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Researching effective catalysts on metal blocks for neutralization of exhaust gases of vehicles

Abstract: Catalysts on metal block carriers were prepared and used in laboratory tests and in the conditions of actual operation. Stability of the carrier and the active phase of the catalysts to poisoning by water vapour was examined. Such poisoning of catalysts promoted with Pt is reversible and the catalysts are again activated by heating at T = 300°C under a stream of dry air for 4 h. The experiments by defining of possibility of interaction of NO with the soot supported on the block catalysts was investigated. Full-size catalyst samples were tested at the diesel engine – generator of Kama Automobile Plant truck running on diesel fuel and at the stand on the basis of diesel generator capacity of 4 Kv. Application the catalytic neutralizer of the fulfilled gases resulted in decrease in harmful emissions in comparison with the engine without neutralizer: in case of Kama Automobile Plant on a mode of the minimal idling (800 rev./min.) efficiency of neutralizer has made on NO_x-59.0 %, C_xH_y-86.0%, CO-99.0%; in case of a stand a degree of cleaning from CO was 100%, hydrocarbons – 99.0%, nitrogen oxides – 61.9%.

Key words: catalyst, exhaust gases, metal block carriers

Introduction

Protection of the environment from industrial and transport pollution poses to humanity demands to improve the synthesis methods of neutralizing catalyst and purification of gas emissions from harmful [1-4]. The most effective means of purifying of the exhaust gases of internal combustion engines of automobiles is a catalytic method [5, 6]. It is possible to use a metal wire, a steel foil, a grid from stainless steel or from bronze, the granulouse carrier – in the form of balls or extrudates, the ceramic carrier from a spodumen, oxide or zirconium nitride, etc. as a primary catalyst carrier for neutralization of exhaust gases of motor transport and the industry. However not all of them are capable to maintain the loadings received in use in actual practice operation (on the car and in the production conditions), and also to correspond requirements imposed to catalytic converters (thermal stability, mechanical strength, gas-dynamic resistance, stable catalytic activity throughout the progressive time of operation). The monolithic ceramic or metallic blocks are the most suitable carriers of the catalysts used for the solution of environmental issues thanks to their principal specifications: to a developed surface, a low pressure drop, high thermal and mechanical stability, ease of an arrangement in the reactor and a possibility of their use as a substrate for a secondary catalyst carrier [7-9]. The development of compositions and methods of catalysts preparation with low content of platinum group metals for complex purification of exhaust gases of motor transport becomes more relevant in the world due to the deteriorating state of the atmosphere, especially in the industrial cities, and the tightening of environmental standards [10, 11].

The work purpose – synthesis of efficient and stable catalysts of neutralization of harmful emissions of the industry and exhaust gases of motor transport on metal block carriers and their testing in the laboratory and in actual application on the diesel engine of Kama Automobile Plant (KamAP) and at the stand on the basis of diesel generator.

Materials and Methods

Preparation of laboratory and full-size examples is carried out by earlier developed technique on the experienced and experimental base where there is a necessary equipment [12]. The primary carrier of catalysts is made of heat-resistant steel foil (corrugated and rolled into a block) brands H23Yu5, H15Yu5 containing about 5% Al, of 50.0 microns thick. The ends of a foil are cut off and welded on the cylindrical block by means of contact welding. The washcoat is a suspension of aluminum salt or of aluminium salt with additives, its quantitative and qualitative compositions are controlled on pH, viscosity and the content of a solid phase. Metal block carriers are completely immersed in suspension till the ending of appearing of air bubbles, then are placed in the centrifuge where surplus of suspension is removed. The promoting metals are applied on the prepared carrier by impregnation from aqueous solutions of salts: cobalt, manganese, nickel, etc. (on a moisture capacity). The active phase based on compounds Mn, Ni, Co, Fe, prepared from acetates and formiates and the platinum group metals converted into colloidal state was used. In fig.1 full-size samples of catalysts for test in the conditions of actual operation are shown.

