Palladium Nanoparticles Supported on Hyperbranched Aramids: Synthesis, Characterization, and Some Applications in the Hydrogenation of Unsaturated Substrates

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ABSTRACT: Hyperbranched (HB) aromatic polyamides (aramids), synthesized from  $A_2 + B_3$  reagents (A = p-phenylenediamine; B = trimesic acid), have been used as polymeric supports for palladium(0) nanoparticles. The chemical-physical properties of these aramids, denoted as **pPDT**, have been compared to those of the polymer **pABZAIA** obtained from the AB<sub>2</sub> monomer 5-(4-aminobenzamido)isophthalic acid. The two HB polymers show structural differences in the shape of the macromolecule as well as the nature of the end groups. The **pPDT** materials exhibit a less regular structure with both amino and carboxy terminal groups, while the **pABZAIA** polymer contains a single amine focal unit per molecule and carboxy end groups. HB aramid-supported Pd<sup>0</sup> nanoparticles were obtained by reduction of polymersupported PdCl<sub>2</sub> with an aqueous solution of NaBH<sub>4</sub>. Some model compounds, mimicking the polymeric hyperbranched structure, were investigated to gain insight into the nature of the interactions occurring between  $PdCl_2$  and the support. The nature of the interactions between the polymeric matrix and  $PdCl_2$ was investigated by means of FT IR and XPS techniques. XPS spectroscopy, performed on both polymers and model molecules, indicated that the interaction between the support and the metallic precursor involves the terminal amino groups. The particle dimensions and the metallic dispersion were determined by TEM analysis. This study showed that the dimensions and dispersion of the metal clusters on pABZAIA are smaller than those on **pPDT**. A preliminary study of the catalytic performance of a specific **Pd**<sup>9</sup>/ **pPDT** catalyst in the hydrogenation of relevant unsaturated substrates (benzene, benzylideneacetone, phenylacetylene, diphenylacetylene, and quinoline) has been carried out in either nonpolar or polar solvents. In most cases, the catalyst proved to be efficient, selective, and recyclable, yet the nature of the solvent affected remarkably the catalysis outcome in terms of both activity and selectivity.

# Introduction

The first example of a metal phase supported on a polymeric matrix dates back to 1956 when Akaburi and co-workers<sup>1</sup> employed a palladium catalyst dispersed on a silk fibroin fiber to obtain optically active amines and amino acids by hydrogenation of appropriate organic precursors. Since then an impressive amount of work has been carried out,<sup>2</sup> especially as regards the use of noble metals supported on polymers as catalysts for hydrogenation reactions.<sup>3–8</sup> It is now apparent that the catalytic activity of such materials is influenced by the nature of both the polymer matrix and the reaction solvent.

The generally low thermal and chemical stability and the poor mechanical properties constitute the major drawbacks of polymeric supports, including polyamides introduced first by Izumi in 1959.<sup>9</sup> In polyamides, which can interact with the metal through the nitrogen atoms, these drawbacks can be partially overcome using materials, containing arylamido groups, such as Nomex

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and Kevlar.<sup>3,5</sup> However, the amido nitrogen atoms in these materials are very weak nucleophiles, and the number of terminal amino groups is too low for binding an acceptable amount of metal. In this respect, dendritic polyamides may be a valid alternative to conventional polymeric supports as they exhibit high chemical and thermal stability as well as excellent functional-group availability/accessibility. In a recent paper, Gröhn et al. showed that dendrimers can be used as polymeric templates to anchor metal nanoclusters.<sup>10</sup> These authors described a system, comprising poly(amidoamine) (PAMAM) molecules dispersed in a hydrophilic crosslinked polymer, in which both the nanoparticles size and the metal loading could be adjusted by simply varying the degree of polymerization of the polymer.

Among dendritic polyamides, the hyperbranched ones constitute a unique class for their easy one-step preparation that can allow for an effective scale-up of the utilization processes. To the best of our knowledge, no report concerning the use of hyperbranched polyamides (aramids) as support material for metal phases has been published so far.

In this paper is reported a study in which aramids, obtained by either  $A_2 + B_3$  reagents or  $AB_2$  monomers, are used as support material for palladium nanoparticles, ultimately generating robust and recyclable hydrogenation catalysts.

