

Microporous poly-*N,N*-dimethylacrylamide-*p*-styrylsulfonate–methylene bis(acrylamide): a promising support for metal catalysis

Milan Králík ^{a,*}, Milan Hronec ^a, Silvano Lora ^b, Giancarlo Palma ^c, Marco Zecca ^d,
Andrea Biffis ^d, Benedetto Corain ^c

^a Department of Organic Technology, Slovak Technical University, Radlinskeho 9, 812 37 Bratislava, Slovak Republic

^b Istituto di Fotochimica e Radiazioni d'Alta Energia, C.N.R., Sezione Di Legnaro, I-35020 Legnaro (Pd.), Italy

^c Dipartimento di Chimica Fisica, via Loredan 2, I-35131 Padova, Italy

^d Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, C.N.R., c/o Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, via Marzolo 1, I-35131 Padova, Italy

^e Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università dell' Aquila, Coppito Due – Via Vetoio, I-67010 L'Aquila, Italy

Received 8 April 1994; accepted 14 December 1994

Abstract

The synthesis of poly-*N,N*-dimethylacrylamide-*p*-styrylsulfonate (DMAA-SS) with 4 mol% of methylene bis(acrylamide) (MBAA) as crosslinker is described. Bulk polymerization of water solution of monomers (DMAA, SS sodium salt, MBAA) was carried out under gamma irradiation. Swellability in water and various organic solvents showed mainly hydrophilic character of the resin. The ion-exchange experiments with 1 M hydrochloric acid and with $[\text{Pd}(\text{NH}_3)_4]^{2+}$ showed very good accessibility of the inner space of the material. Polymer supported $[\text{Pd}(\text{NH}_3)_4]^{2+}$ was reduced by hydrogen in methanol, sodium borohydride in water and sodium borohydride in ethanol. Under these last conditions uniform distribution of Pd throughout the resin particles was observed. The activated material turned out to be a good catalyst for the hydrogenation of *p*-nitrotoluene to *p*-toluidine in methanol under ambient conditions.

Keywords: Accessibility; Crystallite distribution; Gamma rays; ESR; NaBH_4 ; Hydrogenation; Palladium catalysts; Poly-dimethylacrylamide-*p*-styrylsulfonate–methylene bis(acrylamide); Reducing agent; Swellability

1. Introduction

The very large majority of macromolecular supports and, or reagents described so far in the chemical literature, or actually employed in technological applications are polystyrene–divinylbenzene resins, have a cross-linking degree ranging from less than 1% to up to 30%. Relevant

industrial catalytic applications of these materials deal with e.g. the synthesis of MTBE, methyl vinyl ketone, methyl *t*-amyl ether, isoamylene and with phenol alkylation [1]. A rather remarkable application of a palladium catalyst based on is the efficient removal of oxygen, down to the ppb level, from water to be used in power plant installations [1].

N,N-Dimethyl acrylamide (DMAA) based resins are relatively rare, although becoming more

* Corresponding author.

and more popular, especially in the area of biochemical applications, thanks to their moderate hydrophilicity [2–4]. In recent years, we have been describing a variety of DMAA-based resins as macromolecular isocyanides [5], as (macro- and microporous) supports for heterogeneous catalysis, [6], and for IPN (interpenetrating polymer networks) type metal catalysts [5–7].

We report in this paper on the synthesis and the physico-chemical characterization of a DMAA-based ion exchange resin, suitable to be converted, after charging with $(\text{Pd}(\text{NH}_3)_4)^{2+}$, into a fairly widely solvent compatible and molecularly accessible bifunctional catalyst.

2. Experimental

2.1. Materials

Methylene bis(acrylamide) (MBAA), *N,N*-dimethylacrylamide (DMAA) and sodium salt of 4-styrylsulfonic acid (SS) were obtained from Aldrich and were of reagent grade; 4-nitrotoluene, 4-aminotoluene, methanol (MeOH), ethyl acetate (EAC), diethyl ether (DETE) and dichloromethane (DCM) were supplied by Carlo Erba (RPE reagents). Dimethylformamide (DMF), pure ethanol (EtOH), tetrahydrofuran (THF), toluene (TOL), acetone (AC) and sodium borohydride were purchased from Aldrich. $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ was from Strem and palladium acetate was from Fluka. All the products were employed as received, apart from *p*-nitrotoluene which was purified by sublimation under reduced pressure prior to use.

2.2. Apparatus

Grinding of the resin was performed with a Bühler H04 impact grinder and it was followed by sieving (0.18 mm). SEM and XMA analyses were carried out by means of a Cambridge Stereoscan 250 EDX PW 9800 apparatus. A Shimadzu GC-8A gas chromatograph (FID detector) equipped with a SGE 25AQ3 capillary column

(BP10, inner diameter 0.33 mm, film thickness 0.5 μm , length 25 m) was employed for the analysis of the reaction mixtures in the catalytic tests. IR spectra were recorded with Biorad FT7PC spectrometer. ESR spectra were recorded on a Bruker ER 200D X-band spectrometer. About 0.25 g of resin were swollen with a nitrogen saturated 10^{-4} M solution of TEMPONE (2,2,6,6-tetramethyl-4-oxyl-piperidine) in the appropriate solvent. The samples were allowed to reach swelling equilibrium, typically after about 2 h. After the removal of the solution upon filtration, the swollen samples were placed inside the ESR tube and spectra were taken at 295 K. The elemental analyses (C, H, N, S) were carried out by means of a Carlo Erba 1106 Analyzer. Atomic absorption measurements (Na, Pd) were performed with a Perkin Elmer 3030 atomic absorption spectrometer. Samples (ca. 100 mg) were mineralized upon treatment with 1 cm^3 of concentrated nitric acid, 1 cm^3 of concentrated sulfuric acid and 5 cm^3 of concentrated hydrogen peroxide, and the solution obtained after the mineralization was diluted to the concentration suitable for atomic absorption measurements.

