

# Generating palladium nanoclusters inside very lipophilic gel-type functional resins: preliminary catalytic tests in the hydrogenation of 2-ethyl-anthraquinone to 2-ethylanthrahydroquinone

G. Bombi<sup>a</sup>, S. Lora<sup>b</sup>, M. Zancato<sup>c</sup>, A.A. D'Archivio<sup>d</sup>, K. Jerabek<sup>e</sup>, B. Corain<sup>f,\*</sup>

<sup>a</sup> Chelab Srl, Via Fratta 25, 31023 Resana, Italy

<sup>b</sup> Istituto F.R.A.E., C.N.R., Via Romea 4, 35020 Legnaro, Italy

<sup>c</sup> Dipartimento di Scienze Farmaceutiche, Via Marzolo 5, 35131 Padova, Italy

<sup>d</sup> Dipartimento di Chimica, Ingegneria Chimica e Materiali,

Università di L'Aquila, Via Vetoio, Coppito Due, 67010 L'Aquila, Italy

<sup>e</sup> Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojova 135, 16502 Suchdol, Praha 6, Czech Republic

<sup>f</sup> Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Via Marzolo 1, 35131 Padova, Italy

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## Abstract

Four lipophilic polystyrene–methacryloylethylensulfonic acid–divinylbenzene gel-type resins, with 2 and 4% cross-linking degree, are synthesized and used as supports for “atomic” dispersion of Pd(II) finalized to the preparation of resins-supported palladium metal catalysts. Properly performed reduction of Pd(II) to Pd(0) achieves homogeneous dispersion of ca. 3 nm metal nanoclusters inside the supports particles in the more cross-linked resin. Resulting resin-supported palladium catalysts are efficient and moderately chemoselective in the hydrogenation of 2-ethylanthraquinone to 2-ethylanthrahydroquinone.

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## 1. Introduction

Functional resins are currently employed in chemical technologies as ion exchangers and as acidic catalysts under a variety of circumstances [1,2]. They are also employed as supports of palladium metal in some industrial processes such as the syn-

thesis of methyl-isobutyl ketone (MIBK; e.g. Bayer catalyst OC 1038) [3], where the acid centers catalyze the dimerization of acetone to di-acetone alcohol and its dehydration to mesityloxide, which is then hydrogenated on the metal surface to the end product. Similar catalysts based on anion exchange resins (e.g. Bayer catalysts K6333 and VPOC 1063) [3] are employed in industrial heat-exchange units for the reduction of di-oxygen level in water from  $\text{mg dm}^{-3}$  to  $\mu\text{g dm}^{-3}$  levels. Another appli-

\* Corresponding author. Fax: +39-049-8275223.

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

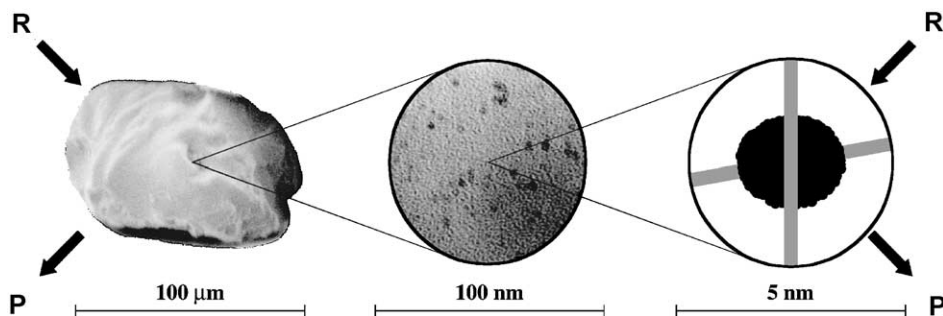


Fig. 1. Schematic representation of a catalyst particle ("microreactor") built-up with a polymer framework and entrapped metal nanoclusters [10–12].

cation is the combined etherification and hydrogenation of mixtures of unsaturated hydrocarbons to give blends of alkanes and MTBE (EC Erdöl-chemie process) [4] or other branched ethers for the manufacture of unleaded petrol (BP etherol process) [5].

In spite of their expected higher costs, resins-based metal catalysts are likely to become economically relevant specialties in view of the gradual extension of metal catalysis to the realm of fine chemistry, also in connection with the need to fulfill more and more strict environmental requirements, which promote the replacement of conventional stoichiometric synthetic routes with catalytic ones [6–9].