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Scheme 1. AB<sub>2</sub> Monomer and Structure of the HB pABZAIA Aramid



Scheme 2. Synthesis and Structure of the  $(A_2 + B_3)$  pPDT Aramids



 
 Table 1. Polymerization Conditions Employed in the Synthesis of the pPDT Samples

sample code	[NH <sub>2</sub> ]/[COOH]	<i>T</i> <sub>p</sub> (°C)	t <sub>p</sub> (min)
pPDT1	1/2	80	90
pPDT2	2/3	80	90
pPDT3	2/3	80	60
pPDT4	1/1	80	90
pPDT5	2/3	80	90

 Table 2. Characterization Data of the HB Polymers

 Described in This Paper

			-		
sample code	t <sub>p</sub> (min)	solubility	$[\eta]^a$ (dL·g <sup>-1</sup> )	$M_{ m w} imes 10^{-3}$ (g·mol $^{-1}$ )	Т <sub>g</sub> (°С)
pPDT1	90	total	0.10		
pPDT2	90	total	0.29	4.25	153
pPDT3	60	total	0.17	23.8	165
PPDT4	90	total	0.40		
pABZAIA	120	total	0.36	100.2	153

<sup>a</sup> In H<sub>2</sub>SO<sub>4</sub> 95-97% at 25 °C.

## **Experimental Section**

**Polymer Synthesis.** The hyperbranched (HB) aramid **polyABZAIA** was obtained following a previously described procedure, which involves the direct polymerization of the AB<sub>2</sub>-type monomer 5-(4-aminobenzamido)isophthalic acid (ABZAIA) (Scheme 1).<sup>11,12</sup>

The procedure used to synthesize the HB aramids **pPDT** from the  $A_2 + B_3$  reagents (A = p-phenylenediamine; B = trimesic acid) (Scheme 2) is given elsewhere.<sup>13</sup>

As shown in Table 1, different  ${\bf pPDT}$  polymers could be prepared by varying the reactant ratio as well as the polymerization time.

Polymer characterization data, including viscosity, solubility in organic solvents (such as DMF, DMSO, NMP), glass transition temperature, and GPC measurements, are provided in Table  $2.^{11-14}$ 

Porosity measurements were performed on two samples of hyperbranched aramids (see later) by an ASAP 2010 Micromeritics apparatus.

The  $AB_2$  monomer ABZAIA and benzene-1,3,5-tricarboxylic acid tris-*p*-tolylamide (**M1,3,5**) (Figure 1) were used as model molecules. **M1,3,5** was prepared from 1,3,5-benzenetricarbox-



Figure 1. Sketch of the model molecule M1,3,5.

ylic acid chloride and p-aminotoluene according to a general synthetic procedure.  $^{\rm 15}$ 

**Preparation of Aramid-Supported Pd<sup>0</sup> Clusters**. Polymer powders were stirred in an aqueous solution of acetic acid<sup>5</sup> containing PdCl<sub>2</sub> (Aldrich, 0.01 wt %) at room temperature for 48 h. The polymer/PdCl<sub>2</sub> ratio was 10/1 (w/w). During the impregnation process, a change in color of both polymer and solution occurred. The powders were filtered, washed several times with deionized water, and dried overnight at 60 °C. Palladium reduction was carried out using an aqueous solution of NaBH<sub>4</sub> (0.1 M) at 50 °C for 2 h. 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 h. The same procedure for impregnation and reduction was followed for the model molecules.

**Characterization of the HB Aramid-Supported Pd<sup>0</sup> Clusters.** TEM measurements were performed with a highresolution transmission electron microscope (JEOL 2010). The polymer/Pd powders were suspended in 2-propanol and a drop of the resultant mixture was deposited on a carbon grid.

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, takeoff angle of 45 deg, and 0.05 eV energy resolution.

Samples were prepared by pressing the polymer/Pd powders onto a thick indium film, then they were set into a prepumping chamber ( $\simeq 10^{-7}$  Torr) for 10 min and then transferred in the main chamber ( $\simeq 10^{-9}$  Torr) for analysis. PHI MultiPak software was used for data treatment and analysis.

Because of 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.

The palladium content in the polymeric support was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Jobin Yvon (series JY24) instrument at a sensitivity level of 500 ppb. Each sample (20–50 mg) was treated in a microwave heated digestion bomb (Milestone, MLS-200) with a mixture of 4 mL of a NaOCI solution (6–14% free chlorine Riedel-de Haën) and 2 mL of 2 M NaOH and heated to boiling temperature for a few minutes. The resulting solutions were analyzed after increasing the volume to 50 mL in a volumetric flask.

