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

Industrial and Engineering Chemistry Research 58.11 (2019): 4355-4363

**DOI:** <https://doi.org/10.1021/acs.iecr.8b06084>

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# N-doped CMK-3 carbons supporting palladium nanoparticles as catalysts for hydrodechlorination

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## ABSTRACT

The effect of nitrogen doping of a carbon support on the activity of Pd catalysts in the hydrodechlorination of 4-chlorophenol in water has been studied. Highly mesoporous CMK-3 carbons have been synthesized by infiltration of a commercial resol resin into SBA-15 silica followed by pyrolysis at 700 °C and removal of the template with NaOH. Nitrogen-doping was achieved by infiltrating 1,10-phenantroline together with the resin. Equivalent porous texture and Pd nanoparticles size were obtained for the catalysts based on undoped and nitrogen-doped CMK-3 carbons. The catalysts allowed fast 4-chlorophenol hydrodechlorination with exclusive selectivity to phenol. A higher activity was observed at 30 °C for the catalyst with the N-doped support ( $76\text{--}81\text{ mmol}\cdot\text{g}^{-1}\text{ Pd}\cdot\text{min}^{-1}$ ), showing the beneficial effect of nitrogen doping of the carbon supports. The different catalytic was also evidenced by the activation energies calculated for the catalysts with undoped ( $53\text{ kJ}\cdot\text{mol}^{-1}$ ) and N-doped CMK-3 carbon ( $36\text{ kJ}\cdot\text{mol}^{-1}$ ) in the 30—70 °C temperature range.

**KEYWORDS:** Hydrodechlorination, carbon, carbon N-doped, catalysis

## 1. INTRODUCTION

The control of hazardous pollutants is one of the main current issues regarding the protection of water bodies. The development of efficient techniques for that purpose has received extensive research attention accordingly. In this context, catalytic treatments have achieved a strong position in the pool of the ready-to-use technologies for the remediation of water pollution <sup>1</sup>. Among them, reductive catalysis usually offers selective conversion of the pollutants to less or non-harmful and more readily biodegradable substances. Thus, catalytic hydrodechlorination with hydrogen is considered as an efficient and environmentally friendly approach to deal with halogenated organics <sup>2</sup>. The operation at mild conditions and the possibility of covering a broad range of pollutants concentration are some of the main advantages of this emerging technology <sup>3</sup>.

Particular attention has been paid to the hydrodechlorination of chlorophenols, a group of toxic and poorly biodegradable pollutants that can be found in different industrial wastewaters <sup>3,4</sup>. Hydrodechlorination can be used as a detoxifying pretreatment prior to biological or advanced oxidation processes <sup>5</sup>. A number of catalytic systems have been reported as active for aqueous phase hydrodechlorination. Pd, Pt and Rh nanoparticles are the most used active phases <sup>6,7</sup>, which are usually supported on silica, carbons, alumina, or clays <sup>7,8</sup>, among other materials. Hydrodechlorination has been claimed as a structure sensitive reaction <sup>6,9,10</sup>, therefore it is important to tailor the catalyst with a well-defined size and shape of the metal nanoparticles, and also to achieve good dispersion and stability of them over the support.

The composition, size and microstructure of the support have also been shown to affect significantly the activity and selectivity of the catalyst. Carbon materials are considered as excellent catalyst supports, especially for hydrodechlorination, due to their textural characteristics, high thermal and chemical stability, availability and modifiable properties <sup>11,12</sup>. The development of support materials with large specific surface area, good flow-through diffusion structure and physicochemical stability has attracted much attention <sup>13</sup>. Conventional porous carbon materials, mainly activated carbons, exhibit a non-structured pore texture with highly prevalent microporosity that can be partially blocked even by the

active phase, hindering the diffusion of reactants and products. However, carbon materials with well-defined and purpose-optimized porous structure can be prepared by templating <sup>14,15</sup>. This is the case of CMK-3 carbons, obtained as the inverse replica of a SBA-15 template. They show large and ordered mesoporosity with morphology of interconnected rods <sup>16,17</sup>. Taking into account that mesoporosity is of great importance in liquid phase heterogeneous catalysis, CMK-3 can be postulated as a good candidate support for metal catalysts used in aqueous phase hydrodechlorination. Valles et al. (2017) <sup>18</sup> showed that CMK-3 carbons with high surface area and pore volume favoured the dispersion of noble metals onto the carbon framework, allowing good activity and selectivity in the hydrogenation of tetralin.

Regarding the composition of carbon supports, doping of carbonaceous materials with heteroatoms (e.g. N, B, or P) has been proven as an effective approach to tailor their surface properties for enhanced performance of the resulting catalyst <sup>19</sup>. Thus, the dispersion of metallic active phases can be improved through the functionalization of the carbon support <sup>20</sup>. Moreover, doping and functionalization of carbon materials with N can contribute to the stability of the supported metal nanoparticles, thus minimizing leaching and loss of catalytic activity <sup>21</sup>.

The aim of the current work it is to study the effect of nitrogen doping of a carbon support on the activity of Pd catalysts in the hydrodechlorination of 4-chlorophenol (4-CP) in aqueous phase. Undoped and N-doped CMK-3 carbons were prepared and used as supports of Pd NPs for the aforementioned reaction. CMK-3 carbons were selected to minimize mass transfer limitations thanks to their mesoporosity and excellent pore interconnectivity.

## 2. EXPERIMENTAL

### 2.1. *Preparation of carbon supports and catalyst*

CMK-3 carbons were prepared by infiltrating 1.5 g of resol resin (Bakelite®PF9934 FL, Hexion Specialty Chemicals Iberica S.A.) into 1 g of SBA-15 (mesostructured, SiO<sub>2</sub> 99%,

Sigma-Aldrich). The resol resin was dissolved in 100 mL of ethanol (99.8%, Sigma-Aldrich) and infiltration was carried out using a rotary vacuum evaporator (100 mbar and 40 °C). Nitrogen-doped CMK-3, named N-CMK-3 hereafter, was prepared adding 0.10 g of 1,10-phenantroline (99%, Sigma-Aldrich) to the resol resin solution. The resin-infiltrated silica samples were heated at 135 °C for 1 h in air to cure the resin, then pyrolyzed at 700 °C for 1 h in nitrogen atmosphere. This temperature was reached at a heating rate of 5 °C min<sup>-1</sup>. The SBA-15 template was removed by washing with NaOH solution (3.5 M) for 15 h and the remaining carbon was filtered (0.45 µm Nylon filter), washed with water until neutral pH and oven-dried at 65 °C. The resulting carbons were grinded gently in a ball mill just to break particle aggregates.

