Catalysis Communications 9 (2008) 2080–2084

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Preparation of carbon nanofibres supported palladium catalysts for hydrodechlorination reactions

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ARTICLE INFO

Article history:
Received 11 February 2008
Received in revised form 19 March 2008
Accepted 7 April 2008
Available online 12 April 2008

Keywords:
Tetrachloroethylene
Hydrodechlorination
Pd catalyst
Carbon nanofibres

ABSTRACT

Palladium catalysts (0.5 and 1 wt%) supported on carbon nanofibres were prepared and tested for tetrachloroethylene (TTCE) catalytic hydrodechlorination working with high organic loadings (using TTCE/toluene mixture, 0.9 M, that simulate real chlorinated wastes). For comparison, a commercial 0.5%-Pd/activated carbon catalyst was also tested for this reaction. CNF-based catalysts showed lower initial activity than the activated carbon-supported catalyst (40% vs. 60% initial conversion) but higher stability (after 25 h on stream activated carbon-based catalyst is completely deactivated whereas CNF-based catalysts show activities of about 15%). The fresh and used catalysts were characterized by BET, TEM, SEM, XRD and XPS. Results obtained suggest that the catalyst deactivation is caused by a combination of coke formation (lower amounts than in the case of conventional supports), and chlorine-poisoning.

1. Introduction

Organic wastes from dry-cleaning facilities and textile industries are an important environmental problem. In the most of the modern installations, tetrachloroethylene-based solvents are used for textile cleaning, generating a waste with high TTCE concentrations (up to 40%) and other hydrocarbons. This waste (viscous liquid or solid, depending on 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) could be a safe alternative treatment for these wastes [3]. Catalytic HDC consists of reacting the organo-chlorinated compounds with hydrogen in the presence of a catalyst, yielding hydrogen chloride, that can be easily removed, and, if HDC is complete, hydrocarbons, which can be burned or even, recovered as valuable chemicals.

Among catalysts proposed for hydrodechlorination reaction in presence of organic compounds, palladium catalysts are considered the most active ones [4]. Catalyst support plays an important role on both catalytic activity and stability. A comparison of activated carbon and alumina supported catalysts [5–7] conclude that the main deactivation cause is the catalyst fouling caused by formation of coke deposits, blocking the micropores of activated carbons. In the case, or inorganic supports (such as γ-Al_2O_3) the strong acid sites, formed by reaction with the HCl released during the reaction, catalyse this coke formation. So, although alumina supports lead to higher amounts of coke, its effect is less marked (slower deactivation), because of their mesoporous structure.

Therefore, other carbonaceous supports for hydrodechlorination, such as carbon nanofibers (CNF) are receiving increasing attention [8]. Its non-microporous character suggests that coke formation (only catalysed by the active metal) might not deactivate Pd/CNF catalysts as dramatically as it occurs with Pd/AC. Amorim et al. [8] studied the hydrodechlorination of chlorobenzene over palladium supported on carbon nanofibres, among other materials. However, in industrial practice, the chlorinated compound is frequently present dissolved in an organic matrix, or is a solid or sludge that must be dissolved before treatment.

The aims of our research are to study the performance of the HDC of TTCE – dissolved in an organic solvent-catalyzed by palladium supported over CNF, and the influence of palladium loading on the catalyst activity and selectivity. Two different metal loadings were tested 0.5 and 1 wt%.

2. Experimental

2.1. Catalysts preparation

A metal-free carbon nanofibre PR-24-HHT (<0.2% Fe), kindly supplied by Applied Sciences (Ohio, USA) was used as catalyst support. Palladium catalysts were prepared by wet impregnation method using $PdCl_2$ as precursor, with a nominal palladium loading of 0.5 and 1 wt%. The impregnation solution consisted of $PdCl_2$ dissolved in 0.1 N HCl to generate H_2PdCl_4, with a solution volume exceeding by 20% the pore volume of the support in each case. The

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doi:10.1016/j.catcom.2008.04.005

use of other precursors, such as palladium nitrate, has been discarded because of their lower water solubility. This precursor solution was dissolved in 60 mL of 0.1 N HCl. 1 g of the carbon nanofibre were added to this solution in a flask under magnetic stirred for 10 min. The flask was then placed in a rota-vapor equipped with a water bath at 70 °C, spun and a vacuum pump for 0.5 h. Next, the powder was dried in a stove at 110 °C for 2 h. Finally, in order to avoid mass-transfer limitations, the catalysts obtained were pelletised (applying two successive cycles at 9.8×10^4 N for 30 s each one), crushed, and sieved in order to obtain particle sizes within the range of 63 and 100 μm. A commercial Pd/activated carbon (ESCAT-26, supplied by Engelhard, 0.5% Pd; 1640 m^2/g), has been also tested in this reaction for comparison purposes.

