On the use of hyperbranched aramids as support of Pt nanoparticles

Orietta Monticelli [1]*, *Andrea Chincarini* [2]

[1]Dipartimento di Chimica e Chimica Industriale, Università di Genova and INSTM NIPLAB Centre, via Dodecaneso, 31, 16146 Genova, Italy; fax: +39 010 353 6198; orietta@chimica.unige.it
[2]INFN Genova unit, via Dodecaneso 33, 16146 Genova, Italy; andrea.chincarini@ge.infn.it

Abstract: A hyperbranched (HB) aromatic polyamide (aramid) synthesized from A_2 (*p*-phenylenediamine) + B_3 (trimesic acid) reactants has been used as Pt nanoparticle support. TEM measurements verified the possibility to obtain a high metallic dispersion (MD) using H_2PtCl_6 as metal precursor. The amount of Pt retained by the polymer support turned out to be lower than the Pd loading deposited on the same HB aramid from a different metal precursor, *i.e.* $PdCl_2$, under the same exchange and reduction conditions, namely by the procedure reported in a previous paper of ours [1]. Moreover, Pt nanoparticle diameters have been found to depend on the reducing agent used. As compared to bubbling H_2, $NaBH_4$ allowed obtaining of metal particles characterized by smaller dimensions.

Introduction

Recently, the application of dendritic macromolecules as metal solid support [1, 2] or nanocluster templates in solution [3-9] has found growing interest. As far as this latter application is concerned, the attention has been mainly focused on the use of poly(amidoamine) (PAMAM) Starbust® dendrimers, which have been found to encapsulate metal nanoclusters such as Cu, Pd, Pt in solution [3-6]. The above studies demonstrated the possibility to finely tune cluster dimensions by varying dendritic molecule generation (*i.e.* the degree of polymerization) [3, 4], as well as the efficiency of the above systems as hydrogenation catalysts [5, 6]. Although the exploitation of hyperbranched polymers is emphasized by the easy one-step preparation [10], only few attempts have been made so far to apply such templates as metal cluster stabilizers. Namely, amphiphilic hyperbranched polyglycerols have been used for the stabilisation of palladium nanoclusters employed as catalysts in hydrogenation reactions [7, 8]. More recently, our group has verified the possibility to form stable palladium solutions using HB aramids as stabilisers [9].

On the other hand, the exploitation of dendritic macromolecules as solid metal supports has not been investigated as extensively as their use for nanocluster stabilization in solution. One of the very few studies on the application of hyperbranched polymers, namely HB aramids, as support of Pd nanoparticles was reported in a previous paper of ours [1]. The aramid-supported palladium systems, studied by various characterization techniques, proved to be effective and robust catalysts for the selective hydrogenation of various unsaturated substrates.

In the present work, we extent the use of HB aramids prepared from $A_2 + B_3$ reactants, also to Pt deposition, using H_2PtCl_6 as metal precursor.

Results and discussion

Pt nanoclusters have been supported on a hyperbranched aramid, coded pPDT, obtained from *p*-phenylenediamine (A_2)+ trimesic acid (B_3) reactants, using H_2PtCl_6 as metal precursor. Both a TEM micrograph, (a) and the histogram of the relative population, (b) as a function of metal particle diameter are shown in Fig. 1 for the sample pPDT/Pt(Na). The notation in brackets refers to the reducing agent used ($NaBH_4$). The micrograph below evidences the formation of small Pt aggregates well distributed on the aramid support.

