



Performance of carbon nanofibres, high surface area graphites, and activated carbons as supports of Pd-based hydrodechlorination catalysts

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ABSTRACT

Palladium catalysts (1 wt%) supported on three different carbonaceous supports (activated carbon, AC; carbon nanofibre, CNF; and high surface area graphite, HSAG) were prepared and tested for tetrachloroethylene (TTCE) catalytic hydrodechlorination at 523 K and 195 h⁻¹ space velocity (WHSV). Organic solutions (0.9 mol/L of TTCE in toluene) were used as feed, simulating real chlorinated wastes. Pd/activated carbon and Pd/CNF have shown a fast deactivation on stream, whereas the HSAG-supported catalyst showed the best performance. Characterization of fresh and used catalysts by BET, TEM, XRD and XPS revealed that the deactivation of Pd/AC catalyst is caused by the micropore blockage because of coke formation, whereas in the case of Pd/CNF, deactivation is caused by a combination of coke deposition (in lower extent than in the case of activated carbon), active phase sintering and chlorine poisoning. The best behaviour of the HSAG-based catalysts is caused by the absence of sintering and coke formation, although chlorine poisoning is still present.

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1. Introduction

Organochlorinated wastes are commonly generated in many dry-cleaning and textile modern installations. Specifically, tetrachloroethylene (TTCE) is used in most cases as solvent, generating wastes containing high TTCE concentrations (up to 40%) and other hydrocarbons. This waste (viscous liquid or solid, depending on the operation conditions), which is water-insoluble and very soluble in organic solvents, is considered as a hazardous waste because of its high TTCE content [1,2]. Catalytic hydrodechlorination (HDC), which consists of treating the chlorinated compound with hydrogen in order to transform it into hydrocarbons and hydrogen chloride (easily absorbed in water or alkali), could be a safe alternative for the treatment of these wastes [3].

Among the catalysts proposed for the hydrodechlorination of TTCE in organic wastes, palladium catalysts are considered the most active ones [4,5]. It is also fully accepted that catalyst support plays a key role on both catalytic activity and stability. Previous studies on Pd supported catalysts on activated carbon conclude that the main deactivation cause is the catalyst fouling caused by formation of coke deposits, blocking the micropores of the activated carbon [6]. However, the activated carbon supported catalysts showed an initial conversion 40% higher than the alumina-supported ones for the same palladium loading, attrib-

uted to the best dispersion of the active phase and the spill-over phenomena, that increases the adsorption of the reactant on the catalyst [6,7]. Concerning the inorganic supports (such as γ -Al₂O₃), they present also important drawbacks, such as high sensibility to the hydrogen chloride generated in the reaction or the catalysis of undesired side reactions by the support acid sites [8].

Therefore, non-microporous carbons, such as carbon nanofibres (CNFs) and high surface area graphites (HSAGs), are receiving increasing attention as catalyst supports [9–12]. Its non-microporous character suggests that coke formation (only catalysed by the active metal) might not deactivate these catalysts as dramatically as it occurs with Pd/AC, and its carbonaceous character confers them high resistance to hydrogen chloride poisoning and high affinity for organic compounds. In this way, Amorim et al. [9] studied the hydrodechlorination of chlorobenzene over CNF-supported palladium catalysts, among other materials, whereas Liu et al. reported an enhanced activity of Pd/CNF when they were treated with gaseous ammonia [10]. All these works were carried out with diluted organochlorinated-hydrogen mixtures, whereas in the industrial practice the chlorinated compounds are usually dissolved in an organic matrix, or as a solid or sludge that must be dissolved before treatment (as the procedure followed in the experiments reported in this work). On the other hand, the performance of HSAG as support for hydrodechlorination catalysts has not been, to the best of our knowledge, studied yet.

In this work, palladium supported on CNF and HSAG were compared to the more conventional Pd/activated carbon for the

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hydrodechlorination of TTCE in organic matrix (toluene). Catalyst deactivation was studied, and fresh and used catalysts were characterized by different techniques in order to determine the deactivation causes.

2. Experimental

2.1. Catalysts preparation

The supports of the catalysts tested in this study are commercially available carbonaceous materials. Activated carbon (GF-40) was supplied by Norit (The Netherlands), CNFs (Pyrograf III, PR-24 HHT) by Applied Sciences (Ohio, USA) and high surface area graphite (HSAG 300) by TIMCAL (Bodio, Switzerland). All the materials were used as purchased. In all the cases, a high purity carbonaceous material was chosen, avoiding the presence of transition metals.

Palladium catalysts were prepared by the wet impregnation method using PdCl₂ as precursor, with a nominal palladium loading of 1 wt%. The impregnation solution consisted of PdCl₂ dissolved in 0.1N HCl to generate H₂PdCl₄, with a solution volume exceeding by 20% the pore volume of the support in each case. This precursor solution was dissolved in 60 cm³ of 0.1N HCl. One gram of the carbonaceous support was added to this solution in a flask under magnetic stirring for 10 min. The flask was then placed in a rota-vapor equipped with a water bath at 343 K, spun and vacuum pumped for 0.5 h. Next, the powder was dried in a stove at 383 K for 2 h. Finally, in order to avoid mass-transfer limitations and pressure gradients inside the catalytic bed, the catalysts obtained were pelletized (applying two successive cycles at 9.8×10^4 N for 30 s each one), crushed, and sieved to particle sizes within the range of 63–100 μm.

