The Mechanism of Reconstruction of Rhodium-Platinum Catalyst Gauzes

AN EXPLANATION OF THE NEW SURFACE MORPHOLOGY

By A. R. McCabe and G. D. W. Smith
Department of Metallurgy and Science of Materials, University of Oxford

and A. S. Pratt
Johnson Matthey Technology Centre

The surface reconstruction on rhodium-platinum catalyst gauzes has been examined using scanning electron microscope techniques. The nucleation and growth of the large cage-like features which develop on the gauze surfaces during operation in the ammonia oxidation process have been studied in detail. It is concluded that a vapour phase mechanism involving transport of platinum oxide is responsible for the observed reaction, and the reason why this process operates only over a limited range of temperature and pressure is explained. Some comments are also made on the related reconstruction observed on gauzes used during the production of hydrogen cyanide by the Andrussow process.

Rhodium-platinum gauzes serve as catalysts for the oxidation of ammonia during the production of nitric acid and for the manufacture of hydrogen cyanide. The former, which is based upon the reaction

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

has given rise to several papers previously published here (1–4), and the manufacture of hydrocyanic acid from methane, ammonia and air by the Andrussow process

$$2CH_4 + 2NH_3 + 3O_2 \rightarrow 2HCN + 6H_2O$$
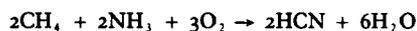
has also been reported (5).

There have been many studies of the surface reconstruction processes which take place when platinum and rhodium-platinum gauzes are used in such catalytic reactions (6, 7). Flytzani-Stephanopoulos and Schmidt have reviewed the available literature on thermal etching and morphological changes (8). Most studies have been carried out on pure platinum, with more limited work on rhodium-platinum. Features observed include facets, pits and more exten-

sive cage-like growths. The latter are particularly common under commercial plant operating conditions and therefore merit special attention. Typical examples of the cage-like growths formed during ammonia oxidation are shown in Figure 1.

