Edited by Kuiling Ding
and Yasuhiro Uozumi

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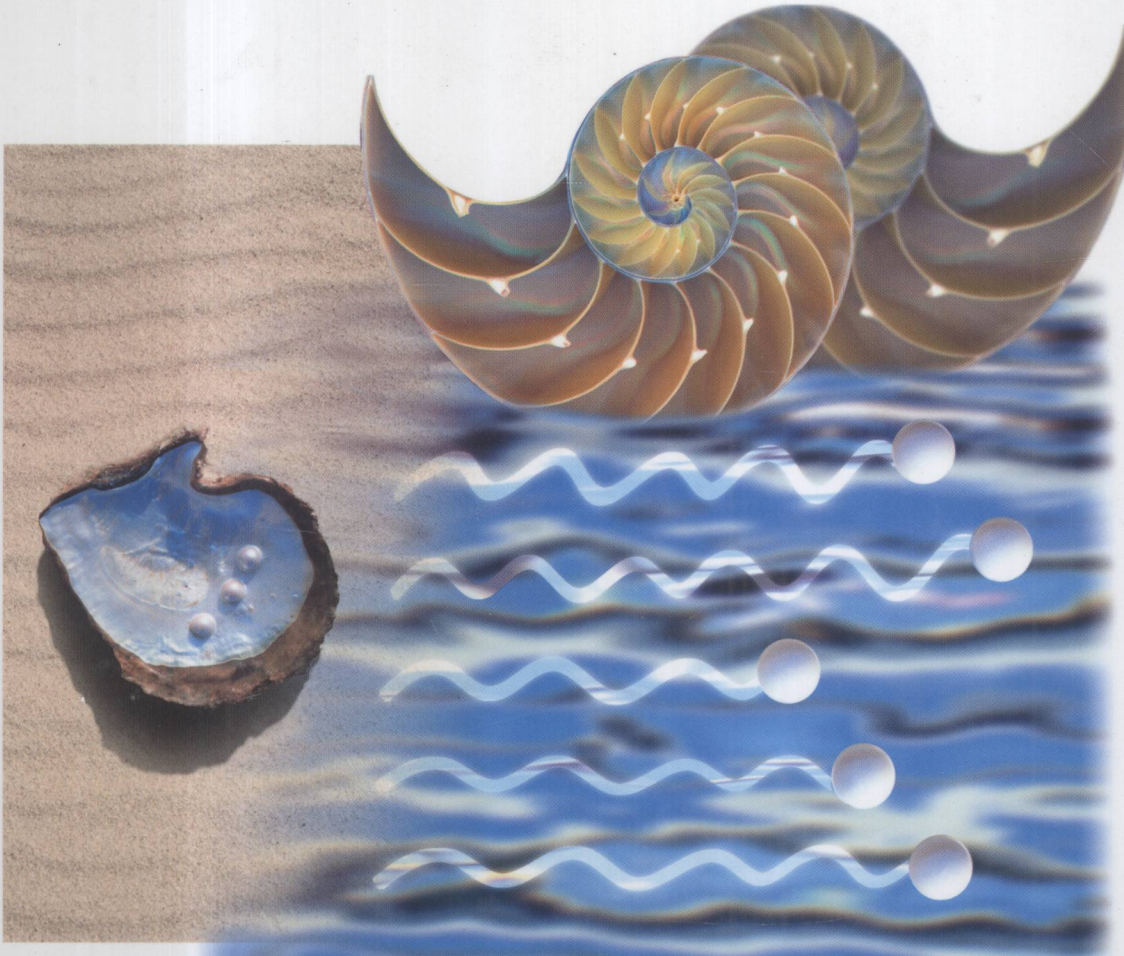
Handbook of Asymmetric Heterogeneous Catalysis



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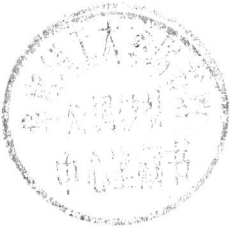

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The Editors

Prof. Dr. Kuiling Ding
Chinese Academy of Sciences
Shanghai Institute of Organic Chemistry
Fenglin Road
Shanghai 200032
China

Prof. Dr. Yasuhiro Uozumi
Institute for Molecular Science (IMS)
Myodaiji
Okazaki 444-8787
Japan

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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.[1)] 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.[2)] 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

[1)] For a review, see: Izumi, Y. (1971) *Angewandte Chemie – International Edition 10*, 871–948.

