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# ASSESSMENT OF THE EFFECTIVENESS OF THE USE OF PALLADIUM IN CATALYTIC SHS-UNITS FOR DIESEL ENGINES

**Abstract.** This paper considers the questions of the purification of exhaust gases of diesel engines from nitrogen oxides, carbon monoxide CO, hydrocarbons CxHy and particulate matter PM, on the catalysts of the porous permeable materials produced by SHS synthesis.

Experimental study on the determination of the effectiveness of catalytic conversion of exhaust gases on the SHS-materials was carried out under the following conditions: the identity of the average diameter, pore size, porosity and pore tortuosity. This was achieved by the fact that the basic structure of the charge contained: alloy steel - 47.5%; chromium oxide - 18%; chromium - 5%; nickel - 4.9%; aluminum - 12%; titanium - 11.5 ... 11.6% and up to 1% by weight of various catalysts.

A comparison of the effectiveness of gas cleaning from particulate matter in the porous SHS-units based on Fe-Al with the same characteristics resulted in quality improvement up to 18-20% using palladium Pd as a part of the material.

Next, the procedure aimed in the assessment of the hazardous diesel emissions on such indicators  $asq_{as\ NOx}, q_{as\ CO}, q_{as\ CH}, q_{as\ PM}$ , the results of which are summarized in Table 1. Here, the estimation of anthropogenic impact values for the same conditions in the case of EURO 4 and EURO 5 emission standards, actual emissions without gas neutralization, and actual emissions with gas neutralization in the presence of porous permeable SHS-units containing palladium Pd.

Keywords: catalyst, self-propagating high temperature synthesis (SHS), exhaust gases.

**Introduction.** The use of palladium Pd in the systems of exhaust gas cleaning at the plants and in the internal combustion engines has been sufficiently studied by researchers. However, the effectiveness of Pd in the composition of the materials obtained by SHS-technology was never investigated. This can be explained both by the high cost of Pd on world markets and a decrease in production volume observed in the world. At the same time, the use of Pdas part of SHS-materials for catalyst units of the catalytic converters for exhaust gas is of interest due to covering a wide range of effective cleaning of the gases from 450 ... 550K to 825 ... 850K with simultaneously cleaning from nitrogen oxides NOx, carbon monoxide CO, hydrocarbons CxHy.

Development of new materials for catalytic converters is connected primarily to the fact that there is a significant deterioration of the catalysts in the process of cleaning gases from the surfaces of the carriers. This is especially true for the materials on the surface of which the catalysts are covered by electrolytic deposition and impregnation, followed by drying [1].

Using of advanced SHS-technology provides durable catalysts resistant to the entrainment of gas supplies (Figure 1).

Researchmethodology. Experimental studies were carried out on the engine of KaMAZ-740 (8Ch 12/12). Recording the external high-speed characteristics were made in speed range of 1400...2600 min-1, and the load characteristics at 2600 min-1 with a pilot plant to assess the effectiveness of treatment of the exhaust gas of diesel engine in porous permeable SHS-catalyst block with all the measurements provided by GOST 14846-81 [2], GOST R 41.49-99 [3], GOST R 41.24-99 [4], GOST R 41.83-99 [5] while working with L-0.2-40 fuel according to GOST 305-82 [5].





B) catalytic converter assembly

Figure 1 – The design of the filter

The duration of the measurement of fuel consumption was not less than 30 seconds. The measurements of opacity, toxicity, temperature and pressure of the exhaust gas were made at least six times for each of the modes using similar devices through the distribution column.

The test program included characterization of diesel engines by test cycle of 13-modes for determining the valuation of specific emissions of nitrogen oxides NOx, carbon monoxide CO, hydrocarbons CxHy and particulate matter PM. This article describes the tests only on nitrogen oxides NOx emissions.

Emissions of harmful substances along with exhaust gases were determined in accordance with GOST R 41.83-99. Exhaust gas opacity and particulate matter emissions were determined in accordance with GOST R 41.24-99.

