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Removal of Nitrogen Oxides from Off-Gases of Diesel Engines: the Problems and the Prospects to Solve Them

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Abstract

Possible application of new technologies to remove nitrogen oxides from off-gases of diesel engines has been considered that is based on the use of steady-state and non-steady catalytic processes to reduce nitrogen oxides by diesel fuel or by the products of its selective conversion into synthesis gas or olefines in compact generators. It has been found that the use of synthesis gas, mixed with the main fuel for petrol or diesel engines, makes it possible to drastically abate emissions of hazardous components and to enhance the efficiency of the engines, in particular, when ultralean mixtures are used. A viability has been revealed to apply complex oxidic systems with high mobility of oxygen as catalysts of the oxidation processes for soot particles with nitrogen oxides involved that facilitate the removal of both types of noxious admixtures.

INTRODUCTION

The prospects for application of diesel engines

Creation and operation of generators of various capacities to transform chemical energy into electric or mechanical one with a high efficiency factor is a priority direction of the development of power industry and highway transport in many developed countries in the new millennium. Although fuel cells are, undoubtedly, the most attractive energy generating units, their putting to work for motor transport requires solving a variety of materiology and engineering problems, which can be achieved not earlier than after 10–20 years. Therefore, the problem to improve the existing types of engines, primarily, to abate their negative environmental impact is still fairly urgent.

It is common knowledge that diesel engines and gas motors are characterized by the peak efficiency among internal combustion engines (ICE). Owing to their economic efficiency and reliability, diesel engines are in general use all over the world as the basic power sources for power generators, on ships, lorries, and buses. In addition, the production of diesel vehicles is growing considerably in the majority of the

European countries, and in certain countries, they comprise a half of all produced means. However, a significant amount of contaminants, specifically, nitrogen oxides and carbon black (particulates), is formed during their operation. Consequently, it is important to develop technologies to abate their emissions from thermally effective diesel engines and gas motors. It appears that such an improvement is the shortest way to enhance the efficiency of the use of mineral combustible for power industry and motor transport.

When monitoring the process of fuel combustion, the efficiency factor of diesel engines comprises 40 % and more; however, it can drop down to 35 %, when certain techniques are applied to decrease the nitrogen oxide emissions, for example, recirculation of the off-gases and monitoring the combustion regime. To generate 1 MW of power with the efficiency factor being equal to 35 %, it is required the quantity of combustible that corresponds to 2.86 MW of chemical energy. On the other hand, with the use of 1 % of fuel as the reduction agent and with no monitoring the burning regime, $2.50(1 + 0.01) = 2.53$ MW of fuel is necessary. Consequently, the efficiency of energy saving for 1 MW of a diesel engine is as great as 11.5 %. In addition, efficiency factor of gas motors comprises 30 % and less, and 3.33 MW of fuel is necessary to generate 1 MW of power. Therefore, the efficiency of energy saving comprises 24.0 % in the event that the necessity disappears to replace a diesel motor by a gas one.

Development of the technologies that help to abate the emission of nitrogen oxides from diesel engines and gas motors with a high efficiency factor will allow an intensive use of the similar engines as the basic energy source and will promote a significant saving in mineral liquid fuels.

Technologies of NO_x removal

Technologies designed to simultaneously strip exhaust gases of ordinary petrol engines from nitrogen oxides, CO, and hydrocarbons are inefficient for diesel and petrol engines, where the oxygen content comprises 10 % and more. The familiar technology for selective catalytic reduction (SCR) of nitrogen oxides under an excess of oxygen, which is applied to neutralize off-gases of thermal power stations, boiler rooms *etc*., uses ammonia as a reducing agent that constitutes a toxic gas, the work with which requires special high-pressure equipment and a careful dosage control to prevent a breakthrough of ammonia. In this connection, the use of the above technology is rather problematic for motor transport that is characterized by a variation of both the composition of the off-gases and their temperature over a wide range (especially, under traffic within city limits). Therefore, it is necessary to conduct investigations and develop systems to neutralize nitrogen oxides with the use of alternative reducers.

For the internal combustion engines that work with leaned mixtures, Toyota Motor Corporation [1, 2] designs a method to remove nitrogen oxides that is based upon the use of so-called adsorbent-catalysts. Basic composition of these systems constitutes a platinum-promoted barium oxide that is applied to aluminium oxide. During the work with leaned mixture, nitrogen oxides are accumulated in the form of nitrates. Periodic introduction of an excess of fuel (impulses of a rich mixture) makes it possible to reduce nitrogen oxides and to recover the adsorbent [1–7].

However, to provide for a possibility of such periodic variation of the mixture ratio for diesel engines, a special modification needs to be introduced into the design of the diesel engine (a system of fuel injection into the off-gases), which hinders a simple transfer of the technology. In addition, in the case when off-gases (OG) of diesel engines are cleared, the problems such as poisoning of catalyst due to a sulphation become substantially complicated because of a greater sulphur content of diesel fuel, and development of new adsorbents of nitrogen oxides is required that would be tolerant of sulphation. Fairly encouraging results in this aspect have been obtained with the use of the sulphated zirconia with applied coarse-dispersion copper oxide and salts of a basic type [5], as well as potassium salts on a mixed oxidic cerium-titanium carrier [7].

