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Preface

Special issue on advances in catalysis in aqueous media

The general perception in the early seventies was that catalytic reactions in aqueous media employing water-soluble organometallic complexes of transition metals to produce commodity chemicals could not take place despite (1) the discovery in 1827 of the first water-soluble transition metal complex, Zeise's salt, $K[PtCl_3(\eta-C_2H_4)] \cdot H_2O$ [1] and (2) the industrial application in 1959 of water-soluble cobalt sulfonated phthalocyanine catalytic complexes in the UOP Extractive Merox™ thiols oxidation process for upgrading oil refining products [2]. Notwithstanding these early contributions, in 1974 two groups independently showed that water-soluble organometallic complexes of transition metals can catalyze different reactions in this green aqueous reaction medium. The group of F. Joó and M.T. Beck carried out the aqueous-phase hydrogenation of pyruvic acid to lactic acid catalyzed by water-soluble Ru/TPPMS complexes [TPPMS, sodium salt of mono-sulfonated triphenylphosphine, $PPh_2(C_6H_4-m-SO_3Na)$], while E.G. Kuntz at Rhône-Poulenc achieved the *proof of principle* showing that the hydroformylation of propene to butyraldehydes catalyzed by water-soluble Rh/TPPTS complexes [TPPTS, sodium salt of trisulfonated triphenylphosphine, $P(C_6H_4-m-SO_3Na)_3$] can be done on a laboratory scale in aqueous/organic biphasic systems. The industrial scale aqueous/organic two-phase propene hydroformylation process using a water-soluble Rh/TPPTS catalyst was developed after successful pilot plant scale tests in 1984 by Cornils et al. at Ruhrchemie which is well known as the Ruhrchemie/Rhône-Poulenc (RCH/RP) process [3,4]. This first major success was followed by additional industrial biphasic processes that, today, have led to an exponential increase of new applications of several water-soluble transition metal complexes modified by numerous ligands, such as sulfonated and carboxylated phosphines, phosphines containing hydroxy and ether functionalities, phosphines with amino, ammonium, phosphonium, phosphonate and phosphate moieties, sulfonated amines, phthalocyanines, porphyrins, phospholes and thioethers or sulfone-based phosphines, and nitrogen-containing ligands. Also included are tenside ligands that catalyze diverse reactions, such as hydroformylations of lower, midrange, higher and functionalized olefins, hydrocarboxylations, carbonylations, alternating copolymerizations of olefins with CO to polyketones, hydrogenations, hydrogenolyses, oxidations, epoxidations, dehydrations, isomerizations, epimerizations, ring-openings, alkylations, and telomerizations, etc. to produce commodity chemicals in aqueous/organic two-phase systems [3].

The pharmaceuticals and fine chemicals companies discovered catalysis in general much later and were still focused on classical stoichiometric technologies in organic synthesis up to the end of the last century producing immense amounts of waste (Table 1) [5] mainly owing to:

- the application of stoichiometric quantities of organic and inorganic reagents [5].
- reliance on organic solvents which constitutes 80–90 % of the total mass of organic compounds used in the production of Active Pharmaceutical Ingredients (APIs), and is responsible for 75–80 % of the organic waste [5,6].

When the pharmaceutical and fine chemical companies finally discovered aqueous-phase (asymmetric) catalysis they began to appreciate the opportunities, as new “tools in the toolbox”. Thus, water as a reaction medium in organic synthesis is rapidly undergoing a shift “*from our worst enemy to our best friend*” [7,8], especially when viewed in tandem with aqueous biocatalysis [9,10]. Moreover, according to the Solvent Selection Guides (SSGs) of the European research and innovation consortium CHEM21 for greening processes in pharmaceutical industries water is the first of the recommended solvents in a list of 51 solvents ranked in four groups: recommended, problematic, hazardous and highly hazardous [6].

From the standpoint of chemocatalysis in water, use of micellar catalysis implies that a surfactant, containing a hydrophobic and hydrophilic component, forms micelles that can solubilize water-insoluble educts and catalysts within the lipophilic inner cores where the reaction takes place. It is the micelles that are water-soluble; hence, both starting materials and reagents (organometallic or otherwise) that are water-insoluble are suitable candidates for this technology.

