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Functional resins as innovative supports for catalytically active metal nanoclusters

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Functional resins are plausible candidates for supporting catalytically active metal nanoclusters alternative, or complementary to conventional supports such as amorphous carbon, metal oxides, zeolites. Mechanical and thermal stabilities are fair and perfectly suitable to application in the realm of fine chemistry. The polymer framework turns out to be a designable template for controlling nanoclusters size and size distributions.
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1. Introduction

Supported metal catalysis is a pivotal tool in modern chemical industry [1–3]. With the remarkable exception of amorphous carbon, currently employed supports are inorganic materials and the traditional role attributed to the supports is the dispersion and stabilization of metal nanoclusters systems deputed to the electronic activation of the employed reagents. However, in recent years the chemical role of the support as a tool for controlling both overall reactivity and selectivity [4] started to become more and more apparent to such an extent to let the support be considered a real promoter of catalytic efficiency [5].

A little group of industrial synthetic technologies [6,7] illustrate the ability of organic resins to act as efficient supports able to exploit the fine chemical action of supported metal nanoclusters towards *multifunctional catalysis*.

We have been exploring in the last 10 years [8] the potential role of functional organic supports in the design of innovative catalysts. In this connection, we like to stress that new-generation resins-based metal catalysts might well be economically convenient in the realm of fine and speciality chemicals [9] and a first-sight complexity of a novel unconventional catalyst has to be judged in the appropriate context.

In fact, in conventional supported metal catalysts, the support is typically an inorganic microphase with

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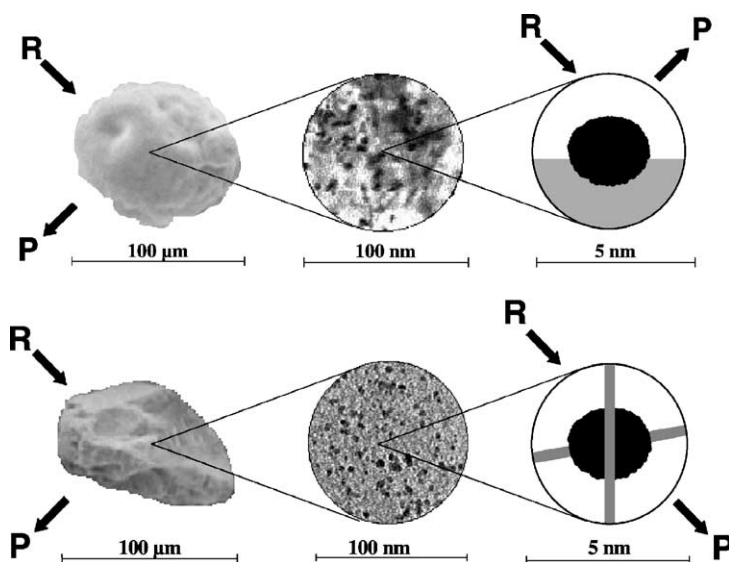*E-mail address:* benedetto.corain@unipd.it (B. Corain).

Fig. 1. Metal catalysis on inorganic supports vs. metal catalysis inside an organic polymer framework.

defined physical and physico-chemical features, being its chemical ones controllable only to some extent. On the contrary, in the case of resins-supported metal nanoclusters, support particles are organic swellable microphases, the physical, physico-chemical and chemical features of which being quite designable and controllable in nature (see Section 2; [8]; Fig. 1).

Thus, reagents involved in a given metal-catalyzed reaction must be able to enter the microreactor (size selectivity), in which they will meet a liquid medium (e.g. a mixture of two different solvents), the composition of which may be quite different from that they experience in the bulk of the reaction medium. Moreover, the kinetics and the thermodynamics of the catalyzed reaction might be significantly different from those existing in the bulk medium itself [8] and even the concentration of the reagents inside the microreactors may be quite different from that existing in the bulk. Consequently, functional resins-supported metal catalysts have to be considered innovative catalysts, in which the support is able to exert promotion or co-catalytic actions that are not so easy to achieve in the case of conventional metal catalysts supported by metal oxides and amorphous carbon, under gas–liquid conditions. A clear illustration of this reasoning was recently offered by the highly chemoselective hydrogenation of 2-ethylanthraquinone to 2-ethylanthrahydroquinone

performed with palladium metal supported on very lipophilic resins, in these laboratories [10] (see later).

