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**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

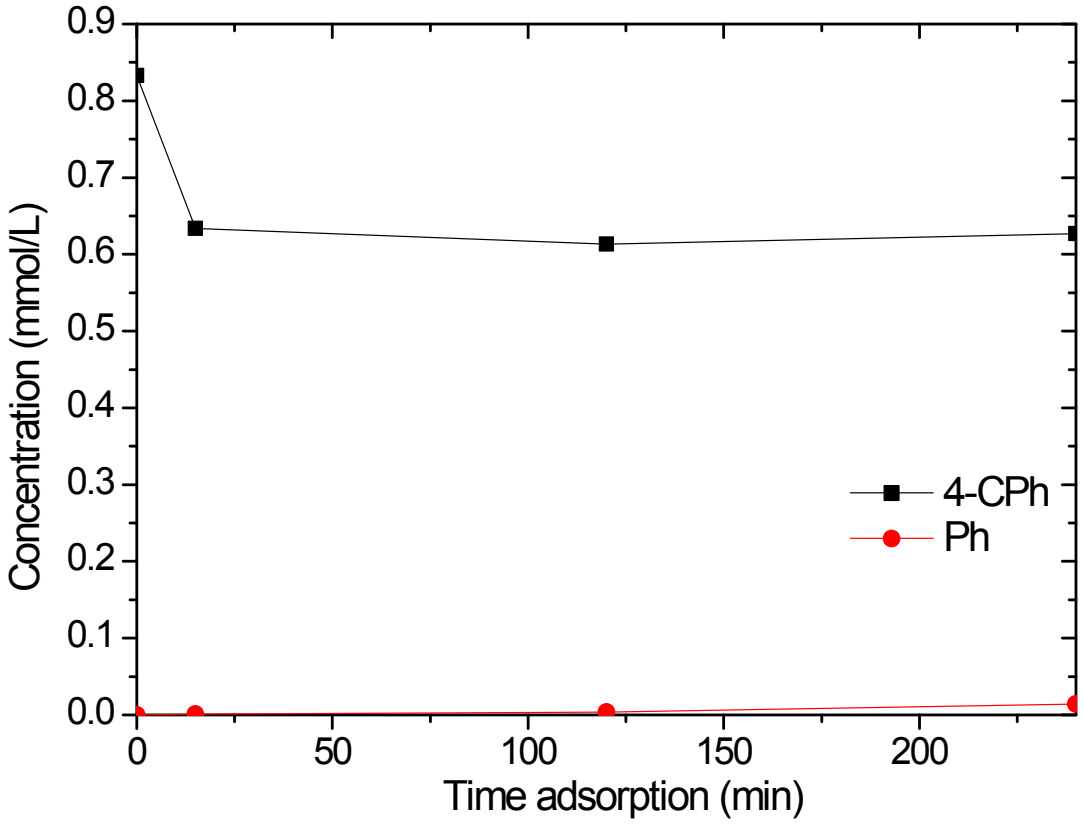


Figure 1S. Hydrodechlorination reaction at 70 ºC using carbon C-17N as catalyst

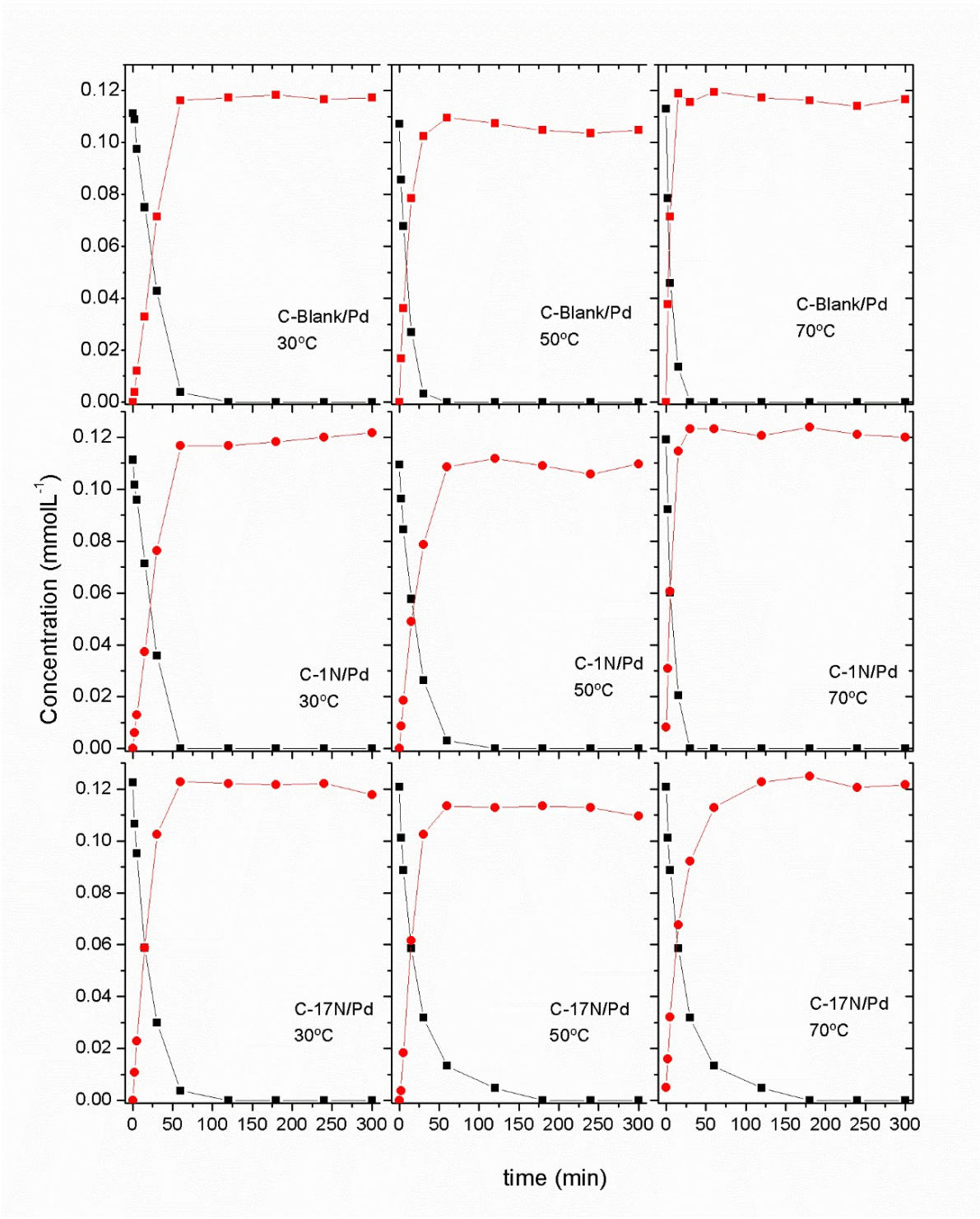


Figure 2S. Time evolution of 4-CPh (■) and phenol (●) concentration in hydrodechlorination reaction at 30, 50 and 70 °C (0.8 g Pd $L^{-1}$)

## 2. Verification of the control regime

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

| | |
|---|---|
| Gas-liquid mass transfer | $D = 7.4 \cdot 10^{-8} \frac{(\varphi M)^{1/2} T}{\mu V_i^{0.6}}$<br>$k_L a = 1.2610^{-5} \left( D m_{H_2} \mu^{-0.9} \rho^{0.9} \sigma^{0.1} N^{1.7} d_i^{1.4} \right)$<br>$Ca_{G-L} = \frac{k}{k_{lav}}$ |
| 4-CP external diffusion | $Re = \frac{\rho N d_I^2}{\mu}$ $Sc = \frac{\mu}{\rho D}$<br>$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}$<br>$Sh = \frac{k_s d_p}{D}$<br>$Ca_{L-S} = \frac{k}{k_S a_p}$ |
| 4-CP Internal diffusion | $D_e \sim \frac{1}{10} D$<br>$(\phi_s)^2 = \left( \frac{d_p}{6} \right)^2 \frac{k}{D_e}$ |

Table 1S. Stages and expressions used to evaluate possible mass transfer limitations.

| 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 coeficient, ($m^2\ s^{-1}$) |
| $D_e$ | effective difusion 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 ($cm^3\ mol^{-1}$) |
| $\varphi$ | association factor, 2.6 for water |
| $\mu$ | viscosity of the liquid phase($kg\ m^{-1}\ s^{-1}$) $7.98\cdot10^{-4}$–$4.04\cdot10^{-4}$ |
| $\rho$ | density of the liquid phase ($kg\ m^{-3}$) 995.71−977.63 |
| $\sigma$ | liquid surface tension of the liquid phase ($kg\ s^{-2}$) $7.18\cdot10^{-2}$–$6.50\cdot10^{-2}$ |
| $\phi_s$ | 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 $H_2$ gas-liquid transfer, as well as $H_2$ 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 ($\phi$)[2].

