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# **Graphical Abstract**

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# "Save Money" During Hydrogenation Reactions by Exploiting the Superior Performance of Pd-NPs Deposited on Carbon Black by Magnetron Sputtering

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# ABSTRACT

The magnetron-sputtering approach was used for the deposition of small (ca. 3.7 nm) and uniformly distributed Pd(0)-*fcc* nanoparticles (Pd-NPs) with partially oxidised surfaces on commercially available carbon black. The pores of the support were uniformly filled by Pd-NPs, and the surface area was drastically reduced by blockage of the pores. The metal concentration increases with the augmentation of the sputtering time without changing the metal NP size. These Pd-nanocatalysts are high efficient for the hydrogenation of nitrobenzene to aniline (TOF up to 141.7 min<sup>-1</sup>), 1,3-cyclohexadiene to cyclohexene (TOF up to 24.0 s<sup>-1</sup>), and cyclohexene to cyclohexane (TOF up to 35.1 s<sup>-1</sup>) under 4 bar of dihydrogen (H<sub>2</sub>) at mild temperatures (75-90 °C). The magnetron sputtering is one of the simplest, reliable, fast, clean and cheap methods for the preparation of Pd/C catalysts.

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## 1. Introduction

Palladium nanostructures, such as Pd nanoparticles (Pd-NPs), have been extensively applied in organic transformations involving dihydrogen (H<sub>2</sub>).<sup>1-11</sup> Efficient industrial implementation of these catalytic processes requires the use of modern synthetic methodologies, which allow precise control over the physical (i.e., size and shape) and chemical (i.e., well-defined composition) properties of these nanostructures.<sup>12-15</sup> Conventionally, the most extensively extended approach is the chemical reduction of metallic salts under non-sustainable conditions (i.e., hazardous reducing agents and generation of large amount of residues).<sup>16-21</sup> The magnetron-sputtering technique is receiving increasing attention during the last decade. This technique is a potential candidate for being considered the most sustainable and efficient method for generating metal nanostructructures.<sup>22-24</sup> Briefly, this technique involves accelerating ions from an *in situ* generated plasma towards high-purity metallic targets, yielding a sputtering beam consisting of metal atoms and small metal clusters. Stabilization of metal nanoparticles (M-NPs) occurs when the incident sputtering beam is directed on the appropriate solid or liquid support.<sup>25-26</sup>

Among the advantages of this technique, the most important are the atomic efficiency of the process and the faster generationisolation of small and well-dispersed nanostructures of high purity, and then, precious metal (money) is saved.<sup>27-32</sup> Recently, our group has developed a new sputtering chamber, which allows the constant mixing of the solid support, and thus, the distribution of the metallic nanoparticles in all spatial planes of the support (Figure 1).<sup>33</sup> Pdand Ru-NPs generated by magnetron-sputtering are small and uniformly distributed.<sup>33-36</sup> Furthermore, access of the reagents to the surface metal-active sites during use of the catalytic materials is facilitated as the M-NPs are deposited on the most external layers of the support. This effect is of crucial importance for catalysts based on highly porous supports (i.e., SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>), and is probably due to hindered diffusion of the metal atoms and clusters through the support pores. To date, the effect of sputtering time on the chemical and physical properties of the formed Pd-NPs deposited on solid supports has not been reported. Here, the use of the magnetronsputtering approach for the deposition of Pd-NPs on commercially available carbon black is reported. A carbon support was selected due to its wide variety of applications.<sup>37</sup> We disclose herein that the sputtering approach can be use with advantages to prepare classical Pd/C catalysts. Moreover, we present the deposition time effect on