2. Why functional resins: chemical and physico-chemical aspects

Resins are isotropic materials, brittle in nature, built with macromolecular chains chemically interconnected by covalent bonds or particularly effective hydrogen bonds or physically interconnected thanks to a thorough entanglement of the same polymer chains. Synthetic resins are typically functional ones, i.e. built with polymer chains bearing molecular pendants aimed at performing a chemical task. FR's exhibit two major micro- and nanoscale morphologies that let them to be classified as microporous (gel-type) and macroporous (macroreticular) [11].

Gel-type resins do not possess any porosity in the dry state (glass-like). They develop an extensive nanoporosity in the swollen state that is the working state of these materials.

Macroreticular resins do possess a microporosity in the dry state. They develop also a certain nanoporosity in the swollen state that is the working state of these materials (Fig. 2).
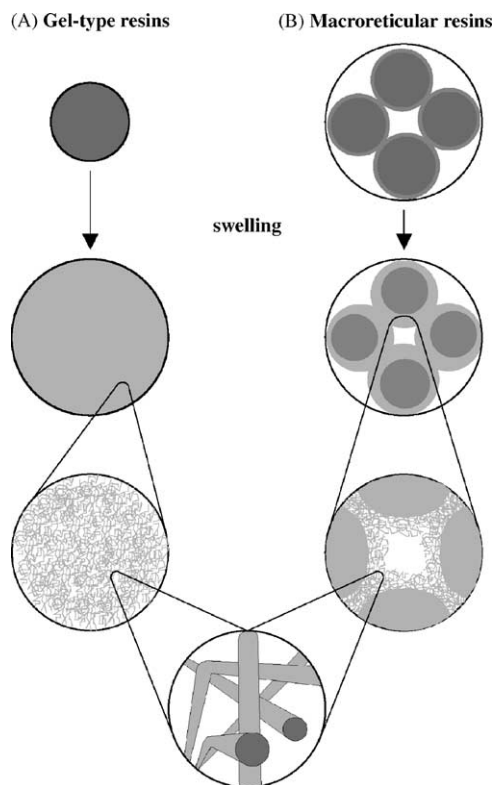
Fig. 2. Schematic representation of the micro- and nanoscale morphology of gel-type and macroreticular resins.

The chemical functionality of FR's is a major molecular tool for controlling a pivotal aspect of their utilization, i.e. their swelling ability in proper fluid media [8,11]. Upon switching from polar to unpolar pendants, specific swelling volume changes dramatically [12] with paramount consequences in chemical utilization of FR's. Pendants play also a critical role in enabling the anchoring of desired metal centres and, consequently, in the dispersion of metal nanoclusters in the body of the FR's particles (see Section 3). Moreover, as anticipated in Section 1, pendants may act in such a way to appreciably modify the thermodynamics [8] and the kinetics [8] of a reaction let to occur in the swollen resin domains, compared with its occurrence inside bulk solvent.

Two other chemical and physico-chemical features of FR's are to be recognized and properly considered and, in case, exploited, i.e. porosity and thermal stability.

The overall nanoporosity of gel-type FR's (Fig. 2) can be reasonably modulated upon controlling resins cross-linking degree [8,12–14] and, consequently, the accessibility of the interior of the microreactor (Fig. 1) may be finely controlled. The same holds for macroreticular reins, the porosity of which can be finely controlled on the basis of synthetic expedients [11].

Finally, somewhat surprisingly for an organic material, the thermal stability of FR's turns out to be quite significant up to 300–400 °C [15] as widely confirmed in these laboratories for polyacrylic resins, under nitrogen.

3. Our contribution to resins synthesis and to physico-chemical characterization

In the frame of our endeavour to resins-supported metal catalysts we found a great benefit in employing γ-rays initiated (and sustained) polymerization of acrylic co-monomers in the presence of suitable cross-linking agents [8]. An overall view of the conditions employed for obtaining the majority of our resins is made possible by Table 1.

Resins are typically built up with a structural co-monomer (DMAA or STY) and with a functional one (e.g. SEMA, MA; Table 1).

