

Edited by Kuiling Ding  
and Yasuhiro Uozumi

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# Handbook of Asymmetric Heterogeneous Catalysis



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*Edited by*  
*Kuiling Ding and Yasuhiro Uozumi*



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*Edited by*  
*Kuiling Ding and*  
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## ***Further Reading***

Ertl, G., Knözinger, H., Schüth, F.,  
Weitkamp, J. (Eds.)

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## Preface

Stereoselective molecular transformation is a central theme in modern organic synthetic chemistry. Among the many strategies applied to prepare desired organic molecules in their optically active forms, catalytic asymmetric synthesis has been widely recognized as a powerful reaction class. Compared to the impressive developments of homogeneous asymmetric catalysis – the most splendid of which were awarded the Nobel Prize of 2001 – enantioselective organic synthesis with *heterogeneous* chiral catalysts has received only scant attention, in spite of the historical appearance of a silk–palladium composite as the first heterogeneous enantioselective catalyst in 1956.<sup>1)</sup> During the past decade, however, in response to increasing environmental concerns about the harmful and resource-consuming waste of the heavy and/or rare metals that are frequently used as the catalytic centers of homogeneous catalysts, the importance of heterogeneous systems has again been realized and this area is presently undergoing very rapid growth.<sup>2)</sup> In addition, the development of heterogeneous chiral catalysts has been attracting significant interest for their practical advantages: the safe and simple manipulation of work-up; reduced contamination by catalyst residues in the products; and the recovery and reuse of the costly chiral and/or metal resources. There is good reason to believe that the development of asymmetric heterogeneous catalysis – including the heterogeneous-switching of given homogeneous asymmetric processes and the chiral-switching of heterogeneous nonasymmetric processes – offers a practical, ‘green’, clean and safe alternative to more conventional methods of accomplishing many asymmetric processes.

This book, which comprises 12 review-type chapters, is intended to provide an overview of the main research areas of asymmetric heterogeneous catalysis, although the arrangement of the chapters is somewhat arbitrary. Chapter 1 (Z. Wang, K. Ding and Y. Uozumi) provides an introductory review to outline this volume, which should give guidance to the broad readership. Chapters 2 (S.S. Thakur, J.E. Lee, S.H. Lee, J.M. Kim and C.E. Song) and 3 (S. Itsuno and N. Haraguchi) mainly describe the development of chiral catalysts bound to

<sup>1)</sup> For a review, see: Izumi, Y. (1971) *Angewandte Chemie – International Edition* 10, 871–948.

<sup>2)</sup> For a review, see: De Vos, D.E., Vankelcom, I.F.J. and Jacobs, P. A. (eds) (2000) *Chiral Catalyst Immobilization and Recycling*, Wiley-VCH, Weinheim.

inorganic and organic (polymeric) supports, respectively, via the heterogenization of chiral organometallic and organic catalysts originally designed for homogeneous counterparts. In Chapter 4, Q.-H. Fan, G.-J. Deng, Y. Feng and Y.M. He present details of dendritic chiral catalysts, where the dendrimer moiety—a new class of highly branched polymer—often provides unique physical as well as chemical properties. Asymmetric heterogeneous catalysis in exotic liquid media is addressed in Chapters 5, 6 and 7. Thus, fluorous liquid–liquid biphasic systems with fluorophilic-modified chiral catalysts are reviewed in Chapter 5 (G. Pozzi), while water-based reactions with hydrophilic (or amphiphilic) polymeric catalysts are described in Chapter 6 (Y. Uozumi). The recent growth of chemistry with ionic liquids and supercritical carbon dioxide is also significant, and nowadays this is applied to heterogeneous asymmetric catalysis, which is detailed in Chapter 7 (S.-G. Lee and Y.J. Zhang). Although organocatalysis is a well-established class of organic transformations, chiral-switching is an up-to-date topic in the area of asymmetric catalysis. M. Benaglia introduces the heterogeneous-switching of asymmetric organocatalysis, mainly with cinchona- and amino acid-derivatives, in Chapter 8. The metal crosslinked assembly of chiral organic ligands forming chiral coordination polymers realized self-supporting systems of chiral complex catalysts where the catalytic activity and heterogeneous property are obtained in a single step (Chapter 9, K. Ding and Z. Wang). The chiral-switching of metal catalysts is a classic, yet immature, approach to asymmetric heterogeneous catalysis. Clearly, while pioneering strides have been made, additional studies on the chiral modification of metal surfaces are warranted, and this topic is reviewed by T. Sugimura in Chapter 10. The chiral-switching of phase-transfer catalysis (PTC) has been another eagerly awaited subject, and a breakthrough in asymmetric PTC was recently brought about by K. Maruoka, who contributes Chapter 11 together with his colleagues, X. Wang and Q. Lan. The final chapter of this volume is provided by H.-U. Blaser and B. Pugin, who introduce the industrial application of heterogeneous asymmetric catalysis.

We gratefully acknowledge the work of all authors in presenting up-to-date and well-referenced contributions; indeed, without their efforts this volume would not have been possible. Furthermore, it was a pleasure to collaborate with the Wiley-VCH ‘crew’ in Weinheim, who not only did an excellent job in producing the book but also helped us in a competent manner in all phases of its preparation. We are also grateful to Dr. Zheng Wang of Shanghai Institute of Organic Chemistry, who put a lot of effort into editing this volume. The collaborative studies of K.D. and Y.U. were partially supported by the Asian Core Program, sponsored by the Japan Society for the Promotion of Science.

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July 2008

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