

Surface Phenomena on Rhodium-Platinum Gauzes

CATALYST ACTIVITY DURING AMMONIA OXIDATION

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The rare occurrence of inactive catalyst gauzes for no obvious reason has led to comparative studies of the structures of rhodium-platinum wires from both active and inactive gauzes. Active gauzes showed the regular development of octagonal crystal faces on the nodular growths on the wires. Inactive gauzes showed no crystal development and an amorphous growth appeared on the wires. Segregation of rhodium and iron at the surface occurred in this case, perhaps due to unusual plant operating conditions, and may have caused deactivation.

The use of rhodium-platinum alloy gauze as the catalyst in the modern process for ammonia oxidation is well established, as shown by the large number of papers reviewed previously in this journal (1) and elsewhere (2). At the present time there are in the world more than 450 nitric acid plants and almost without exception they use platinum alloy catalyst gauzes, usually of 10 per cent rhodium-platinum.

The oxidation process is highly efficient and over a wide range of operating conditions a nearly quantitative conversion of ammonia to nitric oxide can be obtained. Conversion efficiencies of between 92 and 96 per cent are commonplace and are consistently achieved throughout the lifetime of a plant. In general the shortfall from maximum efficiency is probably due to some decomposition of the ammonia feedstock before it reaches the gauzes, rather than to significant yields from possible alternative reactions (1, 2) that can take place on the gauzes.

On rare occasions, however, a case is found of a catalyst gauze pad that is inactive. Although apparently indistinguishable from other gauze pads, the inactive gauze pad does not maintain its initial conversion efficiency

and uneconomical yields are obtained only a short time after igniting the pad. It would appear that the high selectivity of the catalyst gauzes for promoting the desired oxidation reaction steadily declines and that yields from alternative side reactions become significant. Treating the inactive gauzes with constant boiling hydrochloric acid and replacing them in the plant does not improve their performance. Replacement of the inactive pad by a fresh pad of gauzes has always overcome the problem but has done nothing to explain it.

Analytical examinations of inactive gauzes and of the material from which they were woven and cut do not give any indication of the cause of inactivity. The chemical composition of the gauze material has always been found to lie within the tolerance limits. Analysis to determine whether some unusual impurity had been scaled into the wire surface during the wire drawing process, or whether the retention by the gauzes of impurities entrained in the feedstock gas might account for the drop in activity, did not reveal any cause of the inactivity.

Although inactive gauze pads occur infrequently and are more of an occasional



Fig. 1 Careful inspection of gauzes fabricated by Johnson Matthey Metals before dispatch to nitric acid plants. The flat circular gauze will be installed in a medium pressure plant and the smaller hexagonal gauzes in high pressure plants. The large rolled circular gauze will be installed in a plant operating at atmospheric pressure

embarrassment than a constant cause of trouble, a more detailed examination of them was undertaken as part of a research programme to study the fundamental mechanisms involved in ammonia oxidation for nitric acid production.

Examination of Inactive Gauzes

To this end a number of inactive gauzes from two medium pressure plants were examined at various periods in their lifetime and the results, together with the results from a more general examination made of spent gauze pads taken from all types of plant in various parts of the world, were compared with those obtained from an examination of several inactive gauzes from two inactive gauze pads. A description of the results follows with a series of scanning electron microscope and electron microprobe analyser photographs illustrating the state of the gauze surface at various stages.

It has been previously reported (3) that rhodium-platinum gauzes develop nodules or "brussels sprout" growths on their surfaces while in operation in nitric acid plants. The catalytic activity of the gauzes appears to be related to the development of this nodular growth, since fresh gauzes with smooth as-drawn wire surfaces are inactive and need to be activated before they will oxidise ammonia efficiently. For this reason replacement gauzes are usually installed beneath some of the older activated gauzes already in the catalyst pad. When a new pad is being commissioned, each gauze in the new pad is activated by playing a hydrogen flame over its surface until the gauze just glows red. Alternatively, a few activated gauzes obtained from a plant already in commission are inserted on top of the fresh gauze pad and serve to ignite the remainder.

