

The Problem of Toxicity of Gas Engines and their Solutions

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One of the reasons constraining the proliferation of engines powered by natural gas, the methane emission is increased. Methane is a hydrocarbon relatively hard oxidation for to use widespread practice of neutralisation of the fulfilled gases of petrol engines of catalysts, synthesized on the basis of the platinum group metals with established relatively low concentrations, does not always provide the necessary level of exhaust gas from hydrocarbons, especially in a context of ever-tightening environmental standards. Invited to address this focus on Palladium catalysts with high activity in the oxidation of methane. The main factors affecting the oxidation of methane concentration of palladium, gas pressure, geometric surface, as well as the methods of stabilization of palladium catalysts for long-term operation. Proposed and synthesized palladium catalysts with high activity and stability and were tested in the converter for purification of exhaust gas of engines KAMAZ 820.52-260 and Cummings D-260G, confirming the high functional quality developed catalytic compositions.

Key words: vehicle, gas engine, gas fuel, methane, emission, catalytic converter.

The gas fuel usage as the engine fuel of internal combustion engines is one of the most perspective disciplines at the analysis of practicable alternatives for the engine petroleum-product fuels. Within the present work, the "gas fuel" term means the natural (methane) and liquefied (propane, butane) gases. Besides the obvious interest connected with the engine fuels' base expansion, application of gas is considered to be one of perspective directions of control over the motor transport noxious emissions. In

particular, it is assumed that the good mixture formation or carburation within the gas phase allows to achieve qualitative combustion and so or by that to minimize formation of products of poor combustion within the spark ignition engines, and gas introduction into the diesel engine fuel charge practically excludes formation of disperse particles (diesel soot). However, a more detailed analysis of environmental characteristics of the gas fuel engines (complete or partial replacement of traditional petroleum-product fuel) shows that the opinion on ecological safety of such engines is seriously exaggerated. The hydrocarbon emissions with exhaust gases of such engines, as a rule, exceed significantly the allowable level, and the hydrocarbon fraction within the combustion materials is presented mainly by gaseous fuel. This

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conclusion is fair both for conventional spark ignition engines (for example, gasoline ones), and for diesel engines which are fully or partially converted for gas.

Main part

Special problems arise when methane is used as an engine fuel. Among hydrocarbons, methane has the highest CH bond energy (423,2 kJ/mole), in comparison for example with the propane CH bond energy equal to 398,0 kJ/mole; and this highest value complicates methane burning processes within engine cylinders, and that is accompanied by enhanced hydrocarbon emission, and methane makes their main part, more than 90%. Since the operating standards of the European countries, Japan and Russia regulate the general hydrocarbon emission and do not separate emission of methane and/or other saturated hydrocarbons (alkanes) in the form of a separate category of toxic substances, then when using compressed or liquefied gas along with the other components it is necessary to pay special attention to neutralise hydrocarbons. Methane is a gas relatively harmless for human and animal health, however, the greenhouse effect created with its participation is more than 20 times higher than the one of carbon dioxide [EBRD Methodology for Assessment of Greenhouse Gas Emissions, 2010; F.I. Abramchuk *et al.*, 2008].

Therefore, since the EURO-3 level, the European legislators [D. Roth *et al.*, 2000] separate methane out from the general group of hydrocarbons and establish separate limits on its emissions. In particular, the standards on emissions of heavy gas engines establish the methane emission values of not above 1,6 g/kWh (Euro 3), 1,1 g/kWh (Euro 4, 5) and 0,5 (EURO-6).

Meanwhile, the domestic and world experience as to the gas fuel engines' creation shows that at a complete or partial diesel engine converting for the gas fuel (methane), the total hydrocarbon emissions can surpass or exceed manifold the regulatory values. So, as to the diesel engines converted for operation within the gas and diesel cycle (G-10), while the UNECE Regulations #49-01 tests the HC total emission has exceeded the value of 10g/kWh. The results which are a bit less but non-comparable to the requirements of modern standards are received while Isuzu 4HV1 engine testing (the results are

received by AFS (Alternative Fuel Systems, Canada) company, the converted for gas fuel diesel engines produced by Cummins (G-L10-260G) and Caterpillar (C12), USA, and also at gas modifications of some domestic engines. By improving the design and supporting systems (fuel supply, ignition and so forth) within these engines it's possible to reduce the HC emissions significantly, however in this case the hydrocarbon emissions also exceed the allowable (1,1 g/kWh) level many times. Besides, in some cases while diesel engines converting for methane, a noticeable increase of emissions of nitrogen oxides (up to 20-30%) is cognized [N.M. Popova and K. Dosumov, 2007].

