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The Use of the Effect of Synergism to Increase the Activity of Catalysts in deNO$_x$ Process

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Abstract

Formulations of original catalytic compositions have been developed to clear gas emissions of highway transport on the basis of catalysts that are free of precious metals: NTK-10-1, STK, and Ni–Cr oxidic catalyst, the use of which was not made in these processes previously. High activity of the developed catalytic compositions is caused by the effect of synergism that has been discovered and studied for the first time with mechanical mixtures of commercial catalysts. The investigation of the mechanism of the reaction of selective NO$_x$ reduction by propane over individual industrial catalysts has demonstrated that the effect of synergism that can be observed with their binary mechanical mixtures is caused by oxidizing activation of propane that proceeds on the surface of STK and Ni–Cr oxidic catalysts with the formation of more efficient reducing agents, namely, propylene and hydrogen respectively. Owing to the interphase diffusion, the last-mentioned fall on the surface of the NTK-10-1 catalyst through the gas phase, and the catalyst activates NO$_x$.

INTRODUCTION

Present-day power industry and highway transport are the basic sources of the pollution of the environment. In connection with a continuous growth of energy consumption and with an increase in the quantity of cars, the combined proportion of the air pollution by emissions of thermal power stations (TPS) and motor transport in large cities ranges up to 95 % [1, 2].

As of now, the cost of catalysts for gas purifying is of about 10 billion dollars, or 33 % from the total cost of all catalysts produced in the world, and costs for their production will substantially increase every year. A vast majority of the catalysts that are now in use for clearing exhaust gases of motor transport contain Pt and other precious metals that include rhodium in all cases. In addition to their high cost, the basic absolute obstacle on the way of a wide-scale dissemination of catalytic converters of the given type lies in the limited reserves of rhodium. In this connection, investigations are urgent that are directed to develop new effective catalysts, free of precious metals, and methods of neutralization of toxic components on their basis.

Currently, great attention is given to the development of catalysts for the reaction of selective reduction of nitrogen oxides by hydrocarbons with excessive oxygen. One of the promising ways for creating catalytic systems for this process is based on the use of the effect of synergism [3–6]. When multiphase catalytic compositions are used, a principle can be realized to break a composite reaction into stages, each being accelerated by a specific catalyst. The simplest method of generating such systems is a mechanical mixing of two or more components. Previously, it has been found [7–11] that mixtures of industrial catalysts, specifically, Cu–Zn–Al-containing NTK-10-1, Fe–Cr oxidic STK, and Ni–Cr oxidic one, show the effect of synergism in the reaction of selective catalytic reduction (SCR) of nitrogen oxides by hydrocarbons (HC) in excess of O_2 (NO_x HC-SCR).

This work is devoted to the investigation of the nature of synergism with binary mechanical mixtures of STK, Ni–Cr-oxidic, and NTK-10-1 catalysts, the investigation being based on a detailed study of the mechanism of NO_x SCR by propane with individual components and their mixtures.

EXPERIMENTAL

Mechanical mixtures of catalysts, NTK-10-1 + Ni–Cr oxidic (MC_1), NTK-10-1 + STK (MC_2), and NTK-10-1 + VSb/Al_2O_3 were prepared by stirring the individual catalysts taken in equal quantities, without grinding and pressing. A fraction of 1–2 mm was taken for the experiments.

A spectrokinetic method *in situ* was used to determine the mechanism of the NO_x HC-SCR reaction and the nature of synergism; the method implying that simultaneous measuring of the activity of a catalyst and the spectrum of superficial compounds is performed. The purpose of these measurements is the determination of the part played by the observable superficial complexes in the process under study.

Superficial complexes that are formed in the course of the interaction of reagents and their mixtures with the surface of catalyst samples under steady-state conditions were originally identified in the spectrokinetic study. Meanwhile, the concentrations of the components of the reaction mixture and the temperature for conducting the reaction were varied. The properties of the observable superficial complexes under non-stationary conditions were examined at the second stage. To recognize the part played by superficial complexes in the formation of the reaction products, their reactivity of the superficial complexes and kinetic parameters were determined.

Performing spectrokinetic measurements in a steady-state and non-stationary regimes makes it possible to determine the transformation speed for a superficial complex by means of IR spectroscopy methods and to compare it with the reaction rate.

The experimental procedures are described in detail in [7–11]. Chromatographic analysis of N_2O in reaction products (Porapak N phase) was conducted in special experiments.

