

Generating palladium nanoclusters inside functional cross-linked polymer frameworks

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Abstract

The use of functional resins as designable supports for palladium nanoclusters is reviewed. Data are related to the generation of Pd nanoparticles under various conditions and inside gel-type or macroporous frameworks. The combination of different physico-chemical techniques (ISEC, ESR and PGSE NMR) is illustrated as a powerful tool for evaluating nanomorphology and molecular accessibility, mainly of gel-type resins. A few examples of catalytic applications are presented and discussed and prospects for wider utilizations are evaluated. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

A modern approach to tailoring of catalysts based on dispersed metal nanoclusters [1–3] is based on knowledge about catalytic properties of metal particles, their generation and stabilization for catalytic purposes. Functional polymers have good potentialities for supporting and stabilizing metal nanoclusters and additional promoting catalytic effects exerted by functional groups present in the polymer framework may be expected.

1.1. Concepts and definition of polymer supports for catalytic applications

A functional polymer support, in the meaning usually employed in applied macromolecular chemistry,

is a resin, i.e. an organic material built-up with an array of functional cross-linked macromolecular chains that render it insoluble in any conceivable solvent [4,5]. In some cases, the practical insolubility of these materials may be due to extensive hydrogen bonding and, or even to physical chain entanglement (e.g. polybenzimidazole (PBI), see later).

Functional resins contain a variety of diverse functional groups, i.e. anionic (e.g. $-\text{SO}_3\text{H}$, $-\text{COOH}$), cationic (e.g. $-\text{N}(\text{R}_1, \text{R}_2, \text{R}_3)^+$) or more or less complex organic groups like amino, amide, ester, nitrile, epoxy or other reactive centers. In suitable liquid media significant enthalpic interactions occur between the functionalized polymer chains and the solvent molecules and the resulting swelling of the macromolecular framework makes the interior of a given resin particle accessible to reactant molecules. Thus, molecular level dispersion of the carrier offers much higher specific supporting capacity for a given functionality than it is possible to achieve on the pore walls of conventional inorganic supports. This circumstance makes functional resins excellent candidates for

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applications under solid–liquid phase conditions and in fact current applications of these materials [6,7] include ion-exchange [8] as well as acid catalysis [9], supported biocatalysis [10] and solid phase organic synthesis [11].

Organic ion-exchangers have been produced in the hundreds of thousands tonnes per year scale world wide for half of the past century and acidic resins are currently employed as highly designed catalysts for major synthetic processes such as, methyl-*tert*-butyl ether (MTBE) [12] and bisphenol-A synthesis [13]. Moreover, in few significant industrial processes (all based on industrially captive know-how and largely due to Bayer AG), functional resins are used as swollen supports of Pd nanoparticles under liquid phase conditions in (i) the industrial synthesis of methylisobutyl ketone (MIBK) [12,14,15], a semi-commodity produced on the tens of thousands tonnes scale world wide [12,15] and currently utilized as industrial solvent; (ii) the etherification–hydrogenation of mixtures of unsaturated hydrocarbons to give blends of alkanes and MTBE or other branched ethers for the manufacture of unleaded petrol [8]; and (iii) an effective industrial process able to reduce from the ppm's to the ppb's the levels of dioxygen in industrial waters to be employed in heating circuits, microelectronic industries, etc. [14]. Functional resins start to be considered as “intelligent” support for the dispersion of metal nanoclusters by a number of academic research groups [16–22]. Reasonable chemical and thermal stability [9] as well as fine designability and tunability of macro-, meso- and nanostructure and of physico-chemical properties are likely to make resins/metal composites attractive catalysts in highly specialized synthetic, environmentally friendly [23–27] catalytic syntheses in fine chemicals industry. In fact, functional resins are available as two major categories: gel-type (or microporous) and macroporous (or macroreticular) ones. We prefer to pair the terms “gel-type” and “macroreticular”.

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. The macroreticular resins do possess a permanent porosity even in the dry state (hereafter referred to as macroporosity), that supplements the nanoporosity developed by the swelling process (Fig. 1). Gel-type resins are usually lightly

cross-linked (2–8%) materials, while the permanent macroporosity of macroreticular resins require higher cross-linking degrees (8–20%) [1].

Apparently, the interaction of the supported functionality with reactant molecules proceeds in the gel-type resin exclusively in the environment of swollen polymer gel and just in this environment also the majority of the interactions in the macroreticular resins occur. In fact, in these materials only a fraction of the supported functional centers is located at the macropores walls (see Fig. 1) and this fraction would not account for their reactivity.

From a physico-chemical point of view swollen gel can be considered as a tri-dimensional polymer chain framework filled with a liquid. Dimensions of the liquid-filled cavities are close to molecular scale (1–10 nm) and hence, chemical nature of the polymer chains and their morphology influence both the composition and molecular mobility of the liquid. The particles of functional resins may be viewed as “microreactors” designable for variety of purposes, for example, as ion-exchangers [8], sophisticated reagents for “solid phase” synthetic organic chemistry [11], environmentally friendly acid catalysts, e.g. for the industrial synthesis of bisphenol-A [13], or as a chemically passive support for industrial biocatalysis (for example, the production of acrylamide from acrylonitrile with *Rhodococcus* sp. N-774 hydratase, Nitto process [10]). They are used as beads (0.2–1.25 mm) or powders in batch-wise operated suspension reactors or more frequently in fixed-bed flow-through reactors. Their working temperature range spans from room temperature up to about 120°C. The mechanical strength of these solids is modest, but this drawback can be managed by means of various technical solutions [9].

It should be stressed that the potentially rich functionality of the polymer chains offers unique prospects, to resins-based catalysts. In fact, the polymer backbone may contain a variety of pendants finalized to various catalytic, co-catalytic or promotion effects so that polyfunctional catalysis is quite feasible and indeed it is already exploited in the industrial synthesis of MIBK [14]. The appropriate selection of suitable co-monomers will be able to specifically influence the chemical and physico-chemical features of the relevant “microreactors”, thus, providing tools for tailoring these materials for specific purposes.

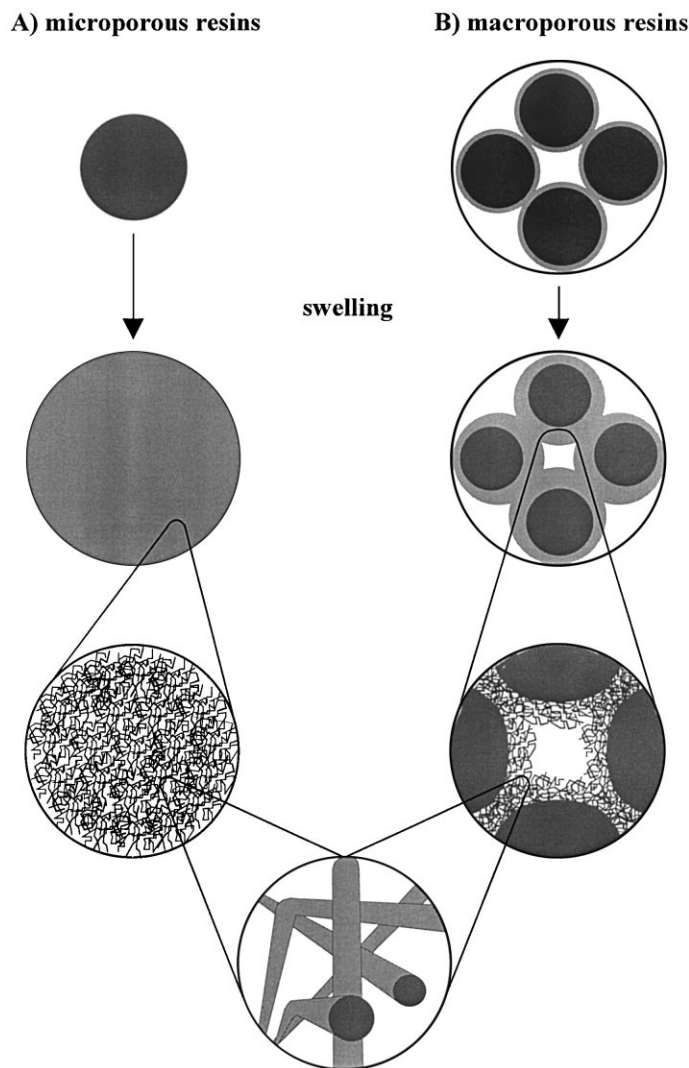


Fig. 1. Schematic picture of the swollen state of gel-type and macroporous functional resins (see text).

