"Heterogenized Homogeneous Catalysts for Fine Chemicals Production: Materials and Processes"

Edited by Pierluigi Barbaro and Francesca Liguori (Istituto di Chimica dei Composti Organo Metallici, Firenze, Italy), Springer, Dordrecht, The Netherlands, 2010,
459 pages, ISBN: 978-90-481-3695-7, £126.00, €139.95, US$189.00 (Print version);
e-ISBN: 978-90-481-3694-4, doi:10.1007/978-90-481-3696-4 (Online version)

doi:10.1595/147106711X581350 http://www.platinummetalsreview.com/

Reviewed by Raghunath V. Chaudhari

The Center for Environmentally Beneficial Catalysis,
The University of Kansas, Lawrence, KS 66047, USA

Email: rvc1948@ku.edu

Introduction

"Heterogenized Homogeneous Catalysts for Fine Chemicals Production" is Volume 33 of the series "Catalysis by Metal Complexes", edited by Claudia Bianchini (Institute of Chemistry of Organometallic Compounds, Sesto Fiorentino, Italy), David J. Cole-Hamilton (University of St Andrews, UK) and Piet W. N. M. van Leeuwen (Institute of Chemical Research of Catalonia, Tarragona, Spain). One of the book's co-editors, Pierluigi Barbaro, is a permanent researcher at Instituto di Chimica dei Composti Organo Metallici (ICCOM), Firenze, Italy, and has research interests in homogeneous and asymmetric catalysis with a focus on supported and nanostructured catalysts for sustainable production processes. The other co-editor, Francesca Liguori, is also at ICCOM and specialises in the chemistry of heterocycles and carbohydrates, organometallic chemistry and the synthesis of heterogenised homogeneous catalysts.

There are 13 chapters by a total of 29 authors, with many years of research experience and expertise in their respective fields. Most of the contributors are from academic institutions or universities, with just one chapter by authors from an industrial background.

The aim of this book is to review the current state of the art on the 'heterogenisation' (or 'immobilisation') of homogeneous catalysts for fine chemicals production, low to medium volume high-value products which are often difficult to separate and purify by conventional techniques such as distillation or extraction. Heterogenisation is a useful technique for developing advanced technologies and green chemical synthesis, as is pointed out in the foreword by David J. Cole-Hamilton and in the introduction to Chapter 1, written by Duncan Macquarrie (University of York, UK).

A number of examples of heterogenised catalytic complexes involving different transition metals are given, but this review will focus on the platinum group metals (pgms). These are grouped by topic. 10 out of the 13 chapters include pgm examples, with the most commonly used metals being ruthenium, rhodium and palladium, although platinum- and iridium-based catalysts are also mentioned.

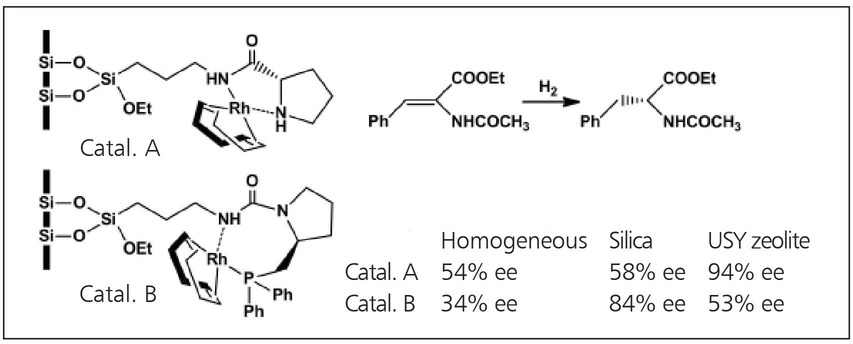
The topics covered are: the synthesis of 'heterogenised' catalysts; asymmetric catalysis; oxidation reactions; polymerisation reactions; reaction engineering; and instrumental techniques for the characterisation of catalytic materials. The design and development of 'heterogenised' catalysts is of great practical significance as it has implications for catalyst–product separation, recycling and the efficient use of pgm catalysts.

Synthesis Methods for Heterogenised Catalysts

The synthesis of 'heterogenised' catalysts is reviewed in 8 out of the book's 13 chapters. Chapters 2–5 are mainly focused on catalyst preparation, with some illustrative examples of model reaction systems. Chapters 3–5 describe catalysts based on pgms, mainly Pd, Rh and Ru with a few Pt catalysts. Chapter 2, by David Xuereb *et al.* (University of Southampton, UK), introduces biomimetic single site heterogeneous catalysts consisting of non-pgms, although the approach may also be useful for pgm catalysts.