Catalysis in aqueous/organic two-phase systems by water-soluble transition metal complexes presents a method of heterogenization of homogeneous catalysis because the highly polar aqueous solvent acts as a fluid, liquid support for the catalyst owing to its immiscibility with most organic starting materials and products and offers a large number of advantages:

- high catalytic activities and selectivities under mild reaction conditions by fine tuning of the coordination sphere of the metal
- facile and quantitative recovery of the catalyst, which resides and operates in water, from organic reaction products by an easy phase separation
- simple catalyst recycling
- due to the easy catalyst recovery and recycling many steps in classical industrial processes are rendered superfluous and process engineering is immensely simplified which leads to energy savings and lower plant emissions
- novel types of reactivities have been observed in water in numerous catalytic reactions

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Table 1

E-factors in various sectors of the chemical industry.

Industry sector	Product capacity (tpa)	E-factor (kgs waste/kg product)
Oil refining products	10 ⁶ –10 ⁸	< 0.1
Bulk chemicals	10 ⁴ –10 ⁶	< 1–5
Fine chemicals	10 ² –10 ⁴	5–50
Pharmaceuticals	10–10 ³	25 to > 100

the inherent large heat capacity of water renders it an ideal solvent to carry out exothermic reactions such as hydroformylations and hydrogenations safer and more selective, especially in industrial large-scale processes that are exothermic

water is a non-toxic, non-inflammable *i.e.* safe, odourless and colorless for easy detection of impurities, ubiquitous, abundantly available, low-cost and a green-sustainable solvent.

Water-dispersed nanoparticle (NP) catalysts are highly versatile and efficient systems used in various chemical processes. They have been applied in environmental remediation, such as breaking down organic pollutants in wastewater treatment and to facilitate eco-friendly chemical synthesis by reducing the use of harmful organic solvents. Biomass conversion to generate biofuels and chemicals is particularly attractive, but NPs immobilized in water have also been used to enhance the production of high-value chemicals. They are particularly attractive as they can be easily adapted for industrial-scale reactions without compromising efficiency and stability issues may be overcome by the use of water-soluble nanoparticle coatings. Compared to NPs immobilized on solid supports, those dispersed in water offer larger active surface area, potentially enhancing catalytic activity and efficiency. These catalysts align with sustainable development goals by reducing energy consumption, enhancing process efficiency, and minimizing environmental impact, but are limited to relatively few metals that form stable metal(0) nanoparticles in water [11,12].

Furthermore, the highly polar nature of water makes it an ideal solvent to perform catalytic conversions of renewable polar biomass and its downstream products, platform chemicals leading to biofuels, and value-added chemicals and materials. From the perspective of a biorefinery, water has several beneficial effects, such as: it accelerates enormously the rates of different types of reactions *e.g.*, hydrogenations and aldol condensations of platform chemicals; it participates in valorization of biomass as a byproduct or as a reagent and acts as a catalyst in hydrothermal liquefaction of biomass under sub- and supercritical conditions [13].

The field of catalysis in aqueous media is consistent with seven of the twelve *Principles of Green Chemistry*: (1) low E-Factors; *i.e.*, high atom economies in synthetic chemistry; (2) less hazardous chemical syntheses; (3) designing safer chemicals; (4) use of innocuous aqueous solvent; (5) effective conversions of renewable polar biomass and its downstream platform chemicals, (6) use of catalytic reagents; and (7) inherently safer chemistry especially in exothermic industrial scale reactions due to the high heat capacity of water. Thus, this field plays an important role in achieving the goal of *sustainability*.

Two of us edited as Guest Editors in 2015 a special issue for *Catalysis Today* in this field entitled “Recent Advances in Catalysis in Green Aqueous Media” with 22 contributions [1]. Important advances continue to appear, especially in emerging and highly innovative subfields in catalysis in water; hence, a special issue on catalysis in aqueous media that addresses such achievements is very timely.

