The Behaviour of Platinum Catalysts for Ammonia Oxidation

STUDIES BY CONTROLLED ATMOSPHERE MICROSCOPY

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Continuous observations by controlled atmosphere microscopy of the effects of heating platinum and rhodium-platinum alloy wires in ammonia-air mixtures indicated that attack on the wire surfaces predominates at the grain boundaries. The alloy wires, including used commercial catalyst gauzes, exhibited the formation of mobile promontories preceding the formation of angular crystalline platelets, whereas pure platinum wires did not show so much promontory growth, even at higher temperatures.

The first stage in the production of nitric acid is the catalytic oxidation of ammonia with air to give nitric oxide. This process is usually carried out over a multi-layered stack of rhodium-platinum alloy gauzes at operating temperatures of 800 to 900°C. Owing to increased demand for nitric acid, relatively high operating pressures (~8 atm) are now being used. Of major concern in this process is the anomalous loss of platinum from the catalyst gauzes. This is a function of such variables as local temperature, oxygen concentration and linear gas velocity, and, consequently, is most pronounced at high pressures. It is thought that adsorption of reactants on the catalyst surface results in a weakening of the Pt-Pt bonds, and at 900°C platinum is lost as platinum oxide, PtO_2 (1, 2).

In the present investigation we have used controlled atmosphere microscopy techniques in an attempt to observe and understand the initial stages in the behaviour of the catalyst when heated in a 10 per cent ammonia-air mixture. In these experiments we have compared the behaviour of pure platinum, 10 per cent rhodium-platinum and specimens of used commercial catalyst gauzes.

Controlled Atmosphere Electron and Optical Microscopy

Transitory features of systems undergoing change often remain unobserved during conventional post-reaction examination. At Harwell we have overcome this restriction with the use of controlled atmosphere electron microscopy (3). The equipment consists of a JEM 7A electron microscope fitted with a gas reaction cell, enabling the specimen to be observed continuously by electron transmission while exposed to gas atmospheres with pressures of up to 230 torr and temperatures of up to 1200°C.

Figure 1 is a schematic representation of the JEOL AGI gas reaction cell (B) and stage (A). Gas passes through a channel in the cell to a region between two 70 μm diameter apertures (C), one in the body of the cell and the other mounted in the top cap. The specimen lies on its heater between these
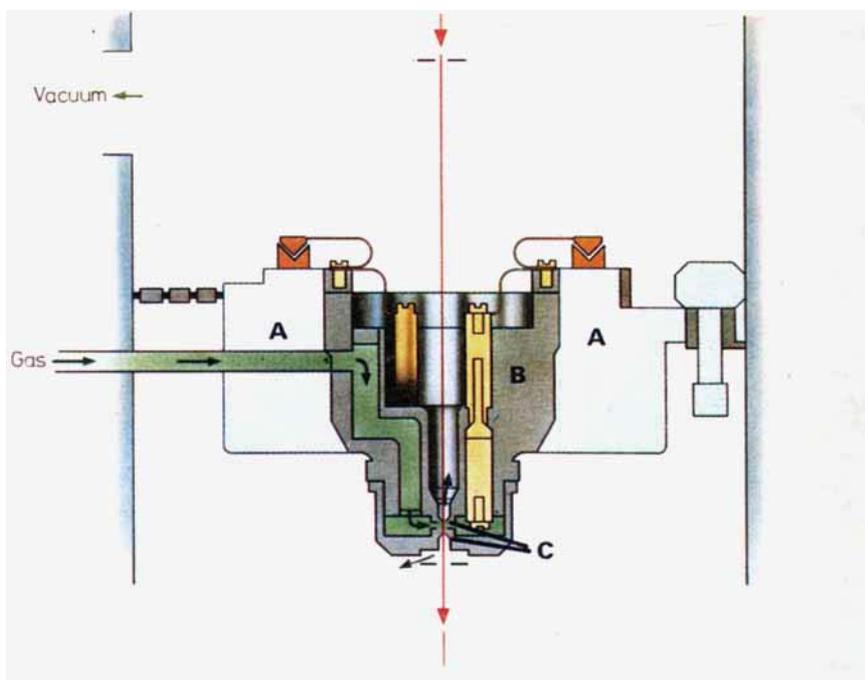
Fig. 1 Diagram of the JEOL AGI gas reaction cell (B) and stage (A) used at Harwell for controlled atmosphere electron microscopy of platinum and rhodium-platinum specimens

apertures. Gas exits into the specimen chamber through the apertures and is all pumped away via an auxiliary vacuum line, thus preventing gas leakage into the main microscope column.

