Metal palladium supported on amphiphilic microporous synthetic organic supports. Part I. Material preparation and textural characterization

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Abstract

Styrene, 2-methacryloxyethylsulfonic acid and methylenebisacrylamide are copolymerized in the presence of dimethylformamide under γ-irradiation at room temperature to give potentially amphiphilic, microporous resins. The molar fraction of methylenebisacrylamide (the cross-linker) ranges from 1 to 6 mol%. The obtained resins, after grinding and sieving, are treated with solutions of $Pd(AcO)_2$ and the ion-exchanged polymers are then treated with $NaBH_4$ in ethanol. The metal content in the materials ranges from 2.1% to 2.4% (w/w). X-ray microprobe analysis shows that Pd(0) is homogeneously dispersed throughout the particles of the polymeric materials. The polymer chain concentration and its distribution in the swollen macromolecular networks are assessed by means of Inverse Steric Exclusion Chromatography (ISEC). In spite of the higher molar proportion of styrene repeating units, the Pd(0)-resin composites swell comparably in water and tetrahydrofurane. Their amphiphilic character is the result of the different swelling properties of the hydrophilic and hydrophobic domains. © 1998 Elsevier Science B.V.

1. Introduction

Synthetic cross-linked macromolecular materials both micro- and macroporous [1] in nature have been recognized as useful supports for catalytically active polydispersed metal phases since 1969 [2]. However, polymer-supported metal (Pd) catalysts have only recently entered the industrial production arena. For instance, Bayer AG produces palladium metal catalysts supported onto anion-exchange resins for the

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chemical removal of dioxygen from water [3]. Deutsche-Texaco has developed a process for the industrial synthesis of methylisobutylketone based on a bifunctional catalyst (palladium metal on sulfonated polystyrene), in which the polymeric network acts as both the support and the acidic component [4].

We have started in 1993 a joint project aimed at (i) proposing new experimental conditions for controlling metal crystallites distribution inside polymeric supports [5], (ii) setting up combined physico–chemical analytical methodologies for defining the nanotextural properties [6] of microporous supports, (iii) proposing new mathematical modelling for defining mass transfer and reactivity inside microporous networks and (iv) searching for reliable correlation between support nanoscopic morphology and catalytic activity [7,8].

In connection with this last point, the focus of our research has been directed so far to hydrophilic materials. However, as solvent–substrate compatibility [1,9] is an important feature of polymer-supported catalysts, we have recently started to investigate on also on materials of different nature in order to extend the scope of our approach. In particular, we designed some potentially amphiphilic functional supports based on hydrophobic (styrene) and hydrophilic (functional sulfonates) monomers, expected to combine a controlled polymer chain concentration [10,11] with essentially the same chemical structure. We report in this paper on the synthesis and thorough characterization of palladium catalysts supported on amphiphilic microporous resins featured by a designed different distribution of polymer chain density and quite similar content of metal phase.

2. Experimental

2.1. Materials

Reagent grade methacryloxyethylsulfonic acid (MESA, Polyscience), styrene (STY,

Aldrich), methylenebisacrylamide (MBAA, Aldrich) and dimethylformamide (DMF, Baker) were used as received. Methanol, ethanol and acetone (Baker), Pd(AcO)$_2$ (Aldrich) were also used as received.

2.2. Apparatus

SEM and XRM analyses were carried out by means of a Cambridge Stereoscan 250 EDX PW 9800 apparatus. Elemental analyses were carried out with a Perkin Elmer 2400 CHN microanalyser, equipped with a Perkin Elmer AD-4 autobalance [1]. IR spectra were recorded on a Biorad FTS7 spectrometer. Atomic absorption spectrometric analyses were carried out with a Perkin Elmer 3030 apparatus. Grinding of the materials was carried out by means of an Edmund-Bühler impact grinder. ISEC measurements were carried out as reported elsewhere [12].