This special issue on *Advances in Catalysis in Aqueous Media* showcases significant advances in chemo- and bio-catalysis in water and consists of 18 papers highlighting recent results and future trends. It exhibits the high potential of catalysis in green and sustainable aqueous environment in relatively new and emerging fields, such as:

- conversions of renewable biomass downstream products and platform chemicals employing water-soluble transition metal catalyst complexes, biocatalysts and heterogeneous catalysts to produce advanced biofuels, value-added bio-based chemicals and intermediates such as furfuryl alcohol and 2,5-furandicarboxylic (2,5-FDCA). The latter has been used, *e.g.*, as a key compound in the YXY® Technology of Avantium to manufacture at a large scale the polyester poly(ethylene 2,5-furandicarboxylate) (PEF). This 100 % bio-based material is known as a novel bio-based plastic with the brand name Releaf® [14,15] possessing superior performance properties compared to the properties of the conventional petroleum-based PET polymer
- conversion of greenhouse gas CO₂ as a feedstock to produce fuels, bulk and value-added chemicals in the presence of water
- applications of highly interesting biocatalysts, such as acyl-transferases (see paper by Bornscheuer *et al.*), that catalyze (trans) esterifications and (trans) amidations in aqueous media
- use of aqueous micellar catalysis to produce APIs, where the involvement of organic solvents and thus, waste generated is minimized, while the loadings of metal catalysts are reduced, thereby lowering costs and extending the accessibility of precious metals, in particular, in the future
- Photocatalytic and electrocatalytic acceleration of organic reactions in water
- use of water-dispersible transition metal(0) catalytic NPs stabilized in the aqueous fluid support
- application of sustainable, low-cost and abundant non-precious metals such as Cu, Ni, Fe, *etc.* as catalysts in aqueous media.

The first paper is by Papadogianakis *et al.* from the National and Kapodistrian University of Athens, Greece, [16] which describes the application of water-soluble platinum catalysts in the aqueous-phase hydrogenation of biorenewable lignocellulose-derived platform chemical furfural which is, after bioethanol, the 2nd highest demanded biomass downstream product. In this investigation, twenty-one different water-soluble phosphines and nitrogen-containing ligands were used for a fine tuning of the coordination sphere around the transition metal in the catalytically active platinum intermediate species. The authors showed that the hydrogenation of multifunctional starting material furfural proceeds with high catalytic activities (TOF > 20,000 h⁻¹) and essentially quantitative selectivities toward the desired value-added multifunctional product furfuryl alcohol (> 99 mol%) with careful optimization of various operating reaction parameters in the presence of platinum modified with the industrially applied benchmark ligand TPPTS under mild and neutral conditions in water. This is the highest catalytic activity with high selectivity towards the desired product furfuryl alcohol exhibited so far by water-soluble transition metal catalysts in the hydrogenation of renewable furfural, run in aqueous media.

In a study conducted by Ordóñez *et al.* from the University of Oviedo, Spain [17] focused on Au/TiO₂-catalyzed synthesis of 2,5-furandicarboxylic (2,5-FDCA) acid from an aqueous solution of 5-hydroxymethylfurfural (HMF) the effects of temperature, O₂ pressure, catalytic loading, and NaOH ratio are probed. Careful optimization of these parameters led to high yields of the target compound with minimal humins formation, enhancing sustainability compared to traditional methods. Additionally, a one-pot process combining fructose dehydration and HMF oxidation was developed.

Gomes *et al.* from the São Carlos Federal University, Brazil [18] carried out the gas-phase hydrogenation of greenhouse gas CO₂ using the sustainable, low-cost and abundant non-precious metal copper as catalyst to produce the value-added chemical ethanol. In this study it was found that the presence of water as steam plays a major role in this reaction, acting as both a source of molecular hydrogen for the hydrogenation reaction of CO₂, and by generating and stabilizing oxidized copper species on the surface of the catalyst. This results in an 80-fold increase in the productivity of ethanol. In sharp contrast, when steam

is absent, the copper oxides were reduced in the conventional copper-catalyzed hydrogenation reaction of CO₂ with externally added molecular hydrogen as a reagent, which gives rise to a dramatic drop in ethanol productivity.

