

# Effect of structural ordering of the carbon support on the behavior of Pd catalysts in aqueous-phase hydrodechlorination

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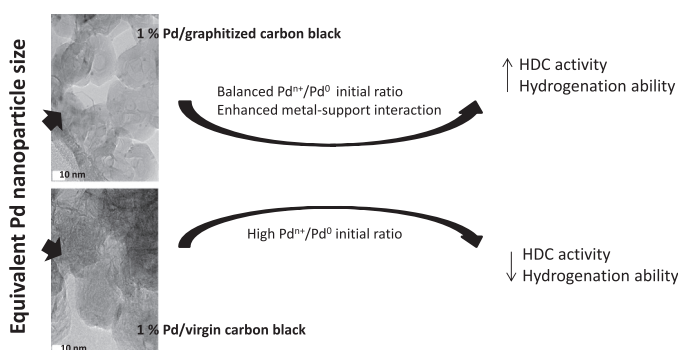
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## HIGHLIGHTS

- Catalysts with graphitized carbon black as support showed the highest activity.
- The graphitization of the support led to catalysts with higher activity.
- This higher activity can be partly related to a well-balanced initial Pd<sup>III</sup>/Pd<sup>0</sup> ratio.
- Graphitized carbon black-based catalysts showed higher ability to hydrogenate phenol.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Catalysts consisting of Pd supported on virgin and heat-treated carbon blacks (homemade and commercial), graphites (natural and synthetic) and commercial carbon nanofibers were prepared and tested in the aqueous phase hydrodechlorination (HDC) of 4-chlorophenol (4-CP) under near ambient conditions (30 °C, 1 atm) in order to explore the effect of the support on the catalytic behavior. The homemade graphitized supports were prepared from commercial carbon black (CB) and from a carbon black-like material (CBPE) obtained from pyrolysis of low-density polyethylene. All the catalysts prepared yielded complete 4-CP conversion, although a wide range of activity was observed (10.7–173.5 mmol g<sub>Pd</sub><sup>-1</sup> min<sup>-1</sup>). The graphitized carbon black provided the most active catalysts, showing Pd nanoparticles around 3 nm in size and a well-balanced contribution of Pd species (Pd<sup>III</sup>/Pd<sup>0</sup> = 0.9). Substantial differences of activity were found between the graphitized and not graphitized supports, even for catalysts with similar Pd nanoparticle size. The higher activity of the catalysts with graphitized supports can be partly associated to a more balanced initial Pd<sup>III</sup> to Pd<sup>0</sup> ratio. Moreover, higher selectivity to hydrogenation products (cyclohexanone) was also achieved with those catalysts due to a higher contribution of the Pd<sup>0</sup> species.

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## 1. Introduction

In the last few years the economic impact of catalysis has been increasing, since the world's demand for catalysts is growing at

almost 6% per year (Hagen, 2015). The relevance of catalysis in the chemical industry is outstanding, taking into account that 85–90% of chemical products needs of a catalyst during their production (Murzin, 2013). Among all the catalytic processes used in the industry, heterogeneous catalysis is by far predominant (80% of the global catalysts market share), compared to homogeneous

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(17%) and enzymatic (3%) Bravo et al., 2013. In heterogeneous catalysis, several materials are used as catalysts supports such as carbon materials, alumina, silica, ceria, zirconia and clays, among others. Carbon materials generate especial interest, being among their main advantages an easily tailorable porous structure and surface chemistry, high resistance to acids and bases, structure stability at high temperatures under inert atmosphere, simple recovery and comparatively low cost in general (Machado and Serp, 2015).

In spite of its availability, graphitic carbons have been much less used than other carbon materials in catalysis due to their low specific surface area ( $10\text{--}50\text{ m}^2\text{ g}^{-1}$ ) and poorly developed pore structure (Machado and Serp, 2015). Nevertheless, graphites have shown fairly good performance as catalysts supports in different reactions, such as the hydrogenation of citral, where higher selectivity towards the unsaturated alcohol was obtained compared to other conventional supports such as alumina, silica or activated carbon (Bailón-García et al., 2013). They have been also used in CO electro-oxidation (Fang et al., 2015), oxidation of alkenes (Bawaked et al., 2011), catalytic decomposition of ammonia (Li et al., 2007) and even as bare catalyst in the Baeyer-Villiger oxidation of cyclohexanone, improving the activity and selectivity towards lactones (Li et al., 2013).

Other related carbon materials, such as graphitized carbon blacks have also been scarcely explored in catalysis for the same reasons as graphite. They have been mostly used in the fuel cell field as catalysts supports, especially in the oxygen reduction reaction, where the catalyst stability was improved due to enhanced resistance to corrosion (Hara et al., 2012; Yano et al., 2013). Similar results were found in methanol oxidation (Jeon et al., 2011). In much less extent, they have been used in other reactions such as CO hydrogenation (Ruiz et al., 1984).

In the case of HDC, considered as a potential solution to deal with toxic chlorinated organic compounds (Keane, 2011), studies on catalysts behavior with graphitic supports are scarce, and there is no conclusive agreement about the effect of these supports on catalyst behavior. Thus, some authors reported lower activity of Pd/C or Ni/C catalyst based on graphite compared to other supports in the gas-phase HDC of chlorobenzene (Amorim et al., 2005; Keane et al., 2003). On the contrary, in liquid-phase HDC of tetrachloroethylene, Díaz et al. (2010) reported enhanced catalytic activity when graphites, mechanically modified to increase the porous structure and specific surface area (so-called “high surface area graphite”), were used as supports in Pd/C catalysts. Particularly, in aqueous phase HDC, which is a suitable process for the treatment of wastewater containing organochlorinated pollutants (Munoz et al., 2016), there is a lack of knowledge on this issue.

