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MAINTENANCE OF THREE WAY CATALYTIC CONVERTER – THERMAL DEACTIVATION

EKSPLOATACJA TRÓJFUNKCYJNYCH REAKTORÓW KATALITYCZNYCH – DEZAKTYWACJA TERMICZNA*

The present paper gives a description of deactivation processes of three way exhaust gas catalytic converters, with special consideration of thermal deactivation. Test results of new (or “fresh”) and aged reactor during five-hours thermal test are presented. Conversion of carbon monoxide, hydrocarbons and nitric oxides is evaluated. Ignition temperatures of catalyst of individual noxious matters are determined, as well for new as for aged catalyst. Results of conversion measurements are correlated with results of physical and chemical tests of catalyst structure changes during ageing test.

Keywords: maintenance of catalytic converter; thermal deactivation, precious metal dispersion.

W pracy opisano procesy dezaktywacji trójfunkcyjnych reaktorów katalitycznych spalin ze szczególnym uwzględnieniem dezaktywacji termicznej. Przedstawiono wyniki badań reaktora nowego i reaktora starzonego w pięciogodzinnym teście termicznym. Oceniono konwersję tlenku węgla, węglowodorów i tlenków azotu. Wyznaczono wartości temperatury zapłonu katalizatora poszczególnych substancji szkodliwych dla katalizatora nowego i starzonego. Wyniki pomiarów konwersji skorelowano z wynikami badań fizyko-chemicznych zmian struktury katalizatora podczas testu starzeniowego.

Słowa kluczowe: eksploatacja reaktorów katalitycznych, dezaktywacja termiczna, dyspersja metali szlachetnych.

1. Introduction

Modern catalytic converters are manufactured on the basis of ceramic or metal monolith, on which subsequent layers are applied, said layers performing different functions. They are composed of more than 5 different metal oxides and 2 - 3 kinds of precious metals. Reduction efficiency of carbon monoxide, hydrocarbons and nitric oxides emission for a fully functional catalytic system, running in steady state at appropriate temperatures and A-F mixture composition close to stoichiometric, 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.

Deactivation of exhaust gas catalytic reactor may result from different processes that may be divided into following groups [3]:

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 above mentioned mechanisms. At 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 [1].

2. Thermal deactivation tests of a converter

Tests were carried out using test stand for converter testing, constructed using electric tubular furnace. In the furnace a catalyst chamber, made of heat-resisting steel, was installed, into which exhaust gas from a Rover 1.4 engine are supplied via a heated gas path. Exhaust gas samples from upstream and downstream the catalyst are taken into exhaust gas analyzers. Exhaust gas temperatures are measured using thermocouples upstream and downstream the catalyst. Exhaust gas from downstream the converter were cooled, and after moisture condensing flowed through a set of rotameters.

Tests were performed using a Pd/Rh - Al₂O₃/CeO₂ catalytic converter for small-engine car, made on the basis of metal monolith (number of ducts: 62 l/cm²) with precious metals amount of 1.46 g Pt/dm³ and 0.3 g Rh/dm³. For test purposes, the car catalyst was transformed into model test catalyst, having $\Phi = 30$ mm (diameter) and $l = 90$ mm (length), then placed inside the tubular furnace. Ageing procedure was performed using exhaust gas [4] having stoichiometric composition (CO₂ = 14.3%, CO = 0.56%, O₂ = 0.65%, HC = 213 ppm, NO_x = 2500 ppm), for 5 hours at 900°C with flow rate corresponding to relative volumetric flow velocity $SV = 6000$ h⁻¹. Before ageing procedure and after its termination a series of tests was performed in order to determine the correlation between the conversion of exhaust gas components and catalytic process temperature. Test results were completed with tests of selected characteristics of catalyst surface, including tests of porosity, palladium dispersion and X-ray structure tests. Tests are presented according to following methods and sequence.

1. Tests of porous structure of catalyst surface before and after ageing were carried out using ASAP 2010 apparatus. Catalyst fragments were examined (steel foil coated with oxide layer

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on both sides with deposited precious metals). Test results refer to 1 g of catalyst mass.