(a)   (b)
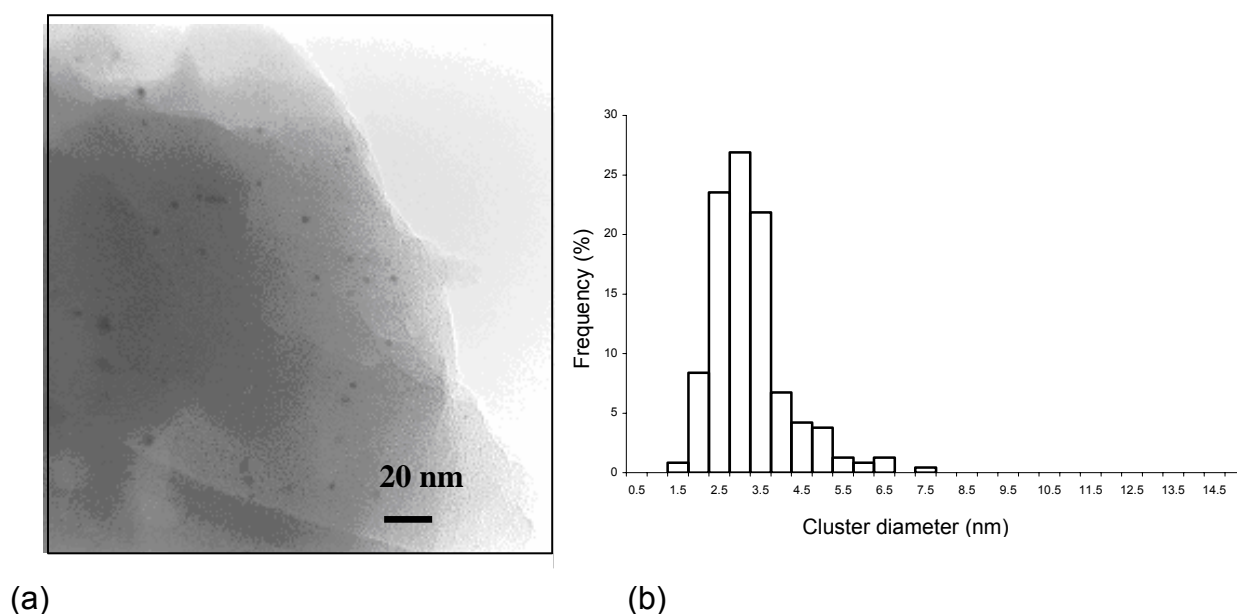
Fig. 1. (a) TEM micrograph of the system pPDT/Pt(Na) and (b) histogram of the relative population as a function of Pt particle diameter.

In order to compare the features of Pt deposited on the HB aramid, in terms of metal concentration and dispersion, to those of Pd nanoclusters, identical exchange conditions, such as temperature, metal/polymer ratio and reduction agent, *i.e.* $NaBH_4$, have been applied for the deposition of each metal on the same aramid.

On comparing the micrograph of the sample pPDT/Pt(Na) with that of the HB aramid containing Pd nanoclusters, *i.e.* pPDT/Pd(Na), shown in Fig. 2, sharp differences between the two systems under study becomes evident. Namely, the concentration of Pd aggregates turns out to be higher than that found in the system pPDT/Pt. Quantitative comparison is given in Table 1, where the visual finding by TEM, shown above, is supported by SEM-EDS and XPS measurements, allowing to evaluate Pt and Pd concentrations on the aramid matrix. By comparing row 3 and 4, it is evident that the values of the metallic concentrations, obtained by XPS and SEM-EDS analysis, are quite different. Indeed, as mentioned in the Experimental Part, the latter technique only allows to obtain a relative concentration. Nevertheless, it is relevant to underline that the ratios between Pt and Pd, calculated by the two methods above, are very similar.

2
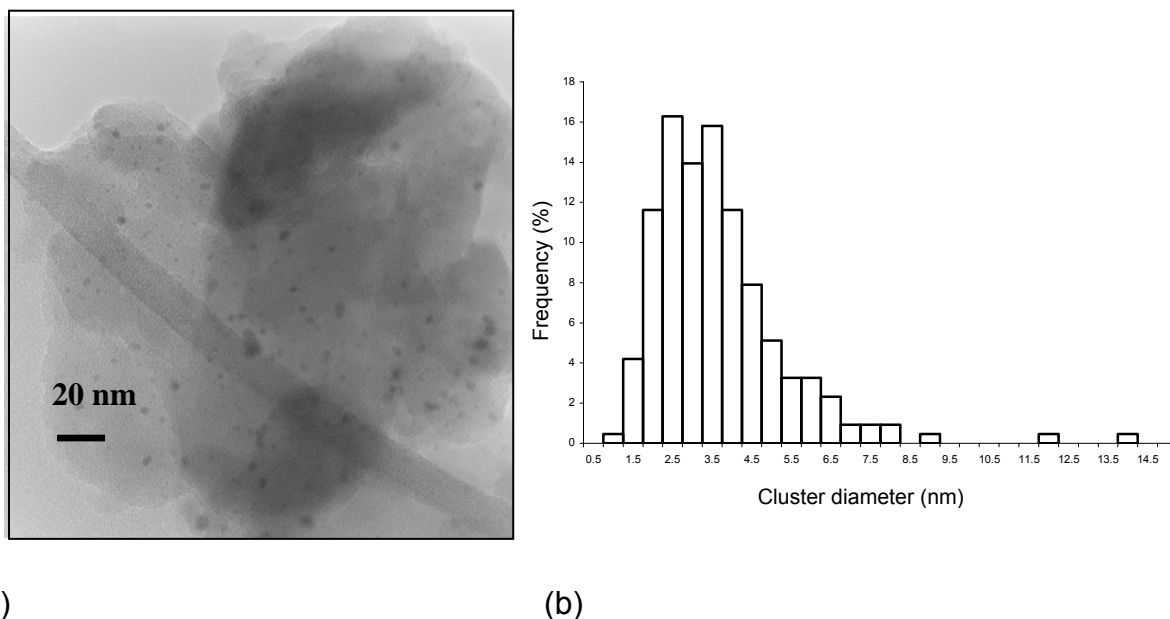
Fig. 2. (a) TEM micrograph of the system pPDT/Pd(Na) and (b) histogram of the relative population as a function of Pd particle diameter.