Synthetic resins are really unique supports for catalytically active metal nanoclusters in that they combine the potentiality of designable multi-functionality and the possibility to control the hydrophilic or lipophilic character of the environment in the vicinity of the active centers with controllable nanomorphology and reasonable thermal and mechanical stability [1,10] (Fig. 1).

This paper and the following one [13] are illustrating these concepts in the chemoselective hydrogenation of 2-ethylantraquinone (AQ) to 2-ethylantrahydroquinone (AH<sub>2</sub>Q), which is a key step in the current industrial synthesis of hydrogen peroxide [14]. This reaction is plagued by the unwanted consecutive hydrogenation of the desired product to, *inter alia*, tetrahydro-2-ethyl-antrahydroquinone and octahydro-2-ethylantrahydroquinone. The current industrial catalyst (Pd/silicoaluminate) provides a chemoselectivity towards AH<sub>2</sub>Q of ca. 95%. Con-

sidering the very large amounts of AQ and AH<sub>2</sub>Q circulating in the process, the losses of AQ due to the conversion of AH<sub>2</sub>Q into unwanted by-products are considerable. Even small increases of the chemoselectivity may have a very significant economical effect.

The strategy for chemoselectivity improvement reported here is based on the synthesis of novel catalysts containing ca. 1% palladium metal dispersed inside very lipophilic, polymer networks. The desired product, AH<sub>2</sub>Q, is less lipophilic than AQ and it is speculated that its expedient removal assisted by the lipophilic character of the polymer network surrounding Pd crystallites might prevent the undesired further hydrogenation steps. Design of this strategy has been based on our work in recent years during which was developed: (i) a general scheme for the dispersion of metal centers inside given polymer networks, (ii) methods for subsequent production of metal crystallites with controlled size and distribution through the catalyst particles, and (iii) a multi-methodological approach to the evaluation of the nanometer size morphology (hereafter referred to as nanomorphology) and of the molecular accessibility of the polymer network [15,16].

For achieving the desired goal we selected the synthetic strategy based on the co-polymerization of lipophilic monomers with a monomer containing a functional group able to anchor ionic palladium. This approach was dictated by the known difficulty met in generating a lightly functionalized polystyrene framework with –SO<sub>3</sub>H groups uniformly located through the body of the resin particles by direct functionalization of a pre-formed polymer.

## 2. Experimental

### 2.1. Materials

Styrene [STY] (99%), sulfoethylmethacrylate or methacryloylethylensulfonic acid [SEMA] (95%) and sodium 4-styrylsulfonate [SSNa], were from Aldrich and Polyscience, respectively. “Divinylbenzene” [DVB] (Aldrich) was the usual mixture of divinylbenzene (55%) and ethylvinylbenzenes (45%). All solvents, of reagent grade, were from C. Erba, Milano. Industrial Pd/silicoaluminate catalyst and technical EAQ were kindly donated by Ausimont (Bussi sul Tirino, Pescara, Italy).

### 2.2. Apparatus

*X-rays microprobe analysis (XRMA)*: Philips IXL40 Model SEM equipped with an EDAX PY99X-RAY energy-dispersive spectrometer.

*ISEC apparatus* consists of Model 7725i syringe loading sample injector (Rheodyne, USA), stainless steel column 4.1 mm × 250 mm, refractometric detector RIDK 101 (LP Praha, Czech Republic) and computer data acquisition system synchronized with the chromatography set-up through a drop counter probe.

*ESR analysis*: JEOL JES-RE1X apparatus at 9.2 GHz (modulation 100 kHz) over the temperature range of 2–40 °C at variable temperature controlled by a unit Stelar VTC91.

*ICP–AES*: IRIS II Radial apparatus with low temperature CID simultaneous detector.

*Catalytic tests* are carried out by means of a Büchi steel/glass thermostated autoclave, of approximately 100 cm<sup>3</sup> in volume, modified in order to perform quasi-constant pressure catalytic runs. The hydrogen pressure is let to decrease till a fixed value during the catalytic run and automatically adjusted to the higher end of pressure interval upon feeding from a constant pressure hydrogen reservoir.

### 2.3. Synthesis

We have prepared two kinds of resin supports, alternatively with SEMA and SSNa as the functionalized co-monomer. SEMA containing resin supports were synthesized with two different cross-linking degrees.

Table 1

Composition of reaction mixtures employed in the preparation of the resins

	STYR (mol%)	DVB (mol%)	SSNa (mol%)	SEMA (mol%)
M2	94	2	–	4
M4	92	4	–	4
S4	92	4	4	–

The description of the resin composition and designation are shown in Table 1.

