ESTIMATION OF NO_X CONVERSION INTO OXIDE, PLATINUM AND COMBINED OXIDE–PLATINUM SCR CATALYST

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Abstract

The paper contains the results of the tests of the oxide, platinum and combined oxide-platinum catalytic reactor model used in the NH_3-SCR system. As regards the combined oxide-platinum catalyst the first reactor block was extracted from the oxide catalyst used in trucks. As the second module of the reactor a block with platinum acting as a catalyst was used with 2.5g/dm^3 platinum load. The only differences between the combined reactor system and the single platinum and oxide catalysts were connected with the reactors volume which in the case of the single reactors was two times higher than the volume of the corresponding blocks of the combined system. During the tests the ammonia concentration in the engine exhaust gases at the inlet of the reactors was set to 400 ppm. The article contains the results of the physical and chemical active surface structure tests of the reactors with their active surface chemical microanalysis and its topographic pictures performed and taken with the Scanning Electron Microscope. The results obtained from the tests of the influence of the reactor type on the NO_X and NO conversion and the content of NO_2 in NO_X are presented in this article in the form of the function of their operating temperature. Additionally, the results of measured ammonia slip at the outlet of the reactors are presented. The obtained results have shown that the usage of the combined oxide-platinum reactor allows for widening the SCR system effective operating temperature range with a low ammonia slip at its outlet. This was achieved by use of the platinum reactor block which features a high nitric oxides conversion efficiency at the operating temperatures which are lower than those of the oxide catalyst and which can also provide the high ammonia spices conversion rangeto lower the ammonia slip at system outlet.

Keywords: *combustion engines, catalytic reactors, selective reduction, nitric oxides, air pollution*

1. Introduction

Currently, the main issues to be resolved as regards reducing the emissions of harmful substances generated in the Diesel engines include reduction of the nitric oxide emissions. The Euro 5 emission standard reduces the road emission of nitric oxides present in the Diesel engine exhaust gases to 0.180 g/km whereas the emission proposed for the future Euro 6 standard equals only to 0.080 g/km. One solution of this problem includes creation of the Diesel engine exhaust gas treatment system of high efficiency to remove nitric oxides present in these gases. The system using the selective catalytic reduction of nitric oxides performed by using ammonia - NH_3-SCR (*NH_3 - Selective Catalytic Reduction*) is the catalytic system, which allows for the effective reduction of the concentration of nitric oxides present in the Diesel engine exhaust gases. This method allows for the reduction of nitric oxides by using ammonia supplied to the exhaust gases before the reduction reactor. The main reactions connected with reducing nitric oxides in the reduction reactor discussed are as follows [1]:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O, \tag{1}$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O, \tag{2}$$

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O. \tag{3}$$

The above-specified reactions are connected with the reactions connected with reducing NO as well as NO_2, because the conventional NH_3-SCR systems include a reduction reactor behind the

OC (*Oxidation Catalyst*) reactor. By using such a catalytic system a part of NO is oxidised to NO_2 and the total concentration of NO_x present in the exhaust gases is a sum of the concentrations of nitrogen compounds present in the exhaust gases according to the following relationship:

$$NO_X = NO + NO_2 \cdot \tag{4}$$

The reactor of the NH_3-SCR system, which is now most widely used in commercial applications, is the oxide reactor, e.g. $V_2O_5/WO_3/TiO_2$ [2,3]. One of its basic disadvantages is the fact that the efficient reduction of NO_x present in the exhaust gases takes place at relatively high temperatures, which are hard to reach as regards the vehicles with Diesel engines in particular when they are used in cities. Another important oxide reactor disadvantage is the fact that great NH_3 escapes are detected during the NH_3-SCR system operation at the reduction reactor outlet almost at all catalytic conversion temperatures. This phenomenon may be controlled by using a platinum reactor or an oxide-platinum reactor system as a reduction reactor. The results of global tests of various types of reduction reactors used in the NH_3-SCR systems have shown that the reactors, which contain platinum acting as a catalyst, feature high NO_x conversion levels at temperatures lower than those of the oxide reactors [4] as well as lower NH_3 escapes when compared to the oxide reactors.