Tab. 1. Characterization data of the systems pPDT/Pd and pPDT/Pt.

| Sample code	Reducing agent	Metallic concentration	Metallic concentration	dva	dn	Metal dispersion (MD)
		$(\%)^a$	$(\%)^b$	(nm)	(nm)	(%)
pPDT/Pd(Na)	NaBH$_4$	13.2	0.42	6.0	3.5	18.7
pPDT/Pt(Na)	NaBH$_4$	4.8	0.20	3.8	3.2	29.6
pPDT/Pt (H$_2$)	H$_2$	4.8	0.20	5.0	2.7	22.7

^{a} from SEM-EDS analysis, ^{b} from XPS analysis

The amounts of the two metals, deposited on the HB aramid under the same exchange conditions, are very different, as the HB aramid is capable to retain a much higher quantity of Pd as compared to Pt. Metal dispersion data, calculated from the volume/area diameter (dva) and given in the same Table, clearly point out that the above difference in metal concentration also affects metal cluster dimensions. The higher Pd amount of the sample pPDT/Pd(Na) is linked to a lower MD, *i.e.* to the formation of nanoclusters characterized by higher dimensions. The relationship between the above two parameters, already found when comparing the metal retaining capability of aramids obtained from AB$_2$ monomers and A$_2$+B$_3$ reactants [1], can be explained by taking in account that a higher amount of metal deposited on the polymer support could favour nanocluster aggregation.

In order to justify the different capabilities of our HB aramid to retain Pt and Pd respectively, some considerations on the interactions between the two metal precursors, *i.e.* H$_2$PtCl$_6$ and PdCl$_2$, and the HB aramid have to be drawn. Namely, taking in account the latter precursor, we have demonstrated by various

characterization techniques that its interactions with the aramid matrix involve exclusively the polyamide NH_2 groups [1]. In a similar manner, also in the case of H_2PtCl_6 it is likely to occur that only the amino groups of the HB aramid, which can be salified by the acidic medium, are capable to interact with $PtCl_6^{2-}$. Both the above salification equilibrium and the relevant dimensions of the Pt precursor anionic species might strongly limit the rate of metal exchange.

In order to better assess the above hypothesis, FTIR and XPS measurements have been carried out on both the neat HB aramid and the sample pPDT/Pt before and after reduction.
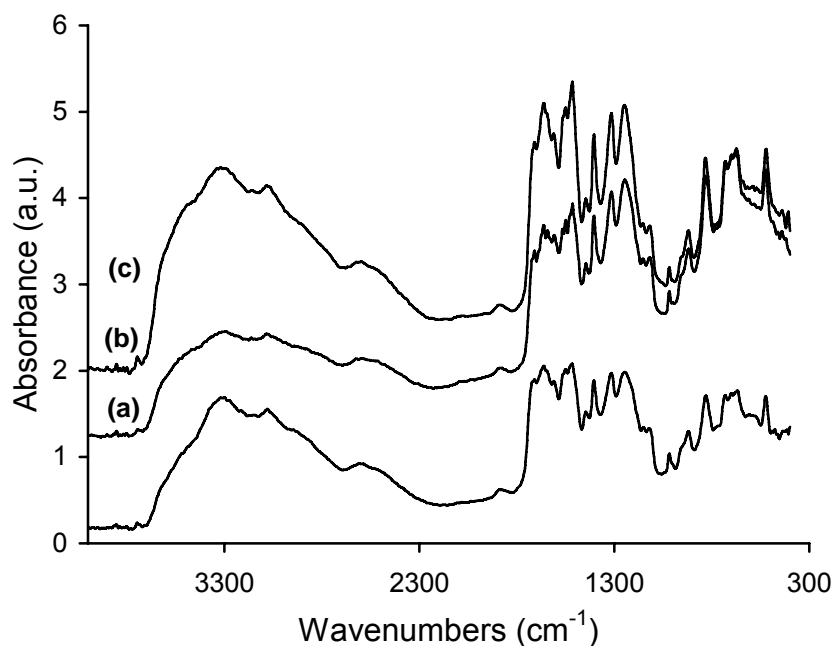
Fig. 3. FTIR spectra of: (a) neat pPDT, (b) pPDT after impregnation with H_2PtCl_6 and (c) after reduction to Pt.