2.3. Synthesis

Resins in the acid form have been coded as SS1MH, SS2MH, SS3MH and SS6MH according to their expected molar cross-linking degree. The compositions of the polymerization mixtures (weights in grams of STY/MESA/MBAA/DMF, in the order; molar fractions of the monomers in parentheses) were as follows:
SS1MH: 6.45 (77), 3.44 (22), 0.12 (1), 5.78
SS2MH: 3.85 (76), 2.15 (22), 0.15 (2), 4.06
SS3MH: 3.78 (75), 2.15 (22), 0.22 (3), 4.00
SS6MH: 3.58 (72), 2.12 (22), 0.44 (6), 4.34
The mixtures were put into 20 ml Pyrex cylindrical vials under nitrogen and then irradiated by γ-rays from a ^{60}Co source at 0.5 Gy s^{-1} for 5 h at 15–18°C. The pale yellow polymeric materials appeared as rubbery cylinders; after

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[1] The microdetermination of C, H and N weight percent fractions has been performed through a procedure optimized in these laboratories for the analysis of samples particularly resistant to combustion.

cutting in slices (ca. 1 mm thick), they were transferred into 50 cm^3 of methanol. Upon two days standing, the slices underwent a partial self-breaking and, after filtration, they were impact-ground in water until particles with diameters of ca 100 μm were obtained. The materials were then washed with methanol (3×30 cm^3), acetone (3×30 cm^3) and diethylether (3×30 cm^3), dried in vacuo (mechanical oil pump, ca 10 Pa, room temperature) up to constant weight of the samples and finally sieved to sizes less than 100 μm.

2.4. 'Palladiation' of resins in the acid form with palladium acetate

Typically 1 g of resin (ca. 1.4 mmol of SO$_3$H functional groups) was let to swell in a methanol–acetone ($1/1$ vol vol^{-1}) mixture and the excess solvent was removed after 4 h upon decantation. The swollen resin was added to a dark brown solution (10^{-2} mol dm^{-3}, 23 cm^3) of Pd(AcO)$_2$ in methanol–acetone ($1/1$ vol vol^{-1}) under vigorous stirring and fast decoloration was observed. At the same time the resin turned out to a very dark brown color. The exchanged resin was washed with methanol (3×30 cm^3) and then dried in vacuo (mechanical oil pump, ca. 10 Pa, room temperature) up to constant weight of the sample.

2.5. Pd(II) reduction to Pd(O) in exchanged resins

Typically 0.5 g of Pd(II)-containing resin (0.11 mmol Pd) was let to swell in the least amount of ethanol for 4 h, after which time it was rapidly poured into 17 cm^3 of an alcoholic solution of NaBH$_4$ ($7.14 \cdot 10^{-2}$ mol dm^{-3}, ethanol) under vigorous stirring. After 2 h the black material was filtered off and washed with ethanol (3×30 cm^3) and dried in vacuo (mechanical oil pump, ca. 10 Pa, room temperature) up to constant weight of the sample.

3. Results and discussion

The monomers and the cross-linker (CL) are not miscible and the addition of ca. 30% DMF (w/w) is necessary. Four mixtures, in which the CL molar fraction has been changed from 10^{-2} to $6 \cdot 10^{-2}$ while keeping constant the fraction of MESA (see Section 2), are co-polymerized under γ-rays irradiation [13]. The relevant data are collected in Table 1.

The hydrogen ions in the resins, which are obtained in the acidic form, are easily replaced by reaction with a solution of Pd(AcO)$_2$ in acetone–methanol mixtures ($1/1$, vol vol^{-1}). The ion-exchange reaction occurs with quantitative uptake of the 'Pd^{2+}' ions from the solution and quantitative release of acetic acid; the final metal load in the catalysts depends on the amount of Pd(AcO)$_2$ available for ion exchange [7]. The ion-exchanged polymers are then treated with an alcoholic solution of NaBH$_4$, in large excess with respect to Pd(II) (Scheme 1).

