



Research paper

Exploring the role of the catalytic support sorption capacity on the hydrodechlorination kinetics by the use of carbide-derived carbons

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ABSTRACT

This work aims at evaluating the effect of the catalytic support sorption capacity on the hydrodechlorination (HDC) process. Carbide-derived carbons (CDCs) have been selected for such goal as their high purity and tunable pore structure makes them a suitable carbon model material. CDCs were synthesized from TiC by chlorination at different extraction temperatures (800–1300 °C) in order to selectively modify their pore structure and crystallinity. Afterwards, the catalysts were produced using a three step process of sulfuric acid treatment, ion-adsorption of palladium precursor and gas phase reduction. Pd/TiC-CDC (1% wt.) catalysts were tested in the HDC of 4-chlorophenol (4-CP) in both aqueous and organic phases under ambient conditions (30 °C, 1 atm, [4-CP]₀ = 2.9 mmol L⁻¹, [Pd-TiC-CDC] = 1 g L⁻¹, 50 N mL H₂ min⁻¹). The experimental results were successfully fitted by an expanded kinetic model which accounts for consecutive reaction and sorption processes in parallel, allowing to deduce true HDC kinetic constants.

The sorption capacity of the support was found to determine the HDC rates in aqueous phase. In this sense, those catalysts showing the highest surface areas and lowered ordered structures led to higher HDC rates, confirming that a high surface density of 4-CP onto the catalyst surface enhances significantly the HDC reaction. The optimum catalyst (Pd/TiC-CDC-1000) led to the complete conversion of 4-CP in 15 min at a HDC rate of $4.1 \times 10^{-2} \text{ L s}^{-1} \text{ g}_{\text{cat}}^{-1}$.

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1. Introduction

The generation of industrial wastewaters has become a problem of increasing concern within the past decades. Particular attention is receiving the discharge of organochlorinated pollutants, highly toxic species for which the environment has low assimilative capacity. These xenobiotic compounds are quite relevant in industry nowadays due to their antimicrobial properties, which make them attractive for the production of herbicides, fungicides, insecticides or broad antibacterial agents [1]. Consequently, their presence in the aquatic environment has inevitably increased during the past few decades [2–5], involving serious implications for both the environment and public health. Since the generation of these hazardous effluents is in most cases unavoidable, the development of

cost-efficient and sustainable processes for organochlorinated pollutants remediation is imperative. In this context, much scientific effort has been put into investigation of catalytic hydrodechlorination (HDC) as a promising alternative to the broadly established conventional methods [6].

Most HDC studies have focused on the active phase and thus, a number of metals such as Pd, Pt, Ni, Cu and Rh have been tested [7–14]. Among them, Pd has been widely accepted by the scientific community as the most effective metal due to its inherent capacity to dissociate hydrogen and promote C–Cl bond scission as well as to its high resistance to the poisoning properties of the chloride ions released during reaction [1,6,15]. Although to a lesser extent, catalytic supports have been also investigated as they play an important role in the activity, selectivity and stability of the catalyst. Inorganic supports such as aluminum- or silicon oxides have been widely employed [8,12,16], but carbonaceous materials and, in particular, activated carbon (AC) are the most frequently used because of their chemical resistance, high surface area and relatively inexpensiveness [1,17–20]. Moreover, their surface chemistry can be appropriately adapted to the reaction demands through activation processes [21,22] although this aspect has not been deeply explored for the HDC reaction. In any case, the effect

Abbreviations: CDC, carbide-derived carbon; MPS, mean pore size; QSDFT, quenched solid density functional theory; SPV, specific pore volume; SSA, specific surface area; TiC-CDC, titanium carbide-derived carbon.

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of functional groups has been mainly related to the dispersion of the active phase [18,22]. For instance, Calvo et al. [18] showed that the presence of carboxylic and lactone groups in Pd/AC catalysts led to enhanced conversion of 4-CP and improved selectivity to cyclohexanol due to a more homogeneous dispersion of the active phase.

Despite its high importance, studying support influences of porous carbons is challenging as for AC the production leads to scattering material properties due to the diverse quality of the raw material (e.g. wood, coal or fruit stones) [23–25]. As a result, performance of catalysts supported on AC can vary strongly. In a recent contribution, we demonstrated that sorption of reaction species, which is mainly related to the properties of the catalytic support, plays a key role on the HDC kinetics dealing with AC-supported catalysts and must be considered to deduce true kinetic constants for the HDC process [26]. Including the sorption processes in an expanded kinetic model resulted in a reasonable fit with both negligible and high adsorption capacity catalysts (Pd/Al₂O₃ and Pd/AC, respectively). Nevertheless, although different commercial Pd/AC catalysts were tested, the role of the textural properties and the crystallinity of the carbon support on the HDC performance remain unclear.

In this context, carbide-derived carbons (CDCs) appear as promising model catalyst supports to study support influence for HDC reactions. CDCs are formed by selective extraction of the metal or metalloid atoms, transforming the carbide structure into pure carbon but maintaining the original shape and volume of the precursor. The resulting carbon structure depends in high reproducibility on the synthesis method, applied temperature, pressure and choice of carbide precursor. In this sense, the pore structure can be accurately tuned ranging from ultramicroporous to mesoporous and from extremely disordered to crystalline structures [27–31]. The applicability of CDC as metal noble support in catalysis has been already demonstrated [32–36] but its application in HDC has not been investigated in the literature so far.

