was calculated by comparing the peak areas of hydrogen absorption determined in the course of the experiment with the TPR peak of the standard sample (NiO).
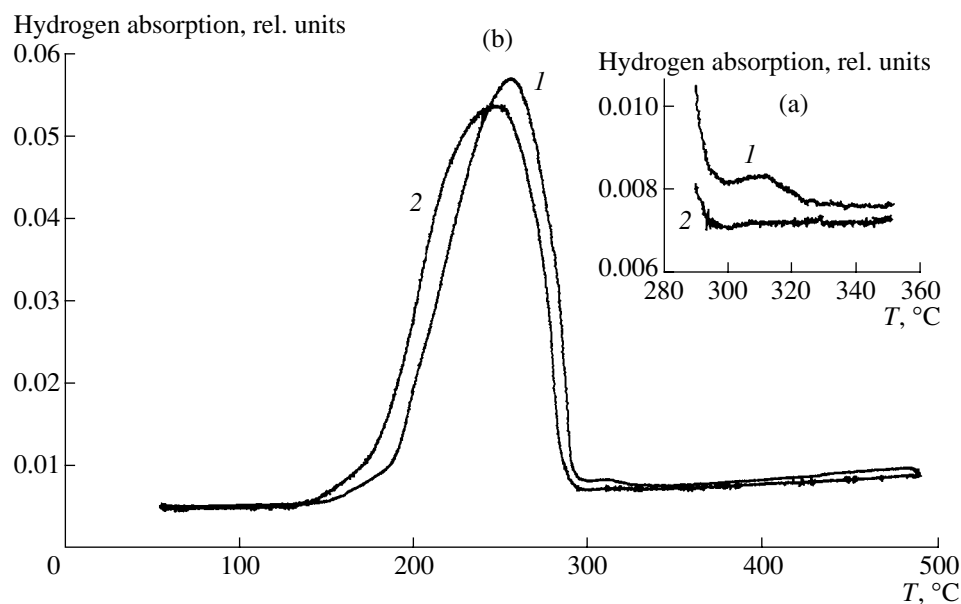
Fig. 1. TPR spectrum of the NTK-10-1 catalyst; (a) enlarged fragment of the spectrum that refers to NiO reduction; (*1*) first cycle and (*2*) second cycle of reduction.

The specific surface area was measured by the chromatographic BET method from thermal argon desorption.

Temperature-programmed desorption (TPD) in a flow IR cell/reactor was combined with recording the IR spectra of surface complexes. Before each TPD experiment, the catalyst was treated in a flow of nitrogen in the IR cell at 400–500°C, cooled to 25°C, and then adsorption of the 0.1% NO/N$_2$ mixture was carried out for 20 min. Excess NO was removed by a flow of nitrogen for 20 min. TPD was carried out in the regime of uninterrupted analysis of NO and NO$_2$ in the gas phase before and after the reactor using a chemiluminescent NO/NO$_x$ Beckman-951A analyzer (nitrogen carrier gas, $W = 9000$ h^{-1}, temperature ramp 5 K/min). In the course of TPD, the spectra of surface compounds were recorded. Each spectrum provided information on changes in the state of the surface in the course of heating for 20°C.

IR transmittance and diffuse-reflectance spectra were obtained using a Spectrum RX I FT-IR Perkin-Elmer system (resolution, 4 cm^{-1}; scan time, 4.2 s). The resulting IR spectra were processed using the Spectrum computer program developed by Perkin-Elmer. The sample weight in diffuse-reflectance spectral measurements was 1000–1200 mg; in the case of transmittance regime, the sample was 40–60 mg. The intensities of absorption bands in diffuse-reflectance and transmittance spectra were in Kubelka–Munk units and in absorbance units (D), respectively. To determine the compositions of desorbing products, experiments were carried out in vacuum with analysis by an MX 7303 mass spectrometer. Before experiments, a catalyst (55 mg) was treated under standard conditions: kept in

a vacuum at room temperature to 10^{-4} Pa, heated to 500°C, kept in a vacuum for 30 min, treated in oxygen ($P = 2 \times 10^2$ Pa) for 30 min, cooled to 20°C, and vacuumed. Before TPD experiments, individual gases (NO or C$_3$H$_8$) were adsorbed for 5 min, and gaseous mixtures (NO + O$_2$, C$_3$H$_8$ + O$_2$, or NO + O$_2$ + C$_3$H$_8$) were absorbed for 30 min. Then, the samples were vacuumed (10 min) and heated at a ramp of 10 K/min with continuous evacuation.

