



Short Communication

Controlled Pd deposition on carbon fibers by electroless plating for the reduction of nitrite in water

M.L. Bosko, F.A. Marchesini, L.M. Cornaglia, E.E. Miró*

Instituto de Investigaciones en Catálisis y Petroquímica (FIQ, UNL-CONICET), Santiago del Estero 2829-3000 Santa Fe, Argentina

ARTICLE INFO

Article history:

Received 24 August 2011

Received in revised form 26 September 2011

Accepted 28 September 2011

Available online 4 October 2011

Keywords:

Pd-carbon fibers
 Nitrite reduction
 Water purification
 Electroless plating
 Particle deposition

ABSTRACT

Pd catalysts supported on activated carbon felts (ACFs) with different metallic loadings were prepared by electroless plating and evaluated for the reduction of nitrite in water in a batch reactor. Homogeneous Pd dispersions were obtained, the plating solution concentration and the seeding step being the key variables that determine particle size and morphology. The formation of Pd crystals of 96 ± 22 nm situated at the external surface of the carbon fibers was obtained for 0.14 wt.% of metal loading, while an incipient formation of a Pd thin layer was detected for 1.9 wt.%. The fresh and used catalysts were characterized by SEM, EDS, XRD and XPS.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The controlled deposition of metallic particles on different supports is an issue of great interest in designing catalysts. A promising method for this purpose is electroless plating (ELP), which is a catalytic process whereby a chemical reducing agent reduces a metallic salt onto specific surface sites of catalytic surface [1]. For many years, this technique was employed to obtain metallic layers of several microns to be applied in the modification of microstructure and properties of materials [2,3]; the synthesis of composite membranes [4]; and in the plating industry to obtain conductive adhesives, metallization of non-conductive materials and metal finishing. The optimization of the deposition variables is required for the application of this technique (ELP) in catalysis [5].

The aim of the present work is to obtain a method for the controlled preparation of nanostructured Pd/Activated Carbon Felts (ACF). To this end, we selected the electroless plating procedure. Although as said above this technique is usually employed for metallic layers synthesis, we applied it to the controlled deposition of Pd crystals on the external surface of carbon fibers. Different ELP conditions were used, in order to assess their effect on the Pd morphology and catalytic properties. In this vein, we investigated the effect of the palladium particle size in the catalytic performance and activity for the nitrite reduction in water, which was selected as a possible application of the Pd/ACF catalysts. Nitrite and nitrate are water pollutants, and catalysts containing noble metals have been extensively studied for their abatement through reduction processes. On the other hand, the cloths and felts from thin

μm -sized fibers allow reducing the diffusion limitations and the pressure drop in reactors; as well as combining an open macrostructure with mechanical flexibility [6,7]. Besides catalytic measurements, the prepared catalysts were characterized by SEM, EDS, XRD and XPS.

2. Experimental

2.1. Preparation of catalytic felts

Commercial activated carbon felts (ACN 211-15) were employed as supports. They were purchased from American Technical Trading, Inc. The felts were pre-treated in aqueous solution of HCl 4.8 M for 2 h at 50 °C [1] and then rinsed in distilled water and dried at 80 °C overnight. The Pd felts were prepared in two steps. First, the surfaces were activated by deposition of catalytic Pd seed nuclei [1]. For this purpose, a conventional two step $\text{SnCl}_2/\text{PdCl}_2$ procedure was employed [8]. Substrates were immersed 5 min in solutions of 0.13 g/l of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (pH 2) and then 0.1 of PdCl_2 (pH 2); this sequence was considered as an activation cycle. Electroless plating (ELP) was used to grow the Pd nuclei. The felts were immersed in the plating bath for 90 min at 50 °C. The as-deposited ones were carefully rinsed with deionized water and finally dried at 80 °C.

Three samples (A, B and C) were prepared by this technique; the synthesis features and Pd loadings are shown in Table 1.

2.2. Catalysis characterization

The XRD patterns of the films were obtained with an XD-D1 Shimadzu instrument, using Cu K α radiation at 30 kV and 40 mA. The scan rate was 1–2° min⁻¹ in the range $2\theta = 30\text{--}90^\circ$. The images were obtained using a

* Corresponding author. Tel.: +54 342 4536861.
 E-mail address: emiro@fiq.unl.edu.ar (E.E. Miró).

JEOL scanning electron microscope, model JSM-35C, equipped with an energy dispersive analytical system (EDS, EDAX™).

X-ray photoelectron spectroscopy (XPS) analyses were performed in a multi-technique system (SPECS) equipped with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with a pass energy of 30 eV and the Mg-K α X-ray source was operated at 200 W and 20 kV. The working pressure in the analyzing chamber was less than 5×10^{-10} kPa. The XPS analyses were performed on the fresh and used catalysts after being exposed to ambient conditions. These solids were heated up in flowing H₂/Ar at 400 °C. The spectral Pd 3d, O 1s, Cl 2p and Na 1s were recorded for each sample. The data treatment was performed with the Casa XPS program (Casa Software Ltd., UK). The peak areas were determined by integration employing a Shirley-type background. Peaks were considered to be a mixture of Gaussian and Lorentzian functions in a 70/30 ratio. For the quantification of the elements, sensitivity factors provided by the manufacturer were used.