Chapter 3 by José Fraile *et al.* (Universidad de Zaragoza, Spain) presents a very comprehensive review of synthesis methods and applications for heterogenised catalysts, mainly focusing on the use of inorganic supports such as silica, alumina, mixed metal oxides, layered solids (clays and layered double hydroxides), crystalline solids (zeolites including mesoporous materials) and nanoparticles, for example gold nanoparticles and carbon nanotubes. The importance of inorganic supports and their structural properties for the development of heterogenised homogeneous catalysts is highlighted with a number of examples. The chapter starts with a general overview of the different materials that have been used classically for immobilisation of metal complex catalysts, followed by the introduction of some new supports consisting of metal oxide nanoparticles, carbon nanotubes, graphite materials and composite matrices. The chapter is well divided into sections with different solid catalysts categorised according to the type of interaction between the support and the active catalyst, for example, support–metal or support–ligand interactions. Synthetic strategies, characterisation techniques and applications for several immobilised pgm and other transition metal complex catalysts are reviewed. The influence of the nature of the support matrices and other conditions are also discussed. Several newer strategies are described, including the silylation of oligo(methylsilane) (OMS) materials to build encapsulated complex catalysts within large mesoporous cages, previously thought possible only with microporous matrices. Concepts such as immobilisation by adsorption and supported liquid phase catalysis (SLPC) are also discussed in detail with several applications showing prospective research directions for fine chemical applications. Several novel Rh-, Ru- and Pd-based catalysts with uses in fine chemicals are included. For example, hydrogenation of (*Z*)-*N*-acetamidocinnamic acid derivatives using Rh complexes with proline derived ligand on ultrastable Y (USY) zeolite (**Figure 1**).

In Chapter 4, an extensive review of the synthesis of immobilised asymmetric catalysts on polymers and nanoparticle supports is presented by Ciril Jimeno *et al.* (Institute of Chemical Research of Catalonia (ICIQ), Spain). The catalytic performance of a selection of Pd, Rh and Ru complexes with immobilised ligands is compared for a range of reactions. An



	Homogeneous	Silica	USY zeolite
Catal. A	54% ee	58% ee	94% ee
Catal. B	34% ee	84% ee	53% ee

Fig. 1. Immobilisation of rhodium complexes with proline derived ligand on USY zeolite

interesting new approach using functional nanoparticles such as gold and magnetic iron(II, III) oxide (Fe_3O_4) as supports for the immobilisation of pgm complexes is presented, which may lead to wider applications. This chapter will help researchers to identify different materials for the innovative and rational design of improved immobilised catalysts.

Chapter 5 reviews the immobilisation of metal complex catalysts on dendrimer supports. These large molecules enable easy separation of the supported catalyst complex by membrane filtration. The design of dendrimers with different functionalisation on the periphery and at the core has opened new horizons for immobilisation using several different functional moieties in a single structure. The synthesis and applications of these materials for epoxidation, coupling and hydrosilylation reactions is well presented in this chapter and there is scope for expansion into other fine chemicals applications. Examples of dendrimer supported pgm complexes include:

(a) A dendrimer supported $[Rh(nbd)_2](ClO_4)$ (ndb = 2,5-norbornadiene) complex for the asymmetric hydrogenation of dimethyl itaconate, which gives high activity, enantioselectivity and stability; and
(b) The asymmetric transfer hydrogenation of acetophenone using $[RuCl_2(p\text{-cymene})]_2$ immobilised on a core-functionalised dendrimeric ligand (**Figure 2**).

In Chapter 6, the preparation and application of membranes for the separation of catalysts is addressed. Although this chapter mainly gives non-pgm examples, the approach is generic and has scope for expansion to pgm-catalysed reactions.

Applications to Fine Chemicals and Speciality Polymers

Asymmetric Catalysis by Heterogenised Chiral Metal Complexes

Chapter 7 by Benoît Pugin and Hans-Ulrich Blaser (Solvias AG, Switzerland) is an important contribution addressing industrial aspects of fine chemicals production with examples of commercialised processes. The authors have extensive experience in the industrialisation of asymmetric catalytic processes. They give examples of industrial enantioselective catalysis using a number of immobilised pgm catalysts which include:

(a) $[Ir(COD)Cl]_2$ on chiral Josiphos (a proprietary ligand from Solvias AG) immobilised on functionalised silica on polystyrene supports (**Figure 3**) for the manufacture of a herbicide, (*S*)-metolachlor, which is produced at >20,000 tonnes per year; and
(b) Rh diphosphine and Ru-BIPHEP (2,2′-bis(diphenylphosphino)-1,1′-biphenyl) immobilised on silica for asymmetric hydrogenation reactions.