Hydrogenation Reactions with Pd%pPDT. All reactions and manipulations were routinely performed under a nitrogen or argon atmosphere by using standard Schlenk techniques. n-Pentane was distilled under nitrogen from LiAlH<sub>4</sub>, while reagent grade MeOH was used as received. Quinoline was distilled in vacuo and stored under argon. Batch reactions under a controlled pressure of gas were performed with a stainless steel Parr 4565 reactor (100 mL) equipped with a Parr 4842 temperature and pressure controller and a paddle stirrer. GC analyses of the reaction mixtures were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25  $\mu$ m film thickness) SPB-1 Supelco fused silica capillary column. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with an identical capillary column. As a general procedure, a 100 mL Parr autoclave was charged with 16 mg of a specific catalyst, Pd<sup>0</sup>/pPDT5, containing 2.02 wt % Pd, (determined by ICP-AES) the desired amount of substrate, 30 mL of solvent (either n-pentane or MeOH), and  $H_2$  (30 bar). The ensemble was heated to the established temperature and then stirred (1500 rpm) for the desired time, after which the vessel was cooled to ambient temperature and depressurized. The liquid contents were analyzed by GC and GC/MS. Above 1500 rpm, the rates were independent of the agitation speed at all the temperatures studied, thus indicating the absence of mass transport limitations. The stability of the catalyst against leaching from the support was tested as follows. (i) After a catalytic run, the catalyst was separated by filtration from the liquid phase under nitrogen, washed with the solvent and then reused for a second, identical run. After the liquid phase was analyzed by GC, the solvent was removed under vacuum and the residue was analyzed by ICP-AES. No trace of metal was detected by ICP-AES. (ii) To refrain from filtering the solid catalyst after each catalytic run, several reactions were carried out in a 100 mL Parr reactor fitted with a dip pipe with a sintered (2  $\mu$ m) metal piece at its dipping end. Upon completion of the reaction, the solution was forced out through the sintered dip pipe by applying a nitrogen pressure of ca. 2 bar at the gas inlet valve of the reactor, thus retaining the catalyst in the reactor under nitrogen. The catalyst was washed with the appropriate solvent (3  $\times$  20 mL). After a sample of the filtrate was analyzed by GC, most of the solvent was distilled out and the residue was analyzed by ICP-AES. A fresh solution of the substrate to be hydrogenated was then loaded through a thin Teflon pipe connected to the reactor. The reactor was then pressurized with hydrogen to 30 bar, heated to the appropriate temperature and then stirred for the desired time.

#### **Results and Discussion**

**Characterization of the Hyperbranched Aramids.** The molar masses of the **pPDT** polymers, determined using a SEC apparatus equipped with a singlecapillary viscosimetry and MALS detectors, are invariably smaller than those of the  $AB_2$  systems in consequence of the short reaction time required to avoid the gel point and obtain a soluble material. Consistently, **pABZAIA** is featured by a greater intrinsic viscosity than any **pPDT** samples.

<sup>1</sup>H NMR and FT IR analyses provided valuable information on the influence of the polymerization conditions on the structure of **pPDT**, especially in terms of degree of branching and structural units concentration.<sup>13</sup> The six structural units from the  $(A_2 + B_3)$  system, as determined by <sup>1</sup>H NMR measurements, are illustrated in Figure 2.

As shown in Table 1, both the polymer structure and the material properties can be modified by varying the reactant ratio and the polymerization time as well. The possibility to finely tune the properties of the polymer matrix represents a considerable advantage over in-



**Figure 2.** Structural units of the  $A_2 + B_3$  HB aramids obtained from *p*-phenylenediamine (A) and trimesic acid (B) (T, L, and D denote terminal, linear and dendritic units, respectively). See ref 13.



Figure 3. FT IR spectra of **pPDT2** alone, after impregnation with  $PdCl_2$  and after reduction to  $Pd^0$ .

Table 3. Porosity Data of pABZAIA and pPDT3 HB Polymers

sample code	surface area (m <sup>2</sup> ·g <sup>-1</sup> )	average pores diameter (nm)
pABZAIA pPDT3	30 10	40 13

organic materials for the exploitation of aramids as catalyst support.

An important characteristic of any catalyst support is the porosity, which can influence the accessibility of the substrate to the active sites. Surface areas and average pore dimension distribution for **pABZAIA** and **pPDT3** are reported in Table 3. Both systems exhibit large surface areas, while the porosity of **pABZAIA** is higher than that of **pPDT3**.