The quantitative reduction of Pd(II) to palladium metal yields black materials (SS1MPd, SS2MPd, SS3MPd, SS6MPd), in which the acidic sites are neutralized at least partially by sodium ions. The elemental analyses of SS1MPd, SS2MPd, SS3MPd and SS6MPd are collected in Table 2.

Table 1
Elemental analyses of resins SS1MH, SS2MH, SS3MH and SS6MH

Code		%C	%H	%N	%S
SS1MH	f.	**66.53**	**7.27**	**1.70**	**4.34**
	t.[a]	71.59	6.71	0.22	5.40
	t.[b]	*66.83*	*7.37*	*1.63*	*4.70*
SS2MH	f.	**66.60**	**7.32**	**1.73**	**4.38**
	t.[a]	71.13	6.70	0.44	5.40
	t.[b]	*66.04*	*7.35*	*1.86*	*4.76*
SS3MH	f.	**63.60**	**7.02**	**2.31**	**4.98**
	t.[a]	70.99	6.70	0.66	5.30
	t.[b]	*65.66*	*7.34*	*2.05*	*4.76*
SS6MH	f.	**63.01**	**7.56**	**2.78**	**4.55**
	t.[a]	69.80	6.66	1.30	5.27
	t.[b]	*64.73*	*7.30*	*2.63*	*4.70*

[a]calculated on the basis of the composition of the monomers mixtures.
[b]calculated on the basis of assumption (i)–(v) (see text).

$$Ⓟ(SO_3)_2Pd + 2NaBH_4 \longrightarrow Pd/Ⓟ(SO_3Na)_2 + B_2H_6 + H_2$$
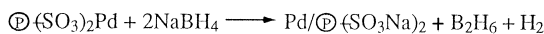
<center>Scheme 1.</center>

The whole of the analytical data deserve some comments. The nitrogen content in SS1MH, SS2MH, SS3MH and SS6MH is much higher than expected on the basis of the composition of the respective monomer mixtures. On the contrary, the content of carbon is always appreciably lower than the theoretical value determined in this way. These results lead us to assume that water and DMA are present in the polymeric materials even after drying. In particular, DMF is supposed to be bound to the polymer network through relatively strong chemical interactions, such as an acid–base reaction with the sulfonic groups. This hypothesis is supported by the observation that a much lower nitrogen content is found in SS1MPd, SS2MPd, SS3MPd and SS6MPd (see below). In conclusion, the composition of the resins depends on the relative amount of the reacted co-monomers and of DMF and water included in the polymer networks. On the basis of a trial and error procedure, we have calculated the theoretical compositions (see t[b], Table 1) of the resins SS1MH, SS2MH, SS3MH and SS6MH and the closer agreement with the experimental data is obtained with the following assumptions:

(i) the cross-linker is quantitatively incorporated into the resins;

(ii) the conversion of MESA in the co-polymerization is equal to 90%; a similar behavior has already been observed for this monomer [7];

(iii) styrene conversion in the co-polymerization is equal to 95%;

(iv) the molar ratio between water and sulfonic groups in the polymers is 2.5;

(v) the molar ratio between DMF and sulfonic groups in the polymers is 0.7.

According to these assumptions, the actual cross-linking degree is 1.0, 2.1, 3.1 and 6.3% (mol mol^{-1}) in SS1MH, SS2MH, SS3MH and SS6MH, respectively. The assumptions (i)–(iv) were applied also to the calculation of the theoretical compositions of SS1MPd, SS2MPd, SS3MPd and SS6MPd (Table 2). These materials are obtained upon treatment of the palladium-exchanged resins with NaBH$_4$, in excess with respect to the stoichiometric amount for the reduction of Pd^{II}. NaBH$_4$ is an alkaline reagent and can displace the molecules of DMF supposed to be held inside the polymer network by acid–base interaction before reduction (see above). Noteworthy, the nitrogen weight fractions in SS1MPd, SS2MPd, SS3MPd and SS6MPd are much lower than in the respective parent resins. The observed values demonstrate that MBAA is the only nitrogen source in the reduced materials and this supports the hypothesis that the molecules of DMF inside the parent resins are actually engaged in acid–base interactions with the sulfonic groups.

