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# Nitrate reduction in water catalysed by Pd–Cu on different supports

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ABSTRACT

Screening tests were carried out in order to study the influence of the support in the performance of Pd monometallic and Pd–Cu bimetallic catalysts for the reduction of nitrate in water. Several metal oxides, as well as metal oxides and activated carbon or carbon nanotube composites were assessed as supports. The catalysts were prepared and tested under the same operation conditions. It was observed that supports play an important role in the catalytic performance and in some cases are directly involved in the reaction mechanism. The Pd–Cu catalysts supported on titanium dioxide and on the composite containing carbon nanotubes and titanium dioxide present the highest conversions, while those supported on ceria materials are the most selective to nitrogen.



## 1. Introduction

Nitrate is a potentially harmful compound to human health because it can be converted into nitrites in the human body and may cause various diseases: blue baby syndrome, cancer or hypertension. The increase of pollution in natural sources of drinking water requires the development of technologies for water remediation. Reverse osmosis, ion exchange and electrodialysis, processes originally developed for drinking water production, are considered the best technologies available to treat water contaminated with nitrate; however, they cannot be used in in-situ applications due to their technological complexity. In addition, these technologies produce nitrate concentrated waste streams, which create a disposal problem due to their high saline content. Other alternative processes that can be potentially used in in-situ applications are catalytic reduction, adsorption and biological denitrification [1].

Since the discovery of Pd–Cu as an effective catalyst for the catalytic reduction of nitrate [2], several studies using bimetallic catalysts, composed by a noble metal (Pd, Pt or Rh) and a promoter metal (Cu, Sn or In) supported on different materials [3–16], have been carried out. It is well known that monometallic catalysts supported on activated carbon are inactive for nitrate reduction [17]. However, some studies have shown that nitrate can also be reduced in the presence of noble monometallic catalysts supported on appropriate metal oxides [18–22]. When nitrate reduction occurs over bimetallic catalysts, it is generally accepted that nitrate is converted into nitrite by a redox reaction on the promoter metal, whereas the role of the noble metal is to activate hydrogen, which reduces the promoter metal, completing the catalytic cycle [23,24]. On the other hand, noble metals are active for nitrite reduction. In the case of monometallic catalysts, the initial step (nitrate reduction to nitrite) is believed to be catalysed by sites on the partially reduced support [25]. High nitrate conversions are obtained in the presence of several catalysts, but also high ammonium and nitrite selectivities, which are the undesirable by-products of this process.

Many supports have been reported in literature, such as alumina [26–28], zirconia, titania and alumina membranes [29], activated carbon [17,30], $SnO_2$ [19,22], $TiO_2$ [5,25], ceria [20] and $SiO_2$ [31], and it has been demonstrated that different supports significantly affect the catalytic activity and selectivity of the process. Several other factors, such as reaction conditions, catalyst preparation method, and the way the noble metal is promoted also have an effect on the performance of the catalysts [16,25,31–34]. Constantinou et al. [35] reported that the catalytic performance of Pd–Cu catalysts supported on various mixed metal oxides, $MO_x/\gamma\text{-}Al_2O_3$ ($MO_x$ = $CeO_2$, SrO, $Mn_2O_3$, $Cr_2O_3$, $Y_2O_3$ or $TiO_2$), varies significantly depending on the support. Yoshinaga et al. [36] observed that Pd–Cu catalysts supported on activated carbon are very selective to nitrogen, and its activity is slightly higher or higher than those supported on silica or alumina, respectively. Recently, we reported that the surface chemistry of carbon materials used as support has a remarkable effect in the performance of Pd–Cu and Pt–Cu catalysts [37]. Nevertheless, more information about the role of the support in the catalyst activity and selectivity is needed.

In this study, the catalytic activity of Pd monometallic and Pd–Cu bimetallic catalysts supported on different materials was assessed

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under the same experimental conditions. Several metal oxides, as well as composites of metal oxides and activated carbon or carbon nanotubes, were used as supports of the mono and bimetallic phases. The corresponding catalytic results were compared with those obtained when activated carbon and carbon nanotubes were used as support. The main goal of this work is to carry out a screening of supports, with the active phases prepared and tested under the same conditions, in order to select the most promising for nitrate reduction, for further developments. Additionally, several supports were used for the first time for this reaction system, namely manganese oxides, composites of activated carbon and ceria or manganese oxides, and composites of carbon nanotubes and titanium dioxide.

## 2. Experimental

### 2.1. Catalyst preparation

The following commercial materials were used as support: activated carbon (NORIT GAC 1240 PLUS) (sample ACo), multiwalled carbon nanotubes (Nanocyl-3100) (sample CNT), cerium(IV) oxide (Fluka) (sample $CeO_2$), manganese(IV) oxide (Sigma-Aldrich) (sample $MnO_2$), titanium dioxide (P25 Degussa) (sample $TiO_2$), γ-alumina (Degussa) (sample $Al_2O_3$), and silica (Saint Gobain NorPro Corporation) (sample $SiO_2$). Some synthesised materials prepared as described elsewhere were also used as supports: cerium oxide [38] (sample Ce–O), cryptomelane (sample K-OMS-2) [39], activated carbon and cerium oxide composite (sample AC–Ce) [38] activated carbon and manganese oxide composite (sample AC–Mn) prepared in a similar way as AC–Ce, carbon nanotubes and titanium dioxide composite (sample CNT–$TiO_2$) [40]. All the supports were finely ground before use ($d_p$<0.1 mm).