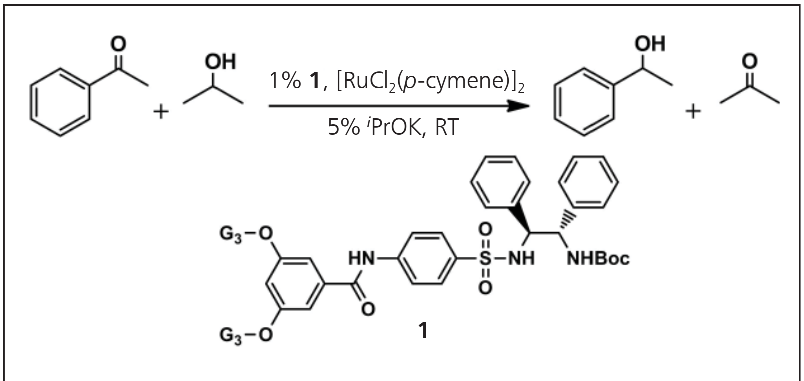


Fig. 2. Asymmetric transfer hydrogenation with ruthenium on dendrimer catalyst. G_3 = generation 3 dendrimer

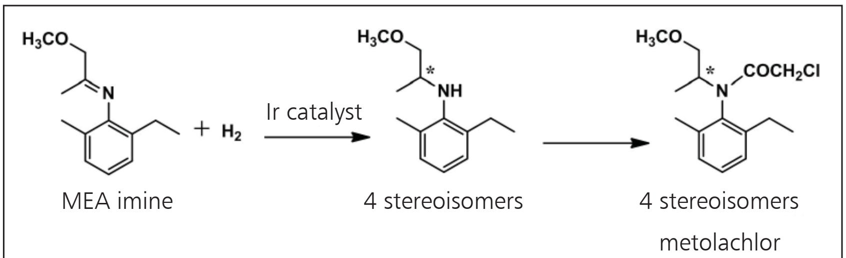


Fig. 3. A process for the preparation of (S)-metolachlor

This chapter is unique in this book with a brief but useful discussion of practical aspects such as catalyst reuse, availability, development time, costs and opportunities for process engineering, which are often difficult to accomplish with immobilised catalysts. It is also the only chapter written by authors working in industrial research and development. It is evident from the references that a more detailed version of the issues addressed in this chapter is available in another book coedited by Hans-Ulrich Blaser (1).

Chapter 9 by Agnes Zsigmond *et al.* (University of Szeged, Hungary) provides a very well written and comprehensive review of the chemoselective and enantioselective hydrogenation of alkenes, aldehydes, diketones and imines using a number of immobilised pgm catalysts, which include some chiral complexes. Different aspects of strategic catalyst design and synthesis are described, including characterisation, applications, recyclability and stability aspects, involving mostly Ru- or Rh-based catalysts. The historical development of industrial technology for enantioselective hydrogenation reactions is reviewed. Topics such as polymer bound and inorganic solid supported Ru or Rh complexes are thoroughly discussed, with emphasis on stability and recyclability. The chapter also includes recent strategies involving the use of designed ionic liquids and/or multiphasic liquid systems, envisioning lower catalyst loss and better recyclability, activity and selectivity. A specific example of the heterogenisation of a Ru-BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) catalyst *via* a spacer is shown (**Figure 4**).

Oxidation Reactions

Chapter 10 summarises a selection of Ru- and Pd-based heterogenised catalysts for oxidation reactions. However, there is limited information about the synthesis and structural characterisation of the complexes. The initial part of the chapter sums up general methodologies to immobilise metal complex catalysts, and there is a good selection of references on oxidation reactions, although there is a much broader spectrum of exciting applications of oxidation in fine chemicals which is not covered here.

