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SURFACE STRUCTURE AND COMPOSITION CHANGES ON PLATINUM - RHODIUM ALLOY CATALYSTS

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Résumé - Les catalyseurs en toile de platine - rhodium utilisés au cours de la fabrication de l'acide nitrique sont l'objet de processus de reconstruction de surface étendus. Ceci a été examiné à l'aide d'un réacteur catalytique miniature et de techniques telles que la sonde à atomes (AF-PIM), la microscopie électronique, et les rayons X. Un mécanisme impliquant le transport en phase vapeur est proposé pour expliquer les principaux traits de la variation du comportement du catalyseur dans les conditions opératoires.

Abstract - Platinum - rhodium gauze catalysts used in the manufacture of nitric acid undergo an extensive surface reconstruction process. This has been investigated using a miniature catalytic reactor, FIM atom probe, electron microscopy and X-ray techniques. A mechanism involving vapour transport is proposed to explain the main features of the variation in catalyst behaviour with operating conditions.

1 - INTRODUCTION In the manufacture of nitric acid, ammonia is oxidised over a platinum - rhodium gauze catalyst, the reaction being both strongly oxidising and highly exothermic. The remarkable surface reconstruction process occurring during operation has long been known to exist [1-4], but no detailed understanding of the mechanism of, or limitations on, this reconstruction are known. We report an investigation of this problem, using a range of microscopical and microanalytical techniques.

2 - EXPERIMENTAL PROCEDURE A miniature catalytic reactor was constructed to simulate the reconstruction taking place, the pressure and flow rates being as for a commercial plant. The apparatus allowed the reaction to be stopped at various stages during the reconstruction process, the gauzes being studied by SEM and EPMA. FIM samples could also be placed in the reactor directly behind the rear gauze, these being examined later using both FIM and atom probe techniques. The gas mixture in the reactor was also varied to investigate the range of conditions over which the reconstruction process occurred.

3 - AIR OXIDATION Initially FIM samples made of the catalyst material were oxidised in air for 1 hour at 800°C giving a 200 - 300Å thick oxide film. A concentration depth profile through this film showed substantial enrichment of the oxide with rhodium. However a similar profile for 600°C indicated that the outer region of the oxide was not as enriched in rhodium as the bulk oxide. The loss of platinum as PtO₂ vapour was suggested (this recondensing on the outer surface under certain cooling conditions), and the possibility that the surface reconstruction on the catalysts was also due to a vapour transport process was suggested. A detailed account of this work has been given previously [5,6].

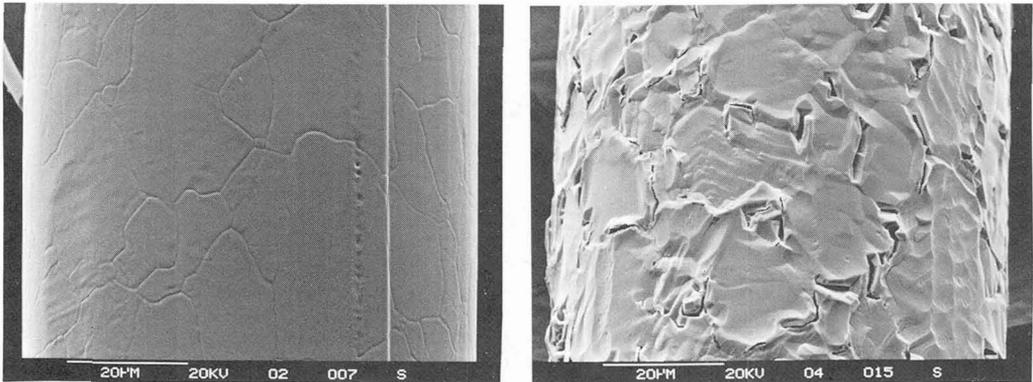


Fig. 1 - Scanning electron micrographs of gauze surfaces.
 (a) Hydrogen flamed, showing recrystallisation and thermal grooving at grain boundaries.
 (b) Exposed to 10% ammonia-air mixture for 2 hours in catalytic reactor, showing development of deep cavities along grain boundaries.

4 - AMMONIA OXIDATION - GAUZES A gauze in its as-received state shows typical wire drawing marks on its surface. However, after pretreatment (which involves flaming with a hydrogen torch), recrystallisation occurs and grains become clearly visible, with grooves along the grain boundaries (figure 1a). After only 2 hours in the catalytic reactor the surface has already started to reconstruct (figure 1b). The development of deep cavities along the grain boundaries is clearly seen.

