

Metal ion implantation onto acidic resins upon reaction of metal acetates and carbamates

Part I. Synthetic results

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Abstract

Moderately cross-linked gel-type resins bearing $-\text{SO}_3\text{H}$, $-\text{COOH}$ and $-\text{OH}$ groups undergo facile metallation with Pd^{II} , Cu^{II} and Ni^{II} acetates with concomitant release of acetic acid. Successful and facile metallation is also observed upon reaction with Pd^{II} , Cu^{II} and Ni^{II} carbamates. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Supported metal catalysts based on synthetic functional resins are currently utilized in at least four industrial processes [1–5], i.e., synthesis of MIBK (Bayer catalyst OC 1038, acetone, 30 bar H_2 , 139–140°C), dioxygen removal from industrial waters (Bayer catalysts K 6333 and VP OC 1063, 1.5–2.0 bar H_2 , 70°C), synthesis of

MTBE (EC Erdoelchemie process) and in the etherification–hydrogenation process of mixtures of unsaturated hydrocarbons to give blends of alkanes and branched ethers for the manufacture of unleaded petrol (BP Etherol Process).

In recent years, we have contributed to the development of the designing criteria of this quite promising type of catalyst upon looking at (i) methods for the dispersion of Pd^{II} inside given polymer networks [6–11]; (ii) protocols for the subsequent production of metal crystallites with controlled size and size distribution through the body of the catalyst particles [6–11], and (iii) multimethodological approaches for the

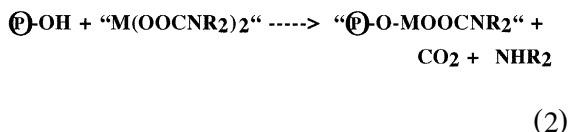
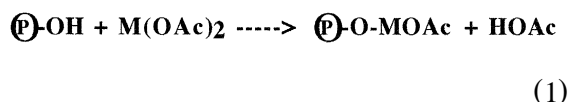
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evaluation of the nanometer-size morphology (hereafter referred to as nanomorphology) and of the molecular accessibility of the polymer network [12–15]. As to point (i), we have illustrated the possibility of implanting “Pd²⁺” under mild conditions and with quantitative yields onto resins bearing –SO₃H groups, upon using Pd(OAc)₂ as the reagent. The reaction is, in fact, a sort of “forced ion exchange” process (exemplified by Eq. 1), which is effectively driven to completion by the formation of the weak acid, HOAc. In this connection, Sommazzi et al. [16,17] reported recently on a related approach aimed at implanting metal species onto the surface of silica, based on the deprotonation of surface –OH groups that promotes the eventual irreversible liberation of CO₂ and the formation of metal–oxygen bonds (Eq. 2):



We report here on the extension of our synthetic approach to other OH-bearing functional resins, i.e., to materials containing –COOH and –OH groups. Moreover, we report also on the application of Sommazzi’s method to the controlled metallation of the same materials.

2. Experimental

2.1. Materials

All chemicals were of reagent-grade. The monomers and cross-linker employed are coded as follows: dimethylacrylamide, DMA; methylenebisacrylamide, MBA; sulfethylmethacrylate (methacryloylethylsulfonic acid) SEMA; methacrylic acid, MA; hydroxyethylmethacrylate, HEMA. All monomers were from Aldrich, apart from SEMA which was from Polyscience.

Commercial methanol (Baker) stored on molecular sieves (Union Carbide, 4 Å) was used without further purification. Dichloromethane (Aldrich) was dried on P₄O₁₀ and distilled prior to use. *Trans*-Pd(O₂CNEt₂)₂(NH₂Et)₂ [18], [Ni(O₂CNEt₂)₂]_x [19] and Cu₂(O₂CNEt₂)₄(NH₂Et)₂ [20] were prepared according to the literature. Anhydrous nickel acetate was obtained by treatment of the commercial hydrated nickel acetate (C. Erba) with acetic anhydride. Commercial Pd(OAc)₂ (Aldrich) and Cu(OAc)₂ · H₂O (Aldrich) were used without further purification. Unless otherwise specified, all the preparations and handlings involving these reagents were carried out under a dinitrogen atmosphere at room temperature.

