

Review

# Dispersing metal nanoclusters inside functional synthetic resins: scope and catalytic prospects

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## Abstract

The use of functional resins as designable supports for metal nanoclusters [G. Schmid, G.L. Hornyak, *Current Opinion in Solid State and Material Science* 2 (1997) 204; G. Schmid, M. Baumle, M. Geerkens, I. Heim, C. Hoseman, T. Sawitowski, *Chem. Soc. Rev.* 28 (1999) 179; J.D. Aiken III, R.G. Finke, *J. Mol. Catal. A: Chemical* 145 (1999) 1] is reviewed, with emphasis on few existing brilliant industrial applications and on the relevant rationale able to boost far more extensive utilizations of these metal/resins composites. The authors' experience in the field is reviewed with regard to resin metallation procedures, to metal ion reduction protocols and to the controlled generation of metal nanoclusters. Moreover, the authors' experience in the evaluation of nanomorphological features of the polymer networks and of its accessibility to molecules of given size is outlined. Prospects in the exploitation of this type of catalysts in the selective hydrogenation processes are briefly described on the basis of results from these and other laboratories. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Metal nanoclusters; Functional resins; Catalysis; Nanomorphology; Accessibility

## 1. Introduction

Macroporous (or macroreticular) and microporous (or gel-type) functional resins (present in the market mostly as polystyrene cross-linked with divinylbenzene) are isotropic materials formed by chemically interconnected polymer chains, normally insoluble in any conceivable solvent. In general, however, strong hydrogen bonding and the mutual entanglement of poly-

mer chains (“physical cross-linking”) may also contribute to the practical insolubility of these materials. They differ significantly in their chemical composition and largely in their micro- and nanostructure. Gel-type resins are usually 2–8% cross-linked, while the macroporous ones are 8–20% cross-linked materials and are normally synthesized in the presence of porogenic components [1]. In the dry state, gel-type materials do not possess any porosity, but they develop an extensive nanometer scale “porosity” (hereafter referred to as nanoporosity) in the swollen state. On the contrary, macroporous resins do possess a permanent micrometer scale

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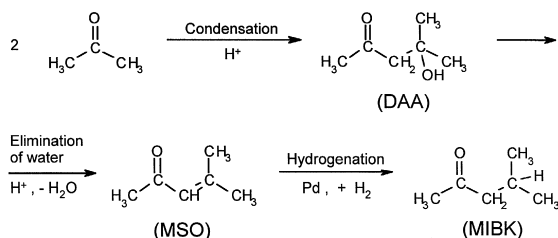
porosity even in the dry state (hereafter referred to as macroporosity), which supplements in the swollen state the nanoporosity developed by the swelling process. In chemical applications, they are used as beads (0.2 to 1.25 mm) or powders in fixed-bed reactors or suspension reactors (often operated batchwise) or more frequently in flow-through reactors [2,3]. The working temperatures range is from room temperature up to about 120°C. The mechanical strength of these solids is relatively poor, but this drawback can be managed by means of various technical solutions [4].

The macro- and nanomorphological aspects of these materials have been reviewed in the literature in recent years [2–6] and we will simply recall some of them when required by the specific subject of this work.

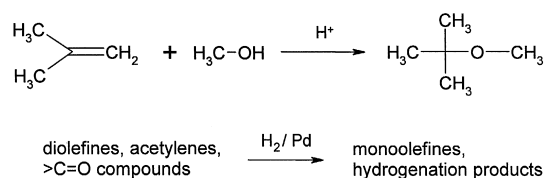
## 2. Resin-based industrial metal catalysts

In the mid-1970s, Deutsche Texaco commercialized a convenient process for the industrial synthesis of methyl isobutyl ketone (MIBK) [7,8], a semicommodity produced on the hundreds of thousands tons scale worldwide [9,10] and currently utilized as industrial solvent (Scheme 1).