RESULTS AND DISCUSSION

STK, Ni–Cr oxidic, and NTK-10-1 industrial catalysts and their mechanical mixtures have been tested in the reaction of selective reduction of nitrogen oxides by propane in excess of O_2. The generated temperature dependences of NO_x conversion are presented in Fig. 1.

For MC_1 mechanical mixture at $T < 400$ °C, the conversion of NO_x represents an additive magnitude of the individual conversion that has been received with the formulation constituents. With further temperature rise, a superadditive increase in the catalytic activity (see Fig. 1, *a*) is evidenced. The analogous phenomenon is observed with MC_2 catalytic system throughout the entire interval of temperatures (see Fig. 1, *b*).

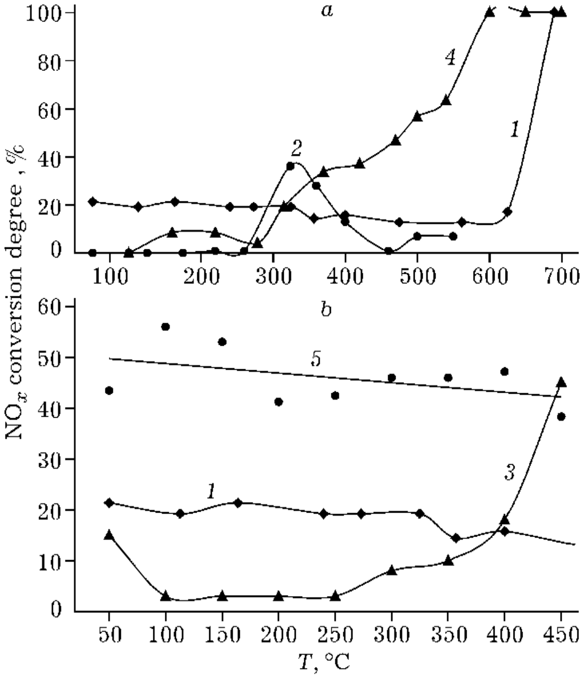

Fig. 1. Temperature dependences of NO_x conversion degree over the NTK-10-1 *(1)*, Ni–Cr oxidic *(2)*, and STK *(3)* catalysts and their MC_1 *(4)* and MC_2 *(5)* mechanical mixtures.

By virtue of the fact that activation of a reducer and oxidizers is essential in oxidation-reduction reactions of the NO_x HC-SCR process, the use of discrete catalytic systems makes it possible to conduct it on spatially separated particles of two different catalysts. The detailed study of the mechanism of selective reduction of NO_x by propane on individual components of mechanical mixtures has made it possible to establish their role in the process.

NTK-10-1 catalyst

Nitrite complexes that desorb at the temperatures of 100–280 °C, nitrate compounds in the field of temperatures of 320–480 °C (on evidence of TPD), nitrite organic compounds, and acetate complexes that form during the adsorption of C_3H_8 are present on the surface of NTK-10-1 catalyst under the conditions of the NO_x SCR reaction by propane.

Quantitative spectrokinetic measurements have demonstrated that when nitrate complex is practically unavailable on the surface, and the temperatures are below 150 °C, the reaction proceeds by consumption of the nitrite complex and the formation of a nitrite-organic compound that yields the reaction products. With an increase of the temperature, the nitrite complex is converted to nitrate one. This process is slowed down in the presence of propane in the gas phase.

At the temperatures above 150 °C, an intermediate nitrate complex is formed at the first stage of the NO_x HC-SCR process and this complex interacts with the acetate complex that has been produced during the activation of propane. Next, the formation of nitrate-organic compound is evidenced that is capable not only to yield reaction products in an oxidizing atmosphere, but also to be additionally oxidized with the release of nitrogen oxides in the gas phase. Nitrogen oxide is not involved in the process of afteroxidation [11].

Consequently, the part of the NTK-10-1 catalyst as a constituent of mechanical mixtures consists in the activation of NO molecules when the reaction of selective reduction of nitrogen oxides is performed by propane in excess of oxygen.