A number of questions remain unanswered from previous investigations. The mechanism for the nucleation and growth of the cage-like structures is not clear, and the reasons why they are observed only over a limited range of temperature and gas mixtures are not explained. Also their relation to the faceting and pitting observed at high temperatures is not understood. Furthermore, the effect of the presence of rhodium on the reconstruction process has not been studied in detail. Identical gauzes are used in hydrogen cyanide production. These run at higher temperatures and they also facet and heavily reconstruct. It has never been fully explained why their reconstructions differ, nor why there is a much lower rate of metal loss in this process—whereas metal loss from ammonia oxidation gauzes is
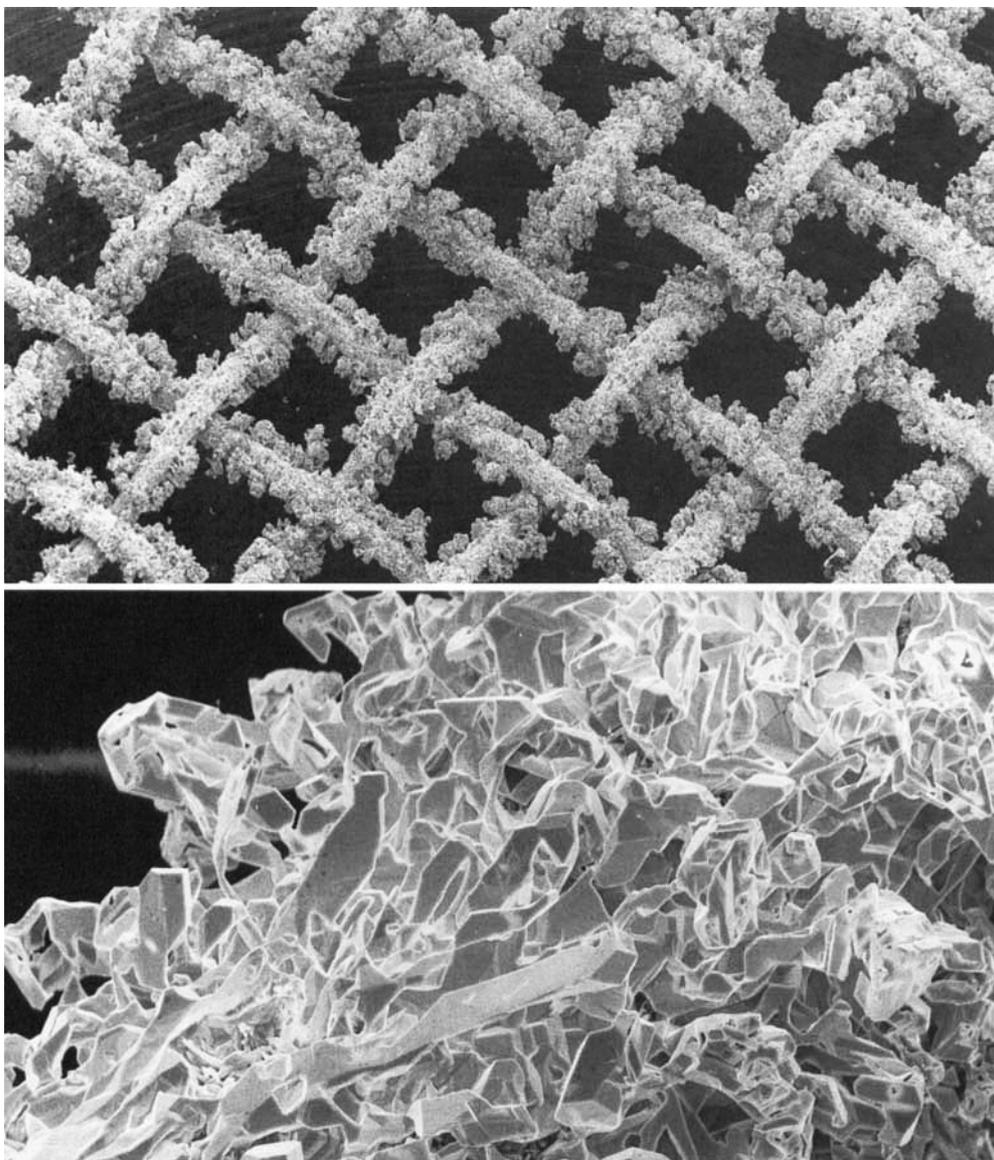
Fig. 1 This section of gauze from a commercial ammonia oxidation plant shows both the general and the detailed reconstruction of the surface of the wires that has taken place during operation. The magnification of the upper electron micrograph is ×64, and that of the lower is ×1250

one of the most important variable cost parameters in the process.

We have carried out a new investigation of these problems using a range of high resolution microscopical and surface microanalytical techniques. In this paper we shall concentrate on the mechanism of development of surface microstructural features, as observed with a scanning electron microscope (SEM). In a subsequent paper (9) we will report on surface chemical changes and the role of rhodium.

A miniature catalytic reactor, with 0.5 inch diameter gauzes, and a larger scale pilot plant using 4 inch gauzes were used to study the ammonia oxidation reaction. The gauzes were exposed to ammonia-air mixtures in the range 6 to

13 per cent ammonia (corresponding to operating temperatures of 650 to 1200°C) for times from 0.5 to 15 hours. Gauze temperatures were measured by pyrometry and conversion efficiencies by wet chemical analysis. A scanning electron microscope was used to study the surface microstructural changes occurring on 10 per cent rhodium-platinum gauzes, with some work being carried out on pure platinum gauzes for comparison. Photoelectron spectroscopy and electron probe microanalysis measurements were also made and these will be reported in our subsequent paper, with data from field ion microscopy and atom probe.

Observation of the Surfaces

The results of exposing rhodium-platinum gauzes to 6, 8, 10 and 12 per cent ammonia-air mixtures in the miniature reactor for fifteen hours are shown in Figure 2. The reconstruction process occurs only over a limited range of gas mixtures. It is particularly interesting to note that at 6 per cent ammonia, the catalytic reaction virtually stopped after only four hours, leaving a herringbone-type of structure on the surface. After operation in 12 per cent ammonia, the gauze surface was smooth with angular holes and cavities. Only at intermediate ammonia concentrations did extensive surface reconstruction occur. All the effects occurred at slightly lower ammonia levels than in a commercial plant, apparently due largely to differences in heat dissipation conditions in the miniature reactor.