The three-step synthesis is catalyzed by a strongly acidic synthetic macroporous resin “doped” [9] with metal palladium dispersed as crystallites inside the polymer network (Bayer catalyst OC 1038, acetone, 30 bar, 130–140°C). The first two synthetic steps would lead to an equilibrium mixture in which only 17% of



Scheme 1. Industrial synthesis of methyl isobutyl ketone (MIBK). DAA — diacetone alcohol, MSO — mesityl oxide.



Scheme 2. Synthesis of methyl-*tert*-butyl ether with parallel hydrogenation of diolefins, acetylenes and carbonyl compounds.

MIBK would be produced. However, the co-presence of the metal polydispersed phase promotes the regioselective hydrogenation of mesityl oxide to give the desired product. This elegant technical solution produces excellent yields and convenient reaction times.

Catalysts of this type are also employed in modern plants [9,10] for the synthesis of MTBE (Scheme 2), the well-known important additive in the production of lead-free gasoline. In fact, the C<sub>4</sub> fraction coming from the traditional MTBE reactor (primarily butene-1, butene-2 and saturated C<sub>4</sub> hydrocarbons, “raffinate II”) turns out to be contaminated by appreciable amounts of diolefins, acetylenes and carbonyl compounds. These compounds can cause considerable troubles during the subsequent transformations of raffinate II and they can be readily eliminated upon hydrogenation in the same MTBE reactor, if these remarkable catalysts do not catalyze the hydrogenation either of isobutene or of butene-1 and butene-2.

It is also worth mentioning the process for the etherification–hydrogenation of mixtures of unsaturated hydrocarbons to give blends of alkanes and branched ethers for the manufacture of unleaded petrol (BP Etherol Process) [1].

Apparently, these catalysts offer a paradigmatic example of selective bifunctional catalysis and the rationale at the basis of their synthesis is very likely to lead to further sophisticated performances (see later) and to innovative catalysts.

In the 1980s, Bayer commercialized an effective and simple industrial process able to reduce the levels of dioxygen (from the ppm’s to the ppb’s) in industrial waters to be employed in

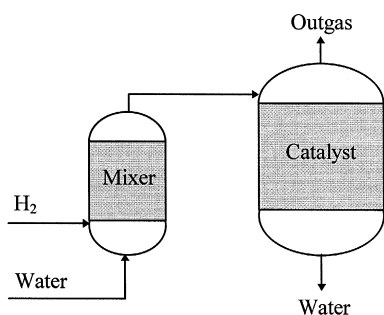


Fig. 1. Schematic flow chart of a catalytic unit for removal of dioxygen present in water (adapted from Ref. [8]).

heating circuits, microelectronic industries, etc. (Fig. 1). The catalyst is an ion-exchange resin, both macroporous and gel-type in nature in beaded form (0.5–1.3 mm in diameter), in which palladium particles are deposited onto the outer shell of the beads (Bayer catalysts K 6333 and VP OC 1063) [8]. Under typical conditions ( $T = 70^{\circ}\text{C}$ ;  $P = 0.15\text{--}0.2\text{ MPa}$ ), the stoichiometric amount of dihydrogen is employed and residual  $\text{O}_2$  is less than 10 ppb. The amount of treated water is approximately 80 bed volumes per hour.

### 3. The rush to the resin-based hybrid phase molecular metal catalyst vs. the carelessness towards the resin-based heterogeneous metal catalysts

The possibility of exploiting macroporous and gel-type functional resins as supports in metal catalysis under solid–liquid phase conditions was proposed by Haag and Whitehurst in 1969 (Mobil Oil) [11] and materialized since then in very numerous examples of macromolecular metal complexes  $\text{P} - \text{L}' - \text{ML}_n$  ( $\text{P}$  = functional resin,  $\text{L}'$  = ligating functionality,  $\text{ML}_n$  = metal complex known to be catalytically active in the homogeneous phase). Complexes  $\text{P} - \text{L}' - \text{ML}_n$  (“hybrid phase catalysts”) [12] resulted to be active in a variety of metal catalyzed organic reactions [13] but they never reached the industrial application in the synthesis of commodities

or even of fine chemicals, at least upon judging from the open literature [14–16]. In spite of this circumstance, thousands of papers, several reviews and a dedicated book [14] do witness an enormous effort which might not be technologically useless if the target of the applications will concentrate on the needs of the fine chemicals industry.

