

Platinum Metals in Catalysis

Catalysis of Organic Reactions

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This book is a compilation from papers and posters presented at the Seventeenth Conference on the Catalysis of Organic Reactions. The wide range of material illustrates the very intense industrial and academic interest in homogeneous and heterogeneous catalysis. About 60 per cent of the articles in this publication deal with the use of platinum group metals, and a selection of these are reviewed here.

Enantioselective Heterogeneous Catalysis

From the number of papers on this topic it is clear that enantioselective heterogeneous catalysis is a growing area of activity. This is due to a need to develop chiral synthetic methods applicable to the production of pharmaceuticals and agrochemicals. Advantages associated with catalyst recovery add to the interest, but the enantiomeric excesses (*ees*) obtained to date in these reactions are usually much lower than when homogeneous catalysts are employed.

Solvent, hydrogen pressure and modifier effects on *ees* were reported by M. Bodmer, T. Mallat and A. Baiker. They obtained *ees* up to 61 per cent for the enantioselective hydrogenation of trifluoroacetophenone on platinum/alumina catalyst.

The majority of modifiers used for heterogeneous enantioselective hydrogenation are cinchonidine and alkaloids of related structure; S. P. Griffiths, P. B. Wells, K. G. Griffin and P. Johnston reported a different class of modifiers: morphine derived alkaloids, in the hydrogenation of methyl pyruvate, but obtained only modest *ees*.

B. Török and co-workers pretreated platinum systems with ultrasound and observed improved enantioselectivity and an enhanced reaction rate in the hydrogenation of ethyl pyruvate.

Factors controlling chemo-, regio- and diastereoselectivity were investigated by S. Coman and colleagues in the diastereoselective hydrogenation

of cyclic β -ketoesters. This was performed over ruthenium-based catalysts on supports of molecular sieves, alumina and carbon, modified with cinchonidine and L(+)-tartaric acid.

Heterogeneous Catalysis

Catalysts based on a shape selective carbon molecular sieve (CMS) which exploits the differences in size and shape between benzene, cyclohexene and cyclohexane were reported by G. Srinivas, D. B. MacQueen, M. Dubovik and R. Mariwala in the selective partial hydrogenation of benzene. Ruthenium/CMS catalysts showed higher selectivity than conventional powdered ruthenium or ruthenium/alumina catalysts.

Two novel heterogeneous catalyst systems: Pt-Pd-CaCO₃ and Pt-C, modified with H₃PO₄, were reported by U. Siegrist, P. Baumeister, H.-U. Blaser and M. Studer. The catalysts were successfully used in the chemoselective hydrogenation of aromatic nitro compounds containing other functional groups, such as iodide, C=C, C \equiv C and C \equiv N, and conditions for the optimum use of both systems are given.

New iridium-based supported catalysts effective in the hydrogenation of halogenated nitro aromatic compounds were discussed by E. Auer, A. Freund, M. Groß, R. Hartung and P. Panster. The corresponding amines were produced and there were accompanying low rates of dehalogenation (< 0.1 weight per cent).

Viscous materials are difficult to hydrogenate without having reaction solvents to reduce viscosity. M. Ebrahimi-Moshkabad and J. M. Winterbottom described using an intermeshing co-rotating twin screw extruder as a 3-phase reactor for the hydrogenation of a dimethyl itaconate model system in viscous media. Alumina-coated screws with a further coat of electroless plated palladium formed the active catalyst.

Heterogeneously catalysed Heck reactions for synthesising commercially relevant compounds

were discussed by A. Eisenstadt. Octylmethoxy cinnamate (a UVB sun screen) was prepared in 75 to 92 per cent yield using a palladium/carbon catalyst. Homo- and hetero-substituted benzophenones, which are monomers and pharmaceutical intermediates, were similarly prepared.