RESULTS

Characteristics of the Catalyst State

X-ray spectral analysis of the initial catalyst and the sample after the reaction of selective reduction of nitrogen oxides by propane showed that the average concentrations of Cu, Zn, Ni, and Ca particles in the bulk are somewhat (up to 1.5 times) higher in the catalyst that operated in the reaction. The concentration of Al particles is the same in both samples and the concentration of oxygen is a little (≤10%) higher in the initial sample. The nonuniform distribution of particles is typical of nickel. Other elements are distributed more uniformly and have no clear-cut inclusions.

According to X-ray phase analysis the catalyst is a mixture of ZnO, CuO, ZnAl$_2$O$_4$ CuAl$_2$O$_4$, and CaCO$_3$. The specific surface area of the sample is 75 m^2/g.

The TPR spectra have a peak corresponding to CuO reduction to metal copper with $T_{max} = 260$°C in the first oxidation–reduction cycle and with $T_{max} = 250$°C in further cycles (Fig. 1). The degree of Cu reduction is 34–36% and does not change in three oxidation–reduction cycles. The rest of the copper enters the composition of complex spinel oxides (anion-modified solid

NO, ppm
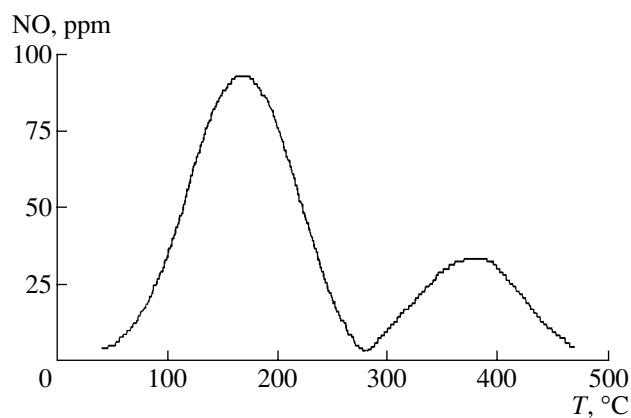
Fig. 2. TPD spectrum after NO adsorption on the surface of the NTK-10-1 catalyst.

solution in zinc oxide [28, 29]) and is reduced at a temperature above >550°C. In the first TPR cycle, a peak with T_{max} = 310°C is registered, which corresponds to the reduction of NiO to metal (Fig. 1a), but the degree of NiO reduction peaked at 2.7%. This peak disappeared in further oxidation–reduction cycles. It is likely that the all the nickel enters the composition of complex oxide (spinel-type) compositions and is reduced at a temperature higher than 550°C. After reaction, the TPR spectrum contains only one maximum associated with the reduction of CuO to Cu⁰. The degree of Cu^{2+} reduction increases to 60% compared to the initial sample.

The results obtained point to the fact that the NTK-10-1 catalyst is a mixture of various oxide forms and $CaCO_3$. Oxygen is rather easy to remove from the surface even under oxidative conditions of the process. Copper oxide is reduced most readily and to the greatest degree. NiO is harder to reduce.

Adsorption of the Components of the Reaction Mixture

NO, NO + O_2. TPD experiments were carried out in a cell for measuring diffuse-reflectance spectra after 0.1 vol % NO/N_2 adsorption (m_{Cat} = 1067 mg). The TPD spectrum contains two peaks (T_{max} = 165 and 390°C) (Fig. 2). The amount of NO molecules desorbed at 165 and 390°C was 1.54×10^{19} and 0.95×10^{19}, respectively.