An excellent review by Bornscheuer et al. from the University of Greifswald, Germany [19] deals with the discovery, mechanism of action and engineering of acyltransferases, a fascinating group of enzymes that catalyze the formation of esters and amides in water. These enzymes, also known as promiscuous hydrolases, form attractive alternatives to the classical use of, e.g., lipases and amidases, in organic solvents.

The paper by Parmentier et al. from the Process Research Groups at Novartis in both Basel, Switzerland, and Jiangsu, China [20] is illustrative of how aqueous micellar catalysis (using TPGS-750-M, 2 wt% in water) can be used to advantage at the kilo scale *en route* to an API. Thus, in a 1-pot process mediated by the sustainable, low-cost and abundant non-precious metal copper added in catalytic amounts as Cu(I), primary amides can initially be formed from net hydration of aromatic nitriles, followed by direct *N*-arylation to ultimately afford the targeted secondary amines. Products can then be isolated by simple filtration and further purified by recrystallization.

Kokotos et al. from the National and Kapodistrian University of Athens, Greece [21] developed a green photochemical protocol for the Michael addition of indoles to β -nitroolefins in aqueous media without requiring external addition of a photocatalyst to achieve good to high yields of the desired products without external heating in reasonable reaction times. Furthermore, the authors note that this approach has a broad scope regarding the nature of the starting materials, as more than twenty 3-substituted indoles are formed. Proposed are two routes outlining possible mechanisms, which could proceed either in tandem or distinct from each other to activate the indole compound.

Roucoux and Denicourt-Nowicki from the University of Rennes, France [22] report on the use of aqueous suspensions containing ruthenium and palladium nanoparticles as catalysts to transform renewable terpenoid compounds selectively into value-added perfume ingredients including cis-pinane, citronellal, and Florsantol®. The authors showed that these scalable and reusable nanocatalysts have significant potential for sustainable industrial applications in the renewable production of perfume ingredients.

Yadav and Shetty from the Institute of Chemical Technology, India [23] examined the industrially attractive hydrogenation of renewable biomass-derived xylose to xylitol using nickel-alumina catalysts supported on hexagonal mesoporous silica. The goal was to achieve high conversions of xylose (98 mol%) with high selectivities (97 mol%) towards xylitol in a solvent mixture consisting of water/isopropanol (1/1), as well as in completely aqueous media. This catalytic system features further advantages, including: it entails the sustainable, low-cost and abundant non-precious metals Ni and Al, it contains a substantial lower metal loading in comparison to conventional Raney nickel catalysts, and it does not suffer from problems associated with metal leaching.

The oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (2,5-FDCA) using O₂ and Au/ZrO₂ catalysts is problematic in terms of carbon balance issues. In a computational study, Michel et al. from the CNRS and ENS de Lyon, France [24] modeled a Au(111) surface to reveal key intermediates and degradation pathways, leading to a two-step experimental approach that achieves over 90 % 2,5-FDCA yield while maintaining a carbon balance above 97 %.

Bhanage et al. from the Institute of Chemical Technology, India [25] developed an efficient hydroformylation reaction of the renewable biomass-derived α -olefin eugenol using water-soluble rhodium catalysts modified with PTABS, an *N*-sulfoalkylated triaza-phosphaadamantane strongly π -accepting phosphine ligand. The cationic surfactant CTAB was required to create micelles as a means of overcoming mass transfer limitations between the apolar organic phase of heavier olefinic substrate eugenol and the highly polar aqueous phase containing the catalyst, in order to accelerate the reaction in this two-phase system. The

Rh/PTABS/CTAB combination, with the apolar promotor ligand Xantphos, proved to be a superior catalyst in the hydroformylation of eugenol to afford at quantitative conversions high yields and regioselectivities to aldehydes; up to 97 mol%, with *n*/*iso* ratios of 93/7, respectively.