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the size, shape, metal dispersion and surface properties of the Pd-NPs catalyst supported on carbon black. The reactivity was evaluated by comparing the catalytic performance of our catalyst with those obtained using a reference catalyst (a commercially available Pd/C catalyst). By increasing the sputtering deposition time our magnetron-sputtering chamber employing the three dimensions' constant device (CMS<sup>3</sup>) allows the production of a series of palladium nanocatalysts of increasing metal content without size variations, i.e., avoiding film formation. The catalytic performances of the Pd-NPs were evaluated in the reduction of the model substrates nitrobenzene, 1,3-cyclohexadiene and cyclohexene under 4 bar of H<sub>2</sub> and compared with a commercially available Pd/C-0 catalyst. The disproportion of 1,3-cyclohexadiene was carried out to address the heterogeneous nature of the as-prepared catalysts. The details described herein are complementary to those described in related studies for the preparation of supported Pd-NPs in other solid materials by sputtering-deposition.33-35



Three Dimensions Constant Mixing Sputter Device (CMS<sup>3</sup>) for the deposition of uniformly distributed metal nanoparticles

**Figure 1.** Illustration of the magnetron-sputtering chamber developed by our group for the deposition of metallic nanoparticles on solid supports. Detailed description is reported elsewhere.<sup>33</sup>

#### 2. Results and Discussion

# 2.1. Sputter deposition

A series of Pd-nanocatalyst (Pd/C-1 to Pd/C-5) supported on commercially available carbon black were synthesized by the magnetron sputtering of Pd-target at 50 W power and with a frequency of optimized 23 Hz for the vibration of the flask. Five samples (Pd/C-1 to Pd/C-5) were obtained using deposition times of 0.5 min, 2.5 min, 5.0 min, 7.5 min and 12.0 min, respectively (see Table 1). ICP-OES analysis revealed that the Pd content increased with the deposition time. This ratio between the deposition time and the Pd content is linear up to 7.5 min (samples Pd/C-1 to Pd/C-4) with an increase of the Pd content in the support of 0.2621 wt. %  $\times$ min<sup>-1</sup> (Table 1 and Figure S1). The sample obtained by using a deposition time of 12 minutes (sample Pd/C-5) displayed a decrease in the deposition rate after 7.5 min. TEM analysis of the Pd/C-1 to Pd/C-5 catalysts indicated the formation of very similar small Pdnanoparticles (i.e., mean diameter between 3.6 and 3.9 nm) with narrow size distributions (Figure 2 and Figure S2).

**Table 1.** Pd-nanocatalyst supported on carbon black (Pd/C-1 to Pd/C-5) prepared by magnetron-sputtering. Deposition time, metal content, mean diameter ( $\emptyset$ ) and metal dispersion. <sup>[a]</sup>

E.	Sample	<mark>Dep.</mark> time/ min	Metal content/ wt. % <sup>[b]</sup>	Ø / nm <sup>[c]</sup>	S <sub>BET</sub> / m <sup>2</sup> g <sup>-1</sup> <sup>[d]</sup>	Metal dispersion / % <sup>[e]</sup>
1	Pd/C-1	0.5	0.15±0.01	3.8±1.5	<mark>25</mark>	-
2	Pd/C-2	2.5	0.73±0.01	3.7±1.4	<mark>22</mark>	25.3
3	Pd/C-3	5.0	1.31±0.01	3.8±1.9	<mark>15</mark>	22.6
4	Pd/C-4	7.5	1.94±0.01	3.7±1.7	<mark>14</mark>	20.4
5	Pd/C-5	12.0	2.36±0.01	3.9±1.9	<mark>10</mark>	14.6

[a] Sputtering-deposition conditions: 100 mg of solid support, 50 W of power, 23 Hz of vibration frequency,  $4 \times 10^{-7}$  mbar vacuum,  $4 \times 10^{-3}$  mbar Ar, and room temperature (25 °C); [b] Metal content (wt. %) determined by ICP-OES; [c] Mean diameter (Ø) and size distributions determined by TEM analysis; [e] The specific surface areas were determined by the BET multipoint method using Tristar 3020 Micromeritics equipment; [e] Metal dispersion determined by H<sub>2</sub>-chemisorption sing a ASAP 2020 Micromeritics equipment.



