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To cite this version:

Claude Grison, Joël Barrault. Editorial overview: Green catalysis. Current opinion in green and sustainable chemistry, 2018, 10, pp.A1-A3. 10.1016/j.cogsc.2018.04.016 . hal-02390343

HAL Id: hal-02390343

https://hal.science/hal-02390343v1

Submitted on 13 Oct 2020

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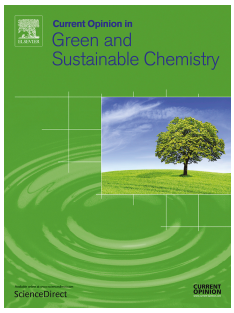

Editorial Green Catalysis

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PII: S2452-2236(18)30053-1

DOI: 10.1016/j.cogsc.2018.04.016

Reference: COGSC 156

To appear in: *Current Opinion in Green and Sustainable Chemistry*

Please cite this article as: C. Grison, J. Barrault, Editorial Green Catalysis, *Current Opinion in Green and Sustainable Chemistry* (2018), doi: 10.1016/j.cogsc.2018.04.016.

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Green Chemistry has created a new thinking in organic synthesis. The design framework of the principles of Green Chemistry is leading to optimize synthetic pathways and product design around minimum toxicity and material/energy efficiency. Catalysis is a pillar of Green Chemistry. Catalysis can reduce material, renewable energy systems, time, temperature and pressure conditions. Catalysis improves selectivity and reduces products from competing reactions, which can simplify downstream processing.

However, catalysts are not necessary green and sustainable. Many catalysts are based on heavy metals and may be toxic. They are not always recyclable and reused. Toxicity of the catalyst, of the catalyst residues and of catalyst degradation products are problematic.

In addition, the sustainable access to mineral resources has become a growing concern in recent years. This situation is particularly critical for some transition metals, such as zinc, nickel, manganese and platinum group elements (PGE), frequently used in industrial processes as catalysts with unique chemical properties. Chemical requirements for these non-renewable resources are increasing steadily, which explains the diminishing exploitable availability. Because of this phenomenon, elements become notably dispersed in the environment, which results in pollution issues and is a supplementary problem. In several countries, governmental authorities have decided to develop innovative technologies of recycling, in order to tackle this increasing concern.

The needed challenges are the design and use of sustainable catalysts and catalytic processes. A key feature of green catalysis is that the catalysts have to be green, manufactured cleanly, sustainably, recyclable and reusable.

This special issue describes different alternatives to produce green catalysts. The first one is the **Ecocatalysis**, a new concept of ecological recycling of mineral resources developed by Grison's group. Ecocatalysis seeks to solve the problem of the phytoremediation. Taking advantage of the adaptive capacity of particular plants to hyperaccumulate the transition metals in their aerial parts, it is possible to address the direct use of metals derived from plants as catalysts in organic chemistry. Plants wastes are directly recovered and transformed into green catalysts, the "ecocatalysts". These original polymetallic systems serve as heterogeneous and homogeneous catalysts in synthetic transformations allowing access to molecules with high added value for fine and industrial chemicals. Homogeneous catalysts can be recycled and reused by bioconcentration of metals in specific plant roots. The approach opens greener and broader perspectives in terms of Green catalysis. In this issue, Pierre-Alexandre Deyris and Claude Grison (https://www.sciencedirect.com/science/article/pii/S2452223617300822) reveal that the development of this new concept is creating a paradigm shift in sustainable and green chemistry: metallic wastes are becoming new ecofriendly and efficient catalytic systems.

Today, there is a general consensus in academic literature that **second generation biomass** is the only valuable carbohydrate resource for non-food applications. In the meantime, fermentation of sugars towards bio-ethanol, mainly from first generation biomass, is becoming widespread at an industrial level. In this issue Bert Sels and Aron Deneyer (https://www.sciencedirect.com/science/article/pii/S2452223618300105) investigate if there is a

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valuable role for edible resources (here: sugars) in the chemical industry without affecting the food security. Moreover, a connection is proposed between a broad range of multiple technologies and sustainable resources, with main attention focused on the native C skeleton and functionality of biomass. Going deeper in sustainability, four criteria (ranging from functionality, through reaction parameters and toxicity to the final end-of-life cycle) are selected, taking into account the entire valorisation route, to apply to the most promising carbohydrate-derived molecules.

