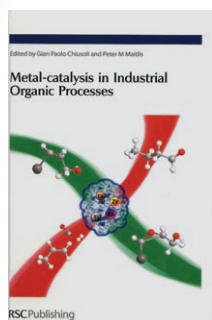




### Metal-Catalysis in Industrial Organic Processes



Edited by *Gian Paolo Chiusoli* and *Peter M. Maitlis*.  
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There is hardly any other field of chemistry that is so clearly connected to industrial applications as organometallic chemistry and catalysis. This close relationship should be emphasized also in teaching courses, because students absorb factual knowledge, complex catalytic cycles, and abstract physicochemical concepts with particular interest when the direct relevance to important industrial processes is emphasized. Therefore, an interestingly written textbook that explains the most important metal-catalyzed industrial processes at a suitably thorough level, but is nevertheless compact enough to be read as a whole, promises to be a very helpful resource. However, the rapid pace of developments in this field makes it difficult to produce such a book. Up-to-date information about industrial processes, if available at all, is only released after a long delay, and the details of many important processes remain hidden in the patent literature and only available to insiders. Gian Paolo Chiusoli and Peter Maitlis, two catalytic chemists with many years of experience, have set themselves the task of producing such a textbook, and have collected together a team of authors

from industry and universities who bring a wide-ranging fund of experience in different areas of organometallic chemistry.

The book *Metal-Catalysis in Industrial Organic Processes*, with just under 300 pages, is relatively compact and handy, but nevertheless covers broad areas of the subject. It consists of seven chapters and two short appendices. Relationships of particular importance are clearly emphasized in special text, and there are exercise problems and suggested topics for discussion.

In the first chapter, "Catalysis in the Chemical Industry", P. Howard, G. Morris, and G. Sunley introduce the subject and discuss the historical development of industrial catalytic processes, criteria for the choice of suitable chemical processes, and methods for studying catalytic reactions and understanding them. In 22 pages of almost pure prose, written in the style of a lecture presentation, the authors discuss many interesting aspects of industrial catalysis. However, from the viewpoint of students it would perhaps have been better to omit some of this information, and instead to break up the text of this introduction with diagrams, pictures, and schemes, to achieve a clearer presentation.

The second chapter, by M. G. Clerici, M. Ricci, and G. Strukul, is entitled "Formation of C–O Bonds by Oxidation", and gives an excellent description of the most important oxidation processes used in the chemical industry. It covers not only the well-established standard processes for the production of basic chemicals such as KA oil and ethylene oxide, but also some newer applications such as the salt-free synthesis of  $\epsilon$ -caprolactam. For asymmetric syntheses, such as epoxidation, *cis*-hydroxylation, and sulfoxidation, as well as explaining the mechanisms, the authors describe some existing industrial applications. Altogether this is an excellent chapter with a good didactical structure and a wealth of up-to-date information.

The next chapter, "Hydrogenation Reactions", by L. A. Oro, D. Carmona, and J. M. Fraile, is also well written and highly informative. After a short introduction to the mechanisms of homogeneous and heterogeneous hydrogenation

processes, the authors describe a wide variety of industrial applications, which range from cracking, reforming, and desulfurization processes in the petrochemical industry to the hydrogenation of fatty acids and to asymmetric syntheses by homogeneous catalysis. As well as the classic examples of L-dopa and menthol, the more recently developed synthesis of metolachlor is mentioned. It would also have been useful to give a few more examples of current industrial applications of asymmetric hydrogenations.

Chapter 4 is entitled "Syntheses Based on Carbon Monoxide". Here again, a large amount of information has been cleverly presented within a remarkably small space. P. Maitlis and A. Haynes have chosen an unconventional sequence of topics, beginning with the carbonylation of alcohols and esters, continuing with reactions such as the alkoxycarbonylation and hydroformylation of alkenes, and ending with Fischer–Tropsch syntheses. This has some advantages from a didactic standpoint, but unfortunately means that the historical connections are sometimes lost. However, this chapter is certainly up-to-date, as shown, for example, by the inclusion of the iridium-catalyzed carbonylation of methanol, in contrast to many older textbooks, which still describe the rhodium-catalyzed method. This is a very informative chapter for students, as it gives valuable insights into the opportunities and problems of carbonylation chemistry.

In the next chapter, "Carbon–Carbon Bond Formation", F. Calderazzo, M. Catellani, and G. P. Chiusoli collect together information about many reactions with widely different mechanisms. These include, for example, Friedel–Crafts-type acid-catalyzed alkylation reactions, palladium-catalyzed cross-coupling reactions, and alkene oligomerizations. Each of these could have filled a chapter by itself, and therefore it has only been possible to discuss the different types of reactions very briefly here. To get a detailed understanding of the mechanisms of the different catalytic reactions, such as the palladium-catalyzed cross-couplings, the reader would also need to refer to a textbook of organometallic chemistry. Also, in the discussions of existing industrial appli-

cations, especially in this chapter, it was necessary to concentrate on a strictly limited selection from the many interesting processes. A very good selection is presented, including even some important and highly topical examples, such as the synthesis of boscalid by a Suzuki coupling reaction. However, it would also have been interesting for readers to be given annual production volumes for industrial processes.

The high level of topicality seen in the previous chapters raises great expectations for Chapter 6, "Metathesis of Olefins" by C. L. Dwyer, as this topic has developed rapidly in the past decade, following the discovery by Grubbs and Schrock of homogeneous catalysts for such reactions. Unfortunately the chapter is very short (17 pp.), and is mainly devoted to the older heterogeneously catalyzed processes, such as the Phillips triolefin process, the SHOP process, and the ethenolysis of cyclic alkenes. In contrast, examples of processes based on the new homogeneous catalysts that are planned or already in operation are only mentioned briefly in passing, and thus the chapter fails to show the importance of the discovery of these catalysts, which resulted in the award of a Nobel Prize in recognition of the potential for wide technological application. Although the

relative emphasis in the chapter might be justified by a strict consideration of current production figures, it probably does not fully meet readers' expectations. In view of the topical importance of the above developments, a detailed discussion of, for example, the Materia poly-DCPD process would have been of interest to readers, and some metathesis-based syntheses of pharmaceutical intermediates could at least have been described under the heading "Recent Progress".

Like the earlier ones, the final chapter, "Polymerization Reactions" by G. Fink and H.-H. Brintzinger, again looks at developments that go beyond existing industrial applications. The authors begin by discussing the mechanisms of the reactions mainly used in polyolefins production, then describe the most important processes for the production of polyethylene and polypropylene. That is followed by a discussion of the types of catalysts that are used, such as the Ziegler–Natta, Phillips, and metallocene catalysts. The main part of the chapter is concerned with current developments and with mechanistic aspects, such as the control of regio- and stereochemistry during polymerization, the phenomenon of chain-walking, the heterogenization of catalysts, and the copolymerization of nonpolar with

polar monomers or CO. The chapter contains a wealth of information, and leaves scarcely any aspect of modern polymerization catalysis untouched—the authors' enthusiasm for the latest developments in the field is clearly evident. However, readers of this chapter need to have some basic knowledge of the subject to understand the relationship between catalyst properties and potential industrial applications.

At the end of the book there are two appendices that contain the basics of homogeneously and heterogeneously catalyzed reactions, so that readers, if needed, can quickly refresh their knowledge of these subjects if they encounter difficult points while reading the book.

In summary, this book offers the reader an interesting survey of metal catalysis as applied in industry. It is didactically well constructed and easy to read, and can be recommended for both students and teachers of organometallic chemistry as a valuable addition to the existing range of standard textbooks.

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