The work aims at determining and comparing the properties of the catalytic reduction reactors of the NH_3-SCR system as regards the ability of these reactors to reduce the NO_x concentration in the Diesel engine exhaust gases. Three types of reactors have been analysed: platinum, oxide and the modular oxide-platinum reactor. Moreover, the NH_3 escape levels have been analysed behind each of the reactors tested to find the solution to achieve the highest NO_x conversion levels at a minimum ammonia escape level.

2. Testing reactors

Three testing reactor models have been selected to test the NO_x conversion properties. Two models: oxide and platinum reactors were uniform cylindrical reactors and their dimensions were as follows: diameter: ϕ = 42 mm and length: l = 90 mm. The active layer composition and the reactor solid construction were as follows:

- the oxide reactor was cut out of the mass-produced NH_3-SCR system reactor insert, which is mounted in trucks. The reactor solid was made of cordierite ($MgOAl_2O_35SiO_2$) with the ducts packing density of 300 cpsi. The exact chemical composition of the active layer of this reactor was not known and it was roughly specified on the basis of the physical and chemical tests,
- the platinum reactor was built on a twisted steel foil carrier with the cell packing density of 400 cpsi (*cpsi – cells per square inch*). The reactor solid was covered with an intermediate layer of aluminium oxide ($Al_2O_{3)}$ in the amount of 47g/dm^3 and then it was impregnated with 2.5g/dm^3 of platinum.

The third tested reactor was a modular oxide-platinum reactor mode of two blocks. The first block was the oxide reactor block and the other one was the platinum reactor block. To prevent the identical dimensions of all the reactors tested the modular reactor blocks were cylindrical and their diameter was ϕ=42mm but its length was half as long as the uniform reactors and equalled to l=45mm. Both modular reactor blocks featured as same base and catalytic coating as those of their equivalents (uniform reactors) mentioned above. The pictures of the reactor models tested are shown in Fig. 1.

The physical and chemical tests of the active surfaces of the oxide and platinum reactors have been performed with SEM (*Scanning Electron Microscope*). The oxide and platinum modular reactor blocks were cut out of their equivalents (uniform reactors). Thus, it was assumed that the construction and composition of the active surfaces were the same as those of the uniform reactors were. The figures below present the topographic pictures of the oxide and platinum reactor surfaces with a magnification of 5,000 x and the results of the local microanalysis of the chemical composition of their active layers.

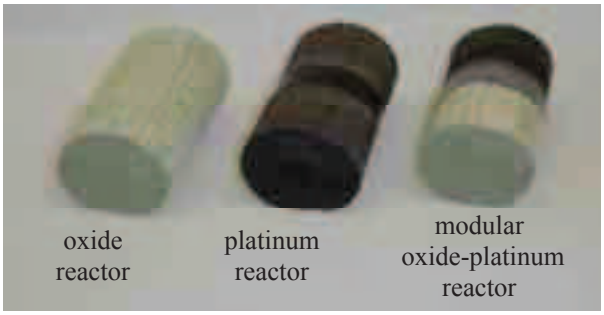

Fig. 1. A picture of three reduction reactor models tested used in the NH_3-SCR system

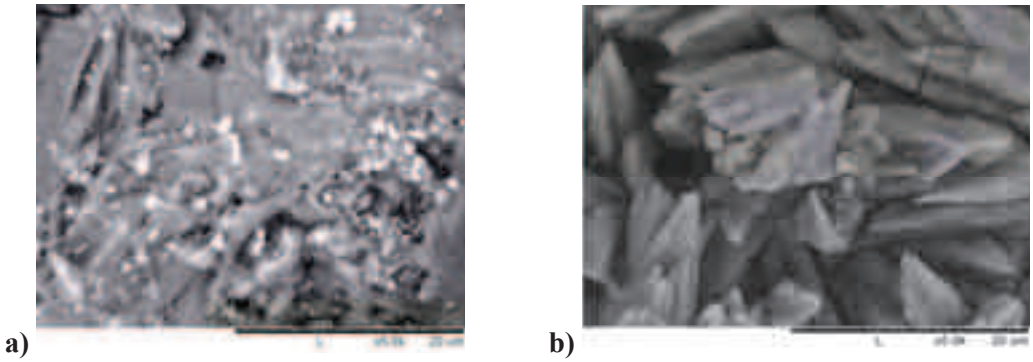

Fig. 2. The topographic pictures of the active surfaces with a magnification of 5,000 x concerning the following reactors: a) oxide reactor, b) platinum reactor

