

Aqueous-Phase Organometallic Catalysis

Concepts and Applications

Edited by
Boys Cornils and Wolfgang A. Herrmann

Second, Completely Revised and Enlarged Edition



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Preface to the Second Edition

Very recently, some colleagues noticed a statement in one of the monthly columns about the state-of-the-art that “in organic chemistry reactions employing the solvent water are still rare [1]” – which is true and untrue at the same time: certainly, water-based conversions are scarce compared to those in the great majority of other solvents. But whoever was sensitive enough to recognize the tremendous possibilities of aqueous-phase catalysis would never ignore the increasing number of publications concerning this field of activity, the progress which has taken place during recent years, and the breakthroughs which have been brought about following these activities.

So it is a great pleasure for us to announce the second edition of our book *Aqueous-Phase Organometallic Catalysis* – in such close proximity to the first edition in 1998. Responsible for this are on the one hand the dramatic successes of industrial realization: production figures are now close to 1 MM tons per year in various applications (with hydroformylations, at approximately 800 000 tpy, in a senior position). On the other hand, the long overdue in-depth occupation with the scientific basis, the exploratory work with the various possibilities of this “immobilization with the liquid support water”, and the exploitation of the immense variability of the method in chemical respects (regarding central atoms and ligands) create an atmosphere of overwhelming interest in this technique.

Thus the sections of this revised edition have been enlarged to different extents. For instance, in respect of the scientific fundamentals and taking into account that the role of water in organometallic conversions is not only purely as a solvent but as a strongly coordinative polar reagent. It contributes considerably to the formation of polar or ionic intermediates or to oxidative additions to lower-valent transition metal complexes (thus explaining the strong pH dependence of many aqueous-phase catalyzed reactions). The work on different central atoms of catalytically active complexes and the search for alternative, highly specialized ligands – including chiral ones – has extended considerably the scope of aqueous-phase organometallic catalysis together with knowledge about coordination catalysis.

The same is true for the application of water-soluble catalysts for quite a bunch of basic organometal-derived chemical reactions ranging from hydrogenations or

hydroformylations to more “exotic” applications such as water-based enantioselective Diels–Alder reactions or kinetic resolutions. It also includes improvements and alternative answers for the chemical reaction engineering of aqueous-phase catalyzed conversions.

Last but not least, the success of aqueous-phase catalysis has drawn the interest of the homogeneous-catalysis community to other biphasic possibilities such as organic/organic separations, fluororous phases, nonaqueous ionic liquids, supercritical solvents, amphiphilic compounds, or water-soluble, polymer-bound catalysts. As in the field of aqueous-phase catalysis, the first textbooks on these developments have been published, not to mention Joó’s book on *Aqueous Organometallic Catalysis* which followed three years after our own publication and which put the spotlight on Joó’s special merits as one of the pioneers in aqueous biphasic catalysis. Up to now, most of the alternatives mentioned are only in a state of intensive development (except for one industrial realization: that of Swan/Chematur for hydrogenations in scCO₂ [2]) but other pilot plant adaptations and even technical operations may be expected in the near future.

This second edition is based mainly on the state-of-the-art as described in the published literature up to the year 2003. To make things easier and to avoid errors, parts of the second edition are revised and updated, rather than rewritten. Thus, in some cases the order of the references is unchanged and new references are added without renumbering the existing ones (or substitute existing refs. by new items). The numbering of structures, equations, etc., was changed if necessary.

Once more we have to express our thanks not only to the authors and coauthors of the volume but also to the team at Wiley-VCH at Weinheim, especially Mrs. Claudia Grössl, for the production and their endless patience, and Dr. Elke Maase, the publishing editor. As with all our books, Mrs. Diana Boatman from Redhill, Surrey (UK), served as freelance copy-editor and was an invaluable help during the difficult process of completion. The Munich research group, especially PD Dr. F. E. Kühn, is acknowledged for scientific and technical assistance.

Hofheim and München
January 2004

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Wolfgang A. Herrmann

References

- [1] *Nachr. Chem.* **2003**, 51(5), 516.
- [2] B. Cornils, W. A. Herrmann, R. Schlögl, C.-H. Wong, *Catalysis from A to Z*, 2nd Edition, Wiley-VCH, Weinheim, **2003**, p. 746.

