



CATALYTIC SYSTEMS ON METAL BLOCK CARRIERS FOR NEUTRALIZATION OF EXHAUST GASES OF MOTOR TRANSPORT

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Catalysts on the basis of various metals on metal substrates with the honey comb structure of channels for neutralization of toxic gases of motor transport are prepared. Reaction $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ at a wide variation of conditions of process is studied. Influence of the nature of the zeolites introduced into composition of the washcoat and the promoting additives of transition metals on activity and properties of block catalysts is researched. The activity of Pd-Mo catalyst is increased at modifying of a washcoat by cations Ce^{4+} , Zr^{4+} . Introduction to the washcoat of titanium dioxide considerably increases the degree of reduction of nitrogen oxides with propylene. The Fe-containing catalyst modified by NaY zeolite possesses high activity. Degree of conversion of NO_x in the studied conditions on synthesized one- and two-component systems reached 80.5-100%, hydrocarbons – from 70.0 to 100%.



INTRODUCTION

The leading place in full satisfaction of needs of the population in transportations belongs to the motor transport and by means of that about 70% of all passengers and over 80% of transportation of goods is performed. In comparison with other means of transport, automobile transport is developed with the advancing rates that, in turn, can lead to ecological disasters. At combustion of fuel in cylinders of the engine of the car are produced non-toxic (water vapor, carbon dioxide) and toxic substances, which are the products of incomplete combustion. These harmful substances with atmospheric precipitation fall on the ground and are the sources of pollution of rivers, bodies of water, green spaces and soil. Finally they reach the drinking water, food. Air pollution leads to a slowing of growth, deterioration in the quality of forests and reduce crop yields, disease of

humans and animals, insects and plants, to accelerate of decomposition process of building materials and metal corrosion.¹ Thus, the problems of environment protection against the harmful effects of motor transport requires an immediate solution. Protection of the environment from industrial and transport pollution is constantly increasing demands put forward to improve the methods of preparation and cleaning catalysts for neutralization of gas emissions from harmful impurities.

The level of air pollution of many industrial cities of Kazakhstan exceeds the existing standard limits several times.² Catalytic cleaning of harmful emissions of cars leads to considerable decrease in contents in the atmosphere of toxic substances and is successfully applied in the developed countries of the world. Pollution of the atmosphere by exhaust gases containing nitrogen oxides (NO_x , NO , NO_2) currently constitutes a global problem. Nitrogen oxides are extremely poisonous. By the

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force of impact on the human body they are the most toxic components of exhaust gases, for this reason, neutralization of nitrogen oxides by the catalytic decomposition or reduction becomes particularly important.³⁻⁷ Production and introduction of highly effective catalysts for decrease in toxic gas emissions will allow to improve a condition of the air basin considerably. Catalysts of neutralization of industrial emissions and exhaust gases of internal combustion engines must have high thermal stability, productivity, mechanical durability, poisons resistance, macroporous structure and low cost. As primary catalyst carrier for neutralization of exhaust gases of motor transport and the industry it is possible to use a metal wire, a steel foil, a grid from stainless steel or bronze, the granulouse carrier - in the form of balls or extrudates, the ceramic carrier from a spodumen, oxide or zirconium nitride, *etc.*⁸⁻¹⁰ Not all of them are capable of withstanding loads produced during operation under actual operating conditions, as well as meet the requirements of the catalytic converters. Monolithic ceramic and metallic blocks - the most suitable substrates of the catalysts used for the solution of environmental problems.¹¹⁻¹³ The task of creating catalysts for environmental protection includes the development of catalyst mass and technology of its supporting on the monolithic honeycomb contactors. Implementation of this research topic is connected with need of the solution of questions of ecological safety and protection of bioresources.

The work purpose is the synthesis of catalysts on the basis of various metals on metal substrates with cellular structure of channels for neutralization of toxic gases of motor transport. Studying of influence of the nature of washcoats on activity and properties of block catalysts in the reaction $\text{NO}_x + \text{C}_3\text{H}_6 + \text{O}_2$.