One of the most perspective ways to solve the problem of enhanced hydrocarbon emissions by diesel engines converted for the natural gas motor fuel is to use oxidising or three-way catalysts (exhaust catalytic converters), which primary goal is oxidation of unreacted or unconverted methane contained within exhaust gases, and restoration of nitrogen oxides if corresponding conditions are organised.

The catalytic neutralisation of uncomplete fuel combustion products including hydrocarbons is well enough developed or worked out and is widely used within the automotive industry for more than 50 years already. Basically, the experience in application of oxidising catalysts was limited to the petroleum-product fuel engines. The hydrocarbon fraction within these engines' exhaust gases is presented mainly by relatively heavy (the number of carbon atoms is more than five) saturated, unsaturated and cyclic hydrocarbons. For this category of catalysts or neutralizers, a wide spectrum of catalysts based on platinum group metals is developed with the assistance of which rather rigid conditions including the values as to hydrocarbon emissions are provided and assured.

However, the usage of such catalysts, which are created mainly based on platinum and platinum-rhodium compositions for methane neutralisation has appeared to be insufficiently effective because of their low activity. In this connection, additional researches were required in order to create the catalysts with enhanced activity in methane oxidising reaction.

The works of FSUE NAMI and some foreign researchers have shown that the most perspective in these processes are the palladium-based catalysts. Picture 1 shows comparative results of methane oxidation on platinum group metals in comparable conditions. The presented data is followed by the conclusion that palladium is the most catalytically active metal capable to deeply acidify methane in the engine exhaust system conditions (temperature, expenses, comprehensible dimensions for in-vehicle arrangement).

At the same time, there is also a number of problem questions demanding quite serious researches regarding optimisation of composition (concentration of palladium and corresponding promoters), gas load (ability to process the

assigned number of exhaust gases), carrier optimisation (carrier type, structure and attributes of the secondary ceramic carrier or header).

A relatively brief experience of usage of palladic catalysts for methane oxidation accumulated not only within the exhaust gases neutralisation practice but also in some other processes accompanied by deep oxidation of methane (heat generators based on methane catalytically assisted combustion, heat and power plant emissions neutralisation and so forth) revealed an effect of some loss of their activity (deactivation). Despite rather a great volume of researches performed in this direction [T. Leprince, 2004], this nature phenomenon still remains insufficiently clear. This circumstance complicates meeting the requirements on catalyst converter

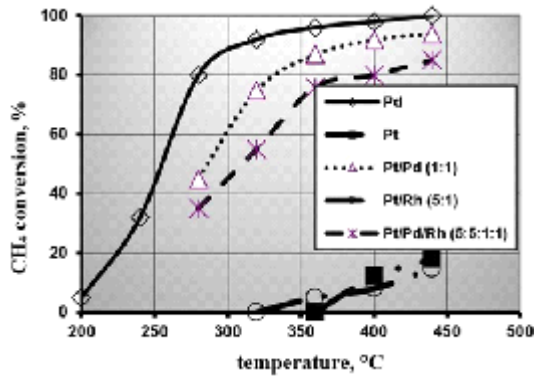


Fig.1. Comparative activity of platinum group metals in methane oxidising reaction ($w = 1.5 \text{ g/dm}^3$; $w = 50,0 \text{ thousand hours}^{-1}$, $\text{CH}_4 - 1,5\%$, $\text{O}_2 - 1,5 \text{ vol } \%$, rest is Ar)

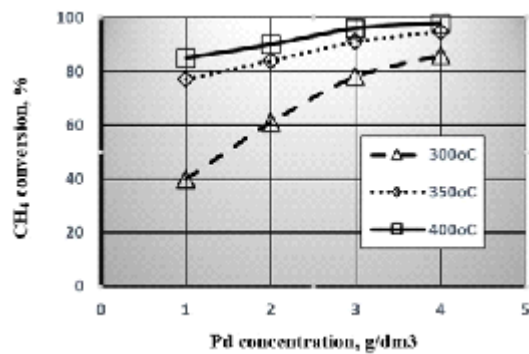


Fig.2. Influence of palladium volume concentration on methane oxidation ($w = 50,0 \text{ thousand hours}^{-1}$)

