EXAMINATION OF THE AMMONIA DOSE INFLUENCE ON NITRIC OXIDES TRANSFORMATIONS INTO COMBINED OXIDE-PLATINUM SCR CATALYST

Wojciech Kamela, Stanisław Kruczyński

Warsaw University of Technology
Institute of Vehicles
Narbutta Street 84, 02-524 Warszawa, Poland
tel.: +48 22 2348781, fax: +48 22 8490303
e-mail: w.kamela@simr.pw.edu.pl, skruczyn@simr.pw.edu.pl

Abstract

This paper presents the test results obtained from the combined oxide-platinum catalytic reactor used in the NH_3-SCR system. 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. During the tests the ammonia concentrations in the engine exhaust gases at the inlet of the reactor system were set to 240, 320 and 400 ppm. The article contains the results of the physical and chemical active surface structure tests of both reactor blocks with their active surface chemical microanalysis and its topographic pictures performed and taken with the Scanning Electron Microscope. The results of the NO_X and NO conversion and the content of NO_2 in NO_X are presented in this paper as the function of combined reactors system operating temperature with three different ammonia concentrations in the exhaust gases. Additionally, the results of the measured ammonia slip at the outlet of the combined reactor were presented. The obtained results have shown that the increase in ammonia dose at the inlet of the system increases the nitric oxides conversion with the minimum influence on the ammonia slip. By using the platinum based catalyst block it was possible to widen the whole reactor system effective operating temperature due to the high nitric oxides conversion efficiency of the platinum block achieved at low operating temperatures. A low ammonia slip at the outlet of the combined catalytic reactor was obtained by use of the platinum reactor block whose properties allow for the high ammonia conversion.

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

1. Introduction

Currently, the main problems to be resolved in terms of reducing the emitted harmful substances which may be found in Diesel engines include the need to create a catalytic system of high efficiency to reduce the concentration of nitric oxides present in the engine exhaust gases. The Euro 5 emission standard which is currently in force reduces the road emission of nitric oxides present in the Diesel engine exhaust gases to 0.180 g/km whereas the value proposed for the Euro 6 standard which is to become effective soon equals only to 0.080 g/km. The selective catalytic reduction of nitric oxides performed by using ammonia - NH_3-SCR (*NH_3 - Selective Catalytic Reduction*) - is one of the solutions to reduce the concentration of nitric oxides present in the Diesel engine exhaust gases. This method includes 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 reactors 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 refer both to the reactions connected with reducing NO and NO_2, because the conventional NH_3-SCR systems include a reduction reactor behind the OC (*Oxidation Catalyst*) reactor. Owing to this solution 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:

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

The most popular reduction reactor of the SCR system of the discussed type is now the oxide reactor e.g.: $V_2O_5/WO_3/TiO_2$ [2, 3]. One of its major 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 at its outlet almost at all catalytic conversion temperatures. This problem may be resolved by using a platinum reactor or an oxide-platinum reactor system as a reduction reactor. The results of global research have shown that the above-mentioned reactor features 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 presented work contains the results of the tests of the modular oxide-platinum reactor used as a reduction reactor of the NH_3-SCR system. The tests were performed with reference to the assessment of the ability of this reactor to convert NO_x present in the engine exhaust gases with various ammonia doses in the exhaust system. The impact of the NH_3 dose on the ammonia escape levels achieved behind the reactor was also assessed.

2. A testing reactor

A testing reactor was the modular reactor with the first block in the form of the oxide reactor and the other block in the form of the platinum reactor. Both block were cylindrical and their dimensions were as follows: diameter: ϕ = 42 mm and length: l = 45 mm. The picture of the testing reactor and its blocks is shown in Fig. 1. The active layers composition and the structure of the individual reactor blocks were as follows:

- the oxide reactor block 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 cell 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 block 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.