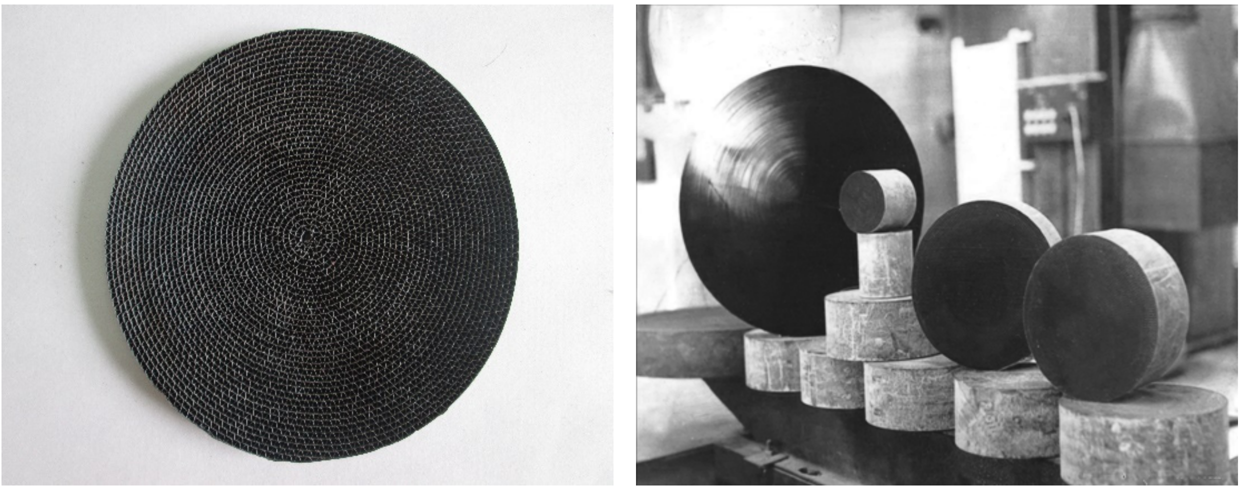

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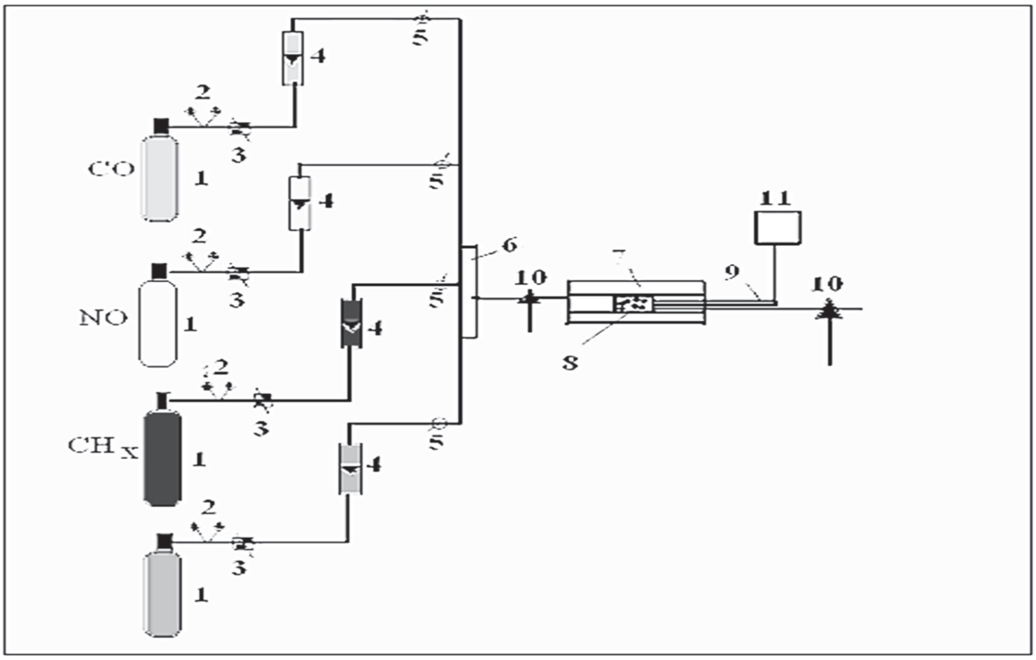
Figure 1 – The full-size samples of catalysts on the metal block: a-cross-section, b-a general view



1 – A gas bag; 2 – Manometer; 3 – Ventile of thin regulation; 4 – Rotameter; 5 – Crane; 6 – Mixer; 7 – Heating system; 8 – Catalyst; 9 – Thermocouple; 10 – Selection of tests before and after the catalyst; 11 – IRT

Figure 2 – Scheme of the flowing installation.