Preface to the First Edition

This book describes homogeneously catalyzed reactions under two major boundary conditions: the catalysts employed are *organometallic* complexes that are used in the *aqueous phase*. In this respect the book is restricted to one area of homogeneous catalysis and therefore – though substantially expanded and more detailed – to one special area of our previous book, *Applied Homogeneous Catalysis with Organometallic Complexes* (VCH, Weinheim, Germany, 1996).

The subject of the book is the use of water-soluble organometallic catalysts for chemical reactions. These catalysts are so far the sole successful means of implementing the idea of *heterogenization* of homogeneous catalysts by *immobilizing* them with the aid of liquid supports. They thus solve the cardinal problem of homogeneous catalysis, which lies in the expensive separation of catalyst as well as product that is inherent in the system: the catalyst used in the homogeneous phase is separated by simply decanting the aqueous catalyst phase from the organic phase of the substrates and reaction products. Since all attempts to heterogenize homogeneous catalysts by immobilizing them on solid supports (“anchoring”) have to varying degrees been unsuccessful, only the use of homogeneous catalysts in aqueous solution and thus on liquid supports (“biphase operation”) leads to a neat, inexpensive solution to the problem that conserves resources and is therefore environmentally friendly.

This book is restricted essentially to *aqueous-phase* catalyses and thus to one area of the more comprehensively defined two-phase catalyses. This restriction to the most recent and successful development of homogeneous catalysis takes account of the rapid technical advances in the process concept first described by Manassen et al. in 1973, which was followed in rapid succession in the 1970s by hesitant basic work and in 1984 by the first commercial implementation. This unusual sequence – industrial implementation in a 100 000 tonnes per year oxo plant for the hydroformylation of propylene **before** years of time-consuming basic research to determine mechanistic, kinetic and other data – demonstrates clearly the great leap forward that this process development represented in the field of homogeneous catalysis and in solving the central problem mentioned earlier. Since then

other processes employing homogeneous catalysis have been converted to an aqueous two-phase procedure.

The development work intensified worldwide in various research groups in the years following the first commercial implementation at Ruhrchemie AG in Oberhausen. The obvious course of action was to let colleagues and specialists themselves report on their developments. This led to the formation of the international circle of contributors from the USA, France, the United Kingdom, China, Italy, Japan, India, Hungary and Germany which gives first-hand reports on its work.

One focus of the book is the hydroformylation process, the process involved in the first commercial implementation of aqueous-phase catalysis with its detailed descriptions of fundamental laws, special process features, and the present state of the art. Further focal points of the book are basic research on the complex catalysts (central atoms, ligands) and on the influence of the reaction conditions, solvents, and co-solvents, and a survey of other aqueous two-phase concepts and of proposed applications, with experimental examples and details. Environmental aspects are also considered.

We are sure that the outline chosen and the wide range of contributions from the authors give a multifaced and informative picture of the present state of developments in the field of aqueous two-phase catalysis, which presents not only the principles and accounts of the latest applications but also many aspects of spin-offs and alternative processes.

This description of ideas and process developments appears to us to be highly important for an appreciation of the potential of aqueous biphasic catalysis. The familiar assessment of the most important aspects of heterogeneous and homogeneous catalysis demonstrates that only in a solution of the problem of continuous separation of catalyst and product, such as becomes possible with the processes involving aqueous immobilized catalysts, is the key to further progress found. Only *homogeneous* catalysts that can be handled without problems will give us scientists and developers confidence that the clear and sure mechanistic understanding of their mode of action and the possibility of easy variability of steric and/or electronic properties can be transferred to other immobilized, and thus easy-to-handle, catalysts. More optimistically, it is hoped that this will apply especially to those heterogenized catalysts that basically are derived from tailor-made homogeneous catalysts.

The sharp line of demarcation between homogeneous and heterogeneous catalysis would thus be blurred and the possibility opened up of combining in one species the advantages of homogeneous catalysts and none of the disadvantages of heterogeneous catalysts: heterogenized homogeneous catalysts would lead to equally advantageous results as homogenized heterogeneous catalysts – the long-awaited dream of catalysis research would be fulfilled!

We thank the team at WILEY-VCH, especially Mrs. Diana Boatman, Dr. Anette Eckerle, and Mrs. Claudia Grössl for their cooperation during preparation of this book and for helpful technical assistance.

Dipl.-Chem. Kolja Wieczorek is acknowledged for preparing all formulas, figures, and schemes; Dipl.-Chem. Thomas Weskamp for the total index.

Frankfurt-Höchst and München
Spring, 1998

Boy Cornils
Wolfgang A. Herrmann

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