2.2. Apparatus

Electronic spectra were recorded from KBr discs with a Perkin Elmer 580 B spectrophotometer in the transmission mode. XRM analyses were carried out by means of a Cambridge Stereoscan 250 EDX PW 9800 apparatus. ESR spectra were recorded on an X-band JEOL JES-RE1X apparatus at 9.2 GHz (modulation 100 kHz) equipped with a variable temperature unit Steler VTC91. PGSE-NMR spectra were recorded on a Bruker SXP 4–100 MHz apparatus operating at 21 MHz for protons, equipped with a variable temperature unit, BRUKER-VT 100.

2.3. Synthesis

2.3.1. Resin preparation

Table 1 reports the composition of the monomer mixtures used to prepare the functionalised resins.

Table 1
Composition of the monomer mixtures used for resin synthesis (the molar percent of each component in the monomer mixture is reported in parentheses)

| Resin | DMA (g) | Functional monomer (g) | MBA (g) |
|------------|-----------|------------------------|----------|
| SPI | 9.27 (92) | SEMA, 0.77 (4) | 0.60 (4) |
| MPI | 9.64 (92) | MA, 0.36 (4) | 0.62 (4) |
| HPI | 9.46 (92) | HEMA, 0.54 (4) | 0.61 (4) |

The clear mixtures were poured into 20 ml Pyrex cylindrical vials under dinitrogen and then irradiated by γ -rays from a ^{160}Co source at 0.5 Gy s^{-1} for 18 h at room temperature, at a distance of 21 cm with a total dose equal to 1 Mrad. The obtained pale yellow glass-like cylinders were suspended in 100 ml methanol (reagent-grade) under vigorous stirring for 24 h, after which time a suspension of millimeter-size colourless particles was obtained. After filtration with a gooch filter, the material was suspended in fresh methanol (50 ml) in a mortar and finely ground, then the suspension was transferred into a beaker with some more methanol (50 ml) and was further stirred for 1 h at room temperature. The suspension was then filtered and the resin was washed with diethyl ether, dried at 10^{-2} Torr over P_4O_{10} and sealed in vials under nitrogen for storing purposes.

Analyses. **SPI**: C, 58.3; H, 10.0; N, 12.4; S, 18.0 (yield = 78%). **MPI**: C, 60.0; H, 10.2; N, 13.3; (yield = 85%). **HPI**: C, 56.6; H, 9.4; N, 12.8 (yield = 87%). **SPI** and **MPI** were titrated with aqueous NaOH and both resulted to contain 0.34 mEq g^{-1} of sulfonic and carboxylic acid, respectively. A second stock of **SPI** contained 0.42 mEq g^{-1} of H^+ .

2.3.2. Implantation of palladium (II), nickel (II) and copper (II) onto **SPI** or **MPI** using the relevant metal acetates as precursors

The metallation reaction was carried out on the basis of two different protocols.

According to protocol A (operations under air), to a pre-swollen (15 min) suspension of 1 g **SPI** (0.34 or 0.42 mEq acidic groups per gram) and **MPI** (0.34 mEq g^{-1}) in 10 ml methanol, 15 ml of methanol solutions of metal acetate ($0.5 \text{ mol M}^{\text{II}}$ to 1 mol H^+) were added under moderate stirring. A rapid (ca. 1 min) colour transfer from the liquid phase onto the solid one was observed with a concomitant development of a marked smell of acetic acid. Filtration and washing with methanol ($2 \times 20 \text{ ml}$) was carried out after ca. 30 min. **MPI-Cu** resulted to be blue, **SPI-Cu** pale blue, **MPI-Ni** and **SPI-Ni**

pale greenish blue in colour. Both **MPI-Pd** and **SPI-Pd**, albeit initially reddish brown in colour, became gradually black even under nominally anhydrous conditions.

According to protocol B (operations under dinitrogen), the dry functional resin (1 g) was added to 20 ml of a solution of the metal acetate under stirring, according to an $8.0 \text{ mol M}^{\text{II}}$ to 1.0 mol H^+ ratio. The resin colour turned gradually to that initially seen under protocol A, but in this case, the reddish yellow colour of **MPI-Pd** and **SPI-Pd** survived for 5 h before filtration and washing with methanol ($2 \times 20 \text{ ml}$) and for months in the dry solid state, even under air.

