Environmentally Benign Micellar Metal Catalysis in Water

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Water as an alternative reaction medium is witnessing a sort of renaissance [1] due to its many advantages compared to other media, in particular low cost, non flammability and environmental compatibility demonstrated by its zero E factor value [2]. However, performing catalysis in water medium entails some challenging drawbacks, like the generally low solubility of organic substrates as well as most metal complex catalysts, together with the possible sensitivity of the latter to the acidity and nucleophilicity of this medium. To circumvent such problems, possible solutions are the use of soft Lewis acid complexes, the synthesis of intrinsically water-soluble catalysts or the employment of micellar supramolecular systems whose role is to cope with reagents and catalysts. Last but not least, the expansion of catalysis in water represents a viable way to try to mimic and better understand enzymatic catalysis, which is the ultimate goal of catalysis in terms of selectivity.

Micellar catalysis is therefore the simplest and at the same time one of the most promising strategies to overcome solubilization problems. Basically micelles behave like cells, isolating species from the bulk solvent, playing several roles at a time [3]: firstly they improve solubilization of organic reagents in water, secondly they favor compartmentalization of reagents thus improving local concentration and reactivity, thirdly in some cases they impart unique chemo- regio- and stereoselectivities [4]. Micellar systems can act as nanoreactors for several organic reactions by virtue of their concentration effect and particular pH values observed on the surface of the micelle that is markedly different from that of the bulk solvent. Micellar catalysis offers the great advantage of using catalysts already developed for use in organic media, while allowing a deep investigation of subtle electronic and steric effects when using the numerous commercially available ligands. Fortunately, this can be rather quickly performed considering that no synthetic steps are required to modify catalysts already developed for use in organic media with hydrophilic functional groups. Besides these properties, compared to common organic media water proved to enhance productivity as well as selectivity at regio-, diastereo- and enantioselective level in several catalytic reactions.

Herein recent progress will be presented in the field of micellar metal catalysis applied to different class of C-C bond forming reactions like hydroformylation, Diels-Alder cycloaddition, C-heteroatom bond forming hydration reaction as well as oxidation and reduction with particular emphasis on product selectivity (chemo, regio and stereo) as well as substrate selectivity which is an aspect seldom investigated in homogeneous catalysis but that makes micelles more similar to enzymes. Hints will be provided on beneficial effects of the employment of aqueous and micellar conditions for the synthesis of bisphosphonates as potential drugs for the treatment of osteoporosis.

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