The monometallic catalysts were prepared by incipient wetness impregnation and the bimetallic catalysts by incipient wetness co-impregnation, from aqueous solutions of the corresponding metal salts ($PdCl_2$, $Cu(NO_3)_2$). After impregnation, the samples were dried at 100 °C for 24 h. The contents of noble metal and copper were fixed at 1%Pd–1%Cu and 1%Pd (weight percent). The catalysts were heat treated under nitrogen flow at 200 °C for 1 h and reduced at 200 °C under hydrogen flow for 3 h.

### 2.2. Catalyst characterisation

The catalysts were characterised using different techniques: $N_2$ adsorption, temperature programmed reduction (TPR) and transmission electron microscopy (TEM).

The textural characterisation of the materials was based on the corresponding $N_2$ adsorption isotherms, determined at −196 °C with a Nova 4200e (Quantachrome Instruments) equipment. BET surface areas ($S_{BET}$) were calculated, as well as mesopore surface areas ($S_{meso}$) and micropore volumes ($V_{micro}$) according to the t-method.

TPR experiments were carried out in an AMI-200 (Altamira Instruments) apparatus; the sample (150 mg) was heated at 5 °C/min up to 600 °C under a flow of 5% (v/v) $H_2$ diluted with He (total flow rate of 30 $Ncm^3$/min). The $H_2$ consumption was followed by a thermal conductivity detector (TCD) and by a mass spectrometer (Dymaxion 200 amu, Ametek).

TEM micrographs were obtained using a LEO 906E microscope operating with an accelerating voltage of 120 kV. Several TEM micrographs were obtained for each catalyst and the metal particle size was determined by measuring all the metal particles present in each micrograph.

### 2.3. Catalyst evaluation

Nitrate reduction was carried out in a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure, and using hydrogen as reducing agent. Initially, 790 mL of deionised water and 400 mg of catalyst were fed into the reactor, the magnetic stirrer was adjusted to 700 rpm and the gas mixture of hydrogen and carbon dioxide (1:1, flow rate = 200 $Ncm^3$/min) was passed through the reactor for 15 min to remove oxygen; $CO_2$ acts as pH buffer (pH = 5.5). After that period, 10 mL of a nitrate solution, prepared from $NaNO_3$, was added to the reactor, in order to obtain an initial $NO_3^-$ concentration equal to 100 mg/L.

Small samples were taken from the reactor for determination of nitrate, nitrite and ammonium concentrations after defined periods. Nitrate and nitrite ions were simultaneously determined by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was a Hamilton PRP-X100 column (150 mm × 4.1 mm) working at room temperature, under isocratic conditions. The mobile phase was a solution of 0.1 M NaCl:$CH_3OH$ (45:55). Two calibration curves (0.01–10 and 10–150 mg/L) were made and linear responses were obtained in these ranges for nitrite and nitrate anions. Ammonium ions were determined by potentiometry using a convenient selective electrode. In this case, a calibration curve with seven points (0.05–50 mg/L) was obtained. pH values were also measured. Selected experiments were carried out in duplicate and the results were found to be reproducible with a maximum error of ca 2.5% relatively to the conversion average.

The amounts of palladium and copper eventually leached during reaction were measured in a UNICAM 939/959 atomic absorption spectrometer, using the remaining solution after each reaction test.

The selectivities to nitrite, ammonium and nitrogen were calculated as:

$$S_{NO_2^-} = \frac{n_{NO_2^-}}{n_{NO_3^- i} - n_{NO_3^-}} \quad (1)$$

$$S_{NH_4^+} = \frac{n_{NH_4^+}}{n_{NO_3^- i} - n_{NO_3^-}} \quad (2)$$

$$S_{N_2} = \frac{2 * n_{N_2}}{n_{NO_3^- i} - n_{NO_3^-}} \quad (3)$$

where $n_{NO_3^- i}$ is the initial amount of nitrate (mmol) and $n_{NO_3^-}$, $n_{NO_2^-}$ and $n_{NH_4^+}$ are the amounts of the respective species (mmol) at time t (min). The amounts of nitrogen ($n_{N_2}$) were calculated by a mole balance, assuming that the amount of NOx produced is negligible [36,41].

## 3. Results and discussion

### 3.1. Catalyst characterization

#### 3.1.1. Textural properties

The textural properties of the supports obtained from the $N_2$ adsorption isotherms at −196 °C are listed in Table 1. The activated carbon (ACo) has the highest BET surface area and is a microporous support. The commercial $CeO_2$ and $MnO_2$ supports present the lowest BET surface areas. The composite samples have surface areas much lower than those observed in the original carbon materials, which was expected considering the low surface areas of the oxides used. From our previous experience [16], the textural parameters of the catalysts were considered to remain practically unchanged compared to the unloaded supports.

#### 3.1.2. TPR

TPR profiles of Pd–Cu catalysts are shown in Fig. 1. Only the comparison among bimetallic catalysts was carried out. It can be observed that the position, width and intensity of the peaks depend