

Editorial

State of the Art in Molecular Catalysis in Europe

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In this editorial, I would like to provide an overview of the eleven contributions to the Special Issue entitled “State of the Art in Molecular Catalysis in Europe”, which is part of the Organic and Polymer Chemistry Section of *Catalysts*. The Special Issue requested contributions involving aspects of heterogeneous and homogeneous catalysis with an emphasis on fundamental and applied research conducted across Europe. As anticipated, the contributions to this Issue cover a wide range of topics with two reviews associated with catalytic aspects of Zn-air batteries and organic dyes. The nine scientific research papers focus on topics ranging from palladium catalysts for C-H functionalisation/C-N bond formation as well as for Suzuki–Miyaura cross-coupling at low temperature, to catalytic acid hydrolysis/dehydration, and to catalysts for polymerization processes (α -olefins and ROP of cyclic esters). There are also contributions discussing catalysts of relevance to the hydrogenation of 2,4-dinitrotoluene and how the use of incorporated Cu into AuPd catalysts can improve H₂O₂ synthesis.

Contribution 1 is a review by Rebrov and Gao entitled “Molecular Catalysts for OER/ORR in Zn-Air Batteries”. The review describes types of catalysts employed for OER/ORR reactions including those based on mixed metal oxides, perovskites, alternative carbons, monometallic noble metals, inorganic–organic composites, and spinels. The limitations and advantages of current systems are discussed, and future directions are proposed. Contribution 2 is a review entitled “Photocatalyzed oxygenation reactions with organic dyes: State of the art and future perspectives” by Conte, Sabuzi et al., which describes recent advances in the use of organo-photocatalysis in the area of the selective oxygenation of organic substrates. The photocatalysts discussed include flavinium salts, cyano-arenes, Eosin Y, Rose Bengal, acridinium salts, and quinone-based dyes, and their deployment in transformations such as the oxygenation of amines, phosphines, silanes, alkanes, alkenes, alkynes, aromatic compounds, and thioethers. Their benefits over metal counterparts are discussed and future perspectives are highlighted.

Contribution 3 is a research article that reports that the palladium species recovered from waste catalyst, namely, [NⁿBu₄]₂[Pd₂I₆], can be readily converted into PdI₂(dppf) (dppf = 1,1'-bis(diphenylphosphino)ferrocene). Both palladium catalysts were found to be active in processes such as Buchwald–Hartwig amination reactions, with the bio-derived solvent cyclopentyl methyl ether offering a more sustainable approach. It was also reported that the catalyst [NⁿBu₄]₂[Pd₂I₆], in the presence of an oxidant, performed well in the oxidative functionalization of benzo[*h*]quinoline to 10-alkoxybenzo[*h*]quinoline and 8-methylquinoline to 8-(methoxymethyl)quinoline, and could be reused multiple times. In contribution 4, a new palladium catalyst bearing a five-membered chelating [N,O] ligand, derived from the condensation of 2,6-diisopropylaniline and maple lactone, is reported. The catalyst was active in the Suzuki–Miyaura cross-coupling reaction and operated under mild conditions for a variety of aryl bromides, as well as boronic acids and pinacol esters. Under slightly more robust conditions, the catalyst was also capable of the cross-coupling of aryl chlorides and phenylboronic acid. In contribution 5, the conversion of *Chlorella vulgaris* biomass into useful materials such as organic acids, sugars, and furanic compounds via hydrolysis–dehydration–rehydration reactions catalyzed by dilute sulfuric acid is discussed. The type of product formed was found to be dependent on the conditions employed. The



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use of metallic ruthenium catalysts supported on activated carbons (5%Ru/C) for the catalytic hydrogenation/hydrogenolysis of this residual carbohydrate biomass is also discussed. Contributions 6 and 7 describe catalysts based on the bis(imino)pyridine ligand set for ethylene polymerization. In particular, non-symmetrical [*N,N*-diaryl-11-phenyl-1,2,3,7,8,9,10-heptahydrocyclohepta[*b*]quinoline-4,6-diimine]iron(II) chloride complexes, upon activation with either MAO or MMAO as a co-catalyst, exhibited exceptional activities with values as high as 35.92×10^6 g (PE) mol⁻¹ (Fe) h⁻¹. β-H elimination and chain transfer to aluminum were identified by ¹H/¹³C NMR spectroscopy. In contribution 7, a family of cobalt bis(imino)pyridine catalysts containing at least one *N*-2,4-bis(dibenzosuberyl)-6-fluorophenyl group is reported. Again, upon activation with either MAO or MMAO, very high activities of the order of 1.15×10^7 g PE mol⁻¹ (Co) h⁻¹ were achievable at 70 °C. Contributions 8 and 9 to this Special Issue also involve the use of catalysts for polymer production. High valent vanadium oxo complexes bearing 6-bis(*o*-hydroxyaryl)pyridine derived ligation were found to be capable of the ring opening polymerization (ROP) of ε-caprolactone (ε-CL), δ-valerolactone (δ-VL), and *rac*-lactide (*r*-LA), with the best results being achieved when the catalysts were deployed in the melt form. These species were also capable, in the presence of DMAC (co-catalyst)/ETA (reactivator), of ethylene polymerization, albeit with moderate activities (≤ 8600 Kg·mol⁻¹·V⁻¹bar⁻¹h⁻¹). In contribution 9, the use of H-bonded molybdenum arrays, which are derived from dianilines, amine-functionalized acids, as catalysts for the ROP of ε-CL and δ-VL is reported. Such systems, when used as melts under N₂ or air, afforded relatively high-molecular-weight polymers (10,420–56,510 Da) with a variety of end groups. The parent dianilines were also capable of the ROP of δ-VL, whilst both PCL and PVL were formed when using the parent acids alone. In contribution 10, the Miskolc Ranking 21 (MIRA21) model was applied to compare 58 catalysts in 2,4-dinitrotoluene catalytic hydrogenation to 2,4-toluenediamine. The results placed eight catalysts in the high (D1) class, and 80% of the catalysts afforded excellent conversions with 45% revealing selectivity above 90% n/n%. A comparison of the various systems revealed that catalysts with oxide and/or magnetic supports performed better than carbon-based supports when utilized under laboratory conditions. Work in contribution 11 found that catalytic activity for H₂O₂ synthesis can be improved by the incorporation of low concentrations of the metals Ni, Cu, or Zn into supported AuPd nanoparticles. The best results were achieved using Cu *versus* the use of a Pt promotor, and this was attributed, based on XPS and CO-DRIFTS experiments, to changes in the surface composition, including the formation of mixed Pd²⁺/Pd⁰ domains and the electronics of the system. Upon reuse, some deactivation was noted, and this was attributed to reduction to Pd⁰ species via H₂ rather than Cl loss.

Finally, we would like to express our sincere thanks to all those who submitted articles of such high quality to this Special Issue on the “State-of-the-art in Molecular Catalysis in Europe”. We hope that you, the readership of *Catalysts*, can also enjoy this Special Issue.

Conflicts of Interest: The authors declare no conflicts of interest.

List of Contributions:

1. Rebrov, E.V.; Gao, P.-Z. Molecular Catalysts for OER/ORR in Zn–Air Batteries. *Catalysts* **2023**, *13*, 1289. <https://doi.org/10.3390/catal13091289>.
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