New ecocatalysts

1. Ecocatalysts: the first bio-based metal catalysts for green chemistry [1]

A crucial feature of green catalysts is their **multi-metallic composition** resulting from the combination of transition elements at very high concentrations (e.g. Zn^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+}, Pd^{2+}, Ce^{2}) with classical elements generally necessary for plant development (e.g. Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Fe^{3+}). The simultaneous presence of a combination of well-defined active sites results from this variety of metallic species. Therefore, sequences of original reaction steps lead to unique selectivities. Indeed, a classic catalyst can be limited to influencing only one or some of the steps of a reaction process, thus limiting the opportunities in organic synthesis. Here, the richness of the different interactions between the present chemical species leads to multiple and unusual metal/ligand interactions in solution.

This peculiarity of composition has been taken advantage of in **multi-component reactions** and in **cascade** leading to the direct preparation of complex heterocyclic compounds of pharmaceutical interest with somewhat barbaric names. , such as 2-*H*-chromenes, 1-*H*-1,5-benzodiazepines, cannabinoids, tetrasubstituted pyridines, polyhydroxy chiral furans, pyrazoles and 1,2,3-substituted triazoles.

2. Innovative, complex and biosourced materials

2.1. New compositions and microstructures

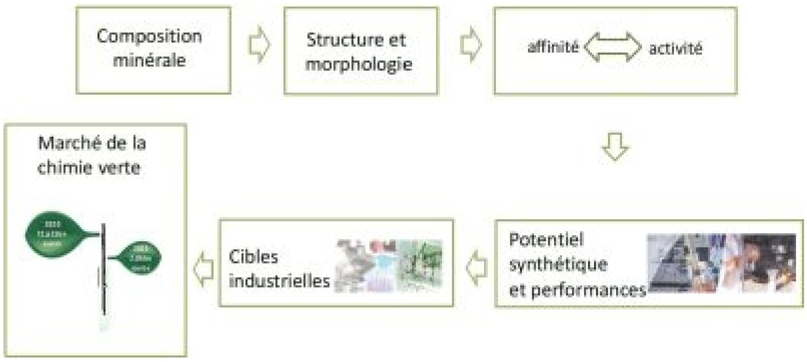

Figure 1. An interdisciplinary approach in chemistry coupling materials chemistry and organic synthesis approaches in green and sustainable chemistry. [Source: © C. Grison]

It has been possible to identify, understand and control polymetallic-molecule interactions up to the catalytic act, through a global approach to materials chemistry and molecular modeling (Figure 1). Ecocatalysts have novel compositions and microstructures resulting from a plant imprint. These salts, often still unknown in catalysis, are the subject of specific studies (bio-inspired catalysis).

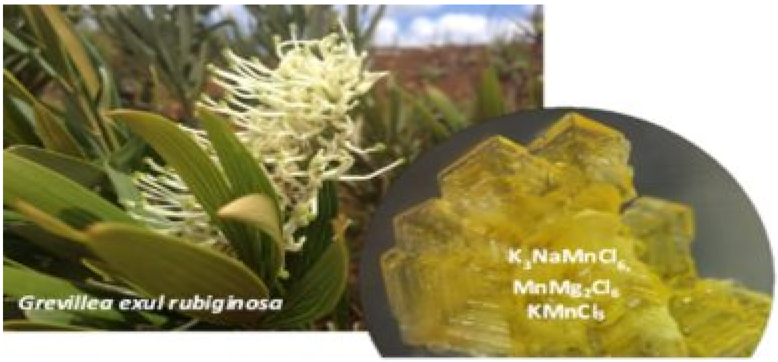

Figure 2. Eco-Mn derived from Grevillea exul rubiginosa: an original structure and a plant footprint. [Source: © C. Grison]

Thus, for example, an Eco-Mn (manganese ecocatalyst) from *Grevillea exul rubuginosa* (Figure 2) consists of unique salts, such as $K_3NaMnCl_6$, $KMnCl_3$ whose interest in catalysis has recently been demonstrated by complex calculations. Three successive generations of Eco-Mn recently developed and studied have shown **promising results (selected as a publication to celebrate the anniversary of the Journal of Green Chemistry)**. A review of all these results completes this publication. It brings together the many results accumulated in the field of epoxidation, oxidative cleavage, oxidations of activated alcohols, and the first example in the literature where Eco-Mn is the catalyst of a reduction reaction. It is the bio-inspired amino-reduction of carbonyl derivatives (including ketones).

