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Review

Metal nanoparticles immobilized on ion-exchange resins: A versatile and effective catalyst platform for sustainable chemistry

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ABSTRACT

This paper reviews the recent achievements in the immobilization of metal nanoparticles on ion-exchange resins and the related catalytic application. The focus is on the production processes for fine and commodity chemicals for which a low environmental impact has been demonstrated. The most significant papers that appeared in the literature from January 2010 to July 2014 have been covered. Their uses in unselective processes, bulk chemicals production, fuel cells components, as well as the use of metal-free ion-exchange resins in acid / base-catalysed reactions, were not included.

1. Introduction

Due to increasingly severe regulations and economic constraints, the development of cost-effective production technology with minimal energy consumption, environmental impact and CO_2 emissions is a major drive at the global level [1,2]. This is particularly urgent in the fine chemical sector where stoichiometric reactions, toxic additives, protecting groups, sophisticated promoters and the number of processing steps required to achieve high selectivity ultimately results in the highest E-factors [3,4]. A solution is to leverage catalysis to increase resource and energy efficiency, by designing novel active materials and green processes through a smarter use of feedstocks and reagents. Among the strategies developed over the last decades, the use of chemical catalysts immobilized on insoluble materials has been preferred by industry owing to the significant benefits in terms of recover and reuse of expensive catalysts, and easier separation and purification procedures [5,6]. Solid-supported metal nanoparticles (MNP) are perfectly suited to this purpose owing to their versatility and because they mimic metal surface activation at the nanoscale, thereby bringing selectivity and efficiency to heterogeneous catalysis [7,8]. However, achieving 100% selectivity and long-term productivity at low energy costs requires careful tuning of the MNP properties, as well as of the interplay with their active environment, including stabilizers, support material and reagents [9,10]. This task is not trivial because the preparation of efficient heterogeneous MNP catalysts is often complicated by multiple issues: (i) lack of control over MNP size and distribution, (ii) lack of reproducibility, (iii) lack of stability under reaction conditions, and (iv) applicability only to specific reaction-support combinations [11,12]. Further drawbacks in MNP synthesis relate to the need of hazardous reducing reagents, toxic modifiers, harsh conditions or sophisticated equipment [13,14].

Compared with other materials, ion-exchange resins offer

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several advantages for the manufacture of supported MNP catalysts, including:

- commercial availability at low cost in various chemical compositions, ionic forms and morphology,
- satisfactory chemical, mechanical and thermal resistance,
- ease of handling and recovery,
- straightforward, non-covalent metal anchoring,
- MNP stabilization due to the dual effects of charged functional groups and porosity,
- potential to engineer bifunctional catalysts, e.g., containing metal and acid sites [15],
- facile integration into existing reactor equipment.

These favourable features explain the variety of ion-exchange resin-supported metals (MNP@resin) described in the literature and the successful application of some of those catalysis in industrial processes [16,17].

This paper reviews the recent achievements in the field of immobilization of MNP on ion-exchange resin and the related catalytic application. The focus is on the production processes for fine and commodity chemicals for which a low environmental impact has been demonstrated. The matter has been partially reviewed up to the end of 2010 [18–21]. Therefore, the present manuscript covers the most notable papers appearing in the literature from January 2010 to July 2014. Their use in unselective processes (e.g., extraction, metal recovery, pyrolysis, pollutants abatement) [22,23], bulk chemical production (e.g., H_2O_2, H_2) [24,25], fuel cell components [26,27], as well as the use of metal-free ion-exchange resins in acid / base-catalysed reactions (e.g., esterifications, hydrolysis, isomerizations) [28,29], were not included.

2. Properties of ion-exchange resins

A comprehensive description of ion-exchange resins is out of the scope of this review [30,31]. Herein a short description of the main features affecting MNP catalyst preparation and performance is provided.