Polymerization yields are usually higher than 95% and the scope of the potential combination of relevant co-monomers is only limited by the need of their mutual miscibility at the start of the polymerization process.

Irradiation is carried out at room temperature so that the transformation of the initial solution into a more and more viscous fluid up to the eventual solidification is expected to occur with convenient graduality in order to reduce structural inhomogeneity. Obtained resins after grinding, washing and sieving (180–400 μm), appear as glassy colourless materials that are used as irregularly shaped particles.

In recent years [13–16] we developed a multi-methodological approach to the evaluation of nanostructure and molecular accessibility of gel-type resins in their swollen state. In fact, inverse steric exclusion chromatography (ISEC) [17,18], ESR evaluation of rotational mobility [19] of the spin probe 2,2, 6,6-tetrametyl-4-oxo-1-oxyl-piperidine (TEMPONE)

Table 1
Gel-type resins synthesized as model supports or as actual supports of catalytically active palladium nanoclusters

Entry (code)	DMAA (%)[a]	SS-Na$^+$ (%)[b]	MA (%)[c]	HEMA (%)[d]	SEMA-K$^+$ (%)[e]	SEMA (%)[f]	STY (%)[g]	MBA (%)[h]	DVB (%)[i]	Solvent (%)
P4N	68	28	–	–	–	–	–	4	–	Water (68% w/w)
M4K	65	–	–	–	31	–	–	4	–	Water (35% w/w)
M4A	70	–	–	–	–	26	–	4	–	Water (35% w/w)
M1–M8	99–92	–	–	–	–	–	–	1–8	–	None
P8N	66	26	–	–	–		–	8	–	Water (40% w/w)
SS1MH	–	–	–	–	–	22	77	1	–	None
SS2MH	–	–	–	–	–	22	76	2	–	None
SS3MH	–	–	–	–	–	22	75	3	–	None
SS6MH	–	–	–	–	–	22	72	6	–	None
SPI	92	–	–	–	–	4	–	4	–	None
MPI	92	–	4	–	–	–	–	4	–	None
HPI	92	–	–	4	–	–	–	4	–	None
M2GB	–	–	–	–	–	4	94	–	2	DMSO (30% w/w)
M4GB	–	–	–	–	–	4	92	–	4	DMSO (30% w/w)
A1–A9	95–87	–	–	–	–	4	–	1–9	–	DMF (10% w/w)
AH	33	–	–	–	–	26	37	4	–	DMF (10% w/w)
BH	–	–	–	–	–	18	78	4	–	Idem
CH	–	–	–	–	–	37	58	–	5	Idem
DH	–	–	–	–	–	17	78	–	5	Idem

[a] *N,N′*-Dimethylacrylamide.

[b] Styrene sulfonate sodium form.

[c] Methacrylic acid.

[d] Hydroxyethylmethacrylate.

[e] Sulfoethylmethacrylate potassium form (i.e. methacryloylethylensulfonate (K$^+$)).

[f] Sulfoethylmethacrylate (i.e. methacryloylethylensulfonate (H$^+$)).

[g] Styrene.

[h] *N,N′*-Methylenebisacrylamide.

[i] Divinylbenzene. % mol/mol, unless otherwise stated.

and pulse field gradient spin echo nuclear magnetic resonance (PGSE-NMR) [13,14] (evaluation of translational mobility of solvents molecules) are found to provide interrelated and convergent pictures of morphology and molecular accessibility at the nanometer level (Fig. 3).

Our overall results provide a robust support to information stemming from various laboratories [20] that permit to depict swollen frameworks as more or less viscous "solutions" of interconnected polymer chains, inside which functional pendants or supported metal nanoclusters are molecularly accessible to given reagents and consequently able to perform chemical work. This unusual feature coupled with reasonable mechanical, thermal and chemical [21] stabilities render functional synthetic resins quite respectable *supports for innovative metal catalysis*.