To take full advantage of the microscope (Fig. 2), sophisticated continuous recording facilities are incorporated. Part of the electron beam falls upon a transmission phosphor screen and this image is focused on to a high sensitivity "Plumbicon" television camera outside the vacuum chamber. The output from the camera is fed to a monitor and is recorded simultaneously on video-tape.

The specimen is mounted over a 300 μm diameter hole in a platinum heater ribbon supported on a mica ring. A platinum: 13 per cent rhodium-platinum thermocouple is spot welded to a point close to the hole. A direct current passed through the heater ribbon heats the specimen.

Controlled atmosphere optical microscopy studies were carried out with a Leitz 1750

heating stage fitted to a Vickers M4a Photoplan microscope (4). This technique enabled the reaction between the ammonia-air mixture and platinum to be examined at higher pressures (2 atm) and over longer periods than was convenient in the electron microscope gas cell.

The platinum catalyst wires used in this work were supplied by Johnson Matthey & Co Limited. The optical studies were carried out with specimens containing a platinum: 10 per cent rhodium-platinum junction. Specimens were connected directly to the electrical leads of the cell and were positioned so that the junction could be observed. The temperature at this point was measured with an optical pyrometer. The 10 per cent ammonia-air mixture was maintained at a pressure of 2 atm and a flow rate of 2 l/min. Contamination of the quartz viewing window of the cell by water vapour prevented continuous observation of the reaction by closed circuit television but the window could be
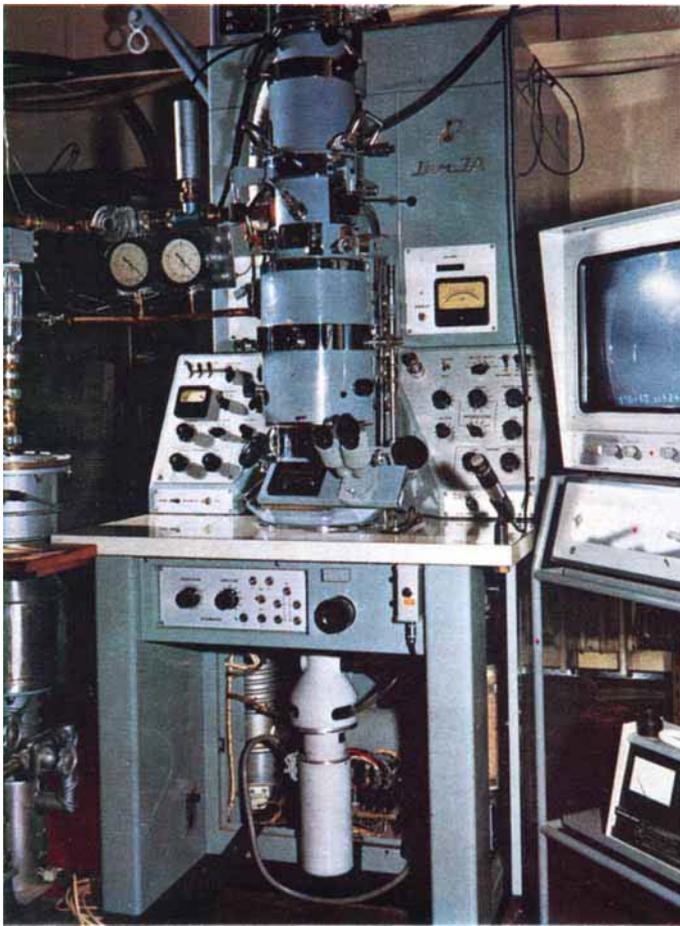
cleared for long enough periods to take photographs at hourly intervals and record the temperature.

Specimens and Studies

Specimens for electron microscopy investigations were prepared by threading platinum wires, 10 per cent rhodium-platinum wires and sections of used gauze through holes in the heater ribbon on either side of the 300 μm diameter viewing hole so that the wire stretched across the central region. In all cases experiments were carried out with specimens in the "as received" condition and also with similar specimens that had received a rigorous cleaning treatment.

The gases used in this work—ammonia and air—were obtained from Air Products Limited and were both of 99.5 per cent purity. They were used without further purification.