Comparing IR spectra of the HB aramid before and after impregnation with H_2PtCl_6, some small differences in the shape of bands in the region above 3300 cm^{-1}, namely in the region of N-H stretch, are consistent with an interaction between H_2PtCl_6 and the amino end groups. Despite the fact that the differences in the spectra are not very evident, the hypothesis of the occurrence of interactions between NH_2 groups of the HB aramid and the metal precursor is supported by the aforementioned work of ours [1] and by other works dealing with oligomeric aramids of Kevlar® type used as polymer-supported catalysts [13]. It is relevant to underline that the behavior of the aromatic polyamides differs from that of the aliphatic polyamides, as in the former molecule the strong electronic stabilization, induced by the aromatic rings, determines a rather poor reactivity of the polymer amide groups. On the contrary, dendrimers such as poly(amidoamine) (PAMAM) turned out to interact with the metal precursor also by amido groups [4].

As far as XPS measurements are concerned, signals of all elements contained in the HB polymer (*i.e.* C, O, N), before and after impregnation with H_2PtCl_6, have not revealed any difference in both line-shape and position. Moreover, platinum peak

position (74.4 eV) corresponds to Pt^0. This result indicates that the exposure of the exchanged sample to X-ray promotes metal reduction. The above phenomenon occurs also when using times of analysis shorter than 20 minutes, *i.e.* the experimental conditions applied for the investigation of palladium-based aramid, which hindered Pd reduction [1]. Taking in account the different behaviors of the two metal-polymer systems, it is possible to conclude that in the case of pPDT/Pt sample, the low concentration of metal on the aramid support may facilitate its reduction.

Metal dispersion and cluster dimension obtained by using H_2 as reducing agent are also shown in Table 1. It is relevant to point out that the above reduction approach leads to the formation of Pt nanoclusters characterized by higher dimensions than those obtained by $NaBH_4$ as reducing agent. This finding, already reported in the case of inorganic supports [14], shows the possibility to vary metal dispersion by changing the catalyst preparation parameters.

Conclusions

The present study has demonstrated the possibility to use HB aramids as Pt metal supports, by using a typical metal precursor, *i.e.* H_2PtCl_6. TEM measurements have proved the formation of Pt nanoclusters characterized by very low dimensions, thus obtaining a high metal dispersion. The HB aramid has been found to retain a much higher amount of Pd as compared to Pt, although the same exchange conditions were applied for the preparation of the two polymer/metal systems. Indeed, the above difference has been interpreted by taking in account the different kinds of interaction of the two metal precursors, namely $PdCl2$ and H_2PtCl_6, with the HB aramid.

$NaBH_4$ turned out to be an effective reducing agent for Pt, allowing formation of a higher metal dispersion as compared to H_2.

Experimental part

HB aramid preparation

The HB aramid, coded pPDT, was obtained according to the procedure given in [11, 12].

Preparation of pPDT/metal system

Aramid powders were stirred in an aqueous solution of H_2PtCl_6 (Aldrich, 0.01 wt.-%) at room temperature for 48 hours. The aramid/H_2PtCl_6 ratio was 10/1 (*w/w*). The powders were filtered, washed several times with deionized water and dried overnight at 60 °C. Pt reduction was carried out using an aqueous solution of $NaBH_4$ (0.1 M) at 50 °C for 2 hours. After reduction, the powders were washed extensively to remove the excess of the reducing agent and dried at 60 °C under vacuum for at least 24 hours. Metal reduction was also carried out at room temperature for 5 hours by using H_2 flux (*ca.* 1 cm^3 s^{-1}).

The preparation of pPDT/Pd system was accomplished following the recipe given in [1].

pPDT/metal system characterization

The amount of palladium or platinum retained by the various samples was measured by SEM-EDS analysis using a Leo Steroscan-440 scanning electron microscopy, equipped with an EDS system (Oxford Link-Gem). The technique does not allow evaluating the absolute atomic amount but only the relative concentration.