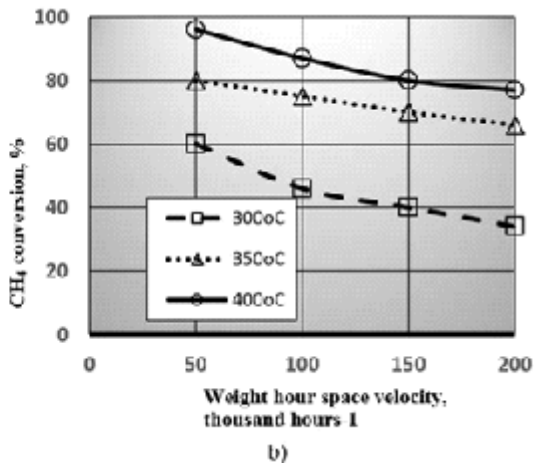
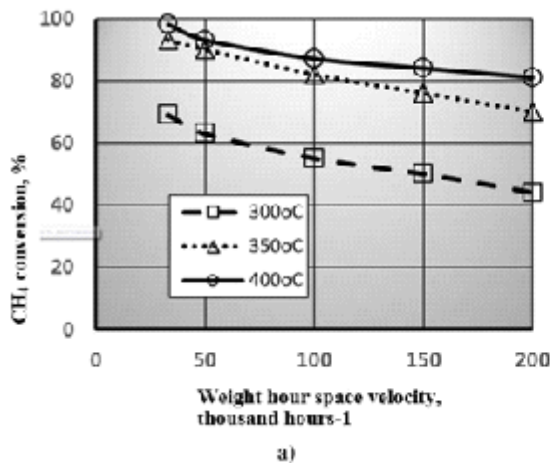


Fig.3. Influence of weight hour space velocity on methane conversion: a) Pd concentration is 4,2 weight %, b) 2,3 weight %

durability (preservation of necessary level of cleaning) at the desired service life (160,0 thousand km).

There is also a number of technological problems of forming of palladic catalysts, they are connected with rather a high concentration of palladium within the reaction zone.

The palladic catalyst peculiarities and its attributes define largely the catalyst design also. Besides ensuring necessary level of cleaning, the catalyst design shall be concurred and coordinated with the engine characteristics (composition, temperature, gas flow rate), shall meet the

requirements on the allowable resistance limited by the gas engine design, weight and dimensional attributes largely defined by the exhaust system design, stability to exposure of severe atmospheres and so forth.

Thus, a catalyst converter for the gas engine is an independent original object different from the others first of all by the catalyst composition or structure, working conditions and to some extent by the design connected with peculiarities of methane oxidation on palladic catalysts.

As was mentioned above, palladium is the most active among the number of precious metal-based catalysts; the other metals and also oxides of transition metals or their combination in the form of spinels, perovskite structures and so forth [T. Leprince, 2004; W. Jansen *et al.*, 2001; T. Kinnunen *et al.*, 2009] which are quite often recommended for deep oxidation processes concede significantly to palladium if operating within comparable conditions. And upon that it should be noted that activity of quite often advertised oxidic catalysts promoted by palladium is actually caused not by oxidic contacts themselves but by the activity of the promoter, i.e. the same palladium [A. S. Ivanova, 1996].

Within the present work, we investigated the palladic catalysts for methane oxidation generated on a metal carrier. A tape made of Kanthal FeCrAl or fechrAl alloy having 0,05mm thickness was used as a carrier. The goffered and flat tapes were rolled into cylindrical samples, were welded