The above measurements have not been extended to the other pPDT samples (pPDT 1, pPDT 2, and pPDT 4), as the main purpose of this specific investigation was confined to a simple comparison of the two classes of materials.

The elevated porosity and the good thermal stability (>400 °C) for the **pPDT** materials), combined with a large number of accessible functional groups, forecast



**Figure 4.** Variation of the XPS signal with time in the Pd 3d region (the appearance of a new signal at low binding energies is indicative of palladium reduction).

a great potential of these HB aramids as support materials for metal phases.

**Characterization of Aramid-Supported PdCl<sub>2</sub>**. Palladium dichloride was supported on either **pPDT** or **pABZAIA** polymers by a standard procedure, which involves the stirring of an aqueous solution of PdCl<sub>2</sub> and acetic acid in the presence of the solid polymer at room temperature for 48 h.<sup>5</sup>

A useful spectroscopic technique to study polymersupported metal compounds is FT IR spectroscopy. The exploitation of this technique has allowed to study the interaction between palladium and some oligomeric aramids featured by a structure similar to the present HB polymers, in terms of the sequence of CO and NH.<sup>5</sup>

The FT IR spectra recorded on **pPDT2** and **pABZAIA** at 120 °C before and after impregnation with  $PdCl_2$  did not show any difference except for the shape of some bands above 3300 cm<sup>-1</sup> in the region of the N–H stretch. Figure 3 shows the IR spectra in the 4000–2000 cm<sup>-1</sup> region for **pPDT2** alone, after impregnation with  $PdCl_2$  and after  $Pd^{II}$  reduction to  $Pd^0$  (vide infra).

The observed spectral changes were clearly consistent with an interaction between  $PdCl_2$  and the terminal groups. Since both the line shape and position of the band due to the carboxy groups (at ca. 1700 cm<sup>-1</sup>) did not change upon  $PdCl_2$  adsorption, it is very likely that only the amino groups are involved in the bonding interaction to palladium(II). The occurrence of nitrogen–palladium bonding interactions has been also reported in model compounds with oligomeric aramids of Kevlar type.<sup>5</sup>

XPS spectroscopy is an important technique for the characterization of polymer-supported metal compounds, especially to study the interactions between the metal and the polymeric matrix as well as determine the oxidation state of the anchored metal.<sup>16–19</sup> Also, XPS spectroscopy can allow one to distinguish between interacting and noninteracting groups in polymers containing different types of nitrogen atoms.<sup>17–19</sup>

In the present case, XPS spectroscopy was used to study the polymer/metal interactions before and after reduction. As shown in Figure 4, the exposure of a **PdCl<sub>2</sub>/pPDT2** sample to X-rays for a long time affected the palladium signal. In particular, the shape of the Pd 3d signal showed a dependence on the analysis time,



Figure 5. TEM micrograph of PdCl<sub>2</sub>/pPDT2 after XPS analysis.

indicated by the appearance of a shoulder at low BE (vertical line in Figure 4), due to the progressive reduction of  $Pd^{II}$  (337.5 and 342.8 eV) to  $Pd^{0}$  (336.0 and 341.3 eV).

A TEM micrograph of **PdCl<sub>2</sub>/pPDT2**, acquired after a long period of XPS analysis, confirmed unambiguously the formation of metal clusters (Figure 5). This drawback of the XPS technique has some precedents<sup>18,19</sup> and was overcome by us using analysis times shorter than 20 min.

Figure 6 shows the N 1s signal peak of the  $(A_2 + B_3)$  polymer **pPDT2**. Since this peak can be well fitted by a single Gaussian curve, any distinction between amino and amido groups in the polymer would be only speculation.



**Figure 6.** N 1s signal fitting for a fresh sample of **pPDT**.

 

 Table 4. Theoretical and XPS Atomic Percentages of the Model Molecules ABZAIA and M1,3,5

ABZAIA		M1,3,5	i	
atom	theoretical	XPS	theoretical	XPS
С	68.3	70.0	83.4	82.5
0	21.3	21.3	8.3	8.3
Ν	9.0	8.2	8.3	9.1

Analogously, a comparison of the XPS signal of all the elements contained in the HB polymer (i.e. C, O, N), before and after impregnation of  $PdCl_2$ , did not reveal any difference in both line shape and position.