In order to achieve the mutual solubility of all co-monomers, DMSO is added to the mixture of the monomers in amount of about 30 wt.% for the series M and 45 wt.% for the S4 resin. Polymerization is carried out by  $\gamma$ -rays irradiation [10,17,18] (<sup>60</sup>Co at 0.28 Gy s<sup>-1</sup> for 72 h at ca. 20 °C). The resins are obtained in the form of transparent rods. Polymers are swollen in THF, then cut in thin slices, ground in a mortar, washed with THF, EtOH, Et<sub>2</sub>O (150 cm<sup>3</sup> each) and dried under vacuum. Polymerization yields determined after this processing are almost quantitative. Resins are sieved to produce a 100–140  $\mu$ m fraction. Composition of selected polymers is confirmed by elemental analysis: M2, C, 85.18, H, 7.49, S, 3.14; M4, C, 83.59, H, 7.49, S, 3.61.

### 2.4. Palladiation

Resins are palladiated typically by reacting 1 g of the polymer (0.4 meq of –SO<sub>3</sub>H groups), swollen in 10 cm<sup>3</sup> of THF under moderate stirring with 25 mg palladium acetate (ca. 0.1 mmol) [10] dissolved in 20 cm<sup>3</sup> THF. After ca. 12 h, the supernatant solution becomes colorless while the resin changes its color to dark brown. The polymer is filtered off, washed with THF, EtOH, Et<sub>2</sub>O (20 cm<sup>3</sup> each) and dried under vacuum.

Resin S4 is modified into the corresponding acidic form by ionic exchange with alcoholic HCl before palladiation.

Palladiated resins (M2Pd(II), M4Pd(II) and S4Pd(II)) are transformed into the final catalysts M2Pd, M4Pd and S4Pd by reduction with an excess of NaBH<sub>4</sub> in ethanol (60 cm<sup>3</sup> of 66 mM solution), under moderate stirring. After 12 h the resulting black materials are filtered off and washed with EtOH

( $2 \times 20 \text{ cm}^3$ ) and  $\text{Et}_2\text{O}$  ( $1 \times 20 \text{ cm}^3$ ) and dried under vacuum.

Palladium content in the resins has been determined with ICP–AES, after complete dissolution of the resins in a mixture of mineral acids (two parts of sulfuric and one part of nitric acid with a few drops of perchloric acid).

### 2.5. Catalytic tests

Catalytic tests are carried out in a mixture of *p*-xylene/2-octanol (1:1). The catalyst is fed into the reactor and covered with  $3 \text{ cm}^3$  of solvent: industrial catalyst is reduced with hydrogen in this step. The working solution of  $50 \text{ cm}^3$  ( $50 \text{ g dm}^{-3}$  of 2-ethylantraquinone in the reaction solvent) are fed in the reactor, air is removed upon gentle bubbling with nitrogen. During this time (ca. 30 min) the apparatus reaches the thermostate temperature of  $25 \text{ }^\circ\text{C}$ .

Hydrogen is fed at a pressure of 200 kPa after removal of nitrogen and the magnetic stirring is operated: the amount of reacted hydrogen is determined from pressure and temperature values that are collected at fixed time intervals while the pressure drops to the lower end of pressure interval (175 kPa) then more hydrogen is fed. The reaction is stopped when hydrogen consumption equals the stoichiometric amount of 2-ethylantraquinone and, at this point, hydrogen is replaced with nitrogen.

The catalyst is recovered upon filtration under nitrogen and eventually water is added ( $50 \text{ cm}^3$ ) and air is bubbled in the resulting mixture for 10 min. The organic phase is then collected and the content of 2-ethylantraquinone is determined by GLC. A complete recovery of the substrate is considered indicative of 100% chemoselectivity.

## 3. Results and discussion

### 3.1. Swelling behavior

Each of the resins is prepared in at least four batches and the polymerization yield is usually 95–100%. Accessibility of metal centers supported in gel-type resins depends on their swelling in the reaction environment. Consequently, proper selection of the solvent for the catalytic reaction is also a part of the overall design.

Table 2  
Swelling of the examined resins in different solvents

Resin	Resin bed expansion in different solvents (%)		
	<i>p</i> -Xylene	2-Octanol	<i>p</i> -Xylene:2-octanol mixture 1:1 (v/v)
M2	152	4	144
M4	85	4	88
S4	159	15	133

It should guarantee: (i) acceptable swellability of catalyst particles, (ii) acceptable solubility of 2-AQ and 2-AH<sub>2</sub>Q in the bulk liquid medium, (iii) preferential absorption of EAQ over 2-AH<sub>2</sub>Q into the swollen polymer matrix. We have tested the swelling behavior of all synthesized resin in *p*-xylene, 2-octanol and in their 1:1 mixture by measurements of expansion of the resin particle bed in transition from dry to swollen state [ $(V_{\text{swollen}} - V_{\text{dry}})/V_{\text{dry}}$ ] (Table 2) [12,19].