The nucleation of reconstruction was studied using a shorter exposure time of two hours. Figure 3 shows the role of recrystallisation and of grain boundaries. The as-received gauze shows surface markings due to wire drawing. However, during pretreatment with a hydrogen torch the gauze recrystallises from its drawn texture, and grain boundary grooves become clearly visible. Following exposure for two hours in the reactor in 10 per cent ammonia, deep cavities develop along grain boundaries, while similar exposure in 13.5 per cent ammonia results in a smooth more rounded surface.

The progressive development with time of the cage-like growths, including the encroachment into grain interiors, can be seen in Figure 4, which shows the effects of exposure for 0.5, 1, 2 and 4 hours in an air 8 per cent ammonia mixture. After only half an hour the previously smooth recrystallised surface shown in Figure 3 (b) has started to reconstruct, Figure 4 (a), this seeming to occur most extensively on some preferred-orientation grains. Figure 4 (b) shows the build up of the growths on these crystals. It is interesting to note the part played in propagating the reconstruction into the grain interiors by the intersection of thermal facets and grain boundary grooves. Figures 4 (c) and 4 (d) show clearly that the reconstruction spreads out from these intersection points. The surface is finally completely covered by the cage-like growths as in Figure 2 (b).

The larger pilot plant was used to compare pure platinum and rhodium-platinum alloy catalyst gauzes. This allowed accurate observation of the two types of catalyst materials under identical operating conditions. The pilot plant gave the same type of reconstruction for a given gas mix as a commercial plant, with a rate of reconstruction somewhat faster than that of a commercial plant but slower than for the miniature laboratory reactor. The reconstruction in the case of pure platinum gauzes was significantly faster than that for identically treated alloy gauzes. For example, Figures 5 (a) and 5 (b) show the microstructures observed on the two types of gauze after a two hour exposure to a 10 per cent ammonia mixture. It is possible that the presence of the rhodium in the surface layer of the catalyst restricts the rate of platinum evaporation, so reducing vapour transport processes. This is considered below.

Discussion

The high vapour pressure of PtO_2 compared to that of platinum (10), along with the observations of weight losses from operational gauzes—and hence the need for catchment gauzes (11)—indicate that there is substantial PtO_2 volatilisation in the ammonia oxidation process. A vapour phase mechanism for reconstruction is therefore likely, as first proposed by