The diffuse-reflectance IR spectra did not contain any absorption bands corresponding to the vibrations in nitrosyl or nitrite–nitrate complexes. Absorption bands of complexes whose desorption gives the observed TPD spectrum is in the region of nitrite–nitrate structures (below 1600 cm⁻¹), where the sensitivity of diffuse-reflectance spectroscopy is low. In connection with this, adsorbed nitrogen oxide species were further studied in experiments using transmittance spectroscopy. In the transmittance spectra obtained in the course of desorption, a broad absorption band is observed at 1215 cm⁻¹, which grows broader toward

lower frequencies. This means that this band consists of at least two individual bands. A decrease in the half-width of this absorption band with an increase in temperature in the course of thermal desorption at 35–100°C and the constant value of the half-width with a further increase in temperature provides further evidence for this conclusion. According to published data [12, 30], absorption bands in this region belong to vibrations in surface nitrite complexes. Furthermore, the spectra contain bands at 1020, 1280, and 1600 cm⁻¹ corresponding to the nitrate surface complex. Figure 3 shows the TPD spectra after NO adsorption at room temperature and a plot reflecting a change in the intensity of absorption bands of surface complexes in the course of desorption. TPD spectra consist of three peaks with T_{max} = 90, 150, and 380°C.

The results of TPD and spectral study of NO + O_2 adsorption at room temperature and at 400°C are qualitatively similar. Note that, in the presence of oxygen, the intensity of the high-temperature desorption peak increases. The amount of desorbed NO molecules at different temperatures are shown in the table.

In the process of thermal desorption, the maximum intensity of absorption band at 1280 cm⁻¹ was observed at 250°C (Fig. 3b). The absorbance at 1215 cm⁻¹ decreased with an increase in temperature and this band disappeared at 200°C. Note that the highest rate of decrease in the intensity of absorption bands at 1280 cm⁻¹ corresponds to the maximum of the high-temperature peak of NO_x evolution. A change in the absorbance in the region of 1215 cm⁻¹ occurs in two stages. This effect is best seen in the experiment described in Fig. 3. In the temperature interval 35–100°C, the intensity of the low-frequency wing of the absorption band at 1215 cm⁻¹ decreases, which corresponds to the low-temperature peak of desorption (Fig. 3). As this takes place, the intensity of high-frequency absorbance at 1215 cm⁻¹ does not change. An increase in temperature above 100°C leads to a decrease in the intensity of the absorption band at 1215 cm⁻¹ and the appearance of the thermal desorption peak at 150°C.

C_3H_8, C_3H_8 + O_2. In the adsorption of a gaseous mixture composed of 0.5 vol % C_3H_8/N_2 at temperatures above 200°C, the diffuse-reflectance spectra contain absorption bands at 3090, 2970, 2930, and 2870 cm⁻¹ (Fig. 4, curves *1, 2*).

The same absorption bands were found in the interaction of the $0.5C_3H_8 + 2.5O_2/N_2$ (vol %) mixture with the surface. However, they appear at lower temperatures (curves *3, 4*). The disappearance of bands coincides with the beginning of the reaction of propane oxidation (Fig. 4, curve *5*). The catalyst shows the high activity in propane oxidation (the temperature of 100% conversion of propane is 370°C).

