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This is an **author produced version** of a paper published in:

Catalysis Science and Technology 8.10 (2018): 2598-2605

DOI: <https://doi.org/10.1039/c8cy00384j>

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Catalysis Science & Technology

ARTICLE

Enhancement of the activity of Pd/C catalysts in aqueous phase hydrodechlorination through doping of carbon supports

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The enhancement of the activity of Pd catalysts for aqueous phase hydrodechlorination (HDC) was studied using N-doped tailored supports. N-doped (1-1.7% N, w) and non-doped mesoporous carbon materials with equivalent pore structure were prepared via templating with MSU-F silica. At 30 °C the doping of the support resulted in a higher catalytic activity (26 vs 49 mmol g⁻¹ Pd min⁻¹ for non-doped and doped support, respectively) in the removal of 4-chlorophenol from water. However, the activity of the catalyst with non-doped carbon increased more with reaction temperature, being even the most active at 70 °C (131 vs 102 mmol g⁻¹ Pd min⁻¹ for non-doped and doped support, respectively). The activation energy of the process was found to decrease from 32 to 16 kJ mol⁻¹ due to nitrogen doping of the support. Nitrogen doping of the carbon support is an interesting strategy to prepare catalysts with high HDC activity at mild temperature conditions, whereas non-doped supports are more convenient for the intensification of the process by increasing the reaction temperature.

Introduction

Catalytic hydrodechlorination (HDC) is a well-recognized process for the removal of organic chlorinated compounds from aqueous phase. A variety of studies have been reported on this topic dealing with the removal of chlorophenols, herbicides, water disinfection by-products, bleaching by-products, etc.¹⁻⁵. Several metals and alloys have been used as active phase in catalytic HDC, being the most common Pd, Pt and Ru^{6,7}. The role of the support in the HDC activity is also important. Thus, noble metal catalysts supported on carbon materials have demonstrated to be more active than silica or alumina-supported ones^{1,7-10}. Likewise, an increased activity in HDC and in further hydrogenation of the reaction products has been observed for catalysts using nitrogen-doped carbon supports¹¹. In spite of the potential of N-doped carbons as supports for HDC catalysts, few works can be found on this topic in the literature so far.

Nitrogen is considered as a good doping agent for carbon materials because nitrogen and carbon are neighbors in the periodic table and both elements show similar sizes, which can help to minimize atomic structural problems. Due to the difference in the total number of electrons, the presence of nitrogen in the carbon matrix

can improve electronic properties, inserting n-type modifications which can be very useful for several kinds of applications where electronic transference plays an important role¹². In the case of catalytic applications, nitrogen doping can improve the hydrophilicity of carbon and materials dispersibility in aqueous media, leading to a better catalytic performance^{13,14}. Furthermore, the electronegativity introduced in the carbon structure by nitrogen atoms seems to play an important role in the dispersion of the metal phase, which may be stabilized and deposited with small nanoparticle size and narrow size distribution. The nitrogen doping can also increase the metal-carbon binding energy, thus contributing to the dispersion of the metal and improving its anchorage and stability during the reaction^{13,15-17}.

Some authors have used catalysts based on templated nitrogen-doped carbons in order to control both the porosity and the chemical composition of the support. Templating is a very interesting technique because it makes possible to design a material with specific size, morphology and porous texture¹⁸⁻²⁰. This method mainly consists in the replication of the structure of a template into the carbon. Two main kinds of templates can be used for this purpose: hard and soft templates²¹. The morphology and pore structure of the resulting carbons are mainly governed by the template used. Silica templates were successfully used to prepare porous carbons having mesopores of different hierarchical order, being MCM-48, MCM-41, SBA-15 and MSU-F among the most used ones²²⁻²⁶. Mesoporous templated carbons are of particular interest as catalyst supports for liquid phase applications due to diminished mass transfer constrains²⁷.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Zhang et al.¹⁷ used soft templating and *m*-aminophenol as both carbon and nitrogen sources to produce high nitrogen content micro and mesoporous carbons, which led to more active HDC catalysts with enhanced hydrogenation activity. Dong et al.¹⁶ used MCM-48 as a silica template and dicyandiamine as carbon and nitrogen source to obtain nitrogen-doped mesoporous microspheres used as supports for more active HDC catalysts. Cui et al. obtained nitrogen doped mesoporous carbons by pyrolysis of a Ni-MOF, showing a good stability and reusability in HDC reactions²⁸, and Zhou et al. attributed to N-doped graphene/Pd a faster hydrodechlorination of 2,4-chlorophenol than the non-doped graphene support²⁹. In spite of those results, there is a lack of knowledge on the effect of nitrogen doping of carbon supports on the activity of HDC catalyst because of the difficulty to compare carbon supports differing in nitrogen content but not in other characteristics such as textural properties.