A mechanism which explains the formation of these cavities is as follows. Consider the boundary between two grains (figure 2). The feed gas contains excess oxygen (the mix used is always less than stoichiometry), so most of the ammonia will be oxidised on initial contact with the outer surface. The gas reaching the bottom of the grain-boundary groove will therefore be strongly oxidising. Platinum oxide will form here, and will migrate outwards, where it meets a more reducing atmosphere, and so platinum is deposited on the outer surface. Thus the grooves deepen, and the surface builds up, resulting in the hollow cage-like growths seen in reconstructed gauzes.

The build up of these structures with time is shown in figure 3a (0.5 hours, some grains start to reconstruct), 3b (encroachment of the growth from the reconstructing grains), and 3c (the entire surface covered). The reconstructed surface is shown at higher magnification in figure 3d.

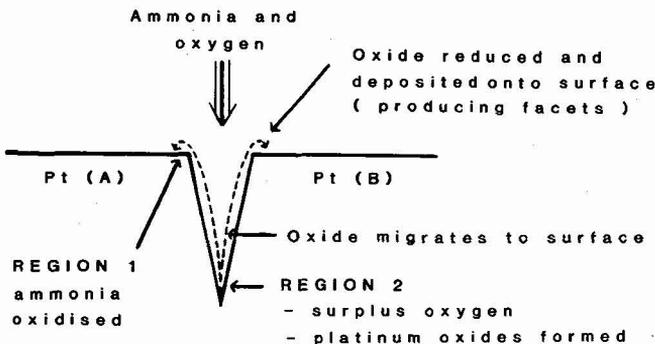


Fig. 2 - Schematic diagram illustrating vapour transport mechanism of surface reconstruction, involving progressive deepening of pre-existing grooves and cavities on the surface of the catalyst.

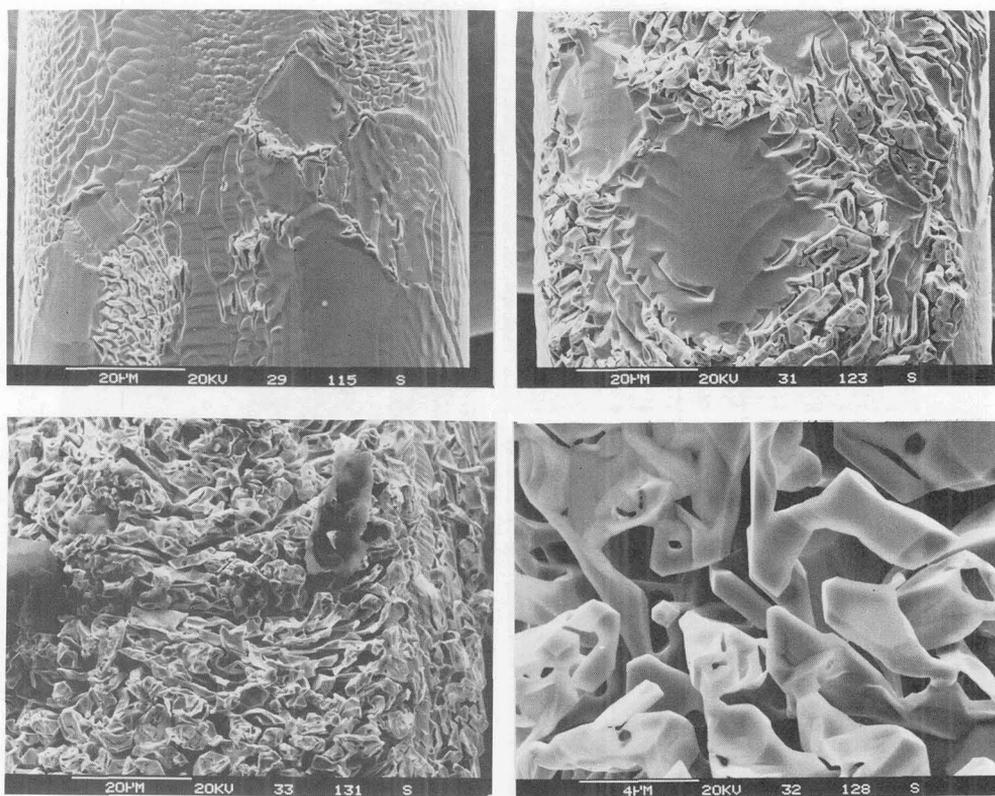


Fig. 3 - Surface structure of gauzes exposed to an 8% ammonia-air for varying lengths of time. (a) 0.5 hours, (b) 2 hours and (c) 8 hours. (d) shows a higher magnification view of the reconstructed surface (after 15 hours).

