

# Platinum Metals Industrial Catalysts

## Catalysis of Organic Reactions

EDITED BY M. G. SCAROS AND M. L. PRUNIER, Marcel Dekker, New York, 1995, 599 pages, ISBN 0-8247-9364-1, U.S. \$195.00

This book comprises a set of papers presented at the 15th Conference on Catalysis of Organic Reactions, held in Phoenix, Arizona, in May 1994. It covers a variety of topics, such as heterogeneous catalysis, asymmetric hydrogenation, hydrogenation, oxidation, hydroformylation, catalyst design and catalyst characterisation. One topic which is emphasised is hydrogenation (alpha to omega), and this is intended to allow a better understanding of the entire process, from choosing a catalyst to the noble metal "loop". There are over 60 papers and 186 contributors, with a healthy number of these being from industry. A large proportion of the papers deal with reactions involving platinum group metal catalysts, reflecting their importance to both academia and industry.

The initial paper, by R. J. McNair from Johnson Matthey, provides an overview of the process of catalyst selection for heterogeneous platinum group metal catalysts in a new hydrogenation process. It includes discussion on the reasons behind the choices of catalytic metal, catalyst support, reactor design, catalyst design, catalyst separation, and spent catalyst recovery and refining. There is a description of the influence of catalyst preparation methodology on the selectivity of supported metal catalysts, exemplified by the hydrogenation of phenylacetylene using 5 per cent palladium on carbon. Other topics that are dealt with include the effect of the preparative method on metal dispersion, distribution and level of reduction and how each can affect the catalyst performance and, in particular, its selectivity.

The effect of reaction conditions on catalyst selectivity is then discussed by F. P. Daly and colleagues from Degussa, with reference to the hydrogenation of oximes and unsaturated C18 acids using supported platinum group metal catalysts. Several factors, such as temperature, pressure, catalyst loading level, solvent system,

reactant purity, agitation and poisons are considered. This is followed by a paper detailing noble metal recovery operations and the various steps involved in the noble metal "loop".

Heterogeneous catalysis in organic synthesis is discussed by R. L. Augustine and colleagues from Seton Hall University, New Jersey. This is illustrated by the platinum catalysed oxidation of alcohols, carbon-carbon bond forming reactions of supported palladium catalysts for the Heck type arylation of allylic groups, and by enantioselective heterogeneous catalysis, which includes the hydrogenation of  $\alpha$ -ketoesters to chiral  $\alpha$ -hydroxyesters using chinchona alkaloid modified platinum catalysts.

A detailed study of the homogeneously palladium catalysed coupling of aryl halides and aryl triflates to itaconate diesters is discussed by M. G. Scaros and co-workers from G. D. Searle and Monsanto. This can provide a convenient route to the intermediate *E*-benzylidene succinate diesters, which in turn can be hydrogenated to chiral *R*-benzylsuccinates with a high degree of optical purity, using rhodium-dipamp complexes as catalysts. In the coupling reactions aryl iodides were more effective than aryl bromides, and the nature of the itaconate diester did not appear to affect the efficiency of the reaction: aryl triflates were more sensitive to the reaction conditions than the aryl halides were.

The DuPont process for the direct combination of hydrogen and oxygen to form hydrogen peroxide is described in a contribution by J. R. Kosak from E. I. DuPont de Nemours. Some of the problems that are associated with the traditional anthraquinone process, such as consecutive hydrogenation and oxidation steps, and also aqueous-organic extractions have been overcome. It has been shown that doping a supported palladium powder with platinum has a synergistic effect, and this has resulted in an improved yield and selectivity to hydrogen

peroxide. The attachment of this catalyst to a stainless steel mesh using washcoating techniques has avoided some of the drawbacks of a slurry catalyst system and has provided an efficient means for directly combining hydrogen and oxygen.

The synthesis of primary amines from olefins, syngas and ammonia is dealt with by J. F. Knifton from Texaco Chemical Company and by J. J. Lin from Shell Development Company. This oxoamination reaction has been extended to butenes and homogeneous cobalt, ruthenium and rhodium systems have all proved effective, with ruthenium being the most productive.

### Asymmetric Catalysis

Several chapters then deal with the topic of asymmetric synthesis. There has been particular interest in this as chiral molecules have become indispensable in the life sciences where there is a drive towards more active, specific drugs which do not have the undesired side effects that are associated with the presence of unwanted isomers. Ruthenium-BINAP complexes have become a popular catalyst system to study, since they have been shown to be effective with a range of substrates. S. Akutagawa from Takasago International Corporation, discusses this area, with reference to the hydrogenation of aliphatic ketones,  $\alpha$ -substituted  $\beta$ -ketoesters, and also the practical application of this technology towards the synthesis of Vitamin E,  $\beta$ -lactam intermediates and biodegradable polymers.

Further chapters deal with the use of ruthenium-BINAP systems for the hydrogenation of unsaturated carboxylic acids and with multinuclear NMR observations on the nature of the catalyst in the reduction of ketoesters.

The homogeneous hydrogenation of imines is discussed by B. R. James from the University of British Columbia, who describes work on asymmetric imine hydrogenation with rhodium phosphine catalysts, and by P. A. Chaloner and colleagues from the University of Sussex who describe the reduction of  $\text{PhN}=\text{CHPh}$  using iridium phosphine complexes.

