

EXAMINING THE SURFACES IN USED PLATINUM CATALYSTS

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Abstract

For the purpose of finding more advanced platinum catalyst manufacturing technologies and achieving a higher degree of ammonia oxidation, metallographic characterization has been done on the surface of catalyst gauzes and catalyst gripper gauzes made from platinum and palladium alloys. For the examined samples of gauzes as well as the cross section of the wires, a chemical analysis was provided.

The purpose of this paper is the metallographic characterization of examined alloys carried out by way of electronic microscopic scanning, X-rays as well as chemical assays which contributed greatly to a better understanding of the surface deactivation, in other words a better consideration of structural changes occurring on the wire surface.

Keywords: Ammonia oxidation; Platinum catalyst; Metallographic characterization

1. Introduction

In the course of ammonia oxidation to nitrogen monoxide, a set of catalyst gauzes made from platinum and platinum based alloys was used. Normal gauze thickness was 1024 apertures/cm² whereas the wire diameter was within the 0.06 – 0.08 mm range. The number of gauzes in one set was 3 – 40, depending on the quantity and pressure of the gas mixture. In the ammonia

oxidation process, the mixture of ammonia with air reacts with the platinum catalyst at the pressure of 0.1 Mpa and $t = 780-920^{\circ}\text{C}$ in a very short time, with $1-2 \cdot 10^{-4}$ sec. During that time, 92-98% of ammonia was oxidized, platinum and rhodium evaporated and catalysts became less active which lead to a reduced life. Depending on the pressure in the gas mixture, gauzes can be used 3 months to one year.

In all nitric acid manufacturing plants

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worldwide, nearly 40-80% of the lost platinum is captured on catalyst gauzes by means of grippers which are mostly made from the following alloys: PdAu20, PdAu10, PdNi5 or from filter mass made from silicone wool and calcium oxide.

Exploitation time for platinum catalysts, platinum and rhodium loss during ammonia oxidation and the degree of ammonia oxidation are the subject of other numerous studies. Different platinum catalyst deactivation mechanisms have been studied by Philpot [1].

We can also find other studies on the phenomena occurring on the catalyst prior to, during and after its use, with a specific accent on the crystallographic orientation of the wire surface and its texture [2-13]. Reduced activities and selectivity of the gauzes have also been studied by other authors [14-19].

Many authors [20-26] have tried to provide characterization of Pt-Rh catalysts after finished exploitation in an industrial environment. However, with numerous studies and submitted papers, new techniques for examining the used catalyst gauzes in order to better understand the reason for the surface deactivation have always arisen interest. The purpose of this paper is to study in more detail and better understand the structural changes on the surface of gauzes and catalyst gripper gauzes, as well as the mechanisms following these changes. The results of these studies have greatly contributed to the selection of new advanced technologies for platinum catalysts. They were created after many years of studying the catalysts as part of technological and development projects in Serbia, TR 19028 (2008), under the sponsorship of the Ministry of Science.

2. Materials and research methods

Catalyst gauzes and catalyst gripper gauzes were created at the Institute of Mining and Metallurgy at Bor, Serbia. The catalysts were used at the nitric acid manufacturing plant for 180 days, at Lukavac, Bosnia-Herzegovina.

In order to examine the structural changes on the catalyst surface, three groups of gauzes and gripper gauzes were used.

The first set of samples were PtRh10 catalyst gauzes and PdAu10 catalyst gripper gauzes, that is the second gripper gauze from the catalyst gripper packaging and the first gripper gauze from the grippers packaging.

The second set comprised of the fourth gripper gauze from the catalyst packaging of the PtRh7.5 content. The gauzes were undergoing the process of ammonia oxidation without the grippers.

The third set consisted of the catalyst gauzes made from PtRh5Pd5 and gripper gauzes of the PdNi5 content. The wire surface in these catalyst gauzes and gripper gripper gauze was examined by an electronic microscopic scanner and X-rays, whereas the chemical analysis was carried out by means of atomic absorption spectrophotometry (AAS).

3. Results and Discussion

The examples of structural changes on the wire surface of catalyst gauzes with PtRh10 content and grippers of PdAu10 with magnification of 100x and 5000x, are shown in figure 1.

