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Catalytic reduction of nitrate on Pt-Cu and Pd-Cu on active carbon using continuous reactor The effect of copper nanoparticles

N. Barrabés [a], J. Just [a], A. Dafinov [a], F. Medina [a,*], J.L.G. Fierro [b], J.E. Sueiras [a], P. Salagre [c], Y. Cesteros [c]

[a] *Departament d'Enginyeria Química, Universitat Rovira i Virgili, Campus sescelades, 43007 Tarragona, Spain*
[b] *Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain*
[c] *Departament de Química Inorgànica, Universitat Rovira i Virgili, Campus sescelades, 43007 Tarragona, Spain*

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Abstract

The increasing pollution of natural sources of drinking water encourages the development of new emerging technologies and processes for water remediation. This work deals with the study of catalytic reduction of contaminated waters containing nitrates (60 ppm) in a continuous reactor working at room temperature and atmospheric pressure and using hydrogen as reducing agent. Optimal proportions of Pt-Cu and Pd-Cu in bimetallic catalysts on activated carbon, obtained by wetness impregnation, have been found. Besides, novel catalysts obtained from copper nanoparticles doped with Pd or Pt and supported on activated carbon, have also been studied. For all catalysts the Pt-Cu pair seems to be more selective in the transformation of the nitrates ions to nitrogen compared to Pd-Cu pair. Furthermore, considering the noble metal amount, the bimetallic nanosphere catalysts are more active (between 20 and 50) than the impregnated ones. The catalysts have been characterized by hydrogen chemisorption, BET, X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) analysis. During the reaction, a considerable amount of the noble metal in its oxidised form has been detected. Based on this result an additional step to the generally accepted reaction mechanism of the nitrate reduction has been proposed.

Keywords: Continuous reactor; Nitrate reduction; Pd-Cu and Pt-Cu/AC catalysts; Activated carbon; Bimetallic catalysts; Copper nanoparticles

1. Introduction

The nitrate compounds are proven to be harmful to the mammalian organisms. In the organism the nitrate is transformed to ammonium. An intermediate step is the partial reduction of nitrate to nitrite. The nitrite can cause a blue baby syndrome in the human and it is also a precursor to the carcinogenic nitrous amine [1,2]. The main sources of nitrate excess are the over usage of fertilisers in agriculture as well as waste effluents from certain industries. Most nitrate salts are soluble in aqueous medium so that nitrate ions are easily distributed to the groundwater sources.

Recently, due to the harmful effects of the nitrate, the European and US legislation have established the maximum admissible concentration for nitrates in drinking water to 50 and 25 mg/l, respectively. Removal of nitrates from drinking water is an important and developing area of research. Although this field of technology is currently a highly developed topic [1–12], there is still a lot of work to do regarding the process in terms of increasing the treating capacity and reducing the cost. In the treatment of nitrate containing effluents, three main types of processes can be distinguished: physical–chemical, biological and catalytic [1].

The main drawback of the physical–chemical treatments, reverse osmosis, electrodialysis and ion exchange is that the nitrates are not transformed into harmless compounds but

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* Corresponding author. Tel.: +34 977559787; fax: +34 977559667.
E-mail address: fmedina@etse.urv.es (F. Medina).

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are only concentrated, therefore the resulting brine should be treated afterwards.

From the ecological point of view, the most promising process is the anaerobic reduction of nitrates to nitrogen gas. The sensibility of the microorganisms to the pH, temperature, other compounds in the effluent, necessity of carbon source for bacterial growing, etc. accompanied by the large residence times and the generation of biological sludge are some of the features that do not always allow the employment of such processes in the nitrate removal.

Recently, there is increasing interest in the development of new processes for nitrate removal such as selective heterogeneous catalytic hydrogenation to nitrogen, which was originally described by Vorlop and co-workers [4,6]. If catalytic hydrogenation is applied to the main characteristics of the final product, the absence of nitrite as well as ammonium ions in the final product should be considered. The European Community permitted levels of ammonia in drinking water of 0.5 and 0.02 mg/l for nitrites ions.