According to literature data [31], the absorption bands at 3090 and 2970 cm⁻¹ can be assigned to the C–H vibrations in the CH_2 group, and the absorption bands at 2930 and 2870 cm⁻¹ can be assigned to C–H
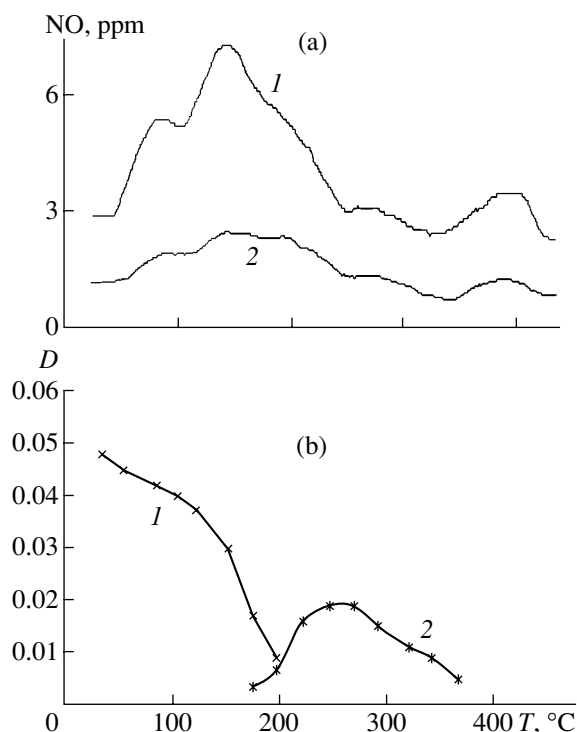
Fig. 3. (a) The TPD spectra of (*1*) NO$_x$ and (*2*) NO after NO adsorption at room temperature on the surface of the NTK-10-1 catalyst; (b) changes in the intensity of the absorption band at (*1*) 1215 and (*2*) 1280 cm^{-1} in the course of desorption.

Fig. 4. Temperature dependence of the intensities of absorption bands at (*1*, *3*) 2870 cm^{-1} and (*2*, *4*) 2970 cm^{-1} after adsorption of the mixtures (*1*, *2*) 0.5% C$_3$H$_8$/N$_2$ and (*3*, *4*) 0.5% C$_3$H$_8$ + 2.5% O$_2$/N$_2$ on the surface of the NTK-10-1 catalyst; (*5*) propane conversion.
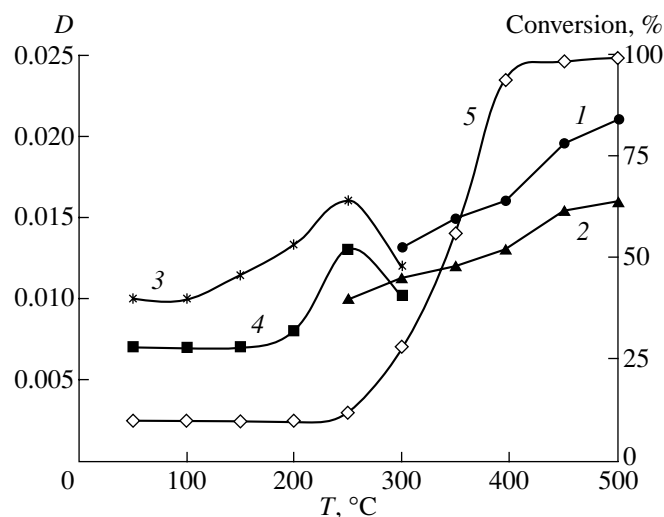
vibrations in the CH$_3$ group of a propane molecule adsorbed on the catalyst surface.

Thermal desorption measurements and mass spectral analyses showed that propane is practically not adsorbed at room temperature. However, after adsorption at 200°C it appears in desorption products (Fig. 5). Moreover, it was found that oxygen is not adsorbed on the catalyst surface.

DISCUSSION

Adsorption Forms of Reactants

At least two surface complexes are formed on the catalyst surface in the course of NO adsorption: nitrite and nitrate. A nitrosyl complex, which can be formed under these conditions, probably rather rapidly transforms into the nitrite complex [30], which is observed in the spectra and characterized by a broad band at 1200–1215 cm^{-1}. However, it is possible that there are nitrite complexes of two types localized at different surface sites. Such an idea is supported by the results of NO thermal desorption with the simultaneous recording of IR spectra of surface compounds (Fig. 3) and data from the measurements of the half-width of this band. A decrease in the intensity of this band of nitrite complexes (Fig. 3, curve *1*) is characterized by two portions with different slopes. These portions correspond to two desorption

peaks in the TPD spectrum. The first corresponds to the desorption of a nitrite complex with a lower band frequency. The second corresponds to the band at 1215 cm^{-1}.