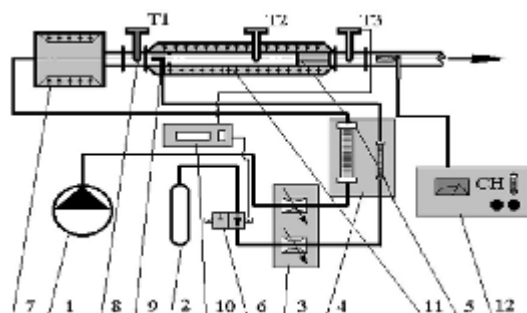
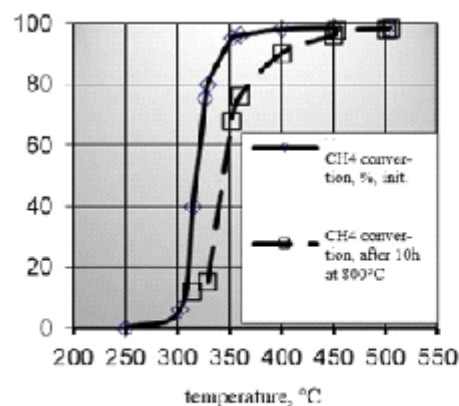
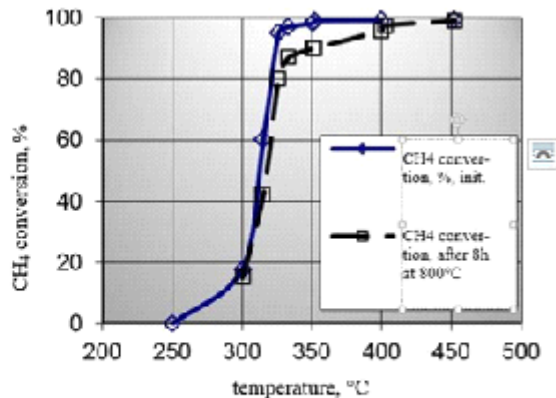


Fig. 4. Diagram of experimental installation in order to research the process of oxidation of compressed natural gas (methane) at the catalyst 1. Air consumption booster; 2. Vessel with CH₄, 3. Gas and air flow control unit; 4. Methane and air flow measurement unit; 5. Catalyst sample; 6. Cut-off valve; 7. Primary heater; 8. Thermocouples; 9. Gas input equipment; 10. Control unit; 11. Secondary heater; 12. Hydrocarbon analyzer with flame ionisation detector



Al₂O₃ annealed at 1000°C, 2g Pd/dm³, restored NaCOOH

a)



Al₂O₃ annealed at 1000°C/h \ 1%ZrO₂/900°C/5h, 2g Pd/dm³, restored NaCOOH

b)

Fig. 5. Efficiency of stabilisation of palladic catalyst within methane oxidising reaction (w- 50, 0 thousand hours⁻¹)

by diffusive method, were annealed at 1000°Ñ within 8 hours. The profiles of the rolls used in order to goffer the tape allowed to change the density of triangular channels within the limits from 20 to 70 cm². After that, the secondary carrier, stabilised aluminium è-oxide and palladium were applied on to the channels' surface. The latter was applied by impregnation of the secondary carrier by sodium tetrachloropalladate with the subsequent restoration by sodium formiate [S.Eriksson, 2006; A. Civera, 2003; T.V Choudhary, 2002].

The palladic catalysts activity was estimated within a laboratory flowing installation with artificially synthesised gas mixtures containing 0,5 vol. % of methane and 1,5 vol. % of oxygen, the rest is argon. When necessary, CO and NO were supplied into the gas stream arriving to the catalyst. The “Beckman-402” gas analyzer with a flame ionisation detector was used for the methane analysis, “Beckman-867” was used for the carbon

oxide analysis, “Beckmann-951A” was used for the nitrogen oxides analysis. The reactor with the catalyst sample were stoved up to 500°Ñ within the reaction mixture current with a continuous ÑÍ₄ concentration registration. The weight hour space velocity (W) were controlled by the catalyst volume (Vct) or gas flow velocity (Vg).The catalysts' efficiency (á) within the methane oxidising reaction was estimated by the conversion level, which was calculated under the following formula:

$$a = 100(C_i - C_o) / C_i \quad \dots(1)$$

where C_i means CH₄ concentration at the reactor inlet;

C_o means CH₄ concentration at the reactor outlet.

The performed researching cycle has shown that the palladic catalysts' activity is influenced by many factors. In particular, the palladic catalysts' activity rather sensitively depends on palladium concentration (picture 2), weight hour space velocity (picture 3a), and there is a relatively small dependence on the geometrical surface (picture 3b), which depends on the density of the carrier channels. It is quite remarkable, that unlike other processes of deep oxidation on platinum group metals, for example, oxidation of CO, more complicated hydrocarbons, nitrogen oxides, etc. the methane oxidation appears to be more sensitive to the above listed factors, and that is on the whole indicative of mainly kinetic constraints typical of this reaction.

