

Editorial Focus on base metal catalysis

Since the establishment of the United Nations' sustainable development goals and the advent of "green chemistry," base metal catalysis has increasingly been a focus of scientific research. Although precious metal catalysts based on Au, Rh, Pt, and Pd have proven robust in industries ranging from transportation and energy to pharmaceuticals and agrochemicals, they are considered scarce and expensive resources. Base metals such as Cu, Zn, Co, and Ni are Earth-abundant and potentially costeffective alternatives to precious metal catalysts, but they require further study to advance their full translation to industry.

Thus far, research has demonstrated the potential for base metal catalysts to fulfill many sustainability goals: reducing dependence on resources that are limited in supply, streamlining synthetic processes, and limiting the generation of hazardous waste. For example, base metal catalysis can be used to employ biofeedstocks, rather than fossil fuels, as starting materials under mild conditions with the assistance of light or electricity. The bigger picture of sustainability, however, can be nuanced, and factors beyond the laboratory—such as mining and extraction—are also vital considerations.

In comparison with precious metals, base metals tend to possess smaller atomic radii, are electropositive, and have the propensity to form high-spin, single-electron complexes. These unique physical and chemical properties can be harnessed in the discovery of new reactions. Recent examples of base metal catalysts enable the formation of radical species, participate in mild redox reactions, and, in the case of metalloenzymes, achieve stereoselectivity. Further studies are needed to expand the repertoire of base-metal-promoted reactions, such that in the near future sustainable methods can be implemented on a global scale.

This focus issue, guest edited by Dr Laura Ackerman-Biegasiewicz, launches with five research articles and one perspective highlighting future directions in the field of base metal catalysis. We are delighted to present a number of papers from early career researchers who are focused on uncovering unique reactivity with base metals, with an emphasis on nickel and cobalt catalysis.

Nickel is one of the most widely studied alternatives to precious metal catalysts. In addition to recapitulating some of the classical reactivity of its heavier cousins, palladium and platinum, it offers unique opportunities, such as through Ni(I)/Ni(III) catalytic cycles, for example. Chuan Wang and colleagues exploit the Ni(I) state to achieve the enantio- and diastereoselective synthesis of 1,2-dihydronaphthalenes by cross-electrophile coupling, involving ring opening of heteroatom-substituted bicyclic alkenes using unactivated alkyl bromides. Conversely, Xiao-Feng Wu and colleagues report that a Ni(0)/Ni(II) cycle drives the synthesis of non-symmetric thioethers by cross-coupling of two different sulfonyl chlorides, involving selective reduction of arylsulfonyl chlorides using manganese.

Widely known for its radical reactivity, cobalt has drawn wide interest in both homogeneous and heterogeneous catalysis as an Earth-abundant element with low toxicity. Daniel Resasco and colleagues explore the rational optimization of





heterogeneous cobalt boride catalysis, using hydrogenation of cinnamaldehyde as a benchmark reaction to systematically explore the role of boron species, different metal supports, and water on selectivity. Meanwhile, Julian West and colleagues exploit the natural organocobalt complex vitamin B12 as a co-catalyst for regioselective ring opening of epoxides, in conjunction with a hydrogen atom transfer catalyst and visible light irradiation.

Main group metals offer fascinating reactivity to complement more widely studied catalysts from the d-block. Calcium offers an inexpensive, Earth-abundant alternative in catalysis and has attracted increasing interest in the past couple of decades. Ashley Basson and Mark McLaughlin provide access to Mannich products by the calcium-catalysed dehydrative coupling of *N*,*O*-acetals and anilines.

Finally, in a perspective, Manar Shoshani highlights the emerging promise of combining late transition metal catalysis with Lewis acidic metals, whether as well-defined heterometallic complexes or as cooperative systems generated *in situ*, for the regioselective C-H functionalisation of pyridines.

The work presented in this focus issue provides a sample of the range of exciting directions in this field, which we expect to only grow. Although these examples focus on emerging strategies in catalysis, there is still a significant amount of information that needs to be gleaned to make progress in sustainable chemical practices. There are limited ligand sets established primarily for the smaller atomic radius of base metals, a small set of heterogeneous platforms to enable selective reactions with reagents without surface degradation, and a lack of holistic information about life cycle assessments of a catalytic process. For example, biocatalysts are exceptionally efficient and selective but require a large amount of energy to produce on a large scale and can be challenging to design. Earth-abundant metal salts are promising as catalysts, yet if they require a complex, expensive ligand in high loading, or unethical mining practices, they might not be considered sustainable. In the future, systematically collating data on base metal catalyst accessibility, reactivity, and recyclability will be essential to accelerating discovery in this field.

We hope the insights contained in this issue can inspire others to focus on developing novel base metal catalysts, improving our understanding of their design and application, and playing a role in creating a sustainable chemistry for the 21st century.

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