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

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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.

Kuiling Ding
Yasuhiro Uozumi

Shanghai and Okazaki
July 2008

List of Contributors

Maurizio Benaglia
Università degli Studi di Milano
Dipartimento di Chimica
Organica e Industriale
via Golgi 19
20133 Milan
Italy

Hans-Ulrich Blaser
Solvias AG
P.O. Box
4002 Basel
Switzerland

Guo-Jun Deng
Chinese Academy of Sciences
Institute of Chemistry
P.R. Beijing 100190
China

Kuiling Ding
Chinese Academy of Sciences
Shanghai Institute of Organic
Chemistry
354 Fenglin Road
Shanghai 200032
P. R. China

Qing-Hua Fan
Chinese Academy of Sciences
Institute of Chemistry
Beijing 100190
P. R. China

Yu Feng
Chinese Academy of Sciences
Institute of Chemistry
Beijing 100190
China

Naoki Haraguchi
Toyohashi University of Technology
Department of Materials Science
Tempaku-cho, Toyohashi, 441-8580
Japan

Yan-Mei He
Chinese Academy of Sciences
Institute of Chemistry
Beijing 100190
P. R. China

Shinichi Itsuno
Toyohashi University of Technology
Department of Materials Science
Tempaku-cho, Toyohashi, 441-8580
Japan

Ji Man Kim
Sungkyunkwan University
Department of Chemistry
Cheoncheon-dong 300, Jangan-gu
440-746 Suwon
Korea

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Quan Lan
Kyoto University
Department of Chemistry
Graduate School of Science
Sakyo
Kyoto 606-8502
Japan

Jae Eun Lee
Sungkyunkwan University
Department of Chemistry
Cheoncheon-dong 300,
Jangan-gu
440-746 Suwon
Korea

Sang-gi Lee
Ewha Womans University
Department of Chemistry and
Nano Science
Seoul 120-750
Korea

Seo Hwan Lee
Sungkyunkwan University
Department of Chemistry
Cheoncheon-dong 300,
Jangan-gu
440-746 Suwon
Korea

Keiji Maruoka
Kyoto University
Department of Chemistry
Graduate School of Science
Sakyo
Kyoto 606-8502
Japan

Gianluca Pozzi
CNR-Istituto di Scienze e
Tecnologie Molecolari
via Golgi 19
20133 Milan
Italy

Benoît Pugin
Solvias AG
P.O. Box
4002 Basel
Switzerland

Choong Eui Song
Sungkyunkwan University
Department of Chemistry
Cheoncheon-dong 300, Jangan-gu
440-746 Suwon
Korea

Takashi Sugimura
University of Hyogo
Graduate School of Material Science
Himeji Institute of Technology
3-2-1 Kohto
Kamigori
Ako-gun
Hyogo 678-1297
Japan

Santosh Singh Thakur
Sungkyunkwan University
Department of Chemistry
Cheoncheon-dong 300, Jangan-gu
440-746 Suwon
Korea

Yasuhiro Uozumi
Institute for Molecular Science (IMS)
Myodaiji
Okazaki 444-8787
Japan

Xisheng Wang
The Scripps Research Institute
Department of Chemistry
10550 North Torrey Pines Road
La Jolla, CA, 92037
USA

Zheng Wang
Chinese Academy of Sciences
Shanghai Institute of Organic Chemistry
354 Fenglin Road
Shanghai 200032
P. R. China

Yong Jian Zhang
Shanghai Jiao Tong University
School of Chemistry and Chemical Technology
800 Dongchuan Road
Shanghai 200240
P. R. China

Contents

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