Fig. 2 These gauzes, which have been exposed to a range of gas mixtures during operation for 15 hours in the miniature reactor, demonstrate that the changes in surface structure are influenced by the gas mixture: (a) air-6 per cent ammonia, this catalyst became inactive during operation, (b) air-8 per cent ammonia, (c) air-10 per cent ammonia, (d) air-12 per cent ammonia ×1000
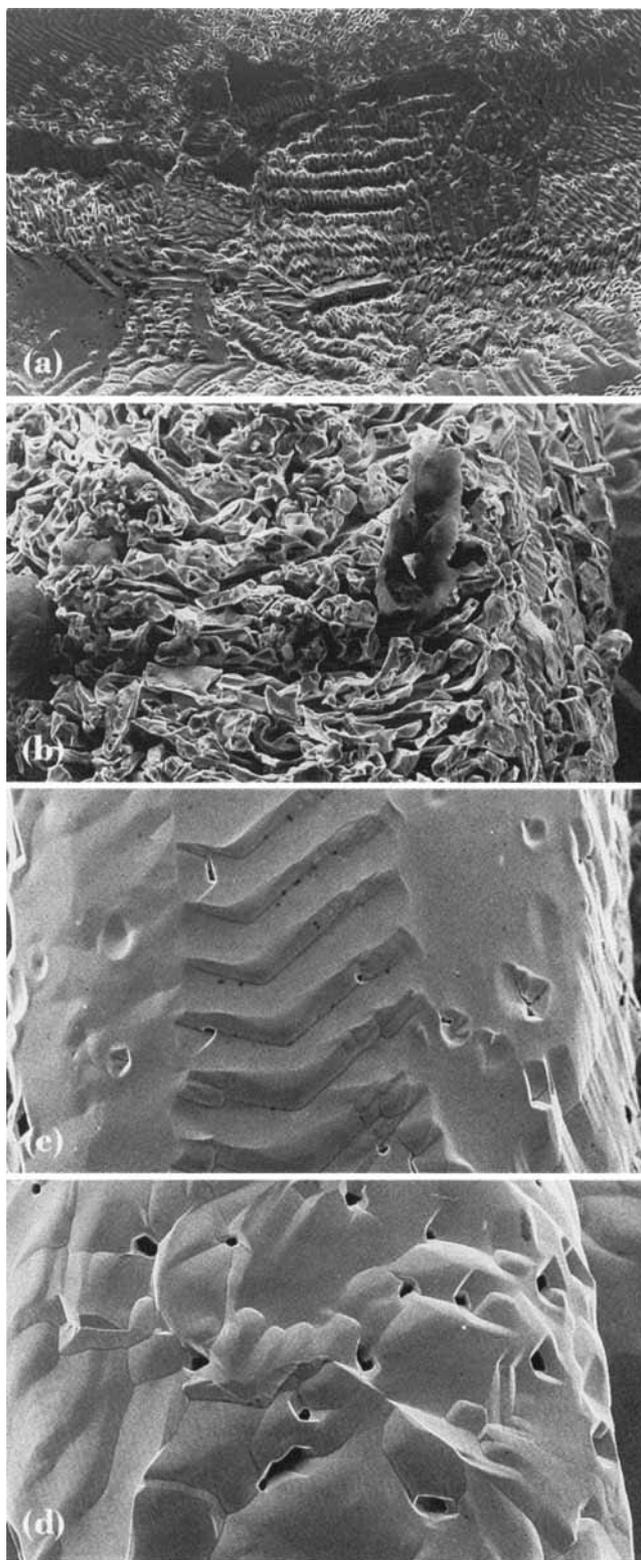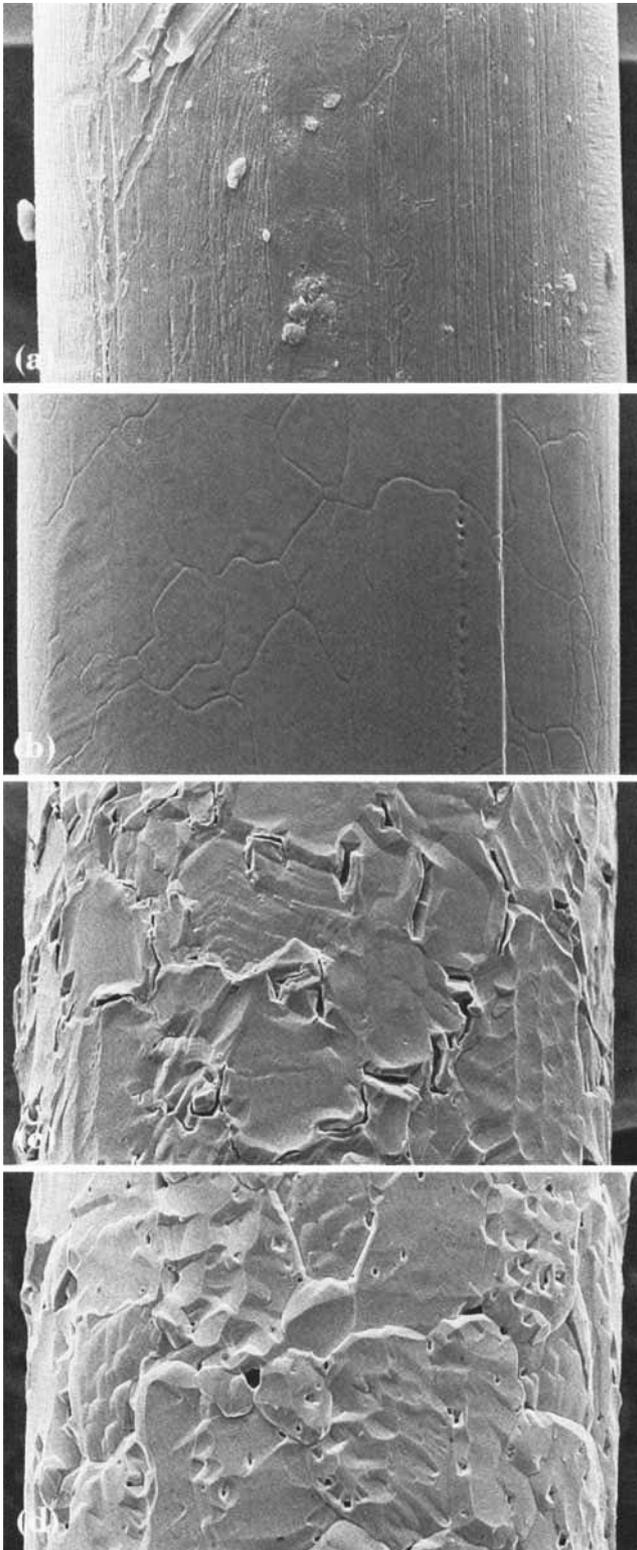
Fig. 3 The nucleation of the reconstruction process was observed on gauzes after two hours in the miniature reactor. (a) Drawing striations are visible on the as-received gauze, but pretreatment in a hydrogen flame causes recrystallisation (b), when grain boundaries become visible. Exposure to air-10 per cent ammonia (c) results in the development of deep cavities along grain boundaries, while in air-13 per cent ammonia (d) more rounded holes develop and the surface is smoother ×1000

