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# Development of technology of synthesis of catalysts for neutralization of emissions of the industry and motor transport

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In the research the technology of preparation of catalysts on block metal carriers was worked out and perfected. As the secondary carrier was used alumina with an additive of zeolite or $Ce^{4+}$, $Ti^{4+}$, $Zr^{4+}$, $La^{3+}$, $Fe^{3+}$. The active phase based on compounds Mn, Ni, Co, Fe and the platinum group metals converted into colloidal state was used. The catalysts were tested in the reactions of the complete oxidation of $NO_x$, CO, $C_3H_8$ and $NOx+C_3H_6+O_2$ reaction. The activity of Pd-Mo catalyst increases when carrier modifying with cations $Ce^{4+}$, $Zr^{4+}$. The activity of a palladium catalyst in oxidation reactions CO - 90-100% and is independent of the concentration of metal, in complete oxidation of $C_3H_8$ at 473-623 K - 78-90%, for Pt - catalyst - 95-100%. For catalysts based on base metals introducing into the secondary carrier of $Ti^{4+}$ significantly increases the degree of reduction of nitrogen oxides with propylene, at 523 K on a Co-Mn-catalyst - 34%, on Fe-Mn - 29%, at 773 K - 33% and 55%, respectively.

**Key words:** catalyst, toxic gases, motor transport, industry, block carriers

## INTRODUCTION

Carbon monoxide, nitrogen oxides, unburned hydrocarbons, and soot are the major toxic components of exhaust gases of industrial enterprises and released during operation of the engine of internal combustion wastes. Decrease of harmful emissions of motor transport and industry to international standards currently is possible only with catalytic methods, which are the most effective means of cleaning [1-5].

As the catalysts of CO and hydrocarbons oxidation and decomposition of nitrogen oxides are used mainly noble metals on carriers having a high catalytic activity and heat resistance to poisons. Complete removal of toxic gases and poisons in the presence of an effective catalyst is possible at the optimum ratio of oxidizing and reducing agents. For the first time monolithic blocks have been used in the end of '60s as the carriers post-combustion catalysts in non-road means of transport, i.e. in mining equipment in a fork lift truck, etc. Later so-called three-route catalysts (TRC) for reduction of $NO_x$ in exhaust gases have been offered. The greatest distribution was gained by catalysts on metal and ceramic carriers of honey comb and cellular structure with an intermediate layer from $\gamma$-$Al_2O_3$ and an active catalytic covering, as a rule, from noble metals (Pt, Pd, Rh) [6,7]. However, the high cost of these metals and their low resistance to poisons stimulate carrying out of scientific research directed at creation of more optimal from an economic and technological point of view, the compositions and methods of catalytic neutralizers preparation. One of the perspective directions in this area - the partial replacement of noble metal on the oxide components [8-10]. Performance of this subject of researches is caused by need of the solution of questions of ecological safety of Kazakhstan and protection of bioresources. The development of effective catalysts of neutralization of harmful emissions of the transport and industrial enterprises is one of the most important ways to reduce emissions of substances that negatively affect the living organism and flora.

The purpose of the work is development of technology of production of the laboratory and full-size samples of catalysts on the block metal carriers and test their efficiency in the processes of neutralization of toxic emissions of the industry and motor transport.

## EXPERIMENTAL

Authors of the present manuscript for many years carry out the researches on synthesis of high-selective stable catalysts of cleaning of exhaust gases of motor transport and harmful emissions of the industry on the basis of monolithic metal block catalysts [11-13]. There is a pilot plant, where all the technological parameters of preparation of neutralizers, as well as technical documentation for the production of neutralizers and drawings on the non-standard equipment have been worked out. The designed monolithic block catalysts with the honey comb structure of channels, developed surface, high thermal and mechanical stability, low pressure

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difference maintain high efficiency of cleaning of exhaust gases from CO, hydrocarbons, nitrogen oxides and correspond to the EURO-3 standard. Degree of cleaning of exhaust gases of cars running on gasoline is equal to: CO-$CH_x$-90-100%, $NO_x$- 80-100%. Block catalysts have a cylindrical shape and are convenient in placing at the source of toxic emissions. High durability of metal and high workability give the chance to make carrier walls rather thin that as a result provides the general significant increase in the geometrical area of a metal substrate. These factors reduce the total catalyst weight by one third in comparison with the neutralizer on the basis of the ceramic at preservation of catalytic effect. Due to the small thickness of the substrate structure may be configured in such a way that the effective cross-section may be significantly higher than when using a ceramic material: at the same time is achieved and the significant decrease of the hydraulic resistance. For preparation of the block carrier the heat-resistant foil with 50 microns thick of need length and width is cut. Then the foil is subjected to goffering, on a smooth foil the corrugated tape is applied then they are rolled into the cylindrical block. The secondary carrier (washcoat) is applied on the prepared block metal carriers with the honey comb structure of channels. In Figures 1 and 2 are shown the laboratory and full-size samples of neutralizers, respectively.