The data in Table 2 indicate that *p*-xylene is a good swelling agent for all the resins but in 2-octanol the resins swell negligibly. Therefore, good swelling in xylene/octanol mixture have to be interpreted as due to a preferential absorption of xylene as the less polar of both solvents. It well illustrates a crucial feature of the polymer supported catalysts, i.e. the ability of the polymer framework to “impose” a liquid medium with a composition that may be very different from that of the bulk solution inside which the resins particles are dispersed.

Swollen state morphology of the investigated resins was thoroughly examined with inverse steric exclusion chromatography (ISEC) [20]. This method is based on measurements of elution volumes of a series of standard solutes of known molecular sizes using chromatographic columns filled with the material to be evaluated. Experiments are performed at conditions aimed at excluding enthalpic interactions between solutes and the stationary phase. By mathematical treatment of the obtained data it is then possible to produce valuable information on the pore morphology of the examined material (from macropores to nanometric micropores). The real pore system is modeled as a set of discrete fractions, each characterized by uniform pores of a simple geometry and size. Swollen polymer gel can be realistically modeled on the basis of the idea developed by Ogston [21] as space in which rigid cylindrical rods representing the polymer chains

are randomly distributed. As the parameter characterizing the pore dimension in ISEC analysis, polymer chain density in units of length per unit of volume, i.e.  $\text{nm}^{-2}$ , is successfully employed. Useful scale of the polymer chain densities spans from  $0.1 \text{ nm}^{-2}$ , corresponding to an extremely expanded network, up to  $2 \text{ nm}^{-2}$ , characterizing very dense polymer into which even the smallest molecules can hardly penetrate. The ISEC analyses were performed alternatively in THF, where the non-polar, lipophilic polymer domains are swollen and the domains containing sulfonic groups are collapsed and, hence “invisible”, and in water, where unswollen and “invisible” are the lipophilic parts of the polymer framework.

ISEC results confirmed that the morphology of the synthesized resins fulfills the design requirements. Hydrophilic domains necessary for anchoring ionic palladium comprise only very small portion of the polymer matrix swelling in water to  $0.10$  and  $0.08 \text{ cm}^3 \text{ g}^{-1}$  in the resins M2 and S4, respectively. On the contrary, do prevail in the resin morphology lipophilic domains swelling in THF, in the resins M2 and S4 to  $3.76$  and  $3.52 \text{ cm}^3 \text{ g}^{-1}$ , respectively.

### 3.2. ESR characterization

ESR spectroscopy was utilized to investigate the rotational mobility of the spin probe TEMPONE (2,2,6,6-tetramethyl-4-oxo-1-oxypiperidine) dispersed in the various toluene-swollen resins with the purpose of evaluating the permeability of the swollen polymer network to solute molecules. The observed ESR spectra collected in the temperature range of  $0\text{--}40^\circ\text{C}$  are typical of “fast-motion” reorientation of the spin probe, whose correlation time ( $\tau$ ) can be computed from line widths on the basis of established relationships [15,16]. The  $\tau$ -values at  $25^\circ\text{C}$  are given in Table 3, together with the activation energies of the rotational diffusion obtained from an Arrhenius plot over the investigated temperature range. These data evidence a relatively good mobility of TEMPONE in the swollen resins even though a reduction of rotational mobility (an increase of  $\tau$ ) is observed in comparison with bulk solution. On the basis of previous work on swollen microporous resins [15,16] the observed  $\tau$ -values are typical of spin probe molecules rotating inside relatively low density swollen polymer network domains, as the ones featured by a

Table 3

Rotational correlation time ( $\tau$ ) of TEMPONE at  $25^\circ\text{C}$  in bulk solution and in various resins swollen in toluene, and apparent activation energies of the rotational diffusion ( $E_a$ ) determined in the temperature range of  $0\text{--}40^\circ\text{C}$

	$\tau$ (ps) $\pm$ 5%	$E_a \pm 0.5$ (kJ mol $^{-1}$ )
Bulk solution	8	5.5
M2	54	6.0
M4	108	5.0
S4	82	6.0

$0.2\text{--}0.4 \text{ nm}^{-2}$  polymer chain density revealed by ISEC in THF-swollen M2 and S4. On the other hand, the swollen polymer part with a polymer chain density  $>1.5 \text{ nm}^{-2}$  is expected to be virtually inaccessible to TEMPONE. The practical constancy of the activation energy also suggests that possible solute–polymer interactions or dynamics of polymer network have a negligible effect on mechanism of reorientation of the spin probe. Consequently, the hindrance of the spin probe rotational diffusion in the swollen resins has to be ascribed mainly to the increase of micro-viscosity of its environment caused by the confinement of the solvent inside the polymer network [15,16].