If the tests are carried out at different gas mixtures, it is found that at lower ammonia levels the catalyst ceases to work, and at higher ammonia levels the surface smooths out due to diffusion [7]. (As the reaction is exothermic, increasing the ammonia content also increases the gauze temperature very markedly).

5 - AMMONIA OXIDATION - X-RAY ANALYSIS. Electron microprobe analysis (using a 20keV incident electron beam) shows that the strong rhodium enrichment seen in air oxidation does not occur in ammonia oxidation, and that in some cases slight platinum enrichment is even observed [7]. A fine wire placed behind the gauzes also shows slight platinum enrichment, this indicating vapour deposition from the gauzes. (It must be noted, however, that the microprobe analysis samples not only the entire surface film but also some of the bulk metal beneath).

6 - AMMONIA OXIDATION - FIM ATOM PROBE ANALYSIS FIM samples made of the catalyst material were inserted directly behind the gauzes, and so were exposed to the reaction environment. An interesting contrast is seen between samples exposed for 10 minutes and those for 30 minutes.

A sequence of FIM images for a sample treated for 10 minutes in the rig is shown in figure 4. A thick oxide film is formed, and both the oxide and the substrate are strongly faceted. A concentration depth profile (figure 5) shows that the oxide is clearly enriched in rhodium compared to the bulk, although there is an indication of platinum deposition on the very outer surface.