2.3. Activity test

The catalytic reduction of nitrite was performed in a three-necked round bottom flask (volume 250 ml) equipped with a magnetic stirrer (700–800 rpm). The pH value was controlled by using a pH controller unit. Experiments were carried out at room temperature, pH between 3 and 7. Hydrogen was fed through a tube into the solution [9]. A stirred batch reactor was loaded with 120 ml of distilled water, 300 mg of catalyst, and different ppm N of nitrite (N-NO₂⁻) as initial concentration. Subsequently, a hydrogen flow of 400 ml min⁻¹ was fed to the batch reactor. The pH was maintained during the reaction time by the addition of small amounts of HCl (~0.1 M) solution [9]. Before the measurements, the samples before reaction tests were reduced in a stream of H₂ at 100 °C to avoid agglomeration of palladium particles [1,10].

Small samples were taken from the vessel for the determination of nitrite and ammonium using Vis spectroscopy (Cole Parmer 1100 Spectrophotometer) combined with colorimetric reagents. The colorimetric Gries reaction was used in the assay for nitrites. Ammonium was analyzed by the adapted Berthelot method. Nitrite conversions were calculated as the amount of nitrite consumed at different reaction times divided by the initial nitrite concentration. The selectivity to N₂ was defined as the amount of N₂ produced (considering NH₄⁺ and N₂ as the main products) divided by the conversion of nitrites [11].

Results are expressed as NO₂⁻ conversion (X,%), selectivity ammonium (S_{NH₄⁺},%) and selectivity to nitrogen (S,%). These parameters are defined as follows:

$$X(\%) = [1 - C/C_0] \times 100$$

$$S_{\text{NH}_4^+}(\%) = [C_{\text{NH}_4^+}/(C_0 - C)] \times 100$$

where C₀ is the initial concentration of nitrites (mg/L N-NO₂⁻), C is the nitrites concentration at time *t*, and C_{NH₄⁺} is the ammonium

concentration at time *t*. Selectivity to gaseous nitrogenated compounds (N_{2(g)}) and some amount of N₂O) is defined as:

$$S_{\text{N}_2}(\%) = 100 - S_{\text{NH}_4^+}(\%)$$

3. Results and discussion

3.1. Catalysts characterization

In order to obtain a homogeneous dispersion of small palladium particles, which act as active sites for nitrate reduction, we prepared three different samples by electroless plating. In the preparation of these catalysts, and taking into account our previous work [4,8] we selected the number of activation cycles and the Pd content of the plating bath as the clue conditions to be modified in order to optimize the size and distribution of the Pd particles.

Surface analysis of the fresh and used catalysts was performed by XPS and the data are shown in Table 2. It can be observed that the Pd percent at volumetric level is in agreement with the Pd concentration in plating solutions (Table 1). On the other hand, as shown in Table 1, the Pd content on the surface compared with the bulk concentration displays a scale factor ca. 10. After the reaction test, no loss of Pd was detected and the bulk metal concentration remained constant in all samples, as measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA 2100.Perkin) (not shown). However, XPS results indicate that the Pd surface concentration decreases in the three samples, probably due to the sinterization of Pd crystals or metal migration inside the support pores. This result is in agreement with that reported in a previous study [12] where it is shown that the simple contact with water and hydrogen makes the dispersion of supported noble metals decrease. Besides Pd, chlorine ions are also present at the fibers surface, and their surface concentrations are also shown in Table 2. These ions come from the salts used during the catalysts preparation and also from the acidified reaction media.

The SEM images show the morphologies of the different samples. It can be observed that the Pd particle size and concentration rise with increasing metal loadings. The distribution of particle sizes and average size was estimated by the SEM images of samples A and B (Fig. 1). When the Pd load was equal to 0.14 wt.%, a high dispersion of Pd particles with a crystal size distribution between 65 and 150 nm was observed (Fig. 1.a and d). Sample B also shows a high dispersion and quantity of the Pd particles, but with larger particle size between 130 and 210 nm (Fig. 1.b and e). The average size estimated of samples A and B was equal to 96 and 169 (Fig. 1) with 95% confidence intervals of 86–106 nm and 160–179 nm, respectively. The particles were counted on the surface for samples A and B, and they were equal to 290 and 680 particles respectively, for an area of 6 μm × 5 μm (Fig. 1.a and b). After reaction, the particles showed two effects which can be observed in the SEM images: the size of the Pd particles grew,

Table 1
Synthesis features and Pd loadings of the prepared samples.

Samples	Sample A	Sample B	Sample C
Number of activation cycles	1	4	4
Composition of plating baths			
PdCl ₂ (g/l)	0.09	0.45	0.9
Na ₂ EDTA (g/l)	10	8.5	16.75
NH ₄ OH (28%) (ml/l)	100	80	160
N ₂ H ₄ (0.021 M) (ml/l)	11	–	–
N ₂ H ₄ (0.25 M) (ml/l)	–	5	10
pH	11	11	11
Pd (wt.%) ^a	0.14	1.8	1.9

^a Data obtained by ICP analysis.

Table 2
Surface features of Pd/ACF catalysts measured by XPS.

Catalysts ^a	100.Pd/C ^b	Pd 3d _{5/2} (eV)	100.Cl/C ^b	Cl 2p (eV)
Sample A	1.49	335.5	0.32	199.8
Used	0.80	335.5	0.59	199.3
Sample B	20.99	335.3	1.58	199.8
Used	7.83	335.4	0.32	199.8
Sample C	20.18	335.4	7.06	200.2
Used	17.61	335.3	0.61	199.3

^a The catalysts were treated in the spectrometer reaction chamber at 400 °C with a 5% H₂/Ar flow.

^b Relation of atomic surface concentrations.

Download English Version:

<https://daneshyari.com/en/article/51588>

Download Persian Version:

<https://daneshyari.com/article/51588>

[Daneshyari.com](https://daneshyari.com)