The idea of exploiting functional resins first for dispersing given metal centers at the atomic level and then for supporting the metal crystallites expected to form upon their chemical reduction was by far less popular in academic and in industrial chemical communities. One could perhaps argue that the awareness of the chemical and physico-chemical potentialities of designed functional resins as well as the thorough knowledge of their micro- and nanomorphologies [2–6] was developed in fact long after the perception of the basic chemical potentialities of functional resins as macromolecular ligands. As a matter of fact, legions of coordination chemists prepared many hundreds of macromolecular metal complexes and used them as molecular catalysts without exhibiting the idea that the reduction of their metal centers under operational conditions to the zerovalent state was not necessarily considered a nuisance but, on the contrary, the way of access to novel potent catalysts under solid–liquid conditions.

To our knowledge, the first authors who appear to have been interested with this specific task in the connection of resin-based catalysts are the German industrial chemists Wöllner and Neier [17]. Among other authors, we mention Sabadie and Germain [18] in the 1970s and Li and Frechet [19,20] in the 1980s. In more recent years, a growth of interest among academies can be appreciated. Thus, Teranishi and Toshima employed in 1994 macroporous styrene-based resins for dispersing Pd nanoclusters (ca. 4 nm) [21] and in 1997. He et al. [22] dispersed Ni–B crystallites on an ion-exchange resin for propanol dehydrogenation and Wu et al. produced Pd–Cu nanoclusters for electro-catalytic applications [23]. Finally, in 1998, Chen et al.

[24] reported on Pt nanoclusters supported at the surface of polystyrene beads, Yu et al. [25] on Pt nanoparticles (ca. 1 nm) dispersed on the surface of macroporous polystyrene beads and Michalska et al. described Pd-heterocyclic polyamides composites [26].

#### 4. Why a functional resin as support for catalytically active metal particles?

Relevant features of synthetic functional resins are listed below:

- (i) suitability to the facile and fine functionalization with chemical groups finalized to the “grafting” of a great variety of metal centers (see below) but also to specific catalytic functions (polyfunctional catalysis);
- (ii) reasonable mechanical robustness, under certain conditions;
- (iii) reasonable thermal stability up to 200–300°C (dry state) and 100–130°C (swollen state) under particular conditions;
- (iv) good chemical stability (e.g. sulphonated polystyrene–divinylbenzene);
- (v) a theoretical specific “surface” area up to 2000 m<sup>2</sup> g<sup>-1</sup> for fully accessible materials;
- (vi) good functionalization degree (up to ca. 5 mmol g<sup>-1</sup>) enabling higher analytical concentrations of active centers with relatively little catalyst volumes;
- (vii) reasonable costs.

A particular emphasis needs to be given to the swelling behavior of (especially) gel-type resins that can swell to the extent of the tens of ml g<sup>-1</sup>! [27]. In the dry state, a particle of these materials can be viewed as a glass particle, with no accessible space even to small gas molecules and all polymer chains are to be imagined as randomly oriented and mutually interwoven, with atoms lying at Van der Waals and London distances. The contact of this particle with a solvent able to solvate the polymer chains produces a gradual expansion of the specific particle volume and a concomitant osmotic pressure,

calling more and more solvent to enter the resin particle. When the osmotic pressure will be balanced by the opposing “elastic” one, the particle volume will stabilize at its maximum value. Expansion volumes up to hundreds ml g<sup>-1</sup> are known, but values ranging from 5 to 10 are more common ones.

From a physico-chemical point of view, a particle of a swollen resin might be considered as :

- (i) a “single” macromolecule dispersed, but not dissolved, in a given solvent;
- (ii) a solution of interconnected macromolecular chains featured by a certain degree of (non-translational) mobility;
- (iii) a low-density peculiar functionalized solid;
- (iv) a solid microvessel filled with a solution of functional polymer chains;
- (v) a droplet of the swelling solvent “solidified”, thanks to the existence of an inner solid framework.