RESULTS AND DISCUSSION

Comparison of Pd-Mo-catalysts on the Al_2O_3 washcoat modified by additives of oxides of cerium, lanthanum, zirconium, iron and titanium (Tab.1) on the block metal substrate shows that the composition of the washcoat has effect on catalytic properties of the supported active agent. In case of Pd-based catalysts the most active compositions were - $\text{PdMo}/\text{Al}_2\text{O}_3+\text{ZrO}_2$, at 623 K - 58% NO_x -conversion degree ($\alpha\text{-NO}_x$) and at 673 K - 52.0%. Less impact on the activity of the additive have the additives of La^{3+} and Fe^{3+} , at 623 K $\alpha\text{-NO}_x$ on the catalysts with the such additives were equal to 17.0% and 26.0%, respectively.

Increase of activity of Pd-Mo catalysts in reaction of $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ as a result of modifying of the carrier can be explained, possibly, with influence of acid superficial OH centers. Supported catalysts based on H^+ form NaY zeolite and ZSM-5 were more active in the reaction of reduction of nitrogen oxide with propylene than at the support based on Al_2O_3 . Thus, $\alpha\text{-NO}_x$ on the catalyst Pt-Cu/HY at 573 K was 25%, at 673 K - 68%, on Pt-Cu/HZSM-5 at the same temperatures and was equal to 32.0 and 70.5%. It was revealed 100% $\alpha\text{-NO}_x$ for catalytic systems PtCu/HY and PtCu/ZSM at 773 K. In case of the catalyst on the basis of FeMn applied on alumina the positive effect of addition of titanium dioxide to alumina in the researched interval of temperatures is noticed. So at temperature 573 K $\alpha\text{-NO}_x$ from 5.0% (for $\text{FeMn}/\text{Al}_2\text{O}_3$) increased to 29.0% ($\text{FeMn}/\text{Al}_2\text{O}_3+\text{TiO}_2$).

A series of oxide catalysts on the block substrate differing with the composition of the washcoat ($\gamma\text{-Al}_2\text{O}_3, \gamma\text{-Al}_2\text{O}_3+\text{TiO}_2$) and the composition of the active substance (Co, Co+Mn, Fe+Mn), promoted and not promoted by platinum is studied. It is found that introduction into the washcoat of titanium dioxide considerably increases extent of reduction of nitrogen oxides by means of propylene on both compositions of oxide catalysts in all interval of the studied temperatures (573-773 K) and was equal to 34% at 573 K on the Co-Mn/ $\text{Al}_2\text{O}_3+\text{TiO}_2$ -catalyst, to 29% -on Fe-Mn/ $\text{Al}_2\text{O}_3+\text{TiO}_2$, and at 773 K -33% and 55%, respectively. Promotion with platinum improves the reduction ability of cobalt-manganese catalyst on Al_2O_3 only at temperatures higher than 673 K. On the titanium-containing sample in the presence of platinum degree of NO conversion was decreased.

The prepared nickel and iron-containing catalysts were tested in the reaction of oxidation of hydrocarbons and reduction of nitrogen oxide (Table 2). Irrespective of the nature of the entered zeolite, noticeable transformation of NO began at a temperature over 473 K, gradually increased with growth of temperature and reached the largest value at T=773 K. In case of the Fe-containing block catalysts the greatest activity at reduction of NO by propylene the catalyst modified by NaY zeolite possesses. The catalyst with the same content was the most active and at oxidation of C_3H_6 . At 473 K degree of C_3H_6 conversion with this catalyst is 35.8% and the complete conversion is observed at 573 K. The degree of conversion of C_3H_6 at 573 K on the catalysts of this series is decreased in the series: $\text{Fe}/\text{NaY} > \text{Fe}/\text{ZSM-5} > \text{Fe}/\text{Al}_2\text{O}_3$.

Table 1

Influence of the nature and composition of the secondary carrier of metal block on activity of oxide systems in reaction $\text{NO}_x + \text{C}_3\text{H}_6 + \text{O}_2$ ($0.05\text{NO}_x + 0.05\text{C}_3\text{H}_6 + \text{O}_2 + \text{Ar}$; $V=24,000 \text{ h}^{-1}$)