The surface of the gauzes made from PtRh10 after used in industrial conditions had the appearance of a „cauliflower“. The surface of the wire gripper gauze was covered with a

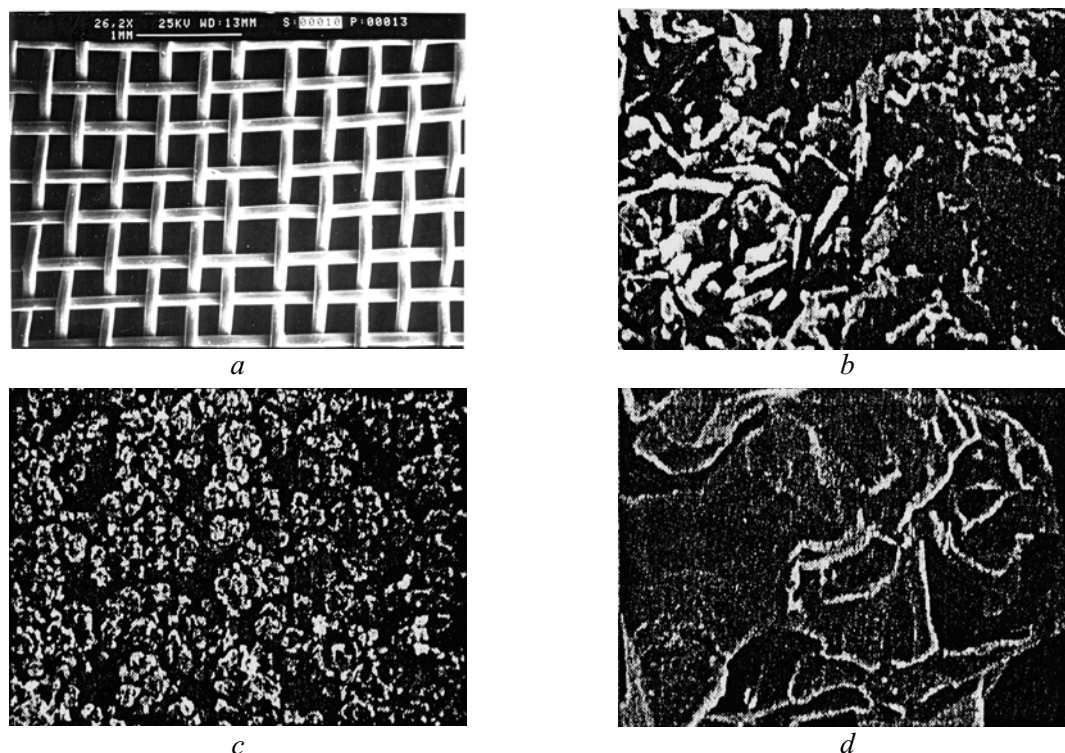


Fig. 1. SEM photograph of the catalyst gauze samples PtRh10 (a, b) and grippers of PdAu10 (c, d). Magnification $\times 100$ (a, b); $\times 5000$ (c, d).

thin needle-like layer. X-rays showed the difference in platinum and rhodium concentrations on the wire surface. The needle-like layer of a larger cauliflower surface was richer in rhodium, rhodium (III) oxide, which was proved by the subsequent analysis.

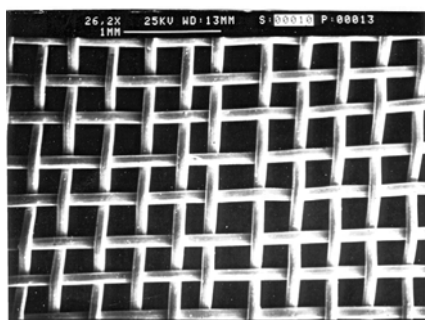
The surface of the first gripper gauze in the set was covered in fine powder. The powder was so thick that the gauze sieves were hardly noticed. Due to a significant reduction in free space between the wires, the layers got larger. The powder had a visibly different shape than the powder on PtRh10 gauzes. It was of a loose structure with finely shaped and smooth walls. On the basis of distribution of elements on the gauze surface, the presence of platinum was proved along with palladium and gold. The presence of impurities was also noted, such as Ca, Mg,

Al, Fe, Si, Cr, Rh which were carried by gas flow and deposited on the gauze surface.