2.3. Synthesis

The ion exchange resin denoted as P4N was prepared from the following monomers:

N,N-dimethylacrylamide (DMAA)

N,N'-methylenebisacrylamide (MBAA)

p-styrylsulfonic acid, sodium salt (SS)

The copolymerization was performed in concentrated water solution, upon gamma irradiation [8]. 5.67 g of DMMA; 4.12 g of SS and 0.49 g of MBAA were dissolved in 6.88 g of water at 40°C in a 20 cm^3 Pyrex cylindrical probe under nitrogen. The closed probe was exposed to gamma rays from a ^{60}Co at 0.5 Gy/s for 48 h at 18°C. After breaking the probe, a cylindrical white–pink rod was obtained. The rod was rinsed in deionized water and cut into slices of about 2 mm thickness, which were washed and decanted with water, methanol and again with water, each washing last-

Table 1
Elemental analysis of P4N

	Element				
	C	H	N	S	Na
Calc. (%)	54.69	6.73	8.66	6.23	4.67
Found (%)	55.48	7.09	9.16	5.28	3.83

ing ca. 30 min. The polymer was rinsed with methanol and dried at 60°C, 5 kPa, for 24 h to constant weight (9.58 g, 93.3% polymerization yield). The analytical data are collected in Table 1. The solution obtained upon collecting all the filtrates was analyzed for the content of sodium.

The material obtained was converted into a conveniently powdered one along two routes, A and B. Route A consisted in suspending the perfectly dry material in water and allowing it to swell and self-break for about one day. Repeating this procedure three times resulted in a fairly uniform powder particles of about 0.1 mm. Route B was based on the mechanical grinding of the water suspended resin, followed by sieving (0.18 mm) and separation of the finest particles upon decantation; this route led to a homogeneous powder made up of particles 0.05–0.15 mm in diameter.

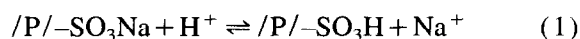
2.4. Swelling behaviour

The solvent compatibility of P4N was evaluated by the measurement of the bulk expanded volumes [3,9]. About 0.3 g of a dry sample were poured into a calibrated cylindrical tube (internal diameter 6 mm) equipped with the frit type G-3. The bottom of the tube was closed and the liquid in which the swellability was to be measured was added. Although swelling was relatively quick (from 1 to 5 min), to be sure that all particles were fully swollen, the polymer was left in contact with the solvent for 60 min, with occasional stirring of the suspension. The stopper from the bottom of the tube was removed and the excess of the liquid was drained through the frit. When the liquid was just at the top of the resin, the height of the swollen polymer was measured and the swellability was so determined. After the measurement, the sample

was washed with methanol and dried to constant weight for the next evaluation.

2.5. Ion exchange

The dynamics of the ion exchange (/P/ denotes the polymer network):



was evaluated quantitatively by means of the apparatus shown in Fig. 1. The column (6 mm internal diameter) was filled with P4N (0.92 g of dry polymer) and then swollen in water. At first, water was allowed to flow through the bed (the valve 1 open, the valves 2 and 3 closed), then the valve 1 was closed and valve 2 was opened. When no liquid was left on the top of the bed, valve 3 was opened (time $t=0$) and after filling the tube above the bed with the solution of acid, valve 2 was closed. The solution flowing from the column was collected in a beaker equipped with a magnetic stirrer and a pH probe. Before starting the experiment, a sufficient amount of water to cover the bulb of the pH probe was poured into the beaker. Samples of the liquid (about 0.3 cm³) were taken from the beaker when the pH started to change and the concentration of sodium was monitored by atomic absorption spectroscopy.

Incorporation of Pd²⁺ into the P4N resin was performed through the ion exchange:

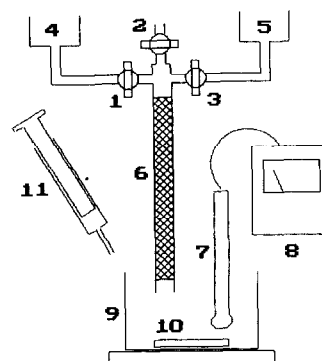
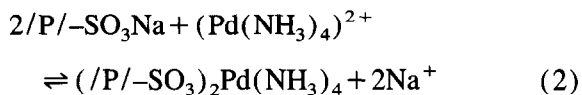


Fig. 1. Apparatus for measuring the ion-exchange dynamics. 1, 2, 3: valves, 4: basin of water, 5: basin of 1 M HCl, 6: glass column packed with a swollen polymer, 7: pH probe, 8: pH meter, 9: beaker, 10: magnetic bar, 11: sampling syringe.



The ion exchange procedure was carried out in a batchwise system using $Pd(NH_3)_4(NO_3)_2$ in three steps as follows: P4N (4.07 g) was swollen in 30 cm³ of water and the suspension was reacted with a solution of $Pd(NH_3)_4(NO_3)_2$ (0.93 g, 90% of the stoichiometric amount) in 25 cm³ of water. The final suspension was vigorously stirred by a magnetic stirrer for one hour and then it was stirred occasionally for the next 4 h. Liquid samples of about 0.3 cm³ were taken from the suspension and concentrations of sodium and palladium were determined by atomic absorption spectroscopy. For the second step, the suspension was filtered, washed with water and transferred to a beaker. 0.260 g of the palladium complex dissolved in the 40 cm³ of water were added to the suspension and the ion exchange was performed for 5 h with occasional stirring. Similarly, the third step was performed with the same amount of palladium complex. The Pd-form of P4N (P4NPd8) was washed with methanol, dried to constant weight and analyzed for the content of sodium and palladium. This procedure made more than 90% of cationic positions available for palladium fixation.