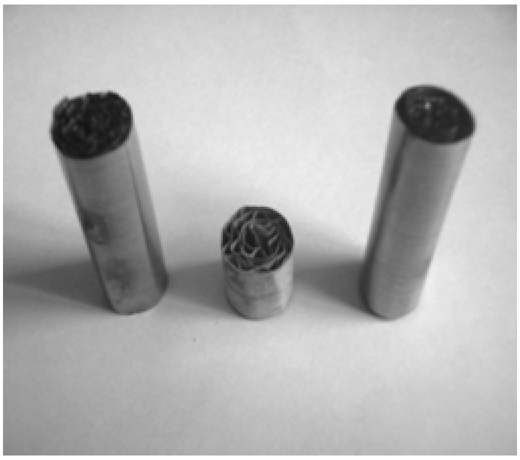


**Fig. 1.** Laboratory samples of neutralizers on metal blocks

Preparation of full-metal catalysts on the block carriers is carried out on the pilot experimental basis. Equipment for the preparation of full-size catalysts on metal carriers on the basis of experimental development is shown on Figures 3, 4. As a secondary carrier is used alumina with the addition of zeolite and alumina modified by additives $Ce^{4+}$, $Ti^{4+}$, $Zr^{4+}$, $La^{3+}$, $Fe^{3+}$. For the preparation of solutions of the active components of the catalysts were applied oxides of Mn, Ni, Co, Fe, prepared from acetates and formates.

