# THERMAL DEACTIVATION OF THREE WAY EXHAUST GASCATALYTIC REACTOR

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## INTRODUCTION

Modern catalytic reactors are manufactured on the basis of ceramic or metal monolith, on which subsequent layers performing different functions are applied. 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 a reactor causes its ageing and unavoidable deactivation process of the catalytic layer. Changes of structure and chemical constitution of the 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 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 present 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.

## THERMAL DEACTIVATION TESTS OF A CATALYST

Tests were carried out using a test stand for catalysts 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 catalyst were cooled, and after moisture condensing flowed through a set of rotameters.

Tests were performed using a Pd/Rh – $Al_2O_3/CeO_2$ catalytic reactor f or a small-engine car, made on the basis of metal monolith (number of ducts: 62 1/cm$^2$) with precious metals amount of 1.46 gPt/dm$^3$ and 0.3 gRh/dm$^3$. For the 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 having stoichiometric composition ($CO_2$ = 14.3%, CO = 0.56%, $O_2$ = 0.65%, HC = 213 ppm, NOx = 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 the 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 on both sides with deposited precious metals). Test results refer to 1 g of catalyst mass.
2. 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.
3. Precious metals dispersion was examined using hydrogen chemical adsorption method. Tests were carried out on powder previously obtained from new and aged catalysts. For a final determination of crystallites dimensions and their degree of dispersion one has to know the concentration of precious metals in the tested catalysts, the concentrations being determined using flame AAS method.

4. 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 h-1 under engine operating conditions corresponding to *n* = 2500 RPM, and *Ne* = 25 kW effective power. Concentration of exhaust gas upstream and downstream the catalyst was measured depending on the temperature of the catalytic process, and the conversion of exhaust gas components was calculated, and then the ignition temperature T50 of the catalyst was determined (the temperature corresponding to 50% conversion of a given component).

## TEST RESULTS

Ad 1. The 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 the thermal 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.

**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<br>Surface of pores - BJH model (adsorption)<br>Surface of pores - BJH model (desorption) | $m^2/g$ | 22.3<br>23.3<br>25.3 | 7.74<br>8.9<br>9.5 |
| Volume of pores - BJH model (adsorption)<br>Volume of pores - BJH model (desorption) | $cm^3/g$ | 0.068<br>0.06 | 0.056<br>0.055 |
| Average diameter of pores - BET model<br>Average diameter of pores - BJH model (adsorption)<br>Average diameter of pores - BJH model (desorption) | Å | 72.82<br>117.1<br>107.6 | 120.1<br>250.0<br>232.0 |

Ad 2. Results of X-ray tests in form of Pd/Rh-$Al_2O_3$/$CeO_2$ catalyst diffraction pattern before ageing test (upper line) and after ageing test (lower line) are shown according to [4] in Figure 1. In preparation Pd/Rh of new catalyst the mixture of γ-$Al_2O_3$ and $CeO_2$ was identified. Metal phases were not identified (except support of layers). In preparation of Pd/Rh catalyst after ageing test, γ-$Al_2O_3$ was also identified, together with the well-crystallized $CeAlO_3$ 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. The low intensity of the observed metal phases reflections, and their superposition with dominating reflections from oxide phases lead to the only possible solution: phases are identifiable. The

measured thickness of layers deposited on the support was equal to 0.045 mm approx., whereas the layers after the test showed a certain irregularity of thickness (within 0.005 mm)

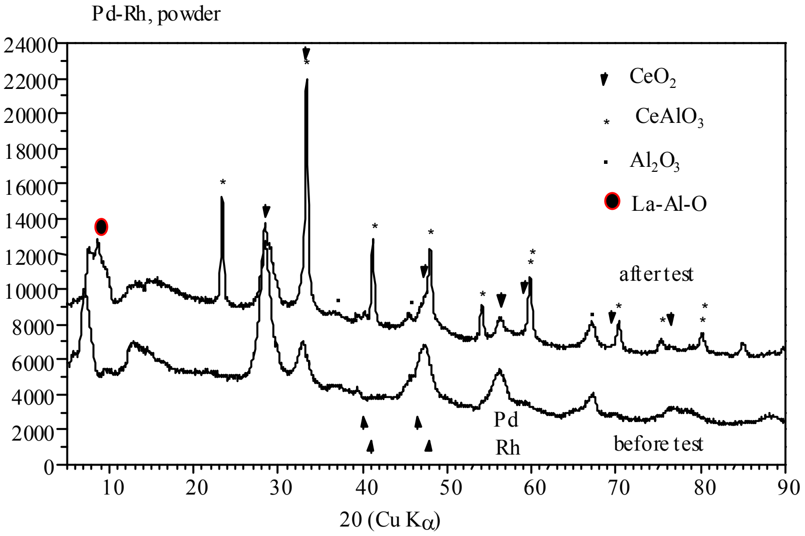

Fig. 1. Diffraction pattern of Pd/Rh - $Al_2O_3/CeO_2$ catalyst before ageing test (lower line) and after ageing test (upper line) [4].

