



Short communication

# Synthesis of palladium nanoparticles on carbon nanotubes and graphene for the chemoselective hydrogenation of para-chloronitrobenzene

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## ABSTRACT

We have studied the synthesis of palladium nanoparticles over carbon nanotubes (Pd/CNT) and graphene (Pd/G) and we have tested their catalytic performance in the liquid phase chemoselective hydrogenation of para-chloronitrobenzene at room temperature. The catalysts were characterized by N<sub>2</sub> adsorption/desorption isotherms, TEM, X-ray diffraction, infrared and X-ray photoelectron spectroscopy and ICP-OES. The palladium particle size on Pd/G (3.4 nm) and Pd/CNT (2.8 nm) was similar though the deposition was higher on Pd/G. Pd/CNT was more active which can be ascribed to the different surface area and electronic properties of the Pd nanoparticles over CNT, while the selectivity was 100% to the corresponding haloaniline over both catalysts and they were quite stable upon recycling.

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## 1. Introduction

The hydrogenation of halonitrocompounds has been traditionally performed by the Béchamp process. However, the increasing production of aromatic haloamines, which are extensively used as intermediates in the fine chemistry industry, requires the development of more environmentally friendly systems [1]. It has been reported that palladium and platinum offer good activities for this hydrogenation [1], but palladium is cheaper and more resistant to deactivation than platinum [2]. However, to achieve yields higher than 99% of the desired aromatic haloamines it is necessary to add modifiers or to employ bimetallic catalysts [3,4]. Moreover, the use of a hydrophobic support as carbon materials may inhibit the formation of aniline [5,6]. In addition, the morphology of carbon nanotubes as rolling graphene layers might influence the adsorption of the molecules and hence the catalytic performance. Besides, their particular electronic properties can induce a positive charge on the metal species due to electron transfer [7], this activating the N=O bond. However, to obtain an optimal size of the nanoparticles a previous oxidation step is frequently needed which may affect the catalytic performance [6]. Therefore alternative methods to synthesize metal nanoparticles have to be developed. The synthesis of heterogeneous catalysts by deposition of pre-synthesized metal nanoparticles has been successfully employed for a variety of catalytic

systems. In these systems the synthesis of the metal nanoparticles is performed by the decomposition of organometallic precursors under H<sub>2</sub> pressure and they are then deposited on the support to obtain a homogeneous particle size distribution [8,9]. On the other hand, recent literature pointed to graphene oxide as an ideal candidate to support metal nanoparticles. The methods of synthesis of the nanoparticles may promote the reduction of graphene oxide, obtaining a more hydrophobic material compared to the parent graphene oxide [2,10].

Therefore, we have explored the synthesis of palladium nanoparticles over graphene and carbon nanotubes and we have tested their catalytic performance on the hydrogenation of p-chloronitrobenzene (p-ClNB).

## 2. Experimental

## 2.1. Catalysts synthesis

As received commercial carbon nanotubes (Nanocyl 3100, >95% purity, CNT) and a lab-prepared graphite oxide (GO) following a modification of the Brodie's method [11] were used as starting material. Two catalysts of 1 wt.% of Pd loading were prepared according to the following procedure: 4.3 mg of Pd<sub>2</sub>(dba)<sub>3</sub> (dba: dibenzylideneacetone) per gram of support was dispersed in 40 ml of tetrahydrofuran THF and submitted to 3 bar of H<sub>2</sub> pressure for 24 h to obtain Pd nanoparticles. Then, the supports, CNT and GO, were suspended in 40 ml of THF along with the previously synthesized Pd nanoparticles and the mixture

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was submitted to 3 bar of hydrogen for 24 h. Finally, the solids were recovered and extensively washed with acetone in a rotatory evaporator and dried under vacuum at 323 K for 16 h. The catalysts were denoted as Pd/CNT and Pd/G.

## 2.2. Characterization

The textural properties of the materials were determined by N<sub>2</sub> adsorption at 77 K on a Micromeritics ASAP 2010 apparatus. X-ray powder diffraction patterns were recorded on a Rigaku diffractometer equipped with a nickel-filtered CuK $\alpha$ 1 radiation ( $\lambda = 1.5418\text{\AA}$ ), using a  $2^\circ \text{ min}^{-1}$  scanning rate and  $1^\circ \text{ min}^{-1}$  for the  $35\text{--}45^\circ$  region. TEM images were taken with a JEOL electron microscope (model JEM-2010) working at 200 kV and it was equipped with an INCA Energy TEM 100 analytical system and a SIS MegaView II camera. 200 nanoparticles were measured to estimate the average particle size. The surface acidity of calcined samples was measured by potentiometric titration of a suspension of the catalyst in acetonitrile with n-butylamine, using an Ag/AgCl electrode [12].

Infrared spectra were collected by using a NicoletNexus FT-IR in the middle range ( $4000\text{--}400 \text{ cm}^{-1}$ ) and recorded by a DTGS detector from 128 scans and with a resolution of  $4 \text{ cm}^{-1}$ . The samples were mixed with predried potassium bromide to a final concentration of approximately 1% (w/w).