Two series of studies were carried out. In the first, experiments were conducted in the optical gas cell on platinum: 10 per cent rhodium-platinum thermocouples and, in the second, experiments were carried out in the electron microscope gas cell with fine wires. All these experiments were conducted in 10 per cent ammonia-air mixtures up to temperatures of at least 900°C.

Optical Microscopy Studies

Figures 3a and 3b show the effect of heating the specimen platinum: 10 per cent rhodium-platinum thermocouple in 10 per cent ammonia-air at 2 atm to 950°C. Before the reaction the surface of the specimen was
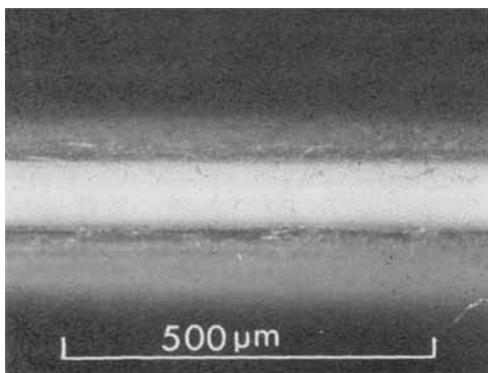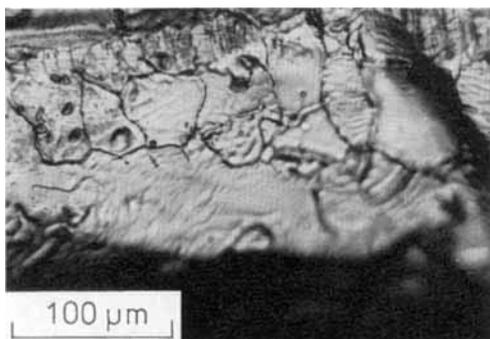
Fig. 3a

Fig. 3b

Fig. 3 Controlled atmosphere optical microscopy of 10 per cent rhodium-platinum thermocouple wire in 10 per cent ammonia-air at 2 atm to 950°C: (a) before reaction, (b) after 12 hours exposure with some indication of the formation of pits or knolls
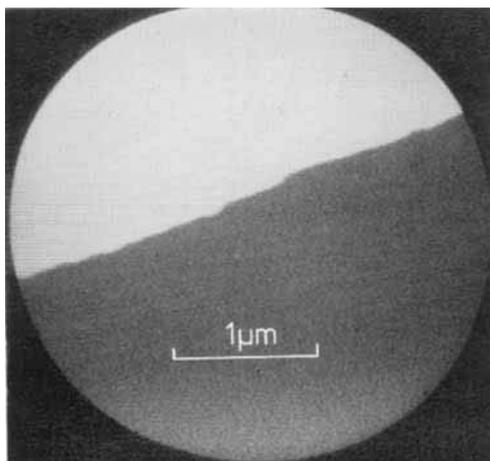

Fig. 4 Controlled atmosphere electron microscopy showed that the 10 per cent rhodium-platinum wire is generally quite smooth before reaction in 10 per cent ammonia-air

quite smooth but after one hour's reaction it was observed to have roughened considerably. Examination after a two-hour period showed that attack had occurred predominantly in the region of grain boundaries.   There are indications from the micrograph in Fig. 3b, taken after 12 hours exposure, of either pits or knoll formation. These two features could not be distinguished by reflectance microscopy

Electron Microscopy Studies

The results reported in this section are in each case taken from five reproducible experiments, and in the cases of platinum and 10 per cent rhodium-platinum wires the behaviour was found to be unaffected by the cleaning treatment.

When a piece of platinum wire was heated in 10 torr of 10 per cent ammonia-air in the gas cell of the electron microscope, the original smooth surface of the specimen did not change until 970°C. At this temperature knolls, some of which appeared to be triangular in shape, were formed on the surface. The size of these growths was observed to increase in width from 50 to 125 nm over a period of 26 min at 970°C.   On raising the temperature to 1100°C secondary growths in the form of needles and platelets appeared on the knolls, giving rise to a more ragged appearance of the original growths.