Catalyst	O ₂ content, vol. %	NO _x conversion, % at the different temperatures, K				
		573	623	673	723	773
Pd-Mo/Al ₂ O ₃	10.0	20.0	10.0	11.0	10.0	5.0-8.0
PdMo/Al ₂ O ₃ +CeO ₂	10.0	19.4	40.0	32.0	12.0	14.0
PdMo/Al ₂ O ₃ +ZrO ₂	10.0	22.5	58.0	52.0	34.0	8.4
PdMo/Al ₂ O ₃ +La ₂ O ₃	10.0	18.0	38.0	17.0	14.0	-
PdMo/Fe ₂ O ₃	10.0	10.0	18.0	26.0	20.0	10.0
PdMo/TiO ₂	10.0	10.0	15.0	30.0	39.0	50.0
PtCu/NaY	5.0	3.0	10.0	21.0	25.0	40.0
PtCu/HY	5.0	18.5	25.6	52.0	68.0	100
PtCu/ZSM	5.0	4.5	15.6	44.0	69.0	100
PtCu/HZSM	5.0	10.2	32.0	53.0	70.5	-
FeMn/Al ₂ O ₃	7.5	5.0	13.0	16.0	24.0	39.0
FeMn/Al ₂ O ₃ +TiO ₂	7.5	29.0	31.0	36.0	49.0	55.0
CoMn/Al ₂ O ₃	7.5	15.0	36.0	18.0	29.6	-
CoMn/Al ₂ O ₃ +TiO ₂	7.5	34.0	22.0	28.0	41.0	33.8
CoMnPt/Al ₂ O ₃	7.5	5.0	16.0	21.6	33.0	43.0
CoMnPt/Al ₂ O ₃ +TiO ₂	7.5	5.0	12.0	15.0	20.0	8.0

Oxidation of propylene on the Ni-containing zeolites happened, in comparison with the Fe-containing block catalysts, to lower extents of conversion: 100% transformation of C₃H₆ was observed on Ni/HY - sample only at 773 K. Other samples of Ni-based catalysts are less active and the degree of conversion of C₃H₆ on them is little varied depending on the nature of the zeolite.

Depending on the nature of the modifying activity zeolite Ni-containing zeolite in the NO reduction reaction at 573 K was decreased in the series: Ni/HY>Ni/NaY>Ni/ZSM-5.

From the two-component systems in the reduction reaction of nitric oxide with propylene in

the presence of oxygen are studied Ni+Pt, Fe+Pt-catalyst (Table 2). For Ni + Pt/HY catalyst the maximum degree of NO conversion is achieved at 673 K, for the sample with addition of NaY a complete conversion of NO is observed only at 773 K. During the oxidation of propylene all Ni-Pt catalysts showed a high activity (100 % at 673 K). In the case of Fe+Pt-catalyst the zeolite additives do not significantly affect the activity of the catalysts in the reduction reaction of NO, and in the oxidation of propylene. In the oxidation reaction of propylene, the catalysts of this series demonstrate low activity.

Table 2

Influence of the promoting additives on the extent of reduction of nitrogen oxide with propylene in the presence of oxygen (350-600 ppm)
Volume speed – $25 \cdot 10^3 \text{ h}^{-1}$, NO concentration -220-400 ppm, C₃H₆ concentration -500-700 ppm

Catalyst	O ₂ Contents, vol.	Degree of transformation at different temperatures, K							Concentration of CO, ppm at different temperatures, K			
		NO, %				C ₃ H ₆ , %						
		473	573	673	773	473	573	673	773	473	573	673
Fe/Al ₂ O ₃	1.0	11.4	18.6	58.1	100	36.0	54.0	73.0	100	0.01	0.00	0.00
	3.0	2.0	19.5	24.7	19.0	2.0	12.0	100	100	0.2	0.01	0.00
	5.0	2.0	10.0	16.6	23.8	10.0	20.0	100	100	0.2	0.01	0.00
Fe/ZSM-5	3.0	3.0	5.7	12.8	18.5	15.0	14.5	100	100	0.03	0.02	0.01
	5.0	0.0	5.0	14.0	13.6	20.0	41.0	100	100	0.02	0.02	0.01
Fe/NaY	3.0	10.0	27.9	59.3	57.3	35.8	100	100	100	0.03	0.02	0.01
Ni/NaY	3.0	15.7	28.7	100	100	20.0	62.0	67.0	70.0	0.03	0.04	0.09
Ni+Pt/NaY	5.0	0	19.2	72.5	100	14.0	54.0	59.7	66	0.05	0.11	0.18
	10	-	10.2	25.0	100	-	100	100	100	0.01	0.01	0.00
Ni/HY	3.0	16.5	58.1	100	100	40.5	70.3	89.2	100	0.01	0.04	0.02
Ni+Pt/HY	5.0	-	27.8	100	100	25.0	40.6	100	100	0.00	0.01	0.00
Ni/ZSM-5	3.0	0	9.2	30.0	100	42.0	50.8	66.6	70.0	0.04	0.06	0.09
Ni+Pt/ZSM-5	3.0	-	32.4	100	80.5	-	100	100	100	-	-	-
Fe+Pt/NaY	3.0	3.5	22.0	32.1	37.6	20.0	66.1	98	100	0.01	0.00	0.00
Fe+Pt/ZSM-5	3.0	0	17.3	30.0	100	-	49.2	68	88	0.01	0.01	0.00