An alternative promising variation of the technology is based on the use of catalysts that are capable to selectively reduce nitrogen oxides by hydrocarbons (HC) under an excess of oxygen [8–22]. Certain systems around zeolites with the applied cations of transition elements and/or platinum metals, especially when moderate loads are used, and within modelling mixtures that are free from water and sulphur dioxide, have shown a sufficiently high efficiency both in steady-state, and periodic processes of SCR of nitrogen oxides by various HCs [8–11]. To take an illustration, a Cu–ZSM-5 catalyst with loads up to 30–50 thousand h^{-1} makes possible conversion up to 80 % of nitrogen oxides with the use of propane as a reducer [10, 23].

However, within the real water-containing mixtures, practically whole assortment of zeolite catalysts is deactivated as a consequence of their hydrothermal instability that leads to dealumination [13, 14], which precludes their application in practice.

For more stable catalysts around aluminium oxides, zirconia, and complex oxidic compositions with the applied platinum metals and/or cations of transition elements, it is possible to provide wanted stability in real mixtures [15–23]. However, in the presence of water vapour and sulphur dioxide, a region of the effective work for the majority of non-platinum catalysts during the reduction of nitrogen oxides by diesel fuel components is shifted to the temperatures that exceed 400–600 °C [24–26], which is above the medium temperature for OG of diesel engines.

It is especially important to reduce nitrogen oxides by methane [24, 25]; therefore, it is impossible to apply this reducer to clear OG of diesel engines from nitrogen oxides for the engines that work on natural gas. To take an illustration, for manganese cations that are applied to sulphated zirconia, conversion level of nitrogen oxides for loads of an order of magnitude of 3000 h^{-1} in the presence of water and sulphur dioxide traces does not exceed 10 % at 500 °C, although it ranges up to ~60 % at 600 °C.

For heavy HCs, for decane as an example, systems around sulphated zirconia with applied copper cations show relatively high activity in a medium-temperature (about 300 °C) region [19, 20]. However, the achievable level of removal of nitrogen oxides (the maximum is of about 40 %) is still insufficient for their practical use, and development of new types of catalytic systems with an enhanced activity in these processes is needed. This can be realized by platinum metals, primarily, the platinum itself, introduced as a constituent of active components [16, 27]. However, platinum shows high selectivity with respect to the formation of an undesirable reduction product, specifically, nitrogen oxide (I), on the majority of carriers [16, 27], which also presents a serious problem.

The problem to remove nitrogen oxides from OG of diesel engines by selective reduction can be solved, if the products with higher reactivity from selective oxidation of fuel (synthesis gas, olefines, alcohols, aldehydes *etc.*) are used as reducers. With their help, effective reduction of nitrogen oxides can be performed in the field of temperatures 100–300 °C with the catalysts such as platinum metals on various carriers (reduction by synthesis gas or by hydrogen [33–40], by a mixture of synthesis gas with olefines or other hydrocarbons on applied silver [41–44]), and of the carriers themselves (zeolites, anatase, aluminium oxide *etc.*) with the use of alcohols and aldehydes as a reducer [28–32].

At first sight, generating alcohols and aldehydes onboard a car by selective oxidation of diesel fuel is rather problematic. Nevertheless, a research that has been performed by the authors [45] has demonstrated that selective oxidation of heavy HCs to yield oxygen-containing compounds occurs with the use of platinum-rhodic grids as catalysts under an autothermal operation with small (milliseconds) times of contact.

Generation of oxygen-containing compounds is also possible, if plasma treatment is applied for OG, where fuel vapours have been introduced [46].

Nevertheless, the technologies on the basis of synthesis gas and olefines that are generated onboard a car and applied as reducers are thought of as the most promising in the aspect of their implementation. Synthesis gas and olefines mixed with hydrogen and CO can be been obtained as a result of selective oxidation of diesel fuel by air oxygen under autothermal conditions at small (milliseconds) times of contact on block catalysts [45, 47–50]. This will make it possible to ensure a compactness of the reactors that is essential for their arrangement onboard a car.

The mixture of olefines can be used, mainly, in a steady-state process of selective reduction of nitrogen oxides, whereas synthesis gas can be used both in a steady-state process and under a periodic regime with accumulation of nitrogen oxides on adsorbents and their subsequent reduction by means of feeding the synthesis gas.

Modifying of hydrocarbon fuel to optimize its combustion in diesel engines

Hydrogen is considered for a long time among the most promising combustibles for ICE, both from the point of view of emission control and in terms of engine run [51–53]. Replacement of part of the basic hydrocarbon combustible with hydrogen or synthesis gas leads to positive effects, such as an increase of power and efficiency factor, a decrease of HC and carbon oxide emissions and smoke opacities. Hydrogen combustion also makes it possible to reduce local overheats, which rank among the basic sources for the formation of nitrogen oxides in ICE. This direction is rather promising, since it allows working on ultra-lean mixtures, which is especially convenient in city driving, when a relatively low engine power is necessary. The examination of the published results [47, 51–53] makes it possible to draw an inference that adding a rather small amount of hydrogen into diesel engine may result in simultaneous abatement of nitrogen oxide emissions and smoke opacity. Application of OG recirculation is a well-known way to reduce emissions of nitrogen oxides; however, an increase in smoke opacity occurs in the process. Partial (10–20 %) replacement of recirculated gases with hydrogen makes it possible to compensate for this effect, with no influence upon the quality of fuel combustion and the engine efficiency.

