CHEMICAL DEACTIVATION OF A THREE WAY EXHAUST GAS CATALYTIC REACTOR USING SULFUR COMPOUNDS

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INTRODUCTION

Reduction efficiency of carbon monoxide, hydrocarbons and nitric oxides emission for a fully functional three way catalytic reactor running in steady state at appropriate temperatures and A-F mixture composition close to stoichiometric, considerably exceeds 90%. Long-lasting use of the reactor causes its ageing and unavoidable deactivation process of catalytic layer. Changes of structure and chemical constitution of catalyst bed take place, with simultaneous deposition of layers of different chemical compounds, blocking the access to the catalyst. Extreme operating conditions, complicated construction and low contents of precious metals may easily make catalysts susceptible to deactivation, at the same time making them a difficult subject of research and tests.

Deactivation of exhaust gas catalytic reactor may result from different processes that may be divided into the following groups [1]:

1. Chemical processes, including adsorption of poison precursors and progressive poisoning, consisting of surface structure modifications and chemical blocking of active areas.
2. Thermal processes, including changes of carrier and metal crystallites structure, sintering, oxidation and creation of precious metals alloys, and evaporation of metals.
3. Mechanical processes, including generation of stresses as a result of thermal shocks and jolts causing friction and crushing of monoliths and carrier.

During normal operation of catalytic reactor, deactivation processes may proceed according to all the above mentioned mechanisms. At the actual level of manufacturing technique and operation of exhaust gas catalytic reactors, deactivation through mechanical processes takes little part to deactivation as a whole. Thermal deactivation together with chemical deactivation predominate.

CATALYST POISONING PROCESSES

Catalysts are poisoned by different matters that can be found in fuel or lubricating oils. Deactivation nature is different, depending on whether the poison acts by bonding with catalyst active phase, or by mechanical blocking catalyst pores and hindering the access of gases to active zone. The most often met catalyst poisoning in normal use is the poisoning with lead, sulfur and phosphorus compounds.

Poisoning with lead. In contact with the catalyst, and depending on temperature, lead may be in volatile form (PbO, $PbCl_2$, $PbBr_2$), or in the form of small particles carried in gas [PbO, $PbSO_4$, $Pb_3(PO_4)_2$], or even in the form of large grain detached from exhaust pipe walls. Vapors penetrate catalyst pores, whereas particles remain on the carrier surface. Most of the lead is deposited on the carrier, and only a small part of the lead is deposited on crystals of precious metals. Palladium is more susceptible to poisoning than platinum. Catalysts poisoned due to chemical effects connected with the coating of precious metals crystals may be regenerated by heating at about 500°C in lead-free atmosphere. In normal use, residual lead contents in lead-free fuel equal to 3 mg/dm^3 does not cause any problems, while 10 mg/dm^3 causes visible deactivation.

Poisoning with sulfur is caused mainly by sulfates being the result of reactions with transitory metals. Creation of sulfates requires oxidation of SO_2 to SO_3. This reaction is catalyzed by oxidizing catalysts as a result of adsorption of sulfur on metal particles and oxidation to SO_3. In this case three way catalysts show lower activity due to rhodium presence. However, SO_2 itself also influences the activity of the three way catalyst, reducing CO, HC and NO_x conversion. Especially cerium is able to adsorb, store and release sulfur. Sulfur may react with carrier oxides, e.g. with Al_2O_3 or CeO_2 giving sulfates of metals. Aluminum and cerium sulfates are formed, but sulfur prefers reacting with CeO_2 in one of the following reactions [2]:

$$2CeO_2 + 3SO_2 + O_2 \rightarrow Ce_2(SO_4)_3$$

$$6CeO_2 + 3SO_2 \rightarrow Ce_2(SO_4)_3 + 2Ce_2O_3$$

$$2SO_2 + CeO_2 + O_2 \rightarrow Ce(SO_4)_2$$

Under reducing conditions, cerium sulfate decomposes in the temperature of about 550-750 K giving sulfur dioxide, that then reacts easily with hydrogen, adsorbed on well-dispersed particles of precious metals, giving hydrogen sulfide:

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$$

Sulfur, stored in the form of hydrogen sulfide, may be rapidly released through variations of exhaust gas composition. During short periods, the concentration of hydrogen sulfide may considerably exceed human smell limit, i.e. 0.02-0.03 ppm.

Poisoning with phosphorus is the result of fuel pollution as well as additives to lubricating oils. Phosphorus contents in lead-free fuels is much lower than in lubricating oils (~0.02 mg/dm^3 of fuel and ~1.2 g/dm^3 of oil). After a mileage of 80 000 km, a three way catalyst may be polluted with 13 g of phosphorus, 93% of which comes from lubricating oil. There is a strong connection between the decrease of CO, HC and NO_x conversion and phosphorus contents in oil. Phosphorus influences the accuracy of lambda sensor, as well as the catalyst's ageing through a decrease of carbon monoxide conversion factor. The influence on conversion of nitric oxide and hydrocarbons is lower. Chemical forms in which phosphorus is retained in the catalysts are still poorly known. Zinc phosphates and aluminum phosphates, as well as phosphates of alkaline earths were discovered, deposited on the carrier's surface.