The incorporation of palladium(II) was also attempted upon reacting the acidic form of P4N (obtained upon the ion exchange of the sodium form with 1 M solution of HCl) with $Pd(CH_3COO)_2$ dissolved in mixture of acetone and water (1:1 volume ratio). Thus 1.00 g of the resin were swollen in 10 cm³ of water, and 10 cm³ of acetone–water solution with 0.019 g of palladium acetate were added. After 1 h occasional stirring, the suspension was filtered and washed with water. The analysis of palladium in solution from filtration and washing showed almost quantitative incorporation of palladium (95%). This result is in accord with observations described in the literature [10]. A disadvantage of this process is some palladium(II) reduction which results in a change of the colour of the resin from white to

black. For this reason we utilized the Pd form of resin prepared with the first procedure.

2.6. Activation of the catalyst

The reduction of palladium(II) to palladium(0) in the P4NPd8 was performed alternatively along four routes:

- (i) H₂ in methanol; atmospheric pressure; 15 h
- (ii) NaBH₄ 0.066 M solution in water; 10 times excess with respect to the palladium content
- (iii) NaBH₄; 0.066 M solution in ethanol; 10 times excess
- (iv) NaBH₄; 0.019 M solution in ethanol; 3 times excess

Typically, dry P4NPd8 was swollen in the chosen liquid (methanol, water or ethanol) and the appropriate amount of reducing agent was added. All reductions were performed under vigorous stirring at room temperature. The end of experiments (ii)–(iv) was revealed by the cessation of the release of gaseous products from the reaction mixture (ca. 3 h from the start). The palladium catalyst (P4NPd8r) was washed with ethanol, methanol, water, rinsed with methanol and dried to constant weight.

2.7. Catalytic tests

Catalytic hydrogenation tests were carried out in vigorously shaken three necked reactors (shaking with a frequency of about 80 min⁻¹) at a pressure of about 100 kPa at room temperature. 10 ml of 1 M 4-nitrotoluene in methanol were poured into the reactor and 40 mg of a Pd/C catalyst (5% of Pd) or 25 mg P4NPd8r were also added. The reactors were then cooled in liquid nitrogen, outgassed by a mechanical vacuum pump and the suspension was then left to melt under hydrogen atmosphere. This procedure was repeated twice. After reaching room temperature, hydrogen was supplied by a rubber balloon through the side of the reactor. Sampling of the reaction mixture was performed by a syringe with a long needle through a rubber cap in the middle neck of the reactor. During the sampling

time (about 2 min), shaking of the reactor was stopped. Easy withdrawal of the solution was possible in the runs with the P4NPd8r catalyst thanks to the rapid settling of the catalyst. On the contrary, in the case of the Pd/C catalyst, 2 min were not sufficient for the sedimentation, and sampling included filtration of aliquot amounts of the suspension before analysis.

3. Results and discussion

The analytical data referring to resin P4N and P4NPd are collected in Table 1. Due to the non-quantitative polymerization, the analytical data for P4N are somewhat different from the theoretical values, the differences being attributable mainly to the incomplete incorporation of sodium SS.

SEM pictures of P4N are reported in Fig. 2. The 'self breaking' procedure produces a smoother (more glass-like) surface than the one involving impact grinding. Although the procedure A (see above) is more straightforward than B, the latter was chosen as being the more time saving and all the data hereafter reported are based on material prepared along the route B. XRMA (Fig. 3) reveals a perfectly homogeneous distribution of sodium and sulphur through a section of a resin particle. The resolution power of the microprobe analytical apparatus is estimated to 1 be μm^2 .

P4N has been carefully examined by FTIR with reference to both polystyrene sodium sulfonate and polydimethylacrylamide. The FTIR spectra of P4N was compared with that of a mechanical mixture of the last mentioned polymers and, apart from minor differences in the range $1000\text{--}1300\text{ cm}^{-1}$, the spectra turned out to be practically identical.

The solvent compatibility [3,9] of P4N, P4NPd8 and P4NPd8r was quantitatively evaluated by bulk expanded volume measurements which are given in Fig. 4.

It is seen that the resin exhibits a marked hydrophilic character and that water, methanol and ethanol (and perhaps dichloromethane) appear to be suitable media for utilizing P4N for chemical applications. In non-polar or scarcely polar solvents P4N exhibits practically no volume expansion, so that no chemical utilization of these materials appears to be likely in these media.

The higher swellability observed in water compares well with some accessibility measurements performed with the stable radical TEMPONE (see Experimental) and recorded with ESR spectrometry [11,12]. Fig. 5 shows rotational correlation times for free solutions of TEMPONE and TEMPONE in the swollen resin.