The prepared nickels and iron-containing zeolite block catalysts had been investigated on thermal stability at T=973 K during 50 h in working gas environment. On the Fe-containing catalyst insignificant decrease of the activity is observed at low temperatures (473 K). The most stable over the entire temperature range is proved to be Ni/HY catalyst at 673 K NO-67.0%.

According electron microscopy and XPS in the initial monodisperse platinum and palladium catalysts are in an oxidized state. EM-data showed that in a sample with Pt the small congestions of dense particles which don't grow together in units and are dispersed on a carrier surface are observed and there are some isolated dense particles (Fig.1).

It was found by XRD, that the oxide catalysts represented spinel with cubic lattice NiMnO_4 with peaks 2 \AA , 52 \AA , 148 \AA , 203 \AA . Also there were

small intensive peaks of CeO_2 (308 \AA) and alumina (160 \AA , 256 \AA). The conducted research of supports and catalysts by means of XRA showed the formation TiO_2 - anatase structure, peaks 3.52; 1.89; 2.38 \AA .

At a diffractogram of catalysts on the basis of a cobalt there are diffraction peaks which are correspond to oxide of a cobalt of structure of a spinel Co_3O_4 (CoCo_2O_4): $2\theta = 31.35; 36.90; 44.90; 59.40; 55.90$. For samples of Pd-Mo catalysts (Fig. 2) there are found Al_2O_3 peaks (25.5, 35.0, 37.8, 43.4, 52.9). It was found that a position of a peak of PdO (it should be at approx. 33.9-34.1) is insignificantly moved to the left, it is apparently due to slight interaction between Mo and Pd. Data XRD don't confirm formation of solid solution or alloy of Pd-Mo.

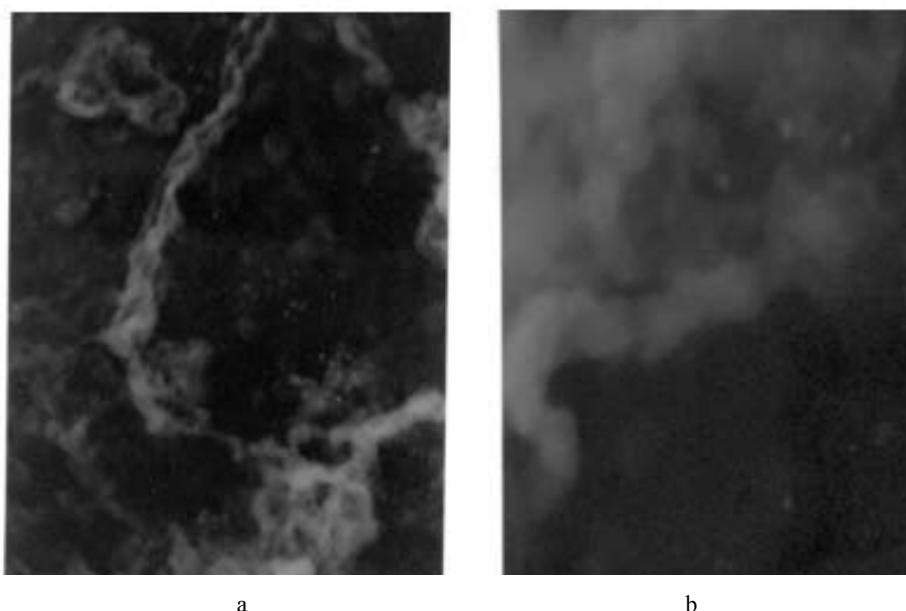


Fig. 1 – the EM - pictures (an increase in 160,000) for catalysts based on noble metals:
a – distribution of Pt on a metal block carrier, b – distribution of Pd to the metal block carrier.