One additional promising variant to remove nitrogen oxides consists in their use for oxidation of carbonaceous materials, the soot particles that are fixed on filters [54–58]. A reoxidation of the formed NO to nitrogen dioxide with the involvement of loosely bonded oxygen of adsorbent-catalysts gives a catalytic nature to the process of carbon black oxidation and removes the problem to provide a contact of the carbon black particles with the catalyst. Creation of self-recovering catalytic filters is made possible due to this circumstance, although to do this, it is necessary to raise the activity of catalysts [59].

The work briefly discusses the results of our investigations over the above directions.

NEW TYPES OF CATALYSTS FOR PROCESSES OF SELECTIVE REDUCTION OF NITROGEN OXIDES BY HEAVY HYDROCARBONS IN AN EXCESS OF OXYGEN

Catalysts around montmorillonite clay that are pillared by zirconia columns are of much interest among promising systems that are tolerant of sulphation under real conditions of diesel emissions. Copper cations that were fixed on these columns and promoted by platinum acted as a combined active component. Methods

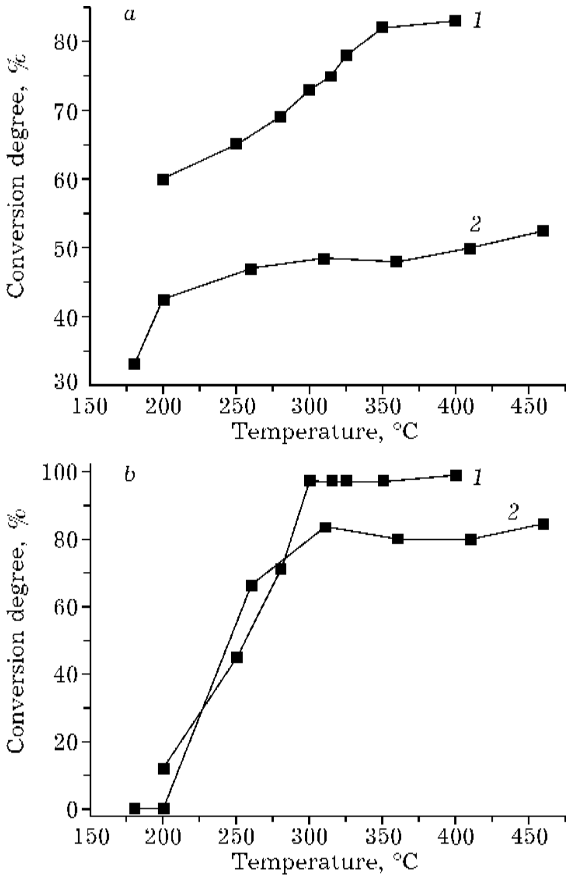

Fig. 1. Temperature dependences of conversion degree of nitrogen oxides (*a*) and decane (*b*) for the catalysts: *1* – 0.2 % Pt + 2.0 % CuO/columnar clay, *2* – 0.5 % Pt/Al_2O_3. The composition of the reaction mixture: 0.1 % NO + 0.05 % $C_{10}H_{22}$ + 1 % H_2O + 10 % O_2, the load is 30 000 h^{-1}.

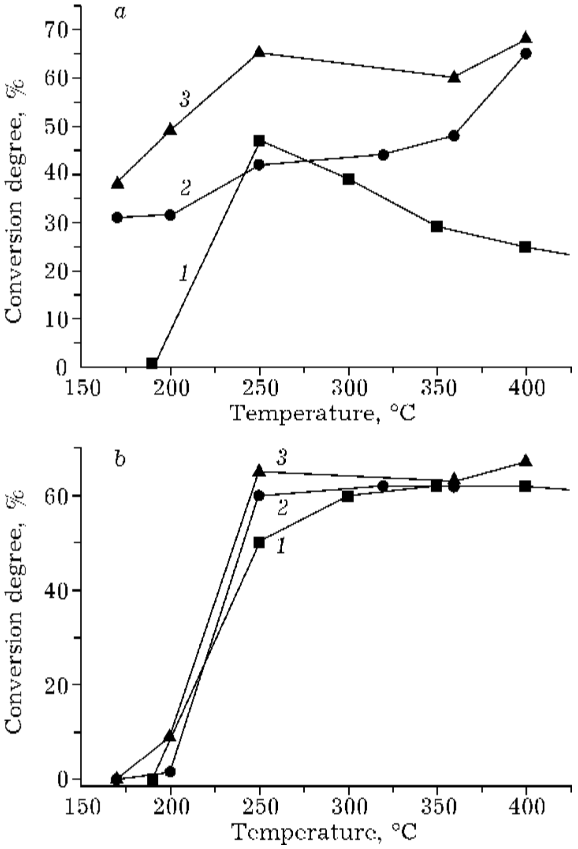

Fig. 2. Effect of H_2O and O_2 concentration in the mixture with 0.1 % NO and 0.05 % $C_{10}H_{22}$ in He with a load of 50 000 h^{-1} on the conversion level of nitrogen oxides (*a*) and decane (*b*) for Pt + Cu/Ca–columnar clay catalyst: *1* – 10 % H_2O + 2 % O_2, *2* – 1 % H_2O + 10 % O_2, *3* – 10 % H_2O + 10 % O_2.