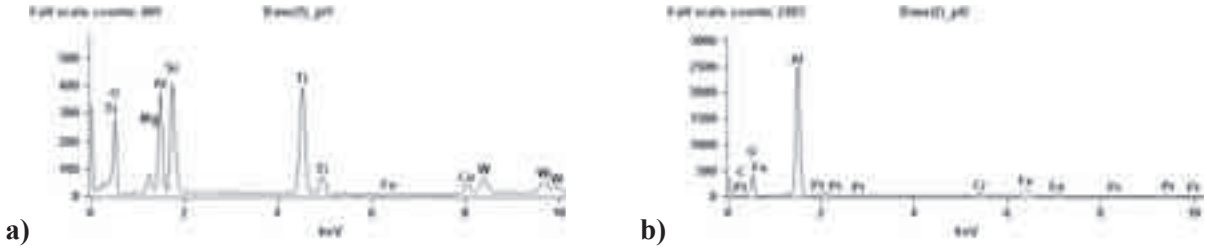

Fig. 3. The results of the local microanalysis of the chemical composition of the active layers of the following reactor: a) oxide reactor, b) platinum reactor

Basing on the results obtained from the tests of the active surface of both reactors, we may say that titanium oxide (TiO_2) and probably tungsten trioxide (WO_3) are the main catalytic compound of the oxide reactor. As regards the platinum reactor platinum (Pt) is the only identified catalytic compound with aluminium oxide (Al_2O_3) as the intermediate layer. The other compounds that may be seen in the spectrum of both reactors probably come from the ceramic oxide reactor solid layer and the steel solid in the case of the platinum reactor.

3. A testing stand

To perform the tests a stand was built as shown in Fig. 4. The Perkins 1104-C engine was used as the exhaust gas generator. During the measurements the engine was operating at a constant rotational speed of n = 1,400 rpm and with a constant load of M_e = 200 Nm. As mentioned in the Introduction during the ammonia NO_x reduction process the reactions connected with reducing NO and NO_2 also take place. Owing to that, the engine exhaust system was equipped with the OC reactor. Its purpose was to oxidise some NO present in the exhaust gases in huge amounts to NO_2. Under such engine, operation conditions NO to NO_2 conversion equalled to 37%. There was a nozzle installed behind the oxidation reactor, which was used to add ammonia of the appropriate concentration to the engine exhaust gases.