The photograph in Fig. 2 shows a gauze of 0.003 inch diameter wire with the wire in

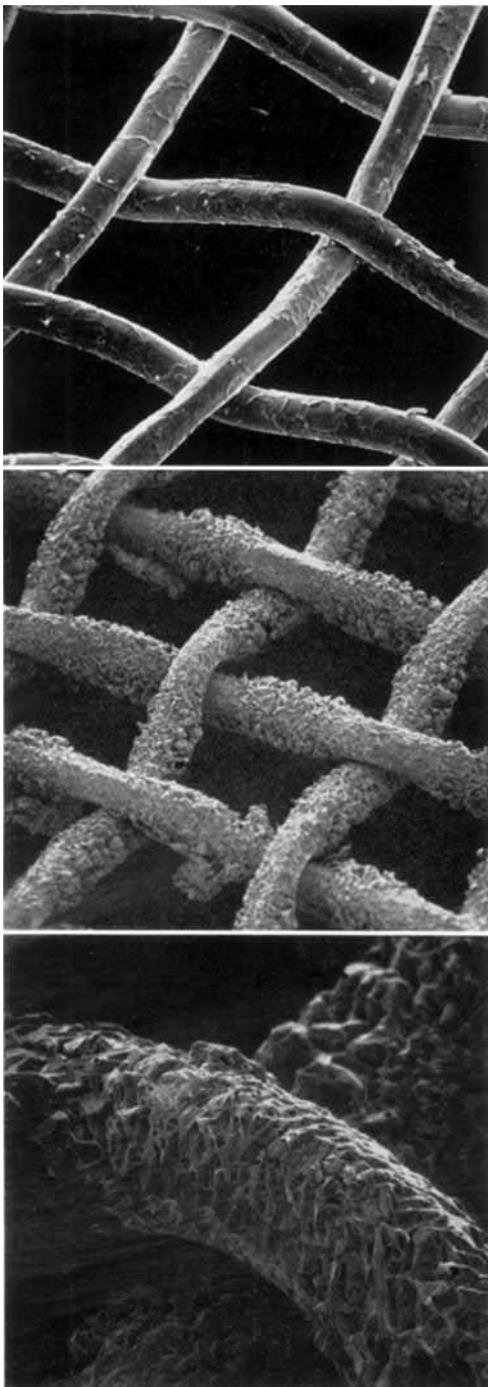


Fig. 2 10% Rh-Pt gauze wire 0.003 inch diameter in the as-drawn condition showing the uniform grain structure and absence of nodules on the wires

Fig. 3 The gauze of Fig. 2 after half the normal gauze life installed in a nitric acid plant showing the nodular pattern typical of an active gauze

Fig. 4 An enlarged view of the crossover point of two gauze wires from the gauze in Fig. 3 showing the octagonal crystal structure and the nodules, which are concentrated on the wire surfaces between crossover points

installed in a nitric acid plant for half the normal gauze life period. Its surface shows the development of the nodular pattern typical of an active gauze. An enlarged view of the crossover point of two gauze wires from the same gauze is seen in Fig. 4. A clearly developed octagonal crystal structure can be seen in the enlargement and also the development of the nodules, which appear to be concentrated on the surfaces between the crossover points. Perhaps nodular growth at crossover points is inhibited by the slight movement of the wires that occurs while the gauze is in service. The structure seen here is generally typical of active gauzes whether they have been operated in low, medium or high pressure plants.

When individual gauzes from an inactive pad are examined, a markedly different structure is observed. The regular development of octagonal crystal faces cannot be distinguished and an amorphous "cauliflower"-like growth as illustrated in Figs. 5 and 6 is seen, in contrast to the "brussels sprout" nodules usual on active gauzes.

Segregation at Wire Surfaces

The obvious visual difference in these highly magnified photographs suggested that electron image determinations might produce interesting results. Accordingly, two sets of active and inactive gauzes were examined, each set taken from one of two different medium pressure plants many thousands of miles apart. The electron image photographs

the as-drawn condition. The uniform grain structure and absence of nodules on the individual wires can easily be seen. Fig. 3 shows the same gauze after it has been

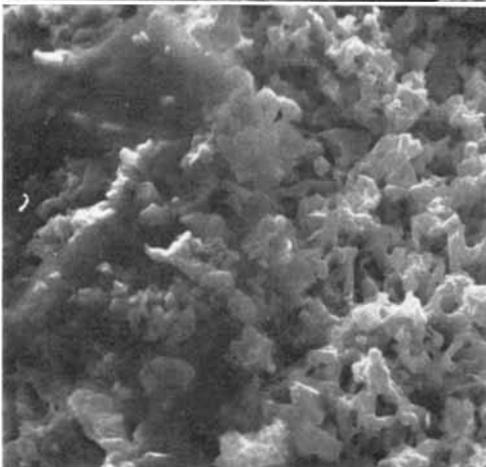
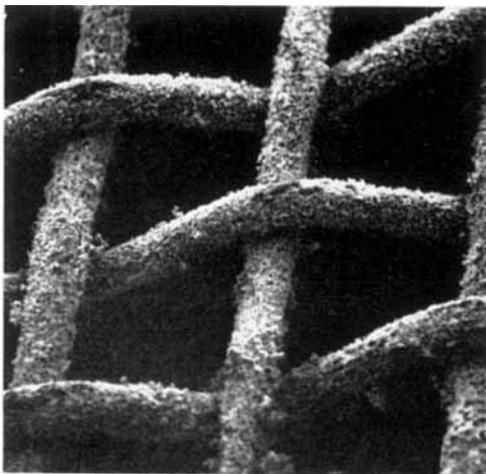


Fig. 5 An inactive gauze after a few days installed in a nitric acid plant showing the absence of octagonal crystal faces

Fig. 6 An enlarged view of the gauze wire shown in Fig. 5 with the cauliflower-like amorphous growth characteristic of inactive gauzes

of both sets of gauzes were similar and those taken from one set are shown.