TEM measurements, which allowed calculation of the metallic dispersion, were performed with a high-resolution transmission electron microscope (JEOL 2010). The powders were suspended in *iso*-propanol and a drop of the resultant mixture was deposited on a carbon grid.

MD was evaluated by high magnification TEM micrographs. In order to obtain a representative value of Pd or Pt nanocluster dimensions, the diameter of at least 200 particles, belonging to different sample regions, was measured. Indeed, many micrographs of the same sample were analyzed. The metallic dispersion was calculated as the ratio between the superficial $(N(s)_m)$ and the total $(N(t)_m)$ number of metallic atoms, while metal particle diameter was reported as both number diameter (dn) and volume/area diameter (dva = $6\sum(V_i)/\sum(A_i)$; V_i; A_i: volume and area of a single cluster). The calculation of dva was performed considering the particles spherical, using the following expression:

$$dva = 6\left[\frac{\sum(V_i)}{\sum(A_i)}\right] = 6\frac{v_M N(t)_m}{a_M N(s)_m} = \frac{6\left(\dfrac{v_M}{a_M}\right)}{MD}$$

where v_M and a_M are $1.47\cdot10^{-29}$ m^3 and $7.87\cdot10^{-20}$ m^2 for Pd and $1.51\cdot10^{-29}$ m^3 and $8.00\cdot10^{-20}$ m^2 for Pt, respectively

XPS analyses have been performed using a PHI 5602 Multitechnique instrument, featuring a charge neutralizer and a monochromated Al X-ray source (1486.6 eV) set at 350 W anode power. The data were acquired in multiregion mode, with 23.50 eV pass energy, take-off angle of 45 deg. and 0.05 eV energy resolution.

Samples were prepared by pressing the aramid/Pd or Pt powders onto a thick indium film; then, they were set into a pre-pumping chamber ($\cong10^{-7}$ torr) for 10 min. and transferred in the main chamber ($\cong10^{-9}$ torr) for analysis. PHI MultiPak software was used for data treatment and analysis.

Due to the intrinsic insulating nature of the samples and the need of a charge neutralization device, all XPS spectra have been software shifted to set the main carbon peak binding energy to 284.7 eV. Curve fits have been performed without smoothing, using Gaussian templates and Shirley background subtraction.

The FT IR spectra were recorded with a Bruker IFS66 spectrometer on KBr pellets.

References

[1] Tabuani, D.; Monticelli, O.; Chincarini, A.; Bianchini, C.; Vizza, F.; Moneti, S.; Russo, S. *Macromolecules* **2003**, 36, 4294.

[2] Gröhn F.; Kim G.; Bauer B.J.; Amis E.J. *Macromolecules* **2001**, 34, 2179.

[3] Zhao M.; Sun L.; Crooks R.M. *J. Am. Chem. Soc.* **1998**, 120, 4877.

[4] Balogh L.; Tomalia D.A. *J. Am. Chem. Soc.* **1998**, 120, 7355.

[5] Zhao M.; Crooks R.M. *Angew. Chem. Int. Ed.* **1999**, 38, 364

[6] Chechik V.; Crooks R.M. *J. Am. Chem. Soc.* **2000**, 122, 1243

[7] Mecking S.; Thomann R.; Frey H.; Sunder A. *Macromolecules* **2000**, 33, 3958.

[8] Mecking S.; Schlotterbeck U.; Thomann R.; Soddemann M.; Stieger M.; Richtering W.; Kautz H. *Polymeric Materials: Science & Engineering* **2001**, 84, 511.

[9] Tabuani D.; Monticelli O.; Komber H.; Russo S. *Macromol. Chem. Phys.* **2003**, 204, 1576.

[10] Voit B. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, 38, 2505.

[11] Monticelli O.; Mariani A.; Voit B.; Komber H.; Mendichi R.; Pitto V.; Tabuani D.; Russo S. *High Performance Polymers* **2001**, 13, 45.

[12]Komber H.; Voit B.; Monticelli O.; Russo S. *Macromolecules* **2001**, 34, 5487.

[13] Capannelli G.; Cum G.; Gallo R.; Spadaro A.*,* Costa G., Piaggio P. *J. Mol. Catal* **1990**, *59*, 39.

[14] Delmon B.; Grange P.; Jacobs P.A.; Poncelet G. "*Preparation of Catalysts IV*", Elsevier, Amsterdam, **1987**.