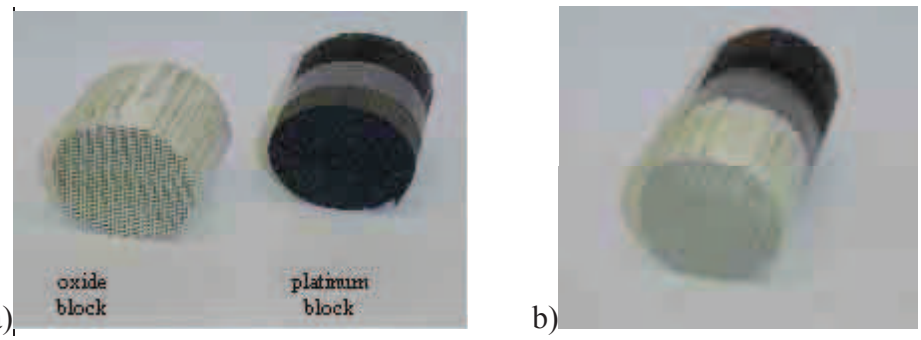
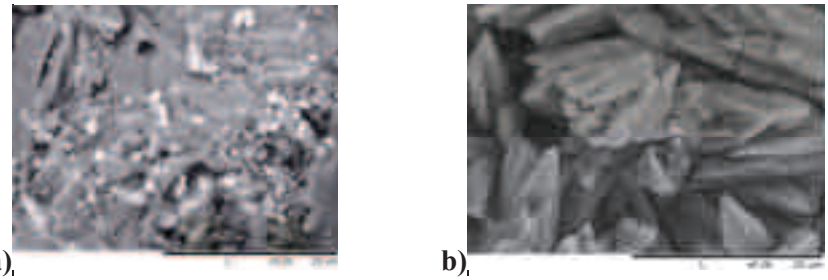


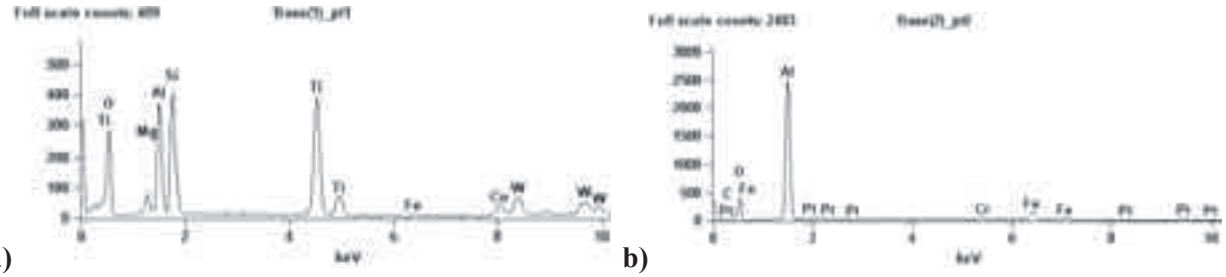
Fig. 1. A picture of the modular oxide-platinum testing reactor: a) reactor blocks, b) reactor

The physical and chemical tests of the active surfaces of both modular reactor blocks have been performed with SEM (*Scanning Electron Microscope*). The figures below present the topographic pictures of the oxide and platinum block surfaces with a magnification of 5,000 x and the results of the local microanalysis of the chemical composition of their active layers.



a) b)

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



a) b)

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

The results of tests of the active surfaces of both modular reactor blocks show 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 block platinum (Pt) is the only identified catalytic compound with aluminium oxide (Al_2O_3) as the intermediate layer. The other compounds which may be seen in the spectrum of both reactors probably come from the ceramic oxide reactor block solid layer and the steel layer in the case of the platinum reactor block.

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 to NO_2 some NO present in the exhaust gases in huge amounts. 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. 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 modular reactor was placed inside the furnace. 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.