At the beginning and at the end of the test program, external speed and load test characteristics were determined, as well as specifications for the 13-mode test cycle.

Experimental study on the determination of the effectiveness of catalytic conversion of exhaust gases on the SHS-materials was carried out under the following conditions: the identity of the average diameter, pore size, porosity and pore tortuosity. This was achieved by the fact that the basic structure of the charge contained: alloy steel - 47.5%; chromium oxide - 18%; chromium - 5%; nickel - 4.9%; aluminum - 12%; titanium - 11.5 ... 11.6% and up to 1% by weight of various catalysts.

The study was conducted in a pilot plant with 8Ch12/12 diesel in the test-bench, equipped in accordance with GOST 21393-75 and GOST 41.49-99 on the fuel according to GOST 308-82 L-0,2-40, MTM-16p oil.

Tests were carried out on the loading characteristics at 2600 min<sup>-1</sup> and the outside speed at 1400 ... 2600 min<sup>-1</sup> at ambient temperature  $T_0 = 300$  ... 303K, atmospheric pressure  $P_0 = 749-752$  mm of Hg col., humidity  $W_0 = 72$  ... 79%.

The porosity of the SHS-materials of catalytic units was  $P = 0.47 \dots 0.49$ ; pore tortuosity  $\xi_i = 1.38 \dots 1.40$ ; the volume of the porous mass was  $2.13 \times 10^{-3} \text{ m}^3$ ; relative area of filter surface for the nominal power regime  $F_{fm} = 1.64 \times 10^{-4} \text{ (m/h)}^2$ .

The pilot plant with SHS-catalytic converter was mounted back to back with one of the exhaust manifold of a diesel engine, so there is no need to preheat the exhaust gases on the load conditions above 50%, where there are higher levels of emissions.

**Results.** Comparative tests showed that on the catalytic SHS-materials with palladium Pd content of about 0.3% by weight at the loading characteristic at 2600 min<sup>-1</sup> for effective pressure values of 0,35..0,55..0,78MPa emissions of nitrogen oxides NOx in the exhaust gases are reduced to 15..60..65% respectively (Figure 2).

Low NOx removal efficiency at low load conditions can be explained by the fact that the exhaust gas temperature of 790K, corresponding to the active influence of Pd catalyst on the process of nitrogen oxidesreduction, is shown starting from the values of the average effective pressure  $P_e = 0.52$  MPa (Figure 2). Hereinafter:  $C_{\text{NOx}}$ ,  $C_{\text{Co}}$ ,  $C_{\text{CxHy}}$ ,  $C_{\text{PM}^-}$  content of nitrogen oxides, carbon monoxide, hydrocarbons,

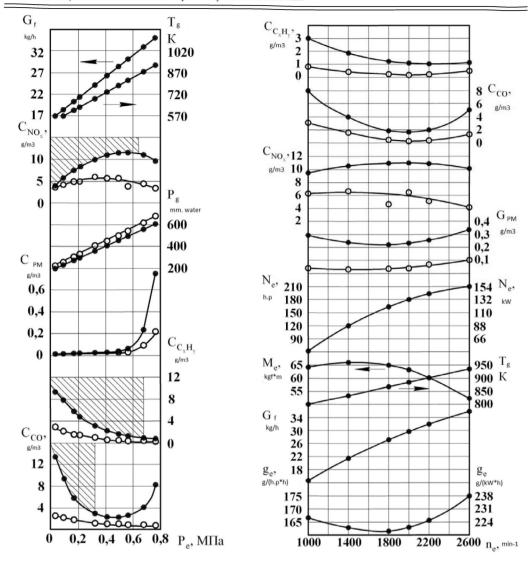


Figure 2 – The effectiveness of cleaning of the exhaust gas of the 8Ch 12/12 diesel engine in SHS-units of the catalyst with the addition of palladium Pd on the loading characteristic at 2600 min<sup>-1</sup>, where ••• - without CN; ••• - with CN

Figure 3 – The effectiveness of cleaning of the exhaustgas of the 8Ch 12/12 dieselengine in SHS-units of the catalyst with the addition of palladium Pd on the loading characteristic, where ••• - without CN: ••• - with CN

particulate matter, respectively, in the exhaust gases, g/m³;  $\alpha$  - coefficient of air excess;  $T_g$  - exhaust gas temperature, K;  $G_a$  - air flow rate, kg/h;  $G_f$  - fuel flow rate, kg/h;  $g_e$ - specific effective fuel flow rate, g/(kW·h).