For test of catalysts in the laboratory the flowing catalytic installation with the tubular reactor of integrated type (fig.2) was used.

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 2.0 to 10.0 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. Duration of analysis-20-30 min. Previously the catalyst was calcinated at 500°C within 4 h. on air in the muffle furnace. The activity of the catalysts was determined at temperatures of 150-500°C. 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.

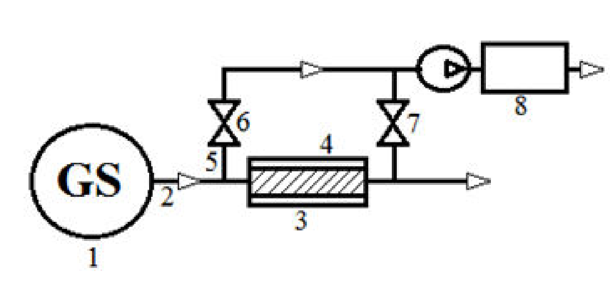
Characteristic of activity of the catalyst was the degree of conversion (α) of initial reagent (hydrocarbon, carbon monoxide, nitric oxide), defined by the formula:

$$\alpha = C\ init.\text{-}Cfin.\cdot Cinit.\cdot 100\ \%,$$

where $C_{init.}$ and $C_{fin.}$ – are the initial and final concentrations of a reagent in volume of a test.

For test the full-size samples of catalysts a stand on the basis of diesel generator (fig.3) was made [13]. As the loading device the rheostats served. Tests before and after the catalyst were selected on all operating modes of the diesel engine (from idle motion up to 4 Kv) directly from an exhaust branch pipe by a gas analyzer «OPTOGAS-500.3». Researches were carried out in a range of loadings from 0 up to 4.0 Kv. The temperature in a zone of work of the catalyst was measured by chromele-alumele thermocouple.

Also as the object of test was served a diesel engine – generator of Kama Automobile Plant (KamAP) of model 820.52-260- is completed with pistons of model 820.52-1004015-40 CB with the chamber of combustion in diameter of 80.0 mm, depth of 25.0 mm, cylinders heads of model 7406.1003040, turbo kompressors «Schweitzer» S2B/7624TAE with cases of turbines with A/R=1.0 and the complete set of the catalytic neutralizers which were elaborated by authors of this article. The neutralizer consists of 2 block catalysts on the metal carrier in diameter of 220 mm and height 90.0 mm everyone with the honey comb structure of channels. 0.1 weight. % Pt was used as an active phase. Neutralizer was tested on the engine working on the diesel fuel with the characteristics: cetane number, not less – 49, density at 150°C-820-860, concentration of sulfur, not more than-500 ppm. In system of greasing oil «Lukoil Super» SAE15W40, APICF4 was used. As cooling liquid (freezing) water was applied. Definition of concentration of gaseous harmful emissions in the waste gases, including, nitrogen oxides (NO_x), total hydrocarbons (C_xH_y), carbon oxide (CO), was made by a multicomponent gas analyzer «Autotest – 02.03» of the I-st class. Calculation of specific emissions was carried out in view of power consumption at n=1500 rev/min., power consumption – 3.5 kVA, at n=2,200 rev./min, power consumption – 11.2 kVA. Definition of harmful emissions in the exhaust gases on a minimal idle motion was carried out on the preliminary preheated engine in a mode of rated power.



1 – Diesel generator; 2 – exhaust pipe; 3 – catalytic reactor; 4 – catalyst sample; 5 – gas operated probe; 6, 7 – sampling valves before and after the catalyst; 8 – a gas analyzer.