Ni–Cr oxidic and Fe–Cr oxidic (STK) catalysts

STK and Ni–Cr oxidic catalysts that enter into the composition of binary mechanical mixtures (the second common component is NTK-10-1 catalyst) show similar adsorption properties. Nitrite, nitrate, and acetate superficial complexes are formed on these catalysts under the conditions of the reactions. On evidence of NO_x TPD, the desorption temperature of nitrite-nitrate complexes on these catalysts is not higher than 200 °C. Nitrite complexes pass into nitrate ones with an increase in temperature. Individual adsorption of oxygen is insignificant; however, the superficial oxygen centres take part in the formation of complexes of the reagents. Under conditions of the $NO + C_3H_8 + O_2$ reaction, the reduction of the surface of the catalysts occurs at elevated temperatures. Interaction of the mentioned reaction mixture or $C_3H_8 + O_2$ mixture with the surface of the Ni–Cr oxidic catalyst gives rise to a significant amount of H_2 [12]. Complexes that constitute the reaction products of oxidizing dehydrogenation or soft oxidation of propane [13] are present on the STK catalyst.

Nitrite-nitrate and acetate complexes are formed on the surface of Ni–Cr oxidic catalyst at the temperatures lower than 200 °C; no conversion of the initial reagents is observed. The reduction rate of nitrogen oxides on the surface of STK catalyst at low temperatures (lower than ~250 °C) is controlled by the interaction of superficial nitrite-nitrate complexes with the activated hydrocarbon.

The quantity of nitrite-nitrate complexes on STK and Ni–Cr oxidic catalysts quickly decreases with the rise in temperature, and the concentration of acetate complexes increases. Two routes are realized in the field of the temperatures higher than 250 °C. The first one consists in the interaction of acetate complexes with nitrate ones and in the formation of the reaction products. The second is determined by the interaction of NO with the reduced surface of the catalysts. Oxygen atoms reoxidize the surface where CO_2 and H_2O are then formed from the activated hydrocarbon. Nitrogen atoms recombine to form molecular nitrogen.

$$H_2(\text{Ni–Cr-oxidic}) \xrightarrow{\text{Interphase diffusion}} H_2(\text{NTK-10-1})$$

$$\text{I.}\quad NO \xrightarrow{O_2} NO_3^- \xrightarrow{H_2} N_2 + H_2O$$

$$\text{II.}\quad NO \longrightarrow N + O$$

$$N + N \longrightarrow N_2$$

$$O + C_3H_8 \longrightarrow CO_2 + H_2O$$

$$O + H_2 \longrightarrow H_2O$$

Scheme 1. Routes of the reactions on the mechanical mixture of NTK-10-1 and Ni–Cr oxidic catalysts under synergism conditions.

Thus, STK and Ni–Cr oxidic catalysts activate propane as a constituent of the reaction mixture under the conditions of the reaction of selective reduction of nitrogen oxides, and more effective reducing agents are obtained.

Mechanical mixture of catalysts, MC_1

H_2 that originates in C_3H_8 oxidation on the Ni–Cr oxidic catalyst plays the part of an active particle that can be favourable for the emergence of the effect of synergism with the mechanical mixture of NTK-10-1 and Ni–Cr oxidic catalysts. The Ni–Cr oxidic catalyst more effectively reduces nitrogen oxides that are adsorbed on the surface of the NTK-10-1 catalyst (Scheme 1).

Figure 2 presents temperature dependences of NO_x and C_3H_8 conversion degree over the NTK-10-1 catalyst in the reaction mixtures that contain H_2 and in those without it. The influence of hydrogen on the conversion of nitrogen oxides becomes apparent at $T > 350$ °C (see Fig. 2, curves *1, 3*); the NO_x conversion level increases from 20 to 100 % in the presence of H_2. Conversion of C_3H_8 is practically independent from the availability of hydrogen in the reaction mixture (see Fig. 2, curves *2, 4*).

Figure 3 displays dependences of the conversion degree of nitrogen oxides on the concentration of H_2 in the reaction mixture at 400 and 500 °C. It is evident that the NO_x conversion degree increases rather sharply (see Fig. 3, curves *1, 3, 4*) at a certain "threshold" H_2 concentration that depends on the temperature and on the O_2 content of the reaction mixture. The influence of H_2 concentration on the reduction of nitrogen oxides grows with an increase of temperature (see Fig. 3, curves *3, 4*) and with a decrease of O_2 concentration (curves *1, 3*).

The similar effect of an increase in the activity of catalysts in the presence of H_2 has been observed for NO_x HC-SCR reactions [14–17].