2.2. Reaction studies

The catalyst (0.25 g) mixed with glass was placed in the mid-section of a fixed-bed reactor over a metal screen introduced inside the reactor (mesh size 60 μm). More details about the catalytic reactor and operating conditions have been described in detail elsewhere [9]. The catalyst was activated in situ before use by passing through the reactor 0.60 L/min (s.t.p.) of hydrogen at 250 °C and 0.5 MPa for 2.5 h. The hydrogen flow used in the reaction ensured a great excess of hydrogen (90:1), so that hydrogen was not a limiting reactant. The organic feed (toluene as solvent and tetrachloroethylene, 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. Repeated catalytic runs generated results that were reproducible to within ±5%. Reaction products were 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%.

2.3. Catalysts characterization

The textural characterization of the materials was based on N_2 adsorption isotherms, measured in a Micromeritics ASAP 2000 surface analyser. The morphology of the catalysts was studied by scanning electron microscopy (SEM) using a Jeol JSM-6100 microscope. Powder X-ray diffraction (XRD) was performed with a Philips PW1710 diffractometer, working with the Cu Kα line ($\lambda = 0.154$ nm). Measurements of the samples were carried out in the range 2θ of 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 39.7°. Likewise, the Pd particle morphology and size distributions were determined by transmission electron microscopy (TEM), in a JEOL JEM2000EXII microscope.

Carbon support structural characteristics as well as the carbonaceous deposits after reaction were characterized by temperature-programmed oxidation (TPO), employing a Micromeritics TPD-2900 apparatus connected to a Pfeiffer Vacuum-300 mass spectrometer. Carbon sample (10 mg) was maintained in a oxygen-stream −2% O_2/98% He – at 50 °C for 30 min, with a flow rate of 50 cm^3/min, and heated from 50 to 100 °C at 10 °C/min. Different heating ramps (10, 15, 20, and 25 °C/min) were used for the characterisation of carbonaceous deposits; coke amount determination was reproducible to better than ±5%.

The chemical composition of the fresh and used catalysts was studied by X-ray photoelectron spectroscopy (XPS) in a SPECS Phoibos 100 MCD5 system equipped with a hemispherical electron analyzer operating in a constant pass energy, using Mg Kα radiation ($h\nu = 1253.6$ eV).

3. Results and discussion

3.1. Characterisation of fresh catalysts

The BET surface areas and pore volume of carbon nanofibres remain unchanged after the impregnation with palladium, maintaining the specific surface area around 32 m^2/g and the volume of mesopores at 0.16 cm^3/g. The morphology of the carbon nanofibres after impregnation was also studied by SEM images, observing that the impregnation does not modify its external appearance and dimensions.

The surface analysis (XPS) shows that the palladium content is of 0.6% and 1.1 wt% for carbon nanofibres with nominal load of 0.5% and 1%. Both Pd and Pd^{2+} species are found in both catalysts after the reduction, the Pd^{2+}/Pd being 0.23 and 0.22 for fresh reduced 0.5%-Pd/CNF and 1%-Pd/CNF catalysts, respectively. Small amounts of chlorine (likely from precursor) have been also found. Although these chlorine atoms could be considered as a catalyst poison, it seems to be not relevant if compared with the large amounts of HCl released during the reaction. Both XPS analyses and separate TPD experiments [10] shows the total absence of functional organic groups on the catalyst surface.

TPO experiments were carried out to achieve the degree of order in carbon materials. A shift from an amorphous to a more graphitic structure is accompanied by a rise in the temperature at which combustion takes place [5,11,12]. The maximum temperature of the gasification peak is 760 °C, both for the carbonaceous support and for the palladium catalysts, so – as was deduced from N_2 isotherms and SEM images – no modification in the structure was produced by the impregnation.

The TEM micrographs show the presence of regular particles on the external surface of the nanofibre, whereas the structure of the nanofibre remains unaltered (Fig. 1). The estimated particle size determined from TEM images (at least 150 measured particles) are 14 and 16 nm, respectively. The application of Scherrer formula to the XRD peak 111 of Pd leads to an average crystallite size of 30 nm in both cases. Thus, Pd particle diameter is similar independently of the metal load. However, significant differences are obtained depending on the technique employed to the measurement, similar discrepancies being found in the literature for this kind of catalysts [8].

3.2. Reaction studies

The only TTCE hydrodechlorination products detected for all the catalysts tested were ethane and trichloroethylene (TCE), formed according to the reactions:

$$C_2Cl_4 + H_2 \rightarrow C_2HCl_3 + HCl \tag{1}$$

$$C_2HCl_3 + 4H_2 \rightarrow C_2H_6 + 3HCl \tag{2}$$

The closure of the chlorine mass-balance was higher than 95% in all the cases. The solvent (toluene) was partially hydrogenated in the first hours on stream, yielding methyl-cyclohexane (MCH). Evolution of TTCE conversion and selectivity for the three studied catalysts is shown in Fig. 2.

In general terms, it is observed that the commercial catalyst is initially more active than the CNFs-supported ones (probably because of the highest metal dispersion), although it suffers faster deactivation. So, after 27 h in stream, the Pd/activated carbon is completely deactivated, whereas the Pd/CNFs have appreciable residual conversions. The differential behaviour of the activated carbon-supported catalysts is caused because of the blockage of its microporous structure because of the coke formation [5]. By contrast, these fouling effects are considered to be less important for catalysts supported on mesoporous materials, such as alumina