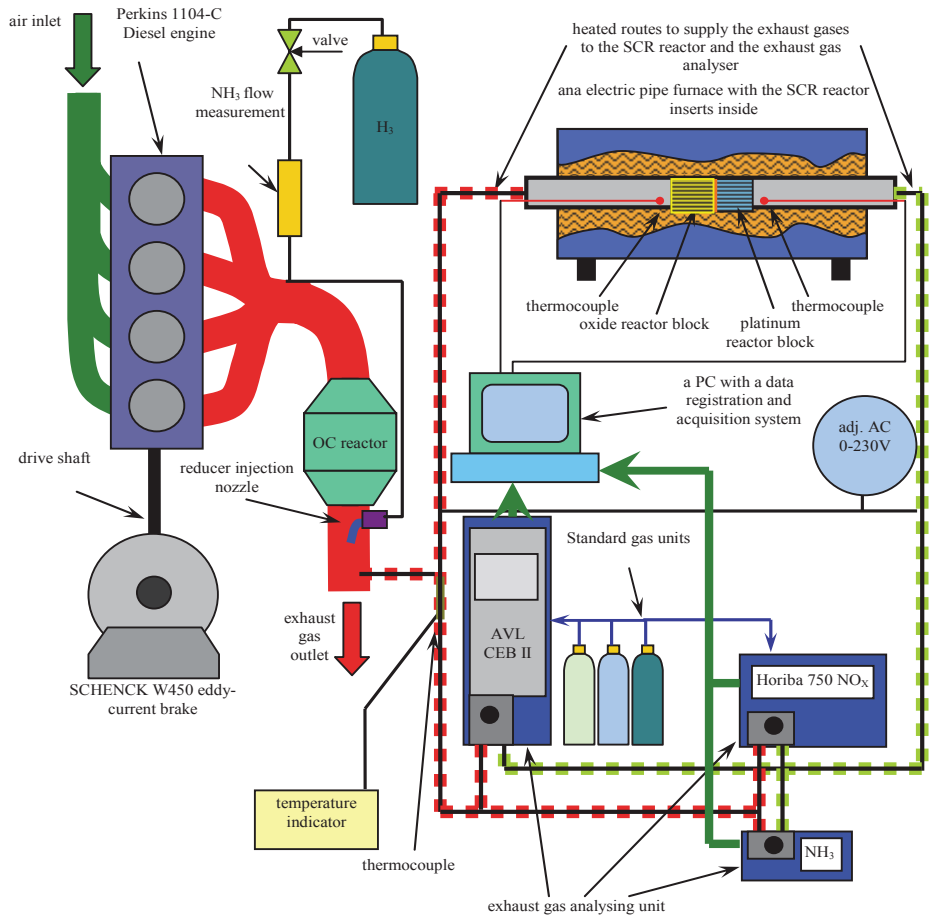


Fig. 4. A block diagram of the testing stand used for testing the catalytic properties of the NH_3-SCR system reactor models

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. Bench test results

Basing on the NO_x, NO and NO_2 concentrations recorded during the tests it was possible to calculate the temporary NO_x and NO conversion values and the content of NO_2 in NO_x by using the reactor operating temperature function. Fig. 5-7 present the test results obtained with the concentrations of ammonia supplied to the reactor inlet of 240, 320 and 400 ppm respectively which equalled to the content of NH_3 in relation to NO_x of 0.5, 0.65 and 0.8 respectively. Moreover, the measured value of the NH_3 escape which takes places behind the reactor is shown in the charts.

The test results obtained have shown that by using the modular oxide-platinum reactor we may achieve the relatively high nitric oxide conversion levels at many temperatures only when the ammonia concentration at its inlet equals to the maximum value out of the three tested values. As shown in Fig. 5 when the ammonia dose at the reactor inlet is increased the 50% conversion temperature (T_{50}) is lowered, the 50% conversion temperature window (ΔT) is widened and the maximum nitric oxide conversion levels (k_{max}) are higher. At the same time, it was observed that when the NH_3 dose is bigger at the reactor inlet, the temperatures at which the maximum nitric oxide conversion takes place (T_{max}) are slightly higher. As it was found in all analysed cases, as soon as the temperature exceeds 200°C the NH_3 escape levels achieved behind the reactor are lower and approach zero. Tab. 1 contains a list of the characteristic parameters of the tested reactor operation. Moreover, it

was observed (Fig. 7) that in the case of a modular reactor with the temperatures of about 250-450°C NO_2 is the main component of NO_x which 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.