In particular, in the light of point (iv), the resin particle can be viewed as a minireactor (vide infra) filled with a “solution” of functional polymer chains with pendant arms bearing chemical groups that render the GR particle an ion-exchanger [28], a sophisticated reagent for “solid-phase” synthetic organic chemistry [29–31], environmentally friendly acid catalysts for the industrial synthesis of bisphenol-A [32] or as chemically non-active supports for industrial biocatalysis (for example, the production of acrylamide from acrylonitrile with *Rhodococcus* sp. N-774 hydratase, Nitto process [33,34]). In order to properly appreciate the physico-chemical grounds of this minireactor view, the remarkable features listed below should be considered. It is apparent that thermodynamic, kinetic and steric features depicted could be effectively exploited to specific synthetic targets, independently of the catalytic properties of the network itself (and of the metal crystallites that

it supports). Advantages can be summarized in the following topics:

- (i) the physico-chemical status of the interior of a gel-type resin swollen particle can significantly affect the concentration of reagents and products inside this sort of minireactor (see above) with respect to the status of solvent bulk [35] with potentially beneficial effects on catalytic specificity and selectivity;
- (ii) the same peculiar status can affect the thermodynamics of a given reaction that we force to occur inside of the polymer gel, again when compared with the same reaction let to occur in solvent bulk [36];
- (iii) the kinetics of a given reaction can be substantially influenced by a solvent–gel mass effect [37,38];
- (iv) the nanoporosity of the polymer network can exert a well defined size-selectivity effect [39] when reagents with various solvated-dynamic radii are put in contact with a catalytically active gel-type resin particle.

On the basis of the above, it is apparent that a wise combination of so many and fine physico-chemical features of a gel-type resin with the catalytic potency of metal crystallites dispersed inside their polymer network is likely to lead to innovative catalysts for the production of at least fine chemicals [40,41].

### **5. Dispersion of metal centers and of corresponding metal crystallites onto the polymer network: our approach**

The dispersion of metal centers inside the polymer network of macroporous and gel-type resins can be achieved along a variety of routes [11,42], among which ion exchange is in principle attractive for its general applicability and expected low cost. In this connection, the protocols employed by Bayer technologists for the preparation of their palladium/resins catalysts (see above) is totally unknown. Therefore, on the basis of our alive interest in the proposal of

functional resins as “intelligent” support for catalytically relevant dispersed metal nanophases, we evaluated various protocols for (i) the homogeneous dispersion of “metal ions” throughout the body of the resins particles and (ii) the subsequent facile production of metal crystallites, possibly designed to give homogeneous and peripheral dispersion (*vide infra*).

We set up recently a very convenient procedure for the quantitative dispersion of Pd<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> inside gel-type resins. Thus, when a solution of the relevant metal acetate is let to equilibrate with swollen resin particles containing sulfonic acid groups (but even carboxylic ones), the quantitative implantation of the metal ions occurs, with concomitant release of acetic acid, just under stoichiometric conditions [43–53].

Interestingly, this approach of “forced” ion exchange should be applicable to the numerous metal ions that exist as handy acetates and it should also hold for metal  $\beta$ -carbonylenolate, alkoxydes and metal compounds able to liberate a relatively stable molecule upon protonation of a suitable anionic ligand. Interestingly, this approach should be quite applicable to disperse different metal centers, thus disclosing the possibility of preparing, after metal ion reduction, “atomically assembled metal alloys” (*vide infra*).

