Rhodium-Platinum Gauzes for Ammonia Oxidation

A STUDY BY SCANNING ELECTRON MICROSCOPY

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In the industrial production of nitric acid by the oxidation of ammonia over rhodium-platinum gauze catalysts the infrequent occurrence of an inactive gauze has prompted a number of investigations into their behaviour. This paper reports on a survey of the surface structure of individual gauzes in a catalyst pack and offers some indications towards the choice of optimum process variables.

The production of nitric acid by the catalytic oxidation of ammonia is of considerable importance to the heavy chemical industry, particularly since large quantities of synthetic ammonia, made by the Haber-Bosch process, are available at a reasonable price on the international market. As originally developed by Ostwald (1) and Brauer at the beginning of the century the industrial process used high purity platinum as catalyst. Subsequently platinum was superseded by rhodium-platinum alloys commonly using 5 and 10 per cent rhodium. Despite considerable research into catalyst composition, these metal alloys have not yet been replaced by any other catalyst capable of reducing the overall production costs for the acid.

The conversion efficiency for nitric oxide production achieved in commercial plants is between 92 and 98 per cent so that little room is left for improvement in this area. Plant operation is reasonably trouble-free and plant design for optimisation of the reaction conditions is well understood. All this in spite of the fact that there is still no certain knowledge as to which of three theories correctly describes the reaction sequence at the catalyst surface.

The ammonia-air mixture is burnt to nitric oxide in the presence of rhodium-platinum alloy gauzes in combustion chambers with diameters up to 4.5 metres. The plants may operate at low, medium, or high pressure corresponding to 1, 3 to 5, or 9 atmospheres

Optimum Operating Data for Ammonia Combustion

Pressure	Gauze temp. °C	NH_3 content, volume per cent	Yield per cent	Pt loss g/ton HNO_3	Operating time, months
Atmospheric	810 to 850	12·0 to 12·5	97·0 to 98·0	0·04 to 0·05	8 to 12
Medium, 3 to 5 atm.	870 to 890	10·5 to 11·0	96·0 to 96·5	0·10 to 0·11	4 to 6
High, 7 to 9 atm.	920 to 940	10·3 to 10·5	94·5 to 95·0	0·25 to 0·30	1½ to 3

respectively. The operating temperatures are different for the different pressures. Factors which can contribute to the operating temperature include plant design, the gas throughput per unit area of the gauze, or gauze loading, and the degree of preheating given to the ammonia-air mixture. The composition of the mixture is also important. The table gives optimised data for different plant types according to the operating pressure used (2).

The heart of each nitric acid plant is its catalyst gauze pack. Two major problem areas exist for both users and the producers of these gauzes. The first concerns the finite life of the catalyst gauzes and the second is apparent in occasional packs of gauze which, after a short life characterised by low conversion efficiency, become inactive.

The authors have made use of scanning electron microscopy to show the definite morphological changes which occur on the surface of the gauze wire under both normal and abnormal operating conditions.

Changes on the Surface of the Catalyst

Normal commercial operating practice uses a 10 to 12 volume per cent ammonia-air mixture. The overall equation describing the production of nitric oxide is:

$$NH_3 + \frac{5}{4}O_2 = NO + \frac{3}{2}H_2O + Q$$

where

$Q = 54,250 - 0.4\,(T - 298)$ cal. Mol^{-1} NH_3

It follows that the reaction is favoured by low pressure and high temperature operating conditions. The good yield also obtained in the high pressure plants is achieved by optimising other conditions such as gas throughput, gauze loading, and ammonia-air ratio.

After a new gauze pack has been installed and ignited a certain time is required to reach the maximum yield of nitric oxide. Several workers have reported (3, 4, 5) examinations of the process of "formation" or activation of the catalyst surface. This process is connected with the restructuring of the gauze surface which is a normal characteristic of used gauzes. Complex outgrowths and deep fissuring of the wire surface result in a greatly increased surface area. It will be shown here, however, that restructuring is not the same for all gauzes of a pack but is most marked on the gauzes with the highest conversion rate.