The main objective of this work is to study the effects of carbon N-doping and the doping level in the activity of Pd/C catalysts in aqueous-phase HDC, in order to assess the potential of this strategy for the preparation of more active catalysts and process intensification. MSU-F silica was used to prepare templated carbons with identical morphology and structure, but different N content (from ~0 to 1.7%, w). The interconnected mesoporosity conferred to the carbon by the template also reduces mass transfer constraints and enables assess the control regime and effect of carbon doping.

Experimental

Preparation of carbon supports and catalyst

Carbon materials were prepared using a resol phenolic resin as carbon precursor, MSU-F as template and 1,10-phenanthroline as doping agent. The resol resin (Bakelite®PF9934 FL) was provided by Hexion Specialty Chemicals Iberica S.A. MSU-F (mesostructured cellular foam, SiO₂ 99%), 1,10-phenanthroline monohidrate (99%) and ethanol (99.8%) were supplied by Sigma-Aldrich. The chemical structure of the resin and 1,10-phenanthroline and the morphology of silica can be seen in Fig. 1. Palladium catalysts were prepared using PdCl₂ (99%) provided by Sigma-Aldrich.

In a typical preparation (Fig. 2) 3 g of resol resin and 1 g of MSU-F template were used. In the case of doped carbons, 0.14 or 0.40 g of 1,10-phenanthroline were added to the resin to achieve different nitrogen contents. The resin/phenanthroline ratios were adjusted in preliminary experiments (not shown) to achieve final nitrogen contents in the doped carbon of 1 and 1.7% (w). These precursors

Fig. 1. Starting materials: A) 1,10-phenanthroline, B) resol resin structure, and C) TEM image of MSU-F

Fig. 2. Procedure for the synthesis of the catalysts.

sample at 130 °C for 1 h in air. The curated resin-silica was treated at 700 °C for 1 h, using a temperature ramp of 5 °C min⁻¹, in inert atmosphere of

N₂. The silica template was removed in 3.5 M NaOH solution for 15 h, and the remaining solid was filtered (0.45 µm Nylon filter), washed with water until neutral pH and oven-dried at 65 °C. The carbons obtained were named as C-blank for non-doped carbon, C-1N and C-17N for the doped carbons, these last with nominal nitrogen contents of 1 and 1.7%, respectively. Pd catalysts were prepared from these carbons by incipient wetness impregnation yielding the catalysts C-blank/Pd, C-1N/Pd and C-17N/Pd. Impregnation of the support was carried out with a solution of palladium chloride in HCl 0.1 M. The impregnated solids were dried at 65 °C overnight and calcined at 200 °C for 2 h, giving rise to catalysts with a nominal load of 1.2% Pd (w). Palladium was reduced at 100 °C in H₂ atmosphere before the characterization of the catalysts and the reaction tests.

Materials Characterization

The porous texture was assessed from the nitrogen adsorption-desorption isotherms obtained in a Tristar II 3020 apparatus (micromeritics). Prior to nitrogen adsorption, the samples were degassed at 130 °C for at least 4 h under vacuum (~0.1 mbar). Surface area was calculated by the Brunauer–Emmet–Teller (BET) equation, external or non-microporous area and micropore volume were obtained from the t-plot and the Barrett-Joyner-Halenda (BJH) method was used for mesopores. Morphology was studied by transmission electron microscopy (TEM) with a JEM 2100 microscope. Chemical elemental analyses were performed in a LECO CHNS-932 apparatus, and thermogravimetric analyses (TGA) were carried out in air atmosphere at a heating rate of 5 °C min⁻¹ until 900 °C, using a Mettler-Toledo TGA/SDTA851e thermobalance. Oxidation state of Pd and chemical environments of N were determined by X-ray photoelectron spectroscopy (XPS) on a K-Alpha-Thermo Scientific spectrometer using monochromatic Al Kα radiation (12 kV, 6 A). The pass energy was 40 eV, energy step size was 0.1 eV and the number of scans were 400 for Pd 3d and N1s. The binding energies of the spectra were corrected using as standard the C 1s peak at 284.6 eV³⁰. The available surface palladium was characterized by CO chemisorption at room

temperature (PulseChemisorb 2705, Micromeritics) to determine metal dispersion assuming a Pd–CO stoichiometry of 1³¹.