One of the advantages of the catalytic reduction of nitrate containing effluents is that the reaction is performed in mild conditions, room temperature and atmospheric pressure. In most procedures hydrogen is used as a reducing agent [1–3,9–12]. Formic acid, which has also been tested [7,8], has two main functions as reducing agent and to maintain the pH of the medium.

Studies of heterogeneous catalytic nitrate reduction have demonstrated that bimetallic catalysts are more efficient in comparison to monometallic ones. The bimetallic catalysts on which research has been focused, consists of a noble metal (Pd, Pt, Ru, Rh and Ir) [13,14] that can easily chemisorb the hydrogen and a promoting metal from the transition group of the periodic table (Cu, Ni, Fe, Sn and In) [15] on different supports [16–24].

The most accepted reaction mechanism for the nitrate reduction is that proposed by Epron et al. [9]. It is assumed that the promoting metal is responsible for the nitrate reduction by red-ox reaction. The main function of the noble metal is to regenerate it by means of activated hydrogen (chemisorbed). The noble metal itself does not present activity for nitrate reduction. On the other hand, the noble metal is effective for the nitrite elimination. It is assumed that the nitrite reduction is realised by the activated hydrogen.

Recently, Corma and co-workers [10] have studied fresh and used Pd-Cu bimetallic catalyst for nitrate reduction by X-ray photoelectron spectroscopy (XPS) detecting Pd(II) in the spent catalysts. Contrarily, there are some studies in which the presence of Pd(II) was not observed [11,12]. For platinum catalysts there are not studies indicating the oxidation state of platinum during the reduction reaction of nitrates. Consequently, more studies are necessary in order to get a better understanding of the role of the metals in this reaction. On the other hand, the majority of these studies were performed in batch or semi-batch equipments [1–26], whereas only a few studies are reported using continuous reactors [27–29].

This work deals with catalytic reduction of water nitrate solution in a continuous three phase reactor at atmospheric pressure and room temperature, using hydrogen as reducing agent. The activity and the selectivity of two pairs of bimetallic catalysts, Pt-Cu and Pd-Cu, in different ratios supported on active carbon have been studied. Two different procedures have been followed for catalysts preparation. First, by incipient-wetness impregnation and reduction, and the second one, the synthesis of copper nanospheres followed by the deposition of noble metal on their surface. Several characterization techniques like scanning electron microscopy (SEM), nitrogen physisorption, hydrogen chemisorption, TPR, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy have been applied.

2. Experimental

2.1. Catalyst preparation

The active metals were supported on active carbon-NoritRox 0.8 with a BET surface area of 790 m^2/g and with an average particle diameter of 0.1 mm. Two main procedures have been followed for the bimetallic catalyst preparation. Firstly, the dried support was impregnated by incipient-wetness technique with an aqueous solution of the corresponding noble metal salts (H_2PtCl_6, $PdCl_2$). After that, the samples were dried at 120 °C for 24 h and then reduced at 350 °C in hydrogen flow for 3 h. The amount of the noble metal was maintained constantly at 1% of weight with respect to the support for all the catalysts. Then, at room temperature, the materials were impregnated with an aqueous solution of copper nitrate. The amount of copper was arranged from 0.05 to 5 wt% with respect to the support. After that, the sample was dried at 120 °C for 24 h and reduced again at 350 °C in hydrogen flow for 3 h. The materials obtained from this procedure are called impregnated catalysts (IC).

The second path for catalysts preparation consists of an initial synthesis of copper nanoparticles (nanospheres) following the procedure described by Sun and Xia [30]. Once obtained, an ethanol solution of copper nanospheres was mixed with an aqueous solution containing appropriate amount of Pd or Pt salts. The mixture was stirred for 2 h at room temperature under inert atmosphere. The corresponding noble metal is reduced by red-ox reaction with the copper nanoparticles, where it is deposited. Then, active carbon was impregnated with the obtained suspensions of Pt-Cu or Pd-Cu nanospheres by incipient-wetness technique. Finally, the materials were dried and then reduced under hydrogen flow at 350 °C for 3 h. The catalysts obtained following this second route were called nanosphere bimetallic catalysts (NSBC). The amount of bimetallic nanoparticles impregnated on active carbon were 5 wt% with respect to the support. The atomic ratios between noble metal and copper in the nanospheres were 1:2700 and 1:670.