Concentration changes due to partition of the reactants between the functional resin and the surrounding bulk solution or changes of the reaction environment polarity due to the influence of functional groups attached to the polymer backbone may positively affect both the supported catalyst activity and selectivity [28–32]. Moreover, steric effects due to the nanoporosity of the polymer network might exert useful size-selectivity effects when the “microreactors” are contacted with reagents featured by different solvated radii [33].

2. Synthesis and metallation of functional polymer frameworks

Preparation of a metal–resin composite can be carried out along two basic routes (i) preparation of a metal colloid and the subsequent fixation of colloid particles into a polymer mass formed from monomers added to the colloid solution [20]; (ii) preparation of a functional resin, metallation either by ion-exchange or impregnation with a metal compound and the

reduction of the metal to zero-valent state. In view of the wider application of the latter route, we focus on this synthetic procedure.

2.1. Commercially available functional resins

Styrenic and acrylic resins are the main representatives of commercially available functional resins [34]. Styrenic resins appeared in the mid-1940s and acrylic ones in the 1960s. To date, ion-exchange market is dominated by styrenic resins, albeit acrylic ones are of growing importance. Phenol-based resins have almost disappeared. Among the producers (and products), Bayer (Wofatit, Lewatit), Dow (Dowexes) and Rohm and Haas (Amberlite, Amberlyst, Duolite) are the best known ones.

While in the case of acrylic resins, a functional group ($-\text{COOH}$) is present from the start of resin preparation as a moiety of the monomer, a post-functionalization approach is typically required for styrenic resins. When this procedure is carried out with the goal to achieve a high degree of conversion (normal requirement in production of commercial resins), usually a homogeneous distribution of active groups is achieved, as each accessible benzene ring then usually contains one functional group. If a lower level of functionalization is required, it is possible to adjust the functional group distribution by selection of suitable reaction conditions. Long reaction times favor homogeneous distribution, while rapid functionalization may preferentially lead to the formation of functional groups near to the surface of polymer particles.

Table 1 collects examples of Dowex type functional resins that we used in our most recent work as supports for palladium catalysts to be used in the reduction of nitroaromatics as well as palladium/copper catalysts applied for the aqueous phase reduction of nitrates.

2.2. Design and synthesis of functional gel-type resins by γ -irradiation

In 1991 we started a long-term research program aimed at providing fundamental know-how about nanomorphology and molecular accessibility of functional resins potentially suitable for supporting metal nanoparticles or catalytically active molecular metal species. To this end we designed the synthesis and physico-chemical characterization of gel-type functional resins aimed at providing convenient, possibly paradigmatic pieces of information. The major groups of resins synthesized in the course of the project are summarized in Table 2.

A general key-point in the project was the production of authentic gel-type frameworks lacking any swollen volume fraction possessing an even rudimentary macroporosity. We tried to avoid (or to limit) any potential porogenic component in the monomer mixture [1] (see the last column in Table 2) and we selected γ -rays irradiation as the most effective and less interfering means for promoting and sustaining the radical polymerization of vinyl monomers [47–56]. The quest of authentic gel-type resins stems from our confidence in the ability of these materials in combining high functionality, somewhat controllable nanoporosity (see Section 2.1), reasonable chemical accessibility and possibility of correlating catalytic productivity with nanomorphology (see Section 2.1).

In terms of lipohydrophilic character, it can be appreciated that we prepared essentially amphiphilic resins [57], with the notable exception of resins M2GB and M4GB [44]. Resins of Table 2 are obtained in almost quantitative yields, under strict mass polymerization conditions apart from the cases where very little amounts of a solvent had to be employed as a means of achieving satisfactory miscibility of the involved co-monomers. The resins, generally obtained as transparent rigid rods, are ground to give

Table 1
Dowex type resins used as precursors of palladium catalysts

References	Commercial code	Cross-linking degree (m, %)	Functional group	Ion-exchange capacity (meq g^{-1})	Particle size (mm)	Code in this work
[35,36]	50W \times 4	4	$-\text{SO}_3\text{H}$	5.0	0.04–0.8	D4
[35]	50W \times 8	8	$-\text{SO}_3\text{H}$	4.9	0.16–0.32	D8
[37]	1 \times 4	4	$-\text{N}(\text{CH}_3)_3^+$	3.5	0.08–0.16	DA4

Table 2
Gel-type resins synthesized as model supports or as actual supports for catalytically active palladium nanoclusters

References	Entry (code)	DMAA (%) ^a	SS-Na ⁺ (%) ^a	SEMA-K ⁺ (%) ^a	SEMA (%) ^a	STY (%) ^a	MBA (%) ^a	DVB (%) ^a	Solvent (%) ^b
[38]	P4N	68	28	—	—	—	4	—	Water (68% w/w)
[39]	M4K	65	—	31	—	—	4	—	Water (35% w/w)
[39]	M4A	70	—	—	26	—	4	—	Water (35% w/w)
[40]	M1-M8	99-92	—	—	—	—	1-8	—	None
[41]	P8N	66	26	—	—	—	8	—	Water (40% w/w)
[42]	SS1MH	—	—	—	22	77	1	—	None
[42]	SS2MH	—	—	—	22	76	2	—	None
[42]	SS3MH	—	—	—	22	75	3	—	None
[42]	SS6MH	—	—	—	22	72	6	—	None
[43]	SPI	92	—	—	4	—	4	—	None
[43]	MPI	92	—	—	4	—	4	—	None
[43]	HPI	92	—	—	4	—	4	—	None
[44]	M2GB	—	—	—	4	94	—	2	DMSO (30% w/w)
[44]	M4GB	—	—	—	4	92	—	4	DMSO (30% w/w)
[45]	A1-A9	87-95	—	—	4	—	1-9	—	DMF (10% w/w)
[46]	AH	33	—	—	26	37	4	—	DMF (10% w/w)
[46]	BH	—	—	—	28	78	4	—	Idem
[46]	CH	—	—	—	37	58	—	5	Idem
[46]	DH	—	—	—	17	78	—	5	Idem

^a Molar (%) with respect to molar content of all monomers.

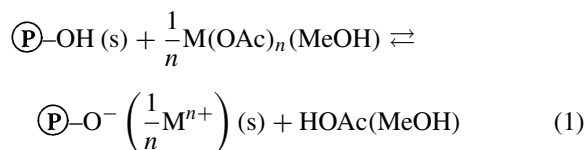
^b Weight (%) to the total weight of the reaction mixture.

sub-millimeter sized particles and, after washing and sieving, utilized as such for further processing. As to their textural characterization, see Section 4.

2.3. Palladiation of functional anionic gel-type resins

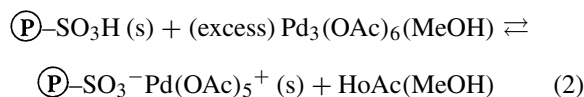
A few well-documented procedures are available to disperse metal centers at an “atomic level” inside polymer frameworks. Thus, ion-exchange, metal coordination by ad hoc functionalized resins (macromolecular ligands) and homo- or co-polymerization of metal-containing monomers have been extensively employed [38–46,58–60]. The most straightforward procedure is undoubtedly ion-exchange, also in the light of the extensive availability of a host of commercial resins. In fact, the ancestor of the resins-supported Pd catalyst mentioned in Section 1.1 was a Pd–resin composite (very roughly described in a “historical” patent by Wöllner and Neier [61]) that was obtained upon treatment with dihydrogen of a strongly acidic ion-exchanger previously exchanged with Pd²⁺ ions, at ca. 100°C. To the best of our knowledge, not a single line dealing with relevant experimental details has ever been published since 1967 about the preparation and micro- and nanomorphology of the Bayer catalysts successfully employed in chemical technology for tens of years [14].

We have developed in recent years a well articulated and widely exploitable “know-how” about metallation procedures of anionic resins under very mild and totally controllable conditions [43,62], based on a rationale that can be very schematically depicted as follows [43]:

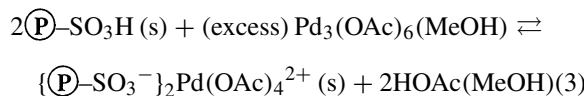


The idea is to react a functional resin possessing an (even very weakly) acidic O–H group with a metal salt containing the conjugated base of a weak acid (e.g. acetic acid). We have recorded a variety of successful tests [43,62] involving Pd(II), Ni(II) and Cu(II) acetates, under various M(OAc)₂/H⁺ initial molar ratios and we have shown that this last condition is a tool for affecting the molecular speciation of the resin-bound metal center [62]. As a significant example, we men-

tion that when Pd(OAc)₂ is used in methanol where it exists as the trimeric species Pd₃(OAc)₆, two quite different situations are observed as the consequence of different initial Pd(II)/H⁺ ratios (*R*). Thus, when *R* = 0.5, quantitative resin metallation (and concomitant Pd(II) partial reduction to Pd(0) caused by the liquid medium itself) occurs and a homogeneous dispersion of palladium through the resin particles is observed (XRMA test). On the contrary, when *R* > 1.0, palladiation is tentatively described by Eqs. (2) and (3) and the palladiated resin exhibits a beautiful and stable orange–red color (λ_{max} = 420 and 530 nm) revealing the survival of the chromophore, i.e. the trimeric Pd(II) entity, in which one or two acetate ligands are replaced by resin-bound carboxylate donating sites. In this case, the dispersion of Pd is seen (XRMA test) to occur mainly at the surface of the resin particles, which observation might be interpreted as due to diffusional problems encountered by the bulky metallation agent inside the polymer framework.