Pd nanoparticles synthesized by incipient wetness impregnation of CMK-3 carbons to obtain a catalyst with a 1.2 %w. Pd nominal load. The CMK-3 and N-CMK-3 carbons were impregnated with a volume of PdCl<sub>2</sub> aqueous solution 1.3 times the pore volume of the support, dried at 65 °C overnight, calcined at 200 °C and reduced at 100 °C in H<sub>2</sub> atmosphere for 1 h (Figure 1).

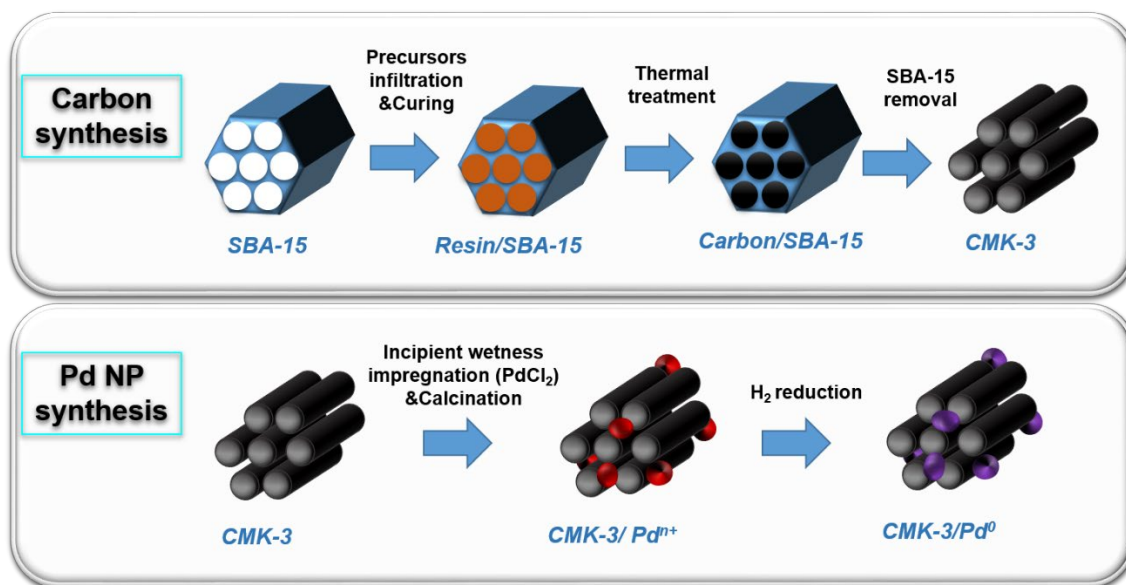


Figure 1. Scheme of the synthesis of CMK-3 carbons and catalysts.

## **2.2. *Materials Characterization***

The chemical elemental analyses were performed in a LECO CHNS-932 apparatus. X-ray photoelectron spectroscopy (XPS) was used to study the elemental composition of surface and the chemical state of nitrogen. A K-Alpha-Thermo Scientific spectrometer with monochromatic Al K $\alpha$  radiation (12 kV, 6 mA) was used with a pass energy of 40 eV, energy step size of 0.1 eV and 150 scans for N 1s. The binding energies of the spectra were corrected using the C 1s peak at 284.6 eV as standard <sup>22</sup>. Nitrogen adsorption-desorption isotherms were obtained at 77 K in a Tristar II 3020 apparatus (Micromeritics). Samples were degassed at 150 °C for at least 4 h under vacuum (~ 0.1 mbar). BET equation and t-plot method were used to calculate the surface area and the external or non-microporous area, respectively. Micropore and mesopore volumes were obtained using the t-plot and the Barrett-Joyner-Halenda (BJH) methods. The morphology of the carbons and the Pd nanoparticles was studied by transmission electron microscopy (TEM) with a JEM 2100 microscope (40 kV).

## **2.3. *Hydrodechlorination experiments***

The catalysts prepared were used in the hydrodechlorination of 4-CP in aqueous phase using a three-necked jacketed glass batch reactor with a reaction volume of 0.150 L. Previous studies carried out with related catalyst showed there were not necessary to employ baffles to avoid vortex formation and swirling flow during the reaction under the operating conditions selected<sup>23</sup>. A magnetic stirrer spinning at a rate of 800 rpm was used to minimize external mass transfer limitations, as it was checked in preliminary experiments. A continuous hydrogen flow of 50 NmL min<sup>-1</sup> was maintained throughout the reaction time. The stripping of 4-CP and reaction products was confirmed negligible. The concentration of metallic Pd in the reaction medium ( $C_{Pd}$ ) was varied between 0.85 and 5.93 mg L<sup>-1</sup>, and the effect of reaction temperature was tested in the 30–70 °C range. Samples were collected at intervals of reaction time, amounting a total withdrawn volume lower than 10% of the initial reaction volume. The samples were filtered and analyzed by HPLC (Prostar, Varian), using a C18 column at 40 °C to determine 4-CP and phenol

concentration ( $C_{4-CP}$  and  $C_P$ ). The concentration of Pd in the reaction medium was below the TXRF detection limit, indicating negligible leaching.

