



Synthesis of palladium nanoparticles over graphite oxide and carbon nanotubes by reduction in ethylene glycol and their catalytic performance on the chemoselective hydrogenation of *para*-chloronitrobenzene

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ABSTRACT

Pd nanoparticles have been synthesized over carbon nanotubes (CNT) and graphite oxide (GO) by reduction with ethylene glycol and by conventional impregnation method. The catalysts were tested on the chemoselective hydrogenation of *p*-chloronitrobenzene and the effect of the synthesis method and surface chemistry on their catalytic performance was evaluated. The catalysts were characterized by N₂ adsorption/desorption isotherms at 77 K, TEM, powder X-ray diffraction, thermogravimetry, infrared and X-ray photoelectron spectroscopy and ICP-OES. It was observed that the synthesis of Pd nanoparticles employing ethylene glycol resulted in metallic palladium particles of smaller size compared to those prepared by the impregnation method and similar for both supports. The presence of oxygen groups on the support surface favored the activity and diminished the selectivity. It seems that ethylene glycol reacted with the surface groups of GO, this favoring the selectivity. The activity was higher over the CNT-based catalysts and both catalysts prepared by reduction in ethylene glycol were quite stable upon recycling.

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1. Introduction

The interest in heterogeneous catalysts being palladium the active phase has increased recently because of its lower price and better resistance to deactivation compared to platinum, among other reasons [1,2]. However, the conventional methods to obtain supported nanoparticles for catalytic applications do not offer good metal dispersion, and alternative methods as the colloidal route have been developed. It consists on the dispersion of the metal precursor into an appropriate solution to which the reducing agent and the support are added under specific conditions. A surfactant or a polymer is generally necessary to avoid aggregation of the nanoparticles [3]. However, in order to optimize the use of the active phase these stabilizers must be removed, which may cause agglomeration of the nanoparticles and, therefore it would be interesting to

develop methodologies that avoid the use of these capping agents. With that aim, the use of a reducing agent and a metal precursor that can be employed under mild conditions to avoid the agglomeration of the nanoparticles is desirable. Organometallic precursors allow for colloidal synthesis at lower temperatures using alcohols as reducing agents, although aggregation cannot always be avoided [4]. Among these methods, the polyol process is based on the decomposition of the polyol (commonly ethylene glycol) by treatment under a certain temperature in a solution containing the metal precursor salt [5–7] to which the support can be also added [8]. In this way, Pt nanoparticles supported on carbon nanotubes (CNT) have been synthesized [9,10]. It has been suggested that the polyol acts as solvent and reducing agent [11], though an additional reducing agent is frequently needed [12,13].

The selective catalytic hydrogenation of aromatic haloamines has been extensively studied to displace the environmentally unfriendly traditional synthetic routes. Although the activation of the N=O bond is relatively easy, the main problem associated with this reaction is the accumulation of intermediates and, depend-

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ing on the metal, the cleavage of the halogen. The accumulation of hydroxylamine may lead to rapid exothermic decomposition and/or formation of condensation products. The most studied metals, i.e. Ni, Pt and Pd, offer good activities for this hydrogenation, but to achieve a high yield of the desired product it might be necessary to work at high temperatures, to add promoters or to employ bimetallic catalysts [14,15]. Palladium is in general less selective than platinum for this reaction due to parallel dehalogenation, and complete inhibition of the C–Cl scission is difficult [16,17]. In this sense it has been reported that the use of a hydrophobic support as activated carbon may inhibit the formation of aniline [17] and an alternative support as CNT can offer further improvement of the catalytic performance [18]. Moreover, recent literature points to graphene oxide as an ideal candidate to act as support for the synthesis Pd nanoparticles [19–21]. This has been achieved by chemical [22], electrochemical [23] or microwave-assisted methods [24]. Some of these methods may also reduce the parent graphene oxide in such a way that the aromatic structure is recovered.

Therefore, we have explored the synthesis of palladium nanoparticles over graphite oxide by the polyol method and compared it with the synthesis over carbon nanotubes. The catalytic performance in the hydrogenation of *p*-chloronitrobenzene (*p*-CINB) was tested and compared with analogous catalysts prepared by conventional impregnation over GO, CNT and previously oxidized CNT.