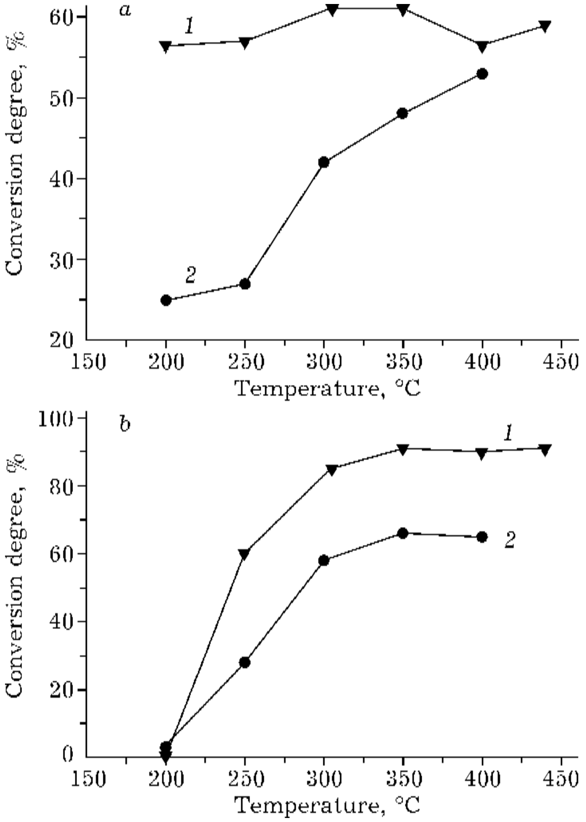

Fig. 3. Effect of sulphation of the catalyst 0.3 % Pt + 5 % Cu/columnar clay (the content of sulphur is 1.5 mass %) upon the conversion level of nitrogen oxides (*a*) and decane (*b*): *1* –Pt + Cu + SO_4, *2* – Pt + Cu. The composition of the mixture: 0.1 % NO + 0.05 % $C_{10}H_{22}$ + 10 % H_2O + 10 % O_2; the load is 30 000 h^{-1}.

of synthesis and physicochemical characteristics of these catalysts are given in detail in works [60, 61]. The most important distinctive features of these systems include: a) high (up to 400 m^2/g) specific surface; b) a developed cellular structure (the availability of supermicropores, cracks between silica-alumina layers with the height of “galleries” up to 10 Å and with the developed network of transport mesopores up to 50 Å in size that are formed by defects of joints of the silica-alumina layers); c) high (up to 700 °C) thermal and hydrothermal stability; d) tolerance for sulphation that is characteristic of both silica-alumina layers and zirconia nanoparticles. The mixed active component that is applied to zirconium dioxide columns is characterized by a greater efficiency as compared to Pt/Al_2O_3 catalyst in the reaction of selective reduction of nitrogen oxides by decane with an excess of oxygen and in the presence of water, the platinum content being essentially smaller (Fig. 1). In so doing, comparable decane conversions for both catalysts are matched by substantially higher conversion degrees of nitrogen oxides on a Cu + Pt/columnar clay sample, especially in a low-temperature field. An additional benefit of the catalyst around columnar clay is a low (that does not exceed 10–15 %) selectivity with respect to nitrogen oxide (I), the formation of which is evidenced only in the field of temperatures of 250–300 °C. Meanwhile, the selectivity with respect to N_2O for Pt/Al_2O_3 catalyst ranges up to 30 % in a wider (200–300 °C) temperature range.

An increase of water and oxygen content in a mixture contributes to a gain in conversion degree of nitrogen oxides, the positive effect of water being more distinct over the region of medium temperatures (~250 °C) (Fig. 2). Within the framework of the familiar schemes for the

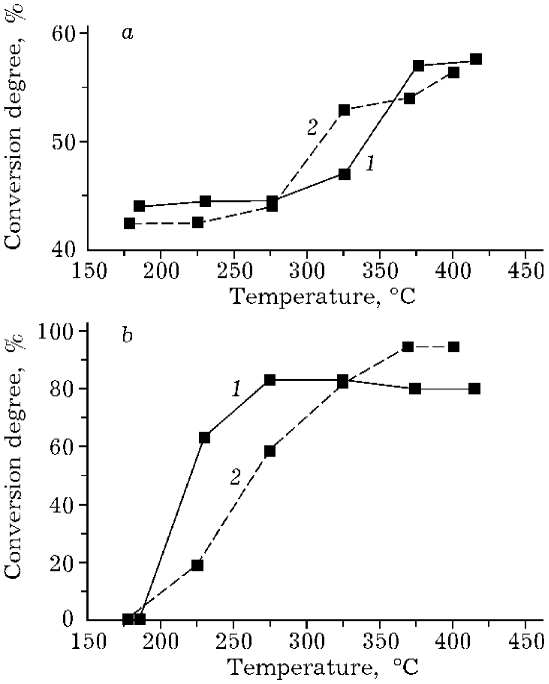

Fig. 4. Effect of sulphur dioxide presence in the reaction mixture upon the conversion level of nitrogen oxides (*a*) and decane (*b*) for the catalyst Pt + Cu/columnar clay: *1* – 0.1 % NO + 0.05 % $C_{10}H_{22}$ + 10 % H_2O + 10 % O_2; the load is 30 000 h^{-1}; *2* – 0.1 % NO + 0.05 % $C_{10}H_{22}$ + 10 % H_2O + 10 % O_2 + 300 ppm SO_2; the load is 90 000 h^{-1}.

