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Short communication

Controlled deposition of Pd and In on carbon fibers by sequential electroless plating for the catalytic reduction of nitrate in water

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ABSTRACT

Catalysts containing 1.8 wt.% of Pd and different In loadings were prepared by sequential electroless plating on activated carbon felts (ACF). Homogeneous structures were obtained, with In particles deposited at the top of a tiny Pd film. The catalyst with the higher In loading (Pd:In ratio of 2.0) presented high activity and good selectivity towards nitrogen, with negligible deactivation after 6 h of time-on-stream and three consecutive nitrate pulses. Besides the promising catalytic behavior, PdIn/ACF have the advantages of an open structure, which is highly accessible to the reactants, with no need of separation after the reaction.

1. Introduction

Nitrate is considered a potentially hazardous when groundwater is used as a supply of drinking water. The maximum levels of nitrate, nitrite and ammonium species recommended in drinking water by the World Health Organization are of 44.0, 0.1 and 0.5 mg/L, respectively.

The catalytic reduction is considered as one of the most promising methods to treat water contaminated with nitrates. In this process, nitrates are reduced to nitrogen using hydrogen or other reducing agents, but undesirable compounds as ammonia and nitrite are also formed, thus the adequate control of activity and selectivity is a key issue for the effectiveness of this method [1]. The controlled deposition of bimetallic particles on different supports is an issue of great interest in designing catalysts for this process [2]. 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 the catalytic surface [3]. In a previous work [4] it was demonstrated that Pd nanoparticles can be homogeneously deposited on the surface of carbon fibers, being active and selective for nitrite reduction with hydrogen. However, while Pd nanoparticles are effective for nitrite reduction, this is not the case for nitrate reduction. For this purpose, another metal must be loaded, for example Cu or In. In is a good candidate, being the optimal Pd:In ratio about 1:0.25 in a weight basis, when alumina or silica are the supports [5].

We have selected carbon fiber felts as the support for PdIn bimetallic catalysts because 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].

The aim of this contribution is to find new ways to control the catalyst performance using a well-defined procedure for its preparation, that is the electroless plating method. To this end, carbon fiber felts were used as a support for Pd,In active phases which were homogeneously deposited by a sequential electroless plating (ELP) technique to obtain active and selective catalysts deposited on a structured support. The catalysts were tested in the nitrate reduction reaction using hydrogen as reducing agent, and the results were compared with those obtained with a conventional PdIn/Al_2O_3 catalyst [5]. They were also characterized by XRD, EDS, SEM and XPS techniques.

2. Experimental

2.1. Preparation of catalytic felts PdIn/ACF (activated carbon felt)

Commercial activated carbon felts (ACN 211-15, American Technical Trading, Inc.; area density: 180 $g \cdot cm^{-2}$, surface area: 1500 $m^2 \cdot g^{-1}$, thickness: 2.00 mm) were used. They were treated in aqueous solutions of HCl 4.8 M for 2 h at 50 °C and then rinsed in distilled water and dried at 80 °C for 12 h. The Pd felts were prepared in two steps. First, the surfaces were activated by deposition of catalytic Pd seed nuclei using a conventional two step $SnCl_2/PdCl_2$ procedure [4]: substrates were immersed for 5 min in a 0.6×10^{-3} M solution of $SnCl_2 \cdot 2H_2O$ (pH 2) and then for another 5 min in a 0.1 M solution of $PdCl_2$ (pH 2); this sequence

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Table 1
Plating Bath compositions.

Composition of plating baths		Samples			
		Pd	$(PdIn)_A$	$(PdIn)_B$	$(PdIn)_C$
Pd bath	$PdCl_2$ (mM)	2.5	2.5	2.5	2.5
	Na_2EDTA (mM)	25.3	25.3	25.3	25.3
	NH_4OH (7.1 M) (mL/L)	80	80	80	80
	N_2H_4 (20 mM) (mL/L)	5	5	5	5
In bath	$In(NO_3)_3$ (mM)	0	0.6	1.5	3.0
	HCl(0.4 M) (mL/L)	0	4	10	20
	N_2H_4(0.2 M) (mL/L)	0	1	1	2

was considered as an activation cycle. Electroless plating (ELP) was used to grow the Pd nuclei. The synthesis features are shown in Table 1.The felts were immersed in the Pd plating bath for 90 min at 50 °C, and a Pd/ACF catalyst sample, with 1.8 wt.% of the noble metal determined by ICP, was obtained. The as-deposited samples were carefully rinsed with deionized water. Then, the felts were immersed in the In plating bath (10 ml/cm^2 felt) with the same reducing agent (N_2H_4, 0.20 M). Three samples (A, B and C) were prepared by this technique with Pd:In ratios determined by EDS of 9.5, 3.5 and 2.0, respectively. Again, the fibers were carefully rinsed with deionized water and finally dried at 80 °C.

