



Deducing kinetic constants for the hydrodechlorination of 4-chlorophenol using high adsorption capacity catalysts



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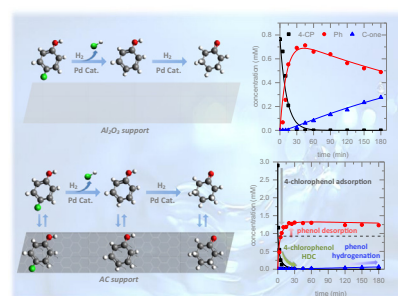
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HIGHLIGHTS

- A new kinetic model accounting for sorption and HDC processes in parallel has been developed.
- Our model allows a good fit of the experimental data regardless of the sorption capacity of the support.
- Sorption must be considered in HDC modelling with AC-based catalysts to close carbon and chlorine balances.
- The selectivity to the reaction products can be successfully predicted.

GRAPHICAL ABSTRACT



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ABSTRACT

Employing high surface area supports for catalytic hydrodechlorination can result in pronounced adsorption of reactants, intermediates and products. The influence of these sorption processes on the activity and selectivity upon 4-chlorophenol (4-CP) hydrodechlorination in aqueous solution has been studied using four commercial Pd/Al₂O₃ and Pd/AC catalysts at ambient pressure within the temperature range of 20–40 °C ([4-CP]₀ = 0.78–2.90 mmol L⁻¹, [catalyst] = 1 g L⁻¹, 50 N mL H₂ min⁻¹). The adsorption capacity of the catalysts was independently evaluated. The Al₂O₃-based catalyst did not show any significant adsorption of those species whereas the activated carbon materials presented in all cases high uptakes (e.g. up to 2.4 mmol_{4-CP} g_{cat}⁻¹). In order to deduce true kinetic constants also for these catalysts, a kinetic model was developed, which accounts for the consecutive reaction and sorption processes in parallel. This expanded model resulted in a reasonable fit, can thus be used for comparison of different catalysts regardless their sorption capacity and allows predicting successfully the selectivity to the reaction products.

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1. Introduction

The increasing social and political concern on environment demands a more rigorous control of industrial wastewaters and thus, the development and implementation of new technologies capable to deal with toxic pollutants resistant to the broadly estab-

lished conventional methods. Among these hazardous pollutants, chlorophenols (CPs) require special attention due to their high toxicity, persistence and low biodegradability. Because of their antimicrobial properties, they are commercially important chemicals with an estimated production of ca. 100 kt per year [1], being widely used in a diversity of industrial processes related to the manufacture of pesticides, pharmaceuticals, dyes and wood preservatives. As a result, they have been detected in both surface and ground waters [2–5], which involves a significant risk for the environment.

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Catalytic hydrodechlorination (HDC) appears as a promising technology for the treatment of wastewater containing organochlorinated pollutants since it shows remarkable advantages when compared to other techniques [6–8]. HDC can operate at mild conditions, not requiring high temperatures and/or pressures as in the case of incineration or wet oxidation processes. Large amounts of reagents, such as in Fenton oxidation, are not needed. It is also efficient within a wide range of concentrations of chlorinated compounds, which is not the case of biological methods. Furthermore, in contrast to oxidation processes, HDC is not strongly affected by the number of atoms of the pollutant [9]. In this process the organochlorinated compound reacts with hydrogen leading to the formation of hydrogen chloride and hydrocarbons. Although HDC does not provide the complete destruction of the pollutants, it leads to their convenient transformation into substantially less harmful species, which involves a significant decrease on the ecotoxicity of the effluent [7]. Accordingly, HDC has been regarded as a detoxifying stage prior to oxidation [9,10] or biological treatments [11]. Nevertheless, from an economic point of view, the formation of valuable non-chlorinated hydrocarbons could be also a potential advantage since they may be reused as raw material, as it is the case of phenol, an important industrial precursor to many materials and useful compounds [12]. On the other hand, the main drawback of this technology, which has limited so far its widespread application, is the relatively low stability of the catalysts due to chloride poisoning [13].

HDC reactions have been studied over a number of metals, being those based on Pd [7,14–19], Pt [16,19] and Rh [16,19–21] with metal loadings ranging from 0.5% to 10% (w/w) the most active ones. Among them, Pd is the metal least affected by the catalyst poisoning properties of the chloride ions released [22,23] and is commonly identified as the most suitable active phase for liquid-phase HDC [22,24]. The catalytic support plays also an important role in both catalytic activity and stability and has been investigated on carbon [7,13,25,26], alumina [16,18,27], zirconia [28,29] and pillared clays [30,31], among other, with alumina and activated carbon being the most reported systems in the literature [17,32,33]. It is generally accepted that alumina presents a high mechanical resistance and a strong interaction with supported metals leading to enhanced metal dispersion but it is also quite sensitive to the HCl formed upon the reaction [22,34]. In contrast, activated carbon is relatively inert to the HCl generated and has been postulated as very suitable support for HDC [22]. Moreover, depending on the catalytic requirements the carbon porosity and surface chemistry can be tuned through the manufacturing and activation processes [25,35].