The initial concentration of 4-CP ( $C_{4-CP_0}$ ) was around  $0.75 \text{ mmol} \cdot \text{L}^{-1}$  and it was determined by analysis in each experiment. In all cases, the experimental data of 4-CP disappearance were fitted to a pseudo-first-order rate equation. The activity ( $a$ ) of the catalysts was calculated from the pseudo-first-order kinetic constants ( $k$ ) as indicated in Equation 2. It reflects the mmol of 4-CP converted per minute and per mass of metal catalyst in the hydrodechlorination reaction. The normalization of the reaction rate using the mass of metal makes possible to compare catalysts tested using different concentration of metal in the reaction medium. The apparent activation energy ( $E_a$ ) was calculated from the Arrhenius's equation:

$$C_{4-CP} = C_{4-CP_0} e^{-kt} \quad (1)$$

$$a \text{ (mmol/ g Pd} \cdot \text{min)} = k \cdot (C_{4-CP_0}/C_{Pd}) \quad (2)$$

$$k = k_0 \cdot e^{(-E_a/RT)} \quad (3)$$

The conditions for mass transfer in the gas-liquid and liquid-solid interphase were evaluated by the  $Ca_{G-L}$  and  $Ca_{L-S}$  Carberry numbers, respectively. <sup>6, 24.</sup>

$$Ca_{G-L} = k/k_L a_v \quad (4)$$

$$Ca_{L-S} = k/k_S a_p \quad (5)$$

The value of the volumetric gas-liquid mass transfer coefficient ( $k_L a_v$ ) was estimated by <sup>25.</sup>

$$k_L a_v = 1.2610^{-5} (Dm_{H_2} \mu^{-0.9} \rho^{0.9} \sigma^{0.1} N^{1.7} d_i^{1.4}) \quad (6)$$

The liquid-to-solid mass transfer coefficient ( $k_s$ ) was estimated from Sherwood (Sh), Reynolds (Re) and Schmidt (Sc) numbers <sup>26</sup> and the diffusion coefficient (D) <sup>27</sup> by:

$$Sh = k_s d_p / D \quad (7)$$

$$Re = \rho N d_i^2 / \mu \quad (8)$$

$$Sc = \mu / \rho D \quad (9)$$

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \quad (10)$$

$$D = 7,4 \cdot 10^{-8} \cdot ((\varphi M)^{1/2} T / \mu V_i^{0.6}) \quad (11)$$

The contribution of internal diffusion to the overall rate was estimated from the Weisz–Prater parameter  $(\phi_s)^2$ , assuming spherical catalyst particles and estimating the effective diffusion coefficient ( $D_e$ ) as 10% of the diffusion coefficient ( $D$ ):

$$(\phi_s)^2 = L^2 \cdot (k/D_e) \quad (12)$$

### 3. RESULTS AND DISCUSSION

#### 3.1. Carbons and catalysts characterization

The undoped and doped carbons prepared did not show any differences in terms of handling and external appearance. The CMK-3 carbon obtained using only resol resin as the starting material contained a small amount of nitrogen (c.a. 0.07 % w, Table 1), which can be attributed to the nitrogen-containing additives of the commercial resin. Nitrogen was successfully inserted in the N-CMK-3 carbon thanks to the co-pyrolysis of the resol resin and 1,10-phenantroline infiltrated in the SBA-15 template. The elemental analysis yielded 1.2 %w of nitrogen.

*Table 1. Elemental analysis and porous texture of the CMK-3 carbons.*

	Chemical elemental analysis			Porous texture				
	C	H	N	S <sub>BET</sub>	S <sub>EXT</sub>	V <sub>meso</sub>	V <sub>micro</sub>	$\bar{d}_{BJH}$
	(%w)			(m <sup>2</sup> ·g <sup>-1</sup> )		(cm <sup>3</sup> ·g <sup>-1</sup> )		(nm)
CMK-3	88.7	2.2	0.07	1226	620	0.58	0.40	3.7
N-CMK-3	85.5	2.3	1.2	1144	671	0.60	0.36	3.5

The **high resolution** XPS spectrum of N 1s region (Figure 2) **can be fitted by three peaks, which can be associated to** pyrrolic (N-5 **at 398.5 eV**), pyridinic (N-6 **at 400.7 eV**) and pyridinic N-oxide (N-6-ox **at 402.5 eV**), **according to literature** <sup>28,29</sup>. The main contribution in terms of atomic content was that of N-5 (54 %), followed by N-6 (36%) and N-6-ox (10%). The presence of these species in N-CMK-3 can be attributed to the doping process, since the corresponding signals were not significant in the spectrum of CMK-3.



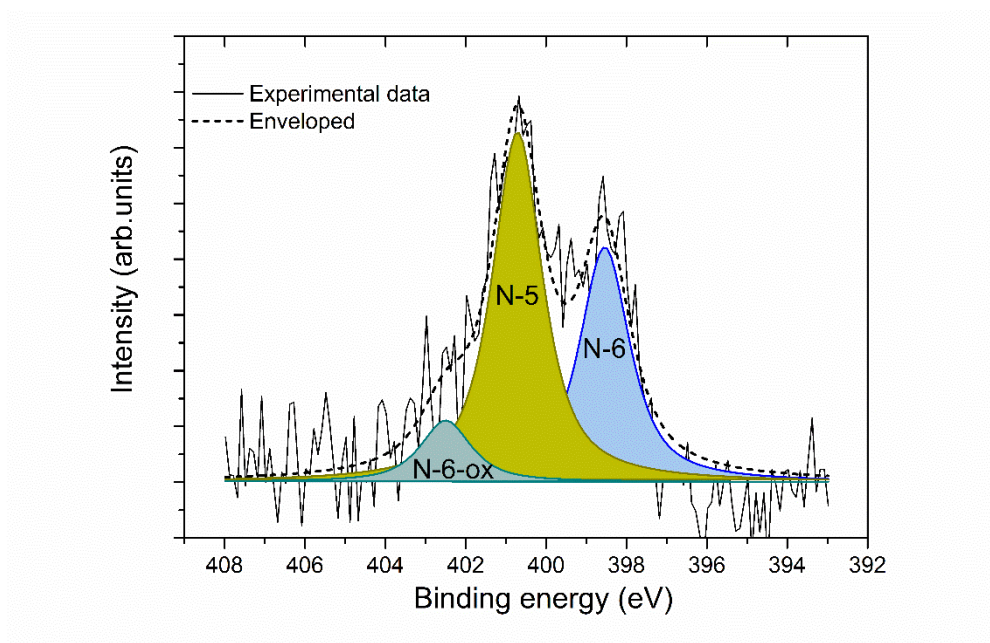


Figure 2. XPS spectrum in the N 1s region of the N-CMK-3 carbon.