**Fig.2.** Full-size catalytic neutralizers on block metal carriers

**Fig. 3.** Centrifuge for impregnating metal on the block carrier

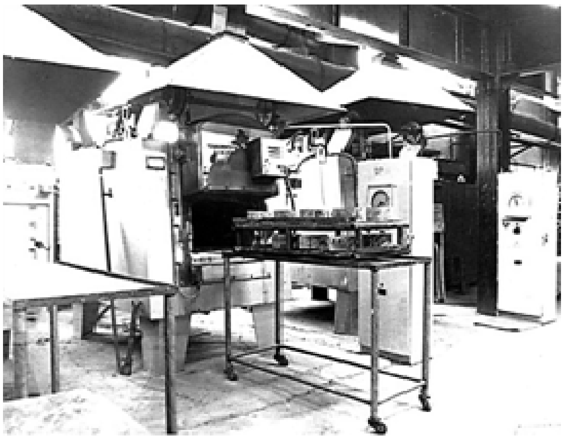


**Fig.4.** The kilns for the full-size metal catalysts

The previously weighed blocks were immersed in a solution of acetate or formate of metal were shaken slightly from the excess solution between the blocks of channels, then were dried at 423 K for 2 hours in a kiln, after which they were calcined in an electric furnace at 873 K for 2 hours. In this case metal salts are decomposed to form metal oxides on the surface of the carrier the block. The blocks were weighed again and by a difference of masses before and after deposition the concentration of the deposited metal was determined. To increase the activity of platinum catalysts in the reactions of oxidation of CO, hydrocarbons and nitrogen oxides decomposition usually platinum metals were transferred to a colloidal state by impregnation of catalysts by the previously prepared solutions of polymers with inclusion of solutions of the deposited metals with the subsequent thermal decomposition. In the work platinum nano-size particles were prepared by reduction with hydrogen in an aqueous solution containing chloroplatinic acid and citric acid. As the stabilizer of colloid platinum particles is used isopropyl alcohol. The obtained colloidal platinum metal by such methods is coated on carrier block. Block carriers supported on metal sols were dried in the furnace for 4 hours at a temperature of 423 K. The catalysts were calcined in a muffle furnace at 773 K for 2 hours. Also in the synthesis of catalysts based on platinum and palladium as active components of catalysts acetates of Pt and Pd and their π-complexes are used. Solutions of acetate of palladium were prepared by dissolution of Pd in the acetic acid containing 3% of $HNO_3$. Nitric acid was removed in the course of evaporation before complete cessation of release of nitrogen oxides. π-complexes of Pd and Pt were prepared by reacting of allyl alcohol with the salts of these metals with subsequent drying of the catalysts at 423 K and calcination at T = 773 K for 2 hours. For increase of thermal stability catalysts were modified with additives of the second metal and oxides of refractory metals. For test of catalysts the flowing catalytic installation with the tubular reactor of integrated type was used [14, 15]. The gas mixture was prepared by feeding of hydrocarbons from container and the compressed air from the line into the mixer. The hydrocarbon content of the mixture was about 0.5. %. The oxygen concentration was varied from 2 to 10 vol. %. The gas mixture was analyzed by GLC and OPTOGAZ gas analyzer before and after the reaction. Crystal 2000M and Chrom 3700 chromatographs with the flame ionization detector are used. Time of analysis-20-30 min. For testing was used a sample of the 2 cm$^3$ colloidal catalyst on the metal carrier. Previously the catalyst was calcinated at 773 K within 4 hours on air in the muffle furnace. The activity of the catalysts was determined at temperatures of 423-773 K. When designing the optimal compositions and methods of preparation of colloid metals were varied its dispersion, the active metals content, their relative proportions and a temperature of the preliminary heat treatment.

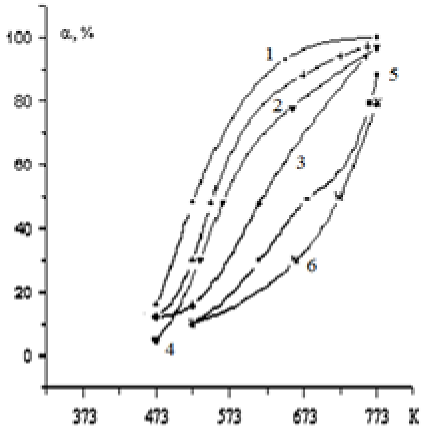
## RESULTS AND DISCUSSIONS

In Table 1 the data by influence of the concentration of the π- allylic complexes of Pt and Pd to activity of the block catalysts in the reaction of CO, $C_3H_8$ oxidation and $NO_x$ reduction are shown. Characteristic of activity of the catalyst was the degree of conversion (α) of initial reagent (hydrocarbon, carbon monoxide, nitric oxide). Apparently from Table, activity of Pd-catalyst in reaction of CO oxidation practically didn't depend on concentration of metal and was about 90-100 % in the investigated interval of temperatures. However, efficiency of Pd-catalyst in reaction of complete oxidation of $C_3H_8$ at low temperatures (623-473 K) was much lower, than that of the Pt-catalyst, and was 78-90 %. The higher activity of the Pt-catalyst in reaction of NO reduction in comparison with Pd the catalyst was observed at contents of Pt equal to 0.1 % and T=773 K.

Research of Pt and Pd catalysts on thermo stability was carried out by maintaining of the catalyst with an interval of 5 hours at T=773 K in a reactionary gas mixture with the contents of 0.5 % of propane-butane with the subsequent analysis of products of reaction. The total time of researches was 100 h. The most stable appeared the catalysts obtained from acetates Pt, less stable - on basis Pd.

**Table 1.** Influence of concentration of π- allylic complexes of Pt and Pd on a degree of conversion of CO, $C_3H_8$,$NO_x$(volumetric speed of a stream of gases- 35000 h$^{-1}$)

| Catalyst | The active metal concentration, % | Conversion degree, % at the different temperatures of research of catalysts, K | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | CO | | | | $C_3H_8$ | | | | $NO_x$ | | | |
| | | 773 | 623 | 523 | 473 | 773 | 623 | 523 | 473 | 773 | 623 | 523 | 473 |
| Pt π-allyl | 0.01 | 100 | 100 | 89 | 16 | 95 | 85 | 50 | 0 | 20 | 20.7 | 13.9 | 0 |
| Pt π-allyl | 0.05 | 100 | 100 | 92 | 50 | 98 | 94 | 73 | 0 | 20.7 | 21.1 | 14.4 | 0 |
| Pt π-allyl | 0.1 | 100 | 100 | 100 | 87 | 100 | 99 | 73 | 17 | 34.2 | 36.7 | 17.1 | 1.2 |
| Pd π-allyl | 0.1 | 100 | 100 | 100 | 83 | 53 | 22 | 5.0 | 0 | 18.4 | 16.8 | 8.0 | 0 |
| Pd π-allyl | 0.15 | 100 | 100 | 100 | 90 | 59 | 32 | 18 | 0 | 24 | 26.6 | 16 | 0.5 |