2. Experimental

2.1. Catalysts preparation

Graphite oxide (GO) was synthesized from graphite powder (99.999% stated purity, 200 mesh, Alfar Aesar) following a modification of the Brodie's method [25]. Graphite was added to a reaction flask containing fuming HNO₃ (20 mL/g of support) which was previously cooled to 273 K in an iced bath. Then, potassium chlorate (8 g/g of support) was slowly added. The reaction was left to proceed for 24 h under stirring, and the final solid was filtered, extensively washed with deionized water until neutral pH, dried under vacuum at 323 K overnight and kept in a desiccator. High purity commercial multi-wall carbon nanotubes (CNT), supplied by Nanocyl (Nanocyl 3100, >95% purity), were also employed. A portion of the CNTs was oxidized with concentrated HNO₃ for 24 h at 403 K (CNTox). The catalysts were prepared employing the necessary amount of the precursor, palladium acetylacetonate Pd(acac)₂ (Sigma–Aldrich, 99%), to obtain a 1 wt.% Pd over GO and CNT. To prepare Pd/GO_{EG} and Pd/CNT_{EG} the support and the Pd precursor were dispersed in ethylene glycol and heated at 373 K for 2 h, filtered off, washed extensively with ethanol and dried under vacuum at 323 K for 16 h. Catalysts Pd/CNT, Pd/CNTox and Pd/G were prepared by incipient impregnation in toluene, followed by drying at 373 K for 24 h and heating under Ar (50 mL/min) at 673 K for 2 h,

with a heating ramp of 5 °C/min. The samples prepared by impregnation were reduced under H₂ (50 mL/min) at 673 K for 2 h prior to the reaction.

2.2. Characterization

The specific surface areas (S_{BET}) of the catalysts were determined from the N₂ adsorption isotherms at 77 K, which were obtained with a Micromeritics ASAP 2010 equipment. Prior to the measurements, the samples were degassed at 473 K for 2 h.

TEM images were obtained with a JEOL electron microscope (model JEM–2010) working at 200 kV. It was equipped with an INCA Energy TEM 100 analytical system and a SIS MegaView II camera. Samples for analysis were suspended in ethanol and placed on copper grids with a holey-carbon film support. The average particle size was obtained from the measurement of 200 nanoparticles.

X-ray powder diffraction patterns were recorded on a Rigaku diffractometer equipped with a nickel-filtered CuK α 1 radiation ($\lambda = 1.5418 \text{ \AA}$), using a 2°/min scanning rate.

The actual Pd loading on the different catalysts was determined by ICP-OES in a PerkinElmer device (Optimal 3000). To this end, the metal was extracted from the catalysts by digestion in HNO₃/H₂O₂ (4:1) for 30 min, in a microwave oven at 473 K.

Thermogravimetric analyses were performed with a Mettler Toledo Thermogravimetric TGA/SDTA 851. The samples were treated under flowing He for 2 h and then heated at a 10 K/min rate up to 1123 K.

X-ray photoelectron spectra (XPS) of the catalysts were obtained on a MicrotechMultilb 3000 spectrometer, equipped with a hemispherical electron analyzer and MgK α ($h\nu = 1253.6 \text{ eV}$) photon source. Prior to the analysis, the catalysts were in situ reduced under the same conditions employed before the catalytic tests. The surface O/C and Pd/C atomic ratios were estimated from the integrated intensities of Pd 3d_{5/2}, C 1s, and O 1s lines after background subtraction and correction by the atomic sensitivity factors. The spectra were fitted to a combination of Gaussian–Lorentzian lines of variable proportions.

Infrared spectra were collected on a NicoletNexus FT-IR in the middle range (4000–400 cm⁻¹), and recorded by a DTGS detector from 128 scans and with a resolution of 4 cm⁻¹. GO and its derivatives were mixed with pre-dried potassium bromide to a final concentration of approximately 1% (w/w).

2.3. Hydrogenation tests

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 were stirred at 20 bar and 298 K. For the recycling studies the amounts were recalculated for each cycle. The concentrations of reactants and products were monitored by gas chromatography

Table 1
Physico-chemical properties of supports and catalysts.

Sample	S_{BET} (m ² g ⁻¹)	dp TEM(nm)	Pd 3d _{5/2} eV	O/C	Pd/C	Pd (%) ICP
GO	–	–	–	0.355	–	–
CNT	300	–	–	0.011	–	–
CNTox	319	–	–	0.088	–	–
Pd/GO _{EG}	–	<2	335.1	0.474	0.002	0.62
Pd/GO _{EG} - used	–	–	335.2	0.455	0.001	–
Pd/G	670	4.1	335.4 (73) 337.1 (27)	0.084	0.002	0.90
Pd/CNT _{EG}	288	<2	335.2	0.096	0.002	0.51
Pd/CNT _{EG} - used	–	–	335.2	0.029	0.001	–
Pd/CNT	285	9.4	335.9	0.022	0.001	1.02
Pd/CNTox	289	2.7	335.7	0.071	0.007	0.91

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