Similar experiments were conducted with 10 per cent rhodium-platinum wire specimens. The appearance of the wire before reaction was generally quite smooth, as seen in Fig. 4, but on heating to 700°C in 10 torr of 10 per cent ammonia-air the surface took on a rippled form.   When the temperature was raised to 855°C, isolated knolls were observed to form. These moved quite freely along the surface, as shown in Figs. 5a and 5b and sometimes collided to form larger growths.   The knolls ranged in width from 100 to 200 nm and were too dense for penetration by the electron beam.   Figures 6a to 6d form a sequence taken from the TV display showing the effect of heating the specimen from 890 to 925°C.   As the temperature was increased
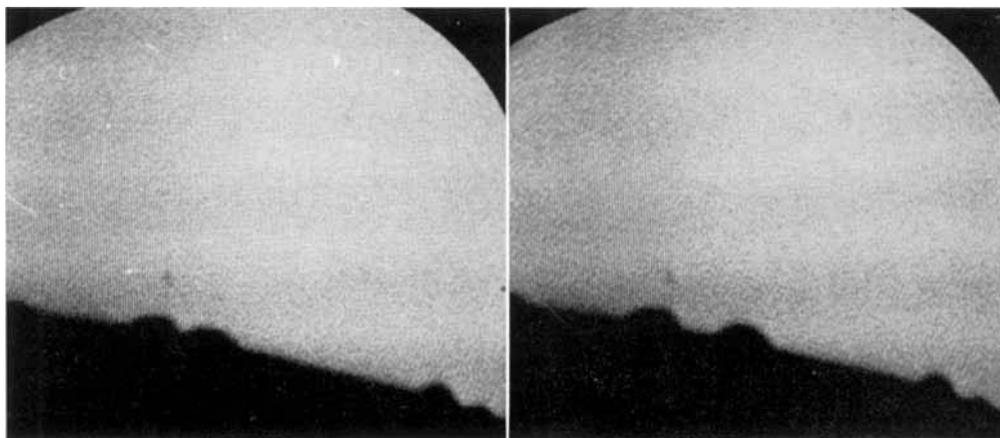
Fig. 5 Knolls formed on the surface of 10 per cent rhodium-platinum wire above 800°C moved quite freely along the wire surface. The interval between frame (a) (left) and frame (b) (right) was 1 s
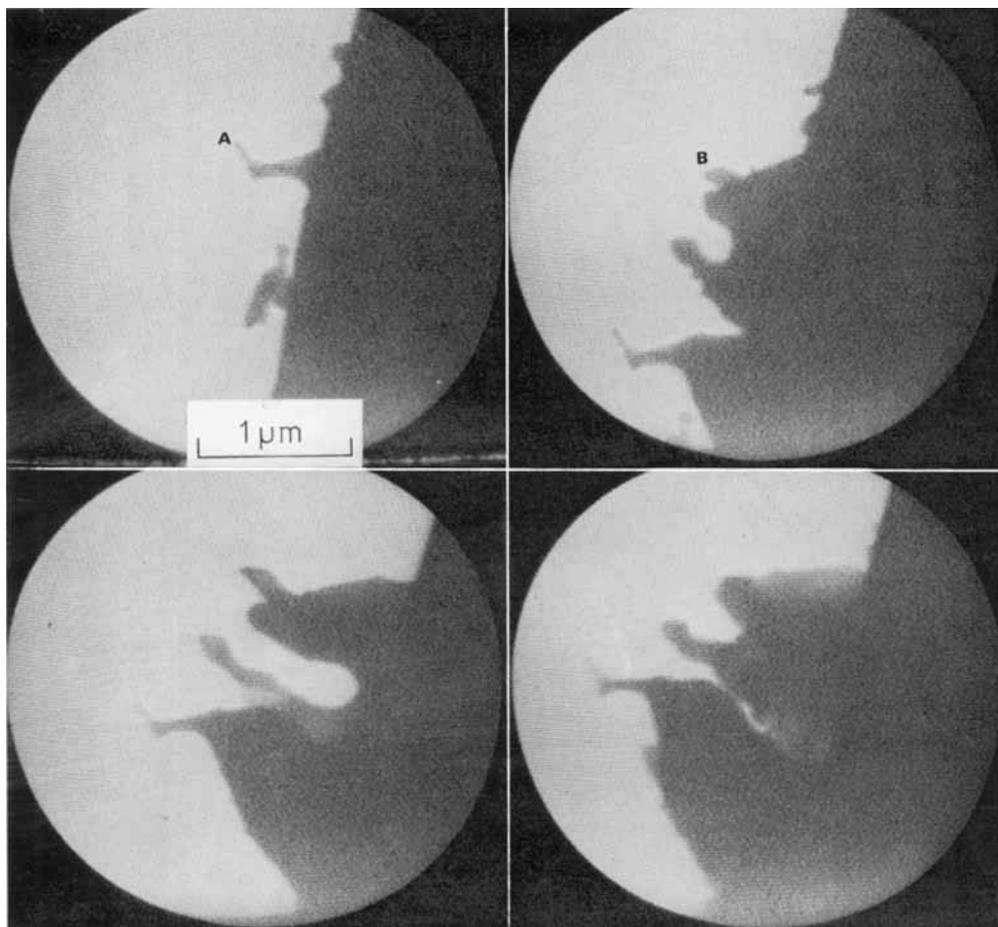
Fig. 6 Promontory formation on 10 % rhodium-platinum wire heated in 10 % ammonia-air at 10 torr. Secondary platelet and needle growth took place on the sides of the promontories, e.g. A and B. (a) (upper left) 890°C, 0 min; (b) (upper right) 890°C, 2.3 min; (c) (lower left) 890°C, 6.1 min; (d) (lower right) 925°C, 8.0 min