The chemical reduction of the metal centers dispersed inside the polymer network of a gel-type resin is expected to produce “bare” metal atoms as many as metal ions are. Obviously, these atoms will immediately tend to aggregate to give nanoclusters, the growth of which is expected to be soon blocked by the network of interwoven chains, which are mutually interconnected by covalent bonds. We set up recently convenient protocols for the mild reduction of the metal centers to the zerovalent state, with the production of nanometric crystallites, the size of which should be conditioned by the polymer chain concentration of the polymer network (see below). Nanoclusters generated with our procedure range from 2 to 4 nm or 3 to 5 nm, depending on experimental conditions (X-

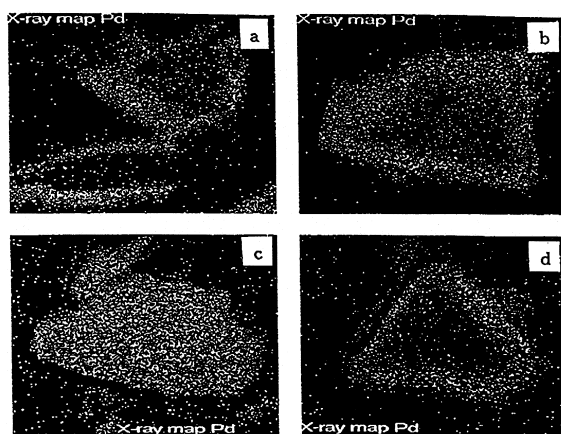


Fig. 2. Distribution of metal palladium in various Pd-resin composites [43]: (a) hydrogen in methanol, 100 KPa; (b)  $\text{NaBH}_4$  0.066 M in water; (c)  $\text{NaBH}_4$  0.066 M in ethanol. Particles size is ca. 0.1  $\mu\text{m}$ . (d)  $\text{NaBH}_4$  0.0189 M in ethanol.

ray diffraction [44] and TEM evaluation [54]). Moreover, we set up also a protocol for controlling the spatial distribution of metal crystallites inside the resin particle (Fig. 2), which can be controlled upon correctly choosing a suitable liquid medium for swelling and adequate reducing agent concentrations [43].

## 6. The issue of nanomorphology and molecular accessibility of the polymer network

This issue is of fundamental importance for the rational exploitation of the fine potentialities of metal catalysts based on functional resins and it has been marginally considered in the almost 30-year long history of catalysis based on hybrid phase catalysts [14]. In 1991, we started to develop a novel approach to these topics and our work is still going on in this connection. In fact, as the catalytic productivity of resin-based catalysts may be diffusion-controlled in nature, the quantitative correlation of catalytic activity (productivity) with nanomorphology (as determined from Inverse Steric Exclusion Chromatography (ISEC [55,56]) and molecular accessibility of the polymer network (as determined from the combination of ISEC and ESR and pulse field-gradient spin-echo NMR (PGSE

NMR) spectroscopies [57–59,47,48,51]), as well as with intrinsic catalytic activity of metal nanoclusters (Fig. 3) are of paramount importance for the best data analysis and catalyst design. Nanomorphology affects the accessibility of the interior of a swollen gel and consequently both the conditions for the formation of catalytic sites (functional groups, e.g. formation sulphonic groups by sulphonation of polystyrene-divinylbenzene; incorporation of metal cluster precursors by ion-exchange, metal nanoclusters generated by reduction) and diffusion of reaction species to/from these catalytic sites are influenced.

Particularly promising appears to be PGSE NMR in that, while the hydrogen nuclei of the polymer network relax very efficiently, they do not interfere with the spin echo signal due to the swelling medium or to a given solute possessing NMR useful nuclei, when proper duration of the pulse is chosen.

Inasmuch as the catalytic productivity of a resin-supported catalyst depends on nanostructure and molecular accessibility of the polymer network, “analytical” tools able to provide direct information are essential. ISEC informs on the nanomorphology (nanoporosity) of the network. ESR of paramagnetic probes with known solvated dynamic radii and dissolved in compatible solvents that are let to penetrate the polymer network inform [57] on molecular rotational