The principal observation is the appearance of a single well defined triplet, whose shape reveals a clear cavity effect [13] and provides information on: (i) the probe (0.64 nm of kinetic diameter [14]) gains access to the microporous domains

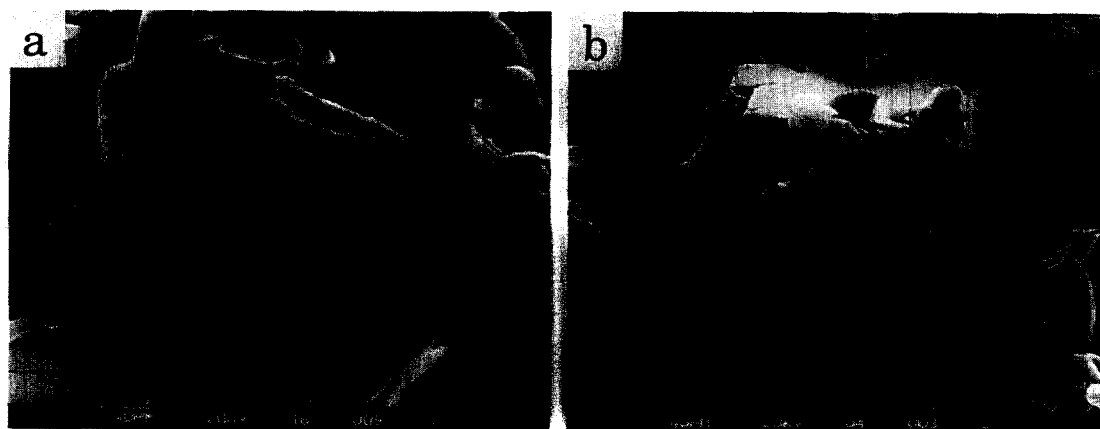


Fig. 2. P4N particles; (a) obtained using self-breaking procedure, (b) obtained using the impact grinder.

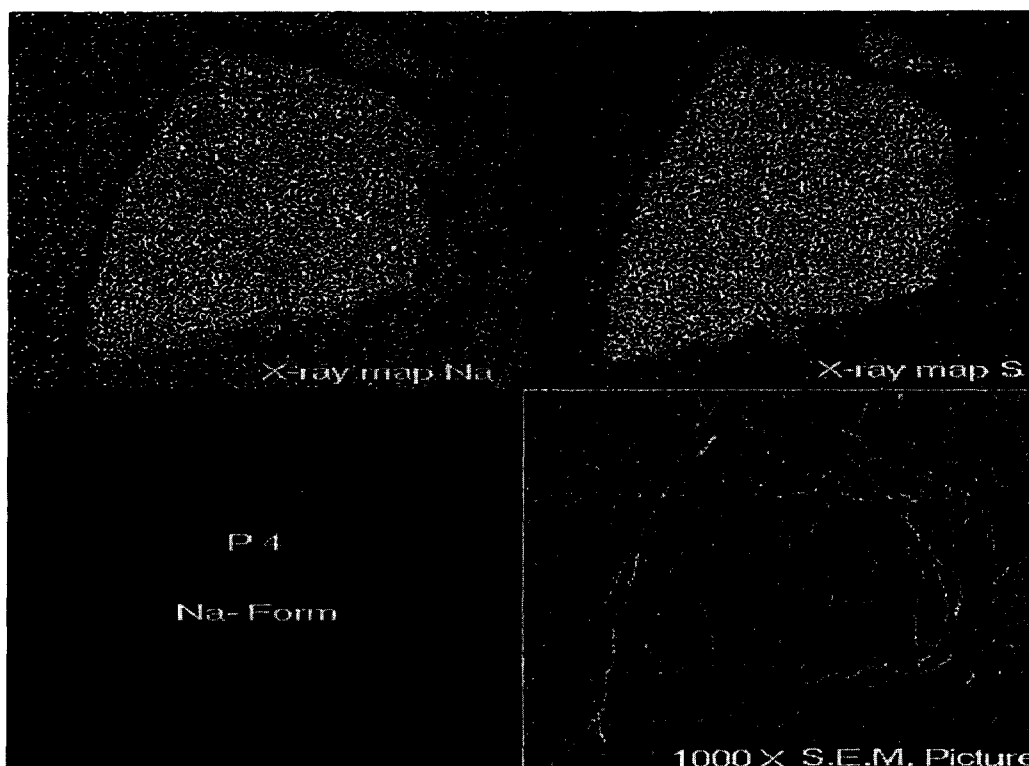


Fig. 3. SEM and XRM maps of sulphur and sodium in P4N. Particle size is about 0.1 mm.

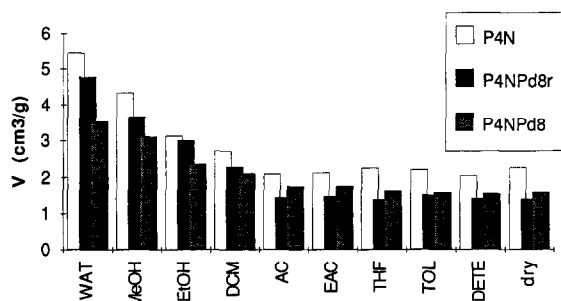


Fig. 4. Specific bulk expanded volumes of P4N in various swelling agents. The size of particles was in the range 0.05–0.15 mm, the average sphere equivalent diameter was 0.11 mm. WAT = water, MeOH = methanol, EtOH = ethanol, DCM = dichloromethane, AC = acetone, EAC = ethyl acetate, THF = tetrahydrofuran, TOL = toluene, DETE = diethyl ether, dry = specific volume of the dry sample.

of P4N after swelling with water, methanol and ethanol; (ii) the rotational correlation time of the probe dispersed inside swollen P4N undergoes a marked decrease with respect to the data obtained when TEMPONE is dissolved in bulk water, methanol and ethanol; (iii) the lowest mobility is observed inside the resin soaked by the less swelling medium – ethanol (higher cavity effect); (iv)

only one average type of domain, in which access and rotation of the probe is possible, is seen. In conclusion, the moderate decrease of rotational mobility revealed by the ESR spectra of TEMPONE inside swollen P4N informs us that this matrix is expected to be a rather viable medium for reactants and products featured by lipophilic–hydrophilic character and molecular size both comparable with those of TEMPONE.