Table 2S. Mass transfer-related coefficients

| T (K) | D $H_2$ ($m^2\ s^{-1}$) | D 4CP ($m^2\ s^{-1}$) | $k_{IL}a$ ($s^{-1}$) | $k_s$ $H_2$ ($s^{-1}$) | $k_s$ 4CP ($s^{-1}$) |
|---|---|---|---|---|---|
| 303 | $3.89\cdot10^{-9}$ | $1.07\cdot10^{-9}$ | $0.46\cdot10^{-1}$ | 13.0 | 5.8 |
| 323 | $6.05\cdot10^{-9}$ | $1.67\cdot10^{-9}$ | $0.70\cdot10^{-1}$ | 21.1 | 9.1 |
| 343 | $8.70\cdot10^{-9}$ | $2.40\cdot10^{-9}$ | $0.97\cdot10^{-1}$ | 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 rpm [6]. 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 (ºC) | | 0.8 mg Pd/L | | | 2.4 mg Pd/L | | |
|---|---|---|---|---|---|---|---|
| | sample | $Ca_{G-L}$ | $Ca_{L-S}$ | | $Ca_{G-L}$ | $Ca_{L-S}$ | |
| | | | $H_2$ | 4-CP | | $H_2$ | 4-CP |
| 30 | C-blank | $1.2\cdot10^{-2}$ | $1.0\cdot10^{-7}$ | $2.5\cdot10^{-7}$ | $5.5\cdot10^{-2}$ | $1.6\cdot10^{-7}$ | $3.9\cdot10^{-7}$ |
| | C-1N | $1.3\cdot10^{-2}$ | $1.0\cdot10^{-7}$ | $2.9\cdot10^{-7}$ | $4.4\cdot10^{-2}$ | $1.3\cdot10^{-7}$ | $3.1\cdot10^{-7}$ |
| | C-17N | $1.7\cdot10^{-2}$ | $1.5\cdot10^{-7}$ | $3.6\cdot10^{-7}$ | $7.1\cdot10^{-2}$ | $2.1\cdot10^{-7}$ | $5.0\cdot10^{-7}$ |
| 50 | C-blank | $2.2\cdot10^{-2}$ | $2.7\cdot10^{-7}$ | $6.3\cdot10^{-7}$ | - | - | - |
| | C-1N | $1.4\cdot10^{-2}$ | $1.7\cdot10^{-7}$ | $4.0\cdot10^{-7}$ | - | - | - |
| | C-17N | $1.7\cdot10^{-2}$ | $2.0\cdot10^{-7}$ | $4.8\cdot10^{-7}$ | - | - | - |
| 70 | C-blank | $2.4\cdot10^{-2}$ | $1.7\cdot10^{-7}$ | $4.2\cdot10^{-7}$ | | | |
| | C-1N | $2.0\cdot10^{-2}$ | $1.5\cdot10^{-7}$ | $3.5\cdot10^{-7}$ | | | |
| | C-17N | $1.7\cdot10^{-2}$ | $1.2\cdot10^{-7}$ | $2.9\cdot10^{-7}$ | | | |

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 (ºC) | samples | $(\phi_s)^2$ | | | |
| | | $H_2$ | 4-CP | $H_2$ | 4-CP |
| 30 | C-blank | $2.3 \cdot 10^{-4}$ | $4.4 \cdot 10^{-4}$ | $5.1 \cdot 10^{-4}$ | $9.6 \cdot 10^{-4}$ |
| | C-1N | $2.5 \cdot 10^{-4}$ | $4.7 \cdot 10^{-4}$ | $4.5 \cdot 10^{-4}$ | $8.6 \cdot 10^{-4}$ |
| | C-17N | $2.8 \cdot 10^{-4}$ | $5.3 \cdot 10^{-4}$ | $5.7 \cdot 10^{-4}$ | $1.1 \cdot 10^{-3}$ |
| 50 | C-blank | $3.9 \cdot 10^{-4}$ | $7.6 \cdot 10^{-4}$ | - | - |
| | C-1N | $3.2 \cdot 10^{-4}$ | $6.0 \cdot 10^{-4}$ | - | - |
| | C-17N | $3.5 \cdot 10^{-4}$ | $6.6 \cdot 10^{-4}$ | - | - |
| 70 | C-blank | $3.8 \cdot 10^{-4}$ | $6.1 \cdot 10^{-4}$ | - | - |
| | C-1N | $3.2 \cdot 10^{-4}$ | $5.6 \cdot 10^{-4}$ | - | - |
| | C-17N | $2.7 \cdot 10^{-4}$ | $5.2 \cdot 10^{-4}$ | - | - |

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

References


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