- X-ray structural tests were carried out using Rigaku Denki X-ray diffractometer, in Bragg-Brentano reflective geometry, using CuK radiation and Ni filter. Tests were carried out on a catalyst in form of powder obtained from new and aged catalysts.
- Precious metals dispersion was examined using hydrogen chemical adsorption method. Tests were carried out on powder previously obtained from new and aged catalysts. For final determination of crystallites dimensions and their degree of dispersion, one has to know the concentration of precious metals in catalysts being tested, said concentrations being determined using flame AAS method.
- Conversion of gases was examined at constant gas flow with stoichiometric composition, controlled in closed loop using oxygen sensor, corresponding to relative volumetric flow velocity of exhaust gas $SV = 12000 \text{ h}^{-1}$ under engine operating conditions corresponding to $n = 2500 \text{ RPM}$, and $N_e = 25 \text{ kW}$ effective power. Concentration of exhaust gas upstream and downstream the catalyst was measured depending on catalytic process temperature, and conversion of exhaust gas components was calculated, and then the ignition temperature T^{50} of catalyst was determined (temperature corresponding to 50% conversion of a given component).

3. Test results

Ad 1. Results of tests concerning determination of specific surface (BET model) and surface and volume of pores (BJH model) for new and aged catalyst are shown in table 1. The result of thermal

Table 1. Results of tests concerning surface area and surface and volume of micro pores

Description	Unit	New catalyst	Aged catalyst
Surface area - BET model	m ² /g	22.3	7.74
Surface of pores - BJH model (adsorption)		23.3	8.9
Surface of pores - BJH model (desorption)		25.3	9.5
Volume of pores - BJH model (adsorption)	cm ³ /g	0.068	0.056
Volume of pores - BJH model (desorption)		0.06	0.055
Average diameter of pores - BET model	Å	72.82	120.1
Average diameter of pores - BJH model (adsorption)		117.1	250.0
Average diameter of pores - BJH model (desorption)		107.6	232.0

deactivation of a catalyst is the loss of its active surface. A decrease of surface area (BET) and surface of pores (BJH) down to approx. 35% of initial value was found. The volume of pores decreased down to approx. 85% of initial value, whereas the average pore diameter increased from about 110 Å up to 240 Å. Such effects are due to the fact that pores having comparatively small diameter disappear as first.

Ad 2. Results of X-ray tests in form of Pd/Rh-Al₂O₃/CeO₂ catalyst diffraction pattern before ageing test (upper line) and after ageing test (lower line) are shown according to [1] in figure 1. In preparation Pd/Rh of new catalyst the mixture of γ -Al₂O₃ and CeO₂ was identified. Metal phases were not identified (except support of layers). In preparation of Pd/Rh catalyst after ageing test, γ -Al₂O₃ was still identified, as well as well-crystallized CeAlO₃ phase. Evaluation of crystallites size for that phase, obtained using Scherrer formula and half-width reflection, was equal from 340 to 400 Å for different reflections. In that preparation, reflection (111) from Pd phase (or rich in Pd alloy) was also observed. Small intensity of metal phases reflections being observed, and their superposition with dominating reflections from oxide phases make possible the only one statement: phases are iden-

tifiable. Measured thickness of layers deposited on the support was equal to 0,045 mm approx., whereas said layers after test showed certain irregularity of thickness (within 0,005 mm)

Ad 3. Test of metals dispersion preceded by temperature-pro-

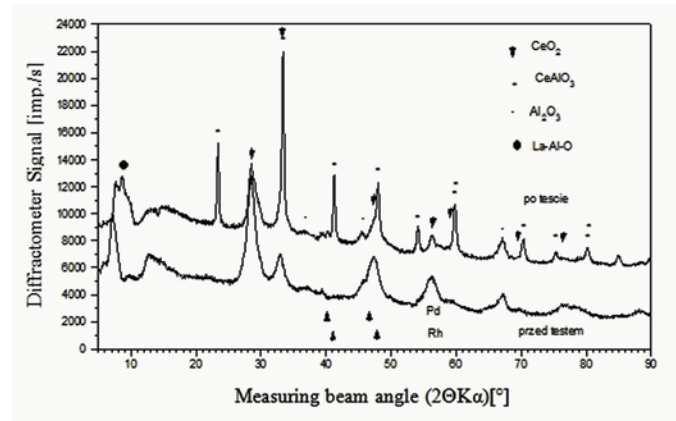


Fig. 1. Diffraction pattern of Pd/Rh - Al₂O₃/CeO₂ catalyst (powder) before ageing test (lower line) and after ageing test (upper line) [1].

grammed reduction (TPR) and temperature-programmed desorption (TPD) were carried out using hydrogen chemical adsorption method. These measurements were performed using impulse method. Hydrogen was injected in form of pulses into argon stream until surface saturation was obtained. Lack of hydrogen chemical adsorption manifested in "passing through" the sample of equal peaks, watched on recorder's screen. Hydrogen is chemically adsorbed in form of monolayer on metal surface. Chemical adsorption of hydrogen on metals of groups 8 – 10 (thus also on palladium and rhodium) takes place with dissociation, so it is assumed that one atom of chemically adsorbed hydrogen $H_{(ads)}$ falls on one surface atom of metal ($H_{ads} / M_{pow} = 1$, where $M = Pd, Rh$).