Figure 3 – A test bench (a stand) on the basis of the diesel-generator

Results and Discussion

The test of the laboratory samples of catalysts

The laboratory test were carried out at the mounted laboratory installation. In exhaust gases of motor transport in the course of combustion of fuel the water vapor is formed therefore in this work the researches of stability of the synthesized catalysts to catalytic poison – water vapor which content was 5% in nitrogen were carried out. Adding to the gas mixture of water vapor was carried out by a saturator, it kept at 50°C in a thermostat and calibrated on changing of volume of water at a constant feed rate of nitrogen giving through it. By adding water vapor, some catalysts sharply reduced its activity (Table 1).

In the presence of water vapor at 400°C the activity of the tested catalysts became unstable. For example, at 300°C on the catalysts which were not promoted Pt, nitrogen oxide degree of conversion was reduced to zero, while in the absence of water vapor on these catalysts degree of nitrogen oxide conversion reached 30.0-38.0%. Co-Mn and Ni-Mn-catalysts promoted with 0.1% Pt, retained a high activity, which is not reduced during the 50 h. experiment. The experimental results show that poisoning by water vapor is reversibly and catalysts are activated by heating again at a temperature of 300°C in a stream of dry air for 4 h.

Table 1 – Change of activity of the catalysts processed by water vapor and in absence of water vapor in reaction of nitrogen oxide reduction by a propylene at 5% the content of oxygen

Samples of catalysts	The degree of conversion of NO at different temperatures		
	300°C	400°C	500°C
Ni+Mn+Pt	70.0	80.0	73.0
Ni+Mn+Pt (H_2O)	64.0	71.0	61.0
Co+Mn+Pt	65.0	77.0	74.0
Co+Mn+Pt (H_2O)	54.0	58.0	49.0
Fe+Mn+Pt	38.0	52.0	50.0
Fe+Mn+Pt (H_2O)	30.0	47.0	40.0
Co+Mn	32.0	54.0	47.0
Co+Mn (H_2O)	28.0	29.0	22.0
Ni+Mn	38.0	53.0	50.0
Ni+Mn (H_2O)	32.0	51.0	48.0
Fe+Mn	25.0	42.0	40.0
Fe+Mn (H_2O)	0.0	10.0	4.0

It is known that soot and nitrogen oxides $(NO)_x$ are combustion by-products on air of any carboniferous material polluting the atmosphere, are capable to chemical interaction with each other and the environment [6, 9, 15].

Main products of interaction of soot with NO_2 is CO_2 and NO:

$$C + 2\,NO_2 = CO_2 + 2\,NO$$

In this regard were made the experiments in which the possibility of interaction of NO with the soot supported on the block catalysts was investigated. Soot was selected by means of the filter from exhaust gases of buses and supported on the surface of the block from alcohol suspension followed by drying at 40°C. The catalyst with the put on it soot was tested in the medium NO + Ar and NO + O2 + Ar at temperatures 100 – 500°C and volume velocity (Vv) = 25•103 h-1.

IR data confirm the presence of residual of organic and sulfur-containing compounds in soot of the exhaust gases. At interaction of the catalyst with gas mixture NO+Ar with temperature increase from 100 to 500°C was observed a decrease of content of NO from 195 ppm to 113 ppm probably due to interaction of NO with the supported soot. In reaction products there were also a trace amount of carbon monoxide formed during the oxidation of carbon in the presence of insufficient oxygen. When passing the gas mixture containing NO+O_2+Ar through the carboniferous metal block with temperature increase from 100 to 300°C excess of amount of NO over initial (from 260 ppm of an initial mixture to 293 ppm at 100-300°C) was observed, and then with increase of temperature from 300 to 500°C – a decrease in content of NO took place. The observed excess, apparently due to the fact that the formed nitrogen dioxide (NO_2) in admixture with NO by passing through the catalyst and soot at 100 – 300°C is first reduced to NO, resulting is observed excess NO content over the initial amount but with further increase in temperature from 300 to 500°C there is the reduction to N_2.