The works [14, 15] have examined the part played by H_2 in the reaction of NO_x reduction by various lower hydrocarbons (CH_4, C_2H_4,

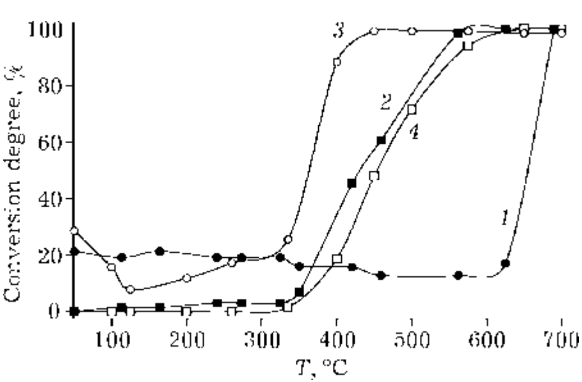

Fig. 2. Dependences of NO_x (*1, 3*) and C_3H_8 (*2, 4*) conversion degree on the temperature during the interaction of mixtures of composition (0.1 % NO + 0.5 % C_3H_8 + 2.5 % O_2)/N_2 with the surface of NTK-10-1 catalyst without H_2 (*1, 2*) and when it is present (*3, 4*).

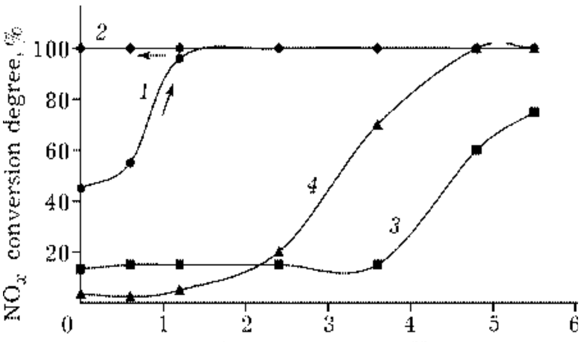

Fig. 3. Dependences of NO_x conversion degree on the H_2 concentration at 400 (*1–3*) and 500 °C (*4*) during the interaction of mixtures of composition (0.1 % NO + 0.5 % C_3H_8 + 2.5 % O_2)/N_2 (*3, 4*) or (0.1 % NO + 0.5 % C_3H_8 + 0.5 % O_2)/N_2 (*1, 2*) and 0–5.5 % H_2 with the surface of NTK-10-1.

C_2H_6, C_3H_6, C_3H_8 and i-C_4H_{10}) on Ag/Al_2O_3. It has been demonstrated that the conversion of NO_x and C_3H_8 considerably increases in H_2-bearing reaction mixtures irrespective of the number of carbon atoms and irrespective of the availability of a double bond in the HC molecule. The authors of [15] believe that high activity of the catalyst in the field of low temperatures in the presence of H_2 is related to an increase of the rates of the formation and consumption of nitrate and acetate superficial compounds. Availability of H_2 accelerates reactions of NO oxidation to NO_2 and C_3H_8 to CO_x [18.]

The analysis of literary data bears witness to the fact that H_2 “keeps” the surface of the catalyst in a reduced state, and both oxygen and nitrogen oxide can dissociate on this surface, which gives rise to highly active oxygen centres. The last-mentioned are involved in an effective activation of both NO with the formation of nitrite-nitrate structures, and HC into acetate superficial complexes.

As we examine the data we obtained from this point of view, we can note that hydrogen has no tangible effect on the concentration of nitrate superficial complexes at low temperatures, and on that of acetate complexes, throughout the entire interval of temperatures on the NTK-10-1 catalyst. The concentration of nitrate structures in the presence of H_2 decreases much quicker with the temperature rise. The data acquired allow a conclusion to be made that one of the routes of the consumption of nitrate complexes on the NTK-10-1 catalyst is their interaction with hydrogen rather than with acetate complexes.

One more, possibly main reason for the H_2 effect on the acceleration of the NO_x SCR process by propane on the NTK-10-1 consists in additional reduction of the surface of the catalyst. The data that are presented in Fig. 3 (curve *2*) bear witness to irreversible changes in the state of the catalyst, since a further decrease of the H_2 concentration in the reaction mixture after its initial puffing onto the surface does not lead to a decrease of NO_x conversion. Results of X-ray phase and X-ray spectral analysis and thermo-programmed reduction (TPR) of the catalyst by hydrogen prove the fact of the reduction of its surface.