4. Functional resins as templates for the production of size-controlled metal nanoclusters

For a number of important reactions, the control of the size of catalytically active metal nanoclusters is essential to control chemical selectivity [22] and also activity, especially in the case of gold nanoparticles [23,24]. Metal nanoclusters are presently prepared in solution along a number of synthetic procedures [25] outside any understandable a priori criterion for size control. This feature is however subsequently controlled by various means, i.e. ionic surfactants, soluble polymers, a peripheral layer of suitable ligands [25].

The approach proposed by our laboratories (Fig. 4) is conceptually quite different and relays on the production of individual metal atoms *inside* a metallated functional resin particle.
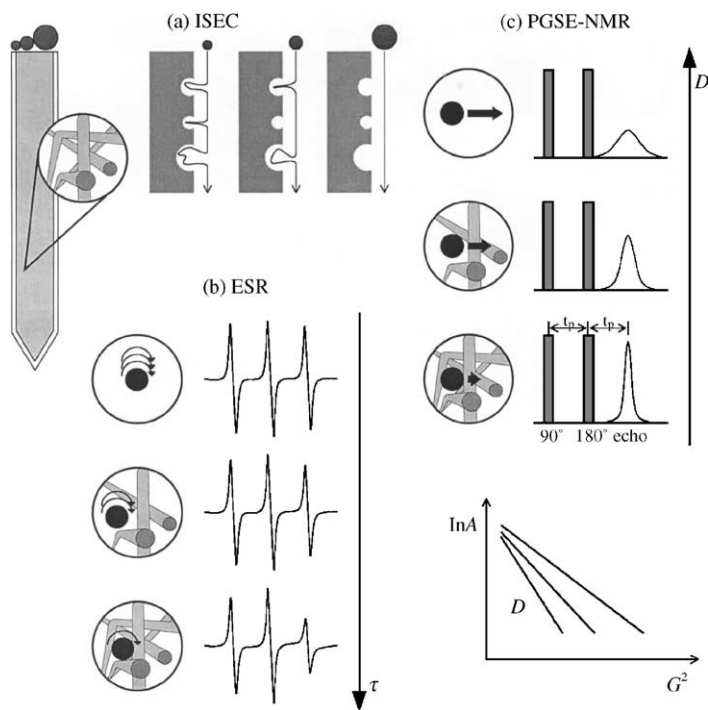
Fig. 3. Expected conceptual interrelation among ISEC, ESR, PGSE-NMR information relevant to catalytic activity of a swollen resin-based metal catalyst.
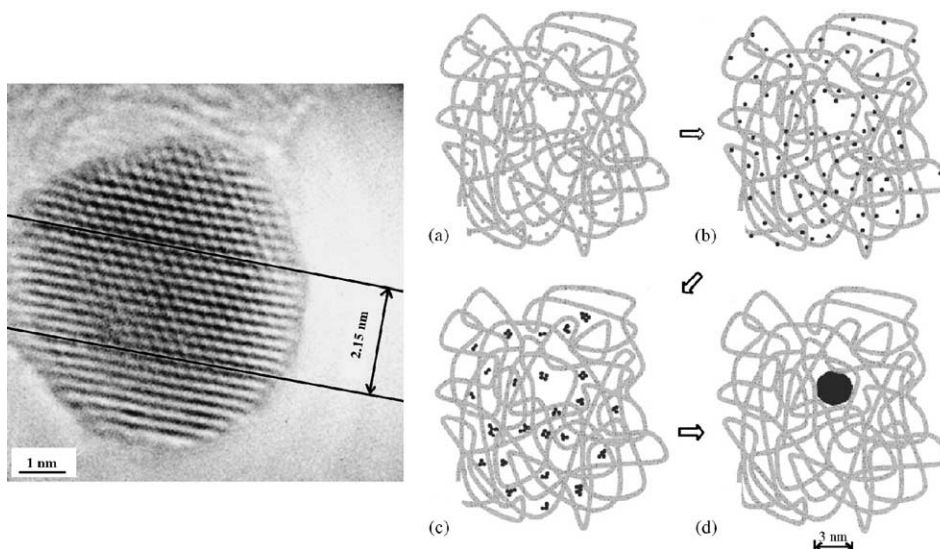

Fig. 4. HRTEM of a relatively large Pd nanocluster generated upon reduction of resin-bound Pd^{2+} to Pd^0 (left) [28] and generation of size-controlled metal nanoparticles inside metallated resins (right). (a) Pd^{2+} is homogeneously dispersed inside the polymer framework; (b) Pd^{2+} is reduced to Pd^0; (c) Pd^0 atoms start to aggregate in subnanoclusters; (d) a single 3 nm nanocluster is formed and "blocked" inside the largest mesh present in that "slice" of polymer framework [27,28].