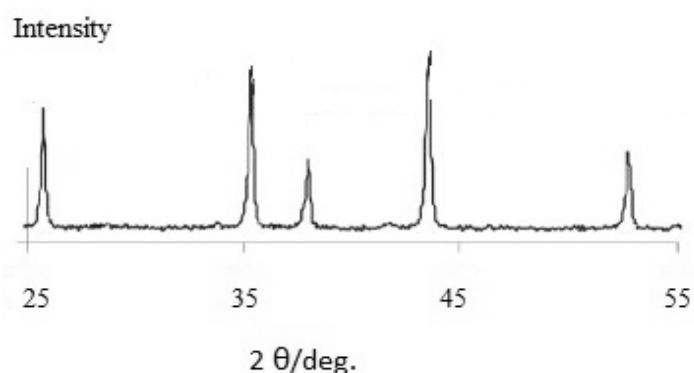
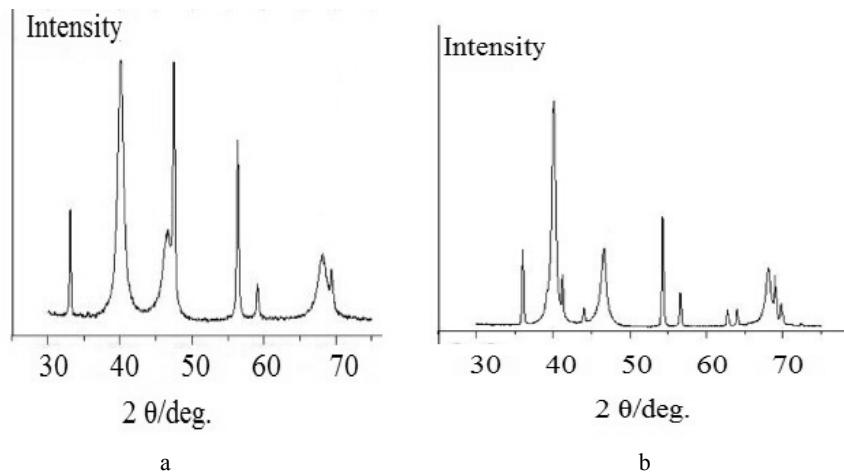


Fig. 2 – XRD image of $\text{Pd-Mo/Al}_2\text{O}_3$ catalyst (after calcination).

Fig. 3 – XRD images of Pd-based catalysts on: a-CeO₂, b-TiO₂.

In case of catalysts on Pd-based catalysts, supported on different washcoats (Fig. 3), it is found (111) peak of Pd (40 20), there are also peaks of Pd 46.5 (plane 200) and 68.2 (plane 220). Results of XRD show that there are clear particles of Pd (Fig. 4).

The TPD method of ammonia has investigated some samples of catalysts on the basis of base metals. The acid centers of the carrier and oxide catalyst are defined.

One - and two-component systems on the basis of Fe and Ni are studied. It was shown by the method of the thermoproduced desorption of ammonia (TPD) that at temperatures up to 523 K ammonia is desorbed from the weak acid sites, in

the range of 523-723 K - from the centres of moderate strength, at temperatures over 723 K - from the strong acid sites.

Characteristic of acid properties of the washcoat γ -Al₂O₃/10%CeO; 5% Co and 5% Co-Mn catalysts is presented in Table 3. As seen from the table, the introduction to the carrier of oxides of cobalt and manganese leads to a small increase in the share of ammonia retentated volume, i.e. strength of the acid centers of the catalyst increases slightly. Apparently, activity of the oxide catalyst is influenced by the structural changes arising at introduction into the washcoat of oxides of cobalt and manganese.

Table 3

The characteristic of acid properties of the washcoat and catalysts determined by ammonia thermal desorption

Sample	Ammonia thermo desorption, mmol/g, % at the different temperature, K				Ammonia adsorption, mmol/g, %
	373	473	573	673	
γ -Al ₂ O ₃ /10%CeO	0.377 61.7	0.128 20.94	0.060 9.84	0.046 7.52	0.611 100
5%Co γ -Al ₂ O ₃ /10%CeO	0.413 65.1	0.092 14.5	0.068 10.72	0.061 9.68	0.634 100
5%Co-Mn γ -Al ₂ O ₃ /10%CeO	0.380 65.0	0.083 14.14	0.062 10.60	0.060 10.26	0.634 100