### 3.3. Palladiation

The uptake palladium is very easy on the resins M2 and M4 synthesized with the sulfonic groups in the hydrogen form. Resin S4 can be palladiated [10] only after conversion into the acidic form.

Tetrahydrofuran is used as the solvent for palladiation of the resins because it is known as one of the best swelling solvents for styrenic polymers and it is compatible with palladium acetate. The complete color fading of the surnatant solution during the

Table 4

Mass fraction of Pd in the examined catalysts

	Pd content (wt.%)	
	Computed	Determined
CoPd <sup>a</sup>	2.0	1.65
M2Pd	1.0	0.95
M4Pd	1.0	0.80
S4Pd	1.0	0.95

<sup>a</sup> Industrial catalyst.

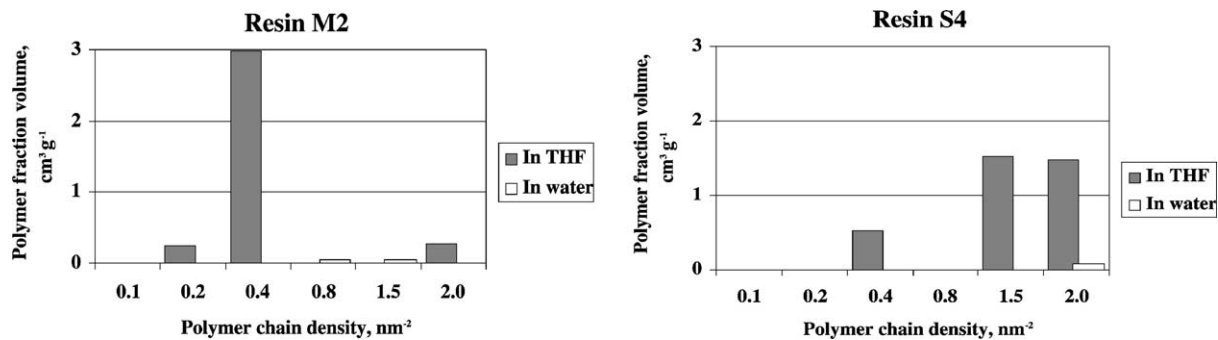


Fig. 2. Comparison of morphology of resins M2 and S4, swollen in water and THF, as determined by ISEC.