The characterization of the materials was completed by scanning electron microscopy (SEM) and X-ray microprobe analysis (XRM). All matrices exhibited the typical vitreous compact structure of microporous resins, as expected on the basis of the polymerization conditions [1,9]. XRM analysis of both Pd(II) and Pd(0) containing materials reveal a homogeneous metal distribution through the resins particles. This observation does fully confirm the suitability of our procedure [5] for controlling the radial distribution of metal crystallites formed upon reduction of the metal ions dispersed in the ion-exchangers (Fig. 1).

Table 2
Elemental analyses of materials SS1MPd, SS2MPd, SS3MPd and SS6MPd after reduction of palladium(II)

		%C	%H	%N	%S	%Na[a]	%Pd
SS1MPd	f.	—	—	—	—	3.35	2.10
	t.[b]	64.63	6.65	0.21	4.81	3.44	2.31
SS2MPd	f.	64.95	6.40	0.39	4.08	3.14	2.34
	t.[b]	63.81	6.62	0.41	4.88	3.50	2.30
SS3MPd	f.	64.04	6.21	0.49	3.79	2.28	2.25
	t.[b]	63.43	6.61	0.61	4.88	3.50	2.31
SS6MPd	f.	64.86	6.47	1.35	4.07	2.13	2.37
	t.[b]	62.48	6.59	1.22	4.91	3.45	2.31

[a]calculated on the basis of complete neutralization of sulfonic groups.
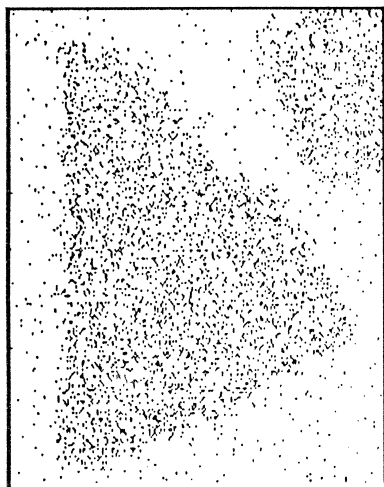[b]calculated on the basis of assumption (i)–(iv) (see text).

Fig. 1. Palladium distribution in SSM3Pd (XRM map).

Apparently, the materials here described do represent cases in which the potentially active metal centers are dispersed throughout the whole polymer network, which possesses a very high surface area [5], when the system of micropores develops, i.e. when it is swollen. Hence, the detailed knowledge of the texture of the polymeric supports in the swollen state can be of great importance in understanding the behavior of this kind of catalysts.

The nanoscopic texture of the polymeric supports in the swollen state have been assessed by means of ISEC after the reduction of palladium(II) to palladium metal. This technique has already proved to be very useful to explain the behavior of macroporous polymeric materials under liquid–solid conditions (including polymeric catalysts) [14,15] and, in particular, of swollen microporous resins [10,16]. In this connection, it has also been shown that conventional dry state techniques, such as BET, are of very little use, if any [17]. Precise values of the Swelling Volume (SV = total volume of swollen polymer per unit mass of dry material) can be obtained very easily from the ISEC data. In addition to S values, ISEC yields a much more valuable evaluation of molecular accessibility and nanoscopic morphology of polymeric materials. This technique was proposed inde-

pendently to this purpose by Halász [18] and Freeman [19]. The swollen polymer is loaded in a column for liquid chromatography and acts as the stationary phase in the partition process of a number of solutes of known molecular size, which are eluted in separate chromatographic runs. A proper mathematical treatment of the elution volume data yields the final ISEC output [11]. The method rests on the following assumptions:

