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Practically relevant catalysis and biocatalysis

Practically relevant and forward looking. These are the two features of the *Catalysis and Biocatalysis* special supplement we had the privilege to edit following the previous issues edited by Ian Grayson in 2016 and Volker Hessel in 2015. Inviting the prominent academic and industrial research chemists who kindly accepted to contribute to this issue, we asked them to present selected recent research from their Labs focusing on outcomes that have "found, or may realistically find soon, practical application in industry".

Reporting the response of fine chemical companies interviewed on the choice of catalyst (enzyme, organo- or metal catalyst) and process (continuous or batch) used for the manufacture of fine chemicals and pharmaceuticals, Grayson last year found that the choice of process as well as of the catalyst depends on the outcomes of a cost-benefit analysis for the whole process (1). In full agreement, along with Teles and Della Pina we have recently argued that a given catalytic chemical synthesis carried out in industry will be replaced by a new one provided that it either *i*) allows a breakthrough in the process economics, or if *ii*) it enables a simple drop-in replacement of the old catalyst (2).

The latter point nicely fits with the excellent contributes in this themed issue. Turner and his team at the University of Manchester report on the application of phenylalanine ammonia lyases (PALs) from *Anabaena variabilis* cyanobacterium to mediate the anti-Michael addition of ammonia with complete regioselectivity, giving access to enantiopure arylalanines from laboratory to industrial scale. Unlike other enzymatic processes, PALs do not require cofactor supplementation or recycling systems, highlighting the synthetic potential of this enzyme.

Paradisi at Nottingham University shows that biocatalysis is "taking to the flow", with the development of stable solid biocatalysts with textural properties suitable for application under flow, in particular for synthesizing amine containing molecules. By focusing on enzymes isolated from the archaeon *H. volcanii* rather than on whole cells, the concern that the biocatalysts may be contaminated by bacterial endotoxins is eliminated, whereas packaging of the enzyme in sequential columns enables the direct synthesis of APIs, with significant environmental and economic benefits.

Stone and co-workers at Johnson-Matthey describe a new process for an existing chiral catalyst, which an eminent example of the drop-in requirement mentioned above. Lopez-Sanchez offers an updated outlook on catalytic routes to glucaric and adipic acid starting from renewable platform chemicals in light of the forthcoming bioeconomy in which chemical industry raw materials will originate from biomass, rather than from oil.

Further showing evidence that photoredox catalysis is consolidating into a source for new selective reactions as well as environmental remediation processes, G. Palmisano and co-workers at Masdar Institute of Science and Technology describe the structure and photocatalytic properties of nanostructured TiO₂ thin films grown by innovative sputtering methodology, aiming to optimize the reactivity and wettability of titania.

Abu-Reziq and Weiss at the Hebrew University of Jerusalem show the excellent performance of polyurea microcapsules doped with Pt nanoparticles in the hydrosilylation, of alkynes, dispersed in water at room temperature. Easily recovered via centrifugation, the capsules are remarkably stable with no significant changes in reactivity and morphology after three consecutive reaction runs.

Albo at Ariel University and colleagues at several Israeli research centres report the excellent results with Ag and Au nanoparticles sol-gel entrapped in organosilica in the environmental remediation of water from highly toxic brominated by-products such as tribromo-acetic acid formed upon water chlorination. The toxic compounds could be quantitatively de-halogenated adding readily available NaBH₄ to the catalyst powder suspended in water. The authors emphasize the ability to obtain reproducible catalysts by using sol-gel technology, and the low catalytic amount of silver and gold used,

and the prolonged stability of their ORMOSIL catalysts in water remediation processes, as "the applicability of a new technology is highly dependent on the cost... of the suggested process". Even more, they conclude, in the field of environmental technologies due to relatively low value of the market.

Finally, Michon, Agbossou and co-workers at Lille University, summarise the recent efforts devoted to apply Ir(III) metallacycle complexes in hydrodefluorination and hydrosilylation highlighting the importance of proper ligand modifications to enable further broad applications of catalysts based on metallacycles.

We are reminded by Turner in his team's contribute that the use of enzymes for chemical synthesis has mitigated several problems faced in the fine chemicals industry including the use of expensive heavy metal catalysts, toxic solvents and the requirement for extensive protection/deprotection chemistry.

This is true, with stable immobilized biocatalysts, metal nanoparticle catalysts, and organocatalysts employed under flow having the potential to produce the breakthrough economic improvements needed for replacing of older technology with scalable, safe, and efficient continuous processing. Industry needs indeed economic, highly active and selective solid catalysts with high turnover numbers and long catalyst lifetime.

The synthetic and environmental remediation routes enabled by the new catalysts described in this issue are part of our common path towards a truly sustainable fine chemical industry offering clear economic and technical advantages (3).

REFERENCES

1. I. Grayson, *Chim. Oggi* 34 (5) (2016) 12-13.
2. R. Ciriminna, C. Della Pina, E. Falletta, J. Henrique Teles, M. Pagliaro, *Angew. Chem. Int. Ed.* 55 (2016) 14210-14217.
3. R. Ciriminna, M. Pagliaro, *Org. Proc. Res. Devel.* 17 (2013) 1479-1484.



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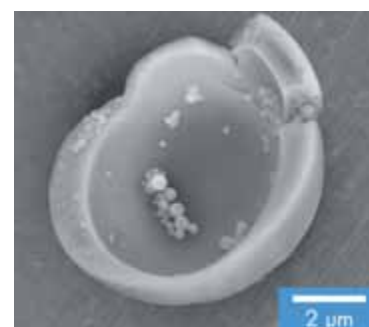
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