Polymerisation Reactions

In Chapter 11, polymerisation reactions using novel immobilised Ru catalysts are reviewed by Matthew D. Jones (University of Bath, UK) with applications in specialty polymers although these are not strictly

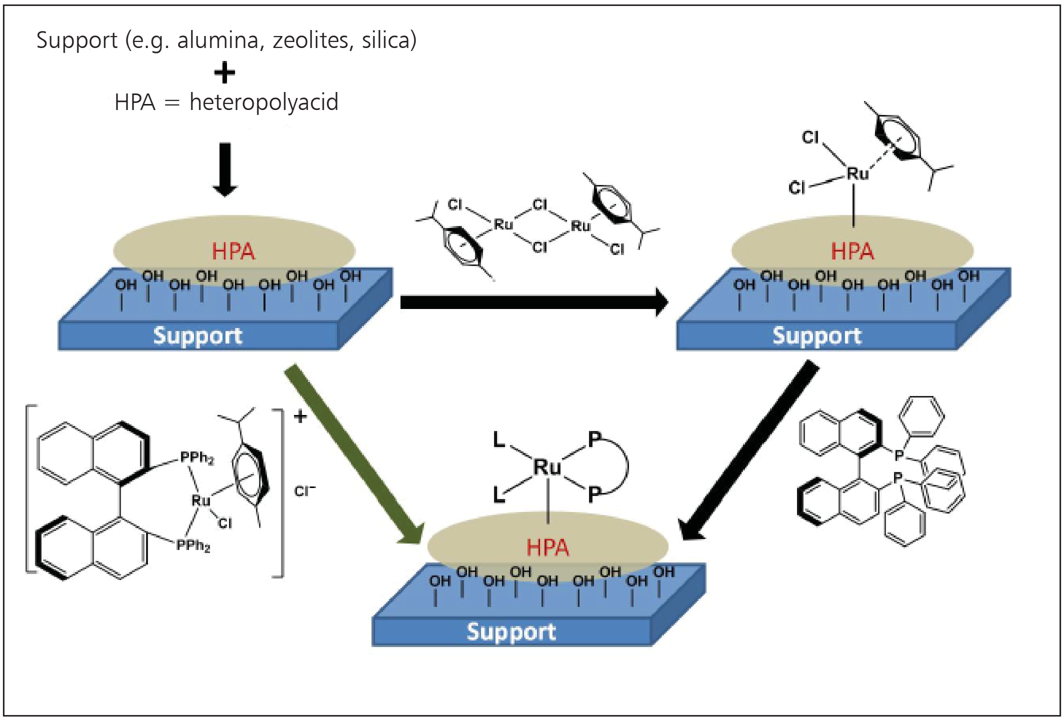


Fig. 4. Heterogenisation approaches for ruthenium-BINAP with spacer

defined as fine chemicals. Immobilising metal complex polymerisation catalysts is a useful strategy for the development of more sustainable processes and 'green technology'. Special emphasis is placed on polymer degradation; the proposed single site catalysts are particularly useful for synthesis of specialty polymers with biodegradable properties, which is significant to the goal of sustainable and green technology. One example of a major breakthrough is the heterogenised Grubb's catalyst (a Ru complex on a silica support) for olefin metathesis (**Figure 5**) which has insignificant leaching. Other examples discussed in this chapter relate to non-pgm catalysts.

Reaction Engineering and Instrumental Techniques

In Chapter 8, Albert Renken (École polytechnique fédérale de Lausanne, Institute of Chemical Sciences and Engineering (EPFL-ISIC), Lausanne, Switzerland) presents an excellent overview of reaction engineering involving heterogenised molecular catalysts, which is useful as an introduction to the subject for chemists and engineers working in this area who are not familiar with the fundamentals of reactor design. The well developed concepts of mass transfer coupled with chemical reactions are described in the context of heterogenised catalytic systems, which generally fall into the class of multiphase catalytic reactions. A selection of relevant examples such as biphasic hydroformylation catalysed by a water soluble Rh complex with triphenylphosphine trisulfonate (TPPTS) ligand, and SLPC reactions catalysed by RhCl(CO)$(PPh_3)_3$ dissolved in dioctyl phthalate containing free PPh_3 supported in porous materials are given. The article also provides a very useful reference source for reaction engineering concepts. In Chapter 12, a brief but essential introduction of molecular simulation is presented which is very timely for understanding molecular interactions in heterogenised catalysts.

Chapter 13 by John Evans and Moniek Tromp (University of Southampton, UK) is a very general introduction to the characterisation of catalytic materials by spectroscopic methods. The characterisation of Pd, Rh, Os and Ru catalysts are described, and the chapter will be useful as a reference source. However the coverage of different techniques is limited, considering the vast progress made in this area in recent years.