2.2. Catalysts characterization

2.2.1. X-ray diffraction (XRD)

The XRD patterns of the films were obtained with an XD-D1 Shimadzu instrument, using CuKα radiation at 30 kV and 40 mA. The scan rate was 2°/min in the range 2θ = 10–90°.

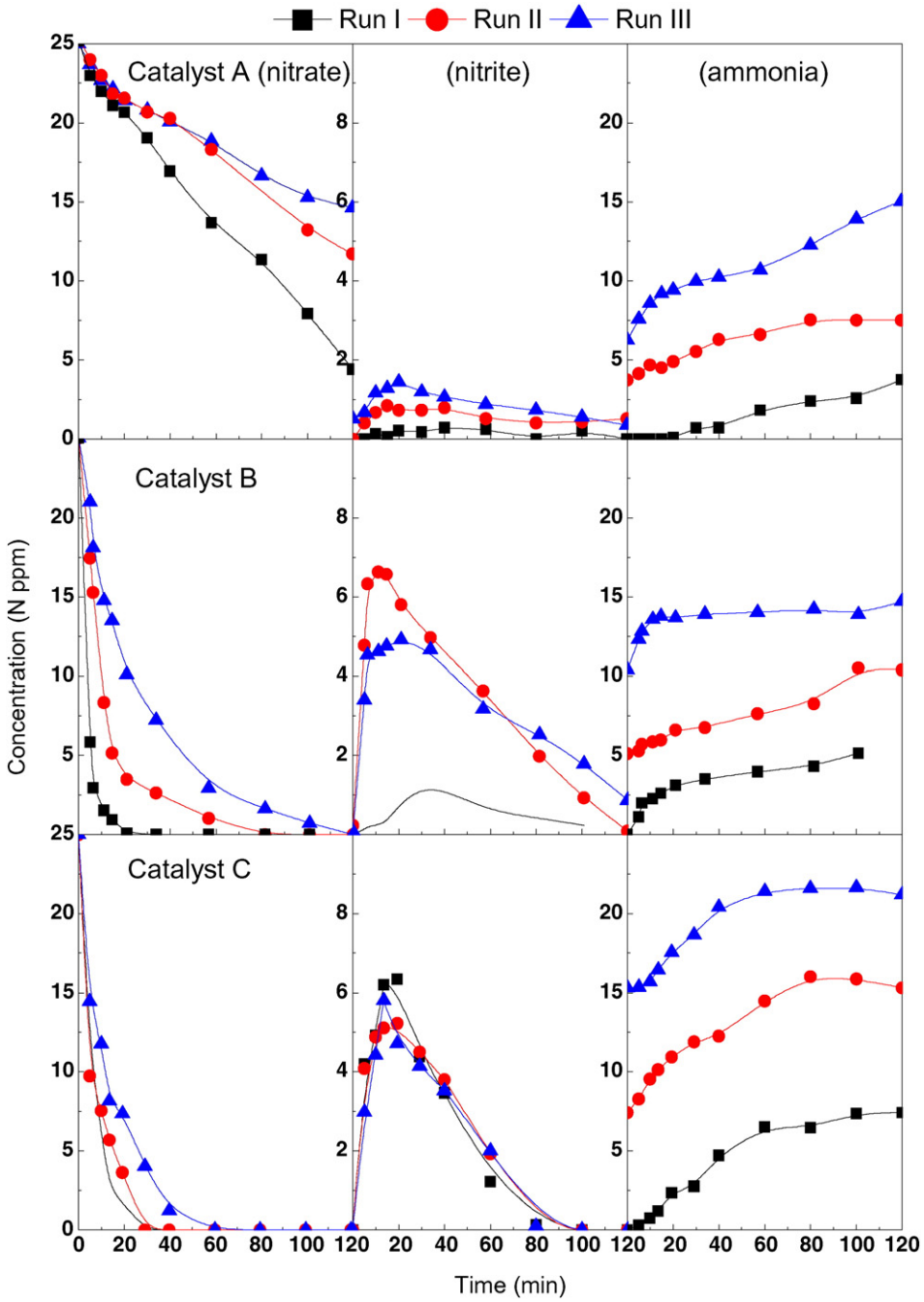

Fig. 1. Concentrations of nitrate, nitrite and ammonium after three consecutive pulses of 25 ppm of nitrate (Catalysts A, B and C), under hydrogen flow.