Hypothetical, typical chemical adsorption image (figure 2) looks as follows: the 1st hydrogen pulse is partially adsorbed, whereas next pulses pass completely through the sample and may be taken as standard. The difference of areas under the first pulse, and average area under next pulses is the measure of adsorbed hydrogen amount. Knowing the amounts of hydrogen pulses injected into argon stream,

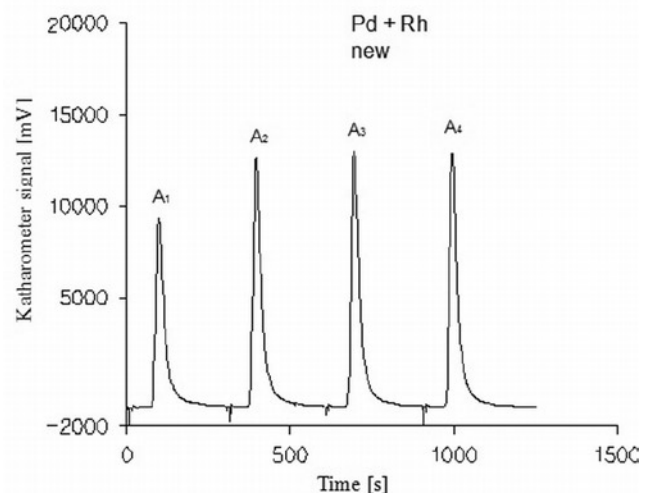


Fig. 2. Example of hydrogen chemical adsorption process on new Pd/Rh catalyst. A_1 , A_2 , A_3 and A_4 mean areas under individual hydrogen pulses

Table 2. Results of metal dispersion measurements according to [2]

catalyst	catalyst mass / number of metal moles in sample	number of moles of adsorbed H ₂		dispersion, D%		average crystallite size [Å]
		chemisorption after TPR	chemisorption after TPD	measurement after TPR	measurement after TPD	
Pd-Rh, new;	0.25157 g/ 13.735e-6	0.875e-6	1.180e-6	12.74	17.18	91
Pd-Rh, aged	0.31443 g/ 16.839e-6	0.591e-6	0.269e-6	7.02	3.19	268

one has calculated from ideal gas law the number of hydrogen moles adsorbed by catalyst sample. Then, assuming that hydrogen is adsorbed by surface metal atoms only, and assuming adsorption model as: 1 hydrogen atom per 1 metal atom, one has calculated average crystallite size and metal dispersion in the catalyst. Results of measurements according [4] are shown in table 2.

Results of metal crystallites size using hydrogen chemical adsorption method (see table 2.) have to be construed very carefully, as the may be distorted by different factors. Said factors are:

- metal crystallites may be enclosed by carrier layer, preventing hydrogen adsorption. Because of this one will calculate a smaller dispersion, thus larger metal crystallites,
- the metal in catalysts being used, even in initial state, may be “decorated” with other components, and additionally in aged catalyst, there may be carbon deposits on metal surface,

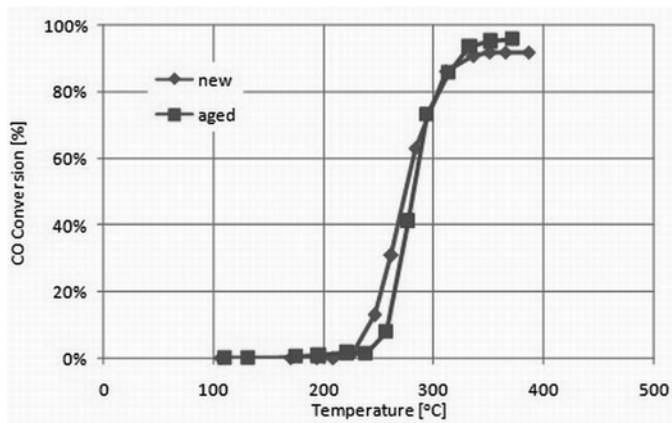


Fig. 3. Carbon monoxide conversion as function of temperature, for new and aged converter