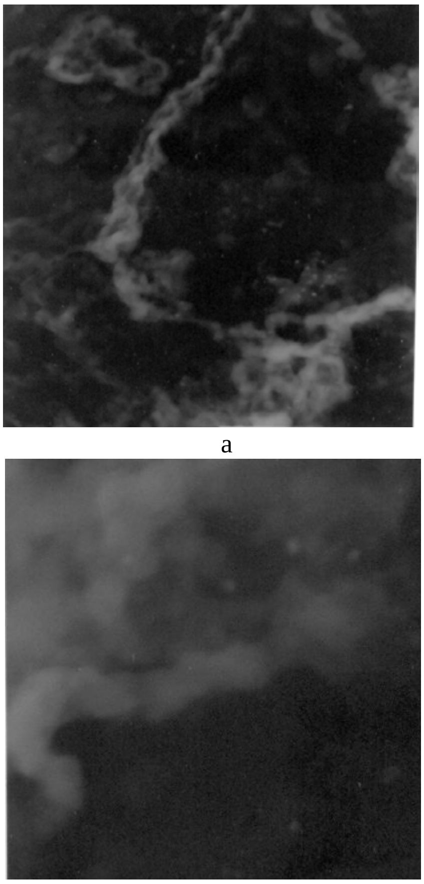
1-0.1% Pt-initial Pt, 2- 0.1% Pt-50 h. of testing, 3-0.1% Pt- 100 h., 4- 0.2% Pd-initial Pd, 5- 0.2% Pd-50 h. of testing , 6- 0.2% Pd-100 h. of testing

**Fig.5.** Dependence of stability of catalysts in reaction of 0.5 % of propane-butane in air oxidation.

Supporting of the secondary oxidic covering on metal blocks of honey comb structure (oxidic washcoat), as a rule, allows to produce carriers with the developed specific surface and porous structure [16, 17]. High thermal stability of the oxidic washcoat is provided with introduction to it of the modifying additives. For example, into the secondary coating alumina are introduced cations of cerium, zirconium, lanthanum, which do not only stabilize $\gamma$-$Al_2O_3$ phase, but also provide resistance to poisons or sintering of Pt, Pd, Rh- active components of the catalysts [18, 19]. In the work metal block Pd-Mo-catalysts on $Al_2O_3$ carrier modified by additives of $Ce^{4+}$, $Ti^{4+}$, $Zr^{4+}$, $La^{3+}$, $Fe^{3+}$ are prepared and investigated in reaction of $NO_x$+$C_3H_6$+$O_2$. Activity of Pd-Mo of catalysts increases when modifying the carrier with cations of $Ce^{4+}$, $Zr^{4+}$. Activity of Pt-Cu catalysts on the zeolite-containing carriers NaY, ZSM-5 and their hydrogen forms is studied. High activity of the catalyst is noticed when supporting of the active phase on the carrier in $H^+$-form. A number of oxidic catalysts with the differing structures of the washcoat ($\gamma$-$Al_2O_3$,$\gamma$-$Al_2O_3$+$TiO_2$) and composition of the active agent (Co+Mn, Fe+Mn) promoted and not promoted by platinum is studied. It is found that introduction into the secondary carrier of titanium dioxide considerably increases extent of reduction of nitrogen oxides by means of propylene on both compositions of oxidic catalysts in all interval of the studied temperatures (423-773 K) and was equal to 34% at 523 K on the Co-Mn-catalyst, to 29% -on Fe-Mn, 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 id decreased.