A chemical evaluation of the accessibility of the matrix P4N was possible by means of dynamic

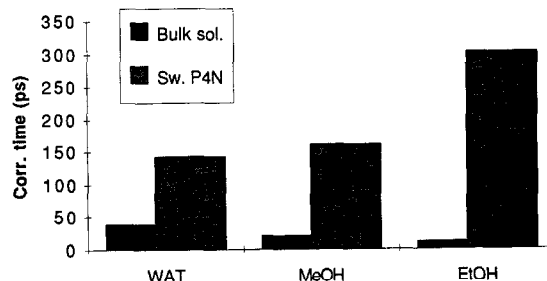


Fig. 5. Rotational correlation time of TEMPONE in free solvent (Bulk sol.) and in the P4N resin swollen with the solution of TEMPONE (Sw. P4N). WAT = water, MeOH = methanol, EtOH = ethanol.

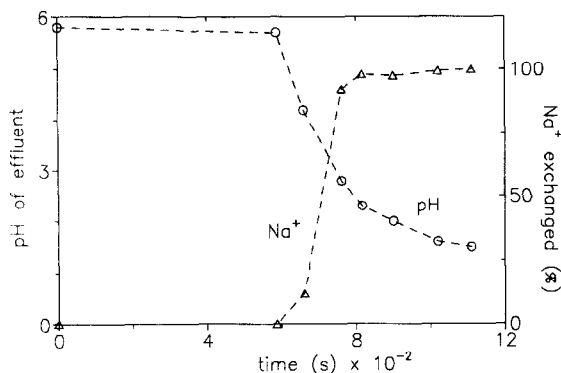


Fig. 6. Dynamics of the ion exchange of Na^+ by H^+ in P4N.

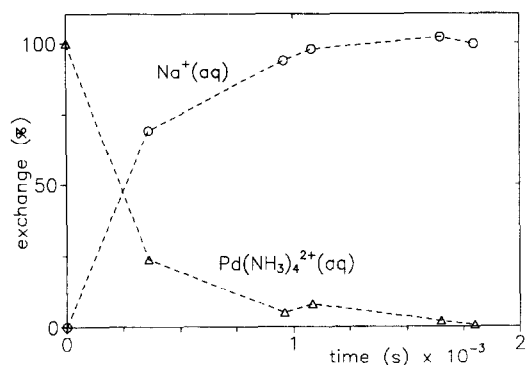


Fig. 7. Dynamics of the ion exchange of Na^+ by $(\text{Pd}(\text{NH}_3)_4)^{2+}$ in P4N. Extent of ion exchange is with respect to the equilibrium (100%).

Table 2
Elemental analysis of P4NPd8

	Element					
	C	H	N	S	Pd	Na
Calc. (%)	50.11	7.31	12.49	4.76	8.00	0.00
Found (%)	49.19	7.46	12.30	4.68	7.60	0.17

ion exchange experiments. Fig. 6 depicts the dynamics of the release of Na^+ , replaced by H^+ , from P4N, the exchange reaction being complete after ca. 600 s in a 0.92 g (dry weight) water swollen sample.

Exchange of Na^+ by $(\text{Pd}(\text{NH}_3)_4)^{2+}$ [15] or exchange reaction of H^+ by Pd^{2+} upon reacting $\text{Pd}(\text{CH}_3\text{COO})_2$ dissolved in acetone/water with P4N in acidic form [10] provided further information on the molecular accessibility of the microporous domains of P4N. In fact, the success of the second procedure supports a good accessi-

bility of P4N but this approach is probably complicated by an undesired side reaction. The first procedure is certainly more cumbersome, but it makes possible the occupation of 95% of the cationic positions after three exchange steps without difficulty. The values calculated for theoretical composition (Calc) and determined by analysis (Found) are given in Table 2. Theoretical values were calculated on the basis of the experimental values from Table 1 for the situation when all sodium would be exchanged with $(\text{Pd}(\text{NH}_3)_4)^{2+}$. In the palladium form of P4N, denoted as P4NPd8, about 5% of cationic positions are occupied by Na^+ . Fig. 7 depicts the dynamics of the ion exchange during the first step (70% of the total ion exchange).

It is seen that equilibration is practically attained after ca. 1500 s. The replacement of univalent Na^+ by $(\text{Pd}(\text{NH}_3)_4)^{2+}$ is accompanied by a marked decrease of swellability of the obtained resin which is now very 'rigid' owing to a predictable 'cross-linking' effect (Fig. 4). However, water, methanol and ethanol exhibit still a moderate swelling ability, which is important for the next synthetic step, i.e. the activation of P4NPd8 upon reduction of palladium(II) to palladium(0). Fig. 8 shows the very homogeneous distribution of the metal centre throughout the polymer network and it also illustrates the residual concentration of sodium ions.