2.3.3. Implantation of palladium (II), nickel (II) and copper (II) onto **SPI** or **MPI** using the relevant metal carbamates as precursors

2.3.3.1. Implantation of palladium (ii) onto **SPI** (and **MPI**) using *trans*- $\text{Pd}(\text{O}_2\text{CNET}_2)_2(\text{NHET}_2)_2$ as precursor. The resin **SPI** (930 mg, 0.316 mmol of $-\text{SO}_3\text{H}$ functionalities) was added to the metal reagent (145 mg, 0.30 mmol) in toluene (100 ml) and addition of methanol (5 ml) produced rapid swelling and colouring of the resin. The mixture was stirred for 8 h at room temperature and then filtered. The final pale yellow solid was washed with methanol (5 ml) and diethyl ether ($2 \times 5 \text{ ml}$), dried in vacuo (10^{-2} Torr) and sealed in vials. Upon using a fully analogous procedure, palladium (II) was implanted onto **MPI** to give a yellow material.

2.3.3.2. Implantation of nickel (ii) onto **MPI** or **HPI** with $[\text{Ni}(\text{O}_2\text{CNET}_2)_2]_x$ as precursor. A saturated solution of $[\text{Ni}(\text{O}_2\text{CNET}_2)_2]_x$ in dichloromethane (about 1.3 mmol in 50 ml) was treated with dry **MPI** (1.091 g , 0.371 mmol of $-\text{COOH}$ functionalities). The resin turned gradually to yellow and the mixture was stirred for 5 h and then filtered. The final bright yellow solid was washed with dichloromethane ($2 \times 10 \text{ ml}$), dried in vacuo and sealed in vials. The same procedure was employed for metallating **HPI** to give again a bright yellow material.

2.3.3.3. *Implantation of copper (ii) onto HPI or MPI upon using $Cu_2(O_2CNEt_2)_4(NHEt_2)_2$ as precursor.* A solution of the metal reagent (574 mg, 0.78 mmol) in dichloromethane (50 ml) was treated with dry HPI (532 mg; ca. 0.2 mmol OH). The resin turned gradually to dark green and the mixture was stirred for 5 h and then filtered. The final dark green solid was washed with dichloromethane (2×10 ml), dried in vacuo and sealed in vials.

Metal analyses were carried out via atomic absorption spectrophotometry after mineralization of the resins with a 1:1 (v/v) concentrated sulfuric and nitric acids mixture. The metal content of the metallated resins is reported in Table 3.

2.4. ESR measurements

About 0.25 g of ground material was swollen with a nitrogen-saturated 10^{-4} M solution of TEMPONE in the required solvent. The samples were allowed to reach the swelling equilibrium and, after pouring the suspension onto filter paper, the swollen material was rapidly transferred into the ESR tube. The ESR spectra were recorded at 25°C; the temperature of the sample during the measurements was controlled to an accuracy of $\pm 0.1^\circ\text{C}$. The rotational correlation times τ were calculated using Eq. 3 [21,22]:

$$\tau = 6.14 \times 10^{-10} \Delta H_0 \times \left[(h_0/h_{+1})^{1/2} + (h_0/h_{-1})^{1/2} - 2 \right] \times \left[1 - 1/5(1 + \omega_c^2 \tau^2) \right]. \quad (3)$$

The parameters, h_0 , h_{+1} and h_{-1} (amplitudes of the low-, centre and high-field spectral lines, respectively) and ΔH_0 (width of the centre-field spectral line) were obtained directly from the derivative spectrum by peak-picking and $\omega_c = 5.70 \times 10^{10}$ Hz. The numerical con-

stant was estimated on the basis of published values from the anisotropic g and A tensor for TEMPONE [23].