J. L. Margitfalvi, from the Central Research Institute for Chemistry of the Hungarian

Academy of Sciences, and R. A. Sheldon and co-workers from Delft University of Technology and the Technical University of Budapest, respectively, revisit the topic of heterogeneous asymmetric hydrogenation catalysts. In the paper by Sheldon the influence of alkaloid-type chiral auxiliaries on the hydrogenation of carbonyl and olefinic groups by supported palladium and platinum catalysts is described, and shows that the highest enantioselectivities, comparable with the previously reported chinchonidine, were obtained with the vinca-type alkaloid vinpocetin®.

The theme of the application of catalysis to the life sciences is continued by D. Forster and co-workers from Monsanto and Searle Discovery Research, who have used homogeneous catalysis including hydroformylation with rhodium, reductive amination with ruthenium, and hydrosilylation with rhodium-phosphines, for reactions on template polymers which can result in the synthesis of tailored polymeric drug delivery systems.

Some catalytic problems relating to rapid deactivation and scale up during the reductive amination of aldehydes and ketones, using palladium or platinum on carbon catalysts, are described by J. J. Birtill from ICI. This is followed by a paper from R. E. Malz and colleagues of Uniroyal Chemical Company and Georgetown Medical School, on the reductive alkylation of acetophenone with aniline. They show that bisulphided catalysts are more effective than their unsulphided counterparts and that a 3 per cent  $\text{Pt}_x$  on carbon catalyst is superior to sulphided rhodium, ruthenium, nickel or palladium systems for that reaction.

The influence of the medium on the nickel catalysed hydrogenation of 2-methyl glutaronitrile is described by G. Cordier from Rhône-Poulenc. In this reaction subsequent dehydrogenation of the intermediate by a catalyst of palladium/silica in a fixed bed configuration gave the desired product,  $\beta$ -picoline, in high yield. A paper by D. G. Blackmond and A. Waghay from the University of Pittsburgh, demonstrates the role that alkali promoters can play in hydrogenation. During the hydrogenation of 3-methyl

2-butenal, catalysed by ruthenium/silica, the addition of potassium results in a shift in selectivity towards the unsaturated alcohol, provided that the potassium is in close proximity to the ruthenium.

Further examples of the influence of promoters in hydrogenations are given in other papers. These include rhodium-tin on silica catalysts, which give high selectivities to crotyl alcohol in the hydrogenation of crotonaldehyde; the selective hydrogenation of carboxylic acids to alcohols by sol-gel ruthenium-tin catalysts; the hydrogenation of bisphenol A using lithium hydroxide as a modifier, and the influence of alloying elements on the selectivity of platinum catalysts in the hydrogenation of phenol. Other topics that are discussed in both papers and/or posters include the influences of the support and the effect of the metal particle size on a variety of reactions catalysed by the platinum group metals.

Investigations by G. Centi and G. Stella from the Department of Industrial Chemistry and Materials, Bologna, on the selective oxidation of 1-butene to 2-butanone on solid Wacker-type catalyst systems comprising palladium supported on oxides, such as vanadium oxide, concluded that the main factors affecting catalyst performance are: the low desorption rate of products and the progressive reduction of vanadium oxide to strongly adsorbed species which inhibit reoxidation.

Catalytic oxidations with air for the clean and

selective transformations of polyols are described by P. Gallezot and colleagues from the Institut de Recherches sur la Catalyse-CNRS. In particular they discuss the oxidation of glyoxal to glyoxylic acids using platinum on carbon, and the conversion of glucose to gluconic acid using a palladium on carbon catalyst impregnated with bismuth. The latter catalyst system possesses some advantages over the commercial enzymatic process in that the reaction is carried out in one step in a single vessel with high yield per catalyst weight.

Papers by G. G. Stanley from Louisiana State University, on the uses of homobimetallic cooperativity with cationic rhodium catalysts are illustrated by the enantioselective hydroformylation of vinyl acetate to give intermediates in the production of L-threonine with enantiomeric excesses of 85 per cent. This is followed by a contribution by S. Wieland and P. Panster from Degussa, on the immobilisation of noble metal complexes and heterogeneous catalysts on polysiloxane supports and their application in organic synthesis.

This volume contains a large number of contributions by experts in various fields of catalysis and as such provides a wealth of information on a wide range of aspects of catalysis. By its very nature the information within the book is somewhat fragmented, and it is difficult to find related themes which recur in the text. Apart from this, it is a useful addition to the bookshelf for those involved in catalysis. M.J.H.R.

## The Fourth Grove Fuel Cell Symposium

Following the pattern of the three earlier highly successful symposia, the fourth meeting will be held at the Commonwealth Institute, London, England, from 19th to 22nd September, 1995. This fuel cell symposium is being organised by a steering committee composed of leading fuel cell scientists from both academia and industry, under the aegis of Elsevier Advanced Technology.

With the increasing interest in the efficient production of electricity combined with the introduction of legislation promoting ultra-low and zero emission vehicles, the potential market for fuel cell systems continues to grow. Internationally invited speakers, all world

authorities on fuel cell technology and exploitation, will provide an up-to-date analysis of technical developments and the opportunities for commercialisation of fuel cells; their contributions have been chosen to provide attendees with a complete picture of the progress achieved and the future prospects for fuel cell technology.

Those who would like to make poster presentations or who require further information about this symposium should contact Sharron Emsley, Fourth Grove Fuel Cell Symposium, Elsevier Advanced Technology, PO Box 150, Kidlington, Oxford OX5 1AS, U.K. Fax: +44(0) 1865 843971.