The reduction of palladium(II) to palladium(0) inside ion exchanges resins has been investigated by various authors for more than two decades [16]. Hydrogen, hydrazine, formaldehyde and ethyl formate [15–17] have been employed by various investigators. An elegant study on the correlation between metal crystallites distribution inside the resin particles and reduction routes was published by Hanson et al. [17]. The distribution of the reduced metal in the resulting catalyst depends on the ratio R of the mobility of the reducing agent to that of metal cation to be reduced as given by Eq. 1.

$$R = - (D_{\text{ra}} dc_{\text{ra}}/dx) / (D_{\text{Pd}^{2+}} dc_{\text{Pd}^{2+}}/dx) \quad (1)$$

where D_{ra} and $D_{\text{Pd}^{2+}}$ are diffusional coefficients

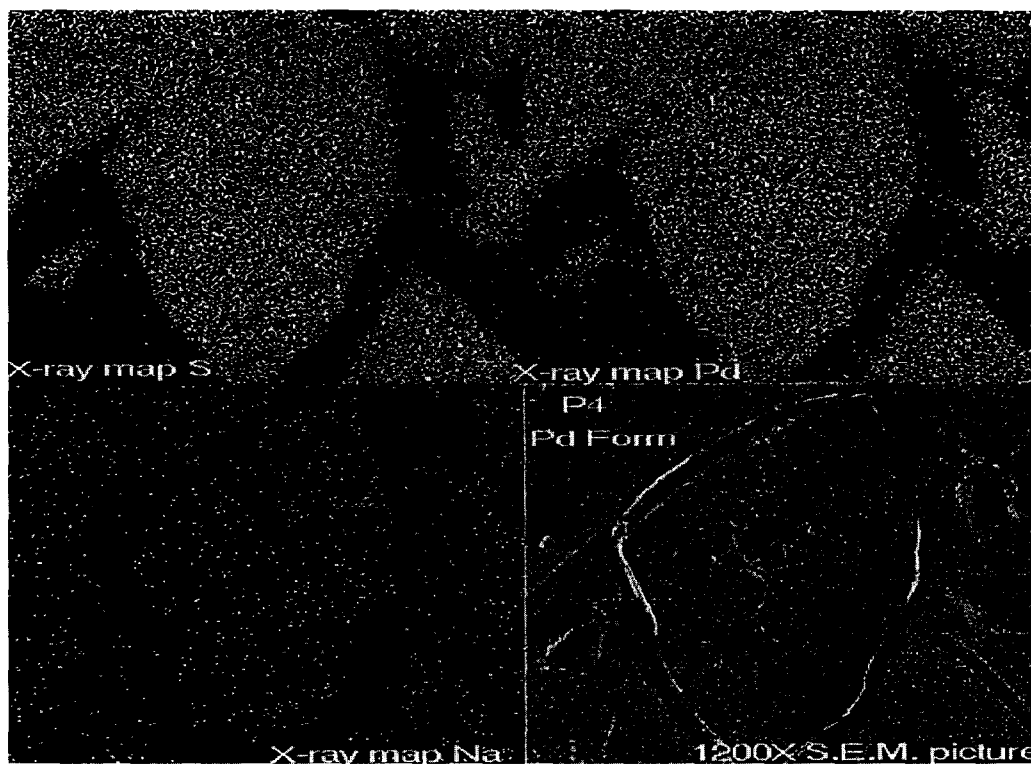


Fig. 8. SEM and XRM maps of sulphur, sodium and palladium in P4NPd8. The particle size is about 0.1 mm.

of the reducing agent and Pd^{2+} respectively and dc/dx expresses the concentration gradients of these species in the polymer particles along the radial coordinate. The minus sign on the right hand side of Eq. 1 is for making positive the value of the ratio R (minus concentration gradient of cationic palladium). When $R \gg 1$, we expect an uniform distribution of metal crystallites (type I – inside the particles) and when $R \ll 1$, we forecast the distribution of the reduced metal at the borders of the resin particle (type E – at the edge of the particle).

On the basis of the above, reduction with H_2 in methanol is expected to produce a type E distribution (Fig. 9a) as it is also observed when a 0.066 M water solution of NaBH_4 in water (Fig. 9b) is employed. When an ethanol 0.066 M solution is employed, type I distribution is observed (Fig. 9c). If the concentration of reducing agent is lowered to 0.019 M, again type E is produced (Fig. 9d). Apparently, these experiments do illustrate in a remarkable way the extreme cases of R values and they also point out both a solvent effect

(i.e. ethanol vs. water) and a concentration effect (i.e. in ethanol). In all these cases, the concentration of metal palladium was practically the same, 7.9%.

SEM analysis provides further complementary information (Figs. 10 a–d). The external surface of resin particles resulting from treatments featured by $R \ll 1$ (Figs. 10a, b, d) appear to be decorated by evident micrometer- (Fig. 10a) and tens of nanometer- (Fig. 10b, d) sized granules, which are likely to be palladium crystallites. Remarkably, the surface of particles obtained under $R \gg 1$ conditions exhibit very few nanometer-sized granules. In this connection TEM analysis will furnish the last word.

The reduced resins were also characterized by bulk expanded volume measurements (Fig. 4). It is seen that the ‘crosslinking effect’ caused by replacement of Na^+ by $\text{Pd}(\text{NH}_3)_4^{2+}$ is substantially reversed by metal reduction. Due to the metal crystallites in the cavities of the polymer, the specific bulk expanded volumes in all cases (even in the dry state) are lower than for the P4N.