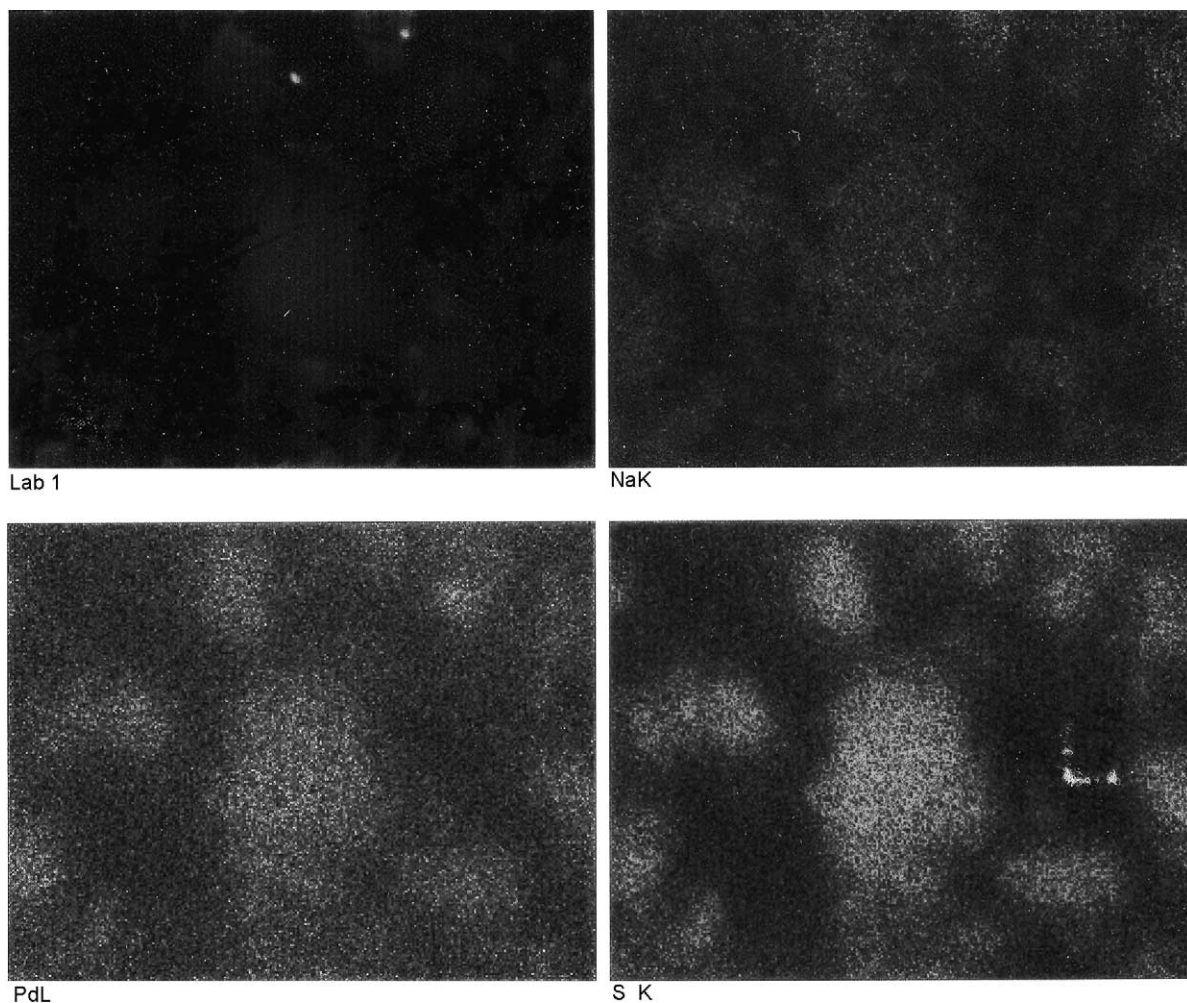


Fig. 3. Catalyst S4Pd: (a) SEM micrograph of a cross-section of a catalyst particle (25 kV, spot 4.0, magnetism 400 $\times$ ); (b) XRMA mapping of sodium (NaK); (c) XRMA mapping of palladium (PdL); (d) XRMA mapping sulfur (SK).