Table 1. Bulk chemical and XPS elemental analysis of carbon samples and catalysts.

	Bulk chemical elemental analysis					Elemental analysis by XPS					
	C	H	N	N/C	H/C	C	O	N	Pd	N/C	Pd/C
	(% w)			(w/w)		(% w)				(w/w)	
C-blank	89.4	1.9	0.15	0.002	0.022	92.5	5.1	-	1.1	-	0.011
C-1N	90.8	1.6	1.06	0.011	0.018	89.8	5.4	0.9	1.0	0.010	0.011
C-17N	82.2	2.0	1.70	0.021	0.025	89.2	6.1	1.7	1.4	0.019	0.011

Hydrodechlorination experiments

The catalysts were tested in the aqueous phase HDC of 4-chlorophenol (4-CP), which was selected as target compound to facilitate comparison of the results with those reported in the literature for other catalysts. This reaction leads to phenol as primary HDC product and can continue through further hydrogenation giving rise to cyclohexanone (C-one) and cyclohexanol (C-ol). Blank experiments carried out with the metal-free support showed negligible 4-CP conversion, as shown in Fig. S1. The experiments were carried out in a glass stirred batch reactor using 0.150 L of ~0.1 g L⁻¹ 4-CP aqueous solution (for each experiment the exact concentration was determined at the initial time), 0.8–2.4 mg L⁻¹ of Pd, 50 NmL min⁻¹ hydrogen flow, constant stirring (800 rpm), ambient pressure and constant temperature within the 30–70 °C range. Homogeneous samples of around 1.2 mL were collected at different reaction times (0, 2, 5, 15, 30 minutes and 1, 2, 3 and 4 hours). The total volume withdrawn was less than 10% of the initial reaction volume. Samples were filtered and analyzed by GC-FID (GC 3900 Varian) using a capillary column (CP-Wax 52 CB, Varian) and N₂ as carrier gas. Mass balances closures of 80–100% were obtained.

A pseudo-first order rate equation was used to fit the experimental data for 4-CP disappearance. To compare the catalysts tested activity (α) was obtained as:

$$\alpha = \frac{k \cdot C_0}{w} \quad (1)$$

where C_0 represents the starting molar concentration of 4-CP, w the catalyst (active phase) concentration expressed as g Pd L⁻¹, and k the first-order rate constant of 4-CP disappearance according to:

$$C = C_0 e^{-k} \quad (2)$$

Results and discussion

Material characterization

The porous carbon materials prepared yielded different nitrogen contents, as shown by the elemental chemical analyses (Table 1). It can be seen that C-blank contains a small amount of nitrogen (0.15% w) that could not be measured by XPS. Although C-blank was synthesized using only the commercial phenolic resin as precursor, the nitrogen content may indicate that the resin contains some N-bearing additives. The elemental analyses from XPS show

equivalent proportions of C and O for all the carbon materials and are in good agreement with the chemical elemental analyses. The nitrogen contents obtained by both methods are very close, indicating a homogeneous distribution of nitrogen in the surface and in the bulk carbon. The XPS profile of N 1s region (Fig. 3) shows mainly pyridinic and pyrrolic N contributions in the case of the N-doped carbons, centered at 398.5 and 400.7 eV, respectively. Both C-1N and C-17N show similar contribution of those two species. Pyridinic oxide (402.8 eV) can also be appreciated in both cases, but in a low proportion. C-blank does not show a signal in the N 1s region, in agreement with the low N content. All the carbons showed quite similar TGA profiles in air (Fig. 4). The main weight loss was observed within the 425–600 °C range, with earlier decomposition in the case of the C-blank sample, but showing identical patterns in the case of the doped carbons. The insertion of nitrogen does not seem to provoke changes in structure leading to substantial differences in the TGA profiles.