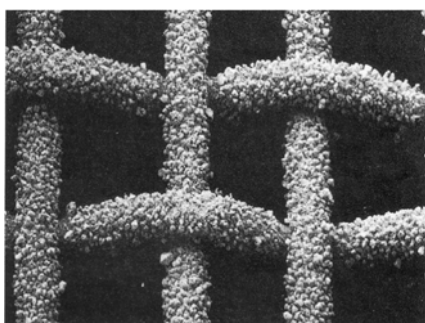
Looking into the surface of the catalyst gauzes wire of PtRh7.5 (the fourth gauze in the packaging), two different surfaces were noticed. Namely, well engraved (deepened) fibres with a regular surface were framed with thin needle-like crystals, as shown in figure 2.

This can be more easily seen in figure 3, showing an electronic photograph of the wire surface with a) deepened areas on the wire and, b) platinum distribution and c) rhodium distribution.

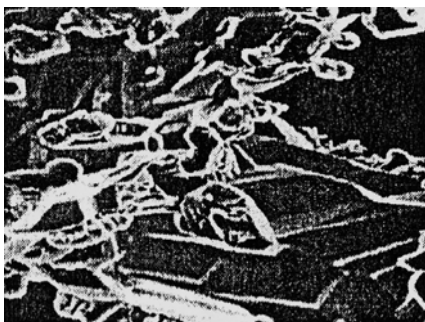
This brings us to the conclusion that the middle area of the wire was rich in platinum, and the surface area in rhodium. Chemical analysis showed that the middle area of the wire contained:



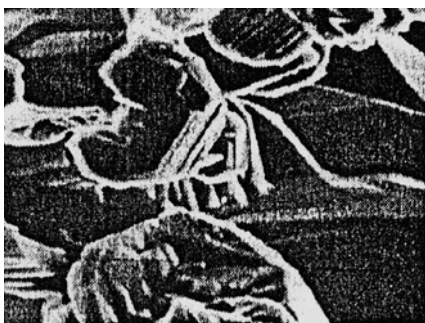
a



b



c



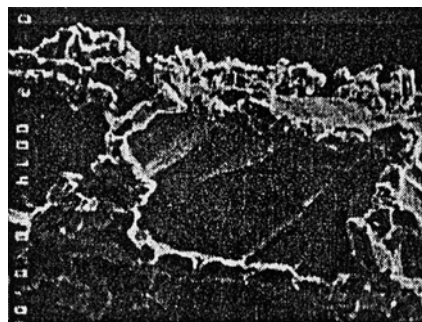
d

Fig. 2. SEM photograph of the used PtRh7.5 catalyst gauze (the fourth in the package); magnified
a) 100x, b) 300x, c) 1000x and d) 4000x

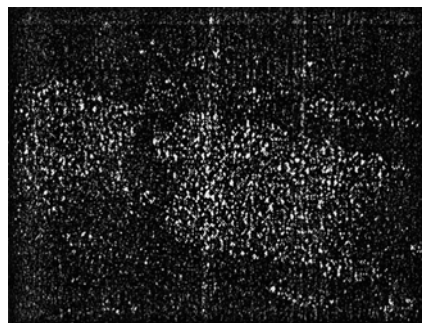
Pt, %	Rh, %
90,5	9,4

The presence of rhodium in the middle of the wire proves that the material the wire was made from was of the Pt Rh7.5 content.

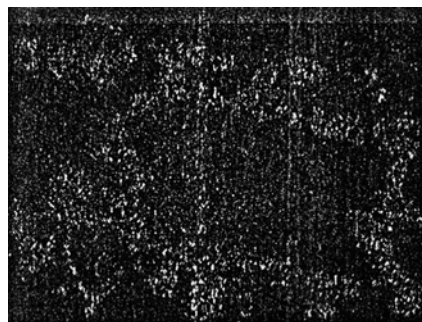
Analysing the chemical content of the wire surface, we have come to the following



a



b



c

Fig. 3. A photograph of the used PtRh7.5 catalyst gauze

a) electronic photograph

b) Pt distribution

c) Rh distribution, magnified 1200x

results:

Rh, %	Pt, %
95,10	1,70

We should add the fact that the results of microanalysis could lead us only to rough estimates of the chemical content, particularly of the wire surface. Chemical content of the PtRh7.5 cross section was determined and shown in tin figure 4.