from 855 to 890°C the knolls increased in size to produce eventually large promontories, and secondary platelet and needle growth took place on the sides of the promontories, e.g. A and B, shown in Figs. 6a and 6b, respectively. The platelets were much thinner than the parent growths and the appearance of extinction contours across their surfaces indicated their crystalline nature. Several features of the reaction are clear from Fig. 6, not least being the dramatic change in morphology of the surface on increasing the temperature from 25 to 890°C. The growth of the promontory with platelet A at its tip can be seen and, moreover, this facet retains the shape of its leading edge, indicating that growth is occurring by transport of material from the bulk rather than by gas phase deposition. There are also indications that material might also be lost at this stage, e.g. platelet B appears to increase in size and then disappears. In one sequence a needle was observed to grow and eventually break off at its base. It was also evident that many of the platelets were quite flexible at 925°C and were getting progressively thinner; the density was decreasing towards the edges, suggesting that material was being lost preferentially from these areas.

Finally, specimens of used commercial catalyst gauze were examined by this technique to discover whether further reaction with 10 torr of 10 per cent ammonia-air took place. An initial survey of the specimen showed that there were a number of promontories on the roughened surface, some of which had platelets associated with them. As the temperature was raised to 700°C, slight changes in the profile of the promontories were noted and these became appreciable at 890°C. The length of promontories increased at the expense of a decrease in width. Platelet growth occurred at the edges of the promontories. High magnification examination of the platelets showed that they were crystalline and had well defined angular shapes, as shown in Fig. 7, and in some cases there was denser material within them. As the reaction
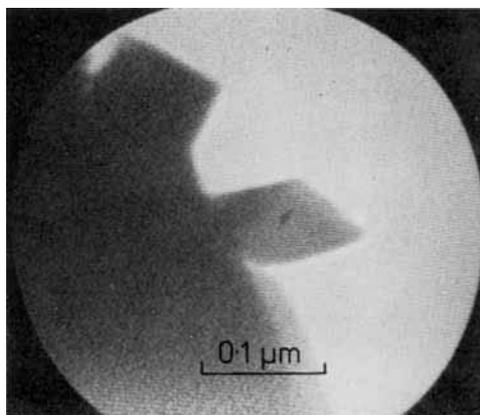
Fig. 7 Crystalline platelets formed on the sides of promontories on a commercial catalyst gauze when heated in 10 % ammonia-air at 10 torr to 980°C

progressed some platelets continued to grow whereas others decreased in size. The sequence shown in Fig. 8 gives an indication of the extent of the reaction. It can be seen that there is a dramatic change in the outline of the tip of the promontory and, although this growth appears to increase in length, this is accompanied by a general decrease in its width. All these observations indicate that there could be appreciable restructuring and transport of material within the bulk.