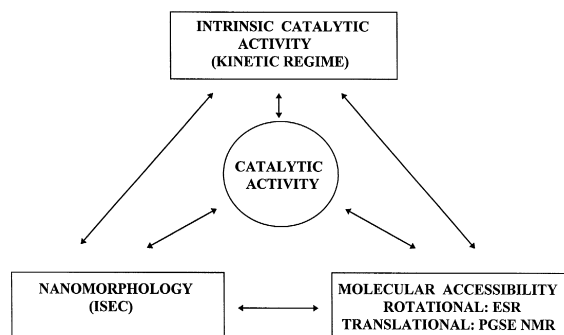


Fig. 3. Relationships among nanomorphology (ISEC), molecular accessibility (rotational and translational mobility; ESR and Pulse Field Gradient Spin Echo NMR-PGSE NMR-measurements, respectively), intrinsic catalytic activity of metal nanoparticles and overall catalytic activity.

mobility. PGSE NMR analysis of compatible solvents dispersed through the polymer network provides self-diffusion coefficients of the solvent itself and of dissolved probes, under convenient conditions [58,59] (translational mobility). This last approach is particularly recommended in that the self-diffusion coefficients so obtained are more reliable than those obtained for inorganic catalytic materials [60] and we believe that it has to become common also in the area of resin-based catalysis.

## 7. Catalytic prospects

To our knowledge, the first paper offering a thorough example of design and synthesis of a resin-based metal catalyst appeared in 1990 [61]. The paper describes the immobilization of preformed Pt nanoclusters (about 2 nm) onto properly designed 2-aminoethylated crosslinked polyacrylamide gel, and illustrates their catalytic activity in the hydrogenation of diverse olefinic compounds. It has been seen that Pt nanoclusters do maintain their catalytic activity after immobilization and they turn out to be one to two orders of magnitude more active (higher initial reaction rate) than commercial Pt on carbon, at ambient conditions.

We have recently evaluated our metal-resin composites as catalysts in some somewhat paradigmatic reactions, including the hydrogenation of cyclohexene (as a model substrate for evaluation the catalytic activity) [44–48], benzene to cyclohexene [49], nitroaromatics [50,51], 2-ethylanthraquinone [62], nitrate and nitrite ions [52]. In order to test the expected relationship between catalytic activity (or productivity) and nanomorphological features (Fig. 3) of our catalysts, we focused our attention [48] on cyclohexene and on two pairs of catalysts based on fairly hydrophilic resins with 1% and 3% cross-linking degree (P1 and P3), containing 2.2% Pd (P1Pd2, P3Pd2) or 0.22% Pd (P1Pd0.2, P3Pd0.2), at ambient conditions. Some relevant

physical data on these materials are collected in Table 1.

It is seen that the polymer networks P1 and P3 are featured by substantially different polymer chains concentrations [55,56] and that the increase in this quantity parallels the increase of rotational correlation time (i.e. viscosity increases with chain concentration) of the spin label utilized as a molecular probe for exploring the microporous network, as well as the expected decrease of the solvent molecules diffusion coefficient.

Our catalytic tests were performed upon using particles featured by well defined sizes, i.e. less than 0.1 mm, from 0.1 to 0.3 mm and from 0.3 to 0.7 mm. The catalytic materials, easily filtrable when particles size is larger than 0.1 mm, are reusable at least three times without appreciable loss of activity, if recovered under hydrogen. Apparently, for the quantitative hydrogenation of the substrate, under conditions of identical analytical palladium concentration, the kinetic behavior of the examined four catalysts depends on support nanostructure, metal loading and catalyst particles size. As shown in Fig. 4, the kinetic behavior is rather complex and the catalytic productivity depends on catalyst particle size. For particle size  $< 0.1$  mm, the hydrogen consumption profile for catalysts P1Pd0.2 and P3Pd0.2 could be kinetics-controlled and it is remarkably independent of the cross-linking degree, i.e. of the nanostructure of the polymer matrix (see Table 1). On the con-

Table 1  
Some physical data referring to catalysts P1Pd2, P3Pd2

Catalyst	Av. pcc <sup>a</sup>	$\tau^b$ (ps)	$D^c \times 10^{+5}$	$\tau/\tau_0^d$	$D_0/D^d$
P1Pd2	0.16	$60 \pm 17$	$1.8 \pm 0.20$	1.6	1.4
P3Pd2	0.24	$115 \pm 18$	$1.1 \pm 0.15$	3.1	2.3

<sup>a</sup>Weighed average polymer chain concentration [55,56] in water ( $\text{nm}/\text{nm}^3$ ).