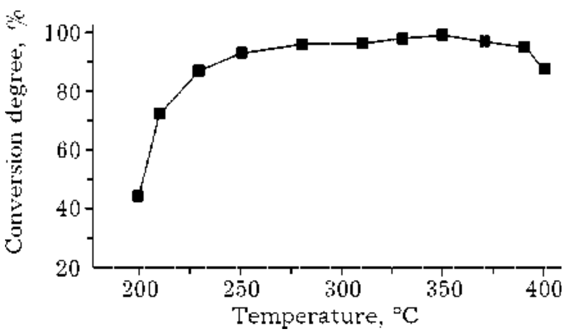

Fig. 5. Temperature dependence of conversion degree of nitrogen oxides when propylene is used as a reducer with a load of 70 000 h^{-1} for the catalyst Pt+Cu/columnar clay. The composition of the mixture: 0.2 % NO + 0.2 % C_3H_6 + 2.5 % O_2 + 200 ppm SO_2 + 3 % H_2O in N_2.

mechanism of SCR reaction, the given effect is attributable to an accelerated hydrolysis of the intermediates such as isocyanates, and to the formation of an effective reducer, specifically, ammonia [62]. Attention is drawn to the fact that the rate of decane conversion has only a weak dependence on water that is present in the mixture, which can be explained by a small sensitivity as regards water presence in the gas phase for the process of HC activation on platinum.

As opposed to catalysts around aluminium oxide [26], sulphation of a catalyst through treatment with ammonium sulphate and the subsequent calcination (the content of sulphur that is fixed on the surface ranges up to 1.5 mass %) leads not to a decrease but to a growth of the fractional conversion of nitrogen oxides and decane (Fig. 3). Consequently, sulphation contributes to a more effective activation of decane, seemingly, due to the involvement of acidic sulphate groups at this stage, these groups being localized on zirconium cations [20, 21]. Under these conditions, an improvement of reduction efficiency for nitrogen oxides is caused, possibly, by the lowered bond strength of intermediates, nitrite-nitrate complexes, with the surface owing to a competition with stronger bound sulphates [63] (for example, going from bidentate, or bridging nitrates, to those monodentate), which raises their reactivity.

The high conversion level of nitrogen oxides is preserved (Fig. 4) upon introduction of sulphur dioxide in the reaction mixture in the quantities that exceed those typically used in such experiments [20, 21], and it increases (Fig. 5) when a more effective reagent, propylene, is used as a reducer [61].

Application of catalysts around columnar clays to cordierite carriers does not result in an appreciable deterioration of their catalytic properties (Fig. 6), although the high conversion level is attained with moderate (about 10 000 h^{-1}) loads and at sufficiently high temperatures.

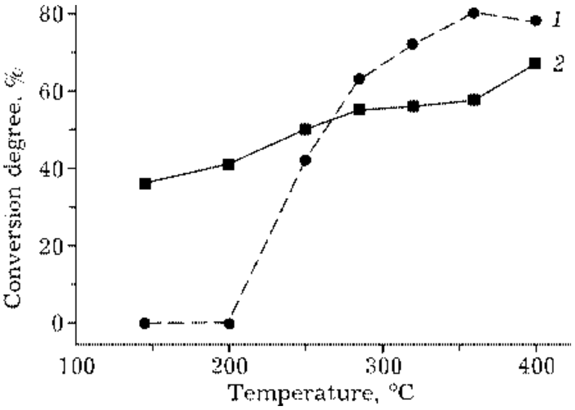

Fig. 6. Temperature dependences of the conversion degree of decane *(1)* and nitrogen oxides *(2)* for the catalyst 0.2 % Pt + 2.0 % CuO/columnar clay, the catalyst being applied to a cordierite microblock (400 cells per square inch). The composition of the mixture: 0.1 % NO + 0.05 % $C_{10}H_{22}$ + 10 % H_2O + 10 % O_2; the load is 13 000 h^{-1}.

A comparable activity level has been obtained for another promising type of active components, skeletal phosphates of zirconium and copper promoted by platinum [23]. Therefore, components of diesel fuel can be used directly as reducers, primarily, to clear OG of large power diesel engines, in particular, those stationary. At the same time, for a mobile application, it is desirable to convert the fuel into reducers with greater efficiency, such as olefines, synthesis gas or their mixture. In this connection, the problem to develop highly effective compact generators of olefines and synthesis gas from diesel fuel components becomes rather urgent.

BLOCK CATALYSTS FOR PROCESSES OF SELECTIVE OXIDATION AT SMALL TIMES OF CONTACT

Processes for oxidation of paraffins to yield synthesis gas

Platinum metals (including those in combination with nickel) that were applied to complex oxidic systems with perovskite or fluorite structures with a sufficiently high mobility of oxygen of the lattice were used as active components for these processes. Activation of HC by C–H bond opening occurred on metal components in the given combination, while an oxidic carrier provided a further transformation of hydrocarbon fragments due to their interaction with the oxygen of its lattice and/or hydroxyl/carbonate groups.