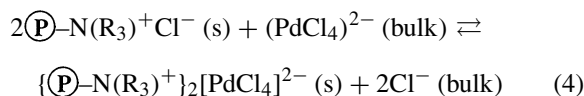


and



2.4. Palladiation of functional cationic resins

In the case of cationic resins, palladiation does not take advantage of the lucky features of palladium acetate seen above. We obtained acceptable results [37] on the basis of the reaction



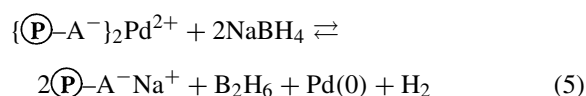
upon using the complex [PdCl₄]²⁻ dissolved in 4 M aqueous HCl. The extent of this ion-exchange was about 60% which is fully comparable with extents of ion-exchange processes based on anionic resins and the cationic complex [Pd(NH₃)₄]²⁺ [38]. This procedure was employed for obtaining Pd/Cu precursors of the catalysts investigated by us for the removal of nitrates dissolved in water [37].

3. Reduction of palladium(II) to palladium(0)

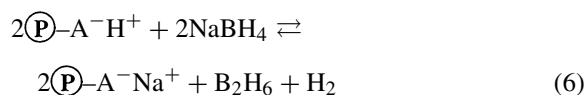
It is well known that chemisorbed or ion-exchanged Pd^{2+} can be easily reduced to $\text{Pd}(0)$ by a variety of reagents such as, dihydrogen, formaldehyde, alcohols, metal hydrides, etc. In our laboratories, sodium borohydride in ethanol, or tetrahydrofuran, and dihydrogen acting on metallated resins were mainly used.

3.1. The reduction with sodium borohydride

The reduction with sodium borohydride is suitable for anionic, cationic, as well as other functional metallated resins, e.g. those prepared by impregnation, or utilization of resins prepared from organometallic monomers [63,64]. In the course of the reduction of an anionic metallated resin, sodium borohydride acts according to the simplified reaction



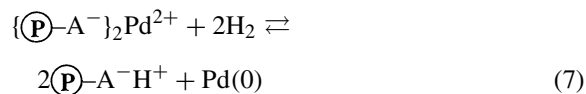
and diborane undergoes further reactions resulting in borate compounds. If the metallated resin contains hydrogen ions, an extra amount of sodium borohydride needs to be employed for the neutralization of acidic sites



As discussed below, the size of metal crystallites as well as their spatial distribution inside the resin particle strongly depend on the concentration of the reducing agent. The reduction procedure with sodium borohydride requires extensive washing to ensure as much as possible removal of boron-containing compounds.

3.2. Reduction of anionic metallated resins with dihydrogen

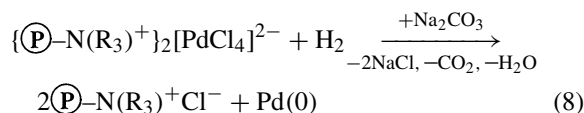
On a technological scale, this process is cheaper and cleaner than the reduction with hydrides so that, inter alia, an extensive washing like in these cases is not necessary. The reduction with dihydrogen obeys the equation



Due to the good solubility of dihydrogen and the good compatibility with the majority of our functional metallated resins, methanol is very often used as a reduction environment [35,65,66]. At temperatures ranging from ca. 20 to 50°C, dihydrogen pressure from 0.1 to 0.5 MPa, the reduction time requires about 0.5 h. Higher dihydrogen pressure allows to reach more uniform spatial distribution of metal crystallites, but it also causes disintegration of the polymer backbone [66], which is also facilitated by higher temperatures and longer reduction times. Metal crystallites generated by the reduction with hydrogen usually have a wider size distribution than it is in the case of catalysts prepared by the reduction with sodium borohydride.

3.3. Reduction of cationic metallated resins with dihydrogen

Cationic metallated resins prepared following Eq. (4) turn out to be redox stable and cannot be reduced with dihydrogen in methanol or water even at pressures up to 5 MPa. We recently observed that a way to circumvent this remarkable redox stability is the action of dihydrogen is the presence of Na_2CO_3 [37] (Eq. (8))



3.4. The generation of Pd nanoparticles and the control of their spatial distribution in gel-type functional resins

In view of the synthetic scale featuring laboratory work, we choose NaBH_4 as the most practical reducing agent [67] in alcohols or in THF [42–47]. It became soon apparent [33] that the actual analytical concentration of NaBH_4 in the reducing solution plays a major role in directing the spacial allocation of the Pd nanoclusters (Fig. 2), at least for 5–8% (w/w) metal loading.

Apparently, when BH_4^- concentration is relatively high, its diffusion rate from the bulk of the reducing solution to the center of the resin particle (the microreactor, see Section 1.1) is sufficiently rapid to prevent an effective diffusion of ions Pd^{2+} already fixed inside the palladiated resin towards the periphery of the resin particle itself, potentially pulled out

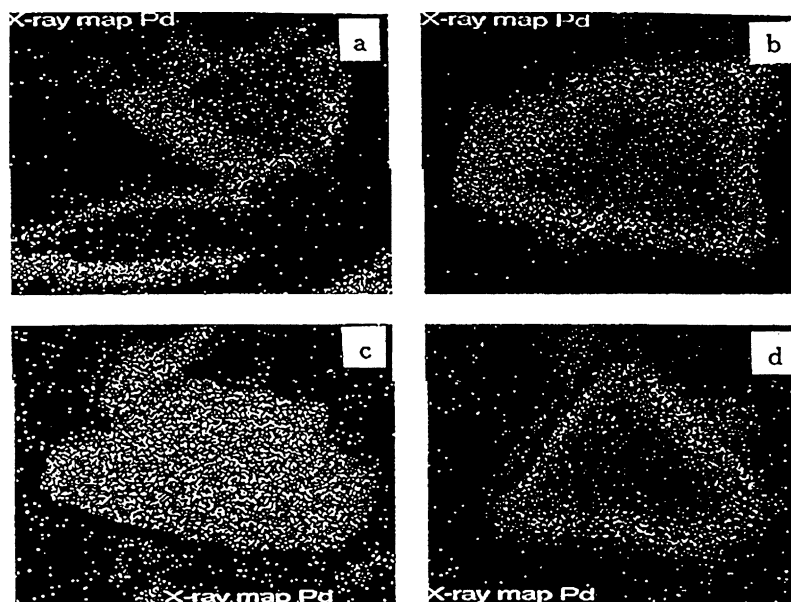


Fig. 2. Distribution of metal palladium in various Pd-resin composites [46]. (a) Hydrogen in methanol 100 KPa; (b) NaBH_4 0.066 M in water; (c) NaBH_4 0.066 M in ethanol. Particles size ca. 0.1 nm; (d) NaBH_4 0.0189 M in ethanol.

by the Pd(II) concentration gradient associated with the reduction of Pd^{2+} to Pd(0) and by the concomitant replacement of Pd^{2+} by Na^+ . Employment of lower reductant concentrations or of dihydrogen (clear diffusional limitations) leads to a paramount peripheral distribution of Pd nanoclusters (Fig. 2b). In the case of lower loading of palladium (0.5–1%) [35,65] a uniform distribution of metal nanoclusters is obtained even after the reduction with hydrogen.

In all our preparations aimed at providing resins-supported Pd catalysts, we usually employed conditions suitable to produce homogeneous distribution of Pd nanoclusters. We faced carefully also the question of nanoclusters size and to this end we took benefit of both X-ray diffraction and of TEM. X-ray analysis provided diameters figures ranging from 2 to 4 nm [39] and a TEM analysis carried out recently on resin-Pd composites based on 2% Pd (w/w) materials and gel-type supports with cross-linking degree ranging from 1 to 9% , gave diameter values equal to 3 ± 1 nm (Fig. 3) [45]. In [45] we speculate that the actual size of the large majority of metal nanoclusters is conditioned by the polymer chain concentration (see [4]) of the polymer framework inside which they are generated (Fig. 4).

