

# Platinum Metals Industrial Catalysis

## Catalysis of Organic Reactions

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This book summarises the proceedings of the sixteenth conference on the Catalysis of Organic Reactions held in Atlanta, Georgia in early 1996. Academic and industrial contributors discussed heterogeneous catalysis: hydrogenations, oxidations and acid catalysis, hydroformylation and asymmetric catalysis. Platinum metals were dealt with in about 70 per cent of the contributions.

## Hydrogenation Reactions

The selective hydrogenation of unsaturated aldehydes, using a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst impregnated with iron or nickel to enhance the selectivity to allylic alcohols, is described by R. L. Augustine and L. Meng, Seton Hall University, U.S.A. J. R. Kosak, Wilmington, discusses noble metal synergism exemplified by modification of a Pd/C catalyst by platinum and iron oxide to produce an active, selective and economical catalyst for the hydrogenation of dinitrotoluenes to aniline. Similarly, doping a Pt/C catalyst with nickel and chromium significantly increases its activity for the hydrogenation of 3,4-dichloronitrotoluene.

The hydrogenation of nitroarenes is described by R. K. Rains and co-workers, Flexsys America L. P., in studies of platinum and palladium catalysts. Hydroxylamine build-up decreases on changing the substituents on the arene ring from electron-withdrawing to electron-donating, thus decreasing the competing side reaction involving ring hydrogenation.

The mechanism of the selective hydrogenation of alkynes to alkenes over Pd/Al<sub>2</sub>O<sub>3</sub> catalysts is discussed by F. King and colleagues, ICI Katalco. Spin trapping techniques as well as the detection of radical products by electron spin resonance indicate that the surface intermediates have free radical character.

A range of soluble rhodium precursors at 1 bar and 20°C are employed by B. R. James and colleagues, University of British Columbia and Pulp and Paper Research Institute of Canada,

to hydrogenate substituted phenols. Over time, rhodium is precipitated causing loss of activity. The true catalyst may be colloidal rhodium.

The removal of protecting groups by catalytic hydrogenation was discussed by K. G. Griffin and co-workers, Johnson Matthey. Palladium is the most effective platinum group metal for the debenylation of ethers and amines, and THF or aliphatic ketones are the preferred solvents.

The selective hydrogenation of fatty esters into unsaturated alcohols over Ru-Sn catalysts is described by A. Piccirilli and colleagues, URA-CNRS 350, France; chemoselective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to allylic alcohols using Rh-Sn, Rh-Sn/SiO<sub>2</sub> and Pt/TiO<sub>2</sub> catalysts is addressed by P. Claus, Institut für Angewandte Chemie, Berlin, while S. K. Tanielyan and R. L. Augustine, Seton Hall University, show that the presence of tin in the support of palladium catalysts is essential for low temperature acetoxylation of toluene.

Asymmetric catalysis is increasingly important and W. S. Knowles, St. Louis, traces the development of useful platinum metals chiral catalysts. Work at Monsanto led to the development of a Rh-DIPAMP system to hydrogenate a pro-chiralenamide in the production of L-DOPA. Later a Rh-BINAP isomerisation catalyst was used by Takasago for menthol manufacture, and Ru-BINAP catalysts were found to hydrogenate  $\alpha$ -arylacrylics. DuPont discovered that C<sub>2</sub>-symmetric phospholanes when complexed to rhodium are effective catalysts for enamide hydrogenation.

F. Spindler and colleagues, Ciba-Geigy, discuss the use of ferrocenyl diphosphines as ligands in iridium systems for the catalytic hydrogenation of N-aryl imines, the products being intermediates for a number of pesticides. The addition of iodide and up to 30 per cent acetic acid results in an effective catalyst system which combines good optical yields with high inherent activity and catalyst longevity.