2.5. PGSE-NMR measurements

The self-diffusion coefficients of the swelling solvents were determined by ^1H Pulsed-Gradient-Spin-Echo Nuclear Magnetic Resonance (PGSE-NMR) measurements [24,25]. In this technique, a spin echo experiment is performed while two magnetic field gradient pulses of magnitude G , duration δ and separation Δ are applied during the dephasing and the rephasing periods, respectively. In the present study, the interval Δ between the magnetic field gradient pulses was kept constant and equal to the interval t between the 90 – 180° radio frequency pulses. In these conditions, for nucleus with diffusion coefficient D , the height of the echo amplitude A is given by [24,25]:

$$A = A_0 \exp \times \left[-2t/T_2 - \gamma^2 G^2 D \delta^2 (\Delta - \delta/3) \right], \quad (4)$$

where γ is the magnetogiric ratio and T_2 is the spin–spin relaxation time of the nucleus. In a typical experiment, A was measured at $\Delta = 20$ ms and $G = 17.5$ G/cm by varying δ up to 6 ms. The gradient strength was calibrated to values of the self-diffusion coefficient of pure water. The chosen t value was sufficient to remove the polymer contribution from the echo signal due to the relatively short T_2 relaxation time of the polymer hydrogens. The solvent diffusion coefficient was obtained from the slope of the logarithmic plot of A vs. the term $\delta^2(\Delta - \delta/3)$. The samples were prepared as described above after swelling in the appropriate solvent and then placed in a 5-mm NMR tube. The spectra were recorded over the temperature range 5 – 35°C at 5° intervals with an accuracy of $\pm 0.25^\circ\text{C}$.

3. Results and discussion

3.1. Resins **SPI** (DMA-SEMA-MBA), **MPI** (DMA-MA-MBA) and **HPI** (DMA-HEMA-MBA)

Functional resins were prepared in high yields upon γ -irradiation [26–28] of relevant homogeneous mixtures of the corresponding monomers (see Section 2). **SPI**, **MPI** and **HPI** were synthesized under conditions aimed at providing a constant (4% m/m) cross-linking degree and a constant molar fraction of acidic groups (corresponding to 0.4 mEq g⁻¹), in the case of a 100% polymerization yield. The observed yields are seen, in fact, to range from 80% to 90%, in line with expectations connected with the established co-polymerization procedure.

The resins do appreciably swell in water, methanol and dichloromethane. The nanomorphology and molecular accessibility of resins **SPI**, **MPI** and **HPI** in these solvents were evaluated on the basis of the translational mobility of solvent molecules within the swollen polymer network (PGSE-NMR) or by considering the rotational behaviour of TEMPONE (2,2,6,6-tetramethyl-4-oxo-1-oxyl-piperidine) dissolved in the swelling solvent. The results are collected in Table 2.

It is seen that the rotational mobility of TEMPONE decreases appreciably (as expected) from the bulk solvent state to the confined state [12–15] for all three investigated swelling media. The confinement effect appears to be somewhat less marked in the case of dichloromethane. The solvent translational mobility is also seen to drop appreciably inside the gel-type polymer network, but the overall cavity effect observed with both ESR and PGSE-NMR is just moderate, quite in line with previous observations [12–15]. Moreover, the constancy of the translational activation energies (obtained from an Arrhenius plot of the solvent self-diffusion coefficient D vs. the temperature) suggests that the reduction in the mobility of the probe is not due to direct enthalpic interactions with the polymer

Table 2

Rotational mobility of TEMPONE (rotational correlation time τ) and translational mobility (self-diffusion coefficient, D) of the solvent inside swollen **SPI**, **MPI** and **HPI**

| Material | Swelling solvent | τ (ps) | D (10 ⁻⁵ cm ² s ⁻¹) | Translational activation energy (± 1) (kJ/mol) |
|------------|------------------|-----------------|---|--|
| None | water | 11 | 2.1 | 19 |
| SPI | water | 48 ^a | 1.3 | 19 |
| MPI | water | 79 ^b | 1.1 | 20 |
| HPI | water | 87 | 1.1 | 19 |
| None | MeOH | 11 | 2.1 | 14 |
| SPI | MeOH | 52 | 1.2 | 14 |
| MPI | MeOH | 36 | 1.0 | 14 |
| HPI | MeOH | 38 | 1.1 | 14 |
| None | DCM | 10 | 3.4 | 10 |
| SPI | DCM | 21 | 1.1 | 13 |
| MPI | DCM | 37 | 1.1 | 10 |
| HPI | DCM | 23 | 1.2 | 10 |

^a[**SPI-Pd**]_B: $\tau = 67$ ps in water; $\tau = 76$ ps in methanol.