The residual weight is around 10% of the initial mass, while the TGA analysis of the resin in air shows a residual weight around 1%, indicating that the templated carbons still contain some silica embedded in the carbon matrix, which was not removed by additional washing with sodium hydroxide. The isotherms show some significant uptake at low relative pressure, indicative of microporosity, and hysteresis loops at medium and high relative pressures indicating a relevant mesoporosity contribution. According to IUPAC classification, the isotherms would be a mix of type I at low pressures and IV isotherm at higher relative pressures

Fig. 3. XPS of N 1s of the carbon supports

Fig. 5. 77 K N₂ adsorption-desorption isotherm of the carbons

Fig. 4. TGA curves in air of carbons

Table 2. Porous texture of the carbons

	S_{BET}	S_{external}	V_{micro}	V_{meso}	$V_{\text{narrow meso}}$
Sample	$(\text{m}^2 \text{g}^{-1})$		$(\text{cm}^3 \text{g}^{-1})$		
C-blank	729	599	0.069	0.608	0.193
C-1N	870	733	0.093	0.739	0.238
C-17N	986	778	0.136	0.747	0.251

Fig. 6. Representative TEM images of prepared carbons: A) C-blank, B) C-1N; C) C-17N

Two well defined hysteresis loops can be identified: one at medium relative pressures, attributed to slit-shaped pores and another at higher relative pressure indicating the presence of layered particles. As can be seen in Table 2, most of the pore volume and surface area is associated to mesopores, being quite similar in all carbons, although nitrogen doping increased the micropore and narrow

mesopore volume. The images obtained by TEM (Fig. 6) show that the carbons prepared have similar morphology derived from the silica template, with no significant effect of nitrogen doping. The XPS spectra in the Pd 3d region (Fig. 7) show the distribution of Pd species in the metal phase. The $\text{Pd}^{\text{II}}/\text{Pd}^0$ ratio was always *circa* 0.8. This fact is important since both zero-valent and electron-deficient palladium species have been reported to contribute to activity in catalytic HDC³³. Elemental analyses from XPS yielded similar proportion of Pd, around 1% (Table 1), in the surface of all catalysts, which is very close to the nominal Pd content and indicates a homogenous distribution of the metallic phase in the catalyst particles. The dispersion of Pd, as obtained from CO chemisorption, is shown in Table 3. The results show similar dispersion values indicating that the metal nanoparticles size are in the same range. The dispersion values were closer in the case of the N-doped carbons. However, it was not possible to measure the nanoparticle size to double checked using TEM images, because of a low contrast between carbon support-Pd nanoparticles. On the basis of the carbon and metal phase characterization, it can be inferred that the catalysts prepared present equivalent textural characteristics in terms of pore distribution and available surface, and also equivalent Pd content and close nanoparticle size.

Fig. 7. XPS of Pd 3d of the catalysts

Table 3. Pd dispersion of the catalysts from CO chemisorption

Sample	Dispersion (%)	Mean Pd particle size (nm)
C-blank/Pd	28	3.9
C-1N/Pd	19	6.0
C-17N/Pd	16	7.0

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Fig. 8. Time course of 4-CP concentration (■), phenol (●) and cyclohexanone (▲) in the HDC experiments (2.4 mg Pd L^{-1} , $[4\text{-CP}]_0 = 100 \text{ mg L}^{-1}$; $T = 30^\circ \text{C}$)

Table 4. Kinetic values of the pseudo first-order rate constant and initial rate of 4-CP disappearance from the preliminary HDC test at 2.4 and 0.8 mg Pd L⁻¹ and 30 °C

Catalysts	2.4 mg L^{-1}			0.8 mg L^{-1}		
	$k \text{ (min}^{-1}\text{)}$	r^2	$a^a \text{ (mmol g}^{-1} \text{ min}^{-1}\text{)}$	$k \text{ (min}^{-1}\text{)}$	r^2	$a^a \text{ (mmol g}^{-1} \text{ min}^{-1}\text{)}$
C-blank/Pd	0.1546	0.997	49	0.032	0.998	26
C-1N/Pd	0.1213	0.97	59	0.037	0.98	35
C-17N/Pd	0.1957	0.98	84	0.046	0.998	49

The most important difference among the three synthesized catalysts is the nitrogen content, thus making them ideal for analyzing the influence of nitrogen doping on the catalytic performance.