The reactive single atoms move rapidly inside the polymer framework to give metal nanoparticles, the size of which is expected to be limited by support nanoscale morphology. Recent work from these laboratories [26–29] does clearly show that this is the case and 2–4 nm palladium nanoclusters are regularly obtained inside 2–6% (mol/mol) cross-linked gel-type resins (Fig. 4).

5. Catalytic prospects of resins-supported metal catalysts

In addition to the first commercially exploited synthesis of methylisobutilketone [6,7] catalyzed by Pd nanoclusters supported on a strongly acidic ion exchanger, resins-supported metal nanoclusters result to be active in a number of model or tecnologically relevant organic reactions (Schemes 1 and 2).

From Schemes 1 and 2 it can be appreciated that these innovative catalyst exhibit a manifold action. In addition to classical hydrogenation of isolated C=C bonds, they catalyze the hydrogenation of acetylenes, carbonyl compounds, dienes, nitroaromatic compounds, NO_3^- and NO_2^- ions, anthraquinone, dioxygen in water from the parts per million to the parts per billion levels [7]. The chemoselective hydrogenation of EAQ to H_2EAQ [10] should be stressed as a paramount example of proper design of the supporting resin matrix.

Entry	Reaction	Catalytic system[a]
1	Hydrogenation of nitroaromatics compounds to the corresponding amines	P4N/Pd^0
2	Hydrogenation of nitroaromatic compounds to the corresponding amines	M4K/Pd^0
3	Hydrogenation of cyclohexene to cyclohexane	SS1MH/Pd^0
4	Hydrogenation of cyclohexene to cyclohexane	SS3MH/Pd^0
5	Hydrogenation of cyclohexen-1-one to cyclohexanone	AH/Pd^0
6	Hydrogenation of cyclohexen-1-one to cyclohexanone	BH/Pd^0
7	Hydrogenation of cyclohexen-1-one to cyclohexanone	CH/Pd^0
8	Hydrogenation of nitroaromatic compounds to the corresponding amines and reduction of aqueous NO_3^- and NO_2^- to N_2.	D4/Pd^0
9	Hydrogenation of nitroaromatic compounds to the corresponding amines	D8/Pd^0
10	Reduction of aqueous NO_3^- and NO_2^- to N_2. D	A4/Pd^0
11	Hydrogenation of 2-ethylanthraquinone (EAQ) to ethylanthrahydroquinone (H_2EAQ)	PDMA MAA/Pd^0

[a]For coding see Table 1.

[b]PDMA MAA = poly-dodecylmethacrylate-methacrylic acid-ethylene dimethylacrylate

Scheme 1. Selection of reactions catalyzed by resins-supported Pd and Pt tested in these laboratories.

Process	Catalyst	References
	Bayer catalyst OC 1038 Strongly acid macroporous resin "doped" with metal palladium dispersed as nano clusters inside the polymer framework	[6, 30]
	idem	[6, 30]
	Bayer catalyst K 6333 and VP OC 1063	[7]
Selective hydrogenation of alkadienes and alkynes to monoenes	Heterocyclic polyamides/Pd	[31]
Selective hydrogenation of cynnamaldehyde to cynnamyl alcohol	Macroporous polystyrene/Pt	[32]
Hydrogenation of allylic alcohol to propanol	Polystyrene microsphere/Pt Polystyrene grafted with poly(N-isopropyl acrylamide)/Pt	[33]

Scheme 2. Selection of reactions catalyzed by resins-supported metal nanoclusters [31–33].

6. Conclusions

Activity and selectivity [10] of innovative catalysts based on metal nanoclusters supported on designable functional resins appear to be prominent and promising. Mechanical stability and re-usability are also very promising [29]. Multifunctional catalysis appears to be quite feasible as in the well-illustrated case of methylisobutylketone synthesis [6,30].

Acknowledgements

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