

Activated carbon cloth-supported Pd–Cu catalyst: Application for continuous water denitrification

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Abstract

Pd–Cu catalysts supported on woven fibrous cloths have been tested for continuous nitrate hydrogenation in water. The results demonstrate that activated carbon cloth (ACC) is an adequate support for the Pd–Cu bimetallic catalysts giving better activity and selectivity than that of supports like glass fibers cloth (GFC) and GFCs coated with Al₂O₃ or SnO₂, which were also studied.

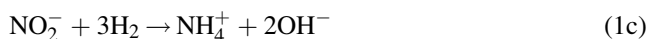
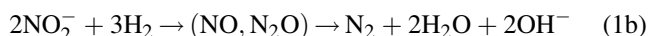
A series of 2% Pd–Cu/ACC catalysts were prepared by selective deposition of Cu on Pd/ACC and examined at steady state in a continuous three-phase radial flow reactor. The activity and selectivity of the bimetallic catalysts depend on the Cu:Pd ratio and the metal loading. The beneficial effect of copper on nitrate hydrogenation activity with a Pd–Cu/ACC catalyst is probably related to the formation of an active Pd–Cu ensembles working as active sites for nitrate-to-nitrite reduction. The maximal nitrate conversion was achieved with 0.6 wt.% Cu–2 wt.% Pd/ACC catalyst showing a 92% selectivity towards gaseous products.

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1. Introduction

Among reductive catalytic processes proposed for water purification [1], the catalytic hydrogenation of nitrates [2] is viewed as a promising emerging technology for removal of nitrates from polluted water; high concentrations of nitrate usually result from over-fertilization [3]. The hydrogenation process can approximately be described by consecutive and parallel reactions:



showing that the nitrates undergo hydrogenation to nitrites and then to gaseous nitrogen (target product) and dissolved ammonia (undesired by product) [4].

Significant effort has been devoted in the past decade for preparation and optimization of catalysts for this process. It has been shown that while single noble metals (Pd, Pt) are active only with respect to nitrite hydrogenation, many

supported noble metals with a metal promoter (Cu, Sn, In), show satisfactory performance for conversion of dissolved nitrate ions [4]. The Pd–Cu catalyst, suggested a decade ago by Horold and Vorlop [2] is still considered to be the best catalyst for the process.

The activity and selectivity of the bimetallic catalyst in nitrate hydrogenation is highly dependent on the preparation method, mode of noble metal promoting, metal-promoter ratio as well as operation conditions. Support selecting is also of importance for this process: various materials such as metal oxides (silica, alumina [5,6], zirconia [7], titania [8]), polymers [9], granular active carbon [10,11] and other materials [12] have been investigated as support for Pd–Cu catalysts and it was shown that the support had greatly affected the catalyst's activity and selectivity towards reaction products.

Currently, there is a growing interest in using novel structured supports like monoliths, foams, membranes as well as fibrous cloths [13]. Cloths woven from thin μm -sized fibers reduce the diffusion distance and produce a low-pressure drop in fixed beds and in multi-phase reactors in which one or more dissolved species have to react with gaseous compounds of limited solubility. Moreover, cloth-

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type catalysts are preferable to monoliths when rapid fluctuations in the flow regime occur, as often-encountered in applications for environmental protection. Catalytic cloths combine an open macrostructure with mechanical flexibility, allowing new options for the design of catalytic reactors.

Recently, we have studied some novel Pd-based catalytic cloths for hydrodechlorination [14] and for nitrite and nitrate hydrogenation [15–17] and obtained promising results. In this aspect it is interesting to support Pd–Cu on the activated carbon cloths (ACC), that have been proven to have a great potential as a catalytic support, especially for the expensive noble metals, since a high metal loading and dispersion can be achieved. In addition to their high apparent surface area (about of 1500 m²/g), ACCs have many other advantageous characteristics when compared with traditional activated carbons, like a morphological network formed by short micro-pores with narrow size distribution, ensuring fast adsorption and desorption, low resistance to the passage of fluid and high fluid permeability.