An assumption can be made that the reduction of NO_x by hydrogen on the NTK-10-1 catalyst proceeds by the mechanism that is typical for the applied platinum metals [19]. In line with this mechanism, the oxides that are constituents of the catalyst are reduced by hydrogen to form metal, where the processes of NO dissociation and recombination of nitrogen atoms are realized with N_2 evolved in the gas phase, whereas oxygen atoms reoxidize the surface of the catalyst that interacts with hydrogen, and H_2O molecules are produced. No formation of NH_3 and N_2O has been recorded in the reaction products.

Mechanical mixture of catalysts, MC_2

The effect of synergism in the case of a mechanical mixture of STK and NTK-10-1 catalysts is caused by the formation of products of propane partial oxidation and/or oxidizing dehydrogenation on the Fe−Cr-oxidic component, these products being more efficient reducing reagents of NO as compared to propane (Scheme 2).

Oxidation of propane to give products of partial oxidation and/or oxidizing dehydrogenation proceeds on the STK catalyst with the involvement of oxygen of the lattice. The proof for this fact is provided, on the one hand, by the reduction of the sample in the NO + C_3H_8 + O_2 reaction mixture and the observed conversion of propane in a certain time after its puffing onto the STK, and on the other hand, by the emergence of N_2 in the products of NO thermal desorption from the reduced surface of the catalyst.

$$C_nH_mO_z/C_3H_6\ (\mathrm{STK}) \xrightarrow{\text{Interphase diffusion}} C_nH_mO_z/C_3H_6\ (\text{NTK-10-1})$$

$$NO \xrightarrow{O_2} NO_3^- \xrightarrow{C_nH_mO_z/C_3H_6} N_2 + CO_2 + H_2O$$

Scheme 2. Routes of reactions with a mechanical mixture of NTK-10-1 and STK catalysts under conditions of synergism.

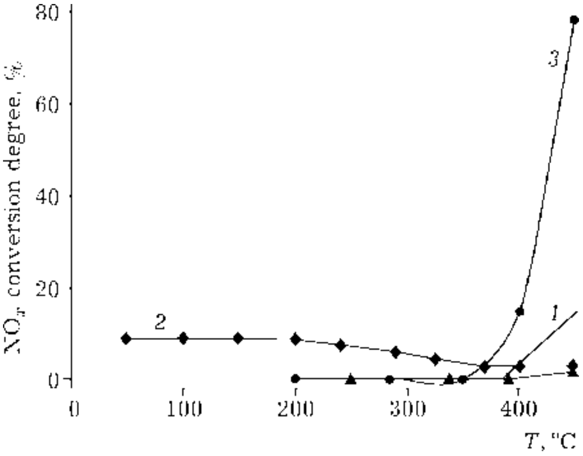

Fig. 4. Temperature functions of the conversion degree of NO_x on VSb/Al_2O_3 (*1*), NTK-10-1 (*2*) catalysts and on their mechanical mixture (*3*) under conditions of the reaction of selective catalytic reduction of NO_x by hydrocarbons for a $(0.1\ NO + 0.9\ C_3H_8 + 2.5\ O_2)/N_2$ mixture.

To provide support to a hypothesis that propylene is one of possible intermediate products of the reaction, experiments have been performed with a mechanical mixture of NTK-10-1 and VSb/Al_2O_3 catalysts. The latter is employed during oxidizing dehydrogenation of propane to form propylene and it shows the greatest efficiency with the ratio $C_3H_8 : O_2 = 3 : 1$ and the temperatures of 450–550 °C.

No conversion of nitrogen oxides in the NO_x SCR reaction by propane is observed on an individual VSb/Al_2O_3 catalyst at the temperatures lower than 450 °C. A mechanical mixture of NTK-10-1 and VSb/Al_2O_3 catalysts also does not show activity at propane concentration of 0.5 vol. % ($C_3H_8 : O_2 = 1 : 5$). However, the conversion level of NO amounts to as much as 80 % with an increase of the volume fraction of propane in the mixture to 0.9 % ($C_3H_8 : O_2 = 1 : 2.8$) at the temperatures above 450 °C (Fig. 4), since the formation of propylene that is an effective reducer of NO occurs on the VSb/Al_2O_3 catalyst, the constituent of the mechanical mixture, under these conditions, propylene being registered chromatographically.