Conclusions

This book presents a comprehensive review of recent developments in the 'heterogenisation' of metal complex catalysts with a focus on synthetic methodology, characterisation and applications in fine chemicals. Many different synthetic approaches are covered, although most of the examples are illustrative rather than real processes used in the fine chemicals industry. It is, however, evident from this book that the pgms have wide ranging applications in fine chemicals and emerging technologies.

The chapters in this book are well written by highly qualified authors and will provide an excellent resource for postgraduate and doctoral students as well as researchers working in the areas of metal complex catalysis, asymmetric catalysis and catalytic process development. A number of known applications using heterogenised metal complex catalysts in commercially relevant hydroformylation, carbonylation and oxidation reactions are not adequately covered (see also (2–8)) and more comparison of the performances of heterogenised catalysts and their homogeneous counterparts would also have been of value.

Overall, the book reads well and covers a subject of interest to both academic and industrial researchers. It should inspire many young researchers to develop novel catalytic materials and make progress towards more sustainable and green chemical processes.

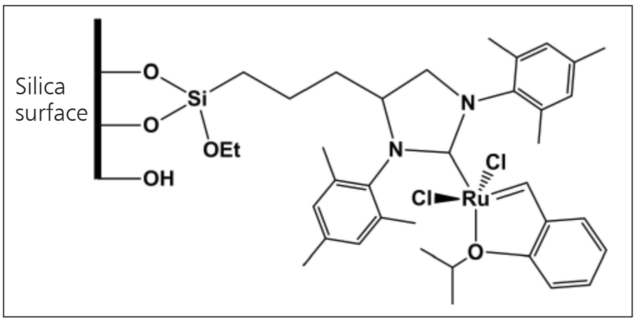
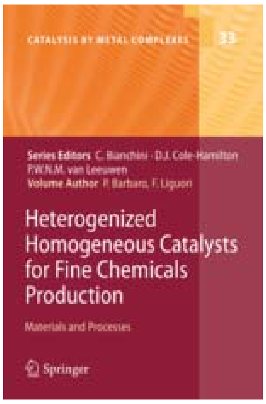


Fig. 5. Heterogenisation of Grubbs olefin metathesis ruthenium catalyst



"Heterogenized Homogeneous Catalysts for Fine Chemicals Production: Materials and Processes"

References

1 "Asymmetric Catalysis on Industrial Scale: Challenges, Approaches and Solutions", 2nd Edn., eds. H.-U. Blaser and H.-J. Federsel, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, 2010

2 G. A. Ozin and C. Gil, *Chem. Rev.*, 1989, **89**, (8), 1749

3 J. M. Andersen, *Platinum Metals Rev.*, 1997, **41**, (3), 132

4 K. Mukhopadhyay, B. R. Sarkar and R. V. Chaudhari, *J. Am. Chem. Soc.*, 2002, **124**, (33), 9692

5 K. Mukhopadhyay, A. B. Mandale and R. V. Chaudhari, *Chem. Mater.*, 2003, **15**, (9), 1766

6 A. J. Sandee, L. A. van der Veen, J. N. H. Reek, P. C. J. Kamer, M. Lutz, A. L. Spek and P. W. N. M. van Leeuwen, *Angew. Chem. Int. Ed.*, 1999, **38**, (21), 3231

7 B. R. Sarkar and R. V. Chaudhari, *J. Catal.*, 2006, **242**, (1), 231

8 R. V. Chaudhari and A. N. Mahajan, Council of Scientific and Industrial Research, 'Novel Catalytic Formulation and its Preparation', *US Patent* 7,026,266; 2006

The Reviewer

Raghunath V. Chaudhari is the Deane E. Ackers Distinguished Professor at the Department of Chemical and Petroleum Engineering, University of Kansas (KU), Lawrence, USA. He worked at the National Chemical Laboratory, Pune, India, for 30 years as Head, Homogeneous Catalysis Division before joining KU in 2007. His research experience covers interdisciplinary fields of homogeneous and heterogeneous catalysis, chemical reaction engineering and modelling of multiphase systems with current activities focused on biomass conversion processes and the design and development of novel catalytic materials. He has authored or co-authored a number of research papers, review articles and two books, the most recent one being on "Trickle Bed Reactors", published in 2011 by Elsevier. He also teaches kinetics, reaction engineering and chemical engineering thermodynamics at graduate and undergraduate levels at KU.