The interaction of oxygen molecules with the surface of the metal is believed to be the major cause of the restructuring of the surface. E. Raub (6) observed surface changes described as "thermal etching" on the surface of platinum heated in enriched oxygen atmospheres. Here it was postulated that surface diffusion of platinum atoms occurred to areas with lower surface free energy. Ultimately this would produce visible changes. H. H. Dunken (7) has used a quantum-chemical approach to attempt to describe the changes which could take place under an adsorbed oxygen layer. The adsorption of oxygen either as atoms or molecules on to the metal surface must therefore be considered as the first step in initiating both the catalytic process and the restructuring process at the gauze surface.

The restructuring effects which occur in use can be studied very conveniently with the scanning electron microscope, making use of the considerable depth of focus available even at high magnifications. A pack of three gauzes from a plant operating at atmospheric pressure was studied first. This pack had been in use for about twelve months under normal conditions and had given a good conversion efficiency.

Examination by Scanning Electron Microscopy

The dependence of surface condition on position in the pack is very well demonstrated by this pack. The greater part of the reaction takes place on the gas inlet side of the first gauze where the reaction load and the gauze temperature reach their highest levels. The second and third gauzes are subject to much lower loadings. Different structures are

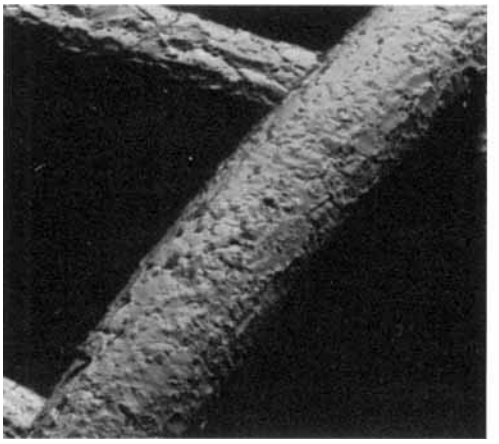

Fig. 1 Rear of gauze 3, backscattered electron image ×440

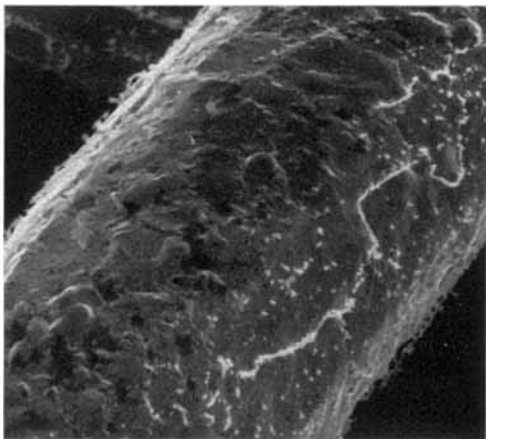

Fig. 2 Rear of gauze 3, secondary electron image ×1100

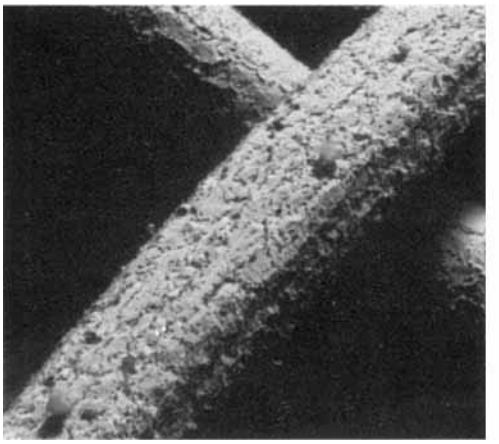

Fig. 3 Front of gauze 3, backscattered electron image ×440

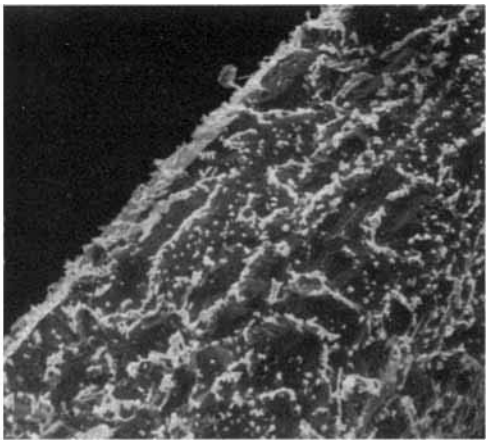