Hydrodechlorination of 4-chlorophenol

Effect of nitrogen doping on the catalytic activity at room temperature. The three catalysts prepared were tested in the HDC of 4-CP. Preliminary reaction tests were carried out using a catalyst concentration of 2.4 mg Pd L^{-1} and 30°C . The evolution of the concentration of 4-CP and the resulting products along the reaction time is shown in Fig. 8. In the three cases a rapid and complete disappearance of 4-CP was observed, being phenol the only reaction product. Some cyclohexanone was also detected in the reaction experiments with C-blank/Pd and C-17N/Pd at reaction times beyond 4 h. Some authors reported that nitrogen-doped carbons promote hydrogenation, but only when the contribution of quaternary nitrogen is relevant¹². In the current study the nitrogen groups identified were mainly pyridinic and pyrrolic.

The experimental data were adjusted to a pseudo-first order rate equation and the values of the kinetic constant and catalytic activity were obtained. The results are summarized in Table 4, showing an increase of the kinetic constant at increasing nitrogen content in the carbon support. The catalytic activity increased from $46 \text{ mmol g}^{-1} \text{ Pd min}^{-1}$ for the catalyst with non-doped support

(C-blank/Pd) to $82 \text{ mmol g}^{-1} \text{ Pd min}^{-1}$ for the catalyst with the support of higher nitrogen content (C-17N/Pd).

On the other hand, carbon doping can affect to the structure of the metal phase³⁴. The heteroatom can create a significant effect over the electronic state of the metal³⁵, providing active sites and affecting the binding energy between doped carbon and the metal³⁶. Baeza et al. studied the hydrodechlorination of 4-CP at 30°C with Pd catalysts supported on N-doped carbon blacks with very low surface area. They reported an enhancement of activity thanks to N-doping, but with lower values, around $56 \text{ mmol g}^{-1} \text{ Pd min}^{-1}$, under equivalent reaction conditions¹¹. The significant differences with the current work may be related to the surface area and the electronic state of nitrogen. **There is no clear consensus in literature on the reasons for the enhancement of activity through N-doped carbons. Some authors indicate that heteroatoms can act as active centers for the adsorption of reactants, particularly with those including -OH groups^{15, 37}. Liu et al.³⁸ attributed higher activity in phenol hydrogenation to the lower size of Pd nanoparticles formed on nitrogen-doped carbon nanotubes. Likewise, Tang et al.³⁹ showed that in addition to Pd dispersion nitrogen doping leads to C-N-C hybrid rings that can interact with substrates containing electron-rich carbon rings, increasing the reaction activity.**

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Table 5. Kinetic parameters and activity values for the HDC of 4-CP with the catalyst tested at different temperatures.

	T (°C)	k (min ⁻¹)	R ²	E _a (kJ mol ⁻¹)	Activity (mmol g ⁻¹ min ⁻¹)
C-blank/Pd	30	0.032	0.998		26
	50	0.11	0.98	32.2±6.8	100
	70	0.13	0.997		131
C-1N/Pd	30	0.037	0.98		35
	50	0.046	0.997	25.1±3.9	44
	70	0.12	0.996		119
C-17N/Pd	30	0.046	0.998		49
	50	0.071	0.97	16.2±0.3	63
	70	0.098	0.995		102

Table 4 also show that when the concentration of metal in the reaction medium decreased from 2.4 to 0.8 mg L⁻¹ the rate constants decreased, but interestingly, the catalytic activity decreased by 39–43%. The specific activity values (metal weight normalized) should not change with Pd concentration, thus the results suggest that some changes in the control regime may have occurred. In this sense, the existence of gas-liquid and liquid-catalyst mass-transfer limitations were evaluated through the estimation of Carberry number, and also the intraparticle mass-transfer limitations using the Weisz-Prater criterion. In all cases the estimations do not support relevant contribution of mass transfer limitations (Electronic Supplementary Information). Regarding the selectivity, phenol was the only product detected in the reactions carried out with a metal concentration of 0.8 mg L⁻¹, regardless the nitrogen concentration in the carbon support. This is probably due to a lower availability of active centers in the reaction medium, and also to the competition between 4-CP HDC and phenol hydrogenation, as it has been previously reported for Pd and Rh catalysts^{40,41}. A metal concentration of 0.8 mg L⁻¹ was selected for the rest of the study in order to focus on the HDC reaction, avoiding subsequent hydrogenation of the phenol primarily produced.