Ad 3. Tests of metals' dispersion preceded by temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) were carried out using the hydrogen chemical adsorption method. These measurements were performed using the impulse method. Hydrogen was injected in the 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 the 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).

Hypothetically, 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 an average area under the next pulses is the measure of the adsorbed hydrogen's amount. Knowing the amounts of hydrogen pulses injected into argon stream, the number of hydrogen moles adsorbed by the catalyst sample was calculated from the ideal gas law. Then, assuming that hydrogen is adsorbed by surface metal atoms only, and assuming the 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 to [5] are shown in Table 2.

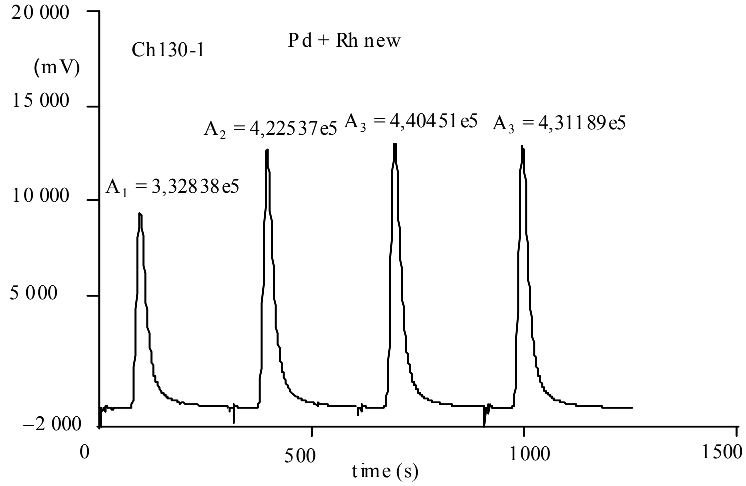

Fig. 2. Example of hydrogen chemical adsorption process on new Pd/Rh catalyst.$A_1$, $A_2$, $A_3$ and $A_4$ mean areas under individual hydrogen pulses

**Table 2. Results of metal dispersion measurements according to [5]**

| catalyst | catalyst mass / number of metal moles in sample | number of moles of adsorbed H2 | | 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 |

Results of metal crystallites size using hydrogen chemical adsorption method (see Table 2) have to be construed very carefully, as they may be distorted by different factors such as:

– metal crystallites may be enclosed by carrier layer, preventing hydrogen adsorption. Because of this one will calculate a smaller dispersion, and thus larger metal crystallites,

– the metal in catalysts being used, even in initial state, may be “decorated” with other components, and additionally, in an aged catalyst there may be carbon deposits on metal surface, coming from the polymerization process of the catalyzed reaction. This situation may make hydrogen adsorption difficult, resulting in the 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.

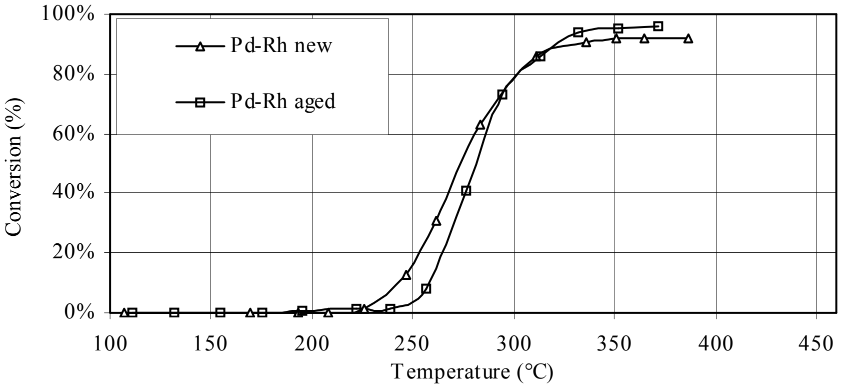

Fig. 3. Carbon monoxide conversion as function of temperature, for new and aged catalyst

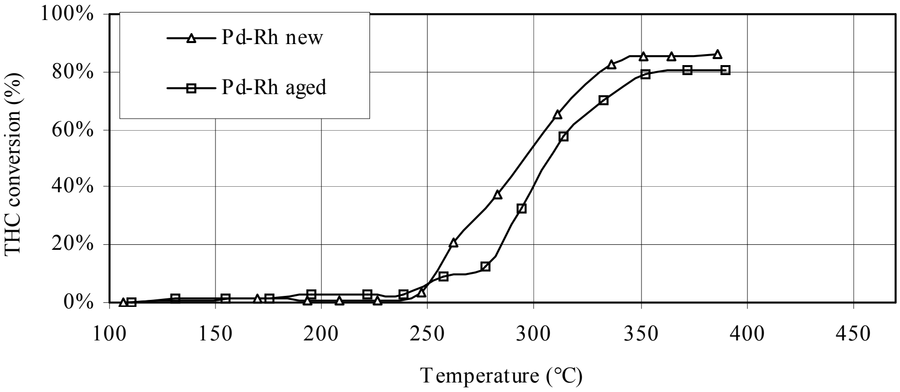

Fig. 4. Conversion of hydrocarbons as function of temperature, for new and aged catalyst

