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Enantioselective Homogeneous Supported Catalysis

During the last two decades, increasing concerns about the sustainability of chemical practices and about the undesirable action of synthetic materials (especially for biomedical applications) have resulted in a growing interest in synthetic methods based on enantioselective catalytic reactions. In this area there has also been an increasing emphasis on efforts directed to the immobilization of catalysts for easy recovery and repeated recycling and reuse. A simple search for the topic "Enantioselective Supported Catalyst(s)" in the ISI Web of Knowledge produced 1253 hits from 1992 on, of which 56% belonged to the period 2007–2012. Thus, it is not surprising that several excellent monographs on the topic have been published in recent years. However, most of these have centered on immobilization on insoluble supports, resulting in heterogeneous supported catalysts.

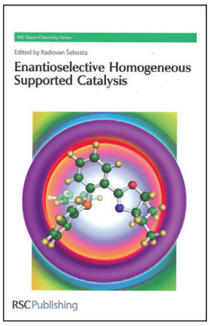
The book *Enantioselective Homogeneous Supported Catalysts*, volume 15 in the RSC Green Chemistry series, follows a different approach, being centered on catalysts immobilized onto solids or liquids in ways that lead to homogenous systems. The editor of the present volume is Radovan Šebesta of Comenius University (Bratislava), an expert in organocatalysis and on the use of ionic liquids as catalyst supports. As the emphasis in the book is on the homogeneous nature of the supported catalytic system, it has mainly been possible to review the published results in a sequence of essentially non-overlapping chapters. There are, however, some areas where the frontier between homogeneous and heterogeneous catalytic systems is not sharply defined, and this leads to inconsistencies between the title of the book and what is discussed in some of its chapters.

The first chapter, by Radovan Šebesta, deals with ionically tagged transition metal catalysts. The roles of the ionic tag are discussed (especially electrosteric activation) and an overview of enantioselective processes mediated by these catalysts and taking place in ionic liquids, supercritical liquids, or biphasic systems is given. The chapter provides a critical analysis of this area of research, discussing the potential of ionically tagged transition-metal catalysts and the present limitations. Although it is rather brief (15 pages), it contains 52 references, thus giving a comprehensive coverage of the present state of development of the field.

The second chapter by S. Toma (34 pages) reviews catalysis with supported organocatalysts, and is structured in three main sections. The first section deals with organocatalysts bearing ionic tags. This is a fast-growing field, and up to now much effort has been devoted to asymmetric aldol and Michael reactions. Progress in these topics is adequately covered. The second section deals with soluble, covalently supported, organocatalysts, and reviews the literature on the use of perfluoroalkyl tags, and on organocatalysts functionalized with low-molecular-weight polyethylene glycols or their monomethyl ethers or with linear polystyrene. The first two topics are well defined, and the literature is adequately covered. However, the third topic (polystyrene) includes a substantial amount of work dealing with organocatalysts immobilized on microporous, slighty crosslinked polystyrene. These materials form gels, but remain insoluble during their catalytic function. Thus, they fall outside the declared scope of the review. The third, rather brief, section of this chapter deals with organocatalytic reactions mediated by organocatalysts immobilized in microenvironments. The section reviews work on ionic immobilization on polymers and on covalent immobilization on silica and magnetic nanoparticles. Again, the criticism can be made that none of these materials are truly homogeneous catalysts. This chapter contains 152 references, including some references from 2011.

The third chapter has been written by P. Goodrich, C. Paun, and C. Hardacre, and deals with asymmetric catalysis in ionic liquids with unmodified catalysts. It has to be mentioned that this approach does not usually involve truly homogeneous conditions: with bulk ionic liquids, biphasic systems are normally used, and with supported ionic liquid phases (SILP) the catalyst is immobilized in a thin layer of ionic liquid on a solid support. However, the SILP strategy offers significant practical advantages and is much used nowadays. The chapter starts with two useful sections on methods for supporting catalysts in ionic liquids and on techniques for the characterization of the catalyst and the ionic liquid. The following description of the use of catalysts immobilized in ionic liquids for some important reaction types (hydrogenation, oxidation, hydroformylation, pericyclic reactions, nucleophilic additions) is very thorough and includes important practical details. This chapter contains 172 references, including work published in 2011.

