

Porous Polymer Scaffolds for the Design of Functional Hybrid Materials and Sustainable Metal Catalysts

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Abstract

This mini-review focuses the attention on the use of nanoporous organic polymers as support of inorganic nanoparticles for the design of metal catalysts active in organic synthesis. The porosity of the support enhances the performance of the metal catalyst, concentrating the reactants at the catalytic sites as a novel example of confined catalysis. Noteworthy metal nanoparticles embedded in nanoporous polymer support have been processed under the form of powder, membrane and monolith in which they found application in batch catalysis and flow chemistry, providing targeted examples of sustainable and green reaction pathways.

Keywords: Polymer; Nanomaterials; Metal catalysts; Nanoporous

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Introduction

Hybrid nanomaterials are one of the most intriguing, stimulating, and exciting research fields in material science and heterogeneous catalysis [1]. These systems typically consist of an organic phase, a host polymer matrix or small guest molecules, compounded with an inorganic material to produce a functional structure defined at a nanometric scale. Two of the most representative examples are inorganic nanoparticles dispersed in an organic polymer phase and functional organic molecules trapped in porous scaffolds (e.g., MOF or zeolites) [2,3]. They are often characterized by extraordinary physical and chemical properties resulting from a synergistic effect of the two phases interacting throughout weak (Coulomb forces, London dispersion forces, hydrogen bonds, dipole-dipole forces, π - π stacking) or strong (Lewis acid-base, covalent, or ionic covalent bonds) chemical bonds; the final properties often differ significantly from those of a simple mixture of the two or more components. Innovative advanced hybrid nanomaterials have thus found a considerable variety of practical applications in Medicine [4,5], Optics [6], Electronics [7], Sensors [8], energy conversion and Storage [9], Mechanics [10], Membranes [11], and finally, in Catalysis [12].

In the latter contest, Metal Nanoparticles (MNPs) embedded/stabilized by polymer scaffolds are emerging as a powerful tool in heterogeneous catalysis to design reusable metal catalysts suitable for a wide range of chemical reactions of interest for industry or fundamental studies [13]. At first sight, organic polymers fare worse than classical inorganic supports such as carbon materials (amorphous carbon, graphene, carbon nanotubes) [14], Metal Oxides (Titania, Ceria, Nano-Silica) to stabilize MNPs vs their aggregation and leaching because of lower thermal stability and worse performances under harsh reaction conditions (elevated reaction temperature; use of strong oxidant or reducing agents; swelling in organic solvents).

However, they offer several practical advantages:

- (i) The hydrophilic and hydrophobic properties of the support can be tuned by appropriate functionalization of the surface, making the catalyst impregnable in solvents

or organic reagents with different polarity;

(ii) Functional groups containing donor atoms can be introduced via common organic reactions to stabilize the MNPs;

(iii) Covalent functionalization of the support with Brønsted acid and base functionalities allows modulation of the pH of the reaction medium, making unnecessary the further addition of acids or bases often required for the catalytic performances;

(iv) Processing of the polymer matrix via conventional procedures allows for the production of the catalysts under the form of films, beads, and foams adequately addressed to the reactor design making easy also the application of these metal catalysts in flow chemistry [12,15,16].

An interesting case is that of Porous Organic Polymers (POPs), that can be obtained via different synthetic approaches among which some representative examples are sketched in (Figure 1).

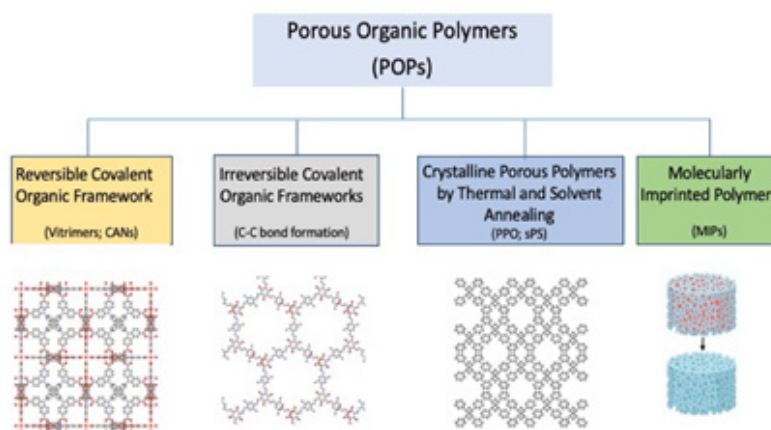


Figure 1: Synthetic pathways leading to the formation of porosity in polymer scaffolds.

