



## Research paper

# Polymer-based spherical activated carbon as catalytic support for hydrodechlorination reactions



Macarena Munoz<sup>a,\*</sup>, Veronika Kolb<sup>b</sup>, Ana Lamolda<sup>a</sup>, Zahara M. de Pedro<sup>a</sup>,  
Antje Modrow<sup>c</sup>, Bastian J.M. Etzold<sup>d,\*</sup>, Juan J. Rodriguez<sup>a</sup>, Jose A. Casas<sup>a</sup>

<sup>a</sup> Sección Departamental de Ingeniería Química, Universidad Autónoma de Madrid, 28049, Madrid, Spain

<sup>b</sup> Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058, Erlangen, Germany

<sup>c</sup> Blücher GmbH, 14727, Premnitz, Germany

<sup>d</sup> Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Technische Universität Darmstadt, 64287, Darmstadt, Germany

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## ABSTRACT

In this work, polymer-based spherical activated carbon (PBSAC) ( $dp = 500 \mu\text{m}$ ) has been used as support to synthesize several Pd/PBSAC (1% wt.) catalysts. These catalysts have been tested in the hydrodechlorination (HDC) of 4-chlorophenol (4-CP) in aqueous phase under ambient-like conditions ( $30^\circ\text{C}$ , 1 atm) at  $[4\text{-CP}]_0 = 3.9 \text{ mmol L}^{-1}$ ;  $[\text{catalyst}]_0 = 1 \text{ g L}^{-1}$  and  $50 \text{ N mL H}_2 \text{ min}^{-1}$ . A sequential calcination ( $200^\circ\text{C}$ , air atmosphere) – reduction ( $80^\circ\text{C}$ ,  $\text{H}_2$  atmosphere) treatment was required to obtain active HDC catalysts with a convenient proportion of zero-valent and electrodeficient Pd species. This catalyst allowed to achieve complete conversion of 4-CP in 90 min reaction time, giving rise to phenol as main reaction product. An expanded kinetic model accounting for both consecutive reaction and sorption processes was used to successfully fit the experimental data. The values obtained for the effective rate constant of 4-CP disappearance ( $3.26\text{--}10.88 \times 10^{-4} \text{ s}^{-1}$ ) and apparent activation energy ( $31.6 \text{ kJ mol}^{-1}$ ) were close to the previously reported for powdered supported Pd catalysts. Remarkably, the catalyst showed a high stability in long-term continuous application (100 h on stream).

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## 1. Introduction

Organochlorinated compounds are among the most distributed pollutants in water [1–4]. The presence of these xenobiotic contaminants in the environment is of increasing concern given their high toxicity, carcinogenic character and long-term persistence in the ecosystems. Their ecological effects and impact on public health have promoted increasingly stringent regulations, being a priority in Europe and the US. Among the potential solutions investigated for the treatment of those pollutants, catalytic hydrodechlorination (HDC) has been claimed as an effective and environmentally-friendly technology, becoming a burgeoning topic in environmental catalysis [3]. HDC allows a fast conversion of a wide range of chlorinated contaminants into less harmful products under ambient-like operating conditions. Apart from the clear environmental benefit, the application of HDC to treat highly concentrated effluents

could be also interesting from an economic point of view since the resulting dechlorinated by-products could be recovered.

A number of catalysts have been tested in HDC, but those based on Pd have received major attention due to their higher activity, selectivity and stability compared to other metals such as Rh, Pt or Ni [5–7]. Meanwhile, activated carbon (AC) has been identified as one of the most suitable supports for HDC catalysts due to its high resistance towards the HCl generated upon reaction. On the other hand, the high adsorption capacity of AC has demonstrated to play a key role on the kinetics of the process. For instance, HDC rate constants were around six times higher with Pd/AC than those obtained with Pd/ $\text{Al}_2\text{O}_3$  (1% wt.;  $dp = 24 \mu\text{m}$ ) commercial catalysts at similar loading and metal particle size [8]. Additional advantages of AC as catalytic support are its high surface area, the tunability of porosity and surface chemistry and the low interaction with catalytically active species [9].