Fig. 4 Front of gauze 3, secondary electron image ×1100

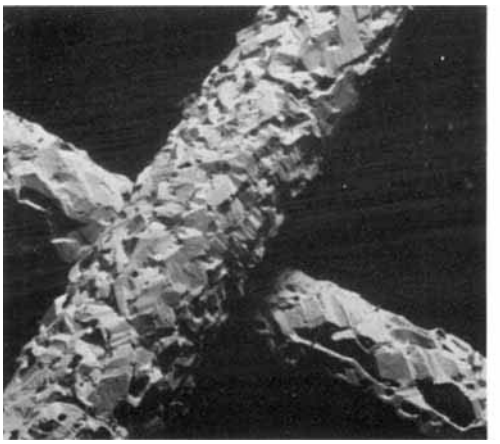

Fig. 5 Rear of gauze 2, backscattered electron image ×440

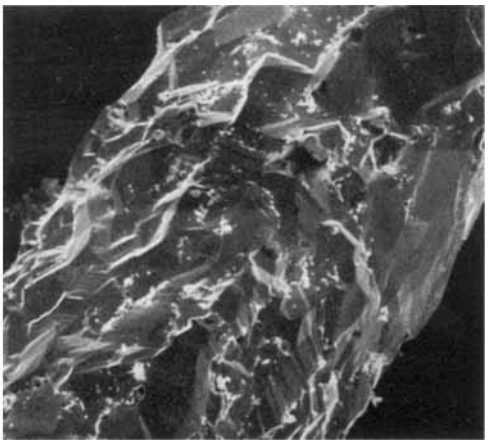

Fig. 6 Rear of gauze 2, secondary electron image ×1100

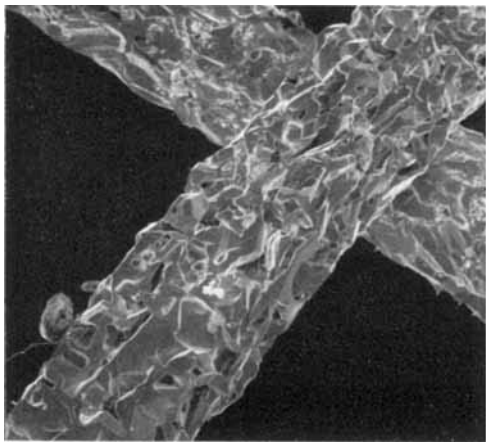

Fig. 7 Front of gauze 2, backscattered electron image ×440

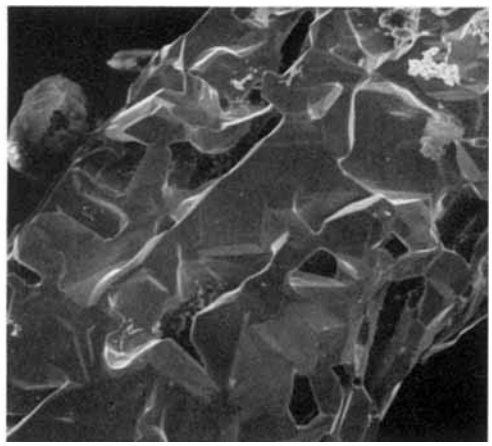

Fig. 8 Front of gauze 2, secondary electron image ×1100

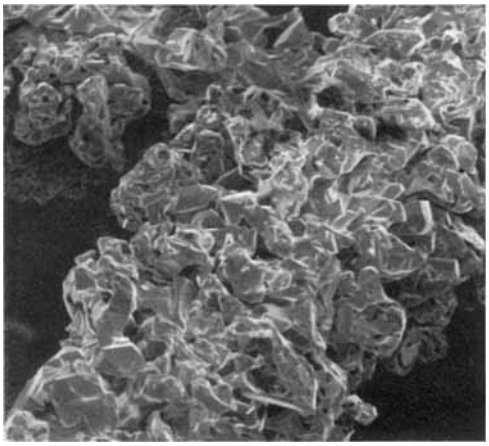

Fig. 9 Rear of gauze 1, backscattered electron image ×440

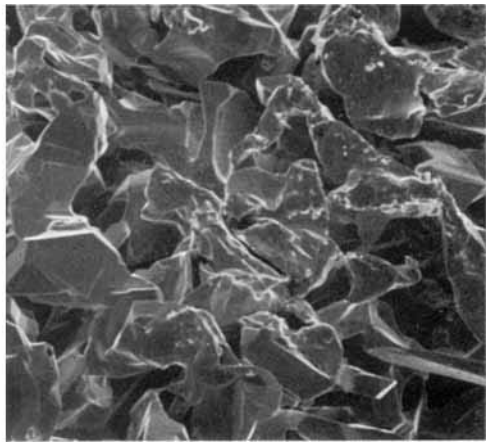

Fig. 10 Rear of gauze 1, secondary electron image ×1100

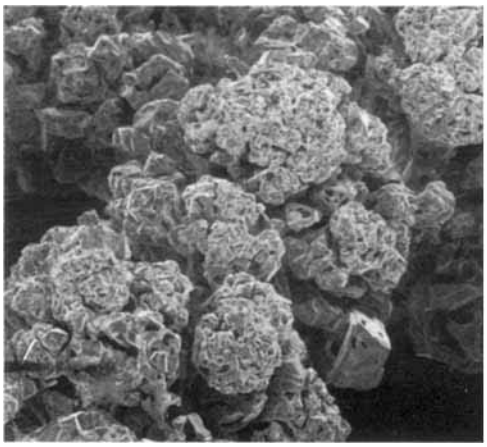

Fig. 11 Front of gauze 1, backscattered electron image ×440

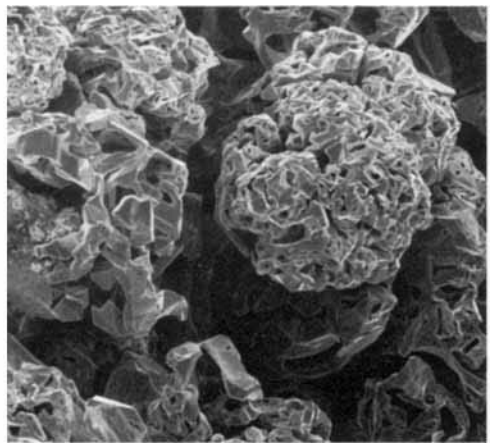

Fig. 12 Front of gauze 1, secondary electron image ×1100

also obtained on the front and back surfaces of each gauze.

The surface structures revealed by the scanning electron microscope will now be considered and an attempt will be made to relate them to the degree of reaction loading on each gauze. The simplest approach is to look at the lower loadings first, since these give the simplest structures. The back face of gauze No. three, away from the gas inlet, shows only an insignificant change compared to the original wire. Examination of Figures 1 and 2 shows an enhancement of the grain boundaries which is very similar to the thermal etching effect already mentioned. On the side facing the gas stream the individual grain facets have become well developed, as shown in Figures 3 and 4. Further development of the same type is apparent on the outlet side of gauze No. two as can be seen from Figures 5 and 6.

This type of structure is clearly indicative of a self-diffusion process with the surface atoms moving to sites with favourable energy. Figures 7 and 8, representing the front of the second gauze, show the first signs of deep fissures between the grains. The detail visible at all levels in these and the subsequent pictures of this series show clearly the great depth of focus available in this technique.