POPs make possible, when hosting catalytically active MNPs, multifunctional confined catalysis mimicking the active pocket in enzymatic catalysis (Figure 2) [13]. When large pores, such as macropores and mesopores, are produced, the enhanced specific surface area allows good permeability of the reagents penetrating

the pores and having access to the metal catalyst site. In contrast, nanoporous polymer supports afford a larger specific surface area but lower accessibility to the pores, making possible size selectivity. Both these features allow the design of efficient catalytic processes.

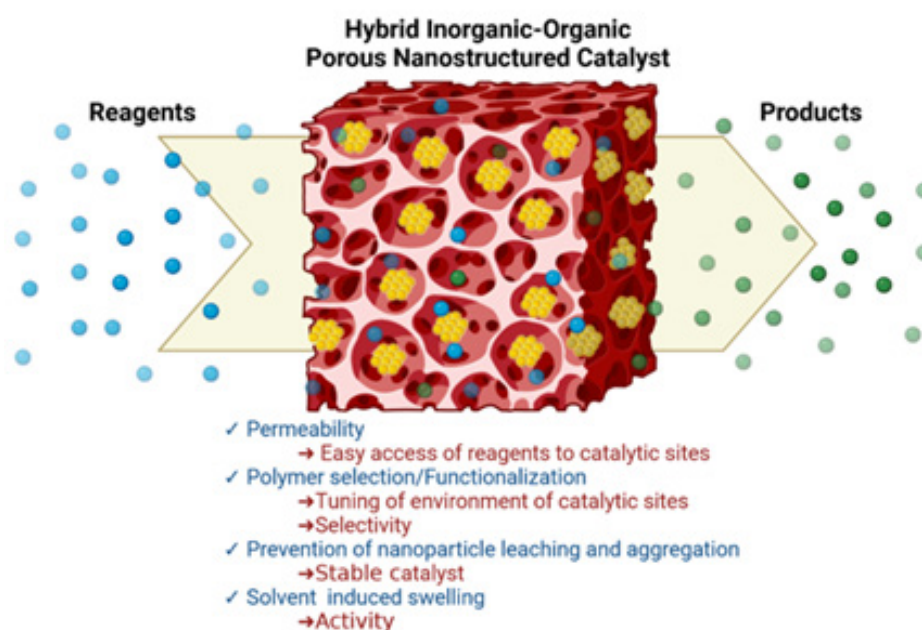


Figure 2: Depiction of chemical transformation promoted by inorganic nanoparticles supported by porous organic polymers.

Survey Methodology

The authors used Scopus, Web of Science, and Google Scholar platforms to search for relevant documents published before April 2023. The keywords used were: “hybrid nanomaterials”, “porous polymer-supported metal catalysts” and “porous polymer-supported gold nanoparticles”. The documents that provided significant advancements or insights on the application of porous polymer-supported metal catalysts were further considered and reviewed. The patents were excluded from the study.

Porous Polymer-Supported Inorganic Nanoparticles

Gold Nanoparticles (AuNPs) currently stand out as very promising candidates in aerobic oxidation catalysis [17-19].

AuNPs incarcerated in crosslinked amorphous polystyrene matrix (AuNPs-PI) resulted very effective in alcohol oxidation to carbonyl derivatives in the presence of Brønsted bases under mild conditions ($T=298\text{K}$; $P_{O_2}=1\text{ bar}$) [20]. A zero-order kinetics for the alcohol to be oxidized, and an induction time of 15min were both observed and interpreted as the confirmation of diffusion-controlled kinetics resulting from the slow permeation of the alcohol through the amorphous phase of the polymer support [21]. Interestingly, AuNPs embedded in porous crystalline polystyrenic matrix (AuNPs-sPSB) with a specific area of $4\text{-}24\text{m}^2/\text{g}$ and nanopore size of $\approx 2\text{nm}$ showed (Figure 3), under the same conditions, no induction time and first-order kinetics in alcohol oxidation to prove the ready accessibility of the reagent to the metal catalyst determining higher catalytic activity [22].

