Available online at www.sciencedirect.com
SCIENCE DIRECT
Catalysis Today 102–103 (2005) 234–241
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Hydrodechlorination of 1,2-dichloroethane on Pd–Ag catalysts supported on tailored texture carbon xerogels

Nathalie Job [a], Benoit Heinrichs [a,*], Fabrice Ferauche [a], Francis Noville [a], José Marien [b], Jean-Paul Pirard [a]

[a] *Laboratoire de Génie Chimique, B6a, Université de Liège, B-4000 Liège, Belgium*
[b] *Laboratoire de Physicochimie des Surfaces, B6c, Université de Liège, B-4000 Liège, Belgium*

Available online 24 March 2005

Abstract

Porous carbon xerogels synthesized in a previous study were investigated as catalysts supports. The support chosen was a micro-mesoporous carbon xerogel obtained from the pyrolysis of a resorcinol–formaldehyde resin whose synthesis variables were fixed at suitable values. Palladium and silver were deposited on this tailored texture carbon by co-impregnation using a solution of palladium and silver nitrates in nitric acid and water. Several catalysts were prepared with various Pd and Ag global contents, the latters being measured experimentally. Alloy particles, detected in all bimetallic samples, were studied by a combination of various techniques that enabled us to obtain their size as well as their bulk and surface composition. When present, the fraction of unalloyed silver was also calculated. The characterization data were related to the results of catalytic tests obtained for selective hydrodechlorination of 1,2-dichloroethane into ethylene. Results show that when the Ag content is too high, pure Ag particles are formed and the alloy composition remains constant. As a consequence, the surface composition of the alloy is constant as well and the catalytic tests lead to similar results.

Keywords: Hydrodechlorination; Carbon xerogels; Tailored texture carbon; 1,2-Dichloroethane

1. Introduction

Carbon porous materials with controlled texture can be synthesized by evaporative drying and pyrolysis of aqueous resorcinol–formaldehyde gels provided that the operating variables are correctly chosen [1–3]. The pore texture of those materials is mainly tailored by the pH of the precursors solution. Gels synthesized with pH values between 5.50 and 6.25 lead to micro-mesoporous carbon materials whose pore volume and maximum pore size increase when the synthesis pH decreases [3]. When the pH is lower than 5.50, the carbon is micro- and macroporous and looses its mechanical properties. When the pH exceeds 6.25, the material obtained is totally non porous. The ability to control their porous texture gives carbon xerogels an advantage with regard to active charcoals whose texture is mainly microporous and strongly depends on the selected raw material. The presence of mesopores should minimize diffusion limitations in catalysts carbon supports synthesized by sol–gel process, and these supports could be designed as desired depending on the considered reaction. In addition, these carbon materials possess a very good mechanical strength and monoliths of various shapes can be easily produced.

Carbon aerogels (i.e. dried by the supercritical method) were successfully used as catalysts supports [4]. Bimetallic Pd–Ag catalysts supported on active charcoals have been proved to be efficient for selective hydrodechlorination of chlorinated alkanes into alkenes [5]. One aim of the present study is to evaluate the potential of Pd–Ag alloys supported on synthetic carbon xerogels for such a reaction. Pd–Ag catalysts have been prepared by wet impregnation of a selected micro-mesoporous carbon xerogel with a solution containing nitric acid, water, $AgNO_3$ and $Pd(NO_3)_2{\cdot}2H_2O$. A series of five catalysts theoretically containing 1.5 wt.% Pd and various amounts of Ag (0–3 wt.%) was prepared. A pure Ag catalyst (1.5 wt.%) was also synthesized as a

* Corresponding author. Tel.: +32 4 366 35 05; fax: +32 4 366 35 45.
E-mail address: b.heinrichs@ulg.ac.be (B. Heinrichs).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.02.021

reference. After drying, samples were reduced under H_2 flow at 350 °C in order to obtain metallic particles.

X-ray diffraction (XRD), transmission electron microscopy (TEM), CO chemisorption and inductively coupled plasma-mass spectroscopy (ICP-MS) analysis enabled us to determine the alloy particles size, the alloy global composition, the alloy surface composition and the actual metals weight percentages. The catalysts were tested for the selective hydrodechlorination of 1,2-dichloroethane into ethylene. Conversion and selectivities were related to the catalysts properties, in particular to the surface composition of the alloy particles in each Pd–Ag sample.