Most ion-exchange resins consist of functionalized cross-linked polystyrene-divinylbenzene copolymers and are conventionally classified into two main groups (Scheme 1) [32,33]:

cation-exchange resins (with anionic functionalities and positively charged mobile ions)

- strong acid exchangers (e.g., containing sulfonic acid groups or the corresponding salts)
- weak acid exchangers (e.g., containing carboxylic acid groups or the corresponding salts)

anion-exchange resins (with cationic functionalities and negatively charged mobile ions)

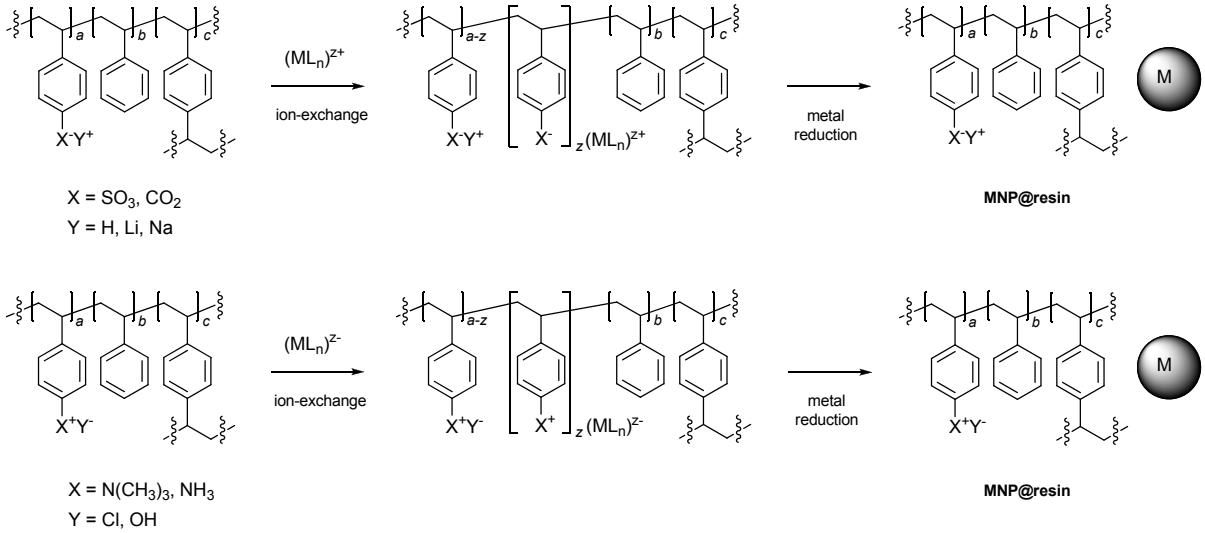
- strong base exchangers (e.g., containing quaternary ammonium groups)
- weak base exchangers (e.g., containing ammonium groups)

Other ion-exchanging materials include acrylic resins [34] and perfluorinated chain polymers bearing sulfonic acid heads, like Nafion® [35] and Aquivion [36].

Cross-linking, typically from 0.5% to 20%, controls resin porosity with low and high cross-linked resins having a gel (microporous) and macroporous structure, respectively [37,38]. In turn, porosity regulates some of the resin properties affecting their catalytic application: swelling, exchange capacity, equilibration rate, and selectivity. Usually, the lower the cross-linking, the higher the moisture content, equilibration rate, loading capacity (typically 1.5–10 meq/g on a dry basis) and the ability to accommodate larger ions.

Swelling of microporous resins is crucial for their catalytic activity. Swelling volumes up to 800% have been found for low cross-linked resins, either in water or methanol [39,40]. Gel type resins are thus generally preferred over macroporous resins owing to better active-sites accessibility to the reactants in solution [41]. However, internal (diffusive) mass transfer limitations, and pressure drops in the case of flow processes [42,43], are usually lower for macroreticular resins [44,45].

The number, type and strength (e.g., acidic) of the functional groups have a direct consequence on both the ease of MNP growth within the resins (see section 3 "Synthesis") and the activity of the MNP@resin catalysts (see section 4 "Application"). Functional groups are crucial in determining site-inhibi-



Scheme 1. Schematic representation of MNP immobilization on cation (top) and anion (bottom)-exchange resins.