Fig. 4 On rhodium-platinum gauzes exposed to air-8 per cent ammonia the progressive build up of the reconstructing surface can be seen with increasing time, until the surface becomes completely covered by cage-like growths. (a) ½ hour, (b) 1 hour, (c) 2 hours and (d) 4 hours   ×1000
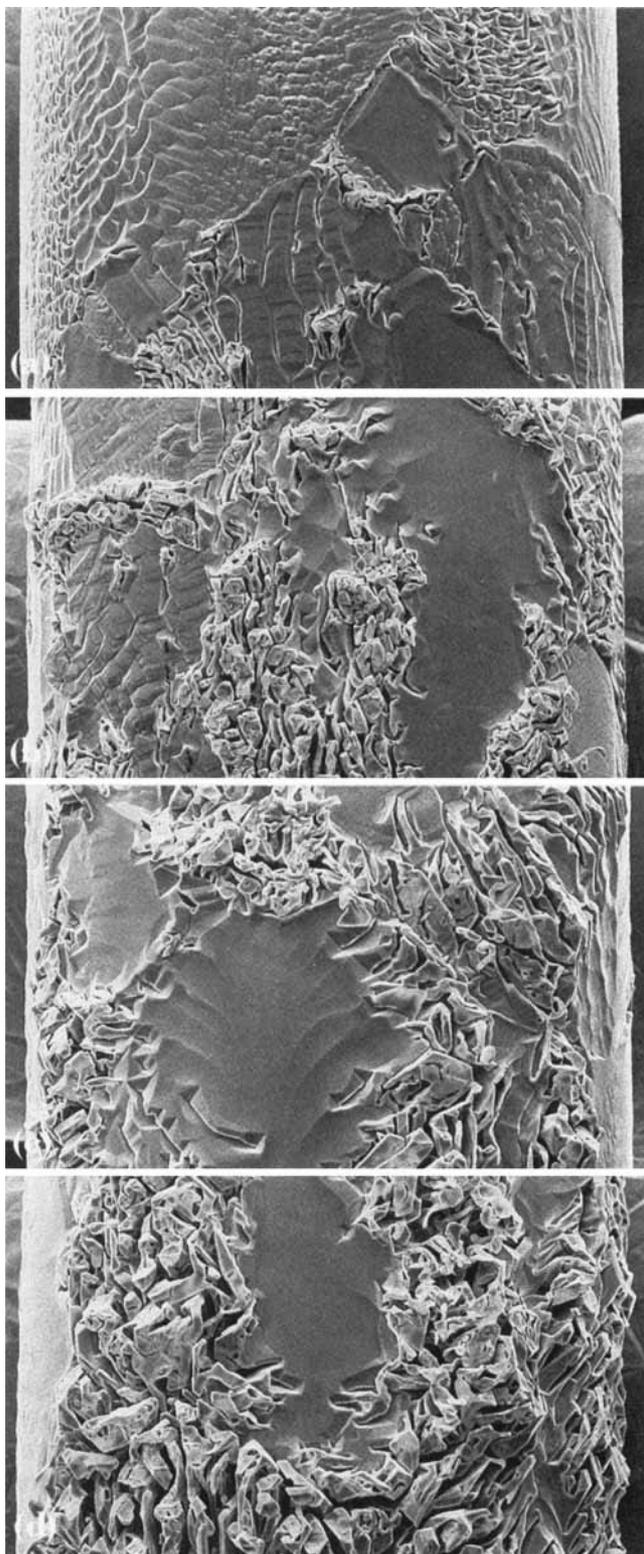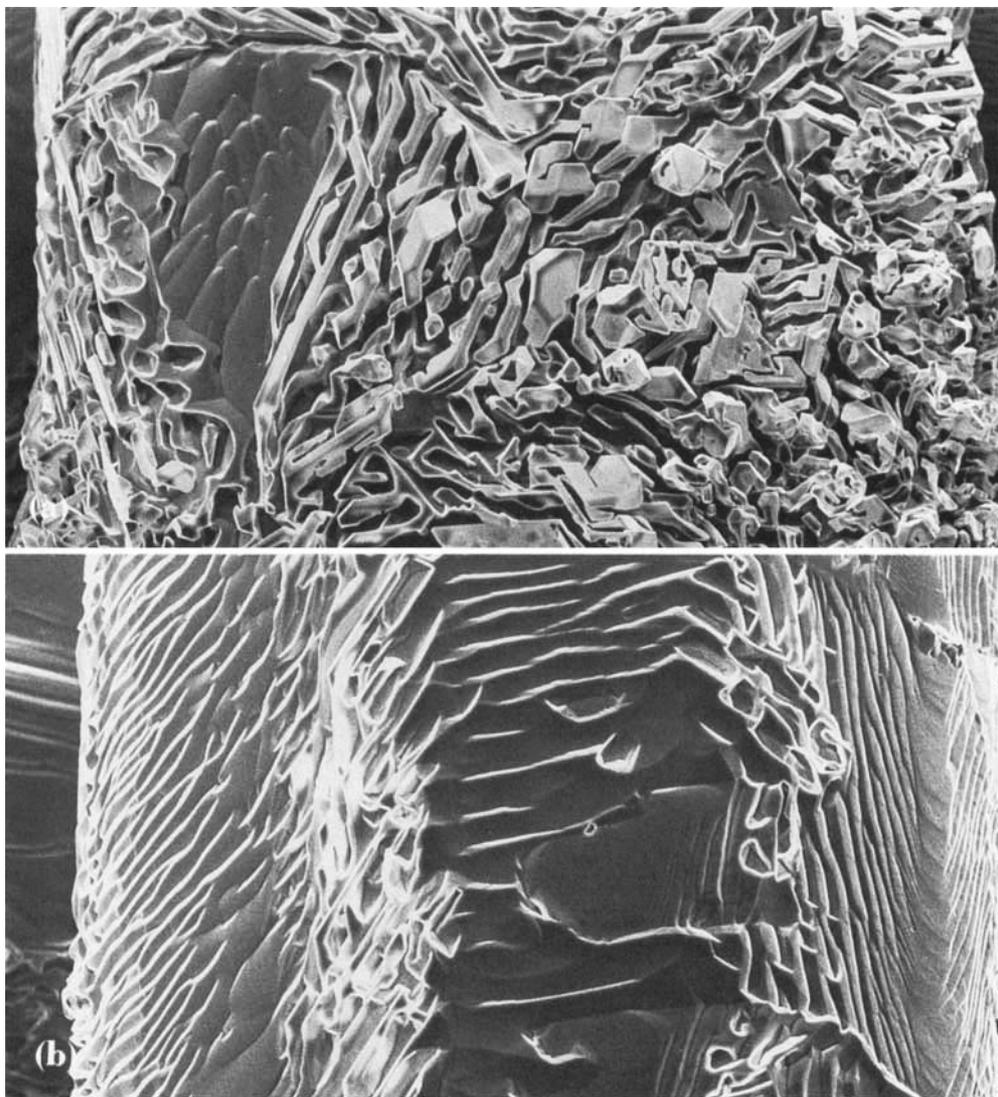
Fig. 5 After reaction in the pilot plant for two hours in an air-10 per cent ammonia mixture it is apparent that the rate of reconstruction of the surfaces of pure platinum and 10 per cent rhodium-platinum are markedly different. In each case the leading face of the third gauze in a pack is shown. (a) pure platinum, (b) rhodium-platinum ×1600