(i) the polymer chains are considered as rigid rods with fixed, uniform diameters;

(ii) the 'pores' are formed by the void spaces among the randomly oriented rods; their 'size' and 'volume' depend on the 'crowding' of the rods in the polymer gel; this is quantitatively expressed as the sum of rod lengths (L_i) per unit volume ($C = \sum L_i / V_g$ = polymer chain concentration, nm^{-2});

(iii) the partition of a solute between the bulk liquid and the gel phase is governed only by polymer chain concentration, as defined above, and molecular size of the solute, i.e. by steric factors only;

(iv) the gel phase is formed by a discrete number of fractions, each one featured by a different single value of polymer chain concentration.

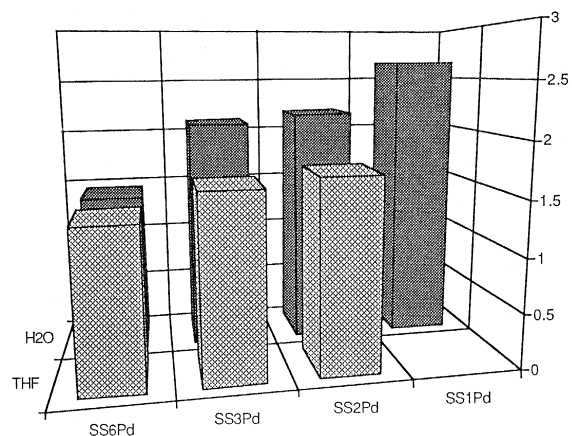The employed swelling agents are water and tetrahydrofuran (THF). Also dichloromethane

Fig. 2. SV values ($cm^3\ g^{-1}$) for SS1MPd, SS2MPd, SS3MPd and SS6MPd in water and THF, as measured by means of ISEC.
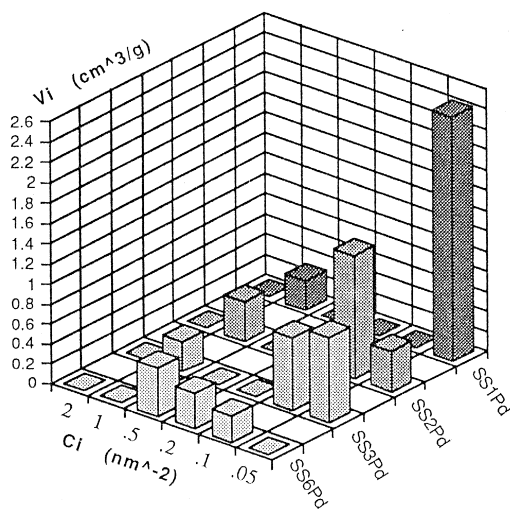
Fig. 3. Distribution of polymer chain concentration in SS1MPd, SS2MPd, SS3MPd and SS6MPd (water).

Table 3
Comparison between SV and GV values for SS1MPd, SS2MPd, SS3MPd and SS6MPd (water and THF)

	H_2O		THF	
	SV	GV	SV	GV
SS1MPd	2.66	2.72	—	—
SS2MPd	2.18	2.05	1.74	1.79
SS3MPd	2.10	1.89	1.66	1.64
SS6MPd	1.46	1.09	1.42	1.63