Combined effect of temperature and N-doping. Activity values were calculated in the 30–70 °C range for a Pd concentration of 0.8 mg L⁻¹ from the kinetic constant obtained by fitting of 4-CP disappearance data (Fig. 25) to a pseudo-first order rate equation. Cyclohexanol and cyclohexanone were not observed among the reaction products even at the highest temperature. The results, given in Table 5, show that the presence of nitrogen in the carbon supports boosts the activity of the catalysts at low temperatures. However, the activity of the catalysts with doped support increased less when the temperature was risen. In fact, at the highest temperature (70 °C) the catalyst with non-doped support (C-blank/Pd) exhibited the highest activity. Therefore, nitrogen doping of the carbon support is of interest if catalysts with high activity at mild temperature conditions are the objective, whereas non-doped supports are more convenient for the intensification of the process

Fig. 9. Adsorption and HDC experiments with C-blank/Pd (up) and C-17N/Pd (down)

by increasing the reaction. Accordingly, the apparent activation energy decreased as the nitrogen content of the carbon support increased. The activation energies for C-blank/Pd (32.2 kJ mol⁻¹) and C-1N/Pd (25.1 kJ mol⁻¹) are in the low range reported for other precious metals catalysts tested in the HDC of 4-CP: 25.42 kJ mol⁻¹ for Rh/pillared-clay⁴²; 85.2 kJ mol⁻¹ for Pd/pillared-clay⁴³; 24.82 kJ mol⁻¹ for Pd/AC⁴⁴; 41.2 kJ mol⁻¹ for Ru/AC⁴⁵; 41.22 kJ mol⁻¹ for Pd/C at 0–30 °C⁴⁶ and 47.51 and 58.2 kJ mol⁻¹ for Pd/Al₂O₃, Rh/AC and Pt/AC, respectively¹. However, the value obtained for C-17N/Pd (16.2 kJ mol⁻¹) is one of the lowest reported in literature so far. The value is also below the typical range for chemical reactions, even though negligible contribution of mass transfer to the overall rate was estimated (Supplementary information). Similar values of activation energy for the adsorption of 4-CP on Pd/C catalysts were reported by Munoz et al.^{47,48}, who indicated that the HDC of 4-CP is highly influenced by adsorption. The possible contribution of the adsorption of 4-CP and phenol was evaluated by suspending C-blank/Pd and C-17N/Pd catalysts in a synthetic reaction medium consisting of a mixture of 4-CP and phenol for 2 h at 70 °C in absence of H₂. C-blank/Pd and C-17N/Pd adsorbed 18 and 11% of initial 4-CP, respectively. In the case of phenol, a higher adsorption was observed for C-blank/Pd (~32%) than for C-17N/Pd (~3%). These results suggest indicate a lower affinity of the catalyst for the compounds studied when the carbon supports are doped. After exposure of the catalysts to the synthetic reaction medium for two hours, hydrogen was introduced in the system. For both catalysts the initial rate was slightly higher than in former experiments due to adsorption of 4-CP, thus showing that phenol adsorption does not cause deactivation or competition (Fig. 9).

Conclusions

Nitrogen-doped and non-doped mesoporous carbon materials were synthesized by templating method with MSU-F silica. This approach allowed us to obtain carbons with different nitrogen content (0.15–1.7%w.), equivalent pore structure and similar N species (mainly pyridinic and pyrrolic groups). The tailored materials were

used to learn about the role of nitrogen doping on the activity of Pd/C catalysts, since the set of catalysts prepared were free from the crossed-effect of chemical composition, textural properties and morphology.

Testing of the catalysts in the hydrodechlorination of 4-CP in aqueous phase showed a clear increase of activity at 30 °C thanks to nitrogen doping of the support. However, intensification of the process by increasing temperature can be better achieved with the catalyst with non-doped supports, as the catalyst with non-doped support were the most active at 70 °C. Low apparent activation energy values were obtained, especially in the case of the catalysts with nitrogen-doped support, supporting contribution of physical phenomena to the overall rate. Nitrogen-doping was also found to decrease the affinity of the catalysts for 4-CP and phenol.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors also thank to Hexion Speciality Chemicals Iberica S.A. for providing them the resol resin Bakelite®PF9934 FL. The authors thank financial support (CTQ2012-32821, CTQ2015-65491_R) and C. Ruiz-García for PhD grant (BES-2013-06608 5) to MINECO.