In the current work, Pd catalysts supported on a set of graphitized and non-graphitized carbons were prepared and tested in the aqueous phase HDC of 4-CP to explore the effect of the structural ordering of the carbon support on the catalysts behavior.

## 2. Experimental

### 2.1. Preparation of supports and catalysts

Homemade graphitized supports (CB2800 and CBPE2600) were prepared from a commercial carbon black (CB; Alfa Aesar, 100% acetylene) and from a carbon black-like material obtained from pyrolysis of low-density polyethylene (CBPE), as described elsewhere (Baeza et al., 2015; Alonso-Morales et al., 2009). Both CB and CBPE supports were heat-treated at temperatures of 2800 and 2600 °C, respectively, during 30 min under He flow. Synthetic graphite (SynG, Fluka), natural graphite (NatG, Ticonderoga, NY, USA) and commercial graphitized carbon black (CBMeso, Sigma-

Aldrich) and carbon nanofibers (CNF, Sigma-Aldrich) were used as received. The catalysts were prepared by wetness impregnation from an aqueous solution of  $\text{PdCl}_2$  in 0.1 N HCl. All the catalysts were prepared with a Pd loading of 1% (w). After the impregnation, the solid was dried for 2 h at room temperature and overnight at 60 °C, then calcined at 200 °C for 2 h and reduced with  $\text{H}_2$  at 100 °C for 1 h.

### 2.2. Characterization of supports and catalysts

The supports were characterized by TEM/STEM at 300 kV (FEI, Tecnai F30), elemental analysis (LECO CHNS-932), nitrogen adsorption-desorption at 77 K (Quantachrome Autosorb I), XRD (X'Pert PRO Panalytical, CuK $\alpha$ -radiation, scanning for  $2\theta = 5\text{--}60^\circ$ , step size  $2\theta = 0.033^\circ$ , count time 200 s), RAMAN spectroscopy (WITex CRM200,  $\lambda = 514\text{ nm}$  and NT-MDT Spectra,  $\lambda = 532\text{ nm}$ ) and pH slurry. The catalysts were characterized by TEM-STEM/EDS at 300 kV (FEI, Tecnai F30). Software ‘ImageJ 1.44i’ was used for counting and measuring NPs on digital STEM images (>200 NPs were measured per sample). Surface-area-weighted mean diameters ( $d_s = \sum n_i d_i^3 / \sum n_i d_i^2$ ) and size distribution, characterized by the standard deviation ( $\sigma_s = \sqrt{\sum (d_i - d_s)^2 / n}$ ), were calculated. Likewise, the catalysts were characterized by XPS (Thermo Scientific, mod. K-Alpha, equipped with an Al K $\alpha$  X-ray excitation source, 1486.68 eV). Spectrograms deconvolution was performed using XPS peak v4.1 software to determine both  $\text{Pd}^{n+}$  and  $\text{Pd}^0$  species. A Shirley background subtraction and mixed Gaussian-Lorentzian by a least-square method curve fitting was used and C 1s peak (284.6 eV) was used as internal standard for binding energies corrections due to sample charging. Doublet separation for Pd 3d was 5.26 eV.

### 2.3. HDC experiments

HDC runs were carried out in a jacketed glass reactor (30 °C, 1 atm) under 50 N mL  $\text{min}^{-1}$   $\text{H}_2$  flow rate, during 4 h. Vigorous stirring (600–800 rpm) was used to facilitate  $\text{H}_2$  distribution through the liquid phase (150 mL). The initial concentration of 4-CP was 100 mg  $\text{L}^{-1}$  and the Pd loading was 2.5 mg  $\text{L}^{-1}$ . Vent was provided with reflux system and no significant stripping was detected. Different catalyst loads and stirring velocities were checked in preliminary experiments in order to confirm that the process takes place under chemical control. The liquid samples (1 mL) were collected and filtered (PTFE filter, pore size 0.22  $\mu\text{m}$ ). High Performance Liquid Chromatography (Varian Prostar, UV-VIS detector) with a C<sub>18</sub> column as stationary phase and a mixture of acetonitrile and water (1:1, v/v) as mobile phase, was used to analyze 4-CP and phenol. Cyclohexanone and cyclohexanol were analyzed by GC/FID (GC 3900 Varian) using a 30 m long  $\times$  0.25 mm i.d. capillary column (CP-Wax 52 CB, Varian) and  $\text{N}_2$  as carrier gas. The quantification of chloride ion was performed by ion chromatography (Metrohm 790 Personal IC). The carbon and chlorine balances matched between 95.3–99.2% and 96.4–99.5%, respectively.

The rate of 4-CP disappearance was calculated from a pseudo-first order equation:

$$\begin{aligned} (-r_{4\text{-cp}}) &= \frac{-dC_{4\text{-cp}}}{dt} = k_1 \times C_{4\text{-cp}} \\ t &= 0; C_{4\text{-cp}} = C_0 \end{aligned} \quad (1)$$

In this model the concentration of  $\text{H}_2$  is included in the pseudo-first-order rate constant ( $k_1$ ), since  $\text{H}_2$  was in great excess. The catalysts activity was calculated from the  $k_1$  values, the 4-CP initial concentration and the Pd dose used in the experiments, according to equation (Murzin, 2013), where  $C_{\text{Pd}}$  corresponds to Pd concentration ( $\text{g L}^{-1}$ ).

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