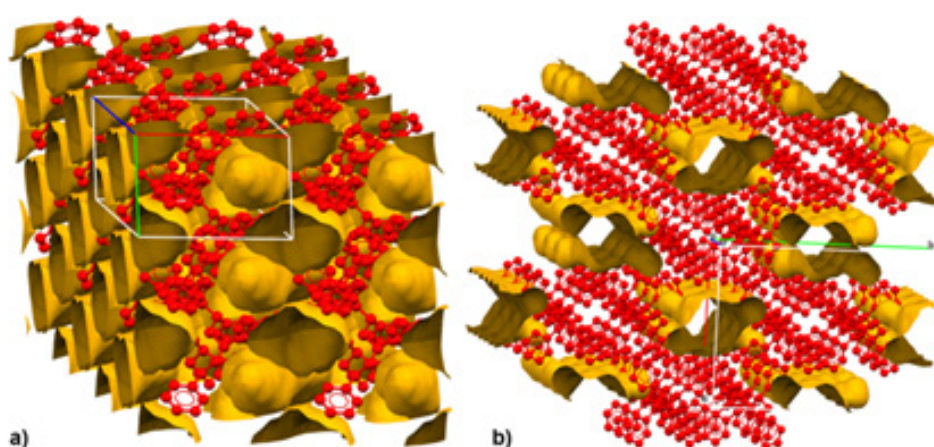


Figure 3: Nanoporous crystalline forms of syndiotactic polystyrene: δ (a) and ϵ (b) forms, respectively, with isolated voids and nanochannels highlighted.

Noteworthy, high selectivity in alcohol oxidation was also assessed. Aliphatic alcohols, which do not penetrate the cavities and channels of the crystalline polymer phase, showed zero-order kinetics and lower oxidizability than the alcohols that this can do. Following these findings, aerobic oxidative esterification of Cinnamyl Alcohol (CA) [23] and 2,5-Hydroxymethyl Furfural (HMF) [24] to the corresponding alkyl esters was successfully obtained. Cascade reactions are one the main sustainable approach in organic synthesis where the reaction product of the first reaction feeds the subsequent reactions, carried out in the same batch reactor, without the need of isolation and purification steps of the products. The selective oxidation of the hydroxy functionality of CA and HMF in the presence of alkyl alcohols such as methanol, 1-butanol, 1-hexanol that are not oxidized, produced cinnamaldehyde or of 2,5-diformylfuran in the first reaction step; the nucleophilic attack of the alkyl alcohol to the carbonyl of the aldehydes, followed by a further oxidation of the resulting emiacetal intermediate produced alkyl cinnamates and dimethyl furan-2,5-dicarboxylate in high yields and excellent selectivity without observing the formation of cinnamic acid and 2,5-furandicarboxylic acid. Also in this case the kinetic order is e.g. zero for the alkyl alcohol and first-order for CA

[24].

The above-mentioned gold catalyst AuNPs-sPSB porous was successfully applied in the intermolecular hydroamination reaction of anilines with phenylacetylenes in high yields and with excellent regio- and stereo-selectivity. The performances of the AuNPs-sPSB catalyst exceed those of the other commercial gold catalysts because of the nanoporous polystyrenic support which allows excellent activity, thermal stability and recyclability of the catalyst. The study of the reaction mechanism, carried out via kinetic investigation supported by DFT modelling, allowed determining interesting features of the hydroamination reaction pathway [25]. On the same topic AuNPs embedded in a highly porous poly(2,6-dimethyl-1,4-phenylene) (PPO) matrix, with a specific area of $4\text{m}^2/\text{g}$, better performed in benzyl alcohol oxidation. The reaction of benzyl alcohol with oxygen at atmospheric pressure afforded benzoic acid (selectivity $>98\%$; $\text{TOF}=2.45\text{ mol}_{\text{Alcohol}}/\text{mol}_{\text{Au}}\text{h}$) or benzaldehyde (selectivity $>99.9\%$; $\text{TOF}=0.80\text{ mol}_{\text{Alcohol}}/\text{mol}_{\text{Au}}\text{h}$) depending on the presence or absence of water in the reaction media [26]. Photocatalytic hydroxylation of benzene to phenol in presence of H_2O_2 oxidant has been studied using a photoreactive polymer composite based on N-doped TiO_2 (N-TiO_2) embedded

into a monolithic syndiotactic polystyrene aerogel (N-TiO₂/sPS, 10/90w/w). The polymer incarcerated N-TiO₂ showed higher phenol selectivity (98%) and yield (57%) compared to bare N-TiO₂ under visible light in acidic conditions (pH=2). The N-TiO₂/sPS catalyst was recovered from the aqueous solution containing the reaction products and reused several times without significant loss of photo reactivity. This example represents a “proof of concept” of innovative green processes for the selective oxidation of aromatic hydrocarbons under mild conditions using a porous polymer-embedded TiO₂ catalyst [27].