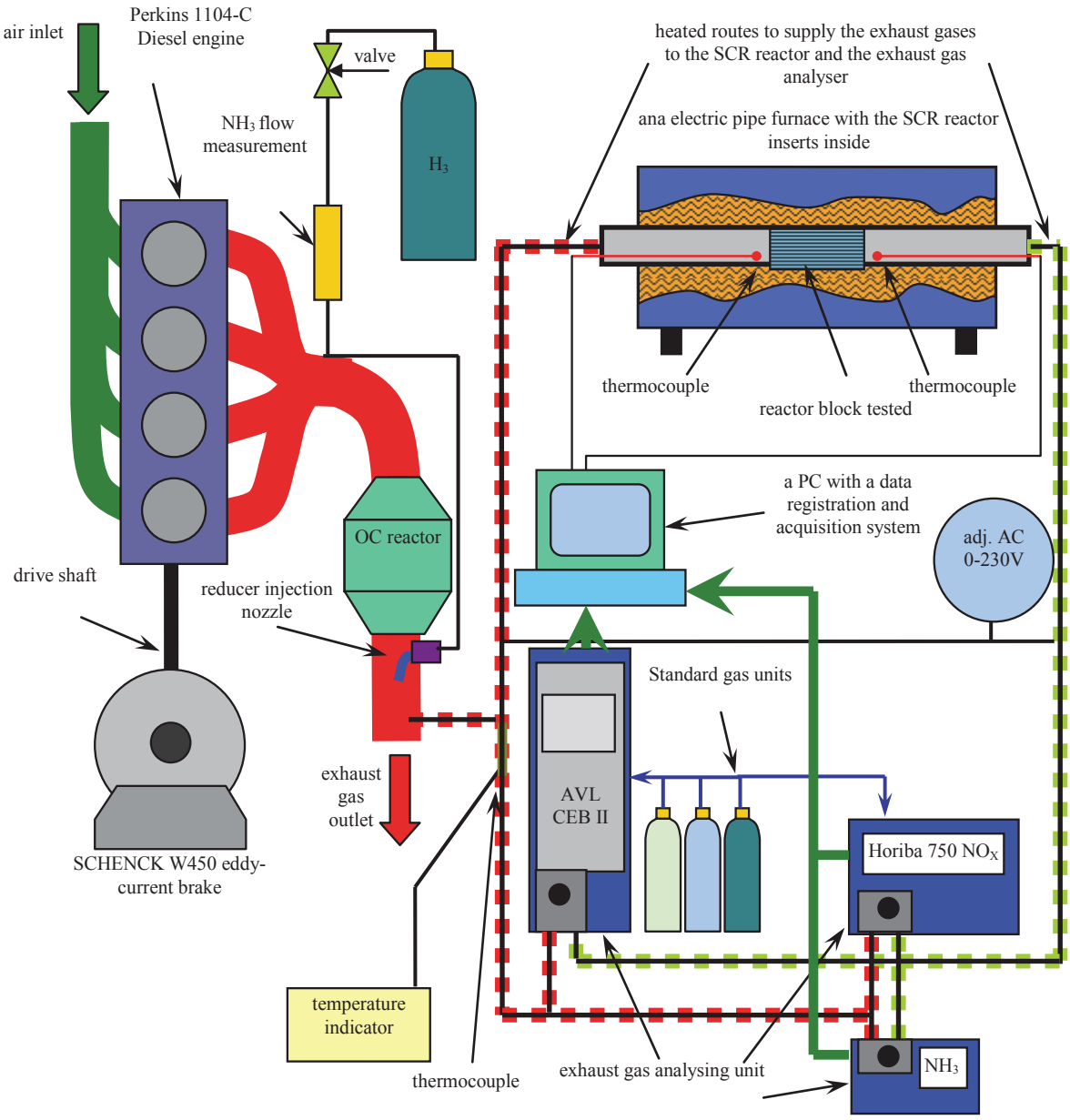

Fig. 4. A diagram of the testing stand used for testing the catalytic properties of the NH_3-SCR system reactor models

To avoid the undesirable connection of ammonia and water (ammonia liquor preparation) NH_3 was dosed into the engine exhaust system when all components of the measurement sections, which contained the exhaust gases, were heated up to over 100°C. The tests were performed with the concentration of ammonia present in the engine exhaust gases of 240, 320 and 400 ppm The ammonia flow was adjusted with a rotameter and controlled with a GFM 430 analyser. The exhaust gases containing ammonia were routed to the exhaust gas analysing units where the concentrations of the individual toxic compounds were recorded. At the next stage of measurements, the exhaust gases were routed to the PR 90/1100 K electric pipe furnace through the heated gas routes and the tested reactor was placed inside the furnace. As regards the tests of the modular reactor, the individual reactor blocks were placed so that the oxide reactor block was the first block at the furnace inlet with the platinum reactor block placed behind it. It was possible to set and adjust the catalytic process temperature precisely by using the electronic furnace controller. The tests were carried out at temperatures of 150-550°C. When the furnace was empty of the exhaust gases these gases were routed to the exhaust gas analysers again where the toxic compound concentrations were continuously recorded. At the same time, the

thermocouples installed before and behind the tested catalytic reactor measured and recorded the exhaust gas temperatures at the reactor inlet and outlet. This was the basis for determining the temporary catalytic process temperature.

4. Test results

The NO_x, NO and NO_2 concentrations recorded during the tests were used to determine the temporary conversions of these compounds by using the tested reactor operating temperature function. Fig. 5-7 show the comparison of the changes in the NO_x and NO conversion and the content of NO_2 in NO_x as regards three tested reduction reactor models used in the NH_3-SCR system. Moreover, Fig. 5 presents the characteristic reactor operating parameters. To make the chart clearer the reactors are marked with the acronyms. The types of the reactors are indicated with the following symbols: T - concerns the oxide reactor, P - concerns the platinum reactor and T/P - concerns the modular oxide-platinum reactor. During the tests, the concentration of ammonia present in the engine exhaust gases equalled to 400 ppm, which meant that the content of NH_3 in relation to NO_x equalled to 0.8. Moreover, the measured values of the NH_3 slip, which takes places behind the reactors, are shown in Fig. 5.