Figure 2. TEM images (a and b) and XRD analysis (c and d) of the sample Pd/C-2.

XRD analysis shows the presence of the Pd(0)-*fcc* planes as a broad signals which are characteristic small Pd(0)-*fcc* nanoparticles (Figure 2c and 2d).<sup>37</sup> N<sub>2</sub>-physorption and H<sub>2</sub>-chemisorption analysis revealed a decrease in specific surface area as compared to the pure support ( $S_{BET} = 30 \text{ m}^2 \text{ g}^{-1}$ ) and a decrease in the metal dispersion with the increase of the metal content at longer deposition times (Figure S3, S4 and Table 1). <sup>38</sup> The same trend was observed for liquid supports, i.e. the augmentation of sputtering time increases the metal concentration without changing the metal NPs size.<sup>31,39</sup> The support pores were filled by Pd-NPs, and after longer deposition times, the surface area was drastically reduced by blockage of the pores, as well as, the access to the metal sites (i.e., reduced metal dispersion).

XPS spectra at the Pd 3d region for the selected samples of Pd NPs supported on carbon, Pd/C-2 and Pd/C-5, freshly prepared and after post-treatment under hydrogenation reaction conditions (i.e., 4 bar  $H_2$  and 75 °C for 1 h) are displayed in Figure 3a and Figure 3b,

respectively. It is possible to observe the presence of two different Pd-chemical components (Pd(0) and Pd( $\delta^+$ ) species) at the Pd-NPs surfaces. The components were identified in accordance to the binding energies reported for similar Pd systems.  $^{40\text{-}42}$  The Pd(0) component appears with a binding energy position around 335.4 eV and with a 0.1 eV maximum variation around 335.4 eV (i.e., 335.3 eV - 335.5 eV) between different samples. The energy shift of these values to higher binding energies than those value typically reported for Pd(0) (i.e., 335.2 eV)<sup>40</sup> was already observed in the literature for Pd/C samples.<sup>43</sup> Pd( $\delta^+$ ) component was fixed at a binding energy value of 1.8 eV higher than the corresponding Pd(0) component of each case. This component was attributed to the oxidation of the Pd-NPs surfaces during experimental manipulation. Moreover, the same samples after post-treatment with H2 displayed lower degree of oxidation (from 48-65% of Pd(0) before to 90% of Pd(0) after post reduction). Similar behaviour was observed for the Ru-NPs prepared by similar sputtering procedures.<sup>36</sup>



**Figure 3.** XPS measurements at Pd 3d region for selected samples **Pd/C-2** and **Pd/C-5**. XPS analysis were performed using the (a) freshly prepared catalysts and (b) after post-treatment under reaction conditions. The black points represent the experimental points, the dash black line the Shirley background used, the grey solid line the fitting performed and the red and blue solid lines represent the Pd(0) and  $Pd(\delta^+)$  components.

A comparison of the two samples revealed that the freshly prepared sample of **Pd/C-2** displayed slightly higher degree of oxidation (65%) than **Pd/C-5** (48%). Probably the higher degree of oxidation of sample **Pd/C-2** is related to its higher metal dispersion (i.e., higher number of metal sites exposed). After hydrogen treatment in both cases the major species are Pd(0).

## 2.2. Hydrogenation reactions

The catalytic performance of the Pd-nanocatalyst supported on carbon black (**Pd/C-1** to **Pd/C-5**) prepared by magnetron sputtering was evaluated and compared with the catalytic performance of commercially available **Pd/C-0** catalyst in the hydrogenation of the model substrates (nitrobenzene and cyclohexene). The reactions were performed under solvent-less conditions at constant H<sub>2</sub> pressure of 4 bar. The reaction kinetics were monitored by quantifying the consumption of H<sub>2</sub>. Substrate conversions and selectivities were also determined by GC-analysis of reaction sample aliquots.