Isomerisation and hydrogenation catalysed by Ru-BINAP and the influence of competitive reactions on enantiomeric excess (ee) are discussed by Y. Sun and co-workers, Merck and Seton Hall University. During geraniol hydrogenation to (*R*) and (*S*)  $\beta$ -citronellol, isomerisation also occurs, giving the homoallylic alcohol,  $\gamma$ -geraniol, which undergoes hydrogenation at a faster rate than the parent compound and causes a lowering of the overall ee, as products of opposite chirality are formed. The isomerisation can be minimised by reducing the time lag between mixing catalyst and substrate and adding hydrogen and by lowering reaction temperature. In contrast to geraniol, nerol does not undergo isomerisation but hydrogenates to citronellol with high ees at low pressures.

Further topics on asymmetric hydrogenations are the diastereoselective hydrogenation of *N*-(2-methylbenzoyl)-(*S*)-proline esters on rhodium metal particles from M. Besson and colleagues, Institut de Recherches sur la Catalyse-CNRS, and the enantioselective hydrogenation of 3-coumarone over chiral centres on a Pt/SiO<sub>2</sub> catalyst by E. Allan and co-workers, Glasgow University, ICI Katalco and Zeneca. In the latter surface chirality is induced by using (*S*) or (*R*)-diamino or dihydroxyl binaphthalene as modifiers.

The use of  $\beta$ -cyclodextrin to achieve enantioselectivity in hydrogenations is discussed. Cationic rhodium diamine complexes combined with the cyclodextrin is described by C. Pinel and colleagues, Institut de Recherches sur la Catalyse et Laboratoire de Catalyse et Synthèse Organique; and G. V. Smith and co-workers, Southern Illinois University, discuss the hydrogenation activity of platinum, palladium, rhodium and ruthenium deposited on the cyclodextrin/epichlorohydrin. The ees in both cases are modest.

### Hydroformylation Reactions

A batch process for the selective production of isovaleraldehyde from isobutene has been developed by A. J. Solodar and colleagues, Monsanto, using a phosphine-free rhodium catalyst at low rhodium concentrations (60 ppm) at 120°C and 450 to 1800 psig. A. G. Abatjoglou and colleagues, Union Carbide Corporation, describe a novel

catalyst-product separation for higher alkenes. Here, the use of the conventional rhodium system is not feasible due to its thermal instability at temperatures where the product volatilises. The system employs monosulfonated triphenylphosphine-rhodium as a catalyst solubilised by addition of an agent, such as *N*-methylpyrrolidone, making the system homogeneous.

A related contribution from H. Olivier and Y. Chauvin, Institut Français du Pétrole, describes the use of imidazolium salts of perchlorate aluminates, borates and phosphates as novel solvents for two phase reactions including rhodium catalysed hydrogenation and hydroformylation. Novel supports and media are discussed by S. Wieland and colleagues, Degussa, who examine sulfonated polysiloxanes as solid catalysts and noble metal supports, and by J. W. Caraway and D. E. Bergbreiter, Texas A & M University, who look at soluble polymers as ligands and supports in catalyst systems, including those of platinum, rhodium and palladium.

Soluble palladium catalysts are studied by several authors; S. A. Godleski, Kodak Research Laboratories, describes palladium(0) complex catalysts for the selective 1,4-addition of nucleophiles to butadiene monoepoxide. When methylamine is the nucleophile, 4-methylamino-1-hydroxy-but-2-ene is converted to *N*-methylpyrrolidone using [RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] as catalyst.

### The Heck Reaction

J. R. Fritch and colleagues, Hoechst Celanese Corporation, describe 4-acetoxy-2-butanone and 4-hydroxy-2-butanone as alternatives to methyl vinyl ketone in the reaction with 2-bromo-6-methoxynaphthalene giving nabumetone. Both are cheaper, less toxic and more stable. S. A. Roberto and R. L. Augustine, Seton Hall University, discuss regioselective control of the arylation and hydrogenation of cinnamaldehyde over Pd/C and Pd/Al<sub>2</sub>O<sub>3</sub> by applying an electric potential to a fine stainless steel screen electrode.

This volume thus provides useful information for those involved in catalysis, and shows the continuing importance here of the platinum group metals.

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