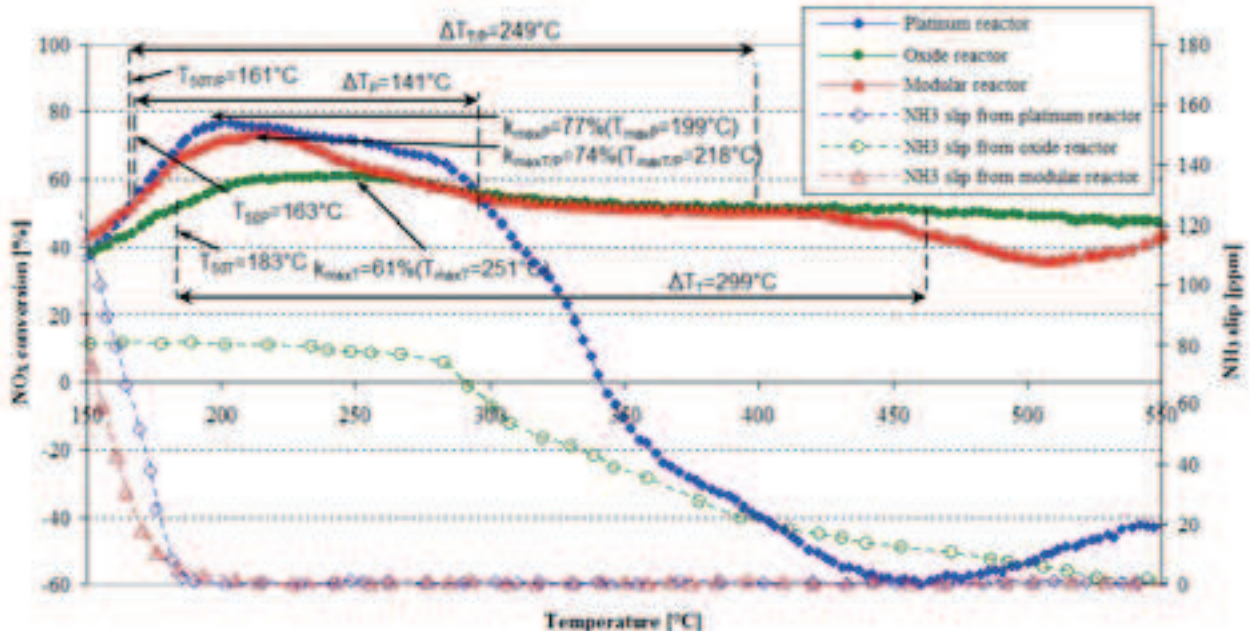

Fig. 5. A comparison of the changes in NO_x conversion in the reduction reactors of the NH_3-SCR system with the NH_3 concentration in the exhaust gases of 400 ppm together with the NH_3 escape values measured

The results of tests of the reduction reactor models used in the NH_3-SCR system have shown that the NOx conversion changes in the case of the modular oxide-platinum reactor are similar to those of the oxide reactor. The main difference between these two reactors is that the efficient conversion of nitric oxides performed with the modular reactor begins at lower temperatures (T_{50}) when compared to the oxide reactor but the conversion temperature range (ΔT) is smaller. When compared to the oxide reactor the maximum NO_x conversion level in the case of the modular reactor is achieved at a lower temperature (T_{max}). The worst nitric oxide conversion parameters as regards the possibility to use such a reactor as a complete NH_3-SCR system reactor were achieved in the case of the platinum reactor where the undesirable negative conversion of this toxic compound takes place at the temperatures of over 345°C. The NH_3 escape results obtained behind the reactors have shown that in the case of the modular and platinum reactors the ammonia escape level decreases rapidly and approaches zero already at the temperatures of about 200°C and this situation is different than that which takes place in the case

of the oxide reactor where the NH_3 concentration behind the reactor decreases gradually and approaches zero only at the last catalytic conversion temperatures. At the same time, it was observed (Fig. 7) that in the case of the modular and platinum reactor with the temperatures of about 250 - 450°C NO_2 is the main component of NO_x that are still present in the exhaust gases. This fact may be used at the next Diesel engine exhaust gas treatment phase in terms of the CRT particulate filters. Tab. 1 presents a list of the characteristic operational parameters of the reactors tested. Moreover, the table presents the average content of NO_2 in NO_X ($U_{NO2śr}$) and the average NH_3 escape ($S_{NH3śr}$) measured at all the reactors tested at all the analysed catalytic conversion temperatures.