In this connection, we stress the circumstance that the generation of Pd nanoclusters, under identical conditions, inside the totally different framework of PBI (see Section 3.5) leads to larger and essentially size-uncontrolled Pd nanoparticles (Fig. 4) [45].

3.5. The generation of Pd nanoparticles inside macroporous supports: the case of PBI and of Bayer UCP 118

In addition to our ad hoc synthesized microporous supports, we paid due attention to classic commercially available macroporous ones, i.e. PBI (Höchst Celanese) and UCP 118 (Bayer). PBI is a peculiar resin in that its lack of solubility in many solvents is not due to covalent cross-links but to the structural rigidity of the polymer chains and to the presence of interchain interactions via hydrogen bonds. PBI is a particularly thermooxidatively stable material (up to 600°C), currently utilized in many high temperature- and chemical-resistant applications such as, fire-blocking applications and thermal-protective coatings. Other uses involve the preparation of membranes for product separations and the application in sorption technologies; PBI for the latter application

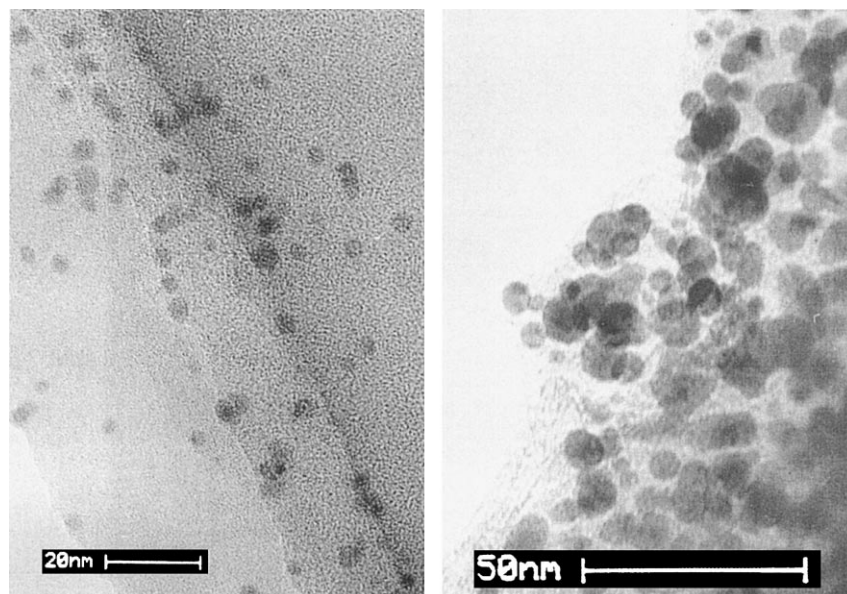


Fig. 3. TEM microphotographs of the Pd nanoclusters generated inside a resin–Pd composite (2% Pd (w/w)) based on a 9% cross-linked gel-type support compared with that of Pd nanoclusters generated inside PBI (see Section 3.5). (Reprinted with permission from: A. Biffis, A.A. D'Archivio, K. Jerabek, G. Schmid, B. Corain, *Adv. Mater* 12 (2000) 1980).

can be manufactured as 250–500 mm beads with a certain degree of macroporosity [68]. On the basis of our results [68] PBI appears to be a macromolecular material that exhibits, both in the dry and swollen state, a peculiar combination of macro- and mesoporous domains so that the generation of Pd nanoparticles, following previous anchoring of Pd^{2+} and chemical reduction of the metal centers, has to occur at the surface of meso- and macropores and not inside the scarcely penetrable nanoporous domains. In accordance with this prediction, Pd nanoclusters turn out to be larger and essentially size-uncontrolled, as anticipated in the previous paragraph (Fig. 4).

Quite different is the case of Pd nanoclusters generation inside resin UCP 118. This material is currently extensively employed as acid catalyst for MTBE synthesis. Its macro- and mesoporous structure has been recently thoroughly investigated by us [69,70] both in the solid and swollen state and the combination of our specific observations with predictions based on the previously accumulated know-how, led us to the conclusion that the generation of Pd nanoclusters has also to occur at the “surface” of the macro- and mesopores. However, in this case such a real physical surface should not occur [71] and Pd nanoclusters had to

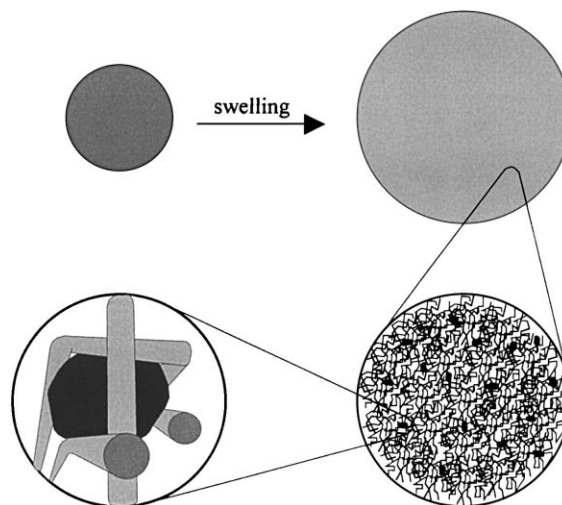


Fig. 4. Polymer chain concentration of the swollen polymer framework as a means of controlling nanoclusters size. (Reprinted with permission from: A. Biffis, A.A. D'Archivio, K. Jerabek, G. Schmid, B. Corain, *Adv. Mater* 12 (2000) 1980).

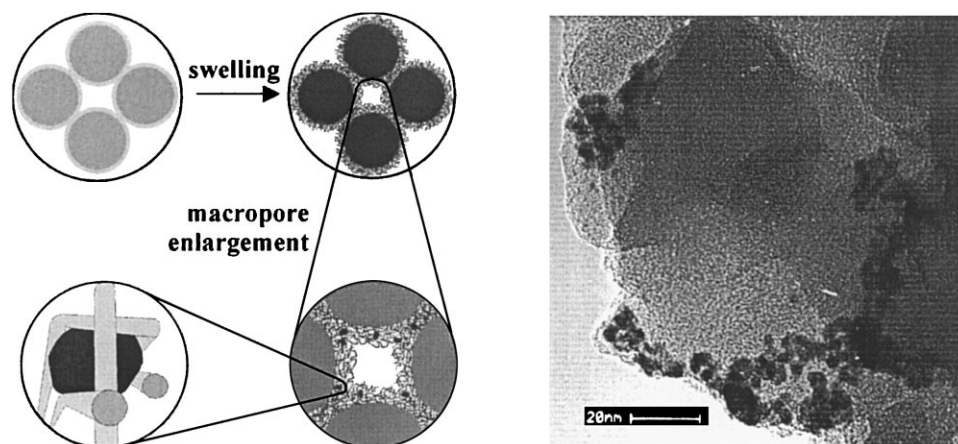


Fig. 5. Graphical model of a macropore of a palladiated resin, with nanocrystallites located at or near the macropore “surface”, and related TEM picture of the UCP 118/Pd composite (2% Pd (w/w)).

form inside a thin layer of gel-type polymer framework. As a matter of fact, the resulting nanoparticles not only do form inside these predicted domains but again they appear size-controlled and close to 3 nm in diameter [69]. It is worth underlining that our results are the first direct published proof of the allocation of Pd nanoclusters in the body of industrially relevant resin-based catalysts (Fig. 5).

4. Nanomorphology and molecular accessibility of the polymer support

When we started this project in the very early 1990s, we felt the opportunity of gathering as many information as possible about what we started to call “nanomorphology and molecular accessibility” of the interior of both gel-type and macroporous resins. At that time, information about macroporous resins was relatively more abundant [1] and for gel-type resins information was available but definitely scattered in nature and not finalized to the understanding of interrelation between nanomorphology and molecular rotational and translational mobility of reagents and products inside them [71].