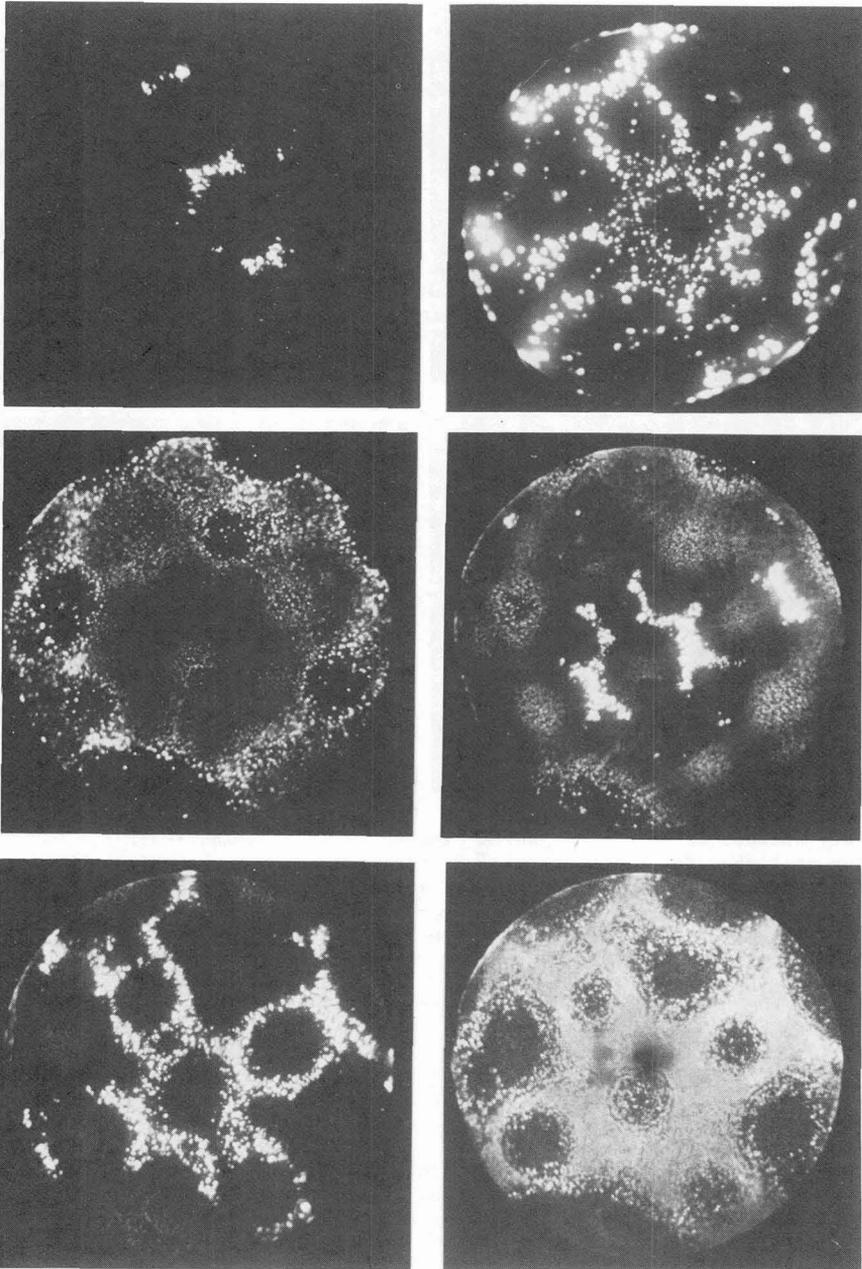


Fig. 4 - Sequence of field ion micrographs showing progressive removal of oxide from a platinum-rhodium specimen exposed for 10 minutes to a 10% ammonia-air mixture in the catalytic reactor. Note the heavy oxide layer, and the strongly faceted nature of the oxide surface, as well as that of the metal substrate. Images (a), (b) and (c) show only the oxide film, while in images (d), (e) and (f) the metal substrate is progressively revealed.

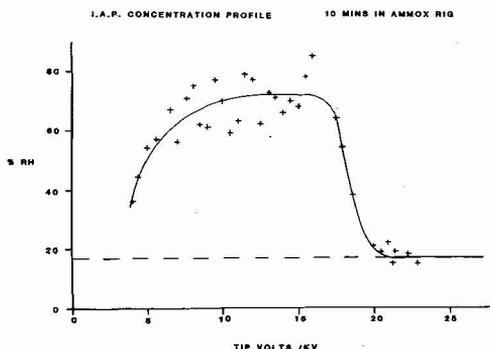


Fig. 5 - Atom probe concentration depth profile through film formed after exposure in the reactor for 10 minutes. Note the strong enrichment in rhodium content of the oxide film.

A sample treated for 30 minutes looks very different (figure 6). The surface region is now metallic, any oxide formed initially having apparently been reduced. A depth profile through this film (figure 7) shows no substantial change in the Pt/Rh ratio from that of the bulk, but large amounts of hydrogen and nitrogen are detected before the bulk metal substrate is reached. This shows that the FIM sample is now acting as a catalyst in the same way as the gauzes.

7 - CONCLUSION AND DISCUSSION The results confirm that the reconstruction process takes place by vapour transport as first suggested by McCabe and Schmidt [8]. Details of events occurring on the platinum - rhodium catalyst surface can now be examined. Six main processes need to be considered in the reconstruction :- 1) PtO_2 vapour formation, migration and decomposition; 2) The selective oxidation of the rhodium species; 3) Thermal faceting; 4) The formation of grain boundary grooves; 5) Surface diffusion; 6) Bulk diffusion in both metal and the oxide.

The extent of each process is dependent on the reaction conditions, the vapour transport process operating 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 which is not catalytically active for nitric oxide formation. If the temperature is too high (high ammonia content), then surface and bulk diffusion dominate, leading to a reduction in surface area and a drop in catalyst efficiency.

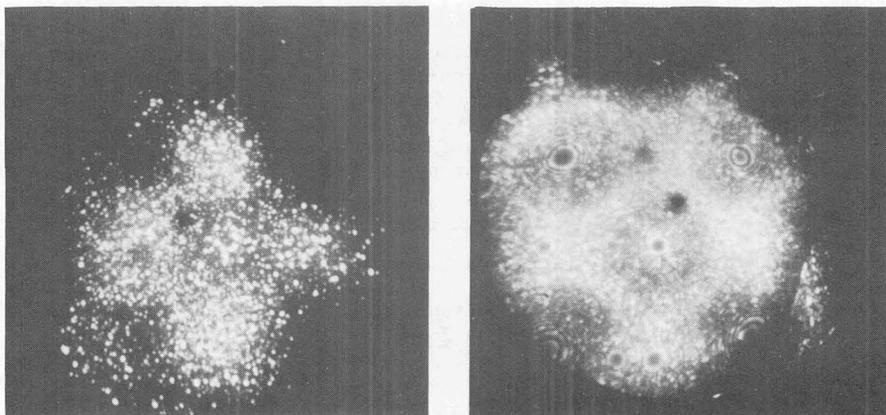


Fig. 6 - Field ion micrographs of a sample exposed for 30 minutes in the catalytic reactor. (a) The surface layer is metallic in nature, any oxide formed having been subsequently reduced. (b) The fully ordered substrate.

