

first. The proposed mechanism implies a competitive adsorption between  $\text{OH}^-$  and  $\text{Cl}^-$  with respect to the free sites of the metal surface prior to the discharge reactions. In other words, the formation of  $[\text{PdCl}_2]_{\text{ad}}$  is inhibited by the presence on the metal surface of  $\text{PdOH}_{\text{ad}}$ , the first step in the anodic passivation of palladium.

## Conclusions

Two reaction mechanisms of anodic dissolution of palladium in acidic chloride solutions are proposed, as functions of the pH value. At lower pH, the effect of chloride ion on electro-dissolution kinetics increases as the hydrogen ion concentration increases. In a critical pH region, the adsorption of  $\text{OH}^-$  competes with  $\text{Cl}^-$ , resulting in the formation of  $\text{PdOH}_{\text{ad}}$  which then inhibits the corrosion process.

# A New Generation of Platinum Metals Catalysts

Supported Metal Complexes, Catalysis by Metal Complexes

BY F. R. HARTLEY, Reidel, Dordrecht, 1985, 318 pages, Dfl.165,00/£45.75

Since 1970 a new area of catalysis has emerged in which the catalyst is supported on a polymer or reactive inorganic support. This book reviews the progress that has resulted from this fresh approach, which has been inspired by the desire to keep the advantages of homogeneous catalysis systems by using every metal atom in the catalysed reaction and yet facilitate recovery of the catalyst, especially from liquid phase reaction systems.

Stoichiometric attachment of platinum metals catalysts to reactive sites on supports via covalent bonding, and their cost effective removal after use, could be important factors in their economic viability. For example, the corrosion and plating out problems experienced in the oxidative acetylation of ethylene to vinyl acetate process could in principle be circumvented using this approach. Potential advantages could also accrue from increased selectivity caused either by promoting preferred orientations for the substrate or by controlling the stereochemistry of the catalytic site.

An illustration of the problems experienced with this approach is seen in the rhodium/methyl iodide catalysed carbonylation of methanol. The homogeneous reaction is very clean giving acetic acid, with 99 per cent selectivity. A supported catalyst having both

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rhodium and a pseudo alkyl halide bonded to a polymer is active, but much less so than its homogeneous counterpart. On continuous use its activity drops due to loss of both rhodium and cocatalyst. An alternative anionic rhodium(I) system supported on polystyrene-poly(4-vinylpyridine) quaternised with methyl iodide has high initial activity but also suffers from rhodium leaching.

Large sections of this book are concerned with the preparation of supported catalyst systems. Further chapters are then devoted to each important type of reaction investigated. For platinum metals catalysts these include hydrogenation, hydrosilylation, carbonylation, hydroformylation and oxidation reactions. The most important commercial applications for this type of catalyst are likely to be where the support is used both to heterogenise the catalyst and to contribute to the total environment of the active site, in a similar manner to that already established in nature for enzyme catalysts. Thus the metal complex and the support would combine to provide a uniquely active and selective catalyst site.

This book consists of a useful review of the present state of the art, but more innovation is required if these techniques are to realise their full potential.

D.T.T.