On the outlet side of the first gauze a general enlargement is seen and further deepening of the fissures is apparent. The individual grains are becoming separated. This is illustrated in Figures 9 and 10. The final stage is shown in Figures 11 and 12 representing the inlet side of the first gauze. The wire surface is now covered with cauliflower-like segregations developed from the original grains. These are so large as to be more conveniently studied at a lower magnification, and the general impression is given in Figure 13. These large structures can be explained by the fact that most of the reaction occurs on the front face of this gauze, resulting in a higher temperature. The deep fissures cause a reduction of the mechanical strength of the gauze by a simple reduction of the cross section available for load bearing. Failure of the gauze by fracture finally occurs.

Gauze Inactivity

Normally rhodium-platinum alloys catalyse the oxidation of ammonia with high efficiency. Occasional cases occur where the gauze pack becomes inactive after a short time and the conversion efficiency drops to an uneconomical value. This drop in performance has been considered to be due mainly to contamination of the catalyst material, the ammonia or the air supply. Careful analyses of all of these have given no direct indication of the presence of catalyst poisons. Another possibility considered was the transfer of rust particles from the pipework, or of ceramic particles from the filter, to the gauzes. These particles would certainly be capable of causing the reduction in efficiency but they can be easily removed by rinsing the gauzes in boiling hydrochloric acid. In some cases, however, this treatment was ineffective and the conversion remained low.