A fairly detailed description of the approaches to a design of these components is set forth in a number of original patents and publications [64–70]. These active components were applied to block carriers of various types, including those filamentary ceramic, metallic (on the basis of a foil from a thermostable alloy), cermet microchannel *etc*. [64–66, 70–73]. It has been demonstrated that catalysts on heat-conducting metal carriers are more preferred to be used for the processes of selective oxidation or for a steam-air conversion of liquid fuel, namely, petrol with a high (up to 40 %) content of aromatic compounds, since they facilitate a more efficient heat transfer from an active zone of exothermal reactions (a deep HC oxidation) in the inlet part of the block to an active zone of endothermic reactions (steam and carbon-dioxide conversion of HC) in the main part of the block. With the inlet temperature being 250–270 °C and time of contact being less than 0.1 s, these catalysts provide full conversion of liquid fuel to yield synthesis gas with the equilibrium composition of the mixture at the outlet [73].

A converted mixture for petrol with optimum component ratios in the inlet mixture ($O_2/C = 0.53$, $H_2O/C = 1.0$) contains as much as 28 % H_2, 17 % CO, 7 % CO_2 calculated with respect to a dry mixture (the rest is nitrogen). Optimization of the composition of an active component and the mixture ratio at the inlet makes it possible to prevent the formation of an undesirable by-product, carbon black. It can be inferred that with a great quantity of aromatic compounds in the petrol after operation, catalysts will also render sustained performance during the course of generating synthesis gas from diesel fuel. The use of metal carriers enables warming up catalysts by passing an electric current from the automobile accumulator, which is important to ensure a quick start.

Thus, with the use of the developed block catalysts, it is possible to effectively generate synthesis gas onboard a car. The use of a fraction of OG as a source of heat, water, and carbon dioxide [53] will make it possible to enhance power efficiency of the generator and a yield of hydrogen with no need to supply motor transport with onboard reserves of distilled water.

Processes of oxidation of paraffins to yield olefines

Owing to high temperatures that develop at the inlet part of a block catalyst, an autothermal process of selective oxidation, or oxidizing dehydrogenation, of paraffins to yield olefines at small times of contact involves cracking processes together with dehydrogenation [45, 47–50]. Therefore, a mixture of light paraffins, hydrogen, and carbon oxides is formed from heavy paraffins and/or aromatic compounds. While the mentioned circumstance is a serious limitation for processes to yield monomers, a mixture of olefines, hydrogen, and CO is quite reasonable to be employed for a process of selective reduction of nitrogen oxides.

It has been demonstrated that mixed skeletal phosphates of zirconium and cobalt (or manganese) that are applied to a block corundum carrier of honeycombed structure are capable to provide a high (up to 70–80 %) conversion of HC (propane) to a mixture of olefines (propylene and ethylene) under autothermal regimes with a yield as high as 50 % provided that the proportion of oxygen in the inlet mixture matches the stoichiometry of oxidizing dehydrogenation (propane/O_2 = 2) [48, 74, 75]. It has been possible to depress the formation of carbon oxides through adding water and CO_2 to the inlet mixture; however, selectivity with respect to methane remains significant (at least 10 %), which is controlled by cracking processes.

Attractive features of these catalysts are their resistance to carbonization and capacity to support the process under an autothermal regime with the inlet temperature of a mixture being 300 °C, even without additional application of platinum to them. This is a favourable distinction of the systems that are developed in the Boreskov Institute of Catalysis, SB RAS (Novosibirsk, Russia) from the recorded analogues that contain as much as 5 % of platinum on foam corundum [45]. Although testing of zirconium-phosphate catalysts in the course of oxidizing dehydrogenation is yet to be performed for HCs that are heavier than propane, it can be inferred by analogy with the results received in the work [45] that these systems will be also efficient in the reactions of diesel fuel conversion.

The use of OG from diesel engines as a source of oxygen, heat, water, and CO_2 will enable one to provide the required autothermal operation for the process and to reduce the probability for undesirable secondary processes of deep oxidation and cracking to occur. There were practically no works in the world in this direction, although these generators of efficient reducers, olefines mixed with synthesis gas, will be much more attractive as to the energy consumptions relative to the methods of fuel activation, such as plasma of corona discharge [46].

CATALYSTS OF SELECTIVE REDUCTION OF NITROGEN OXIDES BY SYNTHESIS GAS

Figure 7 displays a typical example of basic regularities for reduction of nitrogen oxides by synthesis gas in an excess of oxygen on Pd/Al_2O_3 catalyst. Peak efficiency for the removal of nitrogen oxides is achieved in a rather narrow temperature range (100–150 °C) with sufficiently high selectivity of hydrogen consumption for the reduction of nitrogen oxides. At higher temperatures, the complete transformation of synthesis gas leads to a decrease in the reduction efficiency to zero.

The acquired results are mostly in good agreement with the published data into catalytic properties of similar systems [37–40]. Development of the research in the given direction should include optimization of the composition of an active component (with the aim to increase the efficiency of its work under real conditions of OG of diesel engines and to expand the temperature field of the effective work) and methods of its applying to block carriers of various types, as well as parameters of the process of the reduction of nitrogen oxides that can be realized in a steady-state and in a periodic (more efficient) regime [33].