4.1. Morphology of functional resins: an ISEC approach

When functional resins are put in contact with suitable liquids, a swelling of the polymer matrix occurs

and their working-state morphology is substantially different from the dry-state one. Therefore, information based on conventional porosimetric techniques, like nitrogen adsorption or mercury penetration have little to do with their function in the swollen state. Quantitative description of the swollen-state morphology of polymer materials can be obtained using inverse steric exclusion chromatography (ISEC) (for a review paper see [73]). This method is based on measurements of elution volumes of a series of standard solutes of known molecular sizes on chromatographic column filled with the evaluated material. If the experiments are performed in conditions under which the elution behavior of the solutes is governed by steric (entropic) effects only, it is possible by mathematical treatment of obtained data to produce valuable information on the porosity of the swollen polymer mass [72] from 0.2 μm macropores to nanometric micropores. The real pore system is modeled as a set of discrete fractions, each characterized by a simple geometry of uniform size. The macropores are depicted upon using a conventional model of cylindrical pores, but this geometry is unsuitable for the modeling of the porosity of swollen polymer mass. Swollen polymer gel can be realistically modeled on the base of the idea developed by Ogston [74] as space in which rigid cylindrical rods representing the polymer chains are randomly distributed. As parameter characterizing the pore dimension, the concentration of the cylindrical rods in units of length per unit of volume, i.e. nm^{-2}

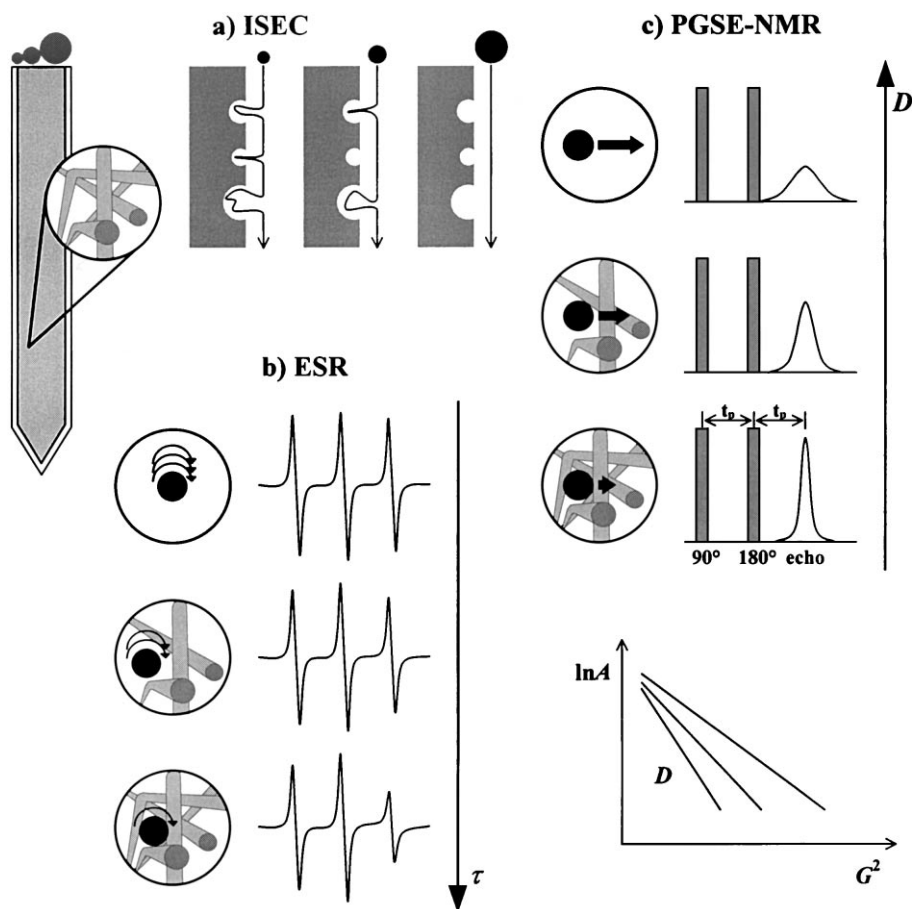


Fig. 6. Expected conceptual interrelation among ISEC, ESR, PGSE NMR information and catalytic activity a swollen resin-based metal catalyst.

is employed. The scale of the polymer chain densities spans from 0.1 nm^{-2} , corresponding to an extremely expanded framework, up to 2 nm^{-2} , characteristic of a very dense polymer framework into which even the smallest molecules can hardly penetrate.

4.2. Molecular mobility versus nanomorphology inside swollen Pd-resins catalysts: a combined ESR-PGSE NMR-ISEC approach

We started from an intuition that is pictorially represented in Fig. 6. From classic literature [75] we were expecting that higher weighed average polymer chain concentration $\langle c_c \rangle$ values had to be associated with lower rotational mobility of dissolved

molecules and with lower translational mobility of the molecules of a given swelling medium. Rotational mobility is relatively easily determined (as τ , rotational correlation time) on the basis of ESR spectra of a paramagnetic molecular probe (e.g. TEMPONE (2,2,6,6-tetramethyl-4-oxo-1-oxyl-piperidine)) dissolved in the swelling medium and let to rotate inside the gel domains of a given resin. Translational mobility is less easily determined on the basis of PGSE NMR (Pulse Field Gradient Spin Echo NMR) measurements that provide self-diffusion coefficient D of solvents dispersed inside the desired swollen resin.

We illustrate our approach on the basis of recent results from our laboratories [75] and we will show its

relevance to the interpretation of catalytic results [76] in Section 5.

To test the feasibility of a quantitative relationship among $\langle c_c \rangle$, τ and D we choose resins M1–M8, Table 2, and water, THF and DCM as swelling media. ISEC–ESR analysis gave for all media a remarkably linear relationship between $\ln(\tau)$ and $\langle c_c \rangle$, thus, confirming our first set of data dealing with water only [40]. Moreover, self-diffusion coefficient D , determined from PGSE NMR both in water and DCM, was also found to linearly correlate with $\langle c_c \rangle$ as

$$\ln\left(\frac{D}{D_0} - 0.15\right) = -\nu\pi r_c^2 \langle c_c \rangle \quad (9)$$

where r_c is the radius of the rigid rods (representing the polymer chains) implied by Ogston's model [65] and ν is an adjustable parameter so that the final relationship between D and τ turns out to be

$$\frac{D}{D_0} = \frac{\tau_0}{\tau} + 0.15 \quad (10)$$

It should therefore, be concluded that ISEC, ESR and PGSE NMR, employed in an integrated fashion, offer an unique overall picture of the relationship between the morphology at the nanometer scale of moderately cross-linked swollen gel-type resins (ISEC) and the rotational and translational dynamics of molecules dispersed inside their polymer framework (ESR and PGSE NMR). The quantitative correlation between the ISEC and ESR analysis described by us for the first time in water [40] is fully confirmed in THF and DCM and ISEC data are seen to quantitatively correlate also with the PGSE NMR ones. These new observations support our multi-methodological approach to the study of structure on the nanometer scale and solutes dynamics of swollen gel-type resins. However, the quantitative correlation between the framework polymer chain concentration (nanoporosity) as provided by ISEC with the translational mobility as given by PGSE NMR is not interpretable on the basis of a pure classic Newtonian hydrodynamic description of molecular mobility and further investigation is required. In essence, the Stokes–Einstein approach to translational mobility does not appear totally adequate for the physico-chemical correlation but a further approach based on tortuosity effects [77] appears to be promising. Indeed, the translational mobility of water, THF and DCM as determined with

PGSE NMR and the rotational mobility of a paramagnetic probe dissolved in the confined solvents are also found to mutually quantitatively correlate. However, the correlation is again not interpretable on the basis of a pure Newtonian picture of the translational and rotational molecular motion of the solvent and the solute, respectively and the physico-chemical model has to be perfected [75].

5. Catalytic results

As anticipated in Section 1, at least four technologically relevant processes are pivoted on the catalytic ability of resins-based metal Pd catalysts, at ambient and also under relatively drastic conditions (MIBK synthesis, 3 MPa, 130–140°C). This circumstance has attracted indeed not only our attention but also that of other international groups. Thus, Michalska et al. [22] have recently described the selective hydrogenation of alkadienes and alkynes to monoenes by Pd/polyamides composites, Teranishi and Toshima dispersed 4 nm Pd nanoclusters on macroporous styrene-based resins [18] and Wu et al. produced resins-supported Pd/Cu nanoclusters for electroanalytical applications [19]. Finally, Li and Frechet produced Pd/PBI composites [17] for the hydrogenation of nitroaromatics and nitroethane.

5.1. Selection of catalytic data

We started our endeavor in 1993 in Padova in the frame of a starting co-operation between the Department of Inorganic, Organometallic and Analytical Chemistry, University of Padova and the Department of Organic Technology, Slovak University of Technology, Bratislava.

Attention was devoted to reactions that can be considered either model ones (e.g. the hydrogenation of cyclohexene) or specific (targeted) ones, i.e. reactions for which the unique features of Pd/functional resins composites were likely to be exploited in order to reach significant (i.e. non-trivial) tasks such as, the selective hydrogenation of nitroaromatics (nitrobenzene, nitrotoluene, nitrophenol, chlorinated nitrobenzenes) to amines, of 2-ethylanthraquinone to 2-ethylanthrahydroquinone and $\text{NO}_3^-/\text{NO}_2^-$ to dinitrogen.