2.2. Reaction studies

The gas phase HDC of TCE at 523 K and 0.5 MPa was carried out in a fixed-bed reactor (WHSV = 195 h⁻¹), with a great excess of hydrogen (90:1, molar) to ensure that it is not a limiting reactant. In previous works with palladium catalysts, deactivation effects were detected at this temperature [6,7]. More details about the catalytic reactor and operating conditions are given elsewhere [13]. Before the catalytic tests, the catalysts were activated in situ by passing through the reactor 0.60 L/min (s.t.p.) of hydrogen at 523 K and 0.5 MPa for 2.5 h. The organic feed (toluene as solvent and tetrachloroethylene, both supplied by Panreac with a minimum purity of 99.5 and 99.9%, respectively) flowed downwards through the reactor, being completely vaporized at reaction conditions. Reaction products were condensed and analyzed by capillary GC in a Shimadzu GC-2010 apparatus equipped with a FID detector, using a 15 m long WCOT silica-fused capillary column as stationary phase. Peak assignment was performed by GC–mass spectra and responses were determined using standard calibration mixtures, being analytical repeatability better than ±0.2%. Non-condensed gases were absorbed in alkaline solution, followed by chloride titration using the Mohr method. Conversion has been calculated in terms of the concentration of tetrachloroethylene in the liquid feed ($C_{TCE,0}$) and in the condensed reactor outlet (C_{TCE}) as $[(C_{TCE,0} - C_{TCE})/C_{TCE,0}]$, and trichloroethylene selectivity has been calculated as mole of trichloroethylene released per mole of tetrachloroethylene reacted $[C_{TCE}/(C_{TCE,0} - C_{TCE})]$. Since ethane and trichloroethylene are the only reaction products, the selectivity for ethane formation is calculated as $[1 - C_{TCE}/(C_{TCE,0} - C_{TCE})]$. The yield for total dechlorination has been calculated as the product of the tetrachloroethylene conversion by the selectivity for ethane formation. Chlorine mass balance was checked in order to ensure the absence of other undetected chlorinated compounds, with balance closures higher than 95% in all cases.

2.3. Catalysts characterization

The textural characterization of the materials (specific surface area and pore volume) was based on N₂ adsorption isotherms, determined with a Micromeritics ASAP 2000 surface analyzer. Powder X-ray diffraction (XRD) was performed with a Philips PW1710 diffractometer, working with the Cu Kα line ($\lambda = 0.154$ nm). Measurements were carried out in the range of 2θ 35–45°, at a scanning rate of 0.002° in 2θ min⁻¹ in order to study the active metal, as the (1 1 1) crystallographic plane of Pd diffract the X-ray beam at 40.1°. Likewise, the Pd particle morphology and size distributions were determined by transmission electron microscopy (TEM), a JEOL JEM2000EXII microscope.

Carbonaceous deposits on the catalysts after reaction were characterized by temperature-programmed oxidation (TPO), employing a Micromeritics TPD-2900 apparatus connected to a Pfeiffer Vacuum-300 mass spectrometer. For this purpose, 10 mg carbon samples were maintained in an oxygen-stream – 2% O₂/98% He – at 50 °C for 30 min, with a flow rate of 50 cm³ min⁻¹, and heated from 323 to 373 K at 10 K min⁻¹.

The chemical composition of the fresh and used catalysts was determined by X-ray photoelectron spectroscopy (XPS). XPS experiments were carried out in a SPECS system equipped with a hemispherical electron analyzer operating in a constant pass energy, using Mg Kα radiation ($h\nu = 1253.6$ eV). The samples were fixed to the sample holder using a carbon adhesive tape. The background pressure in the analysis chamber was kept below 2×10^{-9} mbar during data acquisition. Since samples are conductor (confirmed on observing the position of the C 1s peak at 284.6 eV), there was no need of applying surface neutralization during measurements.

3. Results and discussion

3.1. Characterization of fresh catalysts

The measured BET surface area and pore volume of the studied catalysts are shown in Table 1. The activated carbon catalyst exhibits the highest surface area due to its microporous character, although an important decrease was observed after the impregnation (37.5%). A similar reduction (31%) in surface area was observed for the HSAG-supported catalyst, decreasing the mesopore volume from 0.46 to 0.29 cm³ g⁻¹. Concerning the Pd/CNF, its surface area does not vary significantly after the impregnation with Pd, maintaining also the volume of mesopores at 0.16 cm³ g⁻¹. In all cases, the adsorption isotherms of the Pd catalysts present the same shape as the parent materials [14].

The XPS surface analysis shows that the Pd content is very close to the nominal loading (1 wt%) in all cases. Both Pd and Pd²⁺ species are found after the reduction, with Pd²⁺/Pd ratio around 0.25 for the three catalysts (Table 1). TEM images provided in Fig. 1 illustrate the Pd particle morphology and dispersion on the three carbon catalysts. The Pd/activated carbon catalyst exhibits a globular geometry, with a certain trend to form particle agglomerates, which could be caused by a limited metal–support interaction [9]. Palladium particles on CNF and HSAG present lower

Table 1
Physicochemical characterization of the three carbon supported Pd catalysts.

	Pd/AC	Pd/CNF	Pd/HSAG
S_{BET} (m ² g ⁻¹)	1069	32	222
$V_{mesopores}$ (cm ³ g ⁻¹)	0.36	0.16	0.46
d_{XRD} (nm)	42	31	25
d_{TEM} (nm)	53	16	5

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