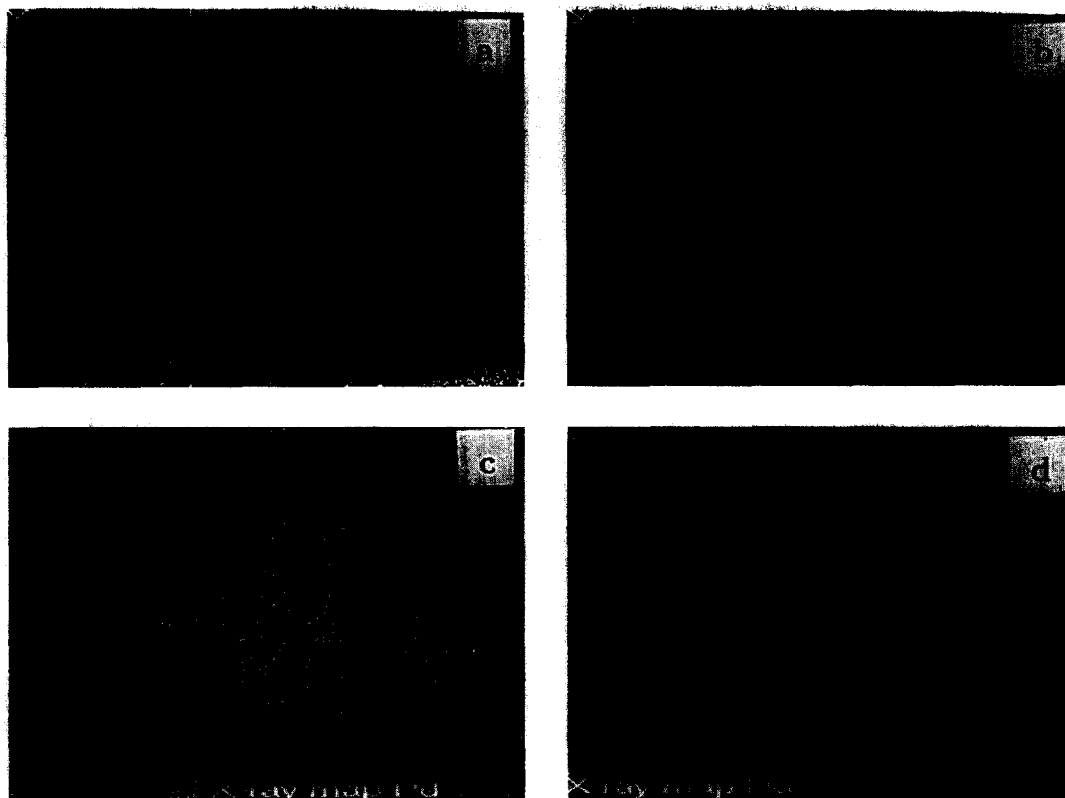


Fig. 9. Distribution of palladium in the reduced P4N ion-exchange resins; (a) hydrogen in methanol (100 kPa), (b) NaBH_4 0.066 M in water, (c) NaBH_4 0.066 M in ethanol, (d) NaBH_4 0.0189 M in ethanol. Particles of about 0.1 μm .

In spite of the lower swellability, P4NPd8r still appears to be a promising material as far as swellability and accessibility are concerned.

For catalytic tests the catalyst with uniform distribution of palladium crystallites was chosen (the catalyst denoted as P4NPd8r). The catalytic potentiality was tested in the hydrogenation of *p*-nitrotoluene to *p*-toluidine at ambient conditions, in methanol, in a shaken batch vessel. For the sake of useful comparison we performed a catalytic experiment also with the commercially available catalyst 5% Pd/C, under identical conditions. In both cases the starting concentration of *p*-nitrotoluene was 1 M and analytical concentration of palladium was 1.88 mM. A typical comparison of catalytic activity is illustrated in Fig. 11. The two catalysts exhibit identical selectivity and comparable overall activity, even though a somewhat detailed comparison is prevented by the different kinetic and diffusional regimes observed in these two cases. Catalyst P4NPd8r is quite easily filter-

able and reusable in ensuing tests, without significant loss of activity for at least three runs.

4. Conclusions

Lightly cross-linked hydrophilic, dimethyl acrylamide-*p*-styrylsulfonate-based microporous ion exchange resins appear to be materials featuring good swellability and chemical accessibility in water, methanol and ethanol. They can be easily and evenly charged with cationic metal complexes and they can be conveniently converted into supported bifunctional metal catalysts which do maintain good swellability and accessibility. An appropriate choice of reducing conditions makes possible fine control of the distribution of metal crystallites inside the support particles. Activity of catalysts obtained is comparable with other palladium catalysts, e.g. palladium on charcoal, but the utilization of polymer supported catalyst is