5.1.1. Nitroaromatics

The selected hydrogenation of aromatic nitroderivatives to the corresponding amines is a coveted goal in synthetic organic industrial chemistry [12]. The currently utilized metal catalyst is Pd supported on carbon or inorganic materials [69] and a well known problem is metal leaching during the process [78,79].

Catalysts based on resins P4N [38], M4K [39] and Dowex (D4, D8) (4 and 8% cross-linking, gel-type) [35] were tested in the hydrogenation of *p*-nitrotoluene (1 M) in methanol under a variety of conditions. Pd(0) analytical concentrations ranging from 0.1 to 2.0 mM were employed with pressures ranging from 0.1 to 0.5 MPa at 20–50°C in a shaken, constant pressure batch reactor. Pd content in the catalysts ranged from 0.5 to 8%. Either diffusion- or kinetics-controlled regimes were attained depending on the hydrogenability of the substrate and content of metal in the catalyst. Selectivity to *p*-aminotoluene was always 100% coupled with moderate rates (about $1 \text{ mol}_{\text{NT}} \text{ kg}_{\text{Pd}}^{-1} \text{ s}^{-1}$) which is higher than in the case of Pd supported on carbon, or other inorganic supports [66]. Unfortunately, Pd leaching was always important under all tested conditions, especially at higher Pd loading. Quite recently [65], we have improved the catalyst performance by addition of Co^{2+} but leaching of palladium was not suppressed totally. Significantly lower leaching of palladium was monitored in the hydrogenation of nitrophenols [65]. Very interesting results were obtained in the hydrogenation of chlorinated nitrobenzenes to chlorinated aminobenzenes, useful intermediates for the synthesis of fine chemicals. In fact, besides good specific activity of the D4/Pd composite (Table 1), also only a moderate hydrogenolysis of C–Cl bonds is observed [80]. Better activity and selectivity properties of resin-supported catalysts in comparison with catalysts supported on carbon are fairly documented in Fig. 7.

5.1.2. Cyclohexene

Hydrogenation of this model uncomplicated olefin is fast and quantitative at ambient conditions. Catalysts mentioned in the previous paragraphs appeared reusable, if filtered under dihydrogen, or nitrogen and immediately re-used. Typical conditions are as seen above for the nitroaromatics reduction.

Preliminary tests carried out on this olefin [41] revealed good accessibility of the entire body of the

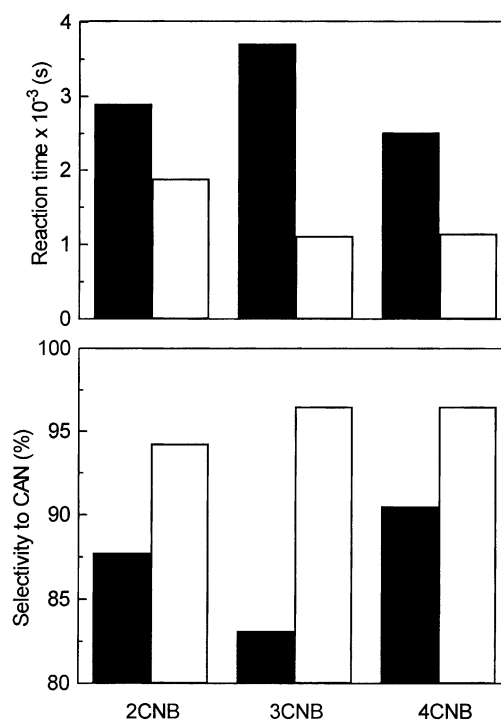


Fig. 7. Reaction time and selectivity to chloroaniline (CAN) of the “stoichiometric hydrogenation”, i.e. $3 \text{ mol H}_2/\text{mol}$ of chlorinated nitrobenzenes (two-, three- and four-position isomers denoted as 2CNB, 3CNB and 4CNB, respectively) over 1 wt.% palladium supported on carbon (black columns) and 1 wt.% palladium supported on gel-type sulphonated poly(styrene-divinylbenzene) commercially denoted as Dowex $50\text{W} \times 4$ (white columns); 1 M solution of CNB in methanol and diethyl ether (1:1 v/v) at the start, 25°C, 0.5 MPa, concentration of palladium in the reaction mixture: $[\text{Pd}] = 7.8 \text{ mol m}^{-3}$.

catalyst particles (therefore, of all present metal nanoclusters) for Pd loading equal to 1 or 0.5%, for catalyst particles sizes $<0.1 \text{ mm}$. More recently, this reaction has been utilized as a mean to evaluate the relevance of the combined ISEC–ESR PGSE NMR approach depicted in [75] to the catalytic productivity of Pd–resins composites (Sections 2.1 and 2.2), in a semiquantitative fashion [76]. To this end, four fairly hydrophilic catalysts containing 2.2% Pd (P1Pd2, P3Pd2) or 0.22% Pd (P1Pd0.2, P3Pd0.2) based on resins SS1MH and SS3MH (Table 2), were investigated with the aim to obtaining a sort of “case history” illustrating the interrelationship among accessibility, mobility and catalytic activity (Table 3).

Table 3
Nanostructural and accessibility (see text) data referring to catalysts P1Pd2, P3Pd2

Catalyst	$\langle c_c \rangle^a$	τ^b (ps)	$D^c \times 10^5$	τ/τ_0^d	D_0/D^d
P1Pd2	0.16	60 ± 17	1.8 ± 0.20	1.6	1.4
P3Pd2	0.24	115 ± 18	1.1 ± 0.15	3.1	2.3

^a Weighed average polymer chain concentration in water (nm/nm³).

^b Rotational correlation time for the paramagnetic probe TEM-PONE rotating in methanol constrained inside the catalyst network.

^c Self-diffusion coefficients (cm² s⁻¹) of methanol constrained inside the catalyst networks.

^d τ_0 and D_0 refer to rotation and diffusion in unconstrained solvent.

Polymer frameworks P1 and P3 are found to be featured by substantially different polymer chains concentrations [42] and it can be noticed 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 framework; concomitantly, the expected decrease of the solvent molecules self-diffusion coefficient is also observed. Catalytic tests, performed upon using particles featured by well-defined sizes, i.e. lower than 0.1 mm, from 0.1 to 0.3 mm and from 0.3 to 0.7 mm revealed that these catalytic materials, are easily filterable when particles size is larger than 0.1 mm and reusable as such 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. The kinetic behavior is seen to be rather complex and the catalytic productivity profile apparently depends on catalyst particles size. For particles size <0.1 mm, the hydrogen consumption profile for catalysts P1Pd0.2 and P3Pd0.2 suggests a possible kinetics-control and it turns out to be remarkably independent of the cross-linking degree, i.e. of the nanostructure of the polymer matrix. On the contrary, for catalysts P1Pd2 and P3Pd2 and particles size ranging from 0.3 to 0.7 mm, a diffusion control is evident, i.e. the reaction is faster inside the polymer framework in which polymer chain concentration is lower and

molecular accessibility (molecular mobility) is higher [76].

5.1.3. Cyclohexene and 2-cyclohexen-1-one

Resins AH, BH and CH (Table 1) are expected to be featured by diverse hydrophilic-hydrophobic properties in view of their substantial differences in co-monomer composition. After palladiation and reduction of Pd(II) to Pd(0), according to Sections 2.3 and 3.1, and concomitant replacement of protons with sodium ions (see Section 3), the so-formed catalysts coded as A, B and C were investigated in the form of resins particles both in terms of molecular accessibility of their interiors to the two olefins and to methanol and as catalysts for the hydrogenation of both substrates in the same medium [46].

Both olefins are found to exhibit in fact similar affinities for the three different polymer frameworks, owing to a leveling effect caused by a strong methanol-support interaction. Hydrogenation was carried out at 25°C, at 1 M substrate concentration and Pd analytical concentration equal to 0.125 M Pd/m³ of the reaction mixture (1.5 MPa) and 0.25 Pd/m³ (0.5 and 1 MPa), in a shaken, constant pressure batch reactor. These conditions enable a kinetic regime to be attained (catalyst particle test) and both olefins are found to be hydrogenated at almost identical rate (determined up to 70% conversion) by a given catalyst. Quite remarkably, reaction rates are found to depend very cleanly on the nitrogen to palladium molar ratio, present in the catalysts, at 0.5, 1 and 1.5 MPa in the 0–80 molar ratio range. In view of the composition of the polymer frameworks, this observation leaves little doubt on the fact that the amido groups present in A and B do exert a specific promotion effect on the reactivity of Pd nanoclusters (Fig. 8) possibly towards dihydrogen, presumably via their nitrogen atoms lone pairs.