A pack of this type was recently examined with the scanning electron microscope. This time the pack was taken from a medium pressure unit where the conversion efficiency had dropped below 90 per cent after a short time. The pack was removed and it and the plant given a thorough examination. It was found that the pack had been run at 50°C below its normal temperature due to a calibration error of a measuring device.

Examination of the gauzes showed very different structures on the surfaces of the second and third gauzes. Figures 14 and 15 show the inlet face of gauze No. two. In addition to the normal well-formed grains a large number of needle-like crystals have formed. These needles are even better defined on gauze No. three, as shown in Figures 16 and 17. Figures 18 and 19 show two different aspects of the needle structure seen on gauze No. three at high magnification.

The structure in Figure 19 resembles that illustrated by J. E. Philpott (8), who concludes that the crystals are rhodium-oxide. We also

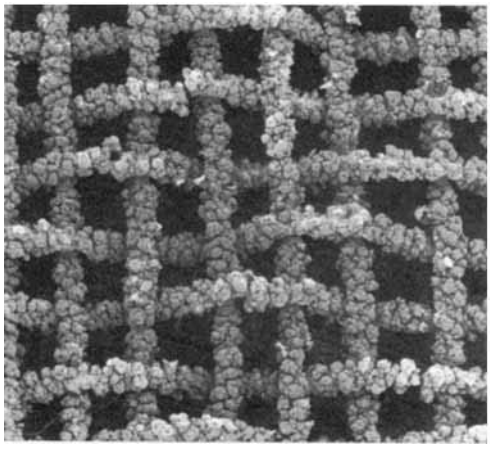

Fig. 13 Front of gauze 1, atmospheric pressure plant, secondary electron image ×44

