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"Handbook of Homogeneous Hydrogenation"

EDITED BY JOHANNES G. DE VRIES (DSM Pharmaceutical Products, The Netherlands) AND CORNELIS J. ELSEVIER (University of Amsterdam, The Netherlands), Wiley-VCH, Weinheim, Germany, 2007, in 3 volumes, 1632 pages, ISBN 978-3-527-31161-3, £280.00, €420.00, U.S.$500.00

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This book reviews the entire field of homogenous hydrogenation over the past forty years. It covers both the research literature and industrial processes, and aims for comprehensive coverage. The target readerships for this book are industrial chemists and chemistry graduates embarking on research in the field. The authors assume a degree-level knowledge of chemistry, but aim to describe the specialist area of homogeneous hydrogenation and provide guidance on the extensive literature available.

The book is unique in covering all aspects of homogenous hydrogenation from unfunctionalised alkene hydrogenation to enantioselective reduction of imines. The two editors are from an industrial chemical company (DSM Pharmaceutical Products, The Netherlands) and a university (University of Amsterdam, The Netherlands). This diversity is also reflected in the authors of the forty-five chapters, who represent a comprehensive cross-section of current industrial and academic research in the field, as well as geographic diversity including Europe, North America and the Far East.

Precious Metal Catalysts

The many uses of precious metal hydrogenation catalysts are reflected throughout the book. These catalysts have been used extensively for enantioselective hydrogenation. The issues of metal recycling and removal from products are covered in topics such as catalyst immobilisation and deactivation.

The initial chapters cover individual precious metals. A chapter on rhodium covers both historical development and reaction mechanisms. Iridium was initially thought to be less catalytically active than rhodium. However, it is in fact slow ligand dissociation that gives rise to apparent lower reaction rates. In suitable non-coordinating solvents, iridium catalysts can produce faster reactions than their rhodium equivalents for some substrates, such as highly substituted alkenes. Further, ruthenium is a uniquely effective catalyst for some hydrogenations, such as the enantioselective reduction of unfunctionalised ketones.

Platinum and palladium catalysts have been used for alkene and alkyne reductions, including partial hydrogenation reactions such as the conversion of dienes to mono-enes. There are also chapters on nickel, lanthanide and actinide catalysts.

Ionic hydrogenations were initially investigated as a way to avoid the use of precious metal catalysts. However, the highest catalytic activities are seen with precious metals such as ruthenium. Precious metal clusters have been studied as an interesting intermediate stage between homogenous and heterogenous catalysts. However, it is often hard to tell whether observed activity is in fact due to small amounts of mononuclear catalyst.

Colloids and nanoparticles are another example of the grey area between homogeneous and heterogeneous catalysis. This chapter describes the use of various stabilisers for these small particles and their applications, such as the use of ruthenium nanocatalysts for the reduction of benzene to cyclohexene.

Chapters on kinetics, spectroscopic methods and the use of parahydrogen to investigate reaction mechanism cover the fundamental characterisation of homogeneous hydrogenation processes.

Hydrogenation of Functional Groups

There is some overlap between the early chapters, which group catalytic processes by the metal catalyst, and later chapters, which cover the hydrogenation of particular functional groups. This is useful, as it ensures that an enquiring reader can find relevant information by several different approaches. There are chapters on the reduction of alkynes and dienes; and of aldehydes, ketones, imines and carboxylic acid derivatives. These reactions often use precious metal catalysts. The chapter on arene and heteroaromatic reduction covers the ruthenium and rhodium complexes used, although these are likely to be acting as heterogeneous catalysts in the harsh conditions normally employed.

The reduction of carbon dioxide is not yet commercialised, but has been carried out with ruthenium, rhodium and palladium catalysts in the research laboratory. A chapter on dehalogenation gives a table of the precious metal catalysts used for various substrates. A chapter on polymer hydrogenation describes how diene based polymers can also be hydrogenated with precious metal catalysts, especially those based on rhodium.

The chapter on transfer hydrogenation covers rhodium, ruthenium and iridium catalysts. It discusses the various donors used, the reaction mechanism and side reactions. Transfer hydrogenation can be used to racemise and thereby recycle the unwanted isomer in dynamic kinetic resolution.

The chapter on diastereoselective hydrogenation is lengthy and tabulates the precious metal catalysts used according to substrate; functional groups in alkene substrates direct the stereochemistry of the hydrogenation.

Rhodium catalysts are unusual in performing hydrogen-mediated carbon–carbon bond formation. The chapter on this reaction covers the cyclisation of enones or aldehydes with cationic rhodium complexes.

Enantioselective Hydrogenation

A substantial part of the book is occupied by enantioselective hydrogenation reactions. This reflects the enormous research interest in this area. These reactions generally use a precious metal catalyst in combination with a chiral ligand. The section on enantioselective alkene hydrogenation begins with an introductory overview. There are then chapters on the different types of chiral ligand used: phospholane, ferrocene-based, other bisphosphines, bidentate phosphine ligands containing heteroatoms, monodentate ligands and bidentate phosphorus–nitrogen ligands. The enantioselective hydrogenation of unfunctionalised alkenes is more difficult and is described in a separate chapter.

The mechanism of enantioselective hydrogenation is not yet fully understood. Details are presented in a chapter which describes mechanisms for rhodium, iridium and ruthenium catalysts and the possible rate determining steps of hydrogen addition and migratory insertion.

Whereas alkene hydrogenation tends to use rhodium or iridium catalysts, ketone hydrogenations more commonly use ruthenium. These are described in chapters on enantioselective ketone and β-keto ester hydrogenations, and the hydrogenation of functionalised ketones.

The enantioselective hydrogenation of imines and enamines is difficult, as amines can act as catalyst poisons and imines are prone to hydrolysis. However, this chapter includes examples of the successful use of iridium, rhodium and ruthenium catalysts for this type of reaction.

Enantioselective transfer hydrogenation has also been carried out with precious metal catalysts. A chapter on high-throughput experimentation and ligand libraries includes an interesting account of how DSM's phosphoramidite ligand library led to a tonne-scale process. The following chapter, on industrial applications, includes details of pilot-scale processes as well as fully commercialised ones. This is useful as many pharmaceutical product syntheses are abandoned at pilot scale despite promising catalytic results.

Phase Separation and Miscellaneous Topics

The separation of product from metal catalysis is a perennial problem in homogeneous catalysis. The issue is addressed in chapters on two-phase

aqueous hydrogenation, supercritical and compressed carbon dioxide as reaction medium, fluorous catalysts and fluorous phase catalysis, ionic liquids and immobilisation techniques. The latter chapter addresses both research results and commercial products such as Johnson Matthey's FibreCat® supported catalysts.

The last part of the book is devoted to miscellaneous topics, which include metal-catalysed regeneration of nicotinamide cofactors, catalyst inhibition and deactivation, and chemical reaction engineering aspects.

Conclusion

The book covers many areas of current research in homogeneous hydrogenation as well as large-scale industrial processes. The information is laid out well; many chapters include useful tables summarising reaction conditions and catalyst activities. The complex structures of chiral ligands are given in clear diagrams. The style inevitably varies between chapters, but most give a clear and comprehensive overview of their subject.

The book comprises three hardback volumes and is accordingly priced quite highly. It is therefore most likely to be bought as a reference work for an academic or industrial library. In this context, I feel it is a useful starting point for future explorations of homogenous hydrogenation. It offers an up-to-date and wide-ranging review of the field.

The Reviewer

Ann Keep is a Principal Scientist at Johnson Matthey Catalysts in Royston, U.K. Her main professional interests are in transition metal catalysts, both homogeneous and heterogeneous.