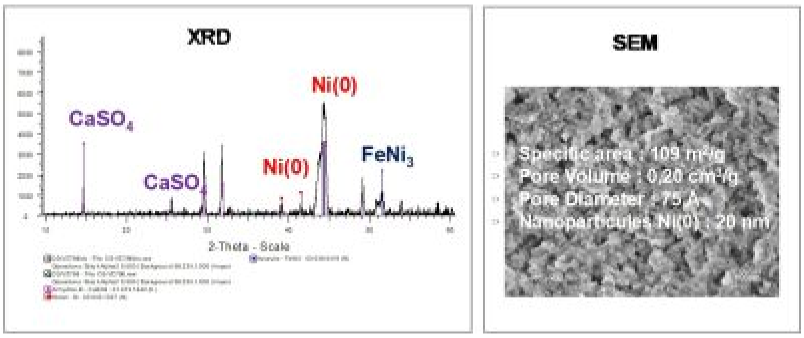

Figure 3. X-Ray Diffraction Spectrum (XRD) of a Eco-Ni(0) and its physicochemical properties. [Source: © C. Grison]

Beyond their original composition, ecocatalysts are not simple catalytic tools for the synthesis of molecules, but **materials in their own right**, innovative, complex and biosourced (their morphology and microstructure bear witness to this). An Eco-Ni prepared by controlled thermal decomposition of a Nickel formate derived from a nickel hyper-accumulating plant, has a morphology worthy of the very reactive clay montmorillonite K10, in terms of specific surface and porosity (Figure 3). It has an original composition ($FeNi_3$) which probably explains its unusual behavior for metallic nickel.

2.2. Catalysts that save expensive transition metals

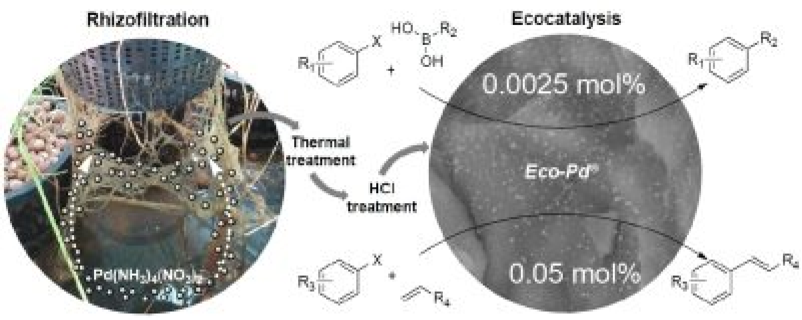

Figure 4. Microstructure of an Eco- Pd and its applications in organic synthesis. [Source: © C. Grison]

The presence of a **mineral matrix** made up of physiological cationic elements makes it possible to disperse and **stabilize** the nanoparticles (2-4nm) formed by transition metals. Their aggregation is thus avoided, and leads to catalyzed reactions with **very small quantities** of catalyst. This is particularly advantageous in the case of very expensive PGMs (Figure 4).

The Suzuki and Heck coupling reactions (Nobel Prize) are carried out without ligands and without additives (important advantage in green chemistry to form carbon-carbon bonds).

2.3. Many mechanisms of organic synthesis revisited

Figure 5. Many mechanisms of organic synthesis revisited thanks to ecocatalysts. [Source: © C. Grison]

Ecocatalysts can present performances and **selectivities much higher** than conventional catalysts. This new concept has made it possible to prepare a wide variety of high-performance ecological catalysts, with adjustable reactivity, while respecting the principles of sustainable chemistry. Ecocatalysts have thus made it possible to revisit all **the major mechanisms of organic synthesis** (Figure 5): Lewis acid catalysis, green reductions, green oxidations, cross-coupling reactions.