Table 1. Results of certification tests of catalyst for KAMAZ-820.52.260 gas engines

Component	Without catalyst	With catalyst	EURO-4 requirements
CO	2,61	0,03	4,0
HC (including CH ₄)	5,84	0,3	1,1
NO _x	4,64	3,2	3,5

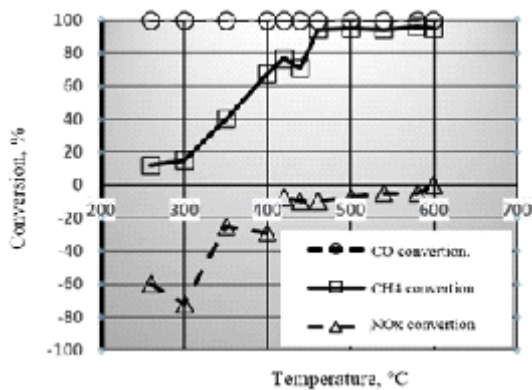


Fig. 6. Temperature dependence of CO and CH₄ conversion on palladic catalyst (lean mixture, aluminium & palladic catalyst stabilised by zirconium oxide, 4,3 g/dm³ palladium concentration, 6 dm³ catalyst volume)

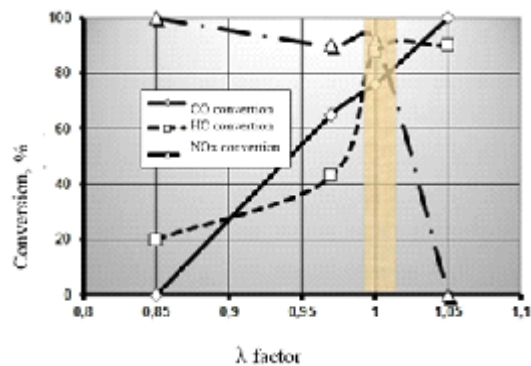


Fig. 7. Influence of the excess air factor on to conversion of toxic components of the gas engine KAMAZ, 820.52-260 converted for natural gas

There are some certain problems concerning the palladic catalysts' durability as well. If exploited or used continuously, some lowering of their activity has been noticed, and the nature of this phenomenon still remains insufficiently clear. There are some versions of explanation of loss of activity of palladic catalysts in the course of continuous exploitation:

- a) Palladic catalysts' poisoning by sulfur compounds;
- b) Thermal sintering or caking of palladic clusters;
- c) Palladium oxidation;
- d) Interaction with the carrier material.

Apparently, all the listed mechanisms take part in the palladic catalysts' deactivation, however they are not prevailing. The main argument forcing to search for further explanations of this phenomenon is a well-known experience of continuous exploitation of palladic or palladium-containing catalysts within automobile catalysts. While continuous operation of the catalysts including the palladic ones, all the listed factors influence and deactivate the catalyst, but along with this its activity remains at rather a high level at the vehicle mileage of up to 100,0-150,0 thousand km. On the other hand, there is experience of the palladic catalysts' successful work in the industrial processes connected with deep oxidation of methane, for example, in processes of heating of technological gases (synthesis of nitric acid, etc.), synthetic gas, dimethyl ether regeneration processes, and so forth. Apparently, the main mechanisms of palladium deactivation are connected with the specificity of its interaction with methane, among which there can be products of decomposition, polymerisation or partial oxidation of CH_4 with formation of stable forms blocking the active component surface or complicating the mass transfer in the catalyst transport pores[D. Ciuparuat *al.*, 2002;Bahmutovand Karpukhin (2012)].

Proceeding from the stated above reasons, a necessity for search for methods of preservation of high activity of the palladic catalysts at continuous exploitation becomes quite clear. Among rather an extensive list of feasible directions in order to solve this task, the primary and dominating attention has been given to stabilisation of the secondary palladium carrier, aluminium oxide. Two directions were considered:

a) thermal stabilisation and b) modification of the carrier by oxides of transition metals. The special attention to the secondary carrier was connected with the peculiarities of the technology being usually used within the automobile catalysts' preparation practice, which assumes application of aluminium oxynitrate, $\text{AlO}(\text{NO}_3)$, as a binder while forming of the secondary carrier on the metal unit surface. As a rule, aluminium oxide received at oxynitrate decomposition has an amorphized structure, which availability not only complicates palladium clusters' mounting, but also while the subsequent catalyst operation promotes palladium migration within the carrier surface, its (palladium) sintering or caking, and finally to its activity lowering. Besides, the amorphized structures' high defectiveness allows to assume formation of solid solutions of palladium ions within a malformed oxide lattice. At the subsequent aluminium oxide sintering and crystallisation, palladium is partially localised within the Al_2O_3 lattice and loses ability to participate in the catalytic process[Terenchenko *at al.*, (2015)].