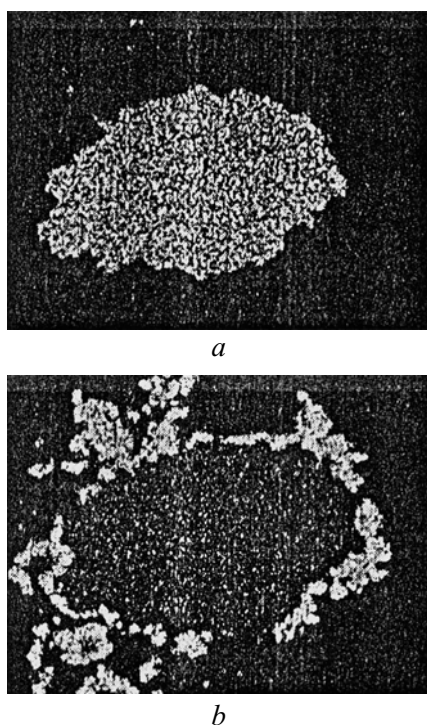


Fig. 4. The appearance of the PtRh7.5 wire cross section: a) platinum distribution; b) rhodium distribution, magnified 1200 x.

Chemical content was determined along the entire cross section of the wire and the results were as follows:

Pt,%	Rh,%	O ₂ ,%
93,2	6,78	0,4

Obtained results were quite satisfactory. What they showed were drastic changes occurring only on the wire surface.

Formation and decomposition of rhodium (III) oxide is closely correlated to the partial oxygen pressure, rhodium content and catalyst temperature. When the rhodium quantity increases, the balance is achieved at higher temperatures with same partial oxygen pressure. This brings us to the conclusion that rhodium (III) oxide will form owing to a reaction temperature drop or an increase in the partial oxygen pressure.

The next series of experiments was performed on the samples of gauzes with the PtRh5Pd content and on catalyst gripper gauzes of the PdNi5 content. In both cases, the wire diameter was 0.06 mm, and thickness of the weave was 1024 apertures/cm². Middle degree of the ammonia oxidation was 96%.

Figure 5. shows a SEM photograph with used catalyst gauzes. The „cauliflower“ structure was noted on both surfaces of the wire. Only with large magnifications, a destroyed crystal structure on smooth surfaces of the walls was noticed.

The chemical content of the first catalyst gauze was determined and the following results were obtained:

Pt,%	Rh,%	Pd,%
95,3-98,6	2,3-4,8	2,4-3,9

We can clearly see from above results that the gauze surface was rich in platinum. We can only suppose that the „cauliflower“ structure was an inactive platinum layer formed due to used platinum gauzes. Also examined was the wire surface on the fourth catalyst gauze, but on the side opposite to the gas flow. Small „cauliflower“ structures were also seen as well as larger quantities of catalyst engraved fibres with crystallographic surfaces regularly oriented.

