

The Manufacture of Fine Chemicals

PLATINUM METALS IN HETEROGENEOUS CATALYSIS

The importance of platinum group metal catalysts in the manufacture of fine chemicals has been recognised for a long time. This was demonstrated in a number of the contributions presented at the Third International Symposium on Heterogeneous Catalysis and Fine Chemicals which was held at Poitiers, France, from 5th to 8th April 1993, and attended by 247 delegates from 27 countries, 28 per cent being from industry. This symposium is held every two years and alternates with that organised by the Organic Reactions Catalysis Society (ORCS) in the U.S.A.

The symposium consisted of 33 papers and 63 poster presentations, platinum group metal catalysts featuring in 13 of the former and 19 of the latter. The lectures and posters were divided into three main sections: hydrogenation, oxidation and acid-base catalysis, with almost all the uses of platinum group metal catalysts being described in the hydrogenation section.

A plenary lecture by I. L. Dodgson of Johnson Matthey described current trends and the opportunities provided by modern hydrogenation catalysts to develop high yield, zero waste processes. Examples given included the change from nickel to ruthenium catalysts for sugar hydrogenation, in order to eliminate nickel-contaminated waste water; the use of palladium catalysts for hydrodechlorination to make CFC substitutes; and bimetallic catalysts to increase both selectivity and activity. The paper reviewed the latest publications on cinchona alkaloid modified platinum group metals catalysts for the increasingly important asymmetric hydrogenation steps in the manufacture of pharmaceuticals and agrochemicals.

There were several other papers on asymmetric hydrogenation. A. Tungler, T. Tarnai, A. Deak, S. Kemeny, A. Gyori, T. Mathe and J. Petro of the University of Budapest, described a kinetic study on enantioselective hydrogenations of isophorone and acetophenone using a palladium on charcoal catalyst modified with the

amino acid (S)-proline to achieve enantiomer excesses of up to 80 per cent.

B. Pugin and M. Müller, Ciba Geigy, described the use of chiral diphosphine-rhodium catalysts bound to silica supports via isocyanato-alkyl-trialkoxysilane linkages for the enantioselective hydrogenation of methylacetamide cinnamate. Enantiomer excesses up to 94.5 per cent were achieved.

A poster by H. U. Blaser and H. P. Jalett of Ciba Geigy described the enantioselective hydrogenation of various α -ketoacids with cinchona-modified platinum catalysts with enantiomer excesses greater than 80 per cent. The effects of catalyst, modifier, solvent, temperature, substrate and substrate concentration were studied and the results were consistent with the "ligand accelerated" catalysis model.

Many of the papers described studies on catalyst selectivity, which is becoming more important than activity in the development of zero-waste processes. M. Besson, L. Bullivant, N. Nicolaus-Dechamp and P. Gallezot of CNRS, Villeurbanne, described a comparative study of charcoal supported platinum, rhodium and iridium catalysts in the stereoselective aromatic ring hydrogenation of thymol to menthones and menthols. The reduction over platinum and rhodium proceeds essentially via the ketone intermediates, whereas the direct route to menthol is predominant over iridium. The formation of *cis* isomers is always highly favoured and iridium gives the highest degree of hydrogenolysis to *p*-menthane.

The screening of a wide variety of catalytic metals for the hydrogenation of an N-oxide function to form 6-chloro-2(1H)-quinoxalinone, which is an important intermediate in a wide variety of pharmaceutical and agrochemicals, was described by R. E. Malz, M. P. Reynolds and C. J. Fagouri of Uniroyal. A platinum sulphide catalyst was shown to be best, but when operating at high temperatures and pressures it

gave a loss of chlorine and lower selectivity and yield.

M. Bankmann, R. Brand, A. Freund and T. Tacke, Degussa, described the evaluation of platinum group metals catalysts prepared on new titania supports in the hydrogenation of substituted aromatic aldehydes. Depending on the choice of catalyst and substrate, the selectivity of the hydrogenation could be directed towards benzyl alcohols when using a low acidity support, benzyl ethers with a strongly acid support or hydrogenolysis.

The paper by T. Mallat, Z. Bodnar and A. Baiker of ETH, Zurich, described a bismuth-promoted platinum on alumina catalyst in the air oxidation of secondary alcohols to ketones. The bismuth-promoted catalyst was not as readily deactivated as a platinum on alumina catalyst, because bismuth suppresses by-product

formation and so modifies the chemisorption properties of platinum. Electrochemical potentials were measured to control the rate of oxygen supply from the gas phase to the catalyst surface and so avoid over-oxidation of the catalyst surface. Conversions of 97 to 99 per cent and selectivities of 95 to 100 per cent to the ketone were achieved for α -tetralol, diphenyl carbinol and 1-phenylethanol.

There were many other interesting papers and posters, too numerous to mention here. The full proceedings of the symposium are to be published by Elsevier in the "Studies in Surface Science and Catalysis" series. The next ORCS conference is from 2nd to 5th May 1994 at Phoenix, Arizona, U.S.A., and the 4th Symposium on Heterogeneous Catalysis and Fine Chemicals will be held at Poitiers in 1995.

I.L.D.

Platinum 1993

A COMPREHENSIVE REVIEW OF THE PLATINUM MARKET

The demand and supply of platinum during 1992 were quite evenly balanced with only a small surplus of 20,000 ounces. Overall, however, demand declined by 6 per cent to 3.8 million ounces although some sectors saw a rise in platinum sales.

Platinum jewellery reached a record 1.51 million ounces troy, assisted by a rise in the sale of wedding rings in the U.S.A., escalating demand in Japan for "low-priced" jewellery and an expanding interest in Swiss platinum watches.

Consumption of platinum and rhodium by the auto industry showed a significant increase over 1991 figures, although this was off-set by supplies being taken from manufacturer's strategic reserves which resulted in lower purchases in the market. Platinum demand in 1993 is expected to increase by at least 200,000 ounces, as both the European Community and the U.S.A. are applying more stringent controls to lower the level of pollutants emitted from motor vehicles. With countries in Eastern Europe, Southeast Asia and South America

gradually adopting emission standards and with the North American vehicle market gaining strength as the recession recedes, the outlook for 1993 is that there will be an increase in platinum group metal sales.

Covering many aspects of the platinum group metals, with particular emphasis on platinum, there is something of interest for most people: from mining and exploration, to applications in the chemical, electrical and glass industries, petroleum refining and biomedical products, platinum investment bars and coins. Past, present and perceived future market trends for each sector are given. All this and more is contained in Johnson Matthey's prestigious annual publication "Platinum 1993" which is in its 9th year of publication.

Readers of *Platinum Metals Review* who do not have access to "Platinum 1993" and who would like to receive this free survey should send their requests for a copy to: Mr J. S. Coombes, Johnson Matthey PLC, 78 Hatton Garden, London EC1N 8JP; Fax: 071-269-8135.