AuNPs were produced in crosslinked Polymeric Inclusion Membranes (PIMs) and Polymeric Nanoporous Membranes (PNMs) composed of cellulose triacetate, 2-nitrophenol octylether and Adogen 364 or Alamine 336 (tertiary amines); the average size of the AuNPs was of 37nm for PIMs and 2.9nm for PNMs. These gold catalysts allowed the reduction of 50 μM aqueous solution of 4-nitrophenol within 25min (PIMs) and 120min (PNMs) using NaBH₄ as a reductant. These results rival those of the most efficient gold catalyst under batch conditions suggesting that the porous polymer support can produce an efficient catalyst under the form of a polymeric membrane [28]. Palladium Nanoparticles (PdNPs) of average size in the range of 6.6-13nm were successfully prepared using porous starch with a surface area of 177m²g⁻¹ and average pore size of 8.2nm. A Pd content between 2.5 and 3 wt% was found to be the optimum for the balance of desirable textural properties and catalytic activity. The starch-supported PdNPs catalysts were tested in the microwave-assisted Heck of iodobenzene with methylmethacrylate and styrene, Suzuki reaction of benzene boronic acid with bromobenzene, and Sonogashira reaction of bromobenzene with phenylacetylene. In all tested reactions, the starch-supported PdNPs performed better than the PdNPs supported on silica. The properties of the PdNPs are reflective of the unique porous environment that these novel polysaccharide-derived porous materials provide, allowing access to a wide range of surface chemistries, thus facilitating the preparation of metal nanoparticles of controllable size and nature. This palladium catalyst is also reusable, preserving the catalytic activity after four reuses [29].

Heterogeneous catalysis usually occurs at the surface of small MNPs. Despite the high surface area to volume ratio, only a few of the metal atoms are catalytically active, determining a reduced metal atom utilization, lower than that of homogeneous molecular catalysts where typically 100% of the metal atoms are active in the catalytic process, a figure that may be orders of magnitude higher than that of heterogeneous catalysts [30,31]. To overcome this drawback, one of the emerging research areas at the cutting edge in heterogeneous catalysis is the Single-Atom Catalysis (SAC), where the reusability of the metal catalyst is preserved along with the high metal atom utilization [10,11]. The increase of the metal atom utilization value of a catalyst is particularly important for heterogeneous catalysts based on platinum group metals (PGM) such as Pd, Pt, Rh, Ir or Ru. A spectacular example of SAC applied in sustainable catalysis is that of Ir embedded in a porous polyamine

scaffold applied in CO₂ reduction [32]. A porous organic polymer with aminopyridine functionalities (AP-POP), with mesopores having an average size of 7.6nm and a surface area of 43m²/g, was designed to fabricate a stable, atomically dispersed Ir catalyst. This Ir-based SAC exhibits excellent catalytic activity during the liquid phase hydrogenation of CO₂ to formate, with a TON value as high as 25,135, representing the best performance for a heterogeneous conversion of CO₂ to formate and well compare the best Ru and Ir homogenous catalysts in the field. The chemical structure of the Ir-SAC is analogous to that of a homogeneous mononuclear catalyst, representing an intermediary between heterogeneous and homogeneous catalysis [32].

Conclusion

The above reported selected examples aim to highlight and substantiate the peculiar properties of the inorganic nanoparticles embedded in porous polymer matrices. These hybrid nanomaterials have been prepared under the form of powder, fiber, membrane, monolith and applied in differ fields of sustainable catalysis showing high catalytic activity, selectivity and thermal stability. Moreover, they were applied in batch condition, or under the form of membrane and monolith in flow chemistry, with conventional heating or microwave irradiation, providing moderate to excellent performances. In our opinion, some of the above cited examples pave the way to novel research fields in catalysis that until a few decades ago seemed to be a peculiar prerogative of porous inorganic supports such as mesoporous silica, zeolites, MOF and others. The careful choice of the porous polymer support and of the inorganic counterpart, the tuning of their morphology and chemical physical properties, the identification of the optimal reaction conditions, all concur to valorize these hybrid nanomaterials in catalysis determining high activity and selectivity in organic transformation of relevance for industry, even disclosing novel reaction pathway, unconceivable with conventional catalytic systems.

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