The N<sub>2</sub> adsorption-desorption isotherms evidence quite similar pore texture for the CMK-3 and N-CMK-3 carbons (Figure 3, Table 1). It can be seen only some small reduction of the total ( $S_{\text{BET}}$ ) surface area upon N-doping, which could be due to the insertion of N functionalities in the mouth of some micropores, as suggested by the small reduction in the micropore volume available for N<sub>2</sub> adsorption. The shape of the isotherms can be interpreted as a combination of type I at low relative pressures and type IV at medium and high relative pressures. Furthermore, a slight hysteresis cycle can be observed, suggesting low contribution of the condensation in mesopores <sup>30,31</sup>. The values of external and non-microporous area were similar for both carbons and indicate a fairly high contribution of mesoporosity, is a very interesting feature for liquid-phase heterogeneous catalysis. The characterization of these materials indicates that the procedure used for the preparation of the N-doped and undoped CMK-3 carbons leads to reproducible and equivalent porous texture and therefore allows studying the effect of N-doping without any interference of the textural characteristics.

The impregnation of Pd at a nominal load as low as 1.2 % (w, carbon basis) can be assumed to cause only minor changes in the porosity of the catalysts respect to the support, mainly in the

mesopore range. This minor change has been observed previously in our previous works where Pd and Pt were impregnated on highly mesoporous supports <sup>32,33</sup>.

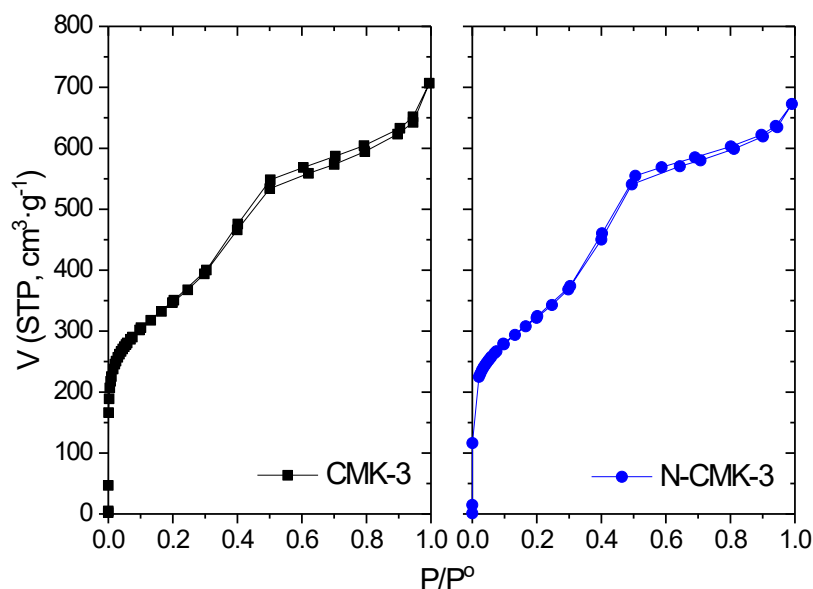


Figure 3. 77 K  $N_2$  adsorption-desorption isotherms of CMK-3 and N-CMK-3.

The carbons and catalysts prepared were also studied by TEM, to examine the internal structure conferred by the support and to learn on the size and morphology of Pd nanoparticles. Figures 4A-4C show representative TEM micrographs of CMK-3 and N-CMK-3. The morphology of the carbon particles, derived from that of the template, can be distinguished. These carbon particles show around 0.6  $\mu\text{m}$  length (Figure 4B), very close to that of the starting SBA-15, indicating that the gentle grinding of the carbon did not affect significantly to the particle size and morphology. The resol resin infiltrated in the cylindrical pores of the SBA-15 template yielded well defined arrays of carbon rods upon pyrolysis.

The mesoporosity of the material is mostly conferred by the void spaces among the nanorods, which also enables a good pore connectivity. Carbon nanorods show high contrast in TEM images due to the high yield (>70%) in the pyrolysis of the phenolic resin precursor. The high magnification imaging of the catalysts (e.g. Figure 4D) shows well-dispersed Pd nanoparticles with globular morphology on the surface of the support. Calculation of metal nanoparticle size is subjected to some uncertainty due to small size

and little difference between the contrast of the metal nanoparticles and the carbon nonorods. The mean size of the nanoparticles in the catalyst N-CMK-3/Pd was  $2.6 \pm 1.0$  nm. A similar situation was observed for CMK-3.

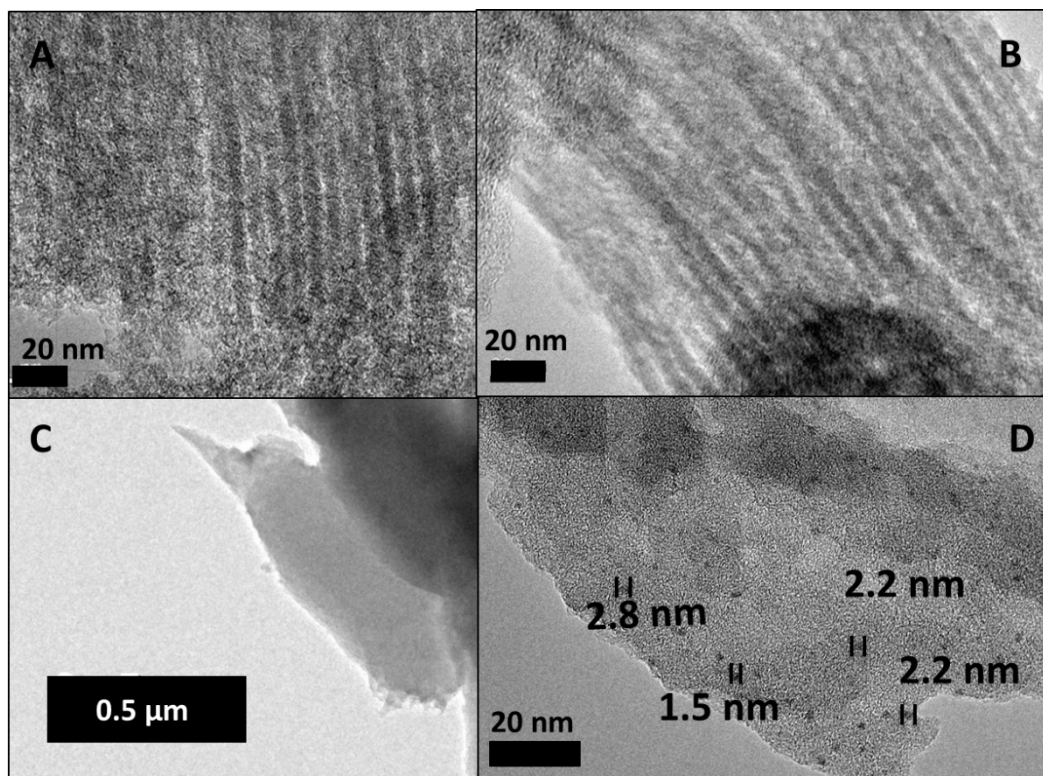


Figure 4. TEM micrographs of A-B) CMK-3, C) N-CMK-3, and D) N-CMK-3/Pd.