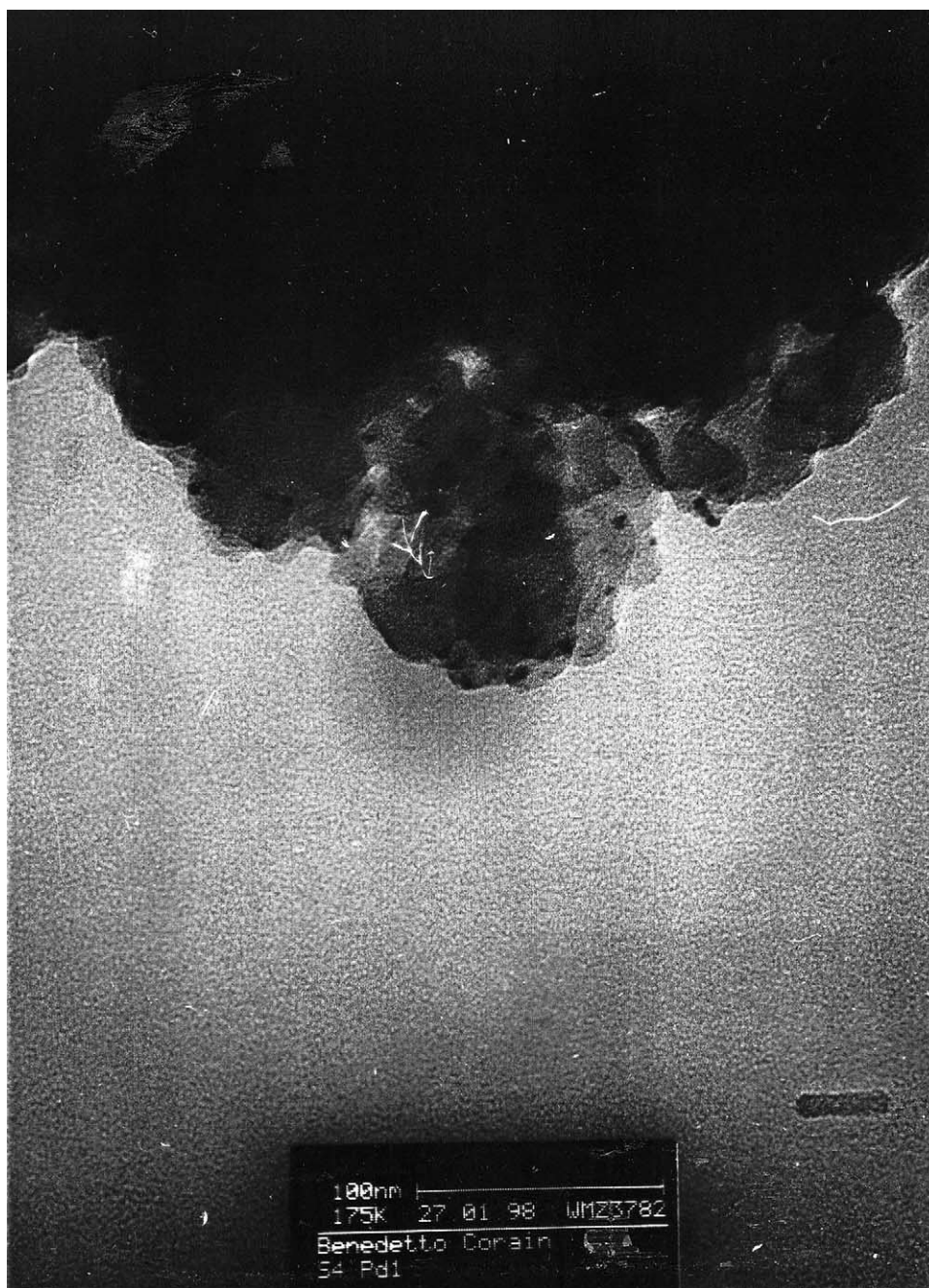


Fig. 4. TEM picture of a particle of S4Pd(I) catalyst. Metal nanocluster are visible in the lower part of the picture.

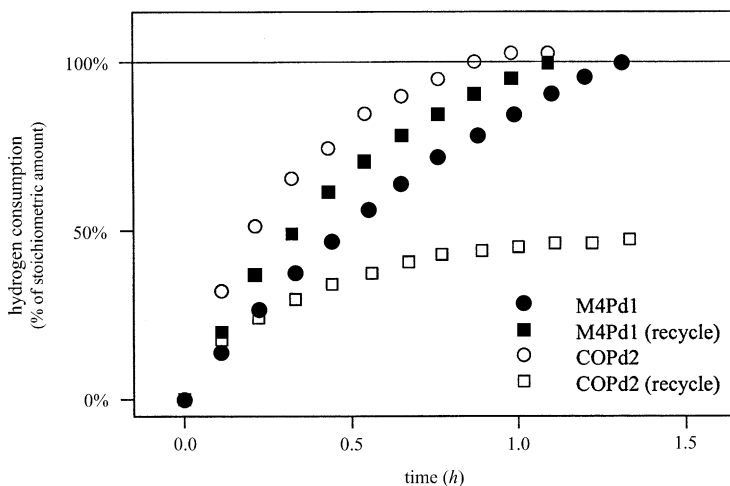


Fig. 5. Kinetic curves of preliminary catalytic tests: comparison between industrial catalyst CoPd and M4Pd.

palladiation of the resin suggests that the incorporation of palladium ions into the polymer support is quantitative. This is confirmed by reasonably good agreement between palladium loading computed from the amount of palladium acetate used and actual palladium content determined by elemental analysis of the resin (Table 4).

X-Ray microprobe analysis (XRMA) of cross-sections of catalysts particles reveals that metal distribution is quite homogeneous through the body of the particles (Figs. 2–4). It confirms also good accessibility of the interior of resins particles expected for moderately cross-linked gel-type resins [15,16] and proves the suitability of our previously described palladiation and reduction protocols [11].

TEM analysis reveals that metal nanoclusters in S4Pd are of fairly regular size ( $3\text{ nm} \pm 1\text{ nm}$ ). This finding agrees with previous results obtained in these laboratories dealing with the generation of Pd crystallites inside amphiphilic resins of similar morphology [12].