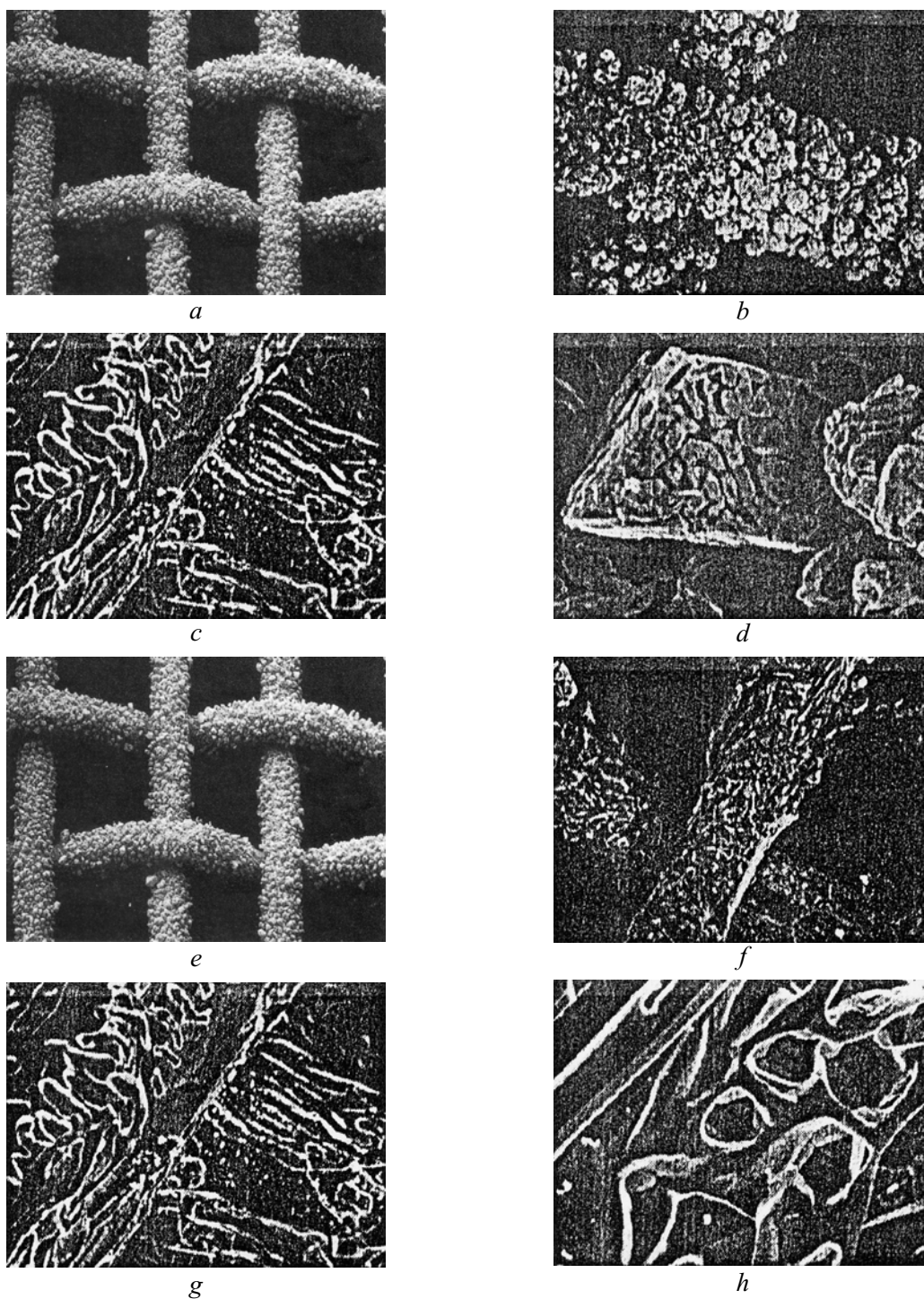


Fig. 5. SEM photograph of the surface catalyst gauzes of the PtRh5Pd content:
 a, b, c, d – the first catalyst gauze in the direction of the gas mixture flow
 e, f, g, h – the fourth catalyst gauze opposite to the gas flow.
 Magnification: a, e – 100x; b, f – 400x; c, g – 1200x; d, k – 3500x.

Analysis of the chemical content of the fourth catalyst gauze was performed and the results were as follows:

Pt, %	Rh, %	Pd, %
86-88	6,5-6,8	5,4-5,9

It can be noticed that the wire surface of the fourth catalyst gauze in the packaging is richer in rhodium, as the case was in the PtRh7.5 gauze. Such gauze surface was characterized by quite an active catalyst which was confirmed by the presence of clearly noticable crystallographic fibre shaped wire walls.

Picture 6 with the SEM photograph shows the surface of the catalyst gripper gauze placed closely behind the packaging of the catalyst gauzes. The presence of deposits was noticed on the surface of the first gauze which largely reduced the activity and purity of the gauzes (as in PdAu10 gauzes). These deposited layers are characterized by the regular shape and smooth walls with clear crystallographic orientation. Analysis of the chemical content produced the following results:

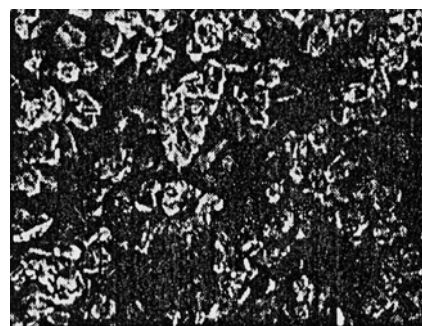
Pd, %	Pt, %
41,7-72,3	34-55,5

We can conclude that deposited layers present the platinum captured from the catalyst gauzes. Also the surface of the last gripper gauze in the packaging in the direction opposite to the gas flow was examined and shown in figure 6 and 7.

In this case we can clearly see some deepened areas on the wire surface.