### 3.2. Hydrodechlorination results

The catalysts prepared were tested in the hydrodechlorination of 4-CP at 30 °C and a concentration corresponding to 2.54 mg Pd·L<sup>-1</sup>. Figure 5 shows a fairly rapid disappearance of 4-CP for both CMK-3/Pd and N-CMK-3/Pd catalysts. It can also be observed the simultaneous generation of phenol, which was the only reaction product apart from chloride ion. Further hydrogenation products like as cyclohexanol or cyclohexanone were not detected, even a trace levels. This is in contrast with the results from other works in the literature with Pd catalysts supported on carbon materials and other supports <sup>6,34,35</sup>. However, there are also some works on 4-CP hydrodechlorination

with Pd catalyst where phenol was the only reaction product detected <sup>13,36</sup>. Total selectivity to phenol has also been observed in the hydrodechlorination of 4-CP using unsupported Pd NPs <sup>37</sup> and Pd nanoparticles supported on sepiolite-carbon nanocomposites <sup>38</sup> and N-doped carbon blacks-like materials <sup>39</sup>. Likewise, Deng et al. <sup>40</sup> and Zhan et al. <sup>41</sup> found total selectivity to phenol when hydrodechlorination of 4-CP was conducted with Pd supported on reduced graphene oxide and rod-like nitrogen-doped ordered mesoporous carbons, respectively. These results show that the type of support and preparation of the catalysts has an important role in the selectivity to hydrogenation products.

Mass balance closures of 92-97% were achieved, suggesting some small adsorption of 4-CP and phenol on the support. Adsorption can also have a contribution to the rapid initial removal of 4-CP, which is then converted on the surface of the catalyst <sup>33</sup>. Faster disappearance of 4-CP was observed for N-CMK-3/Pd than for CMK-3/Pd, with virtually complete conversion is about 15 and 30 min, respectively. Accordingly, high activity values of 76 mmol·g<sup>-1</sup> Pd·min<sup>-1</sup> and 64 mmol·g<sup>-1</sup> Pd·min<sup>-1</sup> were calculated for N-CMK-3/Pd and CMK-3/Pd, respectively. In other works, differences in activity were observed between Pd catalysts supported on boron-doped mesoporous carbon, and was ascribed to differences in Pd<sup>2+</sup>/Pd<sup>0</sup> ratios <sup>19</sup>. However in one of our previous works Pd nanoparticles supported on carbons templated with silicas showed Pd<sup>2+</sup>/Pd<sup>0</sup> ratios around 0.8 for both doped and undoped supports <sup>32</sup>.

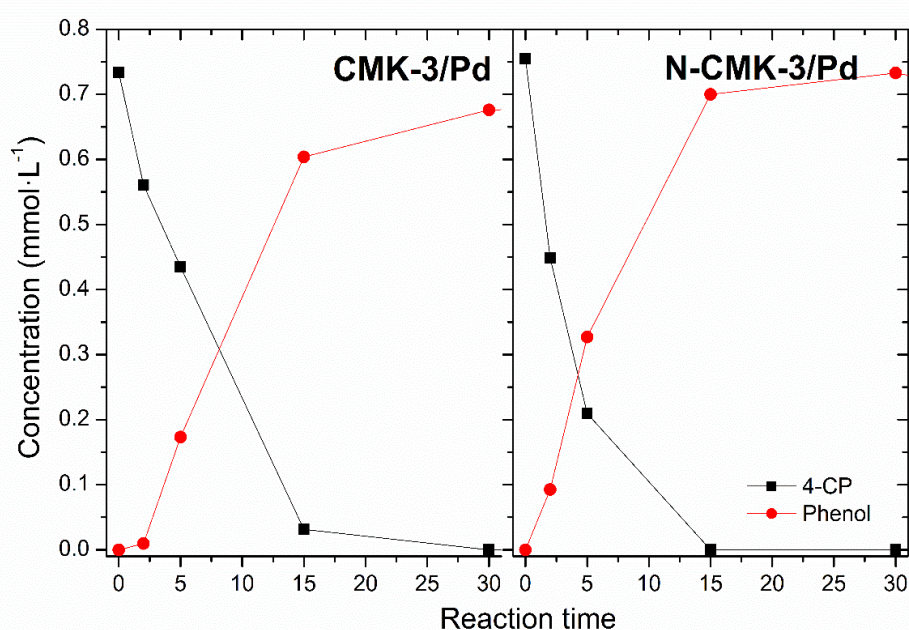


Figure 5. Time-course evolution of 4-CP and phenol upon hydrodechlorination with A) CMK-3/Pd and B) N-CMK-3/Pd (2.54 mg Pd·L<sup>-1</sup>, 30 °C).

