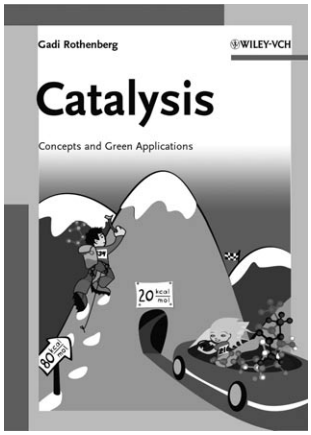
Catalysis: Concepts and Green Applications

Gadi Rothenberg

Wiley-VCH: Weinheim, 2008, 273 pages + XII; ISBN: 978-3-527-31824-7 55,00 €/45,00 £/80,00 $



"How many people do you really think should know how to master this EXAFS characterization technique in Italy? *Ten?… Twelve?*", leading research chemist Giovanni Carturan rhetorically asked a colleague on discussing reform of the educational curriculum for undergraduate chemists. Carturan was complaining that undergraduate teaching of chemistry had shifted its focus from the creation of economic value through the invention of new, useful substances to shaping a class of experts in analytical techniques with a narrow knowledge of their topic.

Focusing on concepts and (green) applications, Gadi Rothenberg now provides one powerful educational tool in the educational tradition invoked by Carturan, father of the BioSil whole-cell encapsulation methodology nowadays used also to catalytically synthesize Paclitaxel from entrapped *Taxus* cells (p 218).

Intended for senior undergraduate students of chemistry and chemical engineering, as well as for chemical researchers in academia and industry, in only 6 chapters this book offers a unified vision of the field dealing with homogeneous, heterogeneous and biocatalysis. Catalysis and green chemistry are first put in the context of our evolution towards sustainable development, explaining (Chapter 1) what they are and why they are important. Ample examples from currently practiced industrial catalytic processes are a book's *leit motif*. For example, the three-step BHC synthesis of ibuprofen (p 22) is used to show how the process provided "an elegant solution" in avoiding the large quantities of solvents and waste associated with traditional stoichiometric reagent usage.

Catalysis is the "key to sustainability" (p 10) and, the author emphasizes in the opening of Chapter 2, that it is a kinetic phenomenon. Hence, the kinetic principles of homogeneous and heterogeneous catalysis are discussed, ending the chapter with a presentation of practical approaches in kinetic studies.

Specific areas of catalysis are then treated in order starting (Chapter 3) from homogeneous catalysis, and particularly catalysis in the liquid phase, both with and without (organocatalysis) metals. The elementary steps in organometallic catalysis and their role in various catalytic cycles are presented along with a qualitative presentation of the main structure/activity concepts in the field. Steric and electronic effects are thus discussed with the help of excellent illustrations. Finally, asymmetric catalysis is presented with examples ranging from Knowles' asymmetric hydrogenation catalyst used in the synthesis of L-Dopa through Noyori's BINAP catalyst for the synthesis of fragrances and pharmaceutical substances. Further practical examples are drawn from bulk and fine chemical synthesis (Shell higher olefins process, Wacker oxidation, Du Pont's synthesis of adiponitrile and Ciba-Geigy's metolachlor process).

Recyclable molecular catalysts made of immobilized homogeneous catalysts are also discussed in this chapter.

Classic gas/solid systems are discussed in the initial part of Chapter 3 dealing with heterogeneous catalysis opening with the development of Haber–Bosch nitrogen fixation and hydrocarbon refinery catalysts. "About 800,000 tons of solid catalysts are used every year worldwide" – writes the author (p 132) - "but this does not mean that we understand how they work". Model (i.e., laboratory) and real catalysts are different and the chapter continues by presenting examples of how catalyst characterization is increasingly being done under conditions that are as close as possible to those of the real process.

After discussing the main preparation routes of solid catalysts and characterization tools, the chapter is concluded with a discussion of liquid/solid and liquid/liquid heterogeneous systems from aqueous to fluorous biphasic catalysis through the use of ionic liquids and phase-transfer catalysis. Examples include BP's AVADA process for the direct synthesis of ethyl acetate from ethene and acetic acid, and the Yellow diesel catalytic distillation process for biodiesel production developed by the author himself.

The three main catalysis methodologies are treated equally in depth. Finally, Chapter 5 deals with a number of new industrial biocatalytic processes, besides well established fermentation methods. Biocatalysis is as green as catalysis gets: reactions conditions are mild, the solvent is water and the catalysts are fully biocompatible. "The question that arises", hence, is not "Why use biocatalysis" but rather "How come there are still any non-biocatalytic processes?" (p 189).

Following the presentation of the basic concepts of biocatalysis, whole-cell and purified enzyme methods are compared in terms of each methodology's advantages and disadvantages. Immobilized enzymes are then presented, either heterogenized at the surface of solid supports or sol-gel entrapped in silica matrices but, alas, the sol-gel entrapment of whole cells is omitted.

Ending the book, directed evolution (the iterative process that mimics the natural evolution process *in vitro*) is presented as a powerful tool to develop new biocatalysts able to meet stringent industrial requirements. The 11 million tons per year isomerization of glucose to fructose, Mitsubishi's biocatalytic hydrolysis of acrylonitrile to acrylamide and the BMS Paclitaxel process are examples from current industrial processes.

Finally, the role of computational modelling of catalytic processes is critically explored showing how computers are actually used as predictive tools in catalysis research (Chapter 6). Models of homogeneous, heterogeneous and enzyme catalysis processes are presented with examples from modelling using both classical mechanics (molecular dynamics, Monte Carlo simulations) and quantum mechanics (Car–Parrinello and Hartree–Fock approaches). Despite admirable efforts to simplify concepts, this chapter is barely understandable for those with no background in computational chemistry.

The author is also an entrepreneur (co-founder of the companies Sorbisense and Yellow Diesel) and this helps him to put the whole discussion of catalysis and green chemistry in the socioeconomical context.

A website (*catalysisbook.org*) complements the book offering answers to selected exercises, a complete reference lists with DOIs, and valued lecture slides that will be useful to teachers and researchers alike. The site also includes the text of the first chapter: Looking at it will be helpful to anyone who is considering buying the book.

In conclusion, the author's highly readable and concise style results in a comprehensive treatment of catalysis that will make of this book a lasting reference for chemistry scholars at all levels: from research practitioners in industry and academia to teachers and their students at graduate and undergraduate level.

Mario Pagliaro
Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via U. La Malfa 153, 90146 Palermo, Italy
Fax: (+39)-091-680-9247;
phone: (+39)-01-680-9370
E-mail: mario.pagliaro@ismn.cnr.it
DOI: 10.1002/adsc.200800426