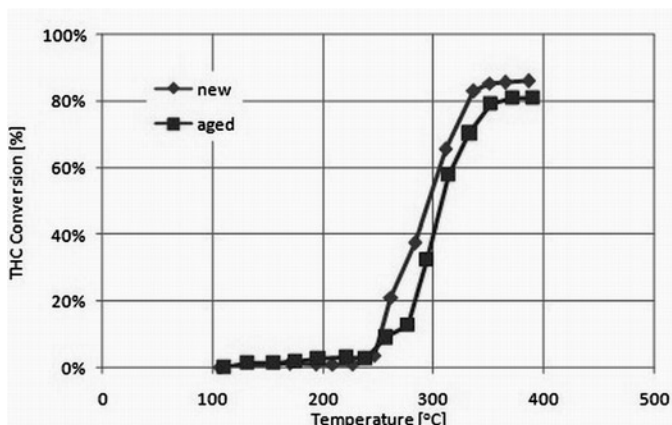


Fig. 4. Conversion of hydrocarbons as function of temperature, for new and aged converter

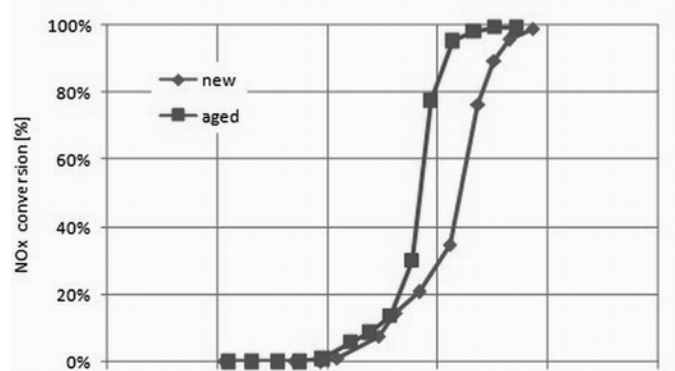


Fig. 5. Conversion of nitric oxides as function of temperature for new and aged converter

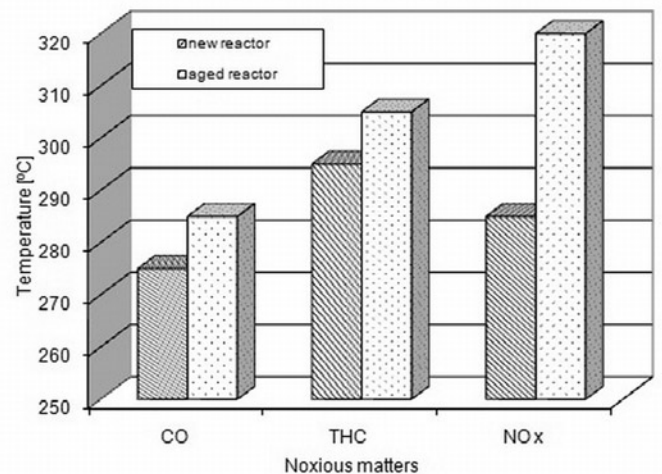


Fig. 6. Temperature comparison for 50% conversion of CO₂, THC and NO_x for new and aged converter

coming from polymerization process of reaction being catalyzed. This situation may make difficult hydrogen adsorption, resulting in calculation of too large values for metal crystallites size.

Ad 4. Results of measurements and calculations of carbon monoxide, hydrocarbons and nitric oxides conversion as function of temperature, for new catalyst and catalyst after ageing test are shown in fig. 3, 4 and 5.

Fig. 6 shows 50% conversion temperatures calculated for individual noxious matters, for new catalyst and catalyst after ageing test.

As a result of thermal deactivation process of a catalyst it was found, that there was a clear increase of 50% conversion temperature for each noxious matter, which was for carbon monoxide, hydrocarbons and nitric oxides 10°C, 10°C and 35°C respectively.

4. Conclusions

1. As a result of thermal deactivation test, the porosity of the catalyst decreased unfavorably, and in the same time small and medium pores were mainly destroyed. Total volume of pores, as well as total surface of pores were decreased.
2. In the catalyst after deactivation test a well-crystallized CeAlO₃ phase was discovered, said phase could contribute to possible decrease of oxygen storage capacity in oxide layer of the carrier. Estimated sizes of crystallites in said phase, obtained using Scherrer formula and half-width reflection, were in the range from 340 to 400 Å for different reflections. In this preparation the appearance of reflection from Pd phase (or rich in Pd alloy) was also observed, a possible indication of Pd-Rh alloy being formed.
3. The thermal deactivation caused a clear increase of average size of precious metals crystallites. Despite reservations concerning the accuracy of this method it can be found, that the decrease of metals dispersion is undeniable and may be essential for catalyst activity.
4. It was found that the thermal deactivation of catalyst under test resulted in essential increase of 50 % conversion temperature of all noxious matters, from about 10°C up to about 30°C, which may cause essential increase of emission during homologation tests including cold engine start-up.

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