**Table 2.** Hydrogenation of nitrobenzene catalysed by Pdnanocatalyst supported on carbon black (Pd/C-1 to Pd/C-5) prepared by magnetron-sputtering.

$$\frac{\text{NO}_2}{\text{Pd cat.}} \xrightarrow{\text{NH}_2} \frac{4 \text{ bar H}_2, 90 \text{ °C}}{\text{Pd cat.}} \xrightarrow{\text{NH}_2} \frac{1}{\text{Pd cat.}} > 99 \% \text{ Sel.}$$

Entry <sup>[a]</sup>	Catalyst	TON <sup>[b]</sup>	TOF <sup>[c]</sup> /min <sup>-1</sup>
1	Pd/C-0	4113	35.5
2	Pd/C-1	1314	2.1
3	Pd/C-2	13 298	141.7
4	Pd/C-3	7410	64.8
5	Pd/C-4	5004	52.9
6	Pd/C-5	4113	55.8

[a] Reaction conditions: Pd/C (10 mg), nitrobenzene (9.1 mmol), 900 r.p.m., 4 bar  $H_2$  and 90 °C; [b] TON defined as the moles of substrate converted per moles of metal; [c] TOF defined as the moles of substrate converted per moles of metal and unit of time at the period of maximum rate of conversion (10-30% conv.).<sup>44</sup>

Table 3. Hydrogenation of cyclohexene catalysed by Pdnanocatalyst supported on carbon black (Pd/C-1 to Pd/C-5) prepared by magnetron-sputtering.



Entry <sup>[a]</sup>	Catalyst	TON <sup>[b]</sup>	$TOF^{[c]}/s^{-1}$
1	Pd/C-0	4443	13.4
2	Pd/C-1	69276	26.3
3	Pd/C-2	14295	35.1
4	Pd/C-3	8003	10.9
5	Pd/C-4	5399	13.3
6	Pd/C-5	4423	12.9

[a] Reaction conditions: Pd/C (10 mg), cyclohexene (9.9 mmol), 900 r.p.m., 4 bar H<sub>2</sub> and 75 °C; [b] TON defined as the moles of substrate converted per moles of metal; [c] TOF defined as the moles of substrate converted per moles of metal and unit of time at the period of maximum rate of conversion (10-30% conv.).<sup>44</sup>

Similar trends were observed in the hydrogenation of nitrobenzene and cyclohexene catalysed by Pd catalysts. The commercial catalyst produced (Pd/C-0) TON and TOF of the same magnitude as those of catalysts Pd/C-3 to Pd/C-5 (See Table 2-3 and Figure S6-S10). The catalysts Pd/C-2 produced higher activity and productivity than the catalyst with higher metal loadings (Pd/C-3 to Pd/C-5) and lower metal loadings (Pd/C-1). This behaviour is attributed to either the higher number of available metal sites in Pd/C-2 than catalysts with higher metal loadings (Pd/C-3 to Pd/C-5), and the reduced level of support metal interactions compared to the catalysts with lower metal content (Pd/C-1). The similar activity displayed by Pd/C-4 and Pd/C-5 was attributed to the fact that

Pd/C-4 displayed similar number of active sites to Pd/C-5, a catalyst with higher metal loading but lower surface area and lower metal dispersion. The remarkable difference of activity and selectivity displayed for Pd/C-1 in the hydrogenation of cyclohexene and in the hydrogenation of nitrobenzene was attributed to both the involvement of different active sites during the hydrogenation steps and its deactivation during the initial reaction stages of the reaction. Analogous deactivation behaviours were previously reported in processes involving similar catalysts and substrates.38,45 It should be highlighted that catalyst Pd/C-2 displayed comparable performances (activity and selectivity) in the hydrogenation of nitroaromatics to anilines to those reported using sub-nanometric Pd clusters on porous nanorods of CeO<sub>2</sub> under similar mild conditions (ca. 80 °C under 5 bar H<sub>2</sub>), a catalyst reported as one of the most active reported so far.<sup>9</sup> The catalytic activity of Pd/C-2 in the hydrogenation of cyclohexene is higher but of the same order of magnitude than those reported in the literature for Pd-NPs supported on carbon materials,<sup>46</sup> and much higher (ca. 10-to-100 times) than those reported for Pd-NPs supported on inorganic oxides and synthesised either by conventional methods<sup>47-49</sup> or by the sputtering approach.<sup>33-35</sup>