Conventional ACs, derived from natural sources like coal or wood, are usually fine powders or low-stable granules, difficult to handle and recover. Their ash contents have also to be considered. In this context, the use of ACs produced from synthetic polymer precursors as starting materials represents a promising alternative given their high and homogeneous quality, their well-

\* Corresponding authors.

E-mail addresses: [macarena.munoz@uam.es](mailto:macarena.munoz@uam.es) (M. Munoz), [etzold@tc1.tu-darmstadt.de](mailto:etzold@tc1.tu-darmstadt.de) (B.J.M. Etzold).

defined pore texture and their very low or practically negligible ash content. Furthermore, polymers can be provided in different shapes, being the sphere one of the most interesting for wastewater treatment applications due to its excellent dynamic behavior and high resistance to abrasion [10,11]. Furthermore, polymers can be provided in different shapes, being the sphere one of the most interesting for wastewater treatment applications due to its excellent dynamic behavior and high resistance to abrasion [10,11]. Polymer-based spherical activated carbons (PBSACs) have been so far mainly used in sorption processes [12–14] but have also proved to be interesting supports in different catalytic applications [15–19]. PBSAC-supported palladium catalysts have been successfully tested in the liquid-phase (ethanol) hydrogenation of cinnamic acid in a recent contribution [20] but its use for the HDC of organochlorinated pollutants in water has not been reported so far.

Recently, we demonstrated that deducing true kinetic constants from catalytic HDC experiments with high surface area supports is only possible if adsorption is considered in the kinetic model [8]. This allows to predict reaction progress and selectivity successfully. Therefore, the application of novel carbon supports should always include a kinetic modelling comprising both sorption and HDC processes to allow the comparison of different catalysts regardless their sorption capacity as well as the estimation of their performance at technical scale.

In the current work, the application of PBSAC-supported palladium catalysts has been investigated in the HDC of 4-chlorophenol (4-CP). The preparation of the catalyst was accomplished by oxidizing the PBSAC support with sulfuric acid in order to break its hydrophobic character and introduce oxygen groups favouring Pd anchorage [20]. Pd was then incorporated by ion-exchange [20]. To investigate the effect of the oxidation state of Pd species on HDC the subsequent thermal treatment of the resulting Pd/PBSAC catalyst was varied. Its activity has been tested under different operating conditions and an expanded kinetic model accounting for sorption and reaction has been accordingly developed to fit the experimental data. Finally, the stability of Pd/PBSAC has been assessed in a long-term continuous experiment.

## 2. Materials and methods

### 2.1. Materials

The PBSAC support (particle size 500  $\mu\text{m}$ ), based on polystyrene-divinylbenzene as precursor, was provided by Blücher GmbH, Germany. Palladium (II) chloride (99%), phenol (99%), cyclohexanone (99%) and cyclohexanol (99%) were supplied by Sigma-Aldrich. Sulfuric acid (96%) and hydrochloric acid (37% wt.) were purchased from Panreac and 4-chlorophenol (99%) from Fluka. All the reagents were used as received without further purification.

### 2.2. Preparation and characterization of Pd/PBSAC catalysts

Prior to metal impregnation, the PBSAC was oxidized for 2 h at 90 °C with 10 mL of sulfuric acid (50% vol.) per gram of carbon. A reflux condenser prevented evaporation. The solid was separated by filtration, washed until neutral filtrate and dried overnight at 60 °C in a vacuum oven.

Immobilization of Pd on the functionalized-PBSAC was carried out by ion-adsorption from an aqueous solution of PdCl<sub>2</sub> and HCl (pH = 1). The ratio of precursor solution to PBSAC was 10 mL g<sup>-1</sup>, to adjust the palladium loading of the catalyst to 1% wt nominal. After the addition of PBSAC, the suspension was slowly stirred at room temperature for 24 h and then filtered and washed with 200 mL of HCl solution of equal pH as the impregnation one. The obtained solid was then dried at 60 °C in a vacuum oven overnight.