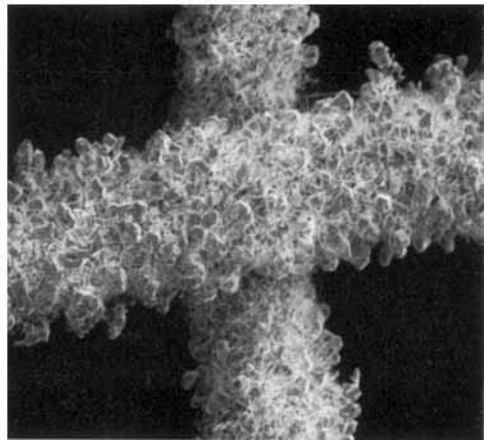

Fig. 14 Front of gauze 2 used in a medium pressure plant ×200

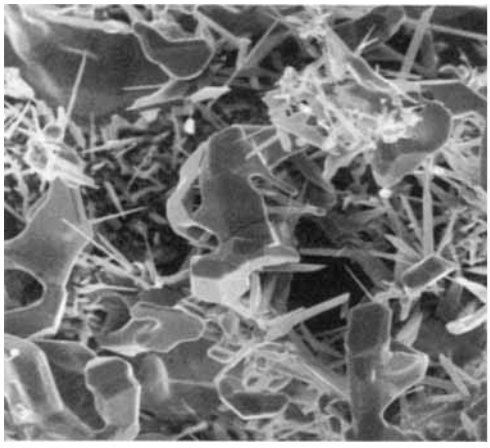

Fig. 15 Section of Fig. 14 ×2000

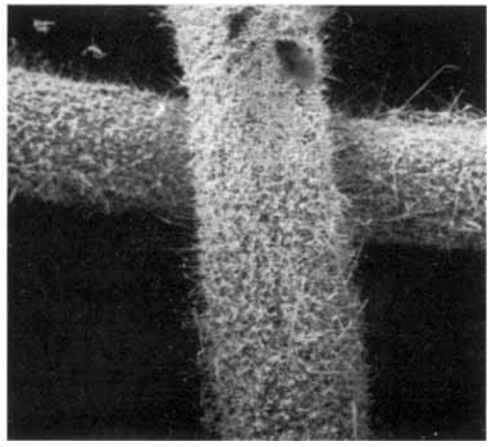

Fig. 16 Front of gauze 3 used in a medium pressure plant ×200

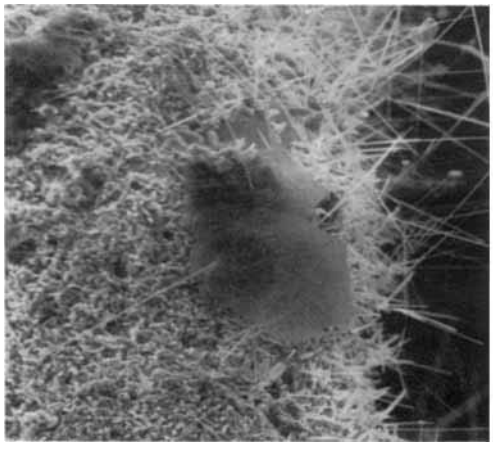

Fig. 17 Section of Fig. 16 ×2000

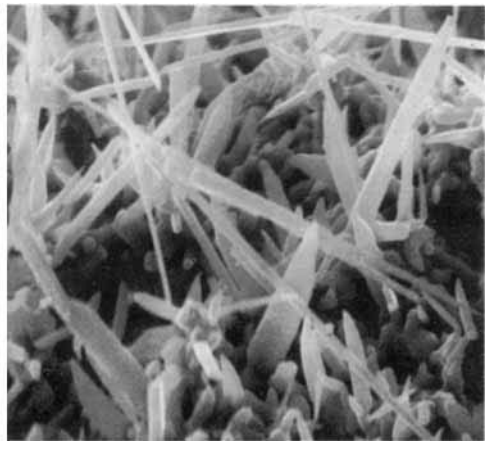

Fig. 18 Section of Fig. 16 ×4000

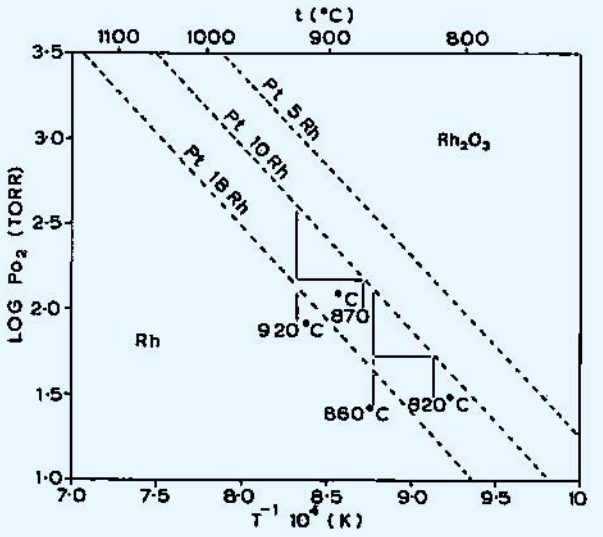

Fig. 20 Temperature dependence of oxygen partial pressure for formation of rhodium oxide on rhodium-platinum alloys

have examined areas with large concentrations of needles using X-ray diffraction methods and confirm the presence of rhodium-oxide.

An explanation for the formation of rhodium oxide under these conditions has been advanced by Schmahl and Minzl (9), who studied the relationship between the decomposition of rhodium-oxide and oxygen pressure and temperature for several rhodium-platinum alloys. From their results, shown graphically in Figure 20 it can be inferred that rhodium-oxide formation on a 10 per cent rhodium-platinum alloy occurs only below 884°C. To a first approximation these figures are also valid for ammonia oxidation, although the presence of nitric oxide must be expected to exert some influence.

As already noted 10 to 12 per cent of ammonia is mixed with the preheated air and it can be calculated that at this instant the oxygen partial pressure will be about 146 Torr. After the conversion has taken place this pressure is reduced to about 53 Torr. Figure 20 also shows a working range, using 10 per cent rhodium-platinum alloy, of 820 to 860°C throughout the pack where the formation of rhodium-oxide will not be expected. These figures agree well with those used in atmospheric pressure plants. For medium pressure plants the temperature range is raised to 870 to 920°C because of the higher oxygen partial pressure. Again these figures are in agreement with normal practice. It will be easily appreciated that a drop in the operating temperature of 50°C could give rise to the formation of rhodium-oxide, as indeed was found on the inactive gauzes examined. Holzmann (10), who studied the effect of rhodium additions to platinum on the catalytic activity, observed that pure rhodium by itself only gives 80 per cent conversion efficiency. He inferred that the large amounts of non-volatile oxide which form will probably obstruct the active chemisorbed layer of oxygen so that the first reaction according to the hydroxylamine theory is restrained:

$$NH_3 + O = NH_2OH$$

When running at low temperatures, diffusion processes will ensure that the surface composition moves automatically towards pure rhodium; the rhodium oxidised at the surface being continuously replaced from inside the wire by diffusion. A rhodium oxide layer of sufficient thickness will act in the same manner as a pure rhodium surface and give a reduced yield.