Monflier et al. from the Université d'Artois, France [26] present in their excellent review the field of cyclodextrin-assisted hydroformylation and hydroaminomethylation reactions in aqueous/organic two-phase systems, covering the period from the early nineties to the present. Native and chemically modified cyclodextrins and more sophisticated cyclodextrin-based systems are attractive materials to break the mass transfer barrier between the apolar organic phase of the heavier starting materials, like higher olefins, and the highly polar aqueous phase containing the water-soluble transition metal catalytic complex to boost the reaction rates in aqueous/organic two-phase systems. The authors describe different stages that have led to the understanding of the behavior of cyclodextrins in these aqueous/organic biphasic catalytic reactions, following optimization of cyclodextrin/water-soluble ligand combinations, as well as the perspectives for development of an industrial scale biphasic viable process.

The article by Raspolli-Galletti et al. from the University of Pisa, Italy [27] describes the use of a combination of chemo- and biocatalysis for upgrading defatted wheat bran, an important food chain waste. This involves fermentation of sugars, formed by chemical or enzymatic hydrolysis of the polysaccharide fraction, to produce high-value fine chemicals, such as carotenoids and lipids.

Low loadings of the heterogeneous Pd catalyst, Pd/C, present in the aqueous micellar media derived from cationic surfactants DTAB or CTAB, are sufficient to effect Suzuki-Miyaura reactions in high yields and, notably, in the absence of a phosphine ligand. Hence, as shown by Beverina et al. from the University of Milano-Bicocca, Italy [28], single cross couplings, and, in particular, double C-C bond-forming reactions generate biaryls containing both aryl and heteroaryl components as highly conjugated "building blocks" that are further amenable to applications to the optoelectronics industry.

In work from the Scarso group in Università Ca' Foscari di Venezia, Italy [29], chiral, nonracemic surfactants were prepared and then used to increase the observed *ee*'s relative to those obtained by conventional means in oxidations of sulfides to sulfoxides. Adding rigidity to the amphiphile enhanced close contact with pro-chiral sulfides, and created an ion-pairing situation, where the surfactant contains anionic head groups derived from a substituted BINOL and the catalyst is derived from a cationic Pt(II) in the presence H₂O₂. The results suggest that improvements will be forthcoming using more rigidly designed surfactants.

Seidensticker et al. from the TU Dortmund University, Germany [30] disclose an interesting concept for the hydroformylation of renewable biomass-derived oleochemicals, such as the heavy internal olefin methyl oleate and the heavy α -olefin methyl 10-undecenoate catalyzed by water-soluble Rh/TPPTS and Rh/sulfoxantphos complexes, respectively. These results were obtained using a continuous reaction/separation operation mode involving a jet-loop reactor to achieve a high degree of mixing for efficient mass transfer in aqueous/organic (isopropanol or butanol) two-phase systems on a mini plant scale. By careful optimization of the reaction/separation parameters the steady-state yields obtained were above 80 % within a duration of continuous operation of longer than 55 h. The extent of leaching of rhodium from the aqueous to the organic phase was 16.7 mg Rh/kg aldehyde, while in the case of the methyl 10-undecenoate hydroformylation, high *n*/*iso* ratios implying excellent regioselectivities towards the desired linear aldehyde product were observed.

Baricelli et al. from the Universidad de Carabobo, Venezuela [31] review the progress made from the early eighties until now in the field of catalytic hydrogenation and hydroformylation reactions mainly of olefinic starting materials. These are available in refinery naphtha cuts and of renewable biomass-derived olefinic compounds employing water-soluble transition metal complexes in aqueous/organic two-phase

systems and present the existing industrial biphasic processes and the potential of several approaches for the development in industrial scale biphasic catalytic processes. Emphasis was placed on various methodologies developed to overcome the inherent mass transfer limitations arising from the lower solubility of heavier starting materials, such as the higher olefins in the polar aqueous medium containing the catalyst.

Zaccheria et al. from the CNR - SCITEC "G. Natta", Italy [32] review recent progress in the field of hydrogenation of renewable biomass-derived mono- and di-saccharides using heterogeneous catalysts based on the sustainable, low-cost and abundant non-precious metal copper in aqueous media to produce polyols of growing interest in the food, pharma and polymer industry. The authors highlighted the significant characteristics of heterogeneous, low loadings of copper-based catalysts, and made comparisons with other more active catalyst counterparts based on the non-precious metal nickel and on the noble metal ruthenium.