The reaction mechanism of chlorophenols hydrodechlorination has been widely studied in the literature [16,18,19,27,36–39]. It is generally accepted that monochlorophenols react with hydrogen to produce phenol (Ph), which is further hydrogenated to cyclohexanone (C-one) [19,27,37–39]. Cyclohexanol (C-ol) can also be formed by hydrogenation of C-one when Rh or Pt are used as active phase [19,27,37] or when activated carbon-supported-Pd catalysts containing high amounts of oxygen surface groups, especially carboxylic acids and lactones, are employed [25]. The experiments of those studies are normally described by simple pseudo-first order rate equations, where the H_2 and catalyst concentration are included in the kinetic constants [16,19,27]. For simplicity the few kinetic studies reported in the literature do not consider the contribution of the adsorption of the pollutant as well as the intermediates onto the support, although it can be highly pronounced when carbon-based catalysts are used. The commonly applied procedure to obtain similar starting reaction conditions for catalysts with different adsorption capacity is to pre-adsorb the reactant onto the catalyst [25,40]. However, this oversimplification is prob-

lematic at strong adsorption since it does not allow closing the mass balance. Thus, the kinetic constants deduced cannot be used for comparison of different catalysts or to estimate the performance at technical scale. Shindler et al. [15] made a first attempt to account for the adsorption of HDC of 4-chlorophenol (4-CP). The work is restricted to the initial stage of adsorption and reaction on one activated carbon fibre supported catalyst.

In this study we compare two kinetic models for HDC of 4-CP, which neglect or account, for the sorption of the reactant 4-CP, the product Ph and the consecutive product C-one. The models are applied to describe experimental data derived from four different commercial Pd/Al₂O₃ and Pd/AC catalysts for the full course of reaction and to deduce the rate constants as a measure for the activity, while only the model accounting for the sorption steps results in a reasonable fit. Finally the kinetic data is used to simulate the course of reaction and selectivity towards the intermediate product Ph, which is strongly affected by ad-/desorption on the catalyst support and is not directly available from the free phase concentration measured during the experiments.

2. Materials and methods

2.1. Catalysts

Commercial catalysts were delivered by Alfa Aesar (AA) and Sigma Aldrich (SA) and were dried before use to remove physisorbed water. The alumina-based catalyst presents 1 wt.% Pd whereas the carbon-supported ones contain 1, 5 and 10 wt.% Pd according to the specification. Correspondingly, the catalysts have been denoted as Pd/Al₂O₃, Pd/AC-AA(1), Pd/AC-SA(5) and Pd/AC-AA(10).

2.2. Catalyst characterization

The porous structure of the catalysts was characterized from nitrogen adsorption–desorption at $-196\text{ }^\circ\text{C}$ using a Micromeritics ASAP 2010 apparatus. The samples were previously degassed overnight at $150\text{ }^\circ\text{C}$. The particle size of the catalysts was measured in aqueous suspensions by dynamic light scattering using a Mastersizer 2000 system (Malvern Instruments).

Table 1 shows the provider, palladium content, particle diameter (dp), surface area, pore volume and PZC of the commercial catalysts used in this work.

2.3. Typical reaction procedure

The aqueous phase HDC runs were performed in a glass slurry-type reactor (250 mL) where hydrogen was continuously fed at 50 N mL min^{-1} . A reaction volume of 150 mL, a catalyst concentration of 1 g L^{-1} and a stirring velocity of 750 rpm were always used, whereas the temperature was investigated within the $20\text{--}40\text{ }^\circ\text{C}$ range. The starting concentration of 4-CP was fixed at 0.78 mmol L^{-1} and 2.90 mmol L^{-1} for Pd-supported on alumina

Table 1
Characterization of the catalysts.

Provider	Pd/Al ₂ O ₃	Pd/AC-AA(1)	Pd/AC-SA(5)	Pd/AC-AA(10)
	Alfa Aesar		Sigma Aldrich	Alfa Aesar
Pd (%)	1	1	5	10
dp (μm)	24	15	10	16
BET (m ² g ⁻¹)	270	875	724	768
Pore volume (cm ³ g ⁻¹)	0.26	0.51	0.68	0.54
PZC	8.7	8.6	8.7	8.3

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