For values of average effective pressure of  $0.35 \dots 0.55 \dots 0.78$ MPa in the cylinders of diesel emissions of carbon monoxide CO are reduced at the loading characteristic, respectively, to 75 ... 86 ... 92%. Active influence of the Pd catalyst on the processes of CO oxidation begins at the exhaust gas temperature of 520K, and this temperature corresponds to the average effective pressure  $P_e = 0.10$ MPa.

At the above mentioned values of average effective pressure at 2600 min<sup>-1</sup> emissions of hydrocarbons CxHy (total)with the exhaust are reduced to 50 ... 84 ... 83%, respectively. The high efficiency of the exhaust gas purification from the CxHy is because the palladium Pd affects the final oxidation processes of hydrocarbons, starting with the temperature of 450 K, corresponding to the specific effective pressure  $P_e = 0.4$ MPa.

Tests carried out on the outside speed at  $1400 \dots 2600 \text{ min}^{-1}$  showed that the efficiency of the Pd catalyst in the reduction of NOx emissions with the exhaust gases at diesel engine speed of n =  $1400 \dots 1800 \dots 2200 \dots 2600 \text{ min}^{-1}$  was respectively 65 ... 58 ... 50 ... 46%. High efficiency of gas cleaning from NOx is because the exhaust gas temperatures are respectively 820 ... 855 ... 890 ... 920K.

The efficiency of the Pd catalyst in the reduction of carbon monoxide CO emissions at the outside speed of  $n = 1400 \dots 1800 \dots 2200 \dots 2600 \text{ min}^{-1}$  was  $95 \dots 92 \dots 91 \dots 86\%$ , respectively. Despite the fact that the range of active influence of Pd on oxidation of the nitrogen lies in the range of  $520 \dots 820K$  and the gas temperature at the outside speed varies within  $820 \dots 920K$ , the catalyst continues to effect the oxidation processes.

The effectiveness of the catalyst for the reduction of hydrocarbon emissions at the outside speed of  $n=1400\dots1800\dots2200\dots2600\ min^{-1}$  is characterized as  $84\dots94\dots96\dots91\%$ , respectively. The temperature range of the highest performance of Pd catalyst varies from 450 to 850K, and the purification efficiency reaches 92%.

Considering the results of reducing particulate matter emissions from the exhaust gases, it should be noted that, in principle, all considered porous permeable catalytic materials having the same porosity, permeability, pore tortuosity, wall thickness and the relative area of the filter surface under the same conditions of the diesel engine should also have the same efficiency of gas cleaning from particulate matter.

However, it was found that the efficiency of purification of exhaust gases using various catalysts differs from each other. This can be explained mainly by the fact that in the presence of some catalysts diesel soot ignition temperature decreases and it burns more complete at the porous permeable surfaces of the converters or particulate filter units.

The efficiency of Pd catalyst on the reduction of the particulate matter emissions at the loading characteristic at  $P_e = 0.35 \dots 0.55 \dots 0.78 \text{MPa}$  and  $1900 \text{ min}^{-1} \text{is } 50 \dots 88 \dots 84\%$ , respectively (Figure 1), at the outside speed of  $n = 1400 \dots 1800 \dots 2200 \dots 2600 \text{ min}^{-1} \text{is } 91 \dots 87 \dots 80 \dots 83\%$ , respectively (Figure 3).