The effect of metal concentration was checked in the 0.85–5.97 mg Pd·L<sup>-1</sup> range, which is representative of the conditions used in the hydrodechlorination literature with Pd catalysts. In these experiments phenol was also the only reaction product found, even at high metal concentration. This result indicates that the absence of activity for further hydrogenation is not related to the availability of metal active sites and competition for them. Previous works have shown that the hydrodechlorination of 4-CP with unsupported Pd and Pd nanoparticles is affected by competition for active sites, with the occurrence of hydrogenation products at 4-CP conversion above 80–90%<sup>43</sup>. Likewise, Pd catalysts prepared by incipient wetness impregnation and supported on a variety of materials including carbon, silica, alumina and clays have been reported to allow the formation of variable amounts of cyclohexanone and/or cyclohexanol during the hydrodechlorination of 4-CP<sup>6,7,34,35,44</sup>. Therefore, the lack of selectivity towards further hydrogenation observed in the current work may be related with the support used. Interestingly, some nitrogen species have been reported to inhibit the activity of metal catalysts in hydrogenation reactions<sup>45,46</sup>, although Pd is more resistant to this type of inhibition<sup>47</sup>. In the current work

the catalyst with the undoped support was also unable to hydrogenate phenol, therefore, the lack of hydrogenation activity cannot be attributed to nitrogen doping of the support. Likewise, Yukihiro et al.<sup>48</sup> prepared catalysts based on Pd nanoparticles supported on nitrogen-doped carbon fibres that were very active and stable in the hydrogenation of a variety of molecules and functional groups. The maximum HCl concentration achievable in the reaction medium is around 30 mg/L. Under these conditions the N-doped carbon support can be considered as stable. Mamtani et al.<sup>49</sup> observed a high stability of N-doped carbons used as catalyst supports in 0.5 M HCl.

Table 2 shows the activity values calculated at different catalyst (Pd) concentrations. A similar trend can be seen for the two catalysts tested, although systematically higher activity values can be observed for the N-CMK-3/Pd catalyst, evidencing the effect of the nitrogen doping of the carbon support. In the case of N-CMK-3/Pd catalyst, the activity increased from 46 to 76 mmol·g<sup>-1</sup> Pd·min<sup>-1</sup> when the concentration of catalyst was raised from 0.89 to 2.54 mgPd·L<sup>-1</sup>. Further increase in the concentration of catalyst resulted in only a slight increase in activity. A wide range of catalytic activity values has been reported in literature for the hydrodechlorination of 4-CP with Pd catalysts. Previous works for Pd supported on  $\gamma$ -alumina and Al-pillared clays<sup>50,51</sup> reported activity values of 0.7 and 0.3 mmol·g<sub>Pd</sub><sup>-1</sup>·min<sup>-1</sup>, respectively, at 30°C. Carbon supports showed to enhance the activity of Pd catalysts, thus at 30°C activity values of 55.6 mmol·g<sub>Pd</sub><sup>-1</sup>·min<sup>-1</sup> were reported for non-porous N-doped carbon<sup>39</sup>, and 10.7-173.5 mmol·g<sub>Pd</sub><sup>-1</sup>·min<sup>-1</sup> for carbon blacks, carbon fibers and graphitized carbons<sup>52</sup>. An activity value of 101 mmol·g<sub>Pd</sub><sup>-1</sup>·min<sup>-1</sup>. Was found by Zhang et al at room temperature for Pd supported on rod-like nitrogen-doped ordered mesoporous carbons<sup>41</sup>. Munoz et al.<sup>42</sup> found at 30°C activity values as high as 700 mmol·g<sub>Pd</sub><sup>-1</sup>·min<sup>-1</sup> for Pd supported on carbide-derived carbons. Therefore, the activity values obtained in the current work, i.e. 42.6 and 65.5 for mmol·g<sub>Pd</sub><sup>-1</sup>·min<sup>-1</sup> for CMK-3 and N-CMK-3, respectively, are in intermediate values among those reported for carbon supported Pd. However, it should be taken into account that the aim of this work is not to optimize the catalyst performance, but to assess the role of carbon N-doping. In spite of the evidences about the influence of N-doping of carbon support on the performance of catalyst, the role of nitrogen species is not fully understood. Potential reasons for the improved characteristics of catalysts based on N-carbon supports are the introduction of basic sites, the increasing of



polarity and the electron-donor properties of the carbons adjacent to N<sup>53,54</sup>. Likewise, some of the C-N bonds formed, specially pyridinic and pyrrolic, act as sites for the nucleation and growth of metal nanoparticles, thus increasing binding energy between N-doped carbon and metal nanoparticles and increasing metal phase stability<sup>55,56</sup>.

In the absence of mass transfer limitations, the specific activity, i.e. Pd weight-normalized and referred to the active centers available, can be expected to remain unchanged when the concentration of catalyst increases<sup>48,57</sup>. Therefore, in the system studied no relevant contribution of mass transfer to the overall rate seems to occur and the differences in activity observed between CMK-3/Pd and N-CMK-3/Pd can be attributed to the catalytic behaviour. Independently of the catalyst concentration used, phenol was the sole reaction product. It has been reported by other authors that phenol could be further hydrogenated to cyclohexanone and/or cyclohexanol with a higher Pd catalyst concentration<sup>58</sup>, with the support having a role in the control of the selectivity.

*Table 2. Values of the kinetic constant and catalytic activity of hydrodechlorination runs at different catalyst concentration (30 °C).*

	C Pd ( $\frac{mg}{L}$ )	$k_{4-CP}$ ( $min^{-1}$ )	R <sup>2</sup>	$a$ ( $\frac{mmol}{gPd \cdot min}$ )
CMK-3/Pd	0.85	0.043	0.980	37
N-CMK-3/Pd		0.054	0.992	46
CMK-3/Pd	2.54	0.216	0.970	62
N-CMK-3/Pd		0.256	0.999	76
CMK-3/Pd	5.93	0.478	0.999	61
N-CMK-3/Pd		0.693	0.960	81

Most of the studies on HDC in aqueous phase have been carried out at ambient-like temperature given the good performance of a number of catalysts under these conditions, and the economy of operation. However, intensification of HDC by increasing the working temperature can be affordable in cases where process streams or effluents are above ambient temperature, e.g. pulp bleaching effluents<sup>59</sup>. Thus, the influence of temperature in the catalytic performance of the catalysts was studied in the 30—70 °C range using a