^b[**MPI-Pd**]_B: $\tau = 90$ ps in water.

backbone but rather to microviscosity or obstruction effects.

The ESR and especially PGSE-NMR observations were particularly useful for designing the experimental conditions for Pd^{II} implantation from metal carbamates (see below). The uncomplicated behaviour of both TEMPONE and dichloromethane inside swollen **SPI**, **MPI** and **HPI** resins was, in fact, a promising prerequisite for an expected successful palladiation of the employed resins. It is worthwhile to note that the rotational correlation time of TEMPONE inside swollen **SPI-Pd** and **MPI-Pd** resin palladiated with the protocol B (see the footnote in Table 2) is appreciably longer than those observed in unmetallated resins, quite in agreement with the “cross-linking effect” expected to occur upon incorporation of “Pd²⁺” units (see below).

3.2. Reactivity of resins **SPI**, **MPI** and **HPI** with metal acetates and carbamates

The essential analytical data are collected in Table 3. As a general comment, we point out that the implantation of metal centers onto func-

Table 3
Analytical data on metallated resins

| Entry | Metallated resin | Colour | Percent metal protocol A (entries 1–6) | Percent metal theoretical for 1 M ^{II} to 2 H ⁺ | Percent metal protocol B (entries 1–6) |
|-------|----------------------------|---|--|---|--|
| 1 | SPI-Pd | orange ^a black ^b | 1.64 | 1.80 2.22 | 0.62 |
| 2 | SPI-Cu | blue | 0.88 | 1.07 | 2.39 |
| 3 | SPI-Ni | pale green | 0.80 | 1.21 | 2.39 |
| 4 | MPI-Pd | orange ^a black ^b | 1.14 | 1.82 1.82 | 1.19 |
| 5 | MPI-Cu | blue | 0.59 | 1.08 | not determined |
| 6 | MPI-Ni | pale green | 0.52 | 0.99 | 1.20 |
| 7 | SPI-PdL_n | pale yellow | – | – | 0.69 |
| 8 | MPI-PdL_n | off white | – | – | 2.16 |
| 9 | MPI-CuL_n | greenish blue | – | – | 2.23 |
| 10 | MPI-NiL_n | greenish yellow | – | – | 0.66 |
| 11 | HPI-CuL_n | green | – | – | 0.57 |
| 12 | HPI-NiL_n | greenish yellow | – | – | 0.71 |

^aProtocol B.

^bProtocol A.

tional resins bearing so diverse acidic functionalities occurs successfully under exceedingly mild conditions. Of course, suitable swelling of the polymer networks able to guarantee reasonable diffusion coefficients for the reacting solutes is to be chosen. In this connection, previous ESR evaluations, when possible, or even simple bulk expanded volume measurements [29] are suggested before performing metal implantation.

Both chemical approaches herein illustrated appear to be effective and of particular interest in the successful implantation of Cu^{II} and Ni^{II} carbamates onto resin **HPI**, which possesses an extremely weakly acidic anchoring group. This specific reaction closely resembles that laying at the basis of Sommazzi's method [16,17] for implanting metal ions onto silica; the release of CO₂ appears to be an effective driving force for the metallation of this exceedingly weakly acidic resin. The release of a stable chemical species associated with the anchoring of the metal center also represents a crucial feature of the other implantation technique employed. Thus, the release of acetic acid concomitant with the formal 2H⁺/M²⁺ "forced" ion exchange using metal acetates makes possible not only the metallation

of strongly acidic resins but also that of carboxylic ones; preliminary tests suggest that the metallation also occurs with resin **HPI**.