POISONING WITH SULFUR COMPONENTS TESTS OF A CATALYST

Tests were carried out using Pd/Rh-Al_2O_3/CeO_2 three way exhaust gas catalytic reactor, used in an exhaust system of a small-engine car. The principal characteristics of the catalyst is given in Table 1.

Table 1. Principal characteristics of catalytic reactor

Monolith material	Heat-resisting steel foil
Reactor volume	1034 cm^3
Number of ducts	62/cm^2
Wall thickness of foil	0,05 mm
Intermediate layer material	$\gamma Al_2O_3/CeO_2$
Precious metals	Pd/Rh = 5/1
Contents of precious metals	1.76 g/dm^3

Tests of chemical deactivation of catalysts were carried out at a test stand fitted with a Rover 1.4 engine, using a test worked out at the Institute of Vehicles [1]. The engine's operating conditions during the test were selected so as to obtain, during 100 hours of the engine run on the test stand, the intensity of ageing and poisoning of the catalyst bed corresponding to a mileage of 100 000 km for a vehicle. The test consists of ten hour cycle, each of them beginning with a six hour engine running period under conditions assuring exhaust gas temperature upstream the catalyst at t_{sp} = 750ºC level. Relative volumetric flow velocity of exhaust gas during that operating period is equal to SV = 44 000 h^{-1}. During that operating period, high instantaneous oxygen concentrations are forced in catalytic reactors through cutting off fuel supply every 10 seconds for 2 seconds, to cylinders 1 and 2, then to cylinders 3 and 4, alternately.

The next four hours of the engine run, assuring exhaust gas temperature upstream the catalyst at t_{sp} = 800ºC level, with relative volumetric flow velocity of exhaust gas equal to SV = 50 000 h^{-1}, are used for stabilizing and intensifying catalyst poisoning processes. During the test the engine consumes approximately 1600 dm^3 of fuel. The measure of catalytic conversion of gases in the reactor is

the relative difference of concentrations of carbon monoxide, hydrocarbons and nitric oxides upstream and downstream the reactor during the test period. This evaluation is performed on the basis of concentration measurements of carbon monoxide using NDIR method, hydrocarbons using FID method, and nitric oxides using CLD method, upstream and downstream the catalyst. Measurements are performed in one or some selected engine working points (constant engine speed (RPM) and constant engine load). Two catalysts were simultaneously tested for ageing and conversion of gases. One catalyst was tested using basic fuel, whereas the other one using basic fuel enriched with sulfur compounds through adding tiophene in an amount assuring concentration of sulfur compounds corresponding to about 1000 ppm pure sulfur. The most important physical and chemical parameters of fuels are given in Table 2.

Table 2. Physical and chemical properties of test fuels

Properties	Measure	Basic fuel	Basic fuel + tiophene
Octane number (LOB)	Unit	52.8	
Lead contents	(% mass)	0.003	
Sulfur contents		0.010	0.101
Fractional structure of sulfur compounds: – up to 60ºC are distillated – from 60 to 100ºC – over 100ºC			 0.10 0.14 0.03
Fractional structure of fuel: – up to 70ºC are distillated – up to 100ºC – up to 180ºC – remainder	(% mass)	 24.5 52.3 96.7 0.5	

Measurement results of carbon monoxide, hydrocarbons and nitric oxides conversion during the test period, for both catalysts under the test, are shown in Fig. 1.

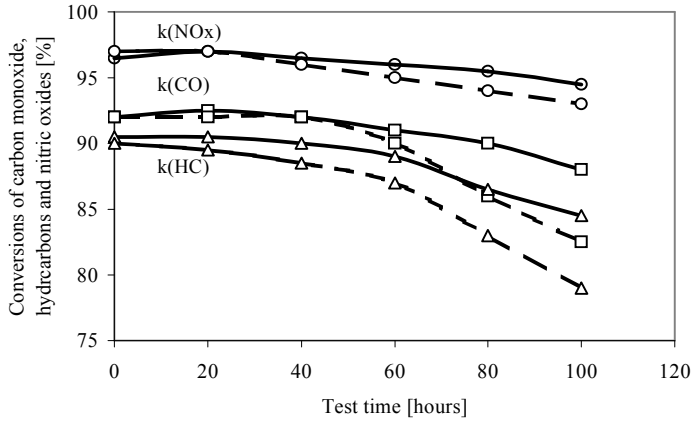

Fig. 1. Conversion of carbon monoxide, hydrocarbons and nitric oxides during 100 hours deactivation test of reactors supplied with basic fuel (solid line) and basic fuel with tiophene added (broken line)

During the test a visible decrease of reactor's catalytic activity may be observed, with reference to all toxic matters being tested. The decrease of catalytic activity is approximately twice bigger in case of the reactor through which the exhaust gas of tiophene containing fuel flows, with relation to a comparative reactor. Such contents of sulfur compounds in exhaust gas causes, after 100 hours of an engine run, a decrease of CO conversion from 92 to 82.5% and 88% respectively, decrease of HC conversion from 91 to 79% and 84.5% respectively, decrease of NO_x conversion from 97 to 93% and 95% respectively.