Table 4

The porous structure and acid properties of the Pt- и Pd-catalysts

Sample of catalyst	Characteristic of the porous structure		Summarized concentration of the acid centres accordingly NH ₃ adsorption, μmol/g
	Specific surface, m ² /g	Volume of the pores, cm ³ /g	
Pt/Al ₂ O ₃	200	0.348	240
Pd/ Al ₂ O ₃	205	0.356	110
Pd/Ni-Mn/Al ₂ O ₃	350	0.274	620
Pt/ Ni-Mn/Al ₂ O ₃	370	0.290	660

Also during the acid properties of the prepared platinum and palladium catalysts were studied with use of a method of TPD of ammonia. Catalysts on basis Pt/Ni-Mn/Al₂O₃ are characterized by the greatest concentration of the strong acid centers (280 μmol/g), at Pd/Ni-Mn/Al₂O₃ catalyst the greatest concentration of the weak acid centers - 250 μmol/g. In Table 4 the characteristics of catalysts on base of Pt and Pd received with use of method TPD NH₃ were resulted. The total concentration of acid sites Pt- and Pd-promoted catalysts of nickel and manganese oxides, higher than that in the initial alumino-platinum and palladium catalysts.

Thus, Pt-and Pd-containing catalysts at close values of the total concentration of the acid centers 660-620 μmol/g are characterized by a distinguished ratio of the centers of different force, that, apparently, determines distinctions in their catalytic properties.

EXPERIMENTAL

In the work were synthesized one and two-component catalytic systems on metal block substrates with honeycomb structure of the channel (Fig. 4) by the technique developed earlier by the authors of the manuscript.¹⁴⁻¹⁸

As inert substrate the tape from a steel foil (goffered and folded into the block) the H23Yu5, H15Yu5 brands containing about 5% of aluminum is used. The foil is subjected to a heat treatment at a temperature 1123-1193 K in air or oxygen during 12-15 h. As the washcoats were used oxide of aluminum of the brand A-1 and NaY (with the module 5.1) and ZSM-5 (with the module 30) zeolites. One - and two-component systems on the basis of Pd, Pt, Cu, Mo, Co, Fe and Ni were prepared. As a binder was used the wet hydrogel of aluminum hydroxide with the humidity 80.0 %. Drawing of an active component was carried out with use of a method of impregnation on a moisture capacity. Adding the modifying cations of Ce, Zr, La, Fe, Ti was carried out by method of impregnation of alumina with the solutions of nitrates of salts of the corresponding metals with the subsequent drying and calcinating of the block with the put washcoat at 773-873 K.

Preparation of a washcoat suspension is controlled by three parameters of pH, viscosity and solids content. The metal block substrates are completely immersed in suspension before the termination of the air bubbles allocation, then they

are placed in a centrifuge, where the surpluses of suspension are removed. The block substrates impregnated with suspension are placed in an electric furnace for 2 h. drying are heated to 423 K. Then the furnace temperature is increased to 873 K, is maintained for 4 h., and there is a decomposition of salts included in the slurry and the formation of the required structure of alumina. The quantity of the washcoat is controlled by a weight method, if necessary the process of the washcoat deposition is repeated. Concentration of the applied metal was determined by a difference of mass of the block before and after applying.

The quantity of the modifying additives was equal to 3.0% in relation to washcoats weight (for example, Al₂O₃). The washcoats were supported on a surface of the metal block, using alumina binder. The hydrogen form of zeolites were obtained by their repeated processing with NH₄Cl solution followed by washing from the chlorine ions, drying at 373-493 K, and calcining at 773 K.

Pt-nanosized particles are synthesized by reduction with hydrogen in an aqueous solution containing chloroplatinic acid and citric acid. As the stabilizer, of colloid platinum particles was used isopropyl alcohol. The metal sols supported on the block substrates were dried in an oven for 4 h. at a temperature of 423 K.

Then the catalysts were calcined in a muffle furnace at 773 K for 2 h. Also at synthesis of catalysts on the basis of platinum and palladium as the active components of catalysts Pt and Pd acetates and their π-complexes were used. The solutions of palladium acetate were prepared by dissolution of Pd in acetic acid containing 3% HNO₃. Nitric acid was removed in the course of evaporation before the complete cessation of selection of nitrogen oxides. π-complexes of Pd and Pt were prepared by reacting of allyl alcohol with the salts of these metals. For increase of thermal stability the catalysts were modified by additives of the second metal and oxides of refractory metals.