S. Sharma, W. Koo-amornpattana, L. Zhang, S. Raymahasay and J. M. Winterbottom examined process optimisation to enhance catalyst activity and selectivity in the hydrogenation of α,β -unsaturated aldehydes, crotonaldehyde and cinnamaldehyde. Selectivities up to 54 per cent for crotyl alcohol and 75 per cent for cinnamyl alcohol hydrogenations were obtained in a 3-phase reactor on modification of the conditions.

The single stage reductive amination of aldehydes and ketones by supported platinum and palladium catalysts was described by J. J. Birtill, M. Chamberlain, J. Hall, R. Wilson and I. Costello. Their paper discussed optimisation of the choice of catalyst and reaction conditions to minimise by-products, such as alcohols.

Homogeneous Catalysis

A new route for enamine synthesis from olefins was reported by M. Beller, M. Eichberger and H. Trauthwein. The amination of aromatic olefins catalysed by cationic rhodium complexes yielded exclusively the *anti*-Markovnikov enamine product. The product yield is dependent on the substituents on the aromatic ring, with more electron donating groups usually giving higher yields.

Supercritical carbon dioxide (scCO₂) as a reaction medium for rhodium catalysed hydroformylation was described by I. Ojima, M. Tzamarioudaki, C.-Y. Chuang, D. M. Iula and Z. Li. They synthesised functionalised nitrogen- and oxygen-heterocycles.

Preliminary findings on the use of homogeneous catalysts of rhodium, ruthenium and palladium anchored to solid supports were reported by S. K. Tanielyan and R. L. Augustine. Such catalysts are highly active and produce good *ees* over a range of hydrogenation reactions. The catalysts have also been applied to allylation and hydroformylation reactions.

Ligand screening applied to the optimisation

of the palladium precursor/ligand combination in the Heck reaction for the synthesis of benzocyclobutene (BCB) derivatives was reported by R. A. DeVries, P. C. Vosejka and M. L. Ash. These BCB derivatives are then thermally polymerised to give materials for electronic, composite and thermal applications.

A new precursor for the *in situ* preparation of hydroboration catalysts [$(\eta^5\text{-C}_6\text{H}_7)\text{Rh}(\text{COD})$] is described by J. A. Brinkman and J. R. Showa. They found that regioselectivity during the hydroboration of styrene was dependent upon the added ligands. Reactions performed in the presence of chiral ligands gave modest *ees*.

Palladium-catalysed Buchwald-Hartwig coupling was used by S. Hayden and J. R. Sowa in the synthesis of fluoroaniline derivatives. The coupling of *N*-methyl piperazine and fluoro-haloarenes using the Pd₂(dba)₃/BINAP/NaO^tBu catalyst system gave the fluoroaniline derivatives in selectivities of > 99 per cent and high isolated yields (> 87 per cent).

Nitrile hydrogenation is used to prepare Nylon products. R. P. Beatty discussed the hydrogenation and reductive hydrolysis of nitriles to amines or alcohols, and the selective hydrogenation of dinitriles to aminonitriles. Ruthenium-based complexes, $[\text{RuH}_2(\text{L})_x(\text{PR}_3)_{4-x}]$, (L = H₂ or N₂, x = 0, 1, 2) were more active and stable for this reaction than ones reported previously.

B. L. Case, J. G. Franchina, Y.-S. Liu and D. E. Bergbreiter described poly(*N*-isopropyl-acrylamide) bound catalysts showing inverse temperature dependent solubility. Amide bonds attach the phosphine ligands to the polymer support. These catalysts were used in the aqueous hydrogenation of allyl alcohol and showed relatively low activity but could be recovered and reused. They examined the use of fluorous biphasic catalysis by preparing neutral rhodium catalysts bound to fluoropolymers. The catalysts had good activity and recyclability for alkene hydrogenation.

This book gives useful, up-to-date details of catalysis. However, the coverage of the platinum metals is mostly on heterogeneous catalysis, particularly enantioselective catalysis; homogeneous catalysis is not well represented, which could lead to disappointment. S. H. ELGAFI