1650 and 1690 m^{-1} absorption bands are observed in the IR spectra that have been measured during the interaction of the $(0.1\ NO + 0.5\ C_3H_8 + 2.5\ O_2)/N_2$ reaction mixture with the STK catalyst and a mechanical mixture of STK and NTK-10-1 catalysts. According to literary data, these bands have been assigned to the vibrations of C=C and C=O bonds in a superficial complex of acrolein [20]. By virtue of the fact that this product is not observed in a chromatographic analysis, an assumption can be made that its concentration in the gas phase is insignificant because of the reactivity.

Thus, the cause of synergism is an interaction of C_3H_8 and O_2 with the formation of a product of partial oxidation (acrolein) and/or oxidizing dehydrogenation of propane (propylene) on the surface of a component (STK) of MC_2 binary mechanical mixture of catalysts and a transfer onto another component (NTK-10-1), the surface of which is filled by adsorbed molecules of NO, due to the interphase diffusion of this product, the effective reducing reagent. Nitrite-nitrate complexes and the products of oxidizing activation of propane interact among themselves with the formation of N_2 and CO_2.

Additional proofs of this mechanism have been received in a series of experiments that have been made during a layer-by-layer loading of NTK-10-1 and STK catalysts into a reactor. If an NTK-10-1 catalyst bed is loaded first along the course of the gas stream, then the conversion of NO is practically the same as for a mechanical mixture of NTK-10-1 and STK catalysts (79 %). As the order of the layer-by-layer loading is changed (*i.e.* when the STK catalyst is arranged as the first layer along the stream), practically full conversion of NO is evidenced, the high conversion level being also preserved upon the catalysts are separated by a layer of quartz, 5 mm in height. If the STK catalyst, on which products of partial oxidation and/or oxidizing dehydrogenation of propane are formed, is arranged first along the course of the reaction stream during the layer-by-layer loading of catalysts in a reactor, the reaction of selective reduction of NO proceeds more effectively than on a mechanical mixture of these catalysts, when the NTK-10-1 catalyst is loaded as the first layer. After oxidation of the products of partial oxidation and/or oxidizing dehydrogenation of propane by oxygen on both components of the binary STK and NTK-10-1 catalytic system is also possible in the system under study.

CONCLUSIONS

Thus, investigation of the mechanism of the reaction of NO_x SCR by propane on NTK-10-1, STK, and Ni–Cr oxidic industrial catalysts has demonstrated that the reason for the synergism that is observed on their binary mechanical mixtures is oxidizing activation of propane that proceeds on the surface of individual Fe–Cr and Ni–Cr oxidic catalysts with the formation of more efficient reducing agents, namely, hydrogen, propylene, and/or acrolein. These compounds are stable and, due to diffusion through the gas phase, they can be transferred onto another component of the mechanical mixture, specifically, onto Cu–Zn–Al oxidic NTK-10-1 catalyst that is responsible for the activation of molecules of nitrogen oxides. That is the surface of the catalyst where the reaction products are formed.

The obtained experimental data confirm the mechanism of synergetic strengthening of catalysis that is described in the literature in mixtures – remote control. According to this mechanism, activation of a reagent on a component of the mechanical mixture occurs with the formation of an active particle that, upon falling through the gas phase onto an alternative component, interacts more effectively with the components of the reaction mixture adsorbed thereon, and the resulting is that a significant acceleration of the reaction occurs [21].

The described results have provided the basis to create a catalytic neutralizer of automobile exhausts that has passed bench tests on a diesel (ZIL-645) and a carburettor (ZIL-508.10) engine in accordance with the UNECE international rules, as well as life cycle tests on the GAS “Volga” car under the operating regime of the real engine of a batch production with standard hydrocarbon fuel. The catalyst provides a decrease in the content of standardized toxic components by 85–95 % and does not lose the activity after a 20 000 km run.

The developed catalytic systems are also effective in the processes of denitration of gas emissions from thermal power stations and diesel engines that are based on the SCR reaction of nitrogen oxides by HC (propane and methane) to nitrogen. The use of propane or methane as reducers as an alternative for the ammoniac technology that is currently in world practice is much more preferred from the point of view of ecology and safety, since highly toxic compounds (ammonia) entering the atmosphere is ruled out even in the case of disturbance in the operating modes of the gas purifying unit.

Taking into consideration that the developed catalytic systems are prepared around the catalysts that are in commercial production, the given purification technology of gas emissions can be realized in short terms in the fuel-and-power complex and in highway transportation.

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