Editorial Catalysts: Supported Metal Catalysts and Their Applications in Fine Chemicals

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Heterogeneous catalysis is an essential tool for the development of both emerging and established chemical processes, as well as for their economic and environmental sustainability. Supported catalysts are largely used in the manufacture of a wide range of fine and specialty chemicals [1,2]. From this perspective, much effort is currently focused toward the rational design of supported catalysts by exploiting innovative approaches aimed at finely-tuning the morphological, structural and textural features of both the active phase and the support [3,4]. Towards the final goal of attaining improved catalytic processes with minimal penalty to the environment, this ambitious objective can be effectively combined with the current, fast progress of other enabling technologies. Among these innovative approaches, the use of non-conventional green reaction media or solvent-free conditions, flow-chemistry, and alternative energy-transfer techniques stand as the most promising strategies [5–9].

This Special Issue tackles some of the topics above, including examples of the development of supported catalysts for either batch or continuous-flow applications, and their use in chemo-, regio-, and stereoselective organic transformations for the synthesis of fine and specialty chemicals, as well as of non-conventional green solvents.

The selective hydrogenation of \( \alpha,\beta \)-unsaturated ketones to the corresponding saturated ketones represents a key transformation step for the synthesis of pharmaceuticals and flavors and fragrances. In this view, Cavuoto et al. [10] report highly efficient silica-supported Cu-based catalysts prepared by chemisorption–hydrolysis (CH) technique as a valid alternative to conventionally used noble metal- or Ni-based systems. Silica-based supports with different surface areas and pore volumes were studied, highlighting the role of the silica support on the efficiency of the catalyst. Moreover, an unprecedented use of heterogeneous Cu-based systems for the chemoselective reduction of \( \alpha,\beta \)-unsaturated sulfones was reported.

Benzimidazole derivatives are largely used in pharmaceutical chemistry. Peng et al. [11] report for the first time the use of \( \text{HfCl}_4 \) supported on carbon as an efficient, recyclable, and easily removable catalyst for the synthesis of 1,2-disubstituted benzimidazoles by condensation of \( N \)-substituted \( o \)-phenylenediamines and aldehydes.

Fusini et al. [12] reported Pd NPs by metal vapor synthesis immobilized on a commercially available poly(4-vinylpyridine) resin, cross-linked with divinylbenzene, as an effective and recyclable supported catalyst in air atmosphere for the Suzuki–Miyaura reaction, one of the most employed and powerful reactions for the synthesis of biaryl and alkene derivatives.

Methoxycarbonylation reactions may be key steps in the production of industrial products, such as detergents, cosmetics, and pharmaceuticals. Aikiri et al. [13] report the application of palladium complexes immobilized on MCM-41 for the methoxycarbonylation of 1-hexene to give mainly linear esters. The heterogeneous nature of the catalyst was confirmed by filtration experiments and poisoning tests, as well as its recyclability.
Glyceric acid derivatives are important biochemical intermediates, that find applications in pharmaceuticals. Wang et al. [14] describe a series of Au-based catalysts supported on mesoporous supports (transition metal oxides or mixed oxides) having different compositions and structures. The role of the support on the selective oxidation of glycerol with hydrogen peroxide to obtain glyceric acid was studied in detail.

Efficiency in the preparation of supported catalysts can be an especially demanding task when the covalent immobilization of an organic ligand is pursued. Pucci et al. [15] disclose an effective and chromatography-free route to tris(triazolyl) units covalently linked to beads or monolithic polystyrene resins. The corresponding Cu(I) complexes proved to be competent catalysts for the Huisgen 1,3-dipolar cycloaddition between azides and alkynes, both in batch and continuous-flow reactors.

On the other hand, Rossi et al. [16] explore the use of 3D printing as enabling tool in organic synthesis. They successfully describe the use of stereolithography to obtain in a cheap and highly reproducible manner 3D-printed thiourea-embedded devices, differing in shape and accessible surface. The microreactors obtained by this approach were tested in the continuous-flow, organocatalyzed Friedel–Crafts alkylation of N-Me-indole with trans-β-nitrostyrene.

Finally, Ding et al. [17] report the synthesis of propylene carbonate as alternative green solvent to be used in organic synthesis. The obtainment of the said cyclic carbonate from 1,2-propylene glycol and urea was conveniently attained by designing a hydrotalcite-derived mixed metal oxide catalysts with tailored acid/base properties.

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