Examination of the electron images from the active gauzes (Fig. 7) shows that the wires were homogeneous and no unusual features are visible. In the electron images of the inactive gauzes (Fig. 8) a clearly defined concentration of material is seen on the surface of the wires. This segregation on the

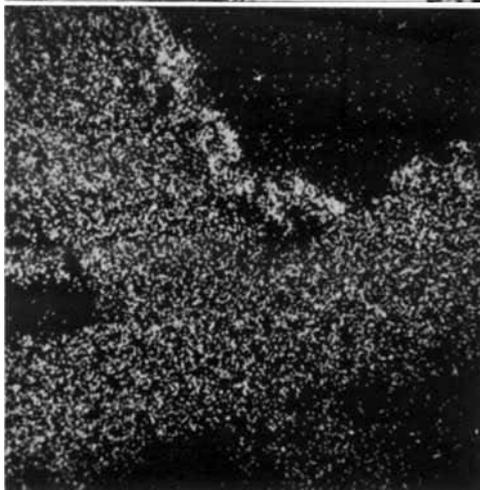
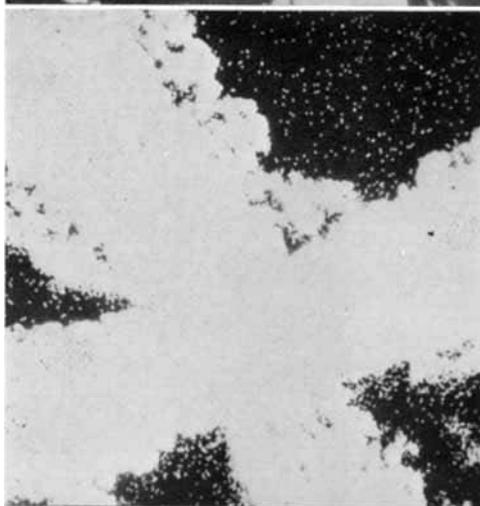
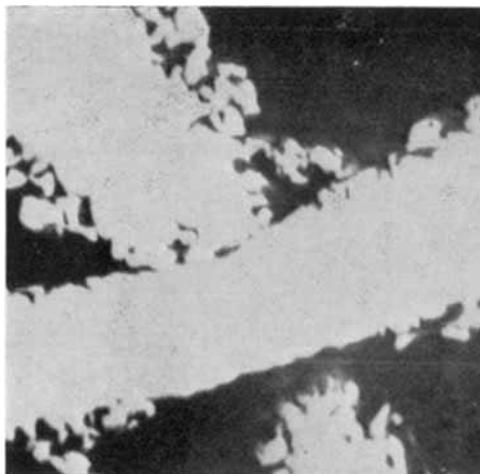


Fig. 7 (right) Electron and X-ray images of spent active gauze showing its homogeneity. a (top) Electron image of cross-section of gauze. b (middle) Pt M α X-ray image. c (bottom) Rh L α X-ray image. $\times 360$