Pd concentration of  $0.85 \text{ g} \cdot \text{L}^{-1}$ . The reaction rate at  $30^\circ\text{C}$  was significantly faster for the catalyst supported on N-CMK-3, showing that the N-doped support is more suitable when Pd catalysts are used at ambient temperature. However, the Pd catalyst supported on non-doped support were more active at high temperature, indicating that intensification of the hydrodechlorination process with temperature can be better achieved for Pd catalysts using non-doped carbon supports. Both CMK-3/Pd and N-CMK-3/Pd catalysts exhibited a substantial increase of activity with temperature (Figure 6, Table 3), whereas exclusive selectivity to phenol was still observed within the whole range of temperature. At  $30^\circ\text{C}$  CMK-3/Pd showed lower activity ( $43 \text{ mmol} \cdot \text{g}^{-1} \text{ Pd} \cdot \text{min}^{-1}$ ) than N-CMK-3/Pd ( $65 \text{ mmol} \cdot \text{g}^{-1} \text{ Pd} \cdot \text{min}^{-1}$ ). At  $70^\circ\text{C}$  the HDC activity was around  $466 \text{ mmol} \cdot \text{g}^{-1} \text{ Pd} \cdot \text{min}^{-1}$  for CMK-3/Pd and  $321 \text{ mmol} \cdot \text{g}^{-1} \text{ Pd} \cdot \text{min}^{-1}$  for N-CMK-3/Pd catalyst. Therefore, intensification of the process by increasing the temperature is better achieved with the catalyst supported on undoped carbon. From these results it follows that the activation energy of 4-CP HDC catalyzed with CMK-3/Pd is higher than with N-CMK-3/Pd ( $53 \text{ vs } 36 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively).

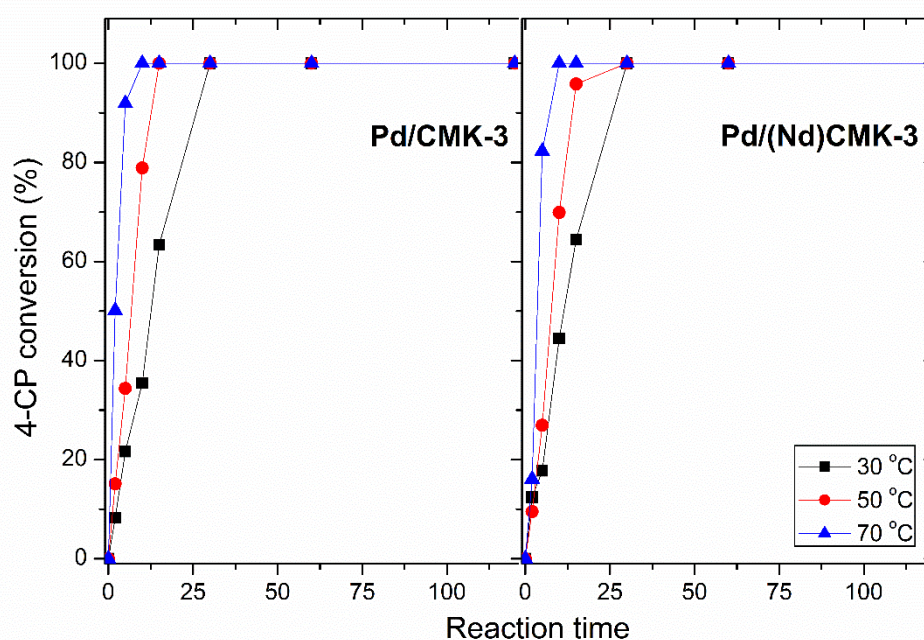


Figure 6. Time course of 4-CP conversion upon catalytic HDC at  $30\text{--}70^\circ\text{C}$  with CMK-3/Pd and N-CMK-3/Pd ( $0.85 \text{ mg Pd} \cdot \text{L}^{-1}$ ).



*Table 3. Values of the kinetic constant and activity in 4-CP HDC at different temperatures (30–70 °C) with CMK-3/Pd and N-CMK-3/Pd (0.85 mg Pd·L<sup>-1</sup>)*

	T (°C)	k <sub>4-CP</sub> (min <sup>-1</sup> )	R <sup>2</sup>	a ( $\frac{\text{mmol}}{\text{gPd} \cdot \text{min}}$ )	Ea ( $\frac{\text{kJ}}{\text{mol}}$ )
CMK-3-Pd	30	0.044	0.995	43	53±1
	50	0.157	0.942	151	
	70	0.511	0.981	466	
N-CMK-3-Pd	30	0.068	0.972	66	36±6
	50	0.206	0.899	186	
	70	0.3608	0.931	321	

These values are close to the reported in the literature within the same temperature range <sup>8,60-63</sup>. However, they appear somewhat low for chemical reaction. This may indicate that some physical step, such as mass transfer or adsorption, could be contributing to the control of the rate of the overall process. Significant differences in mass transfer conditions within the pores of the catalysts of the undoped and doped support are not likely, since they have nearly identical porous texture (see Table 1) thanks to the templating technique used for their preparation. However, the different chemical nature of the undoped and doped support could lead to differences in transport by surface diffusion, which is mostly based on the interaction with the pore walls through an adsorption/desorption mechanism. The potential occurrence of mass transfer limitations **was** evaluated through the estimation of the Carberry numbers and Weisz-Prater parameter. As shown in Table 4, these estimations indicate that at the highest catalyst concentration, i.e. 5.93 mg Pd·L<sup>-1</sup>, mass transfer limitations related to gas-liquid diffusion may be taking place, since the value of  $C_{a_{G-L}}(H^2)$  was higher than 0.1. However, such limitations would not be consistent with the different reaction rate and activity observed between CMK-3/Pd and N-CMK-3/Pd. In the same way, in the reactions at 70 °C limitations in gas-liquid hydrogen transfer may occur, which could be related to a decrease in hydrogen solubility in the reaction medium. Again, these potential limitations can be considered of low relevance taking into account the differences observed between CMK-3/Pd and N-CMK-3/Pd.

Table 4. Carberry ( $C_a$ ) numbers and Weisz-Prater parameter  $(\phi_s)^2$  for the HDC runs carried out.

