



Speciality Grand Challenges in Organometallic Catalysis

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The interaction between a metal center (M) and a molecular moiety (substrate) is the basis of most catalytic processes. The chemical environment surrounding M can equally be a set of suitable ligands (*Coordination Catalysis*) (Crabtree, 2014), a set of properly engineered/functionalized ligands anchored onto a solid support (*Single-Site Surface Coordination Catalysis*) (Copéret et al., 2016), a small cluster of metal atoms as well as a lattice of a material (*Heterogeneous Catalysis*) (Friend and Xu, 2017), and an enzymatic framework (*Biocatalysis*) (Schwizer et al., 2018) (**Figure 1**).

If at least one of the M-environment interactions involves an M–R bond (where R = C and H), all types of catalysis listed above are by definition *Organometallic Catalysis*. Furthermore, even in the absence of a M–R bond in the starting molecule/material, the catalytic process may be still defined as of organometallic nature if a M–R fragment forms in any step of the catalytic cycle. These simple considerations clearly indicate the generality and importance of organometallic catalysis. Relevant examples of organometallic catalysis, for each of category illustrated above, are very well known and reported in the textbooks (Drauz et al., 2012; Bochmann, 2014).

The success of organometallic catalysis may be ascribed to the capability of a metal to activate low-energy reaction pathways along which the deformed substrate, stabilized through coordination at a properly designed L_nM -fragment, is induced to react in a novel and original way. This explains why some reactions are exclusive of coordination/organometallic complexes. In this respect, a classical example is the reductive elimination, which is one of the fundamental steps of organometallic catalytic cycles (Hartwig, 1998; Chen et al., 2017; Chu and Nikonov, 2018; Wolczanski, 2018). It involves the release of R–X from a (L_nMXR) complex, where oxidation state, coordination number and electron of the metal center are reduced by two units.

As a result of this propensity to activate a substrate by opening low-energy reaction pathways, the activity of organometallic catalysts can be so high that a $<10^{-6}$ M active metal concentration is sufficient for carrying out the reaction efficiently: in these cases, catalyst separation and recovery from the products might even be avoided, as it occurs in some industrial polymerization processes (Stürzel et al., 2016). This notwithstanding, catalyst recovery is still necessary in many cases, and typically more easily achievable with heterogeneous rather than molecular systems. For this reason, industrially relevant molecular catalysts are often heterogenized onto suitable supports, as mentioned above, leading to heterogeneous catalysts with similar (ideally the same) activity and selectivity to the molecular counterpart, but with the additional advantage of being easy to separate from the reaction environment and recycle (Schwarz et al., 1995; McNamara et al., 2002; Witzke et al., 2020).

Selectivity is another strong suit of organometallic catalysis, which can be achieved by tailoring the chemical environment of the active metal by proper selection/combination of ligands. As a matter of fact, chemical, regio- and stereo-selectivity approaching 100% have been obtained for many reactions of industrial relevance, even in non-enzymatic systems.

Importantly, the effectiveness of organometallic catalysts stems also from possible M–environment cooperativity. The latter may involve ligands, which may be redox active or bear a handling functionality (a base, an acid, etc.), support, other metallic centers (both in

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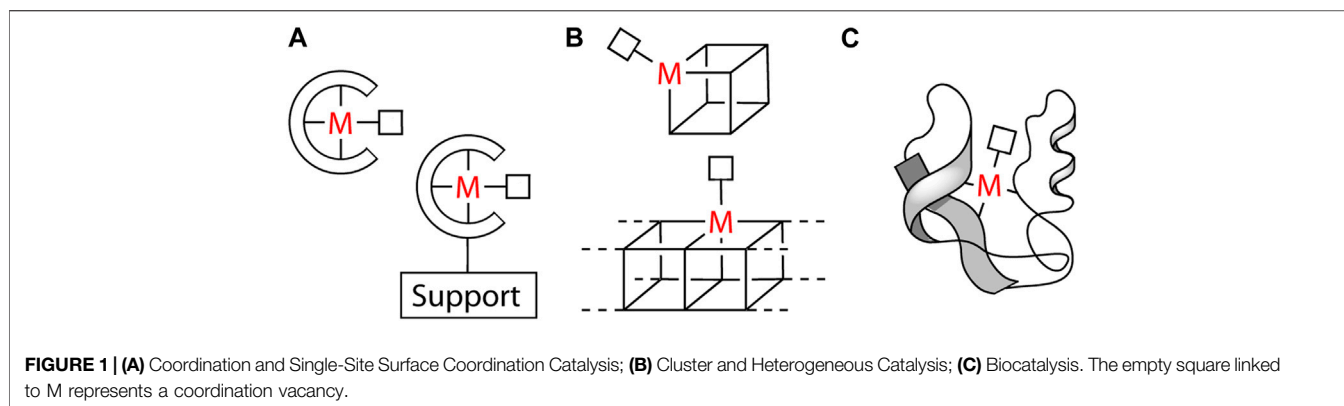
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molecular clusters and extended lattices) and even an enzymatic framework. Notable in the latter respect are the recent developments of artificial metalloenzymes, in which non-native activating metal ions is accommodated in a protein scaffold, to induce selectivity to catalytic process (Schwizer et al., 2018; Lombardi et al., 2019).

