

regarded as the maximum long-term operating temperature of a conventional platinum-clad molybdenum component in the glass industry.

The investigators at Philips paid particular attention to the formation and properties of this molybdenum-rich compound. An alloy containing 28 atomic per cent platinum was shown to be superconducting. The highest superconductive transition temperature for this eutectic composition, 5.6°K, was observed after annealing the alloy at 1800°C.

Other significant features of the diagram include a proposed orthorhombic phase of equiatomic composition, stable at temperatures below 1300°C, and an extensive solubility of platinum in molybdenum. The latter finding is of interest in that it was originally predicted on theoretical grounds by means of the Engel-Brewer correlation (5), and was

confirmed experimentally some time later (1).

At the platinum-rich end of the system, the new diagram indicates the existence of a second orthorhombic phase, of approximate composition Mo Pt₂. This structure appears to be an ordered form of the terminal face-centred cubic platinum solid solution, and occupies the position formerly ascribed to the tetragonally distorted phase denoted α_1 by Raub (4).

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References

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Phosphine Complexes of Rhodium and Ruthenium as Homogeneous Catalysts

HYDROFORMYLATION OF OLEFINS

One of the most rapidly advancing areas of physical-inorganic chemistry is undoubtedly the application of phosphine complexes of the platinum metals as homogeneous catalysts for hydrogenation and hydroformylation of olefins. In a paper presented at the recent symposium on "New Olefin Reactions" at the University of Manchester Institute of Science and Technology, Professor Geoffrey Wilkinson of Imperial College described recent new work in this field: the reactions he discussed are characterised by a degree of specificity not commonly encountered in other catalytic processes.

Perhaps his most startling disclosure was that concerning the rhodium complex *trans*-RhH(CO)(PPh₃)₂ which catalyses the hydroformylation of olefins under ambient conditions. With the widely used cobalt catalyst CoH(CO)₄ temperatures of about 100°C and pressures in excess of 100 atmospheres have to be used. When α -olefins are hydroformylated with the rhodium catalyst, the ratio of straight- to branch-chain aldehyde is

about 20, which is much higher than found with the cobalt catalyst. The reaction is believed to involve the five-coordinate RhH(CO)₂(PPh₃)₂ as an intermediate.

Professor Wilkinson also reported a new, extremely active homogeneous catalyst for olefin hydrogenation: this is the ruthenium complex RuClH(PPh₃)₃, also a five-coordinate species. This complex is even more active than the rhodium complex RhCl(PPh₃)₃ but it is selective for α -olefins, as internal olefins are reduced more slowly by a factor of about a thousand. This specificity is explained by the steric effects of the bulky triphenylphosphine groups. Unfortunately, solutions of the ruthenium complex are very sensitive to air and tend to lose activity during use.

These disclosures give further proof of the power of homogeneous catalysis as a technique for organic reactions, although many difficult technical problems will need to be overcome before reactions such as those described find commercial application.

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