Our results are at variance with those reported by Michalska et al. who observed a shift of the pyridine nitrogen and carboxy oxygen to higher BE upon analysis of Pd<sup>II</sup> complexes formed on heterocyclic polyamides.<sup>18,19</sup> This fact is likely due to the presence of weaker interactions in our systems.

Another route to investigate metal/polymer interactions is to study the amount of metal retained by different polymers and model molecules. To test the reliability of the elemental analysis data obtained from the XPS experiments, the monomer ABZAIA and the model molecule **M1,3,5** were studied by XPS spectroscopy. As shown in Table 4, the experimental analyses for C, O, and N were in good agreement with the theoretical elemental data for all the substrates investigated.

For HB aramids possessing different amounts of functional groups, the retention of palladium compounds is controlled by the chemical structure of the polymer. Since the present **pPDT** polymers have been prepared using different experimental conditions, the percentages of **D**, **L**, and **T** units (Figure 2) (hence, the concentrations of the functional groups in each polymeric product) vary from one sample to another, as determined by <sup>1</sup>H NMR spectroscopy (Table 5).

Consistent with the existence of  $NH_2$ –Pd interactions, as suggested by the FT IR analysis, a correlation between the percentage of the amino terminal groups and the amount of Pd<sup>II</sup> in each HB polymer was observed. As shown in Table 6, the palladium(II) content is proportional to the  $NH_2$  concentration in both **pPDT** and model compounds. In accord with the importance of the  $NH_2$  groups for binding palladium(II) ions, the

Table 5. Percentage of Dendritic, Linear, and Terminal Units as Obtained from <sup>1</sup>H NMR Analysis of Various pPDT Samples

	pPDT1	pPDT2	pPDT3	pPDT4
AA'B(L)	6.1	9.2	15.6	25.8
$A'_{2}B(L)$	45.4	41.7	36.4	23.5
$A'B_2(T)$	30.2	27.0	23.6	12.1
$A_2A'(D)$	0	0	4.4	10.6
A' <sub>3</sub> (D)	12.2	15.4	9.8	6.6
$AA'_2(D)$	6.1	6.7	10.2	21.4

Table 6. Percentage of Amino Groups and Pd (as Weight Percent<sup>b</sup> and Atomic Concentration<sup>c</sup>) of HB Polymers and Model Molecules

sample code	percentage of amino end groups	Pd concn (wt %) <sup>b</sup>	Pd atomic concn (%) <sup>c</sup>
PdCl <sub>2</sub> /pPDT1	12.2 <sup>a</sup>	0.23	1.87
PdCl <sub>2</sub> /pPDT2	15.9 <sup>a</sup>	0.42	3.36
PdCl <sub>2</sub> /pPDT3	30.2 <sup>a</sup>	0.51	4.06
PdCl <sub>2</sub> /pPDT4	57.8 <sup>a</sup>	1.11	8.53
PdCl <sub>2</sub> /pABZAIA		0.15	1.20
PdCl <sub>2</sub> /ABZAIA	33.3	0.68	5.28
<b>PdCl<sub>2</sub> + M 1,3,5</b>	0	0	0

 $^a$  From  $^1H$  NMR analysis, as the total of A units referred to A + A' + B - substituted benzene rings.  $^b$  From XPS analysis.  $^c$  From XPS analysis, considering the atomic weights of C, N, O, and Pd.

molecule **M1,3,5**, devoid of amino groups, did not retain any palladium. This result is a further confirmation that the amido groups do not interact with the metal. This behavior, found also in the case of oligomeric aramids,<sup>5</sup> may be ascribed, as previously mentioned, to the strong electronic stabilization induced by the aromatic ring. It is worth noticing that the metal content in the AB<sub>2</sub> polymer was invariably lower than that retained by any  $(A_2 + B_3)$  sample, which reflects the higher number of amino groups in the latter.

Plotting the percentage of palladium vs the percentage of  $NH_2$  groups for the various **pPDT** samples as well as model compounds, a linear correlation was obtained (Figure 7), while an opposite trend was found for the -COOH units; i.e., by increasing the carboxy group percentage, the amount of retained palladium decreased.

Upon exchange with PdCl<sub>2</sub>, the polymers were no longer soluble in any solvent. As previously observed by Jo et al. for poly(vinylpyridine) matrixes,<sup>20</sup> this effect



**Figure 7.** Percentage of Pd retained by various **pPDT** polymers and model compounds as a function of the percentage of amino groups.