(DCM) has been considered, but its swelling ability is not good enough and the results are not well reproducible. Methanol and ethanol have been ruled out as swelling agents because we are aware from previous experience [20] that strong enthalpic interactions occur in their presence and condition (iii) (steric only interactions) is not fulfilled. This is an unfortunate circumstance, because methanol is often employed as
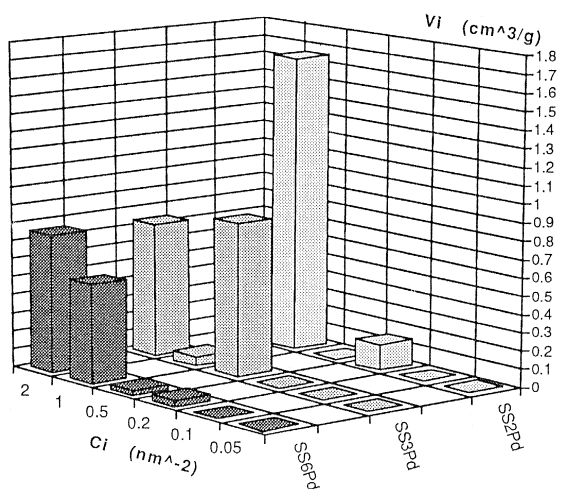
solvent in catalytic hydrogenation reactions [5,7,8,21].

The experimental SV values can be obtained as the difference between the volume of the chromatographic column and the dead volume. For microporous materials, the former is the sum of the volume of the swollen polymer and of the interparticle volume. The dead volume corresponds to the elution volume of a standard solute so large to be totally excluded from the stationary phase (the swollen polymer), to which only the interparticle volumes are accessible. The SV data in water and THF (Fig. 2) underline the amphiphilic character of SS1MPd, SS2MPd, SS3MPd and SS6MPd.

The difference of SV values both in water and THF is apparently small, although the two swelling media have quite different polarity.

The volume distributions of polymer chain concentration in SS1MPd, SS2MPd, SS3MPd and SS6MPd swollen in water and THF are represented in Figs. 3 and 4, respectively.

This distribution is qualitatively equivalent to the pore size distribution according to the conventional description of porous materials. For a given material, the sum of the volumes of the gel fractions represents the volume occupied by the gel phase in the swollen polymer per unit mass of dry material (GV). The values of SV and GV for SS1MPd, SS2MPd, SS3MPd and SS6MPd both in water and THF are collected in Table 3.

The agreement between SV and GV values is very good for all the investigated materials in THF and for SS1MPd in water, which means that the swelling process takes place to such an

Fig. 4. Distribution of polymer chain concentration in SS1MPd, SS2MPd, SS3MPd and SS6MPd (THF).

extent that the whole polymer network is accessible to the ISEC probes and therefore the whole polymer mass is explored. For SS2MPd, SS3MPd and SS6MPd in water SV is higher than GV. This is due to the presence of microporous domains with such a high chain concentration (> 2 nm^{-2}) that they totally exclude all the ISEC probes. However, in the case of SS2MPd and SS3MPd the difference is small and practically their polymer networks are completely detected.

ISEC characterization confirms that these materials are fully microporous in nature, both in water and THF, in that no macropores are detected in the swollen state [11]. Inspection of Figs. 3 and 4 discloses the following general trends:

– all materials are polydispersed in nature, in that they are formed by 2 or 3 domains featured by different chain concentration, in both solvents;

– the relative volume of the fraction with higher chain concentration increases with increasing cross-linking degree;

– the values of both SV and GV decrease with increasing cross-linking degree;

– in general, the gel phases in water and THF are formed mainly by relatively little concentrated ($C_i \leq 0.5$ nm^{-2}) and highly concentrated ($C_i \geq 1$ nm^{-2}) gel fractions, respectively.

The first finding is not surprising, as it is the consequence of the intrinsic kinetics of polymerization [1]; also the second and third observation are not unexpected.
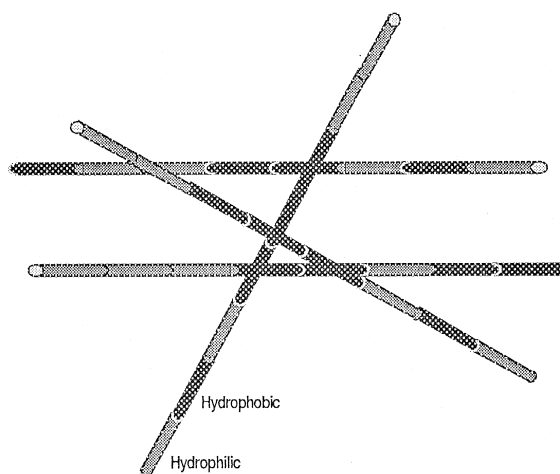

Fig. 5. Schematic picture of polymeric chains.