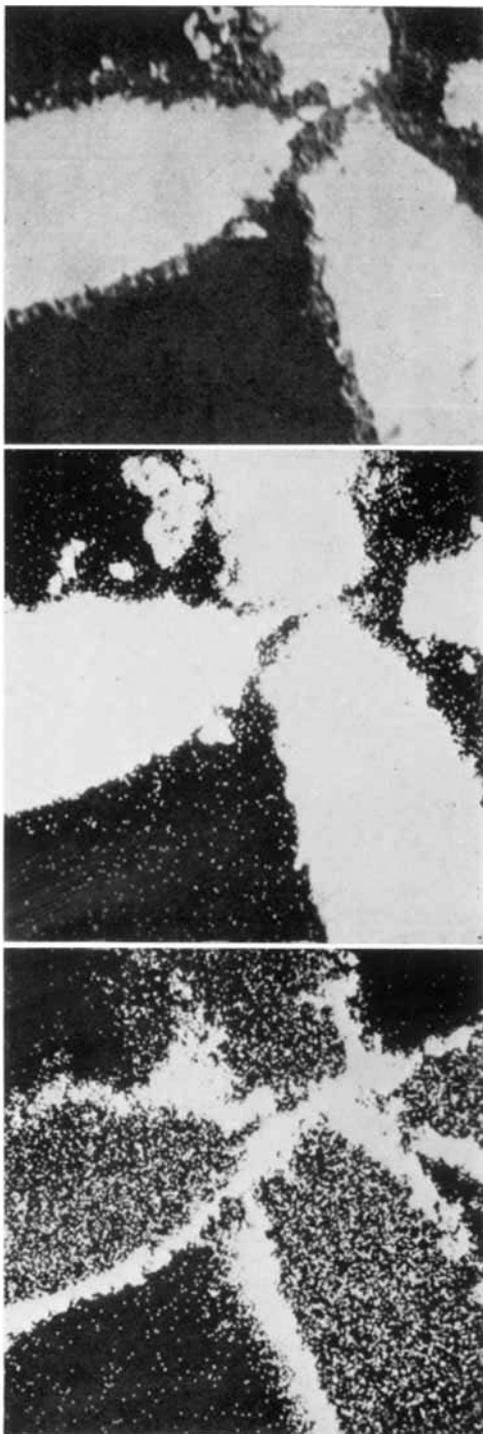


Fig. 8 Electron and X-ray images of spent inactive gauze showing segregation of material at the surface

a Electron image of cross-section of gauze

b Pt $M\alpha$ X-ray image

c Rh $L\alpha$ X-ray image

× 360

the effect is really due to the micro-section being a plane through the middle of the gauze so that more of the wire surfaces is visible at the crossover points where the wires dip and rise in crossing each other.

The composition of the material shown in Fig. 8c is very probably rhodium present as rhodium oxide Rh_2O_3 . A similar electron image was seen showing a concentration of iron, probably as Fe_2O_3 , which was associated with the surface concentration of rhodium. Neither of the active gauzes examined showed any sign of surface concentration of rhodium or iron oxides.

On both sets of inactive gauzes the cauliflower-like nodular structure and the concentration of rhodium and iron oxides on the wire surfaces were found to be present on all the gauzes in the pad although they became less severe from the top gauze downwards.

Surface concentrations of rhodium and iron have not been found on material from which the gauzes are cut out so it is thought that they develop within the plant itself. The factor or factors which initiate the concentrating process may be connected with some flaw in the manufacturing procedure but, since reports of inactive gauzes are related to individual ammonia burners rather than to batches of woven material from individual suppliers, it seems more likely that these factors will be found to lie in some unusual operating condition in the plant itself. A possible cause is a prolonged period of operation at low temperature, thereby encouraging the slow separation and concentration of rhodium oxide on the surface together with the preferential retention of small particles of iron oxide from the feedstock on the rhodium oxide, whereas at temperatures above $900^\circ C$ rhodium oxide would be expected to volatilise.

wire surface appears to be more marked at the crossover points but this is not so because

Fig. 9 Gauze fabrication on the looms in the Johnson Matthey Metals gauze shop. Rhodium-platinum gauzes up to 140 in (3.56 metres) wide are woven from 0.003 in diameter wire



The development of these inactive surfaces is the subject of further research work and in a later article it is hoped that an explanation will be given of the fundamental causes that lie behind these observations.

Acknowledgements

The author is much indebted to Dr G. J. K. Acres for helpful discussions and to Mr J. G. Day, who obtained the scanning electron microscope and electron microprobe analyser photographs.

References

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The Electrodeposition of Rhodium on Titanium

The protection of titanium by a thin coating of platinum is well known in chemical technology but, although platinised titanium anodes are commonly used for industrial electrochemical purposes, little attention has been given to titanium coated with other platinum group metals.

A recent paper by K. P. Batashev and V. P. Zverev (*Tr. Leningrad. Politekh. Inst.*, 1970, (304), 130-134) now reports on studies by the polarisation curve method of the electrodeposition of rhodium on titanium and indicates the feasibility of such plating. It can produce both protective and decorative coatings and also insoluble rhodium/titanium anodes. The features of rhodium for these purposes are its lesser density and greater hardness than platinum.

Titanium alloys were degreased chemically and then were etched in sulphuric acid solution at 60 to 90°C before plating in a bath containing 1.2 to 2.0 g/l rhodium and 40 to 50 g/l sulphuric acid at current densities between 0.1 and 1.5 A/dm² and at temperatures between 20 and 75°C. Insoluble anodes of platinum and rhodium-plated titanium were used and efficiency increased with lower current density and higher bath temperature.

The rhodium coatings obtained at low current density adhered well and were satisfactory as regards hardness, reflectivity (brightness) and corrosion resistance. Tests were carried out to determine the properties, strength and optimum thickness of rhodium coatings on insoluble titanium anodes.