

Editorial

Homogeneous Catalysis and Mechanisms in Water and Biphasic Media

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After its discovery in the early 1980s and successful application on an industrial scale (Ruhchemie/Rhone-Poulenc process) [1–4], water phase and biphasic catalysis have been the subject of fundamental studies in a relatively limited number of research laboratories around the world [5], almost at a curiosity level. During the last 15 years, however, this topic has witnessed a true renaissance, mainly due to the increased attention of industry and academia to more environmentally friendly processes. Water is the green solvent par excellence, and a great deal of research has been carried out to convey the properties of known transition metal catalysts to their water-soluble analogs, maintaining high activity and selectivity [6]. The keys to success have been, among others, the discovery of synthetic pathways to novel molecular metal-based catalysts [7], new mechanistic insights into the role of water as a non-innocent solvent [8], the identification of reaction pathways through experimental and theoretical methods, the application of novel concepts for phase transfer agents in biphasic catalysis and advances in engineering and related techniques applied to various reactions carried out in aqueous media.

Some of the approaches currently used to tackle these problems are described in the present Special Issue, that collects three review articles and six original research papers. The main cutting-edge approaches developed in the field of aqueous biphasic catalysis using cyclodextrins as a supramolecular tool [9] are discussed and compared in the first review [10]. In the second review [11], the topic of the metal-catalyzed addition of carboxylic acids to alkynes [12,13] as a tool for the synthesis of carboxylate-functionalized olefinic compounds is reviewed, with an emphasis on processes run in water. The synthesis of β -oxo esters by the catalytic addition of carboxylic acids to terminal propargylic alcohols in water is also discussed. The third review article [14] describes the use of an advanced analytical method, high-resolution ultrasonic spectroscopy [15], for the non-destructive real-time monitoring of chemical reactions in complex systems such as emulsions, suspensions and gels. This method has the advantage of being applicable to the monitoring of reactions in continuous media and in micro/nano bioreactors (e.g., nanodroplets of microemulsions), enabling measurements of concentrations of substrates and products over the whole course of reaction, evaluation of kinetic mechanisms, and the measurement of kinetic and equilibrium constants and reaction Gibbs energy.

Two research articles [16,17] describe the use of water-soluble Ru(II) complexes [18] for reactions such as C=C and C=N bond transfer hydrogenation [19], and how to minimize the production of CO during HCOOH dehydrogenation reactions in water media, respectively [20]. Other articles describe applications in speciality reactions and materials, for example the use of chitosan aerogel-catalyzed asymmetric aldol reaction of ketones with isatins in the presence of water [21], the use of bismuth oxyhalide as an activator of peroxide for water purification to degrade carbamazepines [22], the study of catalytic activities of nucleic acid enzymes in dilute aqueous solutions [23], the use of iminodiacetic acid-modified Nieuwland catalysts [24] for acetylene dimerization, and the selective conversion of acetylene to monovinylacetylene (MVA) [25].

In summary, this Special Issue provides an uncommon and multifocal point of view on different fields of application where water can be used as a green solvent and/or has implications in the reaction mechanism, the engineering of a process or an analytical technique. These readings can be of interest and help to colleagues working in related research areas, and stimulate the curiosity of others who may think of water processes as viable—albeit sometimes more difficult—alternatives to traditional approaches.

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