The tests of full-size samples of catalysts

Results of tests of the diesel engine of KamAP (Table 2) equipped with the catalytic neutralizer of fulfilled gases which was elaborated by the authors of this article, show, that application the catalytic neutralizer of the fulfilled gases resulted in decrease in harmful emissions in comparison with the engine without neutralizer: on NO_x-33.0 %, C_xH_y -82.0 %, CO-98.0 % (2,200 rev./min.). On a mode of the minimal idling (800 rev./min.) efficiency of neutralizer has made on NO_x-59.0 %, C_xH_y-86.0 %, CO-99.0 %.

Table 2 – Values of specific toxic emissions of engine KamAP without neutralizer and with neutralizer of the fulfilled gases

Number of revolutions, rev./min.	CO, ppm			C_xH_y, ppm			NO_x, ppm		
	without neutralizer	with neutralizer	degree of cleaning, %	with out neutralizer	with neutralizer	degree of cleaning, %	without neutralizer	with neutra lizer	degree of cleaning, %
800	123	1.3	99	3182	445	86	128	75.25	59
2,200	733	8	98	3728	671	82	118	79.06	33

Full-size samples of catalysts on the basis of 0.1% of Pt were tested at the stand on the basis of the diesel generator of 4.0 Kv. The block catalysts on the metal carrier were manufactured with the following dimensions: diameter – 30 mm, height – 90 mm, volume – 63.4 mm^3. According to the accepted methods [2,10, 14] the tests on the toxicity of vehicles, including a catalytic converter envisages the beginning of measurement from a cold condition of the car. In this case for a phase of warming up 80-90% of harmful emissions are allocated. For this reason, the catalysts must have the high degree of conversion at low temperatures. In the case of the developed catalysts in this work the full-sized sample at the tests on the mode «idling» showed efficiency of cleaning from CO even at 20°C – 90.6%, the degree of purification from nitrogen oxides in these conditions was low (3.0%). Effectiveness of the catalyst at 267°C is already more noticeable: degree of transformation of CO was equal to 99.6%, hydrocarbons – 80.7%, nitrogen oxides – 44.4%. Results of experiment show that cleaning from CO begins already at low temperatures while for cleaning from hydrocarbons and nitrogen oxides higher temperatures are required. With increase of engine capacity up to 3-4 Kv the high activity on NO_x (61.1-61.9%) is observed (Table 3). At the power consumption of 4 Kv at 427°C degree of cleaning of CO was amounted to 100%, hydrocarbons – 99.0%, nitrogen oxides – 61.9%. Heat stability of full-size samples of catalysts was defined by determination of activity of the initial catalyst on the diesel generator working under loading in 3.0 Kv with the subsequent fractional calcination of neutralizers at 600°C with an interval of 5 h. in a muffle furnace. During 100-h test the high heat stability of catalysts is revealed.

Table 3 – The test data of the full-size block catalyst on the basis of 0.1% of Pt in the bifunctional mode at the various loadings of the engine operation

The consumed capacity, Kv	Temperature of the exhaust gases, °C	Degree of the exhaust gases cleaning, %		
		CO	CH_x	NO_x
Idle motion	20	90.6	21.5	3.0
2	267	99.6	80.7	44.4
3	308	100	95.6	61.1
4	427	100	99.0	61.9

Conclusions

Thus, the catalysts supported on metal block carriers for cleaning of exhaust gases of motor transport were developed. Laboratory tests and tests in real operating conditions of vehicles of motor transport were carried out. Stability of the carrier and the active phase of the catalysts supported on metal blocks to poisoning by water vapor was researched. At poisoning by water vapor of catalysts promoted with Pt they are activated again under heating at T=300°C under a stream of dry air for 4 h. In the presence of steams degree of transformation of nitrogen oxide on the catalysts which are not promoted by Pt decreases to zero whereas the catalysts promoted by 0.1% of Pt (wt.) kept higher activity during 50 h of an experiment. Full-size catalyst samples were tested on truck of KamAP running on diesel fuel and at the stand on the basis of diesel generator capacity of 4 Kv. Thanks to the use the catalytic converter exhaust emissions are reduced (in comparison with the engine without catalyst), for example, in case of KamAP – on NO_x-33.0%, C_xH_y-82%, CO-98% (at 2,200 rev/min). At a minimum idling mode (800 rev/min.) the efficiency of the neutralizer was on: NO_x-59%, C_xH_y-86%, CO-99%. As for the stand on the basis of diesel generator at the power consumption of 4 Kv at 427°C degree of cleaning from CO was 100%, hydrocarbons – 99.0%, nitrogen oxides – 61.9%.