2. Experimental

2.1. Synthesis of carbon xerogel supported Pd–Ag catalysts

The synthesis process of carbon xerogels was extensively described elsewhere [3]. The selected support was obtained from evaporative drying and pyrolysis of an aqueous resorcinol–formaldehyde gel with a dilution ratio $D = 5.7$ (D = solvent/reactants molar ratio), a resorcinol/formaldehyde molar ratio $R/F = 0.5$, and an initial solution pH = 5.70. The aqueous gel obtained after gelation and ageing at 85 °C was then dried by vacuum evaporation without any pre-treatment. After drying, the gel was pyrolyzed at 800 °C under nitrogen flow in a tubular oven.

The pore texture of the carbon support obtained was determined by analysis of the nitrogen adsorption–desorption isotherms. The main texture parameters are: mesopore volume, $V_{meso} = 1.14$ cm^3/g; micropore volume, $V_{micro} = 0.25$ cm^3/g and $S_{BET} = 575$ m^2/g. No macropores were detected by mercury porosimetry.

The support was then crushed and sieved between 250×10^{-6} and 500×10^{-6} m. Five samples of the obtained pellets were impregnated with nitric acid solutions containing various amounts of $AgNO_3$ and $Pd(NO_3)_2{\cdot}2H_2O$. The metal concentrations of the various impregnating solutions were calculated so that the final Pd wt.% in all catalysts was theoretically maintained at 1.5% whereas Ag wt.% was chosen to be 0%, 0.75%, 1.5% or 3%. A pure Ag catalyst (1.5 wt.%) was also synthesized as a reference. Calculations of theoretical metal contents are based upon two hypothesis: (i) the concentration of the solution in excess after impregnation (eliminated by filtration) is identical to the one of the initial solution; (ii) all the metal that entered the pores after impregnation remains trapped after drying. The actual catalyst composition might of course differ from the theoretical composition.

Five $AgNO_3$ aqueous solutions with various concentrations were first prepared. Five millilitres from a solution containing 0.926 g $Pd(NO_3)_2{\cdot}H_2O$ in 25 ml aqueous nitric acid (69 wt.%) were added to 1.5 ml of each $AgNO_3$ solution. In the case of monometallic samples, one of the metal salt solutions was replaced by its pure solvent. The final composition of the impregnating solutions is reported in Table 1.

Carbon pellets (2 g) were immersed in 4 ml of each solution for 24 h. The samples were then filtered in order to remove the excess of solution and dried under flowing air (ambient temperature) for 24 h. The drying process was completed by vacuum drying (24 h, 150 °C). After drying, the samples to be characterized were reduced in flowing H_2 (H_2 flowrate: 0.025 mmol s^{-1} from room temperature, heating rate: 350 K h^{-1}, final temperature: 623 K, duration: 3 h).

From catalysts nominal metal contents the theoretical atomic ratio $[Pd/(Pd + Ag)]_{th}$ was calculated and the nomenclature of the five samples is related to this variable (Table 1).

2.2. Sample characterization

The pore texture of pure carbon xerogel as well as Pd/C, Ag/C and Pd–Ag/C catalysts was characterized by the analysis of nitrogen adsorption–desorption isotherms performed at 77 K with a sorptomatic Carlo Erba 1900 instrument.

Actual metal contents were determined from inductively coupled plasma-mass spectroscopy. The instrument was a VG Elemental Plasma Quad PQ2. Crushed sample (25 mg) were first digested in 5 ml fuming nitric acid and heated on a hot plate to incipient dryness. Deionised water (500 ml) was then added, and 5 ml of this solution were diluted with 0.75 ml of an internal standard ($^{115}In + {}^{187}Re + {}^{209}Bi$, 50 ng/l) and 19.25 ml water [6].

Metal particles were examined by XRD, TEM and CO chemisorption.

The XRD patterns were obtained with hand-pressed samples mounted on a Siemens D5000 goniometer using the Cu Kα line (Ni filter).

Table 1
Impregnation solution compositions and metal nominal contents

Catalyst	Solution composition				Metal nominal content		
	HNO_3 (69 wt.%) (ml)	H_2O (ml)	$Pd(NO_3)_2{\cdot}H_2O$ (g)	$AgNO_3$ (g)	Pd (wt.%)	Ag (wt.%)	$[Pd/(Pd + Ag)]_{th}$ (at.%)
Pd–Ag (100–0)	5	1.5	0.1852	0	1.5	0	100
Pd–Ag (67–33)	5	1.5	0.1852	0.0673	1.5	0.75	67
Pd–Ag (50–50)	5	1.5	0.1852	0.1347	1.5	1.5	50
Pd–Ag (33–67)	5	1.5	0.1852	0.2694	1.5	3.0	33
Pd–Ag (0–100)	5	1.5	0	0.1347	0	1	0