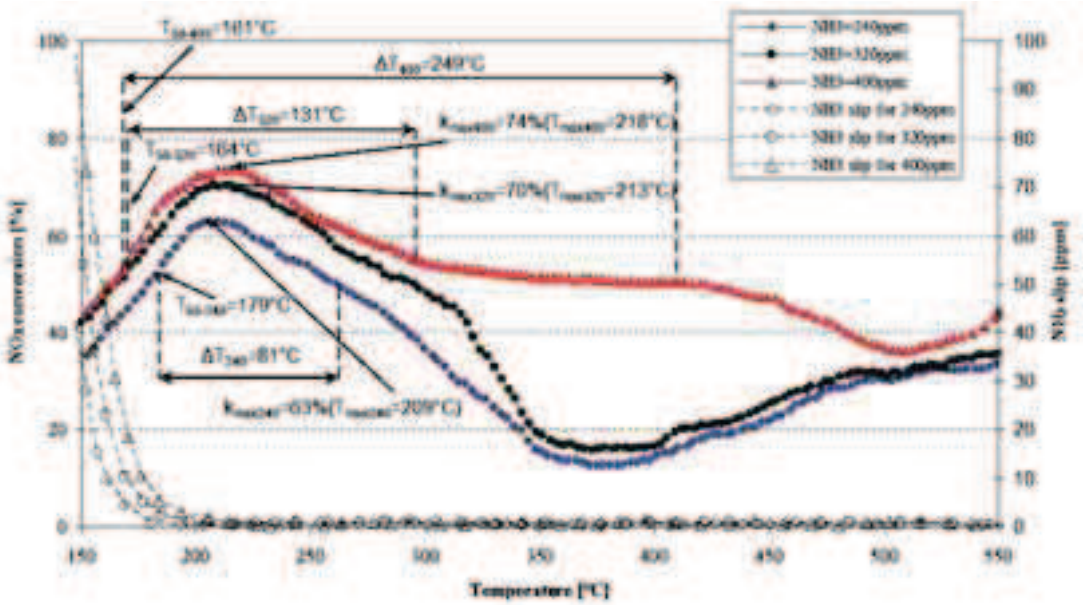


Fig. 5. Changes in NO_x conversion in the modular oxide-platinum reactor of the NH_3-SCR system with the NH_3 concentrations of 240, 320 and 400 ppm together with the NH_3 escape values measured

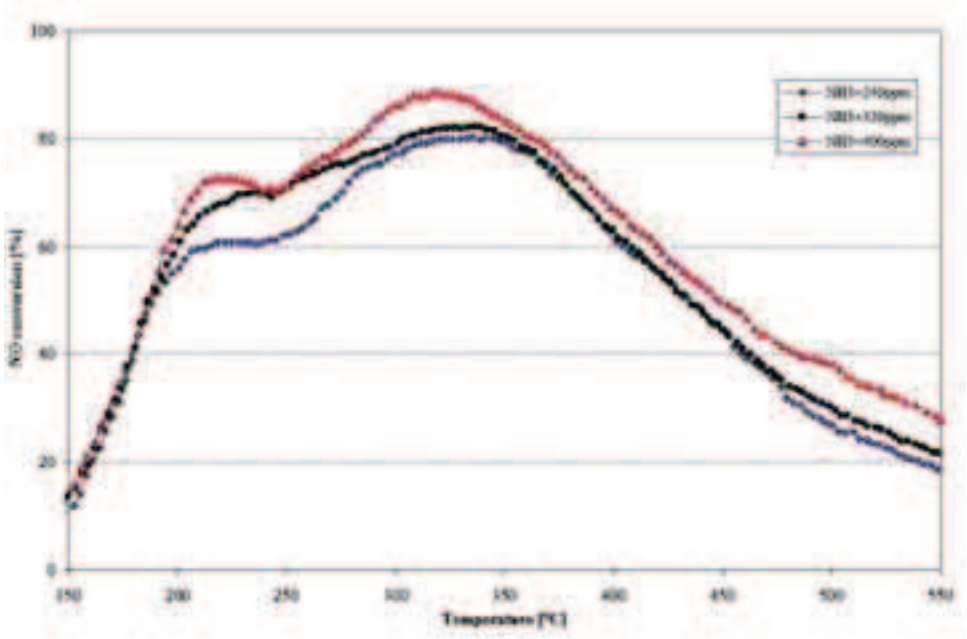


Fig. 6. Changes in NO conversion in the modular oxide-platinum reactor of the NH_3-SCR system with the NH_3 concentrations of 240, 320 and 400 ppm