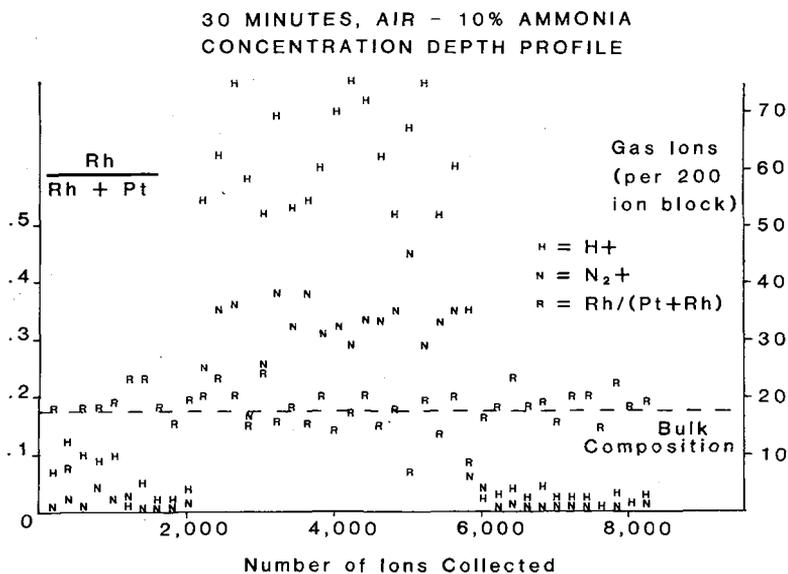


Fig. 7 - Atom probe concentration depth profile through the surface layer formed after exposure for 30 minutes in the reactor. The composition of the metal in the surface region does not differ greatly from that of the bulk, but substantial quantities of hydrogen and nitrogen are detected before the substrate metal is reached.

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The ability to make FIM samples from catalyst material, and to expose them to real reaction conditions so that the FIM sample acts as an actual catalyst, opens up a large area of new work in the study of thin surface films. The use of laser pulsing in the atom probe allows study of these films even if they are not very conducting. The extension of the present work into other catalyst systems such as those used in automobile emission control, chemicals and petrochemicals is now feasible.

8 - ACKNOWLEDGEMENTS This work was carried out in collaboration with Johnson Matthey Group Research Centre. We are particularly indebted to Dr.D.Thompson and Mr.A.Pratt for advice and assistance and Mr.D.Hepburn for extensive help with SEM and electron microprobe work. Dr.C.Grovenor and Mr.A.Cerezo assisted in the laser operation of the atom probe. A.R.McCabe acknowledges the award of an SERC Case studentship. We thank Verlag-Chemie for permission to reproduce illustrations.

REFERENCES

- [1] Handforth S.L. and Tilley J.N., Ind. Eng. Chem. 26 (12) (1934) 1287.
- [2] Busby J.A., Knapton A.G. and Budd A.E.R., Proc. Fertiliser Soc. (1978) 169.
- [3] Pszonicka M. and Dymkowski T., Polish J. Chem. 52 (1978) 121.
- [4] Pielaszek J., Platinum Metals Rev. 28 (1984) 109.
- [5] McCabe A.R. and Smith G.D.W., Proc. 29th Int. Field Emission Symposium Gothenburg, Sweden, Eds. Andren H-O and Norden H, Publ. Almqvist and Wiksell, Stockholm (1982), p.201.
- [6] McCabe A.R. and Smith G.D.W., Platinum Metals Rev. 27 (1983) 19.
- [7] McCabe A.R. and Smith G.D.W., Proc. 8th Int. Catalysis Congress, Berlin, Publ. Verlag-Chemie, Berlin (1984) vol.4, p.73.
- [8] McCabe R.W., Pignet T. and Schmidt L.D., J. Catal. 32 (1974) 114.