Interesting conclusions can be drawn from the last observation if one bears in mind that GV values in water and THF are very close to each other for all the materials. The chains of the investigated polymeric supports are formed by hydrophilic (stemming from MESA) and hydrophobic (from STY) monomeric units. The molar ratios between STY and MESA (i.e. of hydrophobic and hydrophilic monomeric units) in SS1MPd, SS2MPd, SS3MPd and SS6MPd are reported in Table 4. As polymeric chains are depicted as rigid rods, it can be also considered that they are divided in linear hydrophilic and hydrophobic segments of different lengths, according to the sequence of the monomeric units. As a first, rough approximation, the ratio of the sums of the lengths of the hydrophobic and hydrophilic segments in a given material should be close to the molar ratio between the hydrophobic and hydrophilic monomeric units, i.e between STY and MESA incorporated into the copolymer (Fig. 5). The latter can be easily calculated from the starting molar STY/MESA ratio in the polymerization mixture and from the respective conversion figures obtained from the results of the elemental analyses. Therefore it was not necessary to determine the reactivity ratio, which is not known for this couple of monomers.

Table 4

Molar STY/MESA ratio, polymer chain length in water (L_{H_2O}) and THF (L_{THF}) and L_{THF}/L_{H_2O} ratio for SS1MPd, SS2MPd, SS3MPd and SS6MPd

	STY/MESA[a]	L_{H_2O}[b]	L_{THF}[b]	L_{THF}/L_{H_2O}
SS1MPd	3.7	4.3	—	—
SS2MPd	3.5	5.7	16.4	2.9
SS3MPd	3.5	4.6	19.7	4.3
SS6MPd	3.3	4.5	21.7	4.8

[a]Experimental molar ratio of incorporated monomers.
[b]10^8 km g^{-1}.

The ISEC technique allows the determination of the total length of the chains of a swollen polymer ($L = \Sigma V_i \cdot C_i$); the values obtained for the investigated materials in water (L_{H_2O}) and in THF (L_{THF}) are also reported in Table 4, respectively. The ratio L_{THF}/L_{H_2O} ranges approximately from 3 to 5 (Table 4), not very different from the experimental ratio STY/MESA: this is in agreement with the expectation that water strongly interacts with the hydrophilic sections of polymeric chains and poorly with the hydrophobic ones and that THF interacts the other way round. Moreover, water exhibits an apparent swelling power on the hydrophilic domains of polymeric network much greater than the swelling power of THF on the hydrophobic ones. In fact, the aqueous gel has practically the same volume (Fig. 2) as the THF gel, although the length of the hydrophilic sections of polymeric chains is about 3–4 times shorter than the length of the hydrophobic ones.

4. Conclusion

The results reported in this paper confirm [5,7,8] the possibility of (i) introducing 'Pd^{2+}' in amphiphilic microporous ion exchangers in the acid form upon ion-exchange with solutions of Pd(AcO)$_2$ in methanol–acetone and (ii) achieving a homogeneous dispersion of palladium crystallites formed upon reduction of Pd(II) under controlled conditions.

Detailed and subtle information on nanoscopic morphology of microporous resins can be obtained by ISEC measurements. In the case of the amphiphilic resins described herein, we have been able to estimate the relative proportion of hydrophilic and hydrophobic domains and to make a semiquantitative comparison between their relative swelling properties. All these pieces of information are of major importance for understanding how resin-supported metal catalysts work and therefore are relevant for tailoring at the nanoscopic level the microenvironment experienced by the catalytic sites.

Acknowledgements

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