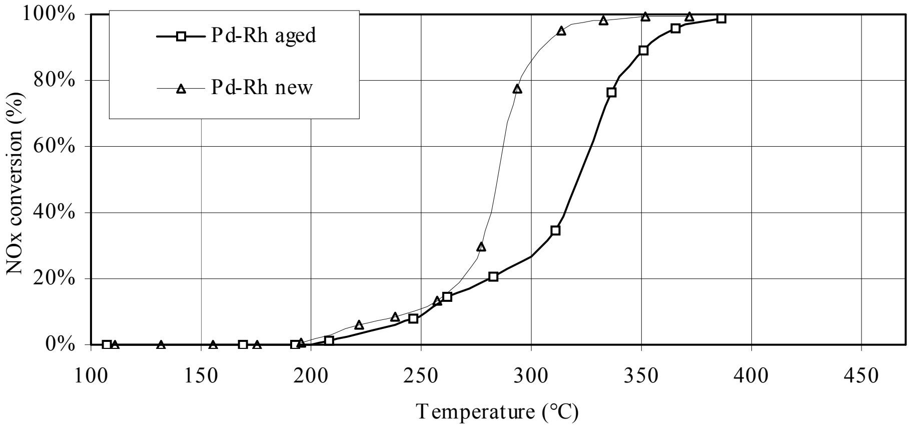

Fig. 5. Conversion of nitric oxides as function of temperature for new and aged catalyst

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

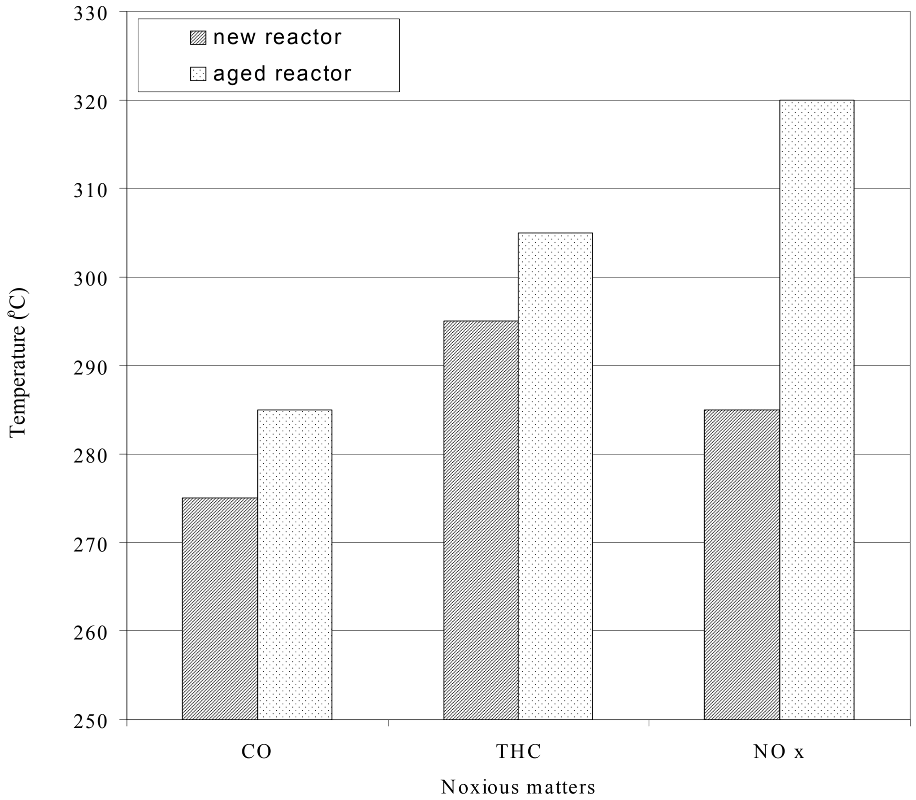

Fig. 6. Temperature comparison for 50% conversion of CO, THC and $NO_X$ for a new and an aged catalyst

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, namely, for carbon monoxide, hydrocarbons and nitric oxides 10°C, 10°C and 35°C respectively.

## CONCLUSIONS

1. As a result of thermal deactivation test, the porosity of the catalyst decreased unfavorably and at 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 $CeAlO_3$ phase was discovered, which could contribute to a possible decrease of oxygen storage capacity in oxide layer of the carrier. The estimated sizes of crystallites in the 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 noticed that the decrease of metals dispersion is undeniable and may be essential for catalyst activity.

4. It was found that the thermal deactivation of the catalyst under test resulted in an 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.

## LITERATURE

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## SUMMARY

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