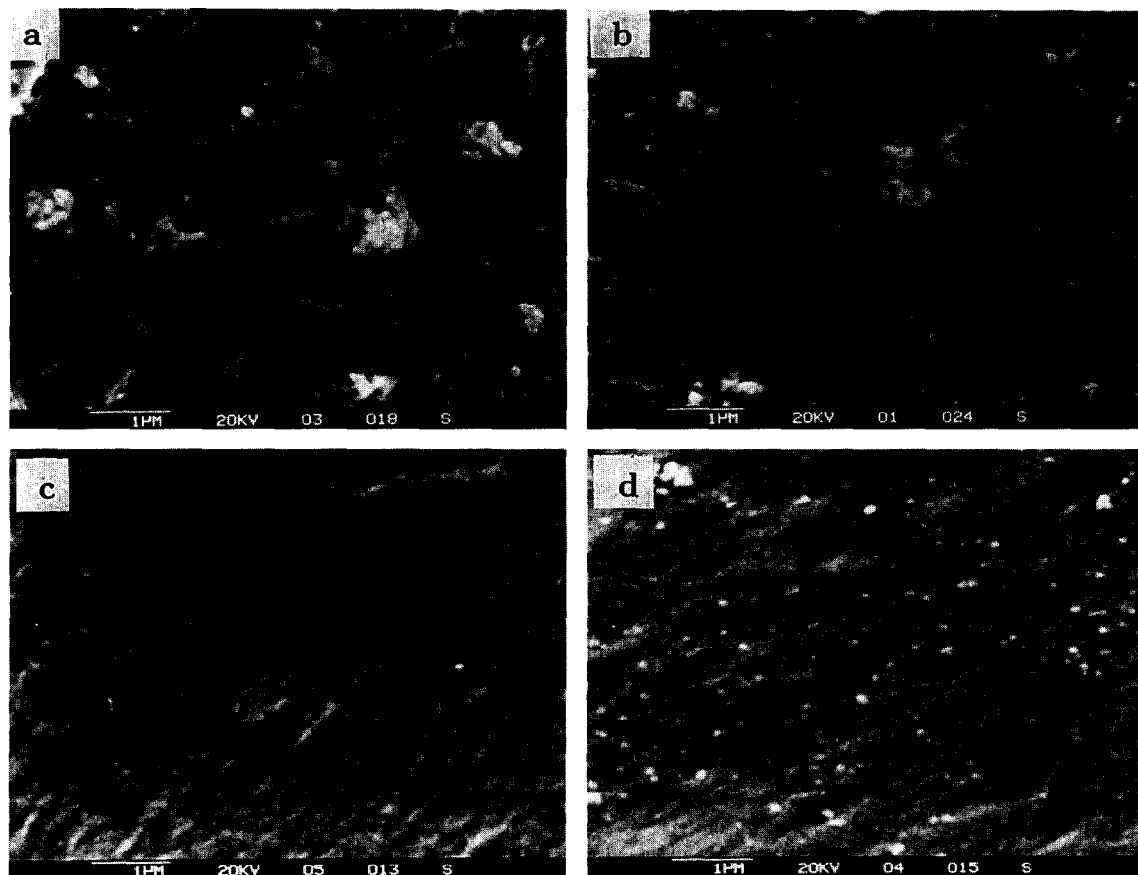


Fig. 10. Particles on the surface of reduced P4N ion-exchange resins; notations as in Fig. 9.

much more comfortable due to their good sedimentation properties which result in easy re-utilization of the catalyst.

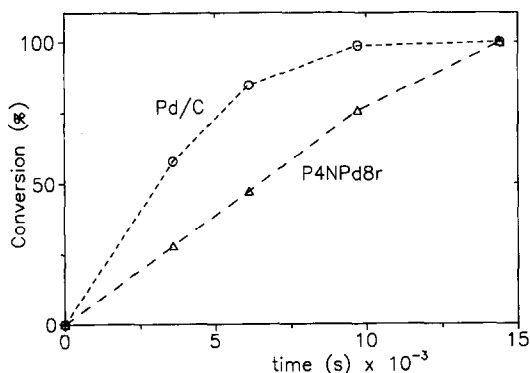


Fig. 11. Conversion of *p*-nitrotoluene vs. time. Pd/C: 5% Pd on Carbon, P4NPd8r: 7.9% Pd in P4NPd8r. 1 M solution of *p*-nitrotoluene at the start, 1.88 mM analytical concentration of Pd in the reaction mixture in both cases.

Acknowledgements

We are grateful to Mr. C. Furlan of C.U.G.A.S. University of Padova for skilful SEM and XRMA. This work was partially supported by 'Progetto Finalizzato Chimica Fine II CNR, Rome' and 'Ministero dell' Università e delle Ricerca Scientifica e Tecnologica, Rome', Fondi 40%. One of us (M.K.) is grateful for a research fellowship granted by the University of Padova.

References

- [1] R. Wagner and P.M. Lange, *Erdöl Erdgas Kohle*, 105 (1989) 414.
- [2] A. Guyot, *Pure Appl. Chem.*, 60 (1988) 365.
- [3] R. Arshady, *Chim. Ind.*, 71 (1989) 84.
- [4] R. Arshady, *Colloid Polym. Sci.*, 268 (1990) 948.
- [5] R. Arshady, M. Basato, B. Corain, L. Della Giustina, S. Lora, G. Palma, M. Roncato and M. Zecca, *J. Mol. Catal.*, 53 (1989) 111 and references therein.

- [6] B. Corain, F.O. Sam, M. Zecca, S. Lora and G. Palma, *Angew. Chem., Int. Ed. Engl.*, 29 (4) (1990) 384.
- [7] L.H. Sperling, *CHEMTECH*, (1988) 104.
- [8] M. Carezza and G. Palma, *Chim. Ind.*, 65 (1983) 261.
- [9] R. Arshady, *Adv. Mater.*, 3 (1991) 182.
- [10] K. Jerabek, *J. Mol. Catal.*, 55 (1989) 247.
- [11] L.J. Berliner (Ed.), *Spin Labelling Theory and Applications*, Academic Press, New York, 1976.
- [12] B. Corain, C. Corvaja, S. Lora, G. Palma and M. Zecca, *Adv. Mater.*, 5 (1993) 367.
- [13] G. Martini and L. Burlamacchi, *Chem. Phys. Lett.*, 41 (1976) 129.
- [14] J.S. Hwang, R.P. Mason, L.P. Hwang and J.H. Freed, *J. Phys. Chem.*, 79 (1975) 489.
- [15] T. Uematsu, M. Umino, S. Shimazu and M. Miura, *Bull. Chem. Soc. Jpn.*, 59 (1986) 3637.
- [16] W.O. Haag and D.D. Whitehurst, *Ger. Pat.* 1800371 (1989), 1800379 (1969), 1800380 (1969)
- [17] D.L. Hanson, J.R. Katzer, B.C. Gates, G.C.A. Schuit and H.F. Harnsberger, *J. Catal.*, 32 (1974) 20.