References

1. O'Neill B.C., J. Science, 2002; 5575 : 1971. DOI 10.1126/science.1071238.

2. Kołodziej A., Łojewska J. chapter in: New and Future Developments in Catalysis, 2013; pp. 257. DOI 10.1016/b978-0-444-53870-3.00010-1.

3. Lee B.Y., Inoue Y., Yasimori I., Bull. Chem. Soc. Jpn., 1981; 54: 3711. DOI 10.1246/bcsj.54.3711.

4. McGrath M. Four major cities move to ban diesel vehicles by 2025. http://www.bbc.com/news/science-environment-38170794.

5. Lucena P., Vadillo J.M., Joserna J.J. Compositional mapping of poisoning elements in automobile three-way catalytic converters by using laser-induced breakdown spectrometry, J.Appl.Spectrosc., 2001, V.55.-N3.-P.267-272.

6. Thomson J., Anstice P.C.J., Price R.D., chapter in : Catalysis in Application, 2003; pp 63-69. DOI 10.1039/9781847550347-00063. ISBN: 978-0-85404-608-9.

7. Rauch S., Harold H.F., Barbante C., Masanori O., Morrison G.M., Peucker-Ehrenbrink B., Wass U. , J. Environ. Sci. Technol., 2005; 1, : 8156. DOI 10.1021/es050784m.

8. Sassykova L.R., Ussenov A., Massenova A.T., Gil'mundinov Sh.A., Rakhmetova K.S., Bunin V.N., Basheva Zh.T. and Kalykberdiyev M.K.. Creation of high effective nanostructured catalysts on base of Pt, Pd for neutralization of motor transport exhaust, Int. J. Chem. Sci., 14(1), 2016, 206-212.

9. Kramer M., Schmidt T., Stowe K., Maier W.F., J. Applied Catalysis A: General, 2006; 302 : 257–263. DOI: http://dx.doi.org/10.1016/j.

10. Val'dberg A.Yu., Kosogorova T.O., Tsedilin A.N., Pokrovskii D.D., Yakimychev A.A., Chemical and Petroleum Engineering, 2007; 5-6: 287.DOI 10.1007/s10556-007-0051-7.

11. Burke N.R., Trimm P.L., Howe R. Cold start vehicle emission control using trapping and catalyst technology. Proceedings. Pt.B. 12th Int.Congress on Catalysis, Granada, 2000, July 9-14: Elsevier 2000, P.1451-1456.

12. Sassykova L.R., Gil'mundinov Sh., Nalibayeva A.&Bogdanova I.O.Catalytic systems on metal block carriers for neutralization of exhaust gases of motor transport, Rev. Roum.Chim, 2017, 62(2) – in print.

13. Sassykova L.R., Massenova A.T., Gilmundinov Sh.A., Bunin V.N., Rakhmetova K.S.,

14. Gilmundinov Sh.A., Sassykova L.R., Nalibayeva A.M., Proceeding of International Symposium on Metastable and Nano Materials, ISMANAM , Corfu, Greece, 2007: 168.

15. Sassykova L.R., Massenova A.T., Gilmundinov Sh.A., Bunin V.N., Rakhmetova K.S., The Effective Catalytic Systems on the Base of Colloid Platinum Metals for Oxidation of CO, Methane and Decomposition of Nitrogen Oxides, DGMK, Tagungsbericht, 3, 181-188 (2014)

16. Burdeinaya T.N., Matyshak V.A., Tret'yakov V.F., Glebov L.S., Zakirova A.G., Carvajal G, M.A., Villanueva A.M.E., J.Applied Catalysis B: Environmental , 2007, 1-4:128. DOI 10.1016/j.apcatb.2005.11.027.