Behaviour of the Wires

The behaviour of the platinum gauze catalyst and of the 10 per cent rhodium-platinum wire appeared to be identical in many respects, whereas platinum wire was significantly less reactive under the same conditions. This difference could be due to a variation in the actual surface temperatures of specimens during reaction, associated with the exothermicity of ammonia oxidation. 10 per cent rhodium-platinum alloy, being the more active catalyst, might be expected to be at the higher temperature and hence exhibit the more active behaviour. Garton and Turkevich (5) have demonstrated that structural changes in platinum occur only in the presence of both ammonia and air, no such changes being observed in either the individual reactants or any of the products.
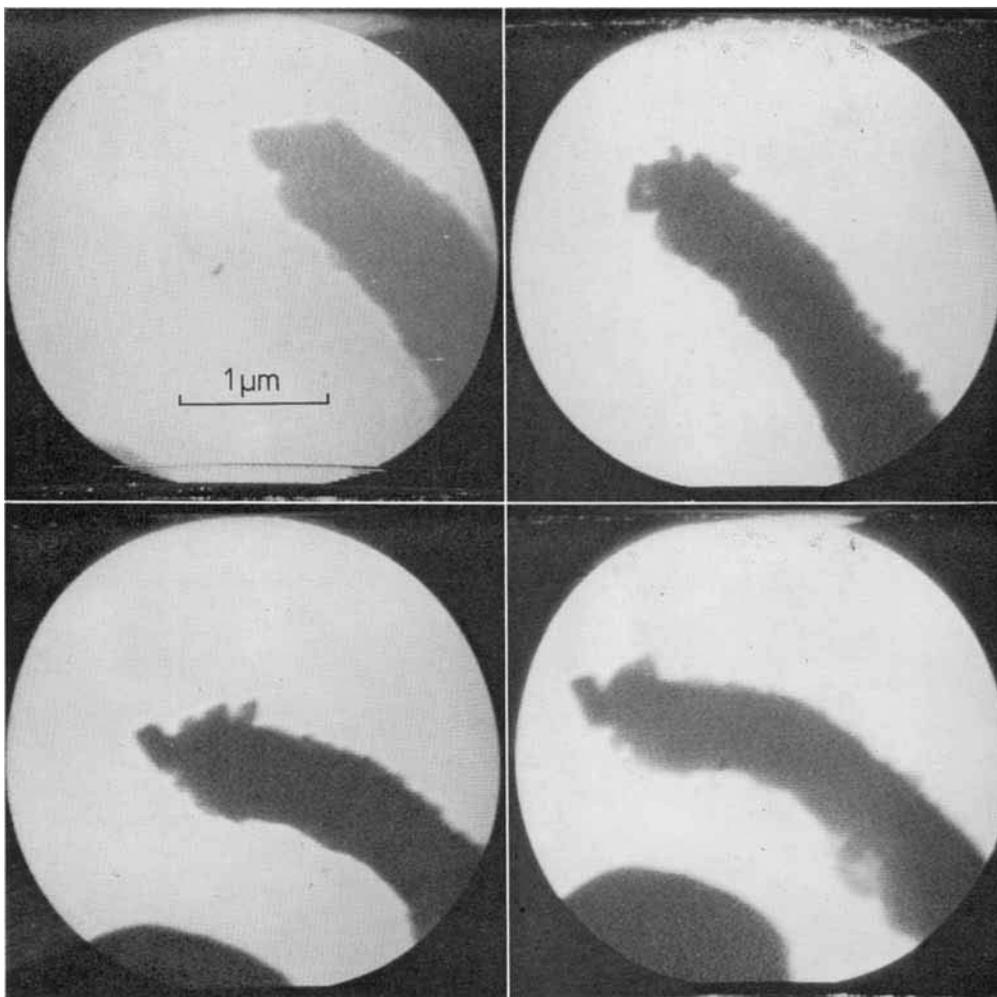
Fig. 8 Increase in length and decrease in width of the tip of a promontory formed on the surface of a used commercial catalyst gauze specimen heated to 890°C in 10 per cent ammonia-air at 10 torr. (a) before reaction, room temperature; (b) 890°C, 2 min; (c) 890°C, 4.5 min; (d) 890°C, 20.0 min

The present experiments clearly indicate that platelets are produced on the edges of the wires by a consecutive process, their growth being preceded by the agglomeration of mobile surface knolls to form promontories, and it was these features which gave rise to platelet formation. Continuous observation of platelet growth suggests that the latter stage involves platinum transport from the bulk rather than vapour transport of volatile platinum oxides.

It is tempting to speculate that attack on the catalyst surface occurs preferentially at grain boundaries with the eventual formation of promontories and the platelet material, and that ultimately platinum is lost from the platelets as volatile compounds.

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