Despite the versatility of organometallic catalysis and its paramount success, many open challenges can be foreseen for the next decades. One that the scientific community is very aware of is the replacement of noble-metal organometallic catalysts with those based on earth-abundant analogues (Bolm, 2009; Chirik and Morris, 2015; Roger et al., 2017). This is not a simple task, due to the typical superior reactivity of the former systems. Traditionally, the best performances in most relevant catalytic processes have been obtained by using the Pt group metals (Albrecht and van Koten, 2001; Johansson Seechurn et al., 2012; Lyons and Sanford, 2010; Seechurn et al., 2012; Labinger and Jay, 2017; Roger et al., 2017). The substitution of a rare and expensive metal of the second and third transition rows (such as Ru, Rh, and Ir) is typically pursued by looking for an abundant and cheap metal of the first transition row belonging to the same triad (e.g., Ru → Fe, Rh → Co, Pd → Ni) (Zhang et al., 2012; Smieja et al., 2013; Tasker et al., 2014; Wenger, 2019) or related by the diagonal relationship (e.g., Ru → Mn, Rh → Fe) (Rayner-Canham, 2011; Zell and Langer, 2018). These replacements are often detrimental but not necessarily dramatic in terms of catalyst TurnOver Frequency (TOF), whereas they are surely more critical in terms of TurnOver Number (TON). Nevertheless, many research groups have obtained remarkable success in some important chemical transformations. For instance, hydroformylation is one of the largest scale processes of the chemical industry, traditionally relying on highly active Rh catalysts. Very recently (2020) Stanley and coworkers reported simple carbonyl Co complexes with performances comparable to those of noble metal systems; the key for high activity appears to be the cationic nature of the Co-complexes (Hood et al., 2020).

Another large-scale industrial field in which it would be important to develop non-noble metal catalysts concerns hydrogenation reactions (Filonenko et al., 2018). Among others, a recent interesting example has been reported by Beller and coworkers, who developed a Mn system for quinolones hydrogenation under mild conditions, consisting of

a very simple and cheap Mn pentacarbonyl bromide complex (Papa et al., 2020). Other first row metals developed for N-heteroarenes reduction include cobalt (Adam et al., 2017; Sahoo et al., 2018) and iron (Chakraborty et al., 2014). The transition from noble-to abundant-metal organometallic catalysts will surely continue to be one of the challenges for the scientific community for the years to come (Bullock, 2010).

For reactions where adequate non-noble metal catalysts are difficult to find, an alternative strategy could be trying to minimize the utilization of such precious elements, by maximizing their performance. In a way, it could be said that the “noble-metal atom economy” is pursued in those cases (Macchioni, 2019). This can be achieved, for instance, by anchoring a well-defined molecular catalyst onto a suitable support, thus facilitating the recovery and reuse of precious catalysts.

To this aim, the most commonly and successfully used supports include silica (Baffert et al., 2011; Wu et al., 2014), organic polymers (Arakawa et al., 2008; McNamara and Hicks, 2014) and metal oxides (Kaboudin et al., 2013). Furthermore, the modification of the surrounding environment of the supported metal complex can be a good opportunity to enhance the catalytic performance of the material (Maeda et al., 2020).

Alternatively, the minimization of precious M-atoms can be achieved by diluting them in a proper porous or layered material based on earth-abundant elements, and having features that maximize M-accessibility and performance. Among the class of materials with these features, metal organic frameworks (MOFs) are surely very attractive and are receiving a lot of attention (Yoon et al., 2012; Furukawa et al., 2013; Liu et al., 2014). For example they can be used as effective porous supports for inorganic catalysts (e.g., to prevent particle aggregation) (Yang et al., 2018) but also in combination with enzymes to reproduce cellular microenvironments (Chen et al., 2018). Importantly, they can also serve directly as catalysts (Zhang et al., 2018) often favoring cooperative effects (An et al., 2019). Also layered double hydroxides (LDHs) meet the requirement to be easily doped with active metals, ensuring a high percentage of active sites, especially after their exfoliation (Fan et al., 2014; Song and Hu, 2014; Cai et al., 2019; Laipan et al., 2019). An example has been recently reported in which micro- and nano-sized iridium-doped zinc-aluminum LDHs,

containing as low as 1 wt% of noble metal, have been exploited in both chemical and electrochemical catalytic water oxidation, exhibiting excellent catalytic performances, comparable only to those of the most efficient molecular iridium catalysts, tested under similar reaction conditions (Fagiolari et al., 2020; Zaccaria et al., 2020). Many scientists are successfully pursuing both approaches to “noble-metal atom economy” that will surely be of great importance for the future.

Other challenges in which the community of catalytic organometallic chemists is likely to engage will be: 1) the development of heterogeneous stereoselective single-site catalysts (Dal Santo et al., 2012); 2) the application of organometallic catalysts in more sustainable, alternative media (Dixneuf and Soule, 2019); and 3) the development of biomimetic catalysts or structural or functional models of enzymatic catalysts (Zakzeski et al., 2010; Beller et al., 2017). These fundamental achievements are a necessary requirement for organometallic catalysis to play a significant role in the trans-disciplinary effort of the scientific community to drive the major societal transformations. In our century, characterized by the climate and energetic crises, this mostly means contributing to implement sustainable production processes based on innovative materials

(Schneiderman and Hillmyer, 2017), energy sources (Armaroli and Balzani, 2007) and chemical feedstocks (Zakzeski et al., 2010).

In conclusion, it is reasonable to think that all the conditions are in place for the future of organometallic catalysis to be as successful as in the past decades. It is also foreseeable that an important key to such success will come from the marked interdisciplinary nature of organometallic catalysis.

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The author confirms being the sole contributor of this work and has approved it for publication.

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Conflict of Interest: The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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