**4 bar H<sub>2</sub>**: TOF up to 24.0 s<sup>-1</sup> 81% Sel. 19% Sel.

**1 bar Ar**: TOF up to 2.4 s<sup>-1</sup> 49% Sel. 51% Sel.

**Scheme 1.** Hydrogenation and disproportionation of 1,3cyclohexadiene catalysed by **Pd/C-2**. Reaction conditions: Pd/C (10 mg), cyclohexene (9.9 mmol), 900 r.p.m. and 75 °C.

In the partial hydrogenation of 1,3-cyclohexadiene (See scheme 1), the Pd catalyst supported on carbon black Pd/C-2 displayed lower cyclohexene selectivity and higher activities than those reported for Pd-NPs supported on inorganic oxides, i.e., SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (ca. TOFs of 1-7 s<sup>-1</sup>, and 90-96 % cyclohexene selectivity).<sup>33-</sup> The Pd/C-2 displayed lower catalytic activities in the hydrogenation of 1,3-cyclohexadiene (24.0 s<sup>-1</sup>) than for the hydrogenation of cyclohexene (35.1 s<sup>-1</sup>). In contrast, Pd-NPs synthesized by sputtering on  $SiO_2$  and  $Al_2O_3$  displayed much higher activity in the hydrogenation of 1,3-cyclohexadiene than in the hydrogenation of cyclohexene. <sup>33-35</sup> Although the higher apparent reactivity of cyclohexene than 1,3-cyclohexadiene, Pd/C-2 was quite selective for the partial hydrogenation of 1,3-cyclohexadiene to cyclohexene (81 % selectivity at >99 % conversion). Palladium surfaces generally displayed high partial hydrogenation selectivities in the hydrogenation of 1,3-dienes because the higher affinity of the diene to the Pd-catalytically active surface sites than the alkene, and thus, the diene reacts to form the partially hydrogenated product.50 The difference of reactivity between the catalysts on different supports is attributed to support effects (mainly electronic factors). XPS analysis of Pd-NPs either on carbon and on SiO2 confirmed that the latter displayed a higher oxidation degree and hence higher electrophilic surfaces, which in turn, facilitated the selective hydrogenation of dienes by increasing the coordination strength to the metal surface active sites of the diene with respect to the alkene. Indeed, these behaviours of Pd-NPs dispersed on carbon and metal oxides and their effect on the catalytic performance were previously reported in related hydrogenation processes.<sup>51-52</sup>

A study of the recyclability and reuse of the catalyst Pd/C-2 revealed high productivities (ca. TON of each cycle up to than 15

000) with a drastic reduction of the catalytic activity in the hydrogenation of cyclohexadiene after successive runs (ca. first run:  $24.0 \text{ s}^{-1}$ , second run:  $16.0 \text{ s}^{-1}$ , third run:  $12.3 \text{ s}^{-1}$  and fourth run:  $9.2 \text{ s}^{-1}$ ) with no variation of the product selectivity (ca. 81 % Sel. cyclohexene, 18-19 % Sel. benzene and 0-1% cyclohexane). The heterogeneous nature of these catalysts was confirmed by their activity to the disproportion of 1,3-cyclohexadiene into benzene and cyclohexene, a reaction typically catalysed by metal surfaces/nanoparticles (See Scheme 1).<sup>50</sup>

These catalysts offer cheaper, simpler and efficient alternative for the classical and largely employed systems such as the Lindlar catalyst.<sup>53-54</sup>