The samples of catalysts have the cylindrical shape, which is suitable for placement directly to the source of the toxic emissions. High durability of metal and high machinability give the chance to make substrate walls rather thin that as a result provides total significant increase in the geometrical area of a metal substrate.

Reaction NO+C₃H₆+O₂ at a wide variation of conditions of process is studied. Catalytic activity of samples was characterized by extent of conversion of NO_x (α-NO_x). Reaction was carried out in the flowing differential reactor under following conditions: reactionary mix (% vol.): 0.05-0.08 NO+0.05C₃H₆ + 5.0 or 10.0 O₂ + argon (nitrogen); volumetric flow rate is 24, 000 h⁻¹. O₂ content of the gas mixture is changed in accordance with the conclusions of earlier studies.¹⁹ For investigation activity of catalysts the flowing installation with a tubular reactor of integrated type was used.^{15, 16}

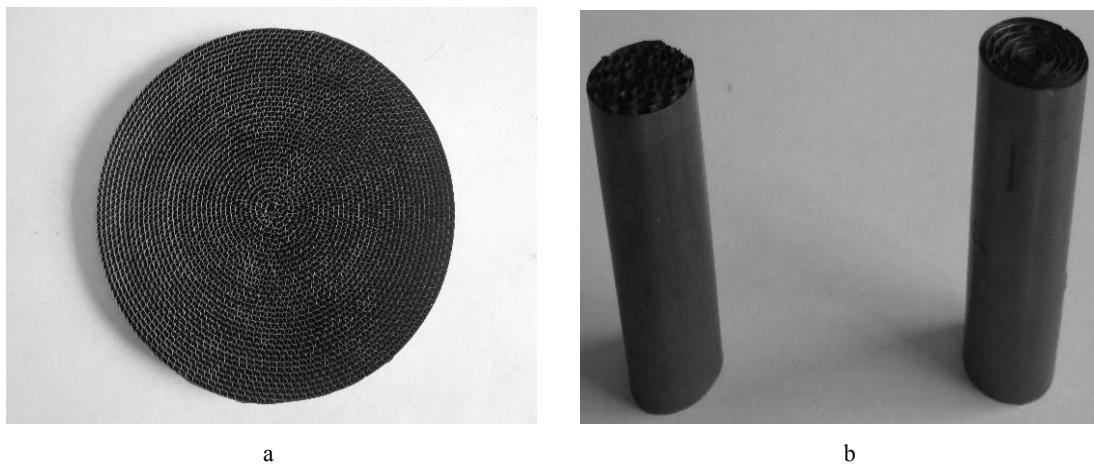


Fig. 4 – The metal block substrates: a – cross-section, b – a general view.

The gas mixture was analyzed by GLC and gas analyzer (OPTOGAZ, GIAM-29M) before and after the reaction. The chromatographs "Crystal 2000M" and Chrom 3700 with a flame ionization detector were used. Time of analysis-20-30 min. Before testing, the catalyst sample was kept in the reactor for 30 min. in the flow of the reaction mixture at 773 K. Thereafter, the gas temperature was lowered to given values, and was determined the conversion of CO, NO and hydrocarbons.

The samples of catalysts based on platinum group metals and base metals were investigated by electron microscope EM-125K with single stage replica method. Acid properties of initial zeolites and catalysts on their basis studied with use of a method of the thermoproduced desorption of ammonia (TPD).

Physical and chemical researches of catalysts on the basis of base metals were carried out by XRD method on x-ray diffractometer DRON-4.0.7 with the copper anode. Samples for research were prepared by mechanical destruction of the catalyst put on a block metal framework. The fallen part of the catalyst was crushed in an agate mortar up to 100 microns and was used for research by method XRA. Identification of microdiffraction patterns was performed with use of ASTM cart index (1986).

CONCLUSIONS

One- and two-component catalytic systems on the basis of various metals on metal substrates with the honey comb structure of channels are prepared and tested in the processes of neutralization of toxic gases of motor transport. Influence of the nature of the zeolites added to composition of the washcoats and the promoting additives of transition

metals on activity and properties of block catalysts in reaction $\text{NO}_x + \text{C}_3\text{H}_6 + \text{O}_2$ is studied. Degree of conversion of NO_x in the studied conditions on synthesized one - and two-component systems reached 80.5-100%, hydrocarbons - from 70.0 to 100%. Catalysts are investigated by a complex of physical and chemical methods of research. Acid properties of initial zeolites and catalysts on their basis are defined.

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