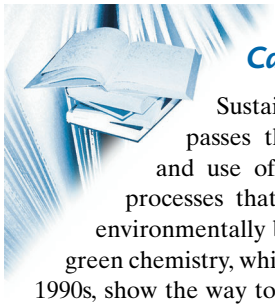


Sustainable Catalysis

Sustainable chemistry encompasses the design, manufacture, and use of chemical products and processes that are efficient, safe, and environmentally benign. The principles of green chemistry, which were developed in the 1990s, show the way towards sustainability. The chemical industry is obviously the final recipient, and also a direct protagonist, of all the progress that is being achieved in this area.

Sustainable catalysis lies at the heart of green chemistry, offering processes that are selective and safe, with energy economy and atom economy, and nowadays it is an essential partner of the pharmaceutical and fine chemicals industries. The book *Sustainable Catalysis* delves into this field, describing a compilation of catalytic transformations that are particularly important for the manufacture of pharmaceuticals and fine chemicals. The topics covered in the book have been judiciously selected from two sources: a list of key reactions identified by the Pharmaceutical Roundtable, a forum created in 2005 by the ACS Green Chemistry Institute and leading pharmaceutical companies, and the topical areas highlighted in the "Challenges" meetings organized jointly by the Applied Catalysis Group of the Royal Society of Chemistry and the Fine Chemicals Group of the Society of Chemical Industry. The editors of this book have done an excellent job in providing a dual approach to most of the topics covered, by presenting first an academic overview, then an industrial case study. This dual approach, which clearly differentiates this book from others previously published, provides a balanced view of the usefulness and limitations of a given process, and of the challenges that must be overcome to cross the bridge from basic research to industrial applications. This would certainly not have been possible without the participation of a panel of authors composed of world-class academic and industrial researchers.

The book comprises 16 chapters. Chapter 1 focuses on the catalytic reduction of amides to amines without the use of metal hydride reagents. After an elegant introduction in which the importance of this process in pharmaceutical synthesis is illustrated with several examples, the authors describe advances in the catalytic hydrogenation and hydrosilylation of amides. The different protocols presently available are compared on the basis of green criteria, and their limitations are clearly indicated.

In Chapter 2, the challenging topic of hydrogenation of esters to alcohols is discussed, but unfortunately only ruthenium-based homogenous catalysts are covered. Chapter 3 is devoted to transaminases, an emerging class of biocatalysts that are finding increasing application in the synthesis of chiral amines through the resolution of racemic mixtures of amines, or by the transamination of ketones. Chapter 4 presents a case study of transaminase evolution for the large-scale production of the antidiabetic compound sitagliptin, a process that was recognized in 2010 by the award of the presidential Green Chemistry prize of the US Environmental Protection Agency (EPA). However, the excessive details given by the author make the reading of this chapter a bit tedious.

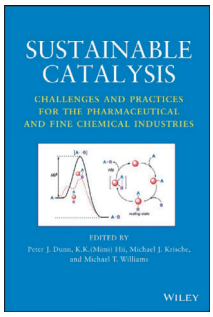
Chapter 5 discusses the direct synthesis of amides from carboxylic acids and amines without the use of stoichiometric coupling reagents. The chapter presents a critical overview of the different catalytic systems capable of promoting this process, paying particular attention to those based on boronic and boric acids. Some industrial applications of these boron-based catalysts are discussed in Chapter 6.

Chapter 7 focuses on the catalytic formation of C–C and C–N bonds from alcohols by the so-called "borrowing hydrogen" methodology. That is followed in Chapter 8 by a discussion of a case study conducted by Pfizer to synthesize an inhibitor for schizophrenia treatment on kilogram scale. The need for more active and cheaper catalytic systems for further large-scale applications is clearly highlighted in both chapters.

Olefin metathesis is covered in Chapter 9, which nicely stresses the efforts devoted to the design of recyclable ruthenium catalysts and development of purification techniques to minimize the metal content in the reaction products—key points for applications in the pharmaceutical industry. The development of a scalable and cost-effective synthesis of ciluprevir, an anti-HCV drug, which involves a ring-closing metathesis reaction, is elegantly presented in the following Chapter 10.

Chapter 11 gives a well-organized review of the arylation, alkenylation, alkynylation, and alkylation of heteroaromatic compounds by catalytic activation of C–H bonds. Particularly valuable is the critical discussion on the scope and limitations of the different strategies presently available. Chapter 12 describes a case study in which an industrial group has developed a new catalytic system for the direct arylation of azoles and applied it to the synthesis of a drug candidate in kilogram quantities.

Chapters 13–15 are devoted to organocatalysis. The first of these discusses the use of diarylprolinol silyl ethers as organocatalysts in a broad range of asymmetric organic transformations, nicely illustrating their potential for the synthesis of natural products and biologically active molecules. The authors, leading protagonists in the field, have done an excellent job of explaining reaction mechanisms,



Sustainable Catalysis
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but failed when discussing the work from other laboratories. Chapter 14 describes a couple of recent applications of organocatalysis on an industrial scale at Merck, while Chapter 15 describes the limited progress made to date in the development of organophosphorus catalysts for Wittig, Mitsunobu, and Appel halogenation reactions, a chemistry that is still in its infancy.

The book ends with a chapter on the catalytic formation of C–C bonds associated with hydrogenation and transfer hydrogenation processes, in which π-unsaturated substrates are reductively coupled to carbonyl compounds and imines. The method offers an appealing alternative to the use of organometallic reagents.

Altogether, this book is an excellent source of information on hot topics in catalysis, for both academic and industrial chemists. For the latter, the discussions of the various challenges encountered and addressed during scale-up studies will undoubtedly be very useful in planning future work. In brief, I have read this book with pleasure and I recommend it to all chemists working or getting started in the field of catalysis.

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