Chapter 4, by M. Bandini, deals with chiral metal catalysts covalently immobilized on soluble polymers. The discussion is divided into "inner-type chiral metal polymers" and "outer-type chiral metal polymers", according to the disposition of the chiral ligand in the polymeric architecture. In polymers of the first type the ligand is at one end of the polymer chain, while in the second type the catalytically active fragment is directly involved in the construction of the polymer chain. This organ-



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ization of the material turns out to be highly effective for describing the present development of the field. The outer-type chiral metal polymers discussed include ligands such as bis(oxazolines), salens, chiral diamines, and phosphines supported on polyethyleneglycol (PEG), on non-cross-linked polystyrene, on polymers formed by the ring-opening metathesis polymerization of norbornene, and on polyesters. Among inner-type chiral metal polymers, binap and binap–binol copolymers, soluble salen polymers, and cinchona alkaloid ligands supported on polyesters and polysiloxanes are covered. This excellent overview of the field, clearly showing its potential and limitations, is supported by 54 references.

The fifth chapter, by R. J. M. Klein Gebbink and M. A. N. Virboul, describes enantioselective catalytic dendrimers. The development of this field has been based on the ideas that the catalytic properties of a particular species will not be altered when supported on a dendrimer, and that catalytic activity will be enhanced through the accumulation of multiple catalytic sites in certain regions of their molecular geometries. Since it is known that the type of dendrimer used for the immobilization exerts an important effect on the activity of the catalyst, the authors have organized this chapter in two main sections according to the position of the metal centers, either inside the dendrimer or on its surface. Within this scheme, the examples discussed are further classified according to the types of ligands used. In this manner, the results from 15 years of research in this field are well described, and all important individual examples are discussed in detail. This chapter includes 75 references.

Chapter 6, by G. Pozzi, deals with fluorous chiral catalysts. These are analogs of standard ligands and organocatalysts that have been modified by the introduction of highly fluorinated fragments, and that can be immobilized in fluorous phases for work in fluorous biphase systems (BFS). This rather comprehensive chapter (43 pages, 124 references) includes a well-written introduction to fluorous technologies, and divides the examples of fluorous catalysis into transition-metal-based catalytic systems and metal-free catalytic systems. Among the metal-based systems, different types of oxidation, reduction, and C−C bond-forming reactions are described in great detail. Among the metal-free catalytic systems, the use of proline derivatives for different organocatalytic applications is thoroughly reviewed.

The seventh chapter of the book, by S. Buda, M. Pasternak, and J. Mlynarski, deals with aqueous-phase asymmetric catalysis, and reviews progress with catalysts whose structure has been modified to include polar groups that increase solubility in water. The reactions discussed take place in water, with or without the addition of organic solvents, and, in general, in homogeneous conditions. The chapter is organized in two sections. The largest one covers metal-assisted asymmetric reactions, and includes work on catalytic hydrogenation (a topic that has received much attention), epoxidation, aldol reactions, and Mannich reactions, in addition to other, less thoroughly studied processes. The second section, on organocatalytic reactions, starts with a description of the pioneer work by MacMillan on Diels–Alder reactions, and covers work on aldol, Michael, and Mannich reactions. Altogether, this chapter gives an excellent overview of the progress achieved in this area, which is key to the development of more sustainable practices in chemical synthesis. This chapter includes 125 references, many of them multiple.

The last chapter of the book, by J. M. Fraile, J. I. García, C. I. Herrerías, J. A. Mayoral, and E. Pires deals with non-covalent immobilization. Again, this topic corresponds to a borderline situation between homogeneous and heterogeneous catalysis: the system undergoing reaction is heterogeneous, but the behavior of the catalysts resembles that of homogeneous species. However, the authors have performed an interesting systematization of the diverse situations where non-covalent immobilization of catalysts operates. Thus, sections on supported liquid phases (some overlapping with Chapter 3), immobilization by physisorption, immobilization by hydrogen bonding, immobilization by entrapment, immobilization by coordinative bonds, and immobilization by electrostatic interactions are included in the chapter, providing an excellent panoramic view of this not so clearly defined area. This chapter includes 84 references.

In accordance with the intention of its editor and authors, this book is not a comprehensive source of information on enantioselective homogeneous supported catalysis, but instead discusses the latest developments in the areas covered, critically evaluating the strengths and weaknesses of these methodologies. The references appear to be up-to-date at the time of editing (early in 2011), and there is a useful index at the back of the book. For these characteristics, and for the many practical details given in the different chapters, this volume will certainly be a useful tool for researchers working in catalysis and a useful addition to the libraries of academic chemists.

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