A related observation was recently reported by Akashi and co-workers who gathered strong evidences (including ESCA data) about a real “coordination interaction” [20] of the amide groups present in poly(*N*-isopropylacrylamide) branches grafted onto the surface of polystyrene microspheres, with the surface of 1.5 nm Pt nanoclusters stabilized by the amidic branches themselves. Moreover, although the role of the support on the performance of metal nanoclusters dispersed on inorganic supports is very

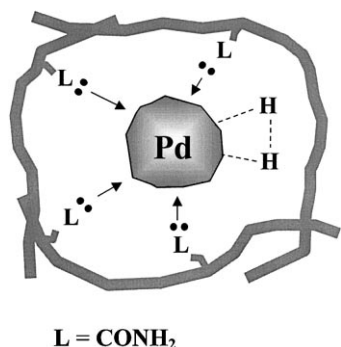


Fig. 8. Schematic picture of the observed interaction of the amidic groups present in the functional organic support with a Pd nanocluster.

well-documented [81], we believe that these observations represent precious relevant pieces of information in the area of polymer-supported metal nanoclusters.

The combination of these two findings lends further credit to the concept of microreactor proposed in Section 1.1 and rises in evidence another feature of the chemistry of the support that might be exploitable in catalytic applications of metal–resins composites.

5.1.4. 2-Ethylanthraquinone

The large majority of the ca. 2 million tonnes per year of hydrogen peroxide produced world wide, is crucially based on the selective hydrogenation of 2-ethylanthraquinone to 2-ethylanthrahydroquinone [12], followed by its reaction with dioxygen that produces hydrogen peroxide and re-generates 2-ethylanthraquinone. The current catalysts, Pd on inorganic supports, offer a ca. 90–95% chemoselectivity in that they also promote also the partial ensuing hydrogenation of 2-ethylanthrahydroquinone to 2-ethyl-5,6,7,8-tetrahydroanthrahydroquinone. In current “anthra process” plants, this unwanted side product is almost quantitatively dehydrogenated by means of a dedicated secondary reactor to regenerate as much as possible the original amount of 2-ethylanthraquinone. In practical terms, the procedure implies systematic addition of fresh substrate and appreciable extra costs.

On the basis of knowledge stemming from our laboratories (see Section 1.1), we have devised a few very lipophilic functional resins aimed at supporting 3–4 nm Pd nanoclusters. Upon playing

with the primary structure of the polymer backbone and with the nature of the reaction medium, we have succeeded in promoting a chemoselectivity to 2-ethylanthrahydroquinone equal to 98%, i.e. slightly, but definitely superior to that provided by a commonly employed commercial catalyst, under identical conditions [82]. We believe that this finding is particularly worthy, in that it follows a precise design of the lipophilic–hydrophilic character of the support targeted to the specific improvement of the chemoselectivity and we feel that these results offer a good paradigm about the potentialities connected with resin-based metal catalysis.

5.1.5. Reduction of $\text{NO}_3^-/\text{NO}_2^-$

The reduction of aqueous nitrates and nitrites by dihydrogen occurs via the formation of nitric oxide and its subsequent reduction either to nitrogen or its “over reduction” to ammonia represents the crux of the problem in environmental catalysis. Palladium-based catalysts do promote the desired reduction of nitrites but the reduction of nitrates requires another metal center such as, copper or tin. The action of Pd/Cu catalysts (2 and 0.5 wt.% of Pd and Cu, respectively) supported on the D4 in its acidic form (Table 1) was reported by Gasparovicova et al. [36]. The basic idea was to use this composite both as catalyst and as a scavenger of ammonium ions formed in the reduction. A good selectivity to dinitrogen is observed, but extensive metal dissolution, mainly during the regeneration of acid sites, is also observed [83]. However, it has been recently noticed that the use of the cationic resin DA4 provides much higher activity and better selectivity to dinitrogen and these catalysts are believed to be able to compete with their counterparts based on inorganic resins [84].

6. Conclusions

Functional resins appear to be very convenient materials for dispersing Pd(II) as designed molecular species through designed polymer frameworks and for their reduction to Pd nanoclusters. Preliminary data strongly indicate that both the allocation of metal nanoparticles inside the body of the resins particles and their actual size can be conveniently controlled. Preliminary catalytic tests reveal that the relevant

Pd–resin composites are active catalysts, sometime reusable, able to promote hydrogenation reactions for which the physico-chemical status of the swollen polymer framework may offer precious chances to designed targets. Significant Pd nanoclusters–support interaction are to be considered.

Acknowledgements

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References

- [1] G. Schmid, G.L. Hornyak, *Curr. Opin. Solid State Mater. Sci.* 2 (1997) 204.
- [2] G. Schmid, M. Bäuml, M. Geerkens, I. Heim, C. Hoseman, T. Sawitowski, *Chem. Soc. Rev.* 28 (1999) 179.
- [3] J.D. Aiken III, R.G. Finke, *J. Mol. Catal. A: Chem.* 145 (1999) 1.
- [4] A. Guyot, in: D.C. Sherrington, P. Hodge (Eds.), *Synthesis and Separations Using Functional Polymers*, Wiley, New York, 1988, p. 1.
- [5] A. Guyot, *Pure Appl. Chem.* 60 (1988) 365.
- [6] P. Hodge, D.C. Sherrington (Eds.), *Polymer-Supported Reactions in Organic Synthesis*, Wiley, New York, 1980.
- [7] D.C. Sherrington, *Chem. Commun.* (1998) 2275.
- [8] C.E. Harland, *Ion-Exchange*, 2nd Edition, Royal Society of Chemistry, Cambridge, UK, 1994.
- [9] H. Widdecke, in: D.C. Sherrington, P. Hodge (Eds.), *Synthesis and Separations Using Functional Polymers*, Wiley, New York, 1988, p. 149.
- [10] A. Tanaka, T. Tosa, T. Kobayashi (Eds.), *Industrial Applications of Immobilized Biocatalysts*, Marcel Dekker, New York, 1993.
- [11] J.S. Früchtel, G. Jung, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 17.
- [12] K. Weissermel, H.-P. Arpe, *Industrial Organic Chemistry*, 3rd Edition, VCH, Weinheim, 1997, Chapter 11, p. 281 (MIBK), Chapter 3, p. 71 (MTBE).
- [13] K. Jerabek, L.G. Hun, K. Setinek, *Czech. Chem. Commun.* 54 (1989) 321.
- [14] R. Wagner, P.M. Lange, *Erdöl Erdgas Kohle* 105 (1989) 414.
- [15] P.M. Lange, F. Martinola, S. Oeckel, *Hydrocarbon Processing*, 1985, pp. 51.
- [16] B. Corain, M. Kralik, *J. Mol. Catal. A: Chem.* 159 (2000) 153 and references therein.
- [17] N.-H. Li, J.M.J. Frechet, *J. Chem. Soc., Chem. Commun.* (1985) 1100.
- [18] T. Teranishi, N. Toshima, *J. Chem. Soc., Dalton Trans.* (1994) 2967.
- [19] L.A.S. Wu, C. Zhu, W. Huang, Lizi Jiaohuan Yu Xifu 13 (1997) 483 (CA 128:246187t, 1998).
- [20] C.-W. Chen, M.-Q. Chen, T. Serizawa, M. Akashi, *Chem. Commun.* (1998) 831.
- [21] W. Yu, H. Liu, X. An, *J. Mol. Catal. A: Chem.* 129 (1998) L9.
- [22] Z.M. Michalska, B. Ostaszewski, J. Zientarska, J.W. Sobczak, *J. Mol. Catal. A: Chem.* 129 (1998) 207.
- [23] R.A. Sheldon, *J. Mol. Catal. A: Chem.* 107 (1996) 75.
- [24] R.A. Sheldon, *Chem. Ind. (London)*, 6 January 1997, 12.
- [25] R.A. Sheldon, R.S. Downing, *Appl. Catal. A: Gen.* 189 (1999) 163.
- [26] H.-U. Blaser, M. Studer, *Appl. Catal. A: Gen.* 189 (1999) 191.
- [27] F. Germani, F. Pizzio, S. Miertus, *Chim. Ind. (Milan)* 82 (2000) 514.
- [28] T. Takagi, *J. Appl. Polym. Sci.* 19 (1975) 1649.
- [29] C. Yaroslavsky, A. Patchornik, E. Katchalski, *Tetrahedron Lett.* 42 (1970) 3629.
- [30] C.H. Harrison, P. Hodge, B.H. Hunt, E. Kashdel, G. Richardson, *J. Org. Chem.* 48 (1983) 3721.
- [31] S. Kondo, S. Kawasoe, M. Ohira, T. Atarashi, K. Ikeda, K. Kusinada, Y. Yuki, *Macromol. Rapid Commun.* 16 (1995) 291.
- [32] H. Hirai, N. Toshima, in: Y. Iwasawa (Ed.), *Tailored Metal Catalysts*, D. Reidel Publishers, Dordrecht, 1986, pp. 107–140.