A reliable evaluation of the quantitative aspects of the metallation procedure and of the actual metal speciation of the metal centers requires further dedicated work, currently in progress in these laboratories. This is especially true in the case of materials prepared starting from the metal carbamates, since in this case it

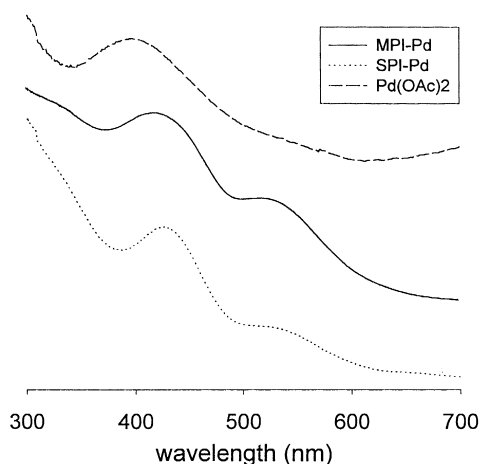


Fig. 1. Electronic spectra of [SPI-Pd]_B and [MPI-Pd]_B compared with that of solid Pd(OAc)₂.

is not clear a priori which ligands are retained in the coordination sphere of the metal ion after the forced ion exchange. Nevertheless, some conclusions can already be drawn from preliminary results.

A rather striking result appears to be the quite different nature of resins **SPI-Pd** and **MPI-Pd** prepared according to protocols A and B. Thus, $[\text{SPI-Pd}]_B$ and $[\text{MPI-Pd}]_B$ resin particles appear quite transparent and featured by a nice orange colour, with almost identical UV–visible spectra (Fig. 1) with λ_{max} at 420 and 530 nm.

In contrast with this observation, $[\text{SPI-Pd}]_A$ and $[\text{MPI-Pd}]_A$ appear as totally black materials, thus strongly suggesting the occurrence of Pd^{II} reduction to Pd^0 after ion exchange has occurred. Moreover, the metal distribution through the body of the metallated resin parti-

cles appears to be markedly different in the two cases (Fig. 2).

It is clearly seen that, while a homogeneous distribution is observed for the resin obtained with the protocol A, a clear peripheral distribution is associated with protocol B.

We interpret this observation in the following terms. Protocol A is aimed at promoting the ion exchange according to Eq. 1. Under these conditions, “ Pd^{2+} ” will experience either the lack of any coordination sphere (in the case of **SPI**) or the “support” of a poor one (in the case of **MPI**). Consequently, trace amounts of water in the liquid medium are expected to produce metal reduction [30]. On the contrary, protocol B offers a significant excess of “ Pd^{2+} ” over H^+ to be exchanged and it is evident that the trimeric unit, $\text{Pd}_3(\text{OAc})_6$, known to be the dominating species in methanol [31,32], turns out to be