The resulting Pd/PBSAC catalyst was submitted to different thermal treatments. In the first set, the catalyst was reduced with hydrogen (50 N mL min<sup>-1</sup>) at 80 °C for 2 h. In the second series, a calcination step at 200 °C in air atmosphere for 4 h was performed prior to reduction. The catalysts were denoted as PBSAC-r and PBSAC-cr, where -r and -cr represent the kind of thermal treatment applied in their preparation (r: reduction (80 °C); cr: calcination (200 °C) followed by reduction (80 °C)).

The porous texture of the PBSAC-based catalysts was characterized from nitrogen adsorption-desorption at -196 °C using a Micromeritics Tristar II 3020 apparatus. The samples were previously outgassed overnight at 150 °C to a residual pressure of <10<sup>-3</sup> Torr. Data evaluation was performed with the software Tristar II version V1.03 using the quenched solid density functional theory (QSDFT) for slit pores. The specific surface area was calculated by the BET equation and the micropore volume was estimated by Dubinin-Radushkevich method. The difference between the N<sub>2</sub> adsorbed volume at a relative pressure of P/P<sup>0</sup> = 0.95 and the micropore volume was taken as mesopore volume. The palladium content of the catalysts was determined by total reflection X-ray fluorescence (TXRF), using a TXRF spectrometer 8030c. Surface palladium species were analysed by X-ray photoelectron spectroscopy (XPS) with a Thermo Scientific K-Alpha apparatus equipped with a K $\alpha$  X-ray excitation source, 1486.68 eV. The software “XPS-Peak” was used for spectrograms deconvolution. Thermogravimetric analyses (TG) were performed with a TGA/SDTA851e (Mettler Toledo) thermogravimetric analyser under air atmosphere at a heating rate of 10 °C min<sup>-1</sup>, from 30 to 900 °C.

### 2.3. Typical reaction procedure

HDC experiments were performed batch-wise in a magnetically stirred glass slurry-type reactor (500 mL) equipped with temperature control. The reaction took place during 3 h under vigorous stirring (1000 rpm) and continuous feeding of H<sub>2</sub> (50 N mL min<sup>-1</sup>). The starting concentration of the target pollutant and the reaction volume were fixed at 3.9 mmol L<sup>-1</sup> and 350 mL, respectively. Unless otherwise indicated, a catalyst concentration of 1 g L<sup>-1</sup> was used whereas the temperature was tested within the 20–50 °C range. Each run was carried out by triplicate being the standard deviation less than 5% in all cases. The long-term continuous experiment (100 h) was performed using the same reactor but including a PTFE blade stirrer instead of the magnetic one. The volume was fixed at 350 mL and the initial concentration of 4-CP at 1.6 mM. The hydrogen flow was maintained at 50 N mL min<sup>-1</sup> while the liquid stream was fed at 1 mL min<sup>-1</sup>, which corresponds to 3.65 kg<sub>cat</sub> h mol<sup>-1</sup> space-time.

The progress of the HDC experiments was followed by periodically withdrawing samples from the reactor. 4-CP, phenol (Ph), cyclohexanone (C-one) and cyclohexanol (C-ol) were analysed by a gas chromatograph with a 25 m length x 0.32 mm i.d. capillary column (CP-FFAP CB, Varian) coupled to a flame ionization detector (GC 3900, Varian).

Equilibrium adsorption tests were also carried out under the same operating conditions as the HDC runs but in the absence of hydrogen. Solutions of 4-CP and the main HDC product, Ph, were prepared at concentrations from 1.5 to 8 mmol L<sup>-1</sup>. The Langmuir equation was used to fit the equilibrium data (Eq. (1)).

$$q_i = \frac{K_{\text{SORP}_i} \cdot q_{mi} \cdot C_i}{1 + K_{\text{SORP}_i} \cdot C_i} \quad (1)$$

*i* = 4-CP, Ph.

where *q<sub>i</sub>* is the amount of the *i* species onto the catalyst at equilibrium (mmol g<sub>cat</sub><sup>-1</sup>); *C<sub>i</sub>* is the equilibrium concentration of that species in the liquid phase (mmol L<sup>-1</sup>); *K<sub>SORP<sub>i</sub></sub>* is the Langmuir

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