Tab. 1. The characteristic parameters of the modular oxide-platinum reactor operation

	The characteristic parameters of the modular oxide-platinum reactor operation			
NH_3 concentration	T_{50}	ΔT	T_{max}	k_{max}
ppm	°C	°C	°C	%
240	179	81	209	63
320	164	131	213	70
400	161	249	218	74

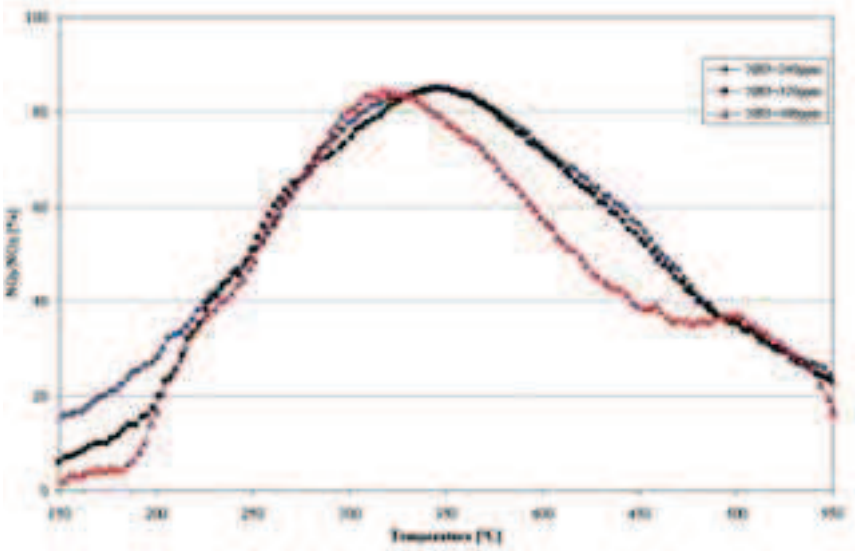


Fig. 7. Changes in the content of NO_2 in NO_x in the modular oxide-platinum reactor of the NH_3-SCR system with the NH_3 concentrations of 240, 320 and 400 ppm

4. Conclusions

Basing on the results obtained from the tests of the reduction, modular oxide-platinum reactor of the NH_3-SCR system the following conclusions have been drawn:

- the tested reactor achieves the positive NO_x conversion levels at all the analysed catalytic conversion temperatures ranging from 150 to 550°C for all the analysed concentrations of NH_3 supplied to its inlet,
- the tested reactor achieves high NO_x conversion levels at many temperatures only for the highest tested concentration of NH_3 supplied to its inlet which equals to 400 ppm,
- when the NH_3 concentration is higher at the reactor inlet the 50% NO_x conversion temperature is lower where this parameter equalled to 161°C for the NH_3 dose of 400 ppm at the reactor inlet,
- when the NH_3 concentration is higher at the reactor inlet the 50% NO_x conversion temperature window is widened. This parameter equalled to 249°C with the highest analysed NH_3 concentration of 400 ppm,
- when the NH_3 concentration is higher the maximum NO_x conversion raises to 74% for the ammonia dose of 400 ppm and the conversion temperature is slightly higher,
- as it was found in all analysed cases, as soon as the temperature exceeds 200°C the NH_3 escape levels achieved behind the reactor are much lower and approach zero. The reason behind such a situation is probably connected with using the platinum reactor block with high oxidizing properties,
- as it was found in all analysed cases where NH_3 was dosed 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

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