#### 3. Conclusions

The magnetron-sputtering approach was revealed as one of the simplest, reliable, fast, clean and cheap methods for the deposition of palladium nanoparticles (Pd-NPs) on a commercially available carbon black. Small (ca. 3.7 nm) and uniformly distributed Pd(0)-fcc nanoparticles with partially oxidised surfaces on the solid supports were obtained. The linear dependence of the deposition time with the final metal content is revealed (increases from 0.15 wt. % after 0.5 min to 1.94 wt. % after 7.5 min) without changing the size and shape of the Pd-NPs. The pores of the support were filled by Pd-NPs, and after longer deposition times, the surface area was drastically reduced by blockage of the pore system, and consequently the access to the metal sites (i.e., reduced metal dispersion). These Pd-NPs catalyse the hydrogenations of nitrobenzene to aniline, cyclohexene to cyclohexane and 1,3-cyclohexadiene to cyclohexene with superior catalytic performance as compared to a commercially available Pd/C and are comparable to the most active catalysts reported so far. Indeed, the highest catalytic activity and productivity was obtained with Pd/C catalyst with palladium content of 0.73 wt%. This behaviour can be due to the higher number of available metal sites than the catalysts with higher metal loadings, and the reduced level of support metal interactions as compared to the catalysts with lower metal loadings. The heterogeneous nature of these Pd-nanocatalysts was revealed by the formation of benzene and cyclohexene from disproportionation of 1,3-cyclohexadienes.

#### 4. Experimental Section

#### 4.1. General procedures

All syntheses were performed using standard Schlenk techniques under argon atmosphere. Chemicals were purchased from Sigma-Aldrich and purified by standard procedures.<sup>55</sup> Carbon black (30 m<sup>2</sup>  $g^{-1}$ ) is a standard material purchased from Micromeritics. **Pd/C-0** catalyst Degussa type E101 NO/W with a Pd content of 5 wt. % was purchased from Sigma-Aldrich. Pd-targets (> 99.99%) were purchased from AJA INTERNATIONAL, Inc. H<sub>2</sub> (> 99.999%), N<sub>2</sub> (> 99.999%) and Ar (> 99.999%) were purchased from White-Martins. ICP-OES analysis for the determination of the Pd content were carried out after sample digestion by using the Thermo Scientific<sup>TM</sup> iCAP<sup>TM</sup> 7400. X-ray diffraction (XRD) experiments were performed by using a Philips X'Pert MPD diffractometer with Bragg-Brentano geometry using a graphite curved-crystal with the Cu Ka X-ray radiation (1.5406 Å). TEM experiments were performed on a JEOL - JEM 1200ExII, operating at an accelerating voltage of 200 kV. Size histograms of the Pd-nanoparticles were obtained by measuring at least 300 particles. N<sub>2</sub> isotherms of the catalysts, previously degassed at 100 °C under vacuum for 3 h, were obtained using Tristar 3020 Micromeritics equipment. Specific