<sup>b</sup>Rotational correlation time for the paramagnetic probe TEM-PONE rotating in methanol constrained inside the catalyst network.

<sup>c</sup>Self-diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ) of methanol constrained inside the catalyst network.

<sup>d</sup> $\tau_0$  and  $D_0$  refer to rotation and diffusion in unconstrained solvent.

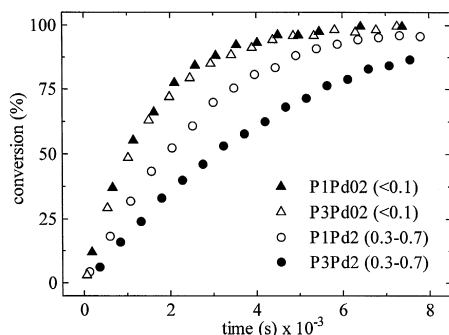


Fig. 4. Conversion profiles for the quantitative hydrogenation of cyclohexene (1 M) in methanol at  $T = 25^{\circ}\text{C}$ ,  $P = 0.5$  MPa. Shaken (6 Hz) constant pressure reactor [48] at a Pd analytical concentration equal to  $2.5 \times 10^{-4}$  M. The particles sizes (in mm) are indicated in parentheses inside the frame of the figure.

trary, for catalysts P1Pd2 and P3Pd2 and particle size ranging from 0.3 to 0.7 mm, a diffusion control is evident and the reaction is faster inside the polymer network in which polymer chain concentration is lower and molecular accessibility (molecular mobility) is higher.

In addition to this system, we have evaluated the catalytic activity of some Ru-resin composites in the partial hydrogenation of benzene to cyclohexene [49] under relatively drastic conditions ( $110^{\circ}\text{C}$ , 15 atm hydrogen) in water–oil liquid phase. Although the obtained results were of some academic interest, the macromolecular support turned out to be unstable owing to extensive hydrogenolysis. Our Pd-resin composites were also investigated in the hydrogenation of nitroaromatics to aromatic amines [50,51], under ambient conditions. The catalysts resulted as active and reusable, but they also exhibited gradual deactivation with concomitant loss of palladium, observation of which could be quantitatively rationalized on the basis of a dissolution mechanism, of the evaluation of intrinsic reaction kinetics and of mass transport [51]. Moreover, we observed subtle changes in the nanomorphology of the support (ISEC tests). Interestingly, however, no measurable changes in molecular accessibility and mobility could be recorded by ESR and PGSE NMR measurements, as well as no change in catalytic activity

to be specifically assigned to these changes. This aspect of resin-based hydrogenation catalysis does need to be thoroughly evaluated and understood in future works. Promising results have been recently obtained in the hydrogenation of nitrates present in drinking water over Pd–Cu-microporous anionic resin [52], bearing an excess of sulfonic acid groups (vide infra). Besides the reduction of nitrate to dinitrogen, the catalysts provide a very efficient means to neutralize the hydroxyl anions that are formed in the reduction reaction and sodium and potassium ions are trapped by the catalytic material, thanks to ion-exchange. After total consumption of the resin capacity, its acidity has to be regenerated conventionally and the catalyst can be conveniently reused. Thus, in a single operational step, it is possible to remove nitrate ions and to control the concentration of relevant cations. This should be a potential advantage over processes based on Pd–Cu-inorganic supports (most frequently alumina) [63,64].