Schmidt and colleagues (12, 13). We have developed this model further, to explain the microstructural features of reconstruction and their dependence on conditions such as gas composition and temperature (14). Our proposed mechanism is illustrated diagrammatically in Figure 6. Consider the boundary between two grains, where a groove will develop on heating simply due to surface tension effects. The feed gas contains excess oxygen and the catalytic reaction is very efficient, so most of the ammonia will be oxidised on initial contact with the outer surface of the gauze. The gas reaching the bottom of the grain boundary groove will therefore be more strongly oxidising than the gas at the surface. Platinum oxide will form here preferentially, and will diffuse outwards, to where it meets a more reducing atmosphere,

and so platinum will be deposited on the outer surface. Thus the grooves will deepen, and the surface will build up, resulting in the hollow cage-like growths seen on reconstructed gauzes, the process being driven by gradients in oxygen potential. The intersections between thermal facets on the grain surfaces and the grain boundary grooves form particularly potent sites for the nucleation and development of the surface growths, since these are the most deeply recessed points on the gauze surfaces.

To understand why the reconstruction occurs only over a limited range of temperature and gas mixtures we have to consider the main physical processes taking place on the gauzes:

   [i] Platinum oxide vapour formation, migration and decomposition

   [ii] The selective oxidation of the rhodium species

   [iii] Thermal faceting

   [iv] The formation of grain boundary grooves

   [v] Surface diffusion

   [vi] Bulk diffusion in both the metal and the oxide.

The extent of each process is dependent on the reaction conditions, the vapour transport process dominating over only a limited range of these conditions. If the temperature is too low (low ammonia content in the gas stream), there is insufficient PtO_2 vapour pressure so the dominant process is the selective oxidation of rhodium to form Rh_2O_3. Under these conditions, the catalyst is rapidly deactivated. If the temperature is too high (high ammonia content), then surface and bulk diffusion are greatly enhanced, leading to a smoothing out of the surface features and a consequent large reduction of surface area. The lower rate of reconstruction observed in the case of rhodium-platinum gauzes suggests that the partial vapour pressure of PtO_2 over the alloy is lower than over pure platinum. This would help to explain the reduced weight losses observed commercially when alloy gauzes are used.

It is interesting to consider how the ideas developed above might be applied to the case of hydrogen cyanide production. In this case the gauze temperatures are 200 to 300°C higher than in the ammonia oxidation reaction, but the equilibrium partial pressure of oxygen in the gas mixture is many orders of magnitude lower. The weight losses from the gauzes are much smaller in comparison. The reconstructions extend much deeper into the gauze, and gauze spaces are eventually blocked during use. Two mechanisms of reconstruction seem possible in this case. First, as the vapour pressure of PtO_2 is orders of magnitude higher than that for platinum (10), even a very small partial pressure of oxygen could produce localised oxide vapour transport. Any volatile oxide formed would be decomposed after travelling only a very limited distance, so metal loss would only be due to direct metal volatilisation. Secondly, there is the possibility of grain boundary and surface diffusion controlling the movement of material, possibly involving the migration of a Pt-O complex. As in the case of the ammonia oxidation process the driving force for reconstruction must be the localised variations in oxygen potential.
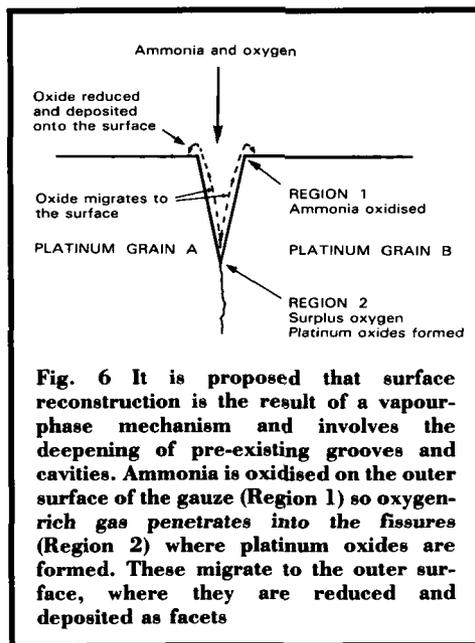
We now have a clearer understanding of the

Fig. 6 It is proposed that surface reconstruction is the result of a vapour-phase mechanism and involves the deepening of pre-existing grooves and cavities. Ammonia is oxidised on the outer surface of the gauze (Region 1) so oxygen-rich gas penetrates into the fissures (Region 2) where platinum oxides are formed. These migrate to the outer surface, where they are reduced and deposited as facets

structural changes occurring on rhodium-platinum gauzes, and the mechanisms involved. The next stage is to look at the surface composition changes involved in more detail. This will be the subject of a later paper.