Ruppert et al. from the Lodz University of Technology, Poland [33] describe the transfer hydrogenation of the renewable lignocellulose-derived platform chemical levulinic acid into value-added chemical γ -valerolactone. This process is catalyzed by ruthenium-palladium nanoalloys immobilized on activated charcoal in the presence of biomass-derived formic acid as a source for molecular dihydrogen in the aqueous solvent.

Finally, we expect that the increasing interest in catalysis in green and sustainable aqueous environment will further inspire new developments in various fields, such as:

1. Using water as the solvent or as the reaction medium offers numerous benefits in synthesis, applicable to the selective chemo- and bio-catalytic conversions of renewable biomass-derived feedstocks to manufacture advanced biofuels, commodity chemicals, value-added chemicals and novel materials.
2. Greenhouse gas CO₂ emissions will be used as a feedstock to produce fuels, bulk and value-added chemicals in aqueous media.
3. Biocatalysts will be used in combination with aqueous micellar catalysis to produce APIs.
4. The photocatalytic acceleration of organic reactions in aqueous media.
5. The use of water-dispersible transition metal(0) catalytic NPs stabilized in the aqueous fluid support.
6. More applications of the sustainable, low-cost and abundant non-precious metals such as Cu, Ni, Fe, etc. as catalysts in aqueous media in the future.