The selective hydrogenation of alkadienes and alkynes to monoenes by Pd-heterocyclic polyamides was successfully performed by Michalska et al. [26] in methanol at ambient conditions. Satisfactory recycling (11 times with 4300 TN's) with negligible loss of activity is reported. The selective hydrogenation of cinnamaldehyde to cinnamyl alcohol in the presence of Pt-macroporous polystyrene (crystallites size 1.1 nm,  $\sigma = 0.30$ ) has been quite recently reported by Yu et al. [25] in ethanol, at 40 atm hydrogen and  $60^{\circ}\text{C}$  for 2 h. In this connection, it is worth mentioning a very recent review paper by Gallezot and Richard [41], which stresses inter alia, not only the particular technological importance of this reaction in fine chemistry (flavors, fragrances, pharmaceuticals) but also the decisive role of the nature of the noble metal employed (e.g. Ir, Rh, Pt, Ru, Pd, conventionally deposited on charcoal, graphite or alumina) in directing the catalytic regioselectivity. The results of Yu et al. [25] appear particularly promising for promoting research interest in metal-resin composites as finely designable cat-



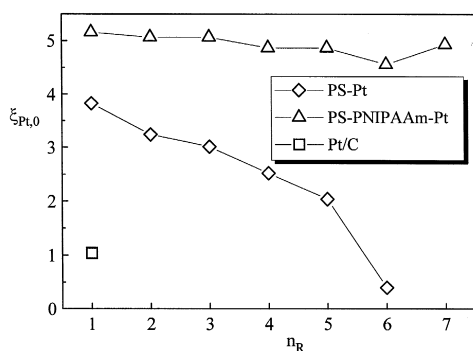


Fig. 5. Initial reaction rate ( $\xi_{Pt,0}$ ; mol $H_2$ /(mol $Pt$  s)) vs. number of catalyst recycling ( $n_R$ ) in the hydrogenation of allylic alcohol (2 mmol) in water (20 ml) solution over platinum nanoclusters immobilized on commercial polystyrene (PS–Pt, 0.005 mmol Pt), stabilized and immobilized by poly(*N*-isopropylacrylamide) on commercial polystyrene (PS–PNIPAAm–Pt, 0.005 mmol), and comparison with Pt/C (0.005 mmol Pt) at 25°C, 1 atm  $H_2$  (data adapted from Ref. [24]).

alysts tailored for this type of hydrogenation reaction. Thus, the preparation of closely related, structurally controlled metal-resin composites in which properly sized, diverse metals nanoclusters can be easily dispersed onto chemically designed supports, should be an easier task along the conceptual and operational routes depicted in this review.

Finally, we like to stress the results obtained by Chen et al. [24] upon using Pt/polystyrene microspheres (600 nm) composites in the hydrogenation of allylic alcohol, in water at 25°C and 1 atm. The best catalyst exhibited a remarkable stability (Fig. 5) through seven recycling tests. A quantitative comparison of catalytic activity among Pt/polystyrene (PS–Pt, metal nanoclusters = 1.5 nm), Pt/polystyrene grafted with poly(*N*-isopropylacrylamide) (PS–PNIPAAm–Pt, metal nanoclusters = 2.1 nm) and commercial Pt/C (Fig. 5), reveals the very promising features of PS–PNIPAAm–Pt and the distinct advantage of its use compared with that of a conventional catalyst.

## 8. Conclusions

The premises, the considerations, the reasoning and the results presented in this review

paper should be considered a message to the catalysis community dealing with a ‘‘Sleeping Beauty’’ who is waiting to be awoken.

Actually, metal catalysis based on synthetic functional resins is well awoken in producing profits in four industrial applications, but the potentialities are innumerable and feasible.

The wise combination of the intrinsic fine physico-chemical features of the swollen polymer gels with the catalytic potency of metal nanoclusters is suitable for producing innovative catalysts in the fine chemicals industry. We feel that the potentialities of these catalysts may be relevant to selective hydrogenation and oxidation reactions, to reactions in which metal-support–substrate interactions can be exploited, to multi-metal catalysis, to the exploitation of polymer chainstethered enantioselective controllers and, in general, to multifunctional catalysis (metal, acidic, redox).

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