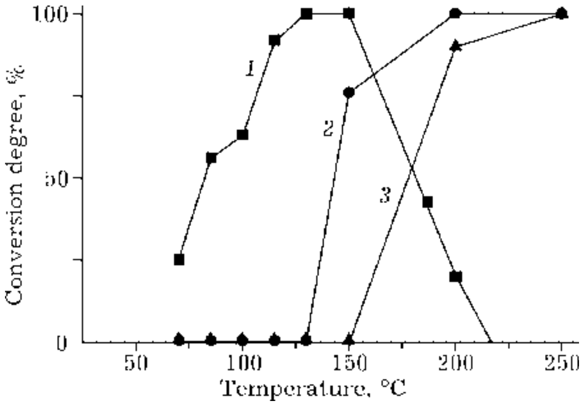

Fig. 7. Temperature dependences of the conversion degree of nitrogen oxides *(1)*, CO *(2)*, and hydrogen *(3)* in a mixture of 0.05 % NO + 0.54 % H_2 + 0.26 % CO + 10 % O_2 in He on Pd/Al_2O_3 catalyst. The load is 120 000 h^{-1}.

INTRODUCTION OF SYNTHESIS GAS IN THE ENGINE TOGETHER WITH THE MAIN FUEL OR INSTEAD OF IT

The synthesis gas generators (SGG) that were developed in the BIC, SB RAS, have been tested at a stand of the Togliatti State Polytechnical University (Togliatti, Russia) within the VAZ-2111 engine–SGG system. An efficiency of the ICE working process has been estimated by the amount of heat brought with the fuel, when it works on pure synthesis gas and at load regimes with its addition to the basic fuel (at a rate of up to 60 %). The efficiency increases: by 20 % at idling, and by 7–10 % at load regimes. With the synthesis gas generator, it is possible to effect the VAZ-2111 engine run on the fuel mixtures that have been leaned to an air excess coefficient (λ) equal to 3. Upon addition of synthesis gas, the content of nitrogen oxides in the leaned mixtures can be lowered down to 20 ppm [76]. With strongly leaned mixtures, the HC emission may somewhat rise; however, this problem can be easily solved by means of a simple oxidizing catalytic decontamination.

By analogy with the known publications [47, 61–63, 77], the given approach is also applied to advantage as regards diesel engines. Accordingly, it has been demonstrated during tests at the Research Institute of Automobile and Motor (Moscow, Russia) stands that the diesel engine runs stably even upon the complete replacement of liquid fuel with synthesis gas, which also ensures a decrease of nitrogen oxide emissions by several times (down to ≈50 ppm).

MIXED OXIDES AS OXIDATION CATALYSTS OF CARBON BLACK WITH NITROGEN DIOXIDE INVOLVED

Disperse oxides with perovskite structure (doped by cerium, bismuth, strontium, iron, or their combination, as well as by lanthanum manganite) or fluorite structure (cerium-zirconium solid oxidic solution doped by cations of manganese, cobalt, bismuth, niobium, and calcium) that were synthesized with the Pekini method [67, 78–80] were used as such oxides. In addition, the surface of these oxides was additionally modified by application of platinum. A sample of carbon black from the diesel engine of Icarus bus was taken for the investigaiton.

It has been found that the temperature of the beginning of the reaction of carbon black oxidation by air that is catalyzed by these systems is rather low (270–400 °C) and drops by 50–100 °C upon NO_2 addition into the mixture with oxygen. Large mobility of surface oxygen in manganites, especially those doped by bismuth [79, 80], promotes the beginning of oxidizing reaction of carbon black by pure oxygen at lowered temperatures. Figure 8 suggests that the reaction products for the latter system, specifically, water and CO_2, appear at the temperatures over 150 °C, and an increase of NO and NO_2 concentration in the gas phase is evidenced under a thermoprogrammed regime.

According to the known concepts [56–58, 81], a disintegration of nitrite-nitrate complexes that are accumulated on the surface of the catalysts is incident to the beginning of oxidizing reaction for carbon black in the given field of temperatures, which is accompanied by evolving of nitrogen oxides and by the formation of reactive speciations of superficial oxygen. It appears that it is these forms of oxygen that initiate oxidation process for a hydrocarbon part of carbon black at low temperatures [81] owing to the formation of oxygen-containing superficial groups.

In spite of an excess of oxygen in the gas phase, NO_2 from the gas phase is also involved in the process of soot oxidation, which is evident from a decrease of the concentration of this component and from an increase of N_2O concentration with growing temperature. Starting with 250–300 °C, oxygen from the gas phase is also involved along with NO_2 in the process of oxidation of carbon black. However, an intensive formation of N_2O, which correlates with the release of water and CO_2 at elevated temperatures too, testifies that nitrogen oxides are also involved in soot oxidation in the high-temperature field. It is believed that a more deep reduction of nitrogen oxides occurs, to form molecular nitrogen. To confirm this assumption, it is necessary to conduct special experiments with mixtures that are free from nitrogen as a diluting agent.

Application of platinum to manganite surface resulted in a relatively appreciable (by 50 °C) decrease of the beginning of the temperature of intensive oxidation of carbon