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A **B** **C**

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147x171mm (300 x 300 DPI)

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Table of Contents

Improved catalytic activity in the hydrodechlorination reaction at room temperature with N-doped carbon as support of Pd nanoparticles

Electronic Supplementary Material

Enhancement of the activity of Pd/C catalysts in aqueous phase hydrodechlorination through doping of carbon supports

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1. Supplementary figures

Figure 1S. Hydrodechlorination reaction at 70 °C using carbon C-17N as catalyst

Figure 2S. Time evolution of 4-CPh (■) and phenol (●) concentration in hydrodechlorination reaction at 30, 50 and 70 °C (0.8 g Pd L⁻¹)

2. Verification of the control regime

The possible existence of mass-transfer limitations was analyzed following the procedure and expressions summarized in Table 1S¹⁻⁵.

		Table
Gas-liquid mass transfer	$D = 7.4 \cdot 10^{-8} \frac{(\varphi M)^{1/2} T}{\mu V_i^{0.6}}$	1S.
	$k_L a = 1.26 10^{-5} (D m_{H_2} \mu^{-0.9} \rho^{0.9} \sigma^{0.1} N^{1.7} d_i^{1.4})$	Stages
	$Ca_{G-L} = \frac{k}{k_{lav}}$	and
4-CP external diffusion		express
		ions
	$Re = \frac{\rho N d_I^2}{\mu} \quad Sc = \frac{\mu}{\rho D}$	used to
	$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}$	evaluat
4-CP Internal diffusion	$Sh = \frac{k_s d_p}{D}$	e
	$Ca_{L-S} = \frac{k}{k_s a_p}$	possibl
	$D_e \sim \frac{1}{10} D$	e mass
	$(\phi_s)^2 = \left(\frac{d_p}{6}\right)^2 \frac{k}{D_e}$	transfe
		r
		limitati
		ons.

Nomenclature	
a_p	volumetric area of the catalyst ($m^2 m^{-3}$)
Ca_{G-L}	Carberry number for gas-liquid mass transport
Ca_{L-S}	Carberry number for liquid-solid mass transport
d_i	diameter of stirrer (m)
d_p	particle diameter of the catalyst (m)
D	diffusion coefficient, ($m^2 s^{-1}$)
D_e	effective diffusion coefficient, ($m^2 s^{-1}$)
k	kinetic constant (s^{-1})
k_{La}	volumetric gas-liquid mass transfer coefficient (s^{-1})
k_s	liquid to solid mass transfer coefficient ($m s^{-1}$)
M	molecular weight
N	stirring velocity (s^{-1})
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
T	temperatura (K)
V_i	volumen of species i in water at normal conditions boiling ($cm^3 mol^{-1}$)
φ	association factor, 2.6 for water
μ	viscosity of the liquid phase($kg m^{-1} s^{-1}$) $7.98 \cdot 10^{-4}$ – $4.04 \cdot 10^{-4}$
ρ	density of the liquid phase ($kg m^{-3}$) 995.71–977.63
σ	liquid surface tension of the liquid phase ($kg s^{-2}$) $7.18 \cdot 10^{-2}$ – $6.50 \cdot 10^{-2}$
ϕ_s	Weisz-Prater parameter

As indicated before, the activation energy values obtained are in the low range reported in the literature, especially in the case of the C-17N/Pd catalyst. One possible cause could be the existence of mass-transfer limitations in the corresponding experiments. The potential contributions to the mass transfer limitations are: i) external diffusion, including H₂ gas-liquid transfer, as well as H₂ and 4-CP transport from the liquid phase to the surface of the catalyst, and ii) intraparticle diffusion throughout the pores of the catalyst. Diffusion coefficients were calculated by the Wilke-Chang correlation ¹, being an important parameter in the estimation of volumetric gas-liquid mass transfer coefficient (k_{La}), liquid to solid mass transfer coefficient (k_s), and Weisz-Prater parameter (ϕ)².

Table 2S. Mass transfer-related coefficients

T (K)	D H ₂ ($m^2 s^{-1}$)	D 4CP ($m^2 s^{-1}$)	k_{La} (s^{-1})	k_s H ₂ (s^{-1})	k_s 4CP (s^{-1})
303	$3.89 \cdot 10^{-9}$	$1.07 \cdot 10^{-9}$	$0.46 \cdot 10^{-1}$	13.0	5.8
323	$6.05 \cdot 10^{-9}$	$1.67 \cdot 10^{-9}$	$0.70 \cdot 10^{-1}$	21.1	9.1
343	$8.70 \cdot 10^{-9}$	$2.40 \cdot 10^{-9}$	$0.97 \cdot 10^{-1}$	31.1	12.0

The values of Table 2S were used to estimate the Carberry number (Ca) in order to learn on the gas-liquid mass transfer. Following the procedure and expressions summarized in Table 1S, the values of the Carberry number shown in Table 3S were obtained. The stirring velocity used in the experiments was 800 rpm, enough to avoid external mass-transfer limitations, according to previous works where an equivalent experimental set-up was used at 600 rpm⁶. This is confirmed by the Ca_{G-L} values obtained, all of them well below 0.1, indicative of no limitations regarding gas-liquid mass transfer.