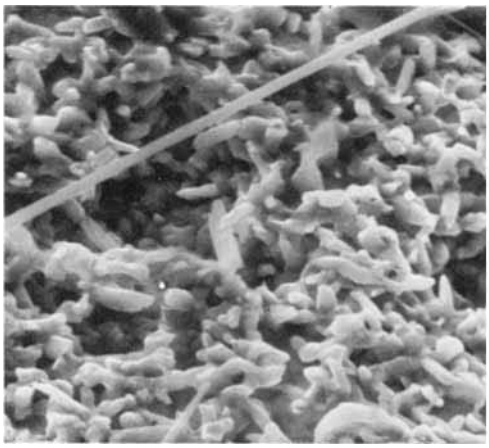

Fig. 19 Section of Fig. 16 ×4000

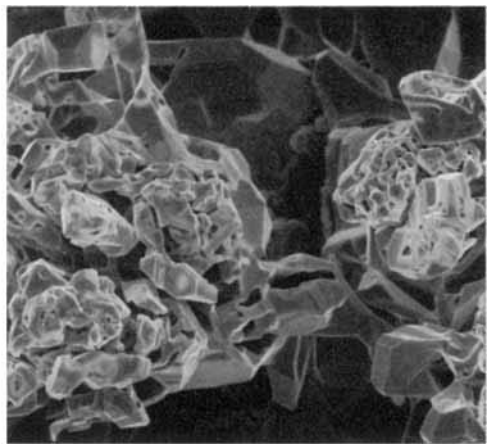

Fig. 21 Front of gauze 1 used in a medium pressure plant, secondary electron image ×2000

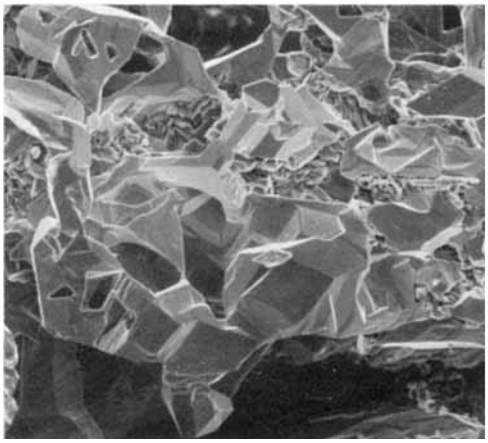

Fig. 22 Rear of gauze 1 used in a medium pressure plant, secondary electron image ×2000

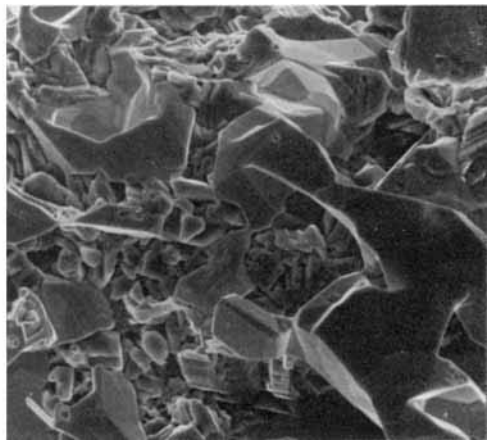

Fig. 23 Front of gauze 2 used in a medium pressure plant, secondary electron image ×2000

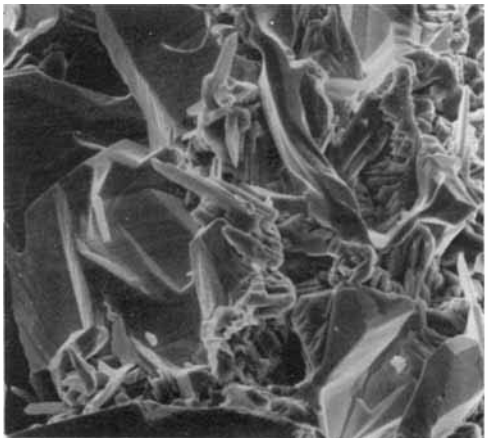

Fig. 24 Rear of gauze 2 used in a medium pressure plant, secondary electron image ×2000