Comparison of TPD and spectral data clearly shows that the high-temperature peak is due to the decomposition of nitrate complexes (Fig. 3, curve *2*). It follows from this figure that the concentration of nitrate complexes passes through the maximum; that is, these complexes are formed when surface reactions occur. One such reaction is between surface nitrites and surface oxygen.

When C$_3$H$_8$/N$_2$ reacts with the catalyst surface, the band at 2870 cm^{-1} is only observed at temperatures higher than 300°C (Fig. 4). In the interaction of C$_3$H$_8$ + O$_2$/N$_2$ with the surface, the same band is observed

Amount of molecules desorbed from the surface of the NTK-10-1 catalyst

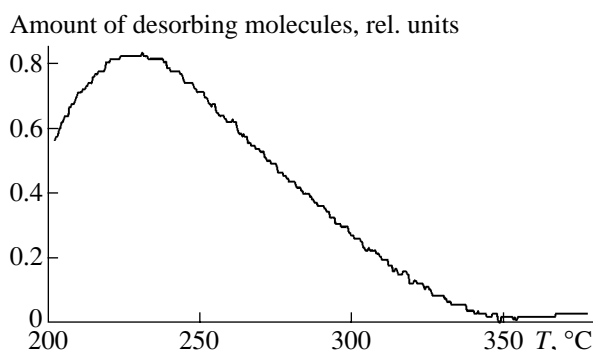| Adsorbate, temperature	T_{max}, °C	Amount of desorbed molecules, $N \times 10^{-19}$
NO, 20°C	90	0.053
	150	0.24
	380	0.032
NO + O$_2$, 20°C	85	0.15
	140	0.14
	365	0.13
NO + O$_2$, 400°C	90	0.18
	140	0.11
	370	0.26

Amount of desorbing molecules, rel. units

Fig. 5. TPD spectrum after propane adsorption at 200°C.

below 300°C (Fig. 4). TPD data with mass spectral analysis show that propane desorption is only observed after its adsorption at temperatures higher than 200°C (Fig. 5). This means that, in propane adsorption at temperatures higher than 200°C, the catalyst surface is probably reduced, leading to the appearance of various propane oxidation products on the surface and coordination-unsaturated copper cations that are capable of binding and activating hydrocarbons. Oxygen plays the critical role in the activation of propane adsorption: its absence leads to a decrease in the adsorption temperature (Fig. 4). Note that, when NO is added, the concentration of adsorbed propane forms increases. The activated adsorption of propane is probably due to the formation of fragments on the surface that are oxidized (by oxygen or NO) and that are analogous to those found in [32].

CONCLUSIONS

According to the data of X-ray phase and X-ray spectral analysis, the NTK-10-1 catalyst is a mixture of ZnO, CuO, NiO, $ZnAl_2O_4$ $CuAl_2O_4$, and $CaCO_3$. Oxygen easily desorbs from the catalyst surface even under oxidative conditions for the process. Copper oxide is reduced most readily and to the greatest degree (the degree of CuO reduction is 34–36%). NiO is reduced to a much smaller degree (up to 2.7%).

In NO adsorption on the NTK-10-1 catalyst surface, two surface complexes are formed: nitrite and nitrate. The TPD spectrum contains two desorption peaks corresponding to these complexes. The low-temperature peak corresponds to desorption of the nitrite complex. Comparison of thermal desorption and spectral data shows that the high-temperature peak is associated with the decomposition of nitrate complexes whose concentration passes through a maximum. The nitrate complex on the surface is formed in the reaction between nitrites and surface oxygen. Propane adsorption is the activated process in which oxygen plays the critical role and decreases the temperature of adsorption. When NO is added, the concentration of adsorption forms of propane increases. Oxygen is not adsorbed on the surface of the NTK-10-1 catalyst.

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