

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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References

1. Cornils, B.; Kuntz, E.G. Introducing TPPTS and related ligands for industrial biphasic processes. *J. Organomet. Chem.* **1987**, *570*, 177–186. [[CrossRef](#)]
2. Kuntz, E. Rhone-Poulenc Recherche. FR Patent 2.314.910, 1975.
3. Kalck, P.; Monteil, F. Use of Water-Soluble Ligands in Homogeneous Catalysis. *Adv. Organomet. Chem.* **1992**, *34*, 219–284.
4. Cornils, B.; Hibbel, J.; Konkol, W.; Lieder, B.; Much, J.; Schmidt, V.; Wiebus, E. (Ruhchemie AG). EP 0.103.810, 1982.
5. Joó, F. *Aqueous Organometallic Catalysis*, 1st ed.; Springer: Dordrecht, The Netherlands, 2001.
6. Cornils, B.; Herrmann, W.A. (Eds.) *Aqueous-Phase Organometallic Catalysis: Concepts and Applications*, 2nd ed.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2004.
7. Shaughnessy, K.H. Hydrophilic ligands and their application in aqueous-phase metal-catalyzed reactions. *Chem. Rev.* **2009**, *109*, 643–710. [[CrossRef](#)] [[PubMed](#)]
8. Dixneuf, P.H.; Cadierno, V. (Eds.) *Metal-Catalyzed Reactions in Water*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2013.
9. Machut, C.; Patigeon, J.; Tilloy, S.; Bricout, H.; Hapiot, F.; Monflier, E. Self-assembled supramolecular bidentate ligands for aqueous organometallic catalysis. *Angew. Chem. Int. Ed.* **2007**, *46*, 3040–3042. [[CrossRef](#)] [[PubMed](#)]
10. Hapiot, F.; Monflier, E. Unconventional Approaches Involving Cyclodextrin-Based, Self-Assembly-Driven Processes for the Conversion of Organic Substrates in Aqueous Biphasic Catalysis. *Catalysts* **2017**, *7*, 173. [[CrossRef](#)]
11. Francos, J.; Cadierno, V. Metal-Catalyzed Intra- and Intermolecular Addition of Carboxylic Acids to Alkynes in Aqueous Media: A Review. *Catalysts* **2017**, *7*, 328. [[CrossRef](#)]
12. Alonso, F.; Beletskaya, I.P.; Yus, M. Transition-metal-catalyzed addition of heteroatom-hydrogen bonds to alkynes. *Chem. Rev.* **2004**, *104*, 3079–3159. [[CrossRef](#)] [[PubMed](#)]
13. Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. Catalytic Markovnikov and anti-Markovnikov functionalization of alkenes and alkynes: Recent developments and trends. *Angew. Chem. Int. Ed.* **2004**, *43*, 3368–3398. [[CrossRef](#)] [[PubMed](#)]
14. Buckin, V.; Altas, M.C. Ultrasonic Monitoring of Biocatalysis in Solutions and Complex Dispersions. *Catalysts* **2017**, *7*, 336. [[CrossRef](#)]
15. Buckin, V. Application of High-Resolution Ultrasonic Spectroscopy for analysis of complex formulations. Compressibility of solutes and solute particles in liquid mixtures. *IOP Conf. Ser. Mater. Sci. Eng.* **2012**, *42*, 1–18. [[CrossRef](#)]
16. Guerriero, A.; Peruzzini, M.; Gonsalvi, L. Ruthenium(II)-Arene Complexes of the Water-Soluble Ligand CAP as Catalysts for Homogeneous Transfer Hydrogenations in Aqueous Phase. *Catalysts* **2018**, *8*, 88. [[CrossRef](#)]
17. Henricks, V.; Yuranov, I.; Autissier, N.; Laurenczy, G. Dehydrogenation of Formic Acid over a Homogeneous Ru-TPPTS Catalyst: Unwanted CO Production and Its Successful Removal by PROX. *Catalysts* **2017**, *7*, 348. [[CrossRef](#)]
18. Guerriero, A.; Peruzzini, M.; Gonsalvi, L. Coordination chemistry of 1,3,5-triaza-7-phosphaadamantane (PTA) and derivatives. Part III. Variations on a theme: Novel architectures, materials and applications. *Coord. Chem. Rev.* **2018**, *355*, 328–361. [[CrossRef](#)]

19. Wang, D.; Astruc, D. The Golden Age of Transfer Hydrogenation. *Chem. Rev.* **2015**, *115*, 6621–6686. [[CrossRef](#)] [[PubMed](#)]
20. Dalebrook, A.F.; Gan, W.; Grasemann, M.; Moret, S.; Laurency, G. Hydrogen Storage: Beyond Conventional Methods. *Chem. Commun.* **2013**, *49*, 8735–8751. [[CrossRef](#)] [[PubMed](#)]
21. Dong, H.; Liu, J.; Ma, L.; Ouyang, L. Chitosan Aerogel Catalyzed Asymmetric Aldol Reaction in Water: Highly Enantioselective Construction of 3-Substituted-3-hydroxy-2-oxindoles. *Catalysts* **2016**, *6*, 186. [[CrossRef](#)]
22. Zhang, T.; Chu, S.; Li, J.; Wang, L.; Chen, R.; Shao, Y.; Liu, X.; Ye, M. Efficient Degradation of Aqueous Carbamazepine by Bismuth Oxybromide-Activated Peroxide Oxidation. *Catalysts* **2017**, *7*, 315. [[CrossRef](#)]
23. Nakano, S.-I.; Horita, M.; Kobayashi, M.; Sugimoto, N. Catalytic Activities of Ribozymes and DNAzymes in Water and Mixed Aqueous Media. *Catalysts* **2017**, *7*, 355. [[CrossRef](#)]
24. Nishiwaki, K.; Kobayashi, M.; Takeuchi, T.; Matuoto, K.; Osakada, K. Nieuwland catalysts: Investigation of structure in the solid state and in solution and performance in the dimerization of acetylene. *J. Mol. Catal. A Chem.* **2001**, *175*, 73–81. [[CrossRef](#)]
25. You, Y.; Luo, J.; Xie, J.; Dai, B. Effect of Iminodiacetic Acid-Modified Nieuwland Catalyst on the Acetylene Dimerization Reaction. *Catalysts* **2017**, *7*, 394. [[CrossRef](#)]



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