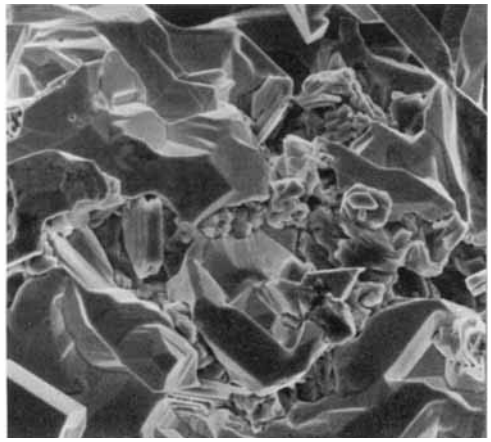

Fig. 25 Front of gauze 3 used in a medium pressure plant, secondary electron image ×2000

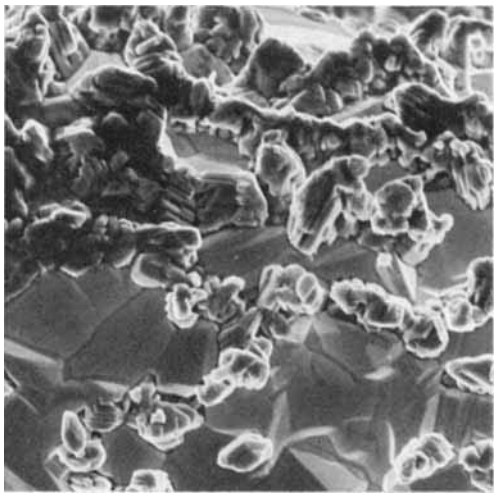

Fig. 26 Rear of gauze 3 used in a medium pressure plant, secondary electron image ×2000

Rinsing in hydrochloric acid will not change the behaviour of this type of surface since rhodium oxide is insoluble even in the boiling acid. The oxide can, however, be reduced with hydrogen or dissociated under nitrogen as suggested by Harbord (11). After these treatments a diffusion anneal should be used to redistribute the rhodium in the gauze alloy. Harbord also mentions that rhodium oxide formation is unavoidable in high pressure plants because of the high oxygen partial pressure. This will only be true where a compromise, between the temperature required to prevent rhodium oxide formation and that necessary to restrict direct metal losses to a tolerable amount, has to be made. Connor (4) states that metal losses increase by a factor of ten if the operating temperature is increased from 820 to 920°C. The effect of such a compromise is shown in the final set of scanning electron micrographs in Figures 21 to 26. These pictures are of gauzes from a medium pressure plant using five gauzes. Nothing unusual was noticed on gauzes No. four and No. five, where thermal etching only was observed, and on the inlet face of the first gauze the usual complex growths are seen (Figure 21). On the back of the first gauze, and on both sides of gauzes Nos. two and three, areas of crystalline rhodium oxide are seen between the metal grain structures. The rhodium oxide appears to reach its maximum development on the back of the second gauze. Provided these areas do not increase in size, the performance of the catalyst will be only slightly affected.

This short account shows how useful the scanning electron microscope is for examinations of catalyst gauzes with good or bad performance. As well as providing spectacular pictures it is possible that the study of the surface structures may come to be a more reliable guide to optimum process operation than the more usual measurements of temperature, pressure and gas compositions.

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Catalytic Purification of Industrial Waste Gases

Too many manufacturing processes still result in the discharge to the atmosphere of noxious gases even though the technology for removing the offending contaminants frequently exists or can readily be developed.

A short communication by T. G. Alanova, A. A. Myagkova and V. N. Kulikova (*Khim. Prom-st.*, 1975, (3), 233), describes work which has been successfully carried out to purify the waste gases resulting from a fermentation process during the manufacture of streptomycin. A comparison of catalytic and high temperature methods showed the superiority of the catalytic process and favoured a platinum on Nichrome catalyst.