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.