Emission tests of noxious components of exhaust gas in ECE test (UDC + EUDC) were carried out using a small engine car fitted with a new ("fresh") catalyst (test 0) and catalyst previously deactivated at an engine test bench, during 100 hour engine run using fuel with sulfur compounds, in an amount corresponding to 1000 ppm of sulfur (tests 1, 2 and 3). All tests were carried out supplying the engine with basic fuel (100 ppm sulfur). Emission measurements in each of the tests were carried out independently for UDC and EUDC parts. Measurement results for UDC part of tests are shown in Fig. 2, whereas in Fig. 3 measurement results for EUDC part of tests are shown. Results of emission measurements for the whole test are shown in Fig. 4.

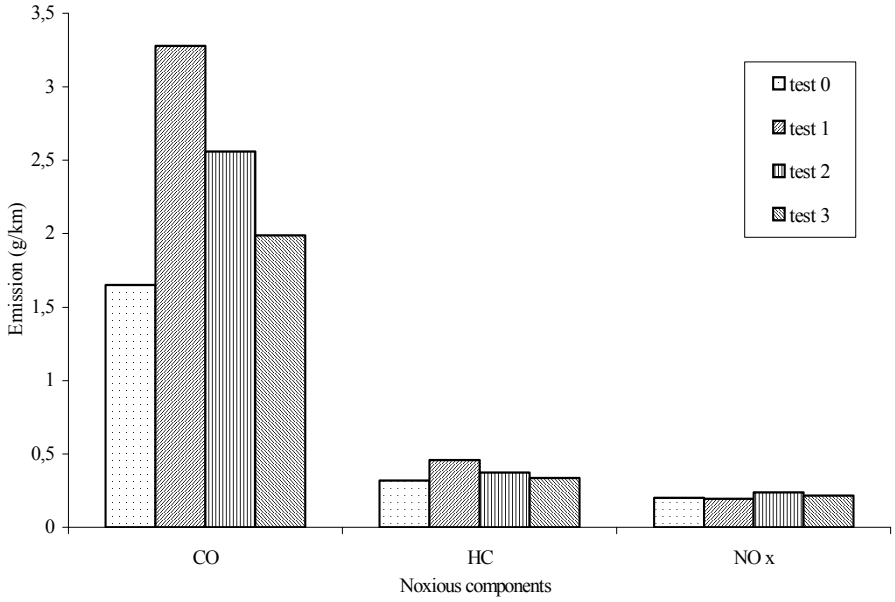

Fig. 2. Results of emission measurements of noxious matters in UDC test of an engine supplied with basic fuel. Symbols: test 0 – new reactor, test 1, 2 and 3 – tests carried out in turn, on reactor deactivated with exhaust gas with high contents of sulfur compounds

The results of tests show an essential emission increase of carbon monoxide and hydrocarbons discharged by the engine with chemically deactivated reactor (test 1) as compared to a new reactor (test 0). On the other hand, results of emis-

sion measurements of noxious matters in subsequent tests 1, 2 and 3 clearly show a decrease of carbon monoxide and hydrocarbons emission from test to test, with ambiguous variations of nitric oxides emission. This trend is the most visible in UDC part of test. This variations result probably from the progressive detoxication of a catalytic reactor during an operation on fuel with low sulfur contents.