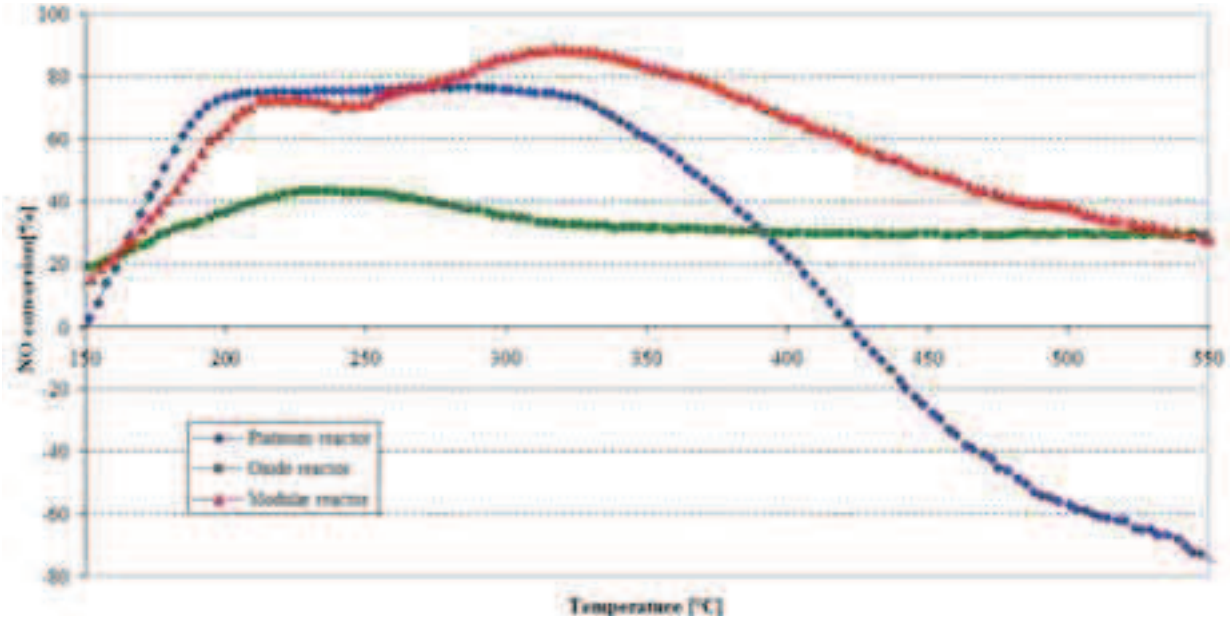

Fig. 6. Changes in NO conversion in the reduction reactors of the NH_3-SCR system with the NH_3 concentration in the exhaust gases of 400 ppm

