

The Solid Oxides of Platinum and Rhodium

FORMATION IN HIGH PRESSURES OF OXYGEN

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At everyday temperatures and in air at normal pressures the solid oxides of the platinum metals are notably of uncertain composition. According to the method of preparation, samples are frequently mixtures of one or more oxides with free platinum and are often partly hydrated. Such uncertainties stem inevitably from the feeble nature of the binding forces in these materials when so close to dissociation.

In view of the importance of these oxides as catalysts, it is surprising that so little has been done in the past to characterise them more strictly. A recent paper (1) by Olaf Muller and Rustum Roy, working in the Materials Research Laboratory of the Pennsylvania State University describes, for instance, the first work that appears ever to have been reported on the use of high pressures of oxygen to stabilise the compounds in reasonably well-crystallised forms for structural examination.

The original intention was to determine the phase equilibria in the system Pt-O at high oxygen pressures. It was soon obvious, however, that it is an almost impossible task to define the phase limits with any certainty owing to sluggishness of the reactions at the temperatures under study. Apparent shifts of up to 50°C were observed in the phase boundaries, depending upon the starting materials used and upon the direction to which the 'equilibrium' temperature was approached.

Platinum black and such compounds as $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ were quite unreactive below about 700°C and at the best produced mix-

tures of platinum metal with small amounts of mixed oxide phases even after several days under pressure. The most consistent results were obtained by heating small quantities of PtI_2 enclosed in platinum (generally 10 mg or less but sometimes up to 0.5 gm), for 1 to 2 days to 400° to 900°C at pressures up to 3500 atm of oxygen. At the end of a run, the "bomb" was cooled in water before releasing the pressure. The samples were examined by X-ray diffraction to determine the structures of the phases produced, but chemical examination was not as thoroughly performed as might have been desired. The authors obviously lacked experience in platinum metal analysis and appear to have been daunted by the insolubility of some of the oxides in aqua regia.

Three platinum oxides were found: α PtO_2 (hexagonal), a new phase, β PtO_2 (CaCl_2 structure) and Pt_3O_4 ($\text{Na}_x\text{Pt}_3\text{O}_4$ structure). Tetragonal PtO and body-centred cubic Pt_3O_4 which have previously been reported in the literature were not found.

The evidence is that hexagonal α PtO_2 is the oxide stable at all pressures below about 570°C, the temperature at which it decomposes at atmospheric pressure. It is not easily produced in well-crystallised form even at the highest oxygen pressure; and it is possible that many months of reaction time might be needed for the growth of perfect specimens. There is a suggestion that the presence of sodium nitrate as a flux may promote crystallisation.

At higher temperatures the new β PtO_2 is formed provided that the oxygen pressure is

sufficiently high—above about 600 atmospheres at 700°C and 1000 atmospheres at 800°C. It is black, relatively stable and completely insoluble in mineral acid mixtures and it would be of interest to know more of its properties—particularly in the field of its catalytic activity.

At intermediate pressures, Pt_3O_4 is the stable oxide. For its preparation in bulk it is suggested that commercial platinum black or fine mesh platinum powder should be heated to 850°C under 200 to 300 atmospheres of oxygen and any unreacted platinum removed by treatment with aqua regia. Its structure appears to be identical with that of $\text{Na}_x\text{Pt}_3\text{O}_4$, the implication being that removal of the sodium atoms leaves empty positions in the lattice.

The work on the Rh-O system described by the authors is less extensive but is remarkable as indicating RhO_2 , a phase not previously described, as the most stable structure. It is easily prepared by heating $\text{Rh}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ at 700 to 850°C at high pressures of oxygen. It is shown to be stable at all temperatures up

to about 1000°C at oxygen pressures above about 20 atmospheres and it is, moreover, the stable phase at atmospheric temperatures below about 700°C. It is a black compound, highly insoluble even in hot aqua regia, and obviously deserves further study. The two other oxide phases, both forms of Rh_2O_3 , have relatively narrow fields of existence at 650 to 900°C and above 950°C respectively.

The interests of the authors as shown by this paper lie in the interpretation of the X-ray data on their samples. The methods of preparation chosen may, however, be of value in a much wider field. High pressure techniques may well help to resolve many outstanding problems of platinum metal chemistry by stabilising transient reactions which otherwise elude study.

Reference

- 1 Olaf Muller and Rustom Roy, Formation and Stability of the Platinum and Rhodium Oxides at High Oxygen Pressures and the Structures of Pt_3O_4 , $\beta\text{-PtO}_3$, and RhO_2 . *J. Less-Common Metals*, 1968, **16**, (2), 129.

Mechanism of the Catalytic Oxidation of Ammonia

The oxidation of ammonia to nitric oxide catalysed by platinum and its alloys forms an essential step in the manufacture of nitric acid, but, because of the high temperature and high space velocity at which the process operates academic investigation of the reaction has only been rarely attempted, and our detailed knowledge of the elementary steps which constitute the total process is very slender. Doubt has often been expressed as to whether the reaction is or is not entirely heterogeneous, and free radical reactions in the gas phase have often been thought to take place, particularly in the formation of nitrogen.

A recent short paper by C. W. Nutt and S. Kapur of the Department of Chemical Engineering, University of Birmingham (*Nature*, 1968, **220**, 697) throws considerable light on the reaction mechanism. These authors examined the reaction in a mass spectrometer by causing an ammonia/oxygen mixture to contact a heated platinum filament:

the reaction products passed under collision-free conditions through molecular beam apertures and thence through an ion source. The ionised products were detected in the usual way.

This technique ensures that only those species actually formed on the catalyst surface are sensed; because of the low background pressure, secondary products which might result from gas-phase collisions do not obtrude.

The reaction was examined with filament temperatures between about 400 and 1600°K. The results are very clear: both nitric oxide and nitrogen are formed on the catalyst surface and cannot arise from secondary processes. The reaction starts at about 500°K, the nitrogen yield is maximum at 700°K and nitric oxide at about 850°K. It is suggested that the rate decreases above this temperature because the residence time of the adsorbed species becomes progressively shorter.

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