Therefore, it was offered to enter the secondary carrier preheating operation into the catalyst preparation technology, and that allows to reduce the number of defects within the Al_2O_3 lattice and to complicate migration of palladium clusters on the unduly developed surface of aluminium oxide and their enlargement, which is accompanied by loss of the number of active centres or sites. Besides, the carrier preliminary quenching or tempering stabilises the porous structure and improves mass transfer between the gas flow or stream and the areas adjoining to the active component. At last, the warmup provides an accelerated crystallisation of amorphized aluminium oxide received from aluminium oxynitrate used within the technological process. Introduction of some modifiers, in particular ceric and zirconium oxides, into the Al_2O_3 crystalline structure stabilizers composition promotes just the same[Fan. X.*at al.*, 2012].

The palladic catalysts' thermal stability was estimated by alteration of activity in a model reaction of methane oxidising through time. The installation presented in picture 4 was used for that. The test results of the catalysts prepared with the usage of the above mentioned (heat treatment and doping) processing methods are shown in

pictures 5a and 5b, and those demonstrate that while doping by zirconium oxide a bit larger effect is reached.

The conducted complex of laboratory researches as to selection of compositions and as to the palladic catalysts' stabilisation methods has allowed to start designing of full-scale catalysts in order to equip the gas engines. Such catalysts have been created for the two gas engines, KAMAZ (mod. 820.52-260) and Cummins (C-260G), and those are the most demanded gas engines in Russia at present. Besides exhaust gases neutralisation these catalysts also perform muffler functions.

Based on these catalysts, a complex of additional researches on updating of attributes of catalysts within full-scale conditions, and also certification tests according to the UNECE Regulation #49-04 have been conducted.

The results of the catalysts' full-scale conditions tests are shown in picture 6 and on the whole confirm the conclusions of the laboratory stage of researches. Dependence of methane and CO conversion from temperature is naturally traced.

The noted growth of toxicity as to nitrogen oxides demands additional researches; presumably, it is connected with changes of initial ("crude") emission of NO_x in the course of the engine consecutive loading in order to increase the exhaust gases' temperature while their flow or consumption rate preservation.

Based on these catalysts, a complex of additional researches on updating of attributes of catalysts within full-scale conditions, and also certification tests according to the UNECE Regulation #49-04 have been conducted.

Remarkable is the possibility to also neutralise NO_x , though the necessary condition in order to realise this reaction is maintenance of the ϕ factor near to 1.0 (stoichiometry). Picture 7 shows these experiments' results and the marked air/fuel ratio area where the catalyst provides more than 80% cleaning of NO_x , CO and NO_x , i.e. it operates in a ternary or three-component mode. Since the gas engines are mainly operated using relatively "poor" or lean mixtures ($\phi > 1.0$), a task of this area expansion was not studied specially. However, under the condition of ensuring of steady, economic and efficient operation of the gas engines using the air-and-fuel mixtures close to the stoichiometric composition, the three-component

cleaning area ("the window of bifunctionality") can be considerably expanded at the expense of the catalyst composition improvement and the air-and-fuel mixture composition regulation system adjustment [Ben W.L. Jangat *et al.*, 1999; S. Gandhiat *et al.*, 2003].

The certification tests as per the UNECE Regulation #49-04 at the KAMAZ 820.52.260 engine have shown high performance and efficiency of the created palladic catalysts and the catalyst design, which have provided performing and meeting the EURO-4 specifications and limits, and as to emissions of hydrocarbons including methane they implement EURO-5 (table 1) also.

CONCLUSIONS

Thus, the conducted work results are as follows: the highly effective palladic catalysts for deep oxidation of methane have been synthesised, methods of their stabilisation have been offered, and the catalyst converters' designs for neutralisation of methane within exhaust gases of the most widespread gas engines in Russia, KAMAZ (mod. 820.52-260) and Cummins (C-260G), have been created. The created catalysts' efficiency has been confirmed by the certification tests of the gas engines equipped with such catalysts for conformity to the EURO-4 requirements.

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