A comparison of the effectiveness of gas cleaning from particulate matter in the porous SHS-units based on Fe-Al with the same characteristics resulted in quality improvement up to 18-20% using palladium Pd as a part of the material.

Next, the procedure aimed in the assessment of the hazardous diesel emissions on such indicators as  $q_{as\; NOx}$ ,  $q_{as\; CO}$ ,  $q_{as\; CH}$ ,  $q_{as\; PM}$ , the results of which are summarized in Table. Here, the estimation of

The values of assessment indicators and technogenic impact				Exceeding	
Emission levels, g/(kW·h)		The values of the technogenic impact, sf/(km²-year)			of anthropogenic impact for
Requirements of EURO-4 EURO-5	Actual without CN with CN	without CN	with CN containing Pd	meeting the requirements of EURO-3 EURO-4 EURO-5	EURO-3 EURO-4 EURO-5
3.50 2.00	8.86 2.64				
1.50 1.50	4.93 1.69	0.242	0.071	0.135	0.526 0.755
0.46 0.25	1.23 0.33	0.242	0.071	0.054	1.315
	Emission levels Requirements of EURO-4 EURO-5 3.50 2.00 1.50 1.50 0.46	Emission levels, g/(kW·h)  Requirements of EURO-4 without CN with CN  3.50 8.86 2.00 2.64  1.50 4.93 1.50 1.69 0.46 1.23	Emission levels, g/(kW·h)  Requirements of EURO-4 without CN with CN  3.50 8.86 2.00 2.64  1.50 4.93 1.50 1.69 0.242	Emission levels, g/(kW·h)         The values of the techno           Requirements of EURO-4 EURO-5         Actual without CN with CN with CN         without CN CN containing Pd           3.50         8.86         2.00         2.64           1.50         4.93         1.50         1.69           0.46         1.23         0.242         0.071	Emission levels, g/(kW·h)   The values of the technogenic impact, sf/(km²·year)

Effectiveness of SHS-catalyst units containing palladium Pd on anthropogenic impacts on the environment posed by harmful emissions of 8Ch12/12 diesel

0.02

0.02

 $q_{as\,T\Psi}$ 

0.40

0.04

anthropogenic impact values for the same conditions in the case of EURO 4 and EURO 5 emission standards, actual emissions without gas neutralization, and actual emissions with gas neutralization in the presence of porous permeable SHS-units containing palladium Pd.

For all estimates of anthropogenic impact generated by 8Ch12/12 diesel on the environment, the same conditions were used:

- height of the discharge pipe from the level of the road surface,  $h_T = 1.00 \text{ m}$ ;
- dilution ratio on the surface layer,  $\pi_d = 2.00$ ;
- average wind speed at a calm, 2.5 m/s;
- average wind speed in the calculations, v = 10 m/s;
- exhaust gas scattering coefficient,  $R_p = 88$ ;
- an indicator of the relative dangers of air pollution, characterizing terrain and macroroughnesses, used for urban areas,  $\sigma_{apd} = 1.0$ ;
  - natural and climatic conditions coefficient,  $d_{NCC} = 2.00$ .

When the Euro-3, Euro-4 and Euro-5 standards are maintained, the share of individual exhaust gas components accounted in the values of the anthropogenic impact coefficient is, respectively, for nitrogen oxides - 97.17 ... 97.5 ... 97.12%; for carbon monoxide - 0.43 ... 0.44 ... 0.76%; for hydrocarbons - 1.68 ... 1.85 ... 1.75%; for particulate matter - 0.72 ... 0.21 ... 0.36%.

Conclusion. Analysis of the data indicates that when using Pd as a catalyst in the composition of SHS-material, it can be noted that the diesel engine meets the standards of EURO-3 and EURO-4 on the integrated indicator of technological load. Achieving the EURO-4 standards on the level of technogenic impact can be reached by both the improvement of work processes of a diesel engine and catalytic converter by selection of the catalysts.