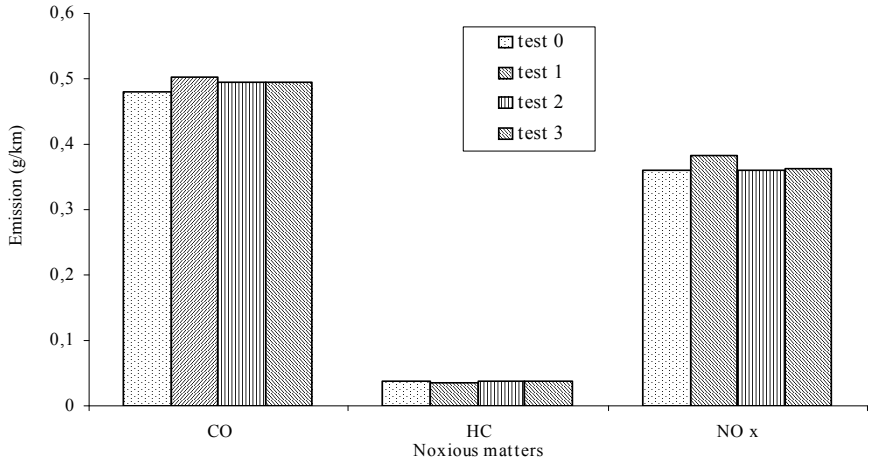

Fig. 3. Results of emission measurements of noxious matters in EUDC test of engine supplied with basic fuel. Symbols: test 0 – new reactor, test 1, 2 and 3 – tests carried out in turn, on reactor deactivated with exhaust gas with high contents of sulfur compounds

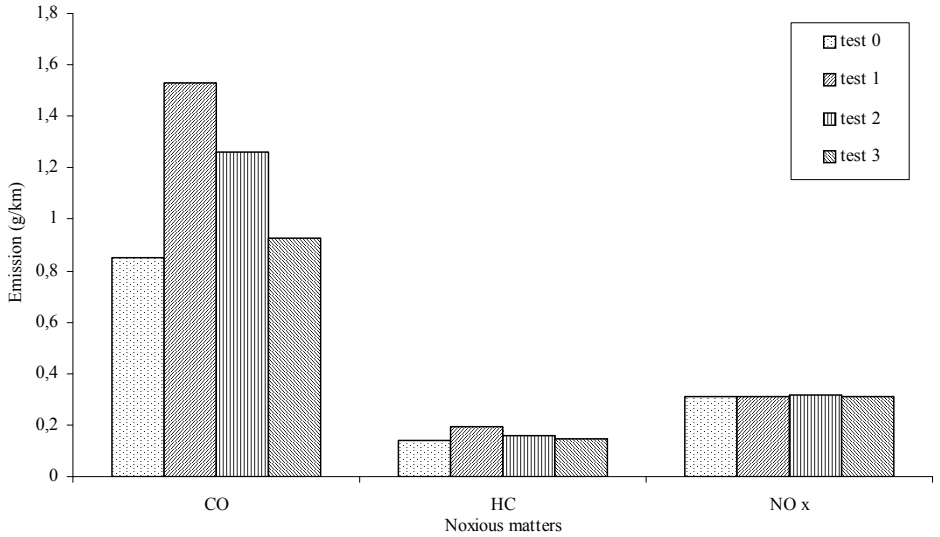

Fig. 4. Results of emission measurements of noxious matters in UDC + EUDC tests of engine supplied with basic fuel. Symbols: test 0 – new reactor, test 1, 2 and 3 – tests carried out in turn, on reactor deactivated with exhaust gas with high contents of sulfur compounds

A similar trend occurs for the whole test, whereas in EUDC part variations of emissions are not big. The obtained results are unequivocally correlated with the results of tests at an engine test bench, wherein the decrease of CO and HC by approx. 6% was obtained, and NO_x conversion by approx. 2% only. Large variations of CO and HC emission in UDC part result probably from an important increase of the reactor's ignition temperature ("light off"), as in this part of the test most of the emission comes from the first 120 seconds of the test, during which period the reactor is warming up.

CONCLUSIONS

1. An decrease of catalytic conversion in reactors tested under steady engine operating conditions, during the 100 hour test depends on sulfur contents in fuel. In case of a reactor operating in exhaust gas from combustion of fuel containing 1000 ppm of sulfur, conversion of carbon monoxide, hydrocarbons and nitric oxides decreases on average by approx. 8% at the end of test, whereas in case of the reactor operating in exhaust gas from the combustion of fuel containing 10 times less sulfur the conversion decreases on average by 4% only.

2. An increase of emission connected with the catalyst's poisoning with sulfur compounds under transient engine operating conditions (ECE R83 test) is much bigger than under steady conditions, and amounts even to 80% for carbon monoxide, and approx. 40% for hydrocarbons. The catalyst's poisoning with sulfur compounds is a reversible effect. Supplying an engine with low-sulfur fuel causes detoxication of catalytic reactor already after a short mileage (a few dozen of kilometers).

REFERENCES

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SUMMARY

The present paper gives the results of research focused on the conversion of carbon monoxide, hydrocarbons and nitric oxides in Pd/Rh catalytic reactor, during 100-hour test carried out using gasoline containing large amounts of sulfur compounds. Conversion values of noxious matters were determined for new (or "fresh") and aged catalysts. Results of conversion measurements obtained from tests at engine test bench were correlated with results of tests concerning emission of noxious matters from a car fitted with a catalyst poisoned with sulfur compounds, the tests being carried out in European test – ECE R83. Detoxication possibility of a catalyst operating on fuel with low sulfur contents was evaluated.