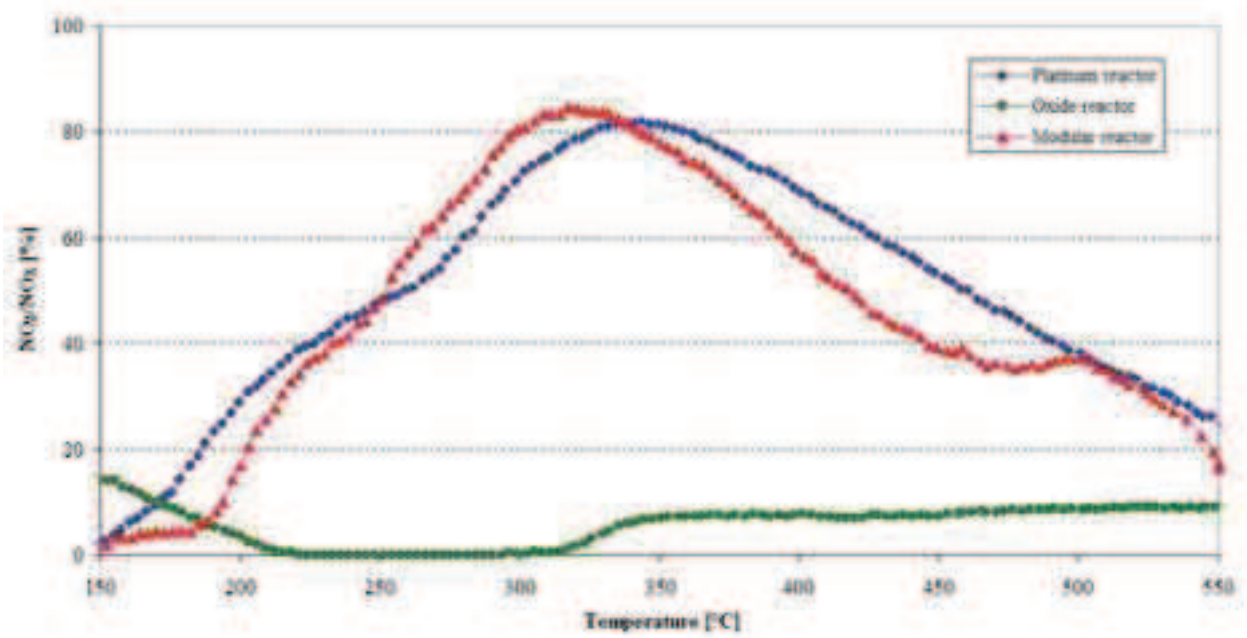

Fig. 7. Changes in the content of NO_2 in NOx in the reduction reactors of the NH_3-SCR system with the NH_3 concentration in the exhaust gases of 400 ppm

Tab. 1. The characteristic operational parameters of the reduction reactors used in the NH_3-SCR system

Reactor type	The characteristic operational parameters of the reduction reactors					
-	T_{50}	ΔT	k_{max}	T_{max}	$S_{NH3śr}$	$U_{NO2śr}$
-	°C	°C	%	°C	ppm	%
platinum	163	141	77	199	14.1	50
oxide	183	299	61	251	43.1	5.5
modular	161	249	74	218	8.5	46

4. Conclusions

Basing on the results obtained from the tests of the reduction reactors used in the NH_3-SCR system the following conclusions have been drawn:

- the modular oxide-platinum reactor features the best properties in terms of the nitrogen compound conversion as regards using of this reactor in the complete catalytic system,
- in the case of the modular oxide-platinum reactor and the oxide reactor the NO_x conversion history is similar and it is positive at all catalytic conversion temperatures (150-550°C),
- when compared to the oxide reactor the higher maximum NO_x conversion level of 70% in the case of the modular oxide-platinum reactor is achieved at a lower operating temperature of 218°C,
- the oxide reactor features the greatest temperature range (299°C) of the efficient NO_x conversion of all the reactors tested,
- the platinum reactor features the highest maximum NO_x conversion level of 77% at the lowest operating temperature of 199°C but in this case the undesirable negative conversion of this toxic compound takes place at the temperature of over 445°C,
- the best performance in terms of reducing the NH_3 escape level was observed in the case of the modular and platinum reactors, which featured the ammonia escape level, which approached zero already at the temperatures of about 200°C. As regards this issue, the operating parameters of the oxide reactor were far worse as the average NH_3 escape level assessed for all operating temperatures of this reactor equalled to 43.1% in relation to the platinum and modular reactors whose levels equalled to 14.1% and 8.5% respectively,
- as it was found in the case of the modular oxide-platinum reactor and the platinum reactor with the temperatures ranging from 250 to 450°C there were high NO to NO_2 conversion levels and this phenomenon may be used at the next phase in terms of the CRT particulate filters mounted in the Diesel engines.

References

[1] Lambert, Ch., Williams, S., Carberry, B., Koehler, E., Tomazic, D., *Urea SCR and CDPF System for a Tier 2 Light-Duty Truck,* Aachener Kolloquium Fahrzeug und Motorentechnik 2006.

[2] Gieshoff, J., *Improved SCR Systems for Heavy Duty Applications*, SAE Paper No. 2000-01-0189, SAE International, Warrendale, PA 2000.

[3] Janssen, J., *Environmental Catalysis – Stationary Sources*, in Handbook of Heterogeneous Catalysis. Ertl G., Wiley J., pp. 1636-1644, New York 1997.
[4] Heck, R. M., *Operating Characteristics and Commercial Operating Experience with High Temperature SCR NO_X Catalyst*, Environmental Progress 13,4, pp. 221-225, 1994.