This makes it possible to reduce significantly the technogenic impacts on the environment posed by diesel.

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# ДИЗЕЛЬДІ ҚОЗҒАЛТҚЫШТАР ҮШІН КАТАЛИТИКАЛЫҚ СВС-БЛОКТАРДА ПАЛЛАДИЙДІ ҚОЛДАНУДЫҢ ТИІМДІЛІГІН БАҒАЛАУ

**Аннотация.** Осы жұмыста дизельді қозғалтқыштардың қалдық газдарын ӨЖС (өздігінен таралатын жоғары температуралық синтез) синтезбен кеуек өткізгіш материалдардан жасалған катализаторларда азот оксидтерінен, көміртек монооксидтерінен СО, көмірсутектілерден СхНужәне катты бөлшектерден тазарту сұрақтары қарастырылған.

СВС- материалдар негізінде қалдық газдарды каталитикалық тазарту тиімділігін анықтау эксперименттік зерттеулер келесі шарттарды орындаумен өткізілді: орта диаметрлер біркелкі, тесіктердің өлшемдері бір, тесіктердің кеуектілігі мен иректілігі бір. Оған себеп болған шихтаның негізгі құрамы: легірленген болат - 47,5%; хром оксиді- 18%; хром - 5%, никель - 4,9%;алюминий - 12%; титан - 11,5...11,6% ден 1% дейін - артурлі катализаторлардың салмағы бойынша.

Кеуекті CBC – блоктарда Fe-Al негізінде газдарды қатты бөлшектерден тазартутиімділігін Pd палладий материалын қолданумен салыстырғанда 18-20% тазарту сапасы артады.

Ары қарай әдіс бойынша келесі көрсеткіштер бойынша дизельдін зиянды шығындысы бағаланды:  $q_{oq}$  NOX,  $q_{oq}$  CO,  $q_{$ 

Түйін сөздер: катализатор, өздігінен таралатын жоғары температуралық синтез (ӨЖС), қалдық газдар.

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## ОЦЕНКА ЭФФЕКТИВНОСТИИСПОЛЬЗОВАНИЯ ПАЛЛАДИЯ В КАТАЛИТИЧЕСКИХ СВС-БЛОКАХ ДЛЯ ДИЗЕЛЬНЫХ ДВИГАТЕЛЕЙ

**Аннотация.** В настоящейработе рассматриваются вопросы очистки выхлопных газов дизельных двигателей от оксидов азота, монооксида углерода СО, углеводородов СхНу и твердых частиц ТЧ в катализаторах из пористых проницаемых материалов, полученных СВС синтезом.

Экспериментальное исследование по определению эффективности каталитической нейтрализации отработавших газов на СВС-материалах было проведено с соблюдением следующих условий: идентичности средних диаметров, размеров пор, пористости и извилистости пор. Это достигалось тем, что базовый состав шихты содержал: легированной стали - 47,5%; оксида хрома - 18%; хрома - 5%; никеля - 4,9%; алюминия - 12%; титана - 11,5…11,6% и до 1% по массе различных катализаторов.

В результате сравнения эффективности очистки газов от твердых частиц в пористых СВС-блоках на основе Fe-Al с теми же характеристиками установлено повышение качества на 18-20 % при использовании в составе материала палладия Pd.

Далее по методике была проведена оценка вредных выбросов дизеля по показателям  $q_{\text{оцNOx}}$ ,  $q_{\text{оцCD}}$ ,  $q_{\text{оцCH}}$ ,  $q_{\text{оц TH}}$ , результаты которой сведены в таблицу. Здесь же выполнена оценка величин техногенной нагрузки для одинаковых условий в случаях выполнения норм выбросов EBPO-4 и EBPO-5, действительных выбросов без нейтрализации газов и действительных выбросов с нейтрализацией газов с присутствием в пористых проницаемых CBC-блоках палладия Pd.

**Ключевые слова**: катализатор, самораспространяющийся высокотемпературный синтез (СВС), выхлопные газы.

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