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References

- [1] G. Papadogianakis, R.A. Sheldon, Preface: special issue on recent advances in catalysis in green aqueous media, *Catal. Today* 247 (2015) 1–3, <https://doi.org/10.1016/j.cattod.2015.02.015>.
- [2] J.C. Bricker, L. Laricchia, Advances in Merox™ process and catalysis for thiol oxidation, *Top. Catal.* 55 (2012) 1315–1323, <https://doi.org/10.1007/s11244-012-9913-0>.
- [3] G. Papadogianakis, R.A. Sheldon, Catalytic conversions in water. An environmentally benign concept for heterogenization of homogeneous catalysis, *Catal. - Spec. Period. Rep. R. Soc. Chem.* 13 (1997) 114–193, <https://doi.org/10.1039/9781847553256-00114>.
- [4] G. Papadogianakis, R.A. Sheldon, Catalytic conversions in water: environmentally attractive processes employing water soluble transition metal complexes, *New J. Chem.* 20 (1996) 175–185. (<http://www.scopus.com/inward/record.url?eid=2-s2.0-0001212031&partnerID=MN8TOARS>).
- [5] R.A. Sheldon, The E factor at 30: a passion for pollution prevention, *Green Chem.* 25 (2023) 1704–1728, <https://doi.org/10.1039/d2gc04747k>.
- [6] R.A. Sheldon, The greening of solvents: towards sustainable organic synthesis, *Curr. Opin. Green Sustain. Chem.* 18 (2019) 13–19, <https://doi.org/10.1016/j.cogsc.2018.11.006>.
- [7] M. Cortes-Clerget, J. Yu, J.R.A. Kincaid, P. Walde, F. Gallou, B.H. Lipshutz, Water as the reaction medium in organic chemistry: from our worst enemy to our best friend, *Chem. Sci.* 12 (2021) 4237–4266, <https://doi.org/10.1039/d0sc06000c>.
- [8] D.K. Romney, F.H. Arnold, B.H. Lipshutz, C.-J. Li, Chemistry takes a bath: reactions in aqueous media, *J. Org. Chem.* 83 (2018) 7319–7322, <https://doi.org/10.1021/acs.joc.8b01412>.
- [9] R.A. Sheldon, Green chemistry and biocatalysis: engineering a sustainable future, *Catal. Today* 431 (2024) 114571, <https://doi.org/10.1016/j.cattod.2024.114571>.
- [10] R.A. Sheldon, Waste valorization in a sustainable bio-based economy: the road to carbon neutrality, *Chem. Eur. J.* 30 (2024) e202402207, <https://doi.org/10.1002/chem.202402207>.
- [11] E. Anagnostopoulou, P. Lilas, P. Diamantopoulou, C. Fakas, I. Krithinakis, E. Patatsi, E. Gabrielatou, A.P. van Muyden, P.J. Dyson, G. Papadogianakis, Hydrogenation of the pivotal biorefinery platform molecule levulinic acid into renewable fuel γ -valerolactone catalyzed by unprecedented highly active and stable ruthenium nanoparticles in aqueous media, *Renew. Energy* 192 (2022) 35–45, <https://doi.org/10.1016/j.renene.2022.04.081>.
- [12] N. Yan, C. Xiao, Y. Kou, Transition metal nanoparticle catalysis in green solvents, *Coord. Chem. Rev.* 254 (2010) 1179–1218, <https://doi.org/10.1016/j.ccr.2010.02.015>.
- [13] G. Papadogianakis, R.A. Sheldon, D.Yu Murzin, Y. Wu, Research topic: aqueous-phase catalytic conversions of renewable feedstocks for sustainable biorefineries, *Front. Chem.* (2020) 1–210, <https://doi.org/10.3389/978-2-88966-447-4> (E-Book with 15 articles, ISBN 978-2-88966-447-4).
- [14] E. de Jong, H.A. Visser, A.S. Dias, C. Harvey, G.-J.M. Gruter, The road to bring FDCA and PEF to the market, *Polymers* 14 (2022) 943, <https://doi.org/10.3390/polym14050943>.
- [15] (<https://www.releaf.bio/>), (Accessed 28 November 2024).
- [16] A. Seretis, I. Mertika, E. Gabrielatou, E. Patatsi, I. Thanou, P. Diamantopoulou, P. Tzevelekidis, C. Fakas, P. Lilas, P.G. Kanellopoulos, E. Chrysoschoy, S.P. Kotsaki, K. Koukoulakis, E. Bakeas, G. Papadogianakis, Novel hydrogenation reaction of renewable furfural into furfuryl alcohol using highly efficient and selective water-soluble platinum catalysts modified with phosphines and nitrogen-containing ligands in green aqueous media, *Catal. Today* 444 (2025) 115019, <https://doi.org/10.1016/j.cattod.2024.115019>.
- [17] P. Rapado, C. Lois, M. Cano, L. Faba, S. Ordóñez, Biomass to plastics: from HMF to fructose for the synthesis of 2,5-furandicarboxylic acid over Au/TiO₂, *Catal. Today* 445 (2025) 115036, <https://doi.org/10.1016/j.cattod.2024.115036>.
- [18] A.C.R. Caldeira, H.O. Alves, A.H.M. da Silva, J.F. Gomes, Influence of water steam and copper oxidation state on the CO₂ hydrogenation to ethanol over copper catalysts, *Catal. Today* 443 (2025) 114971, <https://doi.org/10.1016/j.cattod.2024.114971>.
- [19] B. Baumert, H. Meinert, C. Cziegler, H. Terholsen, T. Bayer, U.T. Bornscheuer, Promiscuous acyltransferases for ester and amide synthesis in aqueous solution, *Catal. Today* 442 (2024) 114925, <https://doi.org/10.1016/j.cattod.2024.114925>.
- [20] M. Parmentier, P. Palamini, B. Gosselin, M. Jakobi, V. Bordes, B. Wu, F. Gallou, One-pot synthesis of substituted amides from nitriles under mild reaction conditions in aqueous surfactant TPGS-750-M, *Catal. Today* 442 (2024) 114915, <https://doi.org/10.1016/j.cattod.2024.114915>.
- [21] P.X. Kolagkis, E.M. Galathri, Ch.G. Kokotos, Light-driven Michael addition of indoles to β -nitroolefins in aqueous medium, *Catal. Today* 441 (2024) 114868, <https://doi.org/10.1016/j.cattod.2024.114868>.
- [22] A. Denicourt-Nowicki, A. Roucoux, Ruthenium and palladium nanocatalysts in water for selective hydrogenation. Scaling up the processes in terpenic renewables chemistry, *Catal. Today* 443 (2025) 114975, <https://doi.org/10.1016/j.cattod.2024.114975>.
- [23] S.R. Shetty, G.D. Yadav, Sustainable hydrogenation of xylose to xylitol using nickel-alumina catalysts supported on hexagonal mesoporous silica in water vis-à-vis aqueous isopropanol as solvent, *Catal. Today* 446 (2025) 115105, <https://doi.org/10.1016/j.cattod.2024.115105>.
- [24] T. Oyegoke, A. Sadier, S. Navarro-Jaén, A. Ventimiglia, N. Dimitratos, F. Dumeignil, B.E.-Y. Jibril, R. Wojcieszak, C. Michel, Enhancing 5-hydroxymethylfurfural oxidation to 2,5-furan-dicarboxylic acid with Au-supported catalysts: optimizing reaction parameters and unraveling degradation mechanism through DFT calculations, *Catal. Today* 445 (2025) 115086, <https://doi.org/10.1016/j.cattod.2024.115086>.
- [25] R.S. Prajapati, A.R. Kapdi, R. Sahu, B.M. Bhanage, Selectivity tuning using Rh/PTABS catalytic system for the hydroformylation of eugenol, *Catal. Today* 438 (2024) 114804, <https://doi.org/10.1016/j.cattod.2024.114804>.
- [26] M. Ferreira, H. Bricout, T.F.H. Roth, T. Seidensticker, S. Tilloy, E. Monflier, Aqueous biphasic hydroformylation and hydroaminomethylation assisted by cyclodextrins: from benchtop to industrial perspective, *Catal. Today* 442 (2024) 114951, <https://doi.org/10.1016/j.cattod.2024.114951>.
- [27] N. Di Fidio, L. Carmassi, G. Kasmiarti, S. Fulignati, D. Licursi, A.M. Raspolli Galletti, C. Antonetti, Chemical and enzymatic hydrolysis of waste wheat bran to sugars and their simultaneous biocatalytic conversion to valuable carotenoids and lipids, *Catal. Today* 442 (2024) 114941, <https://doi.org/10.1016/j.cattod.2024.114941>.
- [28] S. Mattiello, E. Ghiglietti, A. Fappani, A. Fratepietro, M. Ciallella, N. Giulini, M. Sassi, L. Beverina, Sustainable access to π -conjugated molecular building blocks via phosphine-free, ppm palladium level Suzuki-Miyaura reaction in water, *Catal. Today* 442 (2024) 114893, <https://doi.org/10.1016/j.cattod.2024.114893>.