In this work, we explore the role of the sorption capacity of the catalytic support on the HDC kinetics by using well-defined CDCs. These materials were synthesized from titanium carbide at different temperatures in order to vary their textural properties and degree of structural order. Pd was used as active phase due to its outstanding role in HDC [6]. Prior their deposition, CDCs were oxidized in sulfuric acid medium to introduce functional groups providing surface charges and breaking the hydrophobic character [27]. The resulting Pd/TiC-CDC catalysts prepared by ion-exchange were tested in the HDC of 4-chlorophenol (4-CP) in both aqueous and organic (isopropanol) phases.

2. Materials and methods

2.1. Preparation of the Pd/TiC-CDC catalysts

The TiC-CDC supports were synthesized using titanium carbide (TiC, 99.5% purity, 2 μm diameter, Alfa Aesar GmbH & Co KG) as precursor following a reported methodology [30,33]. Briefly, the TiC powder was subjected to chlorination in an alumina tubular reactor, lined by thin graphite foil, at different temperatures (800, 1000, 1200 and 1300 °C) using a mixture of Cl₂ and He (C_{Cl₂} = 1 mol m⁻³, reactor diameter 3.2 cm, superficial velocity of 3 cm s⁻¹). After 5 h the chlorination was stopped by purging with He for 30 min. A hydrogenation post-synthesis treatment (30 min) was then carried out at a temperature equal to the CDC synthesis one to remove residual chlorine and metal chlorides from the pores of the carbon support, obtaining a hydrogen-terminated surface. Typically 5 g of carbide were completely converted to 1 g of TiC-CDC. Materials are denoted according to their chlorination temperature as TiC-CDC-T.

Prior to Pd impregnation, the TiC-CDC supports were functionalized with 50 wt.% H₂SO₄ at 90 °C for 2 h using 50 mL acid per 1 g TiC-CDC. After the treatment, the samples were washed with large amount of distilled water until neutrality and dried overnight at 60 °C.

The deposition of Pd onto the TiC-CDC solids was performed with an ion-adsorption method where the volume of precursor solution exceeds the pore volume of the carbon support. The ratio of solution to carbon was adjusted to 50 mL_{solution} g_{TiC-CDC}⁻¹. An aqueous solution of PdCl₂ (pH = 1) was used as precursor, adjusting the Pd load in the catalyst to a nominal 1 wt.%. The suspension was stirred at room temperature for 24 h. Afterwards the resulting Pd/TiC-CDC catalyst was filtered and washed with 200 mL water (per gram of catalyst) of the same pH as the impregnation solution and dried subsequently at 60 °C overnight. Finally, the catalysts (0.5 g) were reduced for 2 h at 150 °C with 10 L_N h⁻¹ of 30 vol.% H₂ in N₂ in a tubular quartz glass reactor with an inner diameter of 3.2 cm.

2.2. Catalyst characterization

The porous structure of the catalysts was characterized from nitrogen adsorption-desorption at 77 K with a Quantachrome Quadrasorb SI apparatus. The software QuadraWin version 5.02 was employed for subsequent data evaluation using Quenched Solid Density Functional Theory (QSDFT) for slit/cylindrical pores. The mean pore size (MPS) was determined assuming slit pores with the specific pore volume (SPV) and the specific surface area (SSA) calculated with QSDFT from N₂-sorption: MPS = 2·SPV/SSA.

Palladium contents were determined by inductively coupled plasma (ICP-AES, PerkinElmer Plasma 400) after digestion of the samples with a mixture of concentrated HF, HNO₃ and HCl solution in the proportion of 4:1:1. Powder X-ray diffraction (XRD) patterns were recorded in a Philips X'Pert Pro MPD diffractometer operated at 40 kV and 40 mA using Cu Kα radiation in the 2θ range from 10 to 80° (steps: 0.02°, 30 s per step). Raman spectra were recorded in a Horiba Jobin Yvon HR 800 spectrometer using a HeNe laser operating at 633 nm with a power of 20 mW.

The dispersion of Pd on the TiC-CDC supports was determined by measuring the charges (Q_{CO}) associated with electrooxidation (stripping) of adsorbed CO on Pd at saturated coverage. The adsorption of CO was carried out at a constant electrode potential of 0.05 V vs RHE by bubbling CO gas through the electrolyte for 15 min. Subsequently, the remained unadsorbed CO was purged by flowing high purity N₂ for another 15 min. The CO-stripping curves were recorded in 0.5 M H₂SO₄ solution at a scanning rate of 20 mV s⁻¹. The CO-stripping signals were corrected by subtracting the background currents associating with double layer charging and surface oxidation, which were measured in the subsequent anodic scan voltammetry. Given the well-established CO adsorption stoichiometry on a Pd surface (CO: Pd = 1:1), the dispersion can be calculated using the following equation:

$$D = \frac{Q_{CO}}{Q_e} \cdot \frac{W_{Pd} NA}{M_{Pd}} \quad (1)$$

where Q_e is the elementary charge (1.602 × 10⁻¹⁹ C); W_{Pd} is the actual loading of Pd on the electrode; NA is the Avogadro constant (6.02 × 10²³ mol⁻¹); M_{Pd} is the molar weight of Pd (106.42 g mol⁻¹).

2.3. Typical reaction procedure

HDC runs were carried out during 3 h in a glass slurry-type reactor (250 mL), equipped with H₂ supply, a magnetic stirrer (750 rpm) and temperature control. In a typical experiment, 140 mL of 4-CP aqueous solution (2.9 mmol L⁻¹ initial concentration) were placed

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