T (°C)	$C_{Pd} \left( \frac{mg}{L} \right)$		$C_{a_{G-L}} H_2$	$C_{a_{L-S}} H_2$	$C_{a_{L-S}} 4-CP$	$(\phi_s)^2 H_2$	$(\phi_s)^2 4-CP$
30	0.85	CMK-3/Pd	$1.55 \cdot 10^{-2}$	$2.97 \cdot 10^{-8}$	$7.05 \cdot 10^{-8}$	$3.3 \cdot 10^{-8}$	$4.7 \cdot 10^{-7}$
		N-CMK-3/Pd	$1.94 \cdot 10^{-2}$	$3.71 \cdot 10^{-8}$	$8.82 \cdot 10^{-8}$	$4.1 \cdot 10^{-8}$	$5.9 \cdot 10^{-7}$
	2.54	CMK-3/Pd	$7.83 \cdot 10^{-2}$	$4.99 \cdot 10^{-8}$	$1.19 \cdot 10^{-7}$	$6.6 \cdot 10^{-7}$	$6.0 \cdot 10^{-7}$
		N-CMK-3/Pd	$9.28 \cdot 10^{-2}$	$5.92 \cdot 10^{-8}$	$1.41 \cdot 10^{-7}$	$7.8 \cdot 10^{-7}$	$2.8 \cdot 10^{-6}$
	5.93	CMK-3/Pd	$1.73 \cdot 10^{-1}$	$5.10 \cdot 10^{-8}$	$1.21 \cdot 10^{-7}$	$1.4 \cdot 10^{-6}$	$5.3 \cdot 10^{-6}$
		N-CMK-3/Pd	$2.51 \cdot 10^{-1}$	$7.39 \cdot 10^{-8}$	$1.76 \cdot 10^{-7}$	$7.7 \cdot 10^{-6}$	$2.8 \cdot 10^{-3}$
30		CMK-3/Pd	$1.55 \cdot 10^{-2}$	$2.97 \cdot 10^{-8}$	$7.05 \cdot 10^{-8}$	$1.80 \cdot 10^{-4}$	$3.44 \cdot 10^{-4}$
		N-CMK-3/Pd	$1.94 \cdot 10^{-2}$	$3.71 \cdot 10^{-8}$	$8.82 \cdot 10^{-8}$	$2.02 \cdot 10^{-4}$	$3.85 \cdot 10^{-4}$
50	0.63	CMK-3/Pd	$3.74 \cdot 10^{-2}$	$6.92 \cdot 10^{-8}$	$1.64 \cdot 10^{-7}$	$2.77 \cdot 10^{-4}$	$5.28 \cdot 10^{-4}$
		N-CMK-3/Pd	$4.93 \cdot 10^{-2}$	$9.10 \cdot 10^{-8}$	$2.16 \cdot 10^{-7}$	$3.18 \cdot 10^{-4}$	$6.06 \cdot 10^{-4}$
70		CMK-3/Pd	$8.77 \cdot 10^{-2}$	$1.56 \cdot 10^{-7}$	$3.72 \cdot 10^{-7}$	$4.17 \cdot 10^{-4}$	$7.95 \cdot 10^{-4}$
		N-CMK-3/Pd	$6.17 \cdot 10^{-2}$	$1.10 \cdot 10^{-7}$	$2.62 \cdot 10^{-7}$	$3.50 \cdot 10^{-4}$	$6.67 \cdot 10^{-4}$

## CONCLUSIONS

Undoped and nitrogen-doped CMK-3 carbons were prepared by templating and used as supports of Pd catalysts with similar NP size. The templating technique yielded carbons with identical pore structure, but the N-doped carbons incorporated pyrrolic, pyridinic and N-oxide, which were responsible for differences in the behaviour of the catalysts. A clear effect of nitrogen doping on the behaviour of those catalysts was observed at 30 °C, with activity values of 62 and 76 mmol·g<sup>-1</sup> Pd·min<sup>-1</sup> for CMK-3/Pd and N-CMK-3/Pd, respectively, at a catalyst concentration of 2.54 mg Pd·L<sup>-1</sup>. Exclusive selectivity to phenol was reported, in contrast to most common results in the literature, which reported further hydrogenation activity of Pd/C catalysts used in HDC of chlorophenols. The catalytic activity of CMK-3/Pd increased more with temperature than that of N-CMK-3/Pd, which was the most active at 70 °C. Consequently, a higher activation energy was calculated for

CMK-3/Pd ( $53 \text{ kJ}\cdot\text{mol}^{-1}$ ) than for N-CMK-3/Pd ( $36 \text{ kJ}\cdot\text{mol}^{-1}$ ) in the 30—70 °C temperature range, showing the effect of nitrogen doping of the support on the catalytic activity (even though the catalysts with doped and undoped support did not show significant differences in the mean size and electronic state of the Pd nanoparticles).

N-doping has been proved to enhance the activity of Pd/C catalysts at room temperature, showing the potential of this approach for further catalyst synthesis optimization. The carbon preparation technique used and the mesoporous nature of the supports makes possible to assess the role of carbon doping with negligible crossed effect of other variables such as the porosity of the support and the mass transfer limitations.

## Supporting information

**Supplementary data** (Graphical representation of the time evolution of 4-CP conversion in HDC reaction using several amounts of catalyst) is available free of charge via the Internet at <http://pubs.acs.org>.

## Acknowledgements

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

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## Nomenclature

$a_p$	volumetric area of the catalyst ( $\text{m}^2 \text{m}^{-3}$ )
$Ca_{G-L}$	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, ( $\text{m}^2 \text{s}^{-1}$ )
$De$	effective diffusion coefficient, ( $\text{m}^2 \text{s}^{-1}$ )
$k$	kinetic constant ( $\text{s}^{-1}$ )
$k_L a$	volumetric gas-liquid mass transfer coefficient ( $\text{s}^{-1}$ )
$k_s$	liquid to solid mass transfer coefficient ( $\text{m} \cdot \text{s}^{-1}$ )
$M$	molecular weight
$N$	stirring velocity ( $\text{s}^{-1}$ )
$Re$	Reynolds number
$Sc$	Schmidt number
$Sh$	Sherwood number
$T$	temperature (K)
$V_i$	volume of species $i$ in water at normal conditions boiling ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )
$\varphi$	association factor, 2.6 for water
$\mu$	viscosity of the liquid phase: $7.98 \cdot 10^{-4}$ — $4.04 \cdot 10^{-4} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$
$\rho$	density of the liquid phase : $995.71$ — $977.63 \text{ kg} \cdot \text{m}^{-3}$
$\sigma$	liquid surface tension of the liquid phase: $7.18 \cdot 10^{-2}$ — $6.50 \cdot 10^{-2} \text{ kg} \cdot \text{s}^{-2}$



$\phi_s$  Weisz-Prater parameter

### TOC/Abstract Graphic