- [29] D. Frigatti, T. Lorenzetto, C. Stefani, E. Liviero, P. Sgarbossa, F. Fabris, A. Scarso, Chiral surfactants to enhance stereoselectivity in asymmetric catalytic sulfoxidation in water, *Catal. Today* 442 (2024) 114924, <https://doi.org/10.1016/j.cattod.2024.114924>.
- [30] T.F.H. Roth, M. Häusler, D. Vogt, T. Seidensticker, Advancing the aqueous biphasic hydroformylation of oleochemicals in the loop: continuous reaction and separation using a jet-loop reactor concept, *Catal. Today* 439 (2024) 114803, <https://doi.org/10.1016/j.cattod.2024.114803>.
- [31] P.J. Baricelli, J.C. Pereira, M. Rosales, Aqueous-biphasic catalysis: a technological alternative for the use of organometallic complexes in hydrogenation and hydroformylation reactions with possible industrial application, *Catal. Today* 443 (2025) 114969, <https://doi.org/10.1016/j.cattod.2024.114969>.
- [32] F. Zaccheria, L. Vilcoq, V. Pappalardo, N. Scotti, N. Ravasio, The peculiar role of copper in the saccharides hydrogenation in aqueous phase, *Catal. Today* 446 (2025) 115135, <https://doi.org/10.1016/j.cattod.2024.115135>.
- [33] O. Sneká-Platek, M. Jędrzejczyk, W. Kwapiński, A.M. Ruppert, Synthesis driven properties of Ru-Pd nanoalloy for catalytic hydrogenation of levulinic acid with formic acid as hydrogen source in aqueous media, *Catal. Today* 443 (2025) 114970, <https://doi.org/10.1016/j.cattod.2024.114970>.

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