surface areas were determined by the BET multipoint method and average pore size was obtained by BJH method. H<sub>2</sub>-chemisorption analyses were carried out on ASAP 2020 surface area and porosimetry analyser and using of 30 mg of each Pd-catalysts. The pre-treatment of the sample consists of the following steps: (a) He flow at 100 °C for 30 min, (b) two consecutive evacuations under vacuum during 15 min at 100 °C and 350 °C, respectively, (c) three cycles of reduction with H<sub>2</sub> (pressure of 35 KPa) at 100 °C for 5 min and at 350 °C for 120 min, and (d) two consecutive evacuations under vacuum at 350 °C for 120 min and at 100 °C for 30 min. Leak test at the temperature of analysis was performed before starting the analysis. Direct adsorption measurements were made with H<sub>2</sub> at 35 °C and consisted of the determination of the isotherms in the 0.15-60 KPa range (about 5 min per point) separated by an evacuation at the same temperature for 60 min. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos AXIS Ultra DLD instrument. Samples were mounted on the standard Kratos sample bar using double sided tape (sellotape brand), these were inserted into the airlock and pumped down to ~  $3 \times 10^{-7}$  Torr overnight before transfer into the instrument analysis chamber. The analysis chamber pressure during the measurements was better than  $5 \times 10^{-9}$  Torr. Wide energy range survey scans were collected using pass energy 80 eV in hybrid slot lens mode and a step size of 0.5 eV, high resolution data on the Pd 3d, O 1s and C 1s photoelectron peaks was collected at pass energy 20 eV over energy ranges suitable for each peak, and collection times of 5 minutes, step sizes of 0.1 eV. The charge neutraliser filament was used to prevent sample charging over the irradiated area. The X-ray source was a mono-chromated Al K- $\alpha$  emission, run at 10 mA and 12 kV (120W). The data were captured using Kratos VISIONII software and exported into vms format for data processing with CASAXPS (Version 2.3.17). The high-resolution spectra were analysed using a Lorentzian asymmetric line shape convoluted with a Gaussian function for each chemical component. The high-resolution data was charge corrected to adventitious carbon at 284.6 eV. The FWHM value of a given component of the Pd 3d was constrained to be the same for all the measurements. The energy range for each 'pass energy' (resolution) was calibrated using the Kratos Cu  $2p_{3/2}$ , Ag  $3d_{5/2}$  and Au  $4f_{7/2}$  threepoint calibration method. The transmission function was calibrated using a clean gold sample method for all lens modes and the Kratos transmission generator software within Vision II.

#### 4.2. General procedure for the sputtering

As a general procedure, carbon black (100 mg) was loaded in a conical Al flask and placed inside the vacuum chamber. The chamber was closed and evacuated to a base pressure of  $4 \times 10^{-7}$  mbar vacuum for 4 h. Then, the chamber was placed under  $4 \times 10^{-3}$  mbar of Ar at room temperature (25 °C). The **Pd/C-1** to **Pd/C-5** catalysts was obtained by sputtering of Pd-targets (99.99%) at power of 50 W during 0.5, 2.5, 5.0, 7.5 and 12.0 min, respectively. The support was continuously homogenized by revolving the Al flask at a frequency of 23 Hz during the time of sputtering. The chamber was vented with Ar, and the Pd-NPs/C catalysts were recovered and stored under Ar for their further characterization and application.

# 4.3. General procedure for the hydrogenation test

As a general procedure, the substrate (1.12 g of aniline, 0.81 g of cyclohexene or 0.79 g of 1,3-cyclohexadiene) was added to a Fischer-Porter reactor containing the appropriate amount of Pd/C catalyst (10 mg). The reactor was then pressurized and maintained at

constant pressure of 4 bar of  $H_2$  and heated at the desired temperature (90 °C for nitrobenzene and 75 °C for cyclohexene and 1,3-cyclohexadiene). The reaction kinetics were monitored by  $H_2$ consumption. Samples were taken from the reaction mixture at regular intervals, and the conversion and selectivity was corroborated by GC-analysis of the reaction samples using *n*-heptane as internal standard. After the desired reaction time, the reactor was cooled to room temperature and then depressurized. GC analyses were run with an Agilent Technologies GC System 6820 using a DB-17 column. GC conditions were as follows: injector and detector (FID) temperature of 260 °C; N<sub>2</sub> as carrier (1 mL min<sup>-1</sup>), column head pressure of 10 psi and temperature program from 40 °C (10 min) to 250 °C at a heating rate of 10 °C min<sup>-1</sup>.

#### Supplementary data

Detailed experimental procedure, sputtering time vs. metal content, TEM images, size histograms,  $H_2$ -chemisorption isotherms,  $N_2$ -physisorption isotherms, XPS spectra and hydrogenation kinetic data.

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