Table	7.	Metallic	Dispersion	(MD)	and	dva	of	pPDT2	and
			pAB2	ZAIA				-	

sample	metallic	dva <sup>b</sup>	average
code	dispersion <sup>a</sup> (%)	(nm)	diameter (nm)
pPDT2	18.7	6.0	3.5
pABZAIA	25.0	4.5	2.5

<sup>*a*</sup> Calculated as MD =  $N(s)_m/N(t)_m$ .  $N(t)_m$ : total number of metallic atoms.  $N(s)_m$ : number of metallic atoms on the surface. <sup>*b*</sup> Calculated as dva =  $6\sum (V_i)/\sum (A_i)$ ;  $V_i$  and  $A_i$ : volume and area of a single cluster.

may be due to polymer cross-linking promoted by the supported metal species.

**Characterization of Aramid-Supported Pd Nanoparticles**. Palladium nanoparticles on either **pPDT** or **pABZAIA** were obtained by reduction of supported PdCl<sub>2</sub> with an aqueous solution of NaBH<sub>4</sub> at 50 °C for 2 h. High-resolution TEM was employed to determine the dimensions and dispersion of the metallic particles. Indeed, both features are important in determining any catalytic activity as a high metallic dispersion (i.e., low dimensions of the metal particles) generally corresponds to a high number of metal sites on the catalyst surface.

TEM micrographs showed that the concentration of the palladium clusters on **Pd<sup>0</sup>/pPDT2** is quite high, higher than that of **Pd<sup>0</sup>/pABZAIA** (Figures 8 and 9, respectively). In either case, metal particles lower than 1 nm were observed.

The diameter was calculated directly from TEM micrographs, averaging on a large number of Pd particles.

Table 7 summarizes the results obtained from the TEM measurements.

The differences between the two systems are probably due to the larger concentration of the terminal amino groups (responsible for the interaction with the metal) in **pPDT** than in **pABZAIA**.

A perusal of **pPDT** materials containing a large concentration of amino groups such as **pPDT3**,

Scheme 3. Hydrogenation Reactions of Various Unsaturated Substrates with pPDT2



prepared at long polymerization time, confirmed the relationship between the dimensions of the metal clusters and the number of binding groups on the polymer surface.

Finally, it is worth mentioning that the cluster dimensions, in terms of average diameter, observed in the present HB aramids (Table 7) are similar to those obtainable using inorganic supports for palladium catalysts  $(1.1-1.3 \text{ nm on } \text{C}^{21} \text{ and } 3.5 \text{ nm on } \text{Al}_2\text{O}_3)^{22}$  as well as those reported for other polymeric supports (less than 4 nm on nylon<sup>23</sup> and between 2 and 4 nm on other resins).<sup>8</sup>

**Catalytic Hydrogenation Reactions**. The hydrogenation of the unsaturated substrates shown in Scheme 3 was performed in solvents with remarkably different polarity such as *n*-pentane and MeOH at relatively high hydrogen pressure (30 bar) in standard autoclaves. In this preliminary study of the catalytic potential of palladium clusters supported on HB aramids, was employed a specific material, **Pd<sup>0</sup>/pPDT5**, with a palladium content of 2.02 wt % (determined by ICP-AES). In Scheme 3 are also shown all the hydrogenation





20

Pd particles.

the results obtained.

products observed under the present experimental conditions. These are detailed in Table 8 together with

The substrates investigated represent a variety of carbon–carbon and carbon–heteroatom unsaturations, spanning from aromatic, olefinic, and acetylenic C–C bonds to ketonic C–O bonds and to aromatic C–N bonds.

All reactions were reproducible with deviations lower than 1%, and the catalyst was fully recyclable, in terms of both activity and selectivity, for three consecutive runs using the procedures described in the Experimental Section.

For all substrates, **pPDT5/Pd<sup>0</sup>** behaved as an effective catalyst with fairly good activities and excellent selectivities. These latter could be remarkably improved

(a)

0,5 1,0 1,5 2,0 2,5 3,0 3,5 4,0 Cluster diameter (nm) Figure 9. (a) TEM micrograph of Pd<sup>0</sup>/pABZAIA. (b) Histogram of the relative population as a function of the diameter of the Pd particles.

by an appropriate choice of the solvent. In fact, we noticed a remarkable solvent effect: MeOH completely inhibited the hydrogenation of benzene to cyclohexane (entries 1 and 2), yet it allowed for the selective reduction of phenylacetylene to ethylbenzene (entry 6) and of quinoline to 1,2,3,4-tetrahydroquinoline (entry 12). Surprisingly, quinoline was not hydrogenated at all in *n*-pentane (entry 11). A positive influence of MeOH on the catalytic activity was also observed for benzyl-ideneacetone (entry 4).

