

EXAMINING THE SURFACES IN USED PLATINUM CATALYSTS

Dr. Biserka T. Trumić, Ph.D., B.
Mining and Metallurgy Institute Bor,
Zeleni bulevar 33, Serbia

Aleksandra T. Ivanović, B. Technology
Mining and Metallurgy Institute Bor,
Zeleni bulevar 33, Serbia

Dr. Vesna Krstić, Ph.D., B.
Mining and Metallurgy Institute Bor,
Zeleni bulevar 33, Serbia

Dr. Lidija Gomidželović, Ph.D.B.,
Mining and Metallurgy Institute
Bor, Zeleni bulevar 33 Serbia

Silvana B. Dimitrijević, B. Technology
Mining and Metallurgy Institute Bor
Bor, Zeleni Bulevar 33 Serbia

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

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 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 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 [20-24] 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.

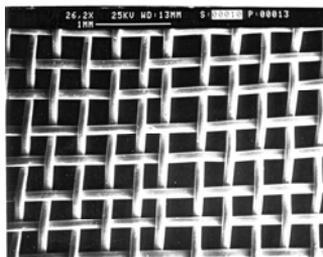
The first set of samples were PtRh10 catalyst gauzes and PdAu10 catalyst gripper gauzes, that is the second gauze from the catalyst gauze packaging and the first gripper from the grippers packaging.

The second set comprised of the fourth 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 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

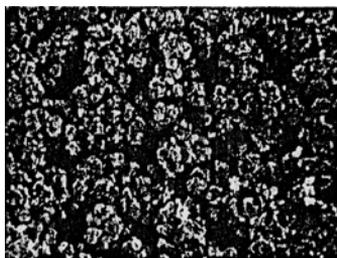
The examples of structural changes on the wire surface of catalyst gauzes with PtRh10 content and grippers of PdAu10 with magnification of 100x and 5000x, are shown in the following picture.



a)



b)



c)



d)

Picture 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).

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

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 PtRhPd gauzes 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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