- [33] R.H. Grubbs, L.C. Kroll, *J. Am. Chem. Soc.* 93 (1971) 3062.
- [34] M. Howe-Grant (Ed.), *Kirk-Othmer's Encyclopedia of Chemical Technology*, Fourth Edition, Vol. 14, Wiley, New York, 1995, p. 737.
- [35] R. Fisera, M. Kralik, J. Annus, V. Kratky, M. Zecca, M. Hronec, *Collect. Czech. Chem. Commun.* 62 (1987) 1763.
- [36] D. Gasparovicova, M. Kralik, M. Hronec, *Collect. Czech. Chem. Commun.* 64 (1999) 502.
- [37] M. Kralik, D. Gasparovicova, in: *Proceedings of the CHISA 2000 Special Symposium on Chemical Technology for Sustainable Future*, 27–31 August 2000, Prague, pp. J2.5.
- [38] M. Kralik, M. Hronec, S. Lora, G. Palma, M. Zecca, A. Biffis, B. Corain, *J. Mol. Catal. A: Chem.* 97 (1995) 145.
- [39] M. Kralik, M. Hronec, V. Jorik, S. Lora, G. Palma, M. Zecca, A. Biffis, B. Corain, *J. Mol. Catal. A: Chem.* 101 (1995) 143.
- [40] A. Biffis, B. Corain, M. Zecca, C. Corvaja, K. Jerabek, *J. Am. Chem. Soc.* 117 (1995) 1603.
- [41] A. Biffis, B. Corain, Z. Cvengrosova, M. Hronec, K. Jerabek, M. Kralik, *Appl. Catal.* 124 (1995) 355.
- [42] M. Zecca, M. Kralik, M. Boaro, G. Palma, S. Lora, M. Zancato, B. Corain, *J. Mol. Catal. A: Chem.* 129 (1998) 27.
- [43] D. Belli, A.A. D'Archivio, L. Galantini, S. Lora, A. Biffis, B. Corain, *J. Mol. Catal. A: Chem.* 157 (2000) 173.
- [44] G. Bombi, *Laurea Thesis*, University of Padova, in press.
- [45] A. Biffis, A.A. D'Archivio, K. Jerabek, G. Schmid, B. Corain, *Adv. Mater.* 12 (2000) 1909.
- [46] M. Zecca, R. Fisera, G. Palma, S. Lora, M. Hronec, M. Kralik, *Chem. Eur. J.* 6 (2000) 1980.
- [47] B. Corain, M. Basato, M. Zecca, S. Lora, G. Palma, *Makromol. Chem. Rapid Commun.* 7 (1986) 651.
- [48] B. Corain, M. Basato, M. Zecca, R. De Pieri, S. Stran, P. Main, R. Arshady, *J. Organomet. Chem.* 326 (1987) C43.
- [49] U. Casellato, B. Corain, M. Zecca, R.A. Michelin, M. Mozzon, R. Graziani, *Inorg. Chim. Acta* 156 (1989) 165.
- [50] R. Arshady, M. Basato, B. Corain, L. Della Giustina, S. Lora, G. Palma, M. Roncato, M. Zecca, *J. Mol. Catal.* 53 (1989) 111.
- [51] B. Corain, F.O. Sam, M. Zecca, A.C. Veronese, G. Palma, S. Lora, *Makromol. Chem. Rapid Commun.* 10 (1990) 697.
- [52] B. Corain, F.O. Sam, M. Zecca, S. Lora, G. Palma, *Angew. Chem. Int. Ed. Engl.* 29 (1990) 384.
- [53] R. Arshady, B. Corain, S. Lora, G. Palma, U. Russo, F.O. Sam, M. Zecca, *Adv. Mater.* 2 (1990) 412.
- [54] B. Corain, M. Basato, M. Zecca, G. Braca, A.M. Raspolli Galletti, S. Lora, G. Palma, E. Guglielminotti, *J. Mol. Catal.* 73 (1992) 23.
- [55] B. Corain, K. Jerabek, S. Lora, G. Palma, M. Zecca, *Adv. Mater.* 4 (1992) 97.
- [56] B. Corain, M. Zecca, S. Lora, G. Palma, *Makromol. Chem. Rapid Commun.* 14 (1993) 799.
- [57] R. Arshady, *Adv. Mater.* 3 (1991) 182.
- [58] F.R. Hartley, *Supported Metal Complexes*, D. Reidel Publishers, Dordrecht, 1985.
- [59] S. Schlick, E. Bortel, K. Dyrek, *Acta Polym.* 47 (1996) 1.
- [60] R. Arshady, B. Corain, M. Zecca, in: R. Arshady (Ed.), *Desk Reference of Functional Polymers: Syntheses and Applications*, American Chemical Society, Washington, DC, USA, 1997, p. 151 and references therein.
- [61] J. Wöllner, W. Neier, *German Patent* 1260454, 1969.
- [62] F. Filippi, *Laurea Thesis*, University of Padova, in press.
- [63] B. Corain, M. Zecca, A. Biffis, S. Lora, G. Palma, *J. Organomet. Chem.* 475 (1994) 283.
- [64] A. Primavera, M. Zecca, B. Corain, *J. Mol. Catal.* 108 (1995) 131.
- [65] M. Kralik, V. Kratky, M. Hronec, M. Zecca, B. Corain, *Stud. Surf. Sci. Catal.* 130 (2000) 2321.
- [66] M. Kralik, R. Fisera, M. Zecca, A.A. D'Archivio, L. Galantini, K. Jerabek, B. Corain, *Collect. Czech. Chem. Commun.* 63 (1998) 1074.
- [67] H. Bönneman, W. Brijoux, R. Brinkmann, R. Fretzen, T. Joussem, R. Köppler, B. Korall, P. Neiterel, J. Richter, *J. Mol. Catal.* 86 (1994) 129.
- [68] A.A. D'Archivio, L. Galantini, A. Biffis, K. Jerabek, B. Corain, *Chem. Eur. J.* 6 (2000) 794.
- [69] A. Biffis, H. Landes, K. Jerabek, B. Corain, *J. Mol. Catal. A: Chem.* 151 (2000) 283.
- [70] A.A. D'Archivio, L. Galantini, E. Tettamanti, A. Panatta, B. Corain, *J. Mol. Catal. A: Chem.* 157 (2000) 269.
- [71] B. Corain, K. Jerabek, *Chim. Ind. (Milan)*, 78 (1996) 563 and references therein.
- [72] K. Jerabek, *Anal. Chem.* 57 (1985) 1598.
- [73] K. Jerabek, in: M. Potschka, P.L. Bubbin (Eds.), *Cross-Evaluation of Strategies in Size-Exclusion Chromatography*, ACS Symposium Series 635, American Chemical Society, Washington, DC, USA, 1996, p. 211.
- [74] A.G. Ogston, *Trans. Faraday Soc.* 54 (1958) 1754.
- [75] A.A. D'Archivio, L. Galantini, A. Panatta, E. Tettamanti, B. Corain, *J. Phys. Chem. B*, 102 (1998) 6779 and references therein.
- [76] M. Kralik, M. Zecca, P. Bianchin, A.A. D'Archivio, L. Galantini, B. Corain, *J. Mol. Catal. A: Chem.* 130 (1998) 85.
- [77] J.S. Mackie, P. Meares, *Proc. R. Soc. London Ser. A* 232 (1955) 498.
- [78] A.J. Bird, D.T. Thomson, in: W.H. Jones (Ed.), *Catalysis in Organic Synthesis*, Academic Press, New York, 1980, p. 61.
- [79] H.J. Janssen, A.J. Kruihof, G.J. Steghuis, K.R. Westerterp, *Ind. Eng. Chem. Res.* 29 (1990) 1822.
- [80] V. Kratky, M. Kralik, M. Hronec, M. Mecarova, in press.
- [81] A.Y. Stakheev, L.M. Kustov, *Appl. Catal. A: Gen.* 188 (1999) 3.
- [82] R. Ricoveri, *Laurea Thesis*, University of Padova, in press.
- [83] M. Kralik, V. Gasparovicova, V. Jorik, M. Hronec, M. Zecca, *Appl. Catal. B: Environ.*, 2000, submitted for publication.
- [84] U. Prusse, M. Hahnlein, J. Daum, K.D. Vorlop, *Appl. Catal.* 55 (2000) 79.