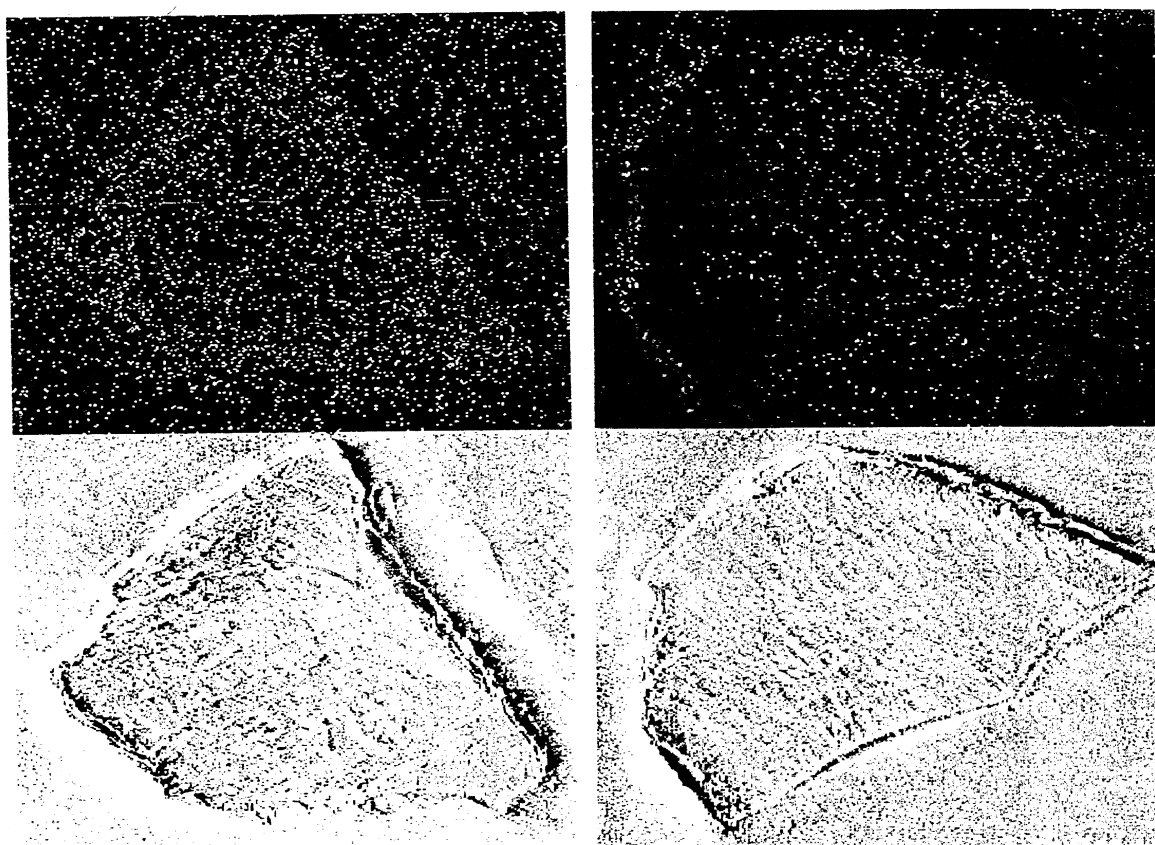
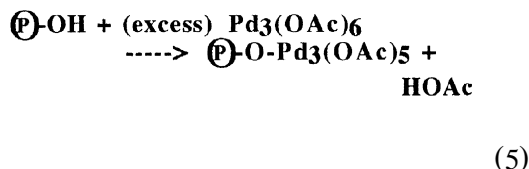
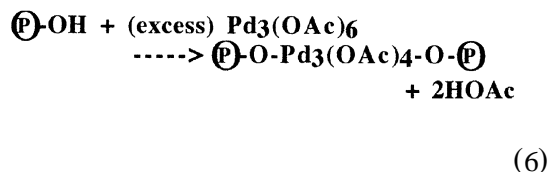


Fig. 2. XRM picture of Pd distribution throughout particles of resin $[\text{SPI-Pd}]_A$ (left) and $[\text{SPI-Pd}]_B$ (right).

“hooked” by the polymer network, thus enabling the survival of the trimeric, reduction-resistant species. The simplest possibility in this connection is depicted by Eq. 5:



but a slightly more complex one is also feasible, i.e.,



It is apparent that this proposal fits with (i) the apparent lack of metal reduction after resin metallation; (ii) the very close similarity of the electronic spectra of $[\text{SPI-Pd}]_B$, $[\text{MPI-Pd}]_B$ and solid $\text{Pd}_3(\text{OAc})_6$; and (iii) the marked contrast between the palladium distributions related to the different synthesis protocols, most probably due to the hampering of $\text{Pd}_3(\text{OAc})_6$ penetration into the body of the particles, which also explains the relatively low palladium loadings achieved with protocol B in spite of the excess metal reagent employed.

4. Conclusions

This paper describes the essential synthetic aspects of two expectedly general strategies for metal implantation onto acidic functional resins. Even very weakly acidic resins, such as materials containing simple hydroxyl groups, can be metallated by these methods. An explanation for some analytical features, such as the loading of the metal and its distribution throughout the resins particles, has been proposed in relation to the reaction conditions employed for the metallation. On the basis of these findings, it appears that the kind of metal speciation inside the

polymer network can be defined by varying the metallation protocol. This is an important task not so much in the perspective of final metal reduction but very much in the perspective of developing a possible and stimulating metal coordination chemistry inside polymer networks.

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