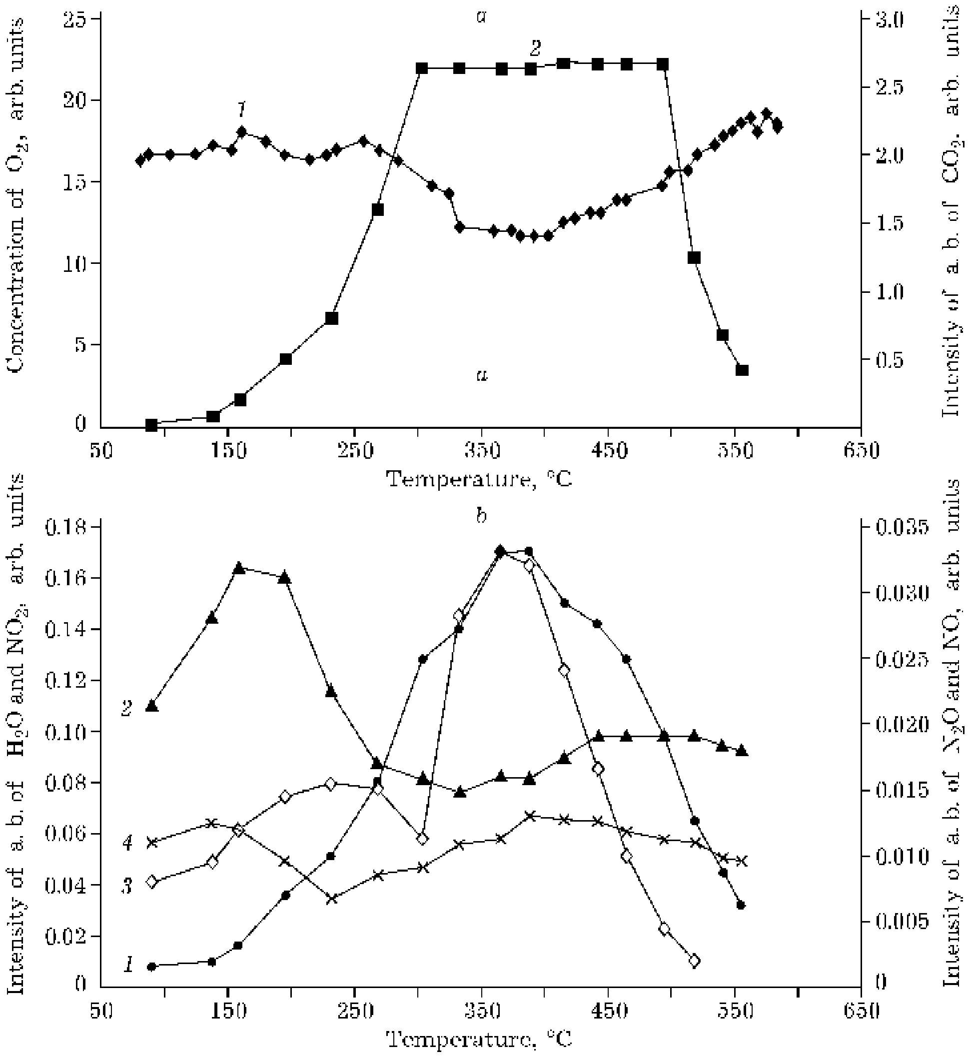

Fig. 8. Dependences of oxygen concentration and of the intensity of CO_2 absorption bands (a. b.), of changing intensity of a. b. of water, NO_2, NO, and N_2O at the outlet from the reactor during the temperatureprogrammed oxidation of carbon black by a mixture of 10.5 % O_2 + 0.5 % NO_2 + N_2, that have been obtained on a lanthanum manganite sample doped by bismuth (a batch of the sample was prepared by easy stirring of 300 mg of a catalyst and 30 mg of carbon black): *a* – O_2 (*1*) and CO_2, 2360 cm^{-1} (*2*); *b* – H_2O, 3730 cm^{-1} (*1*); NO_2, 1630 cm^{-1} (*2*); N_2O, 2210 cm^{-1} (*3*); NO, 1900 cm^{-1} (*4*).

black only for lanthanum manganite doped by iron. Taking into account a sufficiently high adsorption capacity of catalysts around disperse mixed oxides with respect to nitrogen oxides (as high as 1 cm^3 of NO (normal conditions) at ~200 °C), the systems around lanthanum manganite, along with alternative perovskites, can be employed as components of sooty filters for OG of diesel engines both with periodic regeneration and of passive type, that ensure removal of nitrogen oxides and smoke particles [54–58, 82–84].

CONCLUSION

The performed analysis demonstrates that the use of various catalytic processes to clear OG of diesel engines from nitrogen oxides opens prospects for a successful solution of the given problem. Full or partial replacement of diesel fuel with synthesis gas that is produced in compact generators onboard a car is seen to be the most radical approach. In this aspect, block catalysts and synthesis gas generators that are developed in the Institute of catalysis form a basis to conduct the necessary benchmark testing and trial runs.

Along with this technology, the approaches that are related to the use of catalytic methods for decontamination of OG of diesel engines from nitrogen oxides by selective catalytic reduction with diesel fuel or with products of its selective oxidation in compact generators (synthesis gas, olefines, or their mixture) remain rather attractive.

Progress in the development of these methods is due to the successes in the elaboration of new highly active, selective materials that are stable under real conditions of carrying out the catalytic processes, to take an example, such as zirconia-pillared ultramicroporous clays tolerant to sulphation.

Applied platinum metals show a high activity in the field of low temperatures for the process of reduction of nitrogen oxides by synthesis gas or by its mixture with olefines. Investigations in the given field should be directed to expand the temperature field of selective reduction of nitrogen oxides through modification of carrier properties and characteristics of the applied metals. Fluorite- and perovskite-like complex oxidic systems that are resistant to sulphation and capable to activate the oxidation of carbon black due to adsorption and activation of NO to form highly reactive NO_2 dioxide can be used to advantage in various types of sooty filters for a simultaneous removal of smoke particles and nitrogen oxides.

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