References

1 J. Pielaszek, *Platinum Metals Rev.*, 1984, **28**, (3), 109
2 A. R. McCabe and G. D. W. Smith, *Platinum Metals Rev.*, 1983, **27**, (1), 19
3 A. C. Heywood, *Platinum Metals Rev.*, 1982, **26**, (1), 28
4 F. Sperner and W. Hohmann, *Platinum Metals Rev.*, 1976, **20**, (1), 12
5 J. M. Pirie, *Platinum Metals Rev.*, 1958, **2**, (1), 7
6 J. A. Busby, A. G. Knapton and A. E. R. Budd, *Proc. Fertiliser Society*, 1978, 169
7 L. D. Schmidt and D. Luss, *J. Catal.*, 1971, **22**, 269
8 M. Flytzani-Stephanopoulos and L. D. Schmidt, *Prog. Surf. Sci.*, 1979, **9**, 83
9 A. R. McCabe and G. D. W. Smith, to be published.
10 A. S. Darling, *Int. Metall. Rev.*, 1973, **18**, (175), 91
11 H. Holzmann, *Platinum Metals Rev.*, 1969, **13**, (1), 2
12 R. W. McCabe, T. Pignet and L. D. Schmidt, *J. Catal.*, 1974, **32**, 114
13 M. Flytzani-Stephanopoulos, S. Wong and L. D. Schmidt, *J. Catal.*, 1977, **49**, 51
14 A. R. McCabe and G. D. W. Smith, *Proc. 8th Int. Congress on Catalysis*, Berlin, Verlag-Chemie, 1984, Vol. 4, p. 73

A Valuable Contribution to the Literature

IMPRESSIVE NEW PUBLICATION FROM THE LEADING JAPANESE REFINERS AND FABRICATORS OF THE PLATINUM GROUP METALS

As one of the celebrations to commemorate the centenary of the foundation in 1885 of Tanaka Kikinzoku Kogyo K.K., Mr. Jun-ichiro Tanaka the President of the company resolved to publish a comprehensive reference book entitled "Science of Precious Metals". To facilitate this some eighty people, each an authority on a particular subject, were invited to prepare papers covering a wide range of topics on the platinum group metals, and also on gold and silver. Designed to develop further the precious metals industry in Japan, the book will provide users and potential users with a most useful source of scientific and technical information, and with a lesser amount of data on the supply and demand for these metals.

The first volume of this three volume publication serves as a preface, and includes contributions from both industry and academia, a pattern that is followed in the other two volumes.

The majority of the papers in Volume II were written by professors at Japanese universities and are largely devoted to fundamental aspects of the physics and chemistry of the precious metals. The text is ably supported by illustrations and by references to the literature.

The fourteen chapters in Volume III cover the very wide spectrum of applications for the precious metals, including of course the vitally important use of the platinum metals. These range from long established applications such as laboratory apparatus, in the glass and glass fibre industries, and as catalysts and electrodes during the manufacture of chemicals. Their use in petroleum refining, petrochemical processing and C_1 chemistry is also considered, as are recent developments relating to automobile emission control, and the growing electronics and pharmaceutical industries.

In conclusion, the demand and supply of the platinum metals are also considered.

Following its launch on 4 December 1985 at the Industry Club of Japan in Tokyo, the book, which is mainly written in Japanese, was distributed without charge to universities, governmental institutes, laboratories, companies and individuals with an active interest in the precious metals. In his introductory paper Mr. Gordon H. Waddell, Chairman of Rustenburg Platinum Holdings, remarked that in an uncertain world the future of the precious metals seems assured. Undoubtedly the publication of this book by Tanaka Kikinzoku Kogyo will make a most worthwhile contribution to that future.   I.E.C.