Ecocatalysts allow the **synthesis of complex biomolecules** with significant industrial and societal impact. In particular, they allow the synthesis of highly sought-after molecules such as antimitotics, DNA and RNA, biocontrol agents, new generation insecticides, cosmetics and key intermediates in the chemical industry.

2.4. Ecocatalyzed reactions can be performed in green solvents, including water.

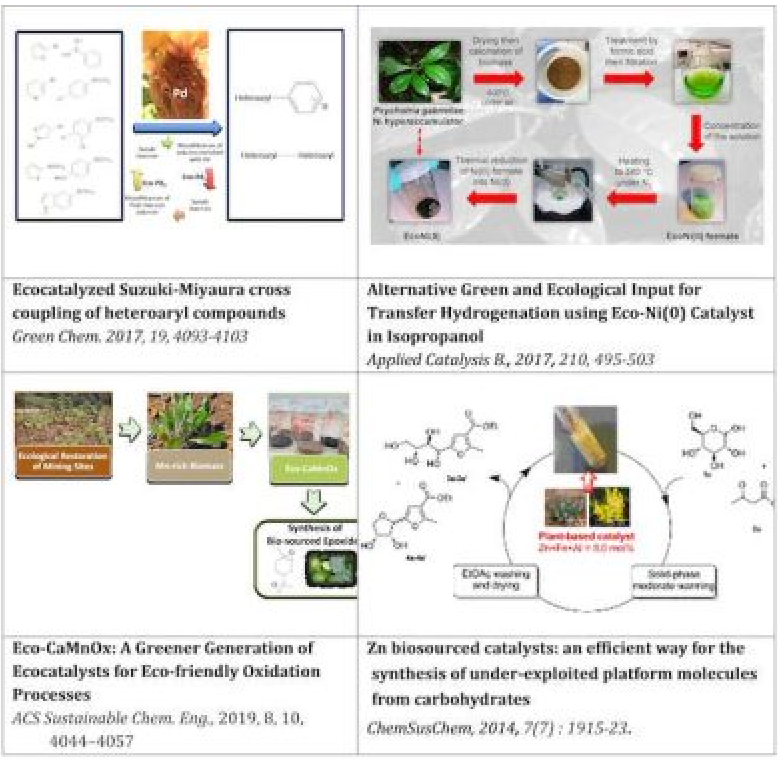

Figure 6. Some examples of ecocatalyzed reactions. [Source : © C. Grison]

Among the many possible examples (Figure 6), we can cite the advantageous example of the heterocyclic series Suzuki reaction carried out in a glycerol/BuOH medium, reductions carried out in isopropanol, oxidizing cuts in butanol or in the water/acetone mixture, or even the Garcia-Gonzalez reaction carried out in a water/EtOH mixture, or even without solvent.

Thanks to the biosorption process (retention of metals on the biomass), it is possible to **recycle and reuse** the ecocatalysts, including in the **homogeneous phase.** This unusual possibility has been tested with the copper-catalyzed alkyne-azide cycloaddition, Suzuki and Sonogashira couplings**.**

3. Conclusion

The concept of ecocatalysis now makes it possible to free ourselves from all the limitations specific to existing methods thanks to a **new generation of functional, ecological, stable and recyclable materials**. They present several reactive interfaces whose properties can be controlled from the intensity and the nature of the desired metal/substrate interaction. These are linked to the biodiversity of plant species used in ecological restoration and biosorption. Ecocatalysts are therefore not simple substitutes for catalysts derived from metallurgy, but new tools that integrate a triple vision: **chemistry, ecology, environment for sustainable chemistry**.

Notes and references

Cover image. Ecocatalysis, developed over the past 10 years, represents an unprecedented way of promoting phytoextraction, rhizofiltration and other pollution control phytotechnologies. [Source: © C. Grison]

[1] Grison C., Y. Lock Toy Ki. Ecocatalysis, a new vision of Green and Sustainable Chemistry, Current Opinion in Green and Sustainable Chemistry, 2021, 29, 100461. https://doi.org/10.1016/j.cogsc.2021.100461.