Reactions at 80 °C were performed for phenylacetylene (entries 7 and 8) to show that the hydrogenation of the triple bond can be stopped selectively in MeOH to give styrene.

Phenylacetylene was hydrogenated in *n*-pentane to a mixture of ethylbenzene and ethylcyclohexane (entry 5), whereas diphenylacetylene was selectively reduced

entry	$T(^{\circ}C)$ ; time (h)	solvent	substrate	substrate/M	$\mathrm{TOF}, {}^{b,c} \mathrm{product}^d$
1	100; 1	<i>n</i> -pentane	benzene	866	303, CY
2	100; 1	MeOH	benzene	866	0
3	100; 1	<i>n</i> -pentane	benzylideneacetone	165	143, BA
4	100; 1	MeOH	benzylideneacetone	165	165, BA
5	100; 1	<i>n</i> -pentane	phenylacetylene	165	145, EB; 20, EC
6	100; 1	MeOH	phenylacetylene	165	165, EB
7	80; 1	<i>n</i> -pentane	phenylacetylene	165	75, EB; 8, EC
8	80; 1	MeOH	phenylacetylene	165	110, ST; 55, EB
9	100; 1	<i>n</i> -pentane	diphenylacetylene	165	140, DPE
10	100; 6	<i>n</i> -pentane	diphenylacetylene	165	27, DPE
11	130; 1	<i>n</i> -pentane	quinoline	1650	0
12	130; 1	MeOH	quinoline	1650	348, <sup>1</sup> THQ
13	130; 8	MeOH	1,2,3,4-tetrahydroquinoline	1650	0

<sup>*a*</sup> Experimental conditions: **Pd<sup>0</sup>/pPDT5**, 2.02 wt % Pd; 30 bar H<sub>2</sub>; 30 mL of solvent; 1500 rpm. <sup>*b*</sup> Average values over at least three runs. <sup>*c*</sup> Mole product: (mol Pd)<sup>-1</sup> h<sup>-1</sup>. <sup>*d*</sup> CY = cyclohexane, BA = benzylacetone, ST = styrene, EB = ethylbenzene, EC = ethylcyclohexane, DPE = 1,2-diphenylacetylene, and <sup>1</sup>THQ = 1,2,3,4-tetrahydroquinoline.

to 1,2-diphenylethane (entry 9), which seems to reflect steric effects. Indeed, the selective and quantitative formation of 1,2-diphenylethane was observed also by increasing the reaction time to 6 h (entry 10).

Studies are currently under way in our laboratories with the aim of elucidating the role played by the solvent/substrate ensemble in controlling the catalytic activity and selectivity of the hydrogenation reactions assisted by  $Pd^{0}/pPDT$  materials as well as other HB aramid-supported metal phases.

## Conclusions

For the first time hyperbranched polyamides with terminal amino and carboxy functional groups have been used as support materials for metal nanoparticles. The preparation of these innovative materials involves anchoring of PdCl<sub>2</sub> to the support prior to reduction with NaBH<sub>4</sub> in water. Although XPS and IR results are preliminary, these techniques allowed us to assess the most appropriate class of polymers to be used as catalyst support. XPS spectroscopy (together with IR) has shown that the interaction between the polymer matrices and the PdCl<sub>2</sub> precursor involves exclusively the NH<sub>2</sub> groups. Therefore, pPDT polymers turned out to be good candidates for catalytic supports. Furthermore, by means of XPS analysis, it was possible to determine the oxidation state of the anchored metal. TEM spectroscopy has revealed that the cluster dimensions and the metal dispersion are greatly influenced the nature of the polymeric support. In particular, the number of amino groups has been found to control the size of the Pd clusters as well as the metal loading.

The aramid-supported palladium materials proved to be effective and robust catalysts for the selective hydrogenation of various unsaturated substrates, spanning from arenes, to  $\alpha,\beta$ -unsaturated ketones, to alkynes, to aromatic heterocycles. Notably, it was observed that the polarity of the solvent (either MeOH or *n*-pentane) can control either the activity or the selectivity of the hydrogenation reactions.

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