### 3.4. Preliminary hydrogenation tests

Preliminary tests were carried out on 2-ethylanthraquinone and M4 catalyst exhibits good activity and moderate selectivity in a mixture of *p*-xylene/2-octanol (1:1) compared with the industrial catalyst. Some selected data are shown in Fig. 5 (hydrogen consumption is referred to the stoichiometric amount needed for complete conversion into 2-ethylanthrahydroquinone).

Fig. 5 shows that the industrial catalyst (CoPd) is just moderately more active than M4Pd that turns to be in fact far more stable (reusable). The high reactivity of M4Pd is already per se a remarkable result in that the very large majority of metal nanoclusters appears to be reachable by hydrogen and substrate in spite of being surrounded by the gel mass. Apparently, the employed solvent turns out to be particularly well selected in that confinement effects are seen to only moderately reduce the rotational mobility of the paramagnetic probe. On the basis of previous studies from these laboratories [11], rotational mobility well correlates with translational mobility and these direct evidences of molecular accessibility of the resin particles parallels the good activity levels exhibited by catalyst M4Pd.

The chemoselectivity of M4Pd in favor of 2-ethylanthrahydroquinone results to be only moderate (estimated value of 60–70% indicated by GLC analysis of final solutions). These values are still definitely lower than those provided by the industrial catalyst, but they encourage attempts of further perfecting the basic idea of embedding Pd nanoparticles inside lipophilic matrices.

## 4. Conclusions

The whole of these preliminary data referring to the metallation of very lipophilic matrices confirm a number of previous observation from our



group, mainly dealing so far with essentially hydrophilic or amphiphilic resins. In particular,  $\gamma$ -rays co-polymerization of designed co-monomers affords quantitatively functional resins based on pre-functionalized monomers, that enable the even dispersion of acidic groups and, consequently, of metal centers and metal nanoclusters, inside the resins particles. The obtained Pd catalysts, after swelling in a properly chosen solvent mixture, result to be efficient and moderately chemoselective towards the hydrogenation of 2-ethylantraquinone to 2-ethylantrahydroquinone.

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### References

- [1] D.C. Sherrington, P. Hodge (Eds.), *Synthesis and Separations Using Functional Polymers*, Wiley, New York, 1988.
- [2] C.E. Harland, *Ion Exchange*, 2nd ed., Royal Society of Chemistry, Cambridge, UK, 1994.
- [3] R. Wagner, P.M. Lange, *Erdol Erdgas Kohle* 105 (1989) 414.
- [4] P.M. Lange, F. Martinola, S. Oeckel, *Hydrocarbon Processing*, December 1985, p. 51 (and references therein).
- [5] D.C. Sherrington, *Chem. Commun.* (1998) 2275.
- [6] R.A. Sheldon, *J. Mol. Catal. Part A. Chem.* 107 (1996) 75.
- [7] R.A. Sheldon, *Chem. Ind. (London)* (1997) 12–15.
- [8] R.A. Sheldon, R.S. Downing, *Appl. Catal. Part A. Gen.* 189 (1999) 163.
- [9] H.-U. Blaser, M. Studer, *Appl. Catal. Part A. Gen.* 189 (1999) 191.
- [10] B. Corain, M. Kralik, *J. Mol. Catal. Part A. Chem.* 173 (2001) 113 (and references therein).
- [11] B. Corain, M. Kralik, *J. Mol. Catal. Part A. Chem.* 159 (2000) 153.
- [12] A. Biffis, A.A. D'Archivio, K. Jerabek, G. Schmid, B. Corain, *Adv. Mater.* 12 (2000) 1909.
- [13] A. Biffis, R. Ricoveri, S. Campestrini, M. Kralik, K. Jerabek, B. Corain, *Chem. Eur. J.* 8 (2002) 2962.
- [14] *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., UCH, Weinheim, 1998.
- [15] A. Biffis, B. Corain, M. Zecca, C. Corvaja, K. Jerabek, *J. Am. Chem. Soc.* 117 (1995) 1603.
- [16] A.A. D'Archivio, L. Galantini, A. Panatta, E. Tettamanti, B. Corain, *J. Phys. Chem. B* 102 (1998) 6779 (and references therein).
- [17] I. Kaetsu, *Radiat. Phys. Chem.* 18 (1991) 343.
- [18] I. Kaetsu, *Radiat. Phys. Chem.* 46 (1995) 1025.
- [19] R. Arshady, *Adv. Mater.* 3 (1991) 182.
- [20] 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, pp. 211–224.
- [21] A.G. Ogston, *Trans. Faraday Soc.* 54 (1958) 1754.