Table 3S. Values of the Carberry numbers (Ca) at different temperature and catalyst concentrations

T (°C)	sample	0.8 mg Pd/L			2.4 mg Pd/L		
		Ca_{G-L}	Ca_{L-S}		Ca_{G-L}	Ca_{L-S}	
			H ₂	4-CP		H ₂	4-CP
30	C-blank	$1.2 \cdot 10^{-2}$	$1.0 \cdot 10^{-7}$	$2.5 \cdot 10^{-7}$	$5.5 \cdot 10^{-2}$	$1.6 \cdot 10^{-7}$	$3.9 \cdot 10^{-7}$
	C-1N	$1.3 \cdot 10^{-2}$	$1.0 \cdot 10^{-7}$	$2.9 \cdot 10^{-7}$	$4.4 \cdot 10^{-2}$	$1.3 \cdot 10^{-7}$	$3.1 \cdot 10^{-7}$
	C-17N	$1.7 \cdot 10^{-2}$	$1.5 \cdot 10^{-7}$	$3.6 \cdot 10^{-7}$	$7.1 \cdot 10^{-2}$	$2.1 \cdot 10^{-7}$	$5.0 \cdot 10^{-7}$
50	C-blank	$2.2 \cdot 10^{-2}$	$2.7 \cdot 10^{-7}$	$6.3 \cdot 10^{-7}$	-	-	-
	C-1N	$1.4 \cdot 10^{-2}$	$1.7 \cdot 10^{-7}$	$4.0 \cdot 10^{-7}$	-	-	-
	C-17N	$1.7 \cdot 10^{-2}$	$2.0 \cdot 10^{-7}$	$4.8 \cdot 10^{-7}$	-	-	-
70	C-blank	$2.4 \cdot 10^{-2}$	$1.7 \cdot 10^{-7}$	$4.2 \cdot 10^{-7}$			
	C-1N	$2.0 \cdot 10^{-2}$	$1.5 \cdot 10^{-7}$	$3.5 \cdot 10^{-7}$			
	C-17N	$1.7 \cdot 10^{-2}$	$1.2 \cdot 10^{-7}$	$2.9 \cdot 10^{-7}$			

The possible occurrence of intraparticle mass-transfer limitations was evaluated from the Weisz-Prater criterion assuming spherical catalyst particles. The values obtained for the Weisz-Prater parameter (Table 4S) were always much lower than 1, which means that intraparticle diffusion limitations can be neglected for all the catalyst tested within the experimental temperatures range.

Table 4S. Weisz-Prater parameter $(\phi_s)^2$ to check intraparticle mass transfer limitation at different temperatures and catalyst concentrations

		0.8 mg Pd L ⁻¹		2.4 mg Pd L ⁻¹	
T (°C)	samples	$(\phi_s)^2$			
		H ₂	4-CP	H ₂	4-CP
30	C-blank	2.3·10 ⁻⁴	4.4·10 ⁻⁴	5.1·10 ⁻⁴	9.6·10 ⁻⁴
	C-1N	2.5·10 ⁻⁴	4.7·10 ⁻⁴	4.5·10 ⁻⁴	8.6·10 ⁻⁴
	C-17N	2.8·10 ⁻⁴	5.3·10 ⁻⁴	5.7·10 ⁻⁴	1.1·10 ⁻³
50	C-blank	3.9·10 ⁻⁴	7.6·10 ⁻⁴	-	-
	C-1N	3.2·10 ⁻⁴	6.0·10 ⁻⁴	-	-
	C-17N	3.5·10 ⁻⁴	6.6·10 ⁻⁴	-	-
70	C-blank	3.8·10 ⁻⁴	6.1·10 ⁻⁴	-	-
	C-1N	3.2·10 ⁻⁴	5.6·10 ⁻⁴	-	-
	C-17N	2.7·10 ⁻⁴	5.2·10 ⁻⁴	-	-

The estimations above supports that the HDC experiments took place absence or with low contribution of mass transfer limitations.

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