Metal-Catalyzed Reactions in Water

Until recently, and in contrast to organic chemistry, reactions in water as solvent were important only for ionic reactions in inorganic chemistry—most likely are hydrogenations or transfer hydrogenations over heterogeneous catalysts as examples of large-scale and economically important transformations. This changed as a consequence of the development of water-soluble ligands (or ligands soluble in other media) and their application in novel homogeneously catalyzed biphasic processes such as SHOP (Shell) or the Ruhrchemie/Rhône-Poulenc process. In parallel, a series of reviews (e.g., that by Li and Chan) appeared, promoting water as a "green" solvent, thus claiming the fashionable advantages of "green synthesis" or "green catalysis". The various reports about special developments in the use of water deal with reactions "on water", or with supercritical water, or with water as catalyst, or other related topics.

With regard to the past background, this book is in certain ways an extended and updated version of the book *Aqueous-Phase Organometallic Catalysis*, issued in 2004 by the same publisher. While that book concentrated on the announcement and introduction of the then novel methodology of aqueous catalysis by transition metals according to the applications known at that time—with the focus on the most important process, aqueous biphasic hydroformylation—this book edited by Dixneuf and Cadierno describes the many widely different basic metal-catalyzed reactions in water that are known at present.

Accordingly, the book has chapters covering the following chemical transformations: Metal-Catalyzed Cross-Couplings of Aryl Halides to Form C−C Bonds (Shaughnessy); Metal-Catalyzed C−H Bond Activation and C−C Bond Formation (Li and Dixneuf); Catalytic Nucleophilic Additions of Alkynes (Yao and Li); Water-Soluble Hydroformylation Catalysis (Nguyen, Urrutigoity, and Kalck); Green Catalytic Oxidations (Sheldon); Hydrogenation and Transfer Hydrogenation (Wu and Xiao); Catalytic Rearrangements and Allylation Reactions (Cadierno, García-Alvarez, and García-Garrido); Alkene Metathesis (Grela, Gulajski, and Skowerski); and Nanocatalysis in Water (Baig and Varma. All chapters present an up-to-date description of the corresponding reactions and of the exciting spectrum of the homogeneous catalysis involved, and discuss the advantages of the method with regard to yield, selectivity, and the possibility of separating the reaction products from the catalyst immediately after the reaction.

This review will not describe the book's content in detail. Instead I draw attention to some particular aspects. Firstly, large-scale applications are only touched on, even where they are known (for example, for the Suzuki coupling or for some oxidations). The exception is the interesting chapter on hydroformylation by Kalck and co-authors. It doesn't matter that the relevant industrial process that has been known for 30 years is incorrectly described in another chapter as the "Rhône-Poulenc process" (p. 3): this is only half of the truth and just demonstrates the incompleteness of the writer's knowledge. The inclusion of nanocatalysts in the book by Dixneuf and Cadierno is debatable. The authors Nasir Baig and Rajender Varma justify this decision by their opinion that nanocatalysts are a kind of heterogenized homogeneous catalysts, which fits into the book's structure in view of their size and the availability of the active centers. Obviously this is not wrong, but for consistency it would also fit for other variants of the heterogenization of homogeneous catalysts, e.g., for clusters. In general, this is a matter of definition: other books draw the line differently. With the above definition, many heterogeneously catalyzed reactions in water ought to be subsumed under the book's title.

Another conspicuous feature of the book—the incessant reference to the adjective "green" for operations in water—seems rather labored and artificial. To improve yield and selectivity was always the aim of each generation of chemists, even those who developed multistep syntheses that take time and only achieve marginal improvements of a few percent. A certain arrogance and disregard for chemists of the past is thus the basis of today's overestimation of "green" processes, which in former times were treated by the same principles and methodologies, but under other honest names. Dixneuf and Cadierno prove with their book that metal-catalyzed reactions in water are one of the most successful principles of a sustainable chemistry, which does not need the trivialities of the "green chemistry" of Anastas and his epigones.

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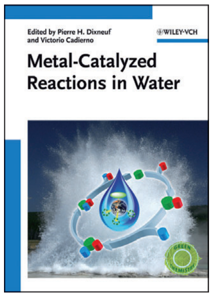

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