The actual metal loading of Pd on the different catalysts was determined by ICP-OES in a Perkin–Elmer device (Optimal 3000). The metal was extracted from the catalysts by digestion in HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (4:1) for 30 min, in a microwave oven at 473 K. X-ray photoelectron spectroscopy (XPS) analyses were performed with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and a

Mg-K $\alpha$  ( $h = 1253.6 \text{ eV}$ ;  $1 \text{ eV} = 1.6302 \cdot 10^{-19} \text{ J}$ ) X-ray source operated at 10 mA and 12 kV.

## 2.3. Hydrogenation reaction

Catalytic tests were performed in a stainless steel Parr-type batch reactor, equipped with a glass sleeve and a magnetic stirrer set at 1000 rpm. The hydrogenations were performed with 50 mg of catalyst, 320 mg of p-chloronitrobenzene and 50 ml of ethanol at 20 bar and 298 K. For the recycling studies the catalysts were recovered by filtration and dried under vacuum. The amounts of p-CINB, and ethanol were recalculated according to the recovered mass of catalyst to preserve the initial concentration and S/C ratio. Details on the analyses of reactants and products can be found elsewhere [6]. Additional experiments were performed to verify that the reaction was heterogeneously catalyzed: the reaction was stopped at 50% conversion and the liquid filtrate was submitted to the reaction conditions.

## 3. Results

### 3.1. Characterization

Representative TEM images of the catalysts are shown in Fig. 1. They show that palladium nanoparticles were homogeneously distributed on the surface of CNT and G supports with a narrow size distribution, as can be observed in the histograms. The average particle size was similar and the values, in Table 1, were 2.8 and 3.4 nm for Pd/CNT and Pd/G respectively which are in the range of values previously reported in literature for Pd nanoparticles over graphene and graphene oxide [13,14], and

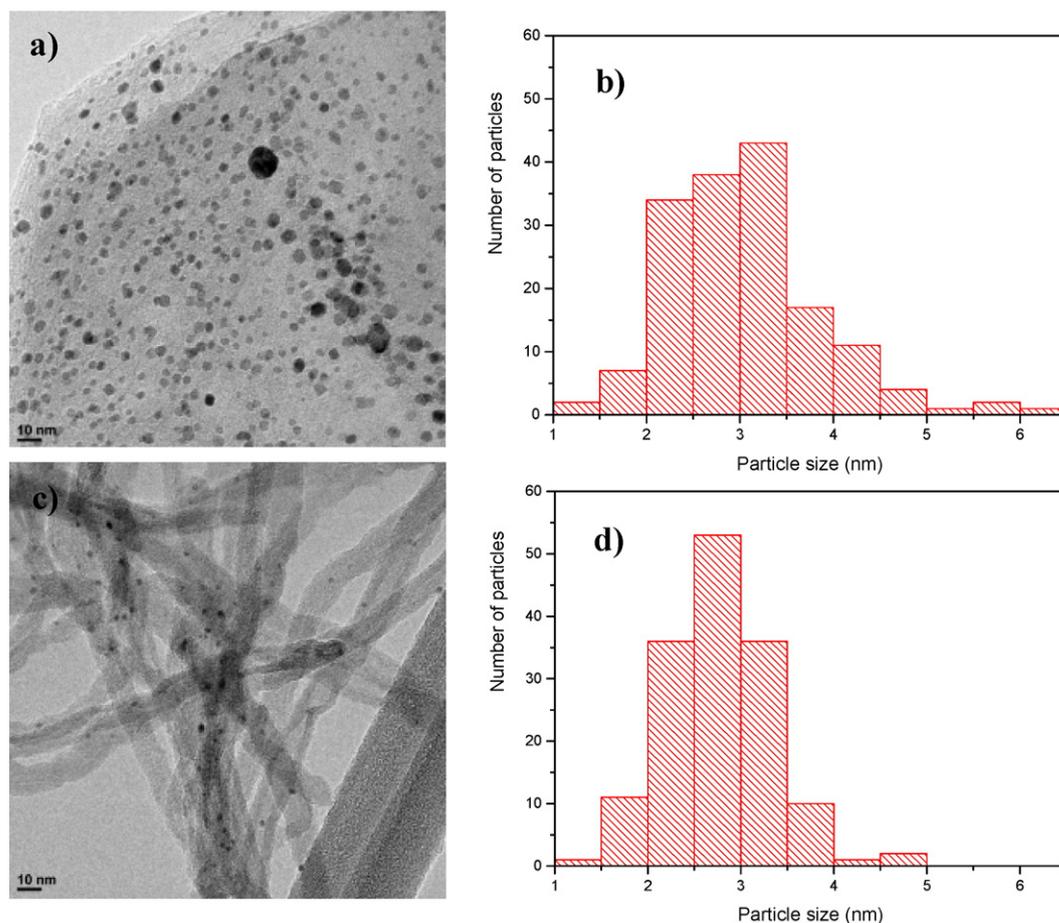


Fig. 1. TEM micrographs and histograms of a), b) Pd/G and c), d) Pd/CNT. Scale bar: 10 nm.

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