Analysis of the chemical content was performed and the results were as follows:

Pd, %	Pt, %
86,8-93,2	7,95-13,02



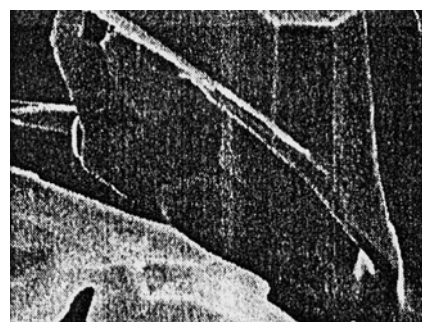
a



b

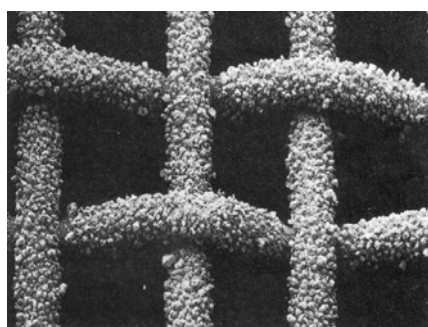


c

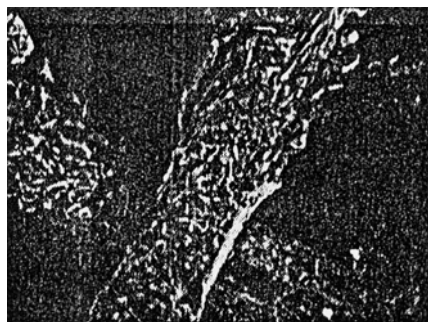


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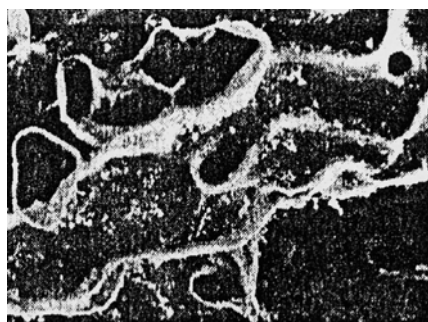
Fig. 6. SEM photograph of the PtRh5Pd5 surface of the catalyst gauze and PtRh5Pd gripper: a, b, c d – the first catalyst gauze in the packaging in the gas flow direction
Enlargement: a–100x; b–400x; c–200x; d– 3500x



e



f



g



h

Fig. 7. SEM photograph of the PtRh5Pd5 surface of the catalyst gauze and PtRh5Pd gripper: e, f, g, h – the last gauze in the packaging opposite to the gas flow direction
Enlargement: e–100x; f–400x; g–200x; h– 3500x

The palladium gripper surface was richer in platinum in this case. Obtained results showed a high efficiency of the platinum captured on the catalyst gauzes by means of grippers made from the PdNi5 alloy. After the entire balance of the material had been done, the analysis showed that over 70% of the platinum evaporated off the catalyst gauzes was captured with catalyst gripper gauzes.

4. Conclusion

Based on the chemical content and metallographic testing of the used catalyst gauzes, the following conclusion can be reached:

By using catalysts in the ammonia oxidation process in very strict and rigorous conditions (high temperature, pressure, gas flow, presence of oxygen) changes occur in the crystal structure on the surface layers of catalysts as well as in the Pt : Rh chemical ratio which becomes disturbed. The consequence is the loss of the platinum metal, reduction in catalytic activation and creation of the finely grained and very porous rhodium (III) oxide. Formation of the rhodium (III) oxide on the wire surface resulted in the drop of the partial oxygen pressure or the increase of temperature in comparison to the regular. Increase in the partial oxygen pressure or a temperature drop could occur due to the lack of platinum during the catalysis which could result in the smaller wire diameter. For that reason, it is necessary to reach a compromise between the temperature which prevents the formation of rhodium (III) oxide and the temperature which limits the loss of platinum in the allowed quantities. This is characteristic to the process of catalytic

ammonia oxidation on PtRh and PtRhP dgauzes which is followed by a selective decomposition of the sub-grain walls and evaporation of platinum along the crystallographic surface. Namely, platinum atoms evaporate off the surface layers of the wire in the form of platinum (II) oxide and make possible catalytic oxidation just beneath the surface, not directly on the surface of the catalyst.

Platinum atoms formed in this way are carried away by the gas flow, deposited on the surface of the catalyst gripper, thus reducing the catalytic activity or agglomerated in larger particles which represents the primary loss. Platinum deposits on the catalysts and catalyst grippers have a thick (dense) structure with subgrain wall layers which are crystallographically oriented.

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