The samples of catalysts based on platinum group metals were investigated by electron microscope EM-125K with single stage replica method. 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. The particles size is predominantly 10.0 nm, 5.0 nm and less 9.0 nm (Fig.6, a). In the sample with Pd there are some isolated dense particles in size 12.0 nm-15.0 nm (Fig.6, b). The platinum produced by reduction in solution has the sizes about 15.0-18.0 nm, at the same time, the platinum colloid obtained by reduction with lemon acid had almost monodisperse distribution, the average size of particles was equal to 8.0 nm. It is found that the organometallic complexes of Pd and Pt at magnification of 33,000 times represent translucent areas of the clots of polymer filled with dispersed particles of 3.0 nm. At higher magnification (in the 62,000 times) also small rare congestions of more dense particles of 5.0 nm in size are observed.

Investigation of Pt and Pd-containing catalyst by means of XPA showed X-ray scattering, which confirms the high dispersion of catalysts obtained by thermal decomposition of organometallic complexes. 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 XPA. It was found, that the oxide catalysts represented spinel with cubic lattice $NiMnO_4$ with reflexes 2Å, 52Å, 148Å, 203Å. Also there were small intensive reflexes of $CeO_2$ (308Å) and alumina (160Å, 256Å). The conducted research of supports and catalysts by means of XPA showed the formation $TiO_2$- anatase structure, reflexes 3.52; 1.89; 2,38 Å. The carrier based on $V_2O_5$-$WO_3$- peaks 4.38, 3.4, 2.8 Å, it has an orthorhombic lattice. In the active phase NiO-crystal lattice is not formed. Catalysts based on base metals had been investigated with an electron microscope EM-on device 125M single by stage replica method. On a nickel-vanadium-tungsten sample the congestions of dense particles which don't grow together in units and are dispersed on a carrier surface are observed. The sizes of particles were mainly 15.0-20.0 nm.



a

b

**Fig.6.** EM - pictures of distribution of noble metals on the metal carrier: a- Pt on carrier, b-Pd on carrier.

## CONCLUSION

Catalysts for neutralization of toxic gases of the industry and motor transport on metal carriers with the honey comb structure of channels are prepared. As the secondary carrier was used alumina with an additive of zeolite or $Ce^{4+}$, $Ti^{4+}$, $Zr^{4+}$, $La^{3+}$, $Fe^{3+}$. For preparation of solutions of the active components of catalysts are applied oxides of Mn, Ni, Co, Fe, obtained from acetates and formates. Also were synthesized the samples of catalysts based on metals of the platinum group converted into colloidal state. It was shown that the activity of the palladium catalyst does not depend on the metal concentration in the CO oxidation reaction and is about 90-100%. The effectiveness of the Pd-catalyst in the $C_3H_8$ complete oxidation reaction at low temperatures (623-473 K) is significantly lower than of Pt-catalyst, and is 78-90%. For catalysts based on base metals introducing into the secondary carrier of $Ti^{4+}$ significantly increases the degree of reduction of nitrogen oxides with propylene, at 523 K on a Co-Mn-catalyst - 34%, on Fe-Mn - 29%, at 773 K - 33% and 55%, respectively.

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# РАЗРАБОТВАНЕ НА ТЕХНОЛОГИЯ ЗА СИНТЕЗ НА КАТАЛИЗАТОРИ ЗА ОБЕЗВРЕЖДАНЕ НА ЕМИСИИ В ИНДУСТРИЯТА И АВТОТРАНСПОРТА

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(Резюме)

Разработена е и е усъвършенствана технология за приготвяне на катализатори върху блокови метални носители. Като вторичен носител е използван алуминиев оксид с добавки на зеолити или йоните $Ce^{4+}$, $Ti^{4+}$, $Zr^{4+}$, $La^{3+}$, $Fe^{3+}$. Активната фаза се състои от съединения на Mn, Ni, Co, Fe и метали от платиновата група в колоидно състояние. Катализаторите са изпитани за реакциите на пълно окисление на $NO_x$, CO, $C_3H_8$ и $NO_x$+$C_3H_6$+$O_2$. Активността на катализатора Pd-Mo нараства, когато носителят е модифициран с $Ce^{4+}$ или $Zr^{4+}$. Активността на паладиевия катализатор при окислението на CO достига 90-100% и е независима от концентрацията на метала; при пълното окисление на $C_3H_8$ при 473-623 K превръщането е 78-90%, а за платинов катализатор - 95-100%. При катализатори с вторичен носител $Ti^{4+}$ значително се повишава намаляването на азотните окиси с пропилен при 523 K върху катализатор от Co-Mn (34%); при катализатор върху Fe-Mn - 29% при 773 K - 33% и съответно 55%.