For the development of the selective conversion of this second generation of biomass, novel heterogeneous catalysts are needed and ab initio modelling, that provides in-depth mechanistic studies as well as in silico screening of catalysts, strongly emerges as a necessity. In this issue, Carine Michel and Romain Reocreux (https://www.sciencedirect.com/science/article/pii/S2452223617301116) highlight the recent contributions of ab initio modeling in the field of catalytic biomass valorization, with a restriction to metal supported catalysts as an illustrative domain. Focused on the metallic active site, most of the studies neglect support effects, solvent effects and coverage effects on the overall catalytic process. Although if most research has concentrated on noble metals catalysts, the partial replacement of these metals and the use of more accessible elements such as Mo, Fe, Co, are also under investigation.
Among the materials which could be selected as supports, zeolites and zeotypes, which are defined as microcrystalline structures, are an important class. This is because it is possible to control and/or tune the acid-base properties as well as their redox properties from various isomorphic substitutions. Moreover, microporous as well as mesoporous properties can be also controlled so that zeolites can be used as microreactors for shape and chemical selectivity; for example, in the manufacture of drugs from natural products (medicinal chemistry). In this issue Patrick Pale et al. (https://www.sciencedirect.com/science/article/pii/S2452223617301086) report an overview of the syntheses of O,N or S-heterocycles mediated by zeolites and show the current and future trends in this area.

Combination of different domains, in what we called assisted- metal-catalyzed reactions; for example photochemistry, should enable synergy effects for green catalysis. Although pronounced recently, a lot of the research activities (i.e. studies from Norbert Hoffmann and Clement Michelin, https://www.sciencedirect.com/science/article/pii/S2452223617300858) have already been focused on **photocatalysis** applied to organic synthesis. Electronic excitation by light absorption modifies the chemical reactivity of chemical compounds. When this technique is applied to organometallic or coordination compounds as catalysts, their activity can be increased or chemical reactivity can even be induced. Several catalytic reactions with expensive catalysts can also be performed using less expensive compounds when they are performed under photochemical conditions. Various elementary steps of catalytic processes, such as ligand exchange, electron transfer, or transformations in the ligand sphere, are selectively addressed. Thus, photochemical reaction conditions, using visible or UV light irradiation, considerably enlarge the scope of catalytic transformations.

Another alternative is **Metal free catalysis**. It offers several advantages: the organocatalyst is often a natural or biobased component and its structure can be chiral and induce asymmetric catalysis. **Organocatalysis** is an interesting contribution to green chemistry and numerous studies have been focused on types of organocatalysis that rely on the use of hydrogen bonding interactions to promote organic reactions. In this issue, Jakub Iwanejko, Elżbieta Wojaczyńska and Tomasz K.Olszewski (https://www.sciencedirect.com/science/article/pii/S2452223617301049) focused on the catalysis in Mannich reaction to illustrate this approach.

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Other important principles of green chemistry concern experimental reaction conditions in order to decrease energy consumption, co-products and of green and sustainable chemistry. In recent years, a lot of research was done to replace usual, well known and efficient petrochemical compounds with biomass derived products. But in this issue, a rather new and original system "compressed CO_2 and H_2O" proposed by Fengyu Zhao and, Haiyang Cheng (https://www.sciencedirect.com/science/article/pii/S2452223618300282), is presented as a green solvent. Such a solvent has been studied extensively not only because both CO_2 and H_2O are non-toxic, nonflammable, abundant, cheap, renewable and easy to handle, but also due to the fact that they are efficient promoters in the organic catalysis reactions.

A complementary fast-growing research area concerns Earth-abundant molecular transition metal photosensitizers and catalysts for dye sensitized photoelectrochemical cells for direct solar energy storage. The possibility of direct conversion of solar energy into solvents or gases in a cost efficient way is considered a disruptive breakthrough for large-scale implementation of solar fuel technologies. This is covered by the paper by Sutra and Igau (https://www.sciencedirect.com/science/article/pii/S2452223617300998).

Finally, we focus on the design and the activity of **new hybrid materials**, such as mixed ionic minerals for green chemistry. They can be considered as designer materials, which are interesting for applications in catalysis. In this issue, Peter Hesemann (https://www.sciencedirect.com/science/article/pii/S245222361830004X) describes different approaches for obtaining ionosilica-derived heterogeneous catalysts. Ionosilicas appear as highly versatile phases for the preparation of various types of heterogeneous catalysts that open interesting perspectives both in transition metal catalysis and organocatalysis. In addition, Carlos Aspesteguia and his colleagues (https://www.sciencedirect.com/science/article/pii/S2452223617301104) studied the synthesis of fine chemicals by FAME metathesis from the immobilization of homogeneous catalysts on high surface area porous supports, which may combine advantages of homogeneous and heterogeneous catalysts and allows the Ru recovery. The immobilization procedure should be achieved without modification of the catalyst to keep the optimized ligand systems of the homogeneous catalysts.

Biographies

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Claude Grison is CNRS Research Director. She is leading the Laboratory of Bio-inspired Chemistry and Ecological Innovations (Montpellier, France), which is dedicated to the implementation of new ecological solutions and innovative chemical tools for the ambitions of tomorrow's chemistry. Dr Grison is the pioneer of the ecocatalysis concept, which represents a major break-through at the interface between ecology and chemistry. An author and co-author of more than 181 scientific articles and patents, she has received 9 Awards for Innovation.

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Joel Barrault is an international expert in green chemistry with expertise in the fields of Catalysis and dedicated catalytic materials, Green chemistry, Renewables and wastes. He is a former CNRS Research

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