In this work, following a previously reports on use Pd–Cu/glass fiber cloth (GFC) as a catalyst for nitrate hydrogenation [16] and Pd/ACC for nitrite hydrogenation [17], we extend the study of a Pd–Cu catalytic cloths for nitrate removal in a radial-flow reactor operated in steady state with pre-dissolved hydrogen in the water. Most previous studies used batch reactor. Pd–Cu catalysts used in this work were prepared by the controlled reduction of copper salt on Pd/ACC, in order to obtain optimal contact of the two metals. We examined systematically the effect of the support material, and for the best Pd–Cu/ACC catalyst we optimized the metal content and the Pd/Cu ratio required for good catalytic activity and selectivity. Results of catalytic experiments are discussed along with catalyst characterization by HRSEM and CO chemisorption.

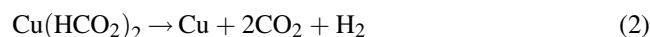
2. Experimental

2.1. Preparation of catalytic cloths

As a support, activated carbon cloth (ACC 523-15) employed in this study was purchased from Nippon KynolTM. The ACC was pre-treated in aqueous solution (4.5 wt.%) of HNO₃ and then rinsed in distilled water. For comparative purposes woven cloth made from glass fibers (GFC YO212 from Fothergil Engineered Fabrics, UK) was also used. In order to increase the specific surface area, GFC YO212 was pre-treated first with hot aqueous HCl solution (3–4 wt.%) to leaching non-silica components (support GFC). Then, the surface of fibrous glass was modified by aluminum oxide (support AlO–FC) or by tin oxide (support SnO–FC) using impregnation with aqueous solutions of Al(NO₃)₃ or SnCl₂, followed by calcination in air at 200 °C for 12 h.

Bimetallic catalytic cloths were prepared in two stages. First, Pd/cloth was obtained by incipient wetness impregnation method using H₂PdCl₄ (dihydrogen tetrachloropalladate(II)) from solution of PdCl₂ (pure, Fluka) in hydrochloric acid). In this impregnation technique the volume of the metal precursor solution does not exceed the water adsorption capacity that was determined for each support during exposure to water for overnight at room temperature. After impregnation, cloth was heat first at 90 °C overnight to eliminate of solvent and calcined at 300 °C for 5 h in flowing argon, and then was washed to remove chloride ions, which become both from decomposition of H₂PdCl₄ during calcination. Final concentration of chloride ions in rising waters was detected using AgNO₃/HNO₃. After drying at 120 °C for 2 h, the samples were reduced at 200 °C for 1 h under flowing hydrogen.

In the second step, a given amount of Pd/cloth was placed on a rotating drum and immersed into a solution of copper formate (Cu(HCO₂)₂, reagent grade Aldrich) required concentration under flowed argon. The copper formate catalytically decomposes only at the surface of Pd particles even at room temperature, according reaction scheme [18]:



which thereby is generating the metallic Cu selective only at the Pd surface. This preparation technique can be regarded as a controlled surface reaction. The solution regularly checked spectrometrically at $\lambda_{\text{max}} = 778 \text{ nm}$ for presence of copper ions in solution. Then cloth was separated from the liquid and dried overnight under argon stream at 90 °C. The metal composition of fresh and used cloths (after dissolution in concentrated HNO₃/HCl) was verified by elementary analysis performed with inductively coupled plasma emission spectrometry (ICP-ES Perkin-Elmer Optima 3000 DV instrument).

2.2. Catalytic hydrogenation

Catalytic cloths were tested for nitrate hydrogenation in flow reactor system operated with pre-dissolved hydrogen in the water [19]. In a typical run, a solution of nitrate (1.82 mmol/l from NaNO₃, reagent grade, Aldrich) in distilled water saturated with gaseous H₂ (>99.99%, Orgim, Israel) was fed into radial flow tubular reactor with rolled catalytic cloth at 25 °C.

In order to avoid hydrogen limitations in the reactor, saturation of hydrogen in nitrate solution was performed under pressure before reactor. The equilibrium concentration of the dissolved concentration of hydrogen (C_{H₂}) in water follows Henri's law:

$$C_{\text{H}_2} = P_{\text{H}_2} \alpha$$

where P_{H_2} is the hydrogen pressure and α is the hydrogen solubility constant (for water at 25 °C $\alpha = 0.89 \text{ mmol H}_2 / (\text{l}_{\text{H}_2\text{O}} \text{ bar})$). According to the reaction stoichiometry the concentration of dissolved hydrogen at the reactor inlet

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