

Enhancement of Pd-based catalysts for the removal of nitrite and nitrate from water

A. H. Pizarro, I. Torija and V. M. Monsalvo

ABSTRACT

Mono- and bimetallic catalysts have been evaluated in the catalytic reduction of NO_2^- and NO_3^- . The activity and selectivity of the catalysts based on Pd, Pd-In and Pd-Sn supported on different materials such as basic Al_2O_3 , SiO_2 and SnO_2 have been evaluated under mild operation conditions (25 °C, 1 atm). NO_2^- hydrogenation was efficiently achieved with monometallic Pd catalyst supported on SnO_2 and the bimetallic Pd-In catalysts supported on Al_2O_3 and SiO_2 which led to the highest NO_2^- conversion (80%). Pd/ SnO_2 and bimetallic Pd-In supported catalysts completely transformed NO_3^- while Pd-Sn catalyst showed a lower activity. Initial rates between 0.5 and 2.6 $\text{mmol}\cdot\text{min}^{-1}\cdot\text{g}_{\text{Pd}}^{-1}$ were obtained for NO_3^- reduction. The lowest selectivity to NH_4^+ was observed with the Pd-In/ Al_2O_3 catalyst, which also showed a high stability in long-term experiments. The operation at low relative H_2 fractions in the gas feed greatly diminishes the selectivity to NH_4^+ , reaching concentrations below the maximum concentration allowed in drinking water (0.5 mg/L).

Key words | catalytic reduction, denitration, drinking water, indium, nitrate, nitrite

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INTRODUCTION

Nitrate pollution is one of the most important issues in water quality (Gupta & Ali 2012). The European Commission highlighted the situation of some hypertrophic rivers, lakes and ground waters where NO_3^- exceeds legal limits in more than 10% of the sampling points in the European Union (EU) (Eurostat 2012). Supranational organizations such as the European Commission and the World Health Organization (WHO) have developed some regulations and guidelines regarding NO_3^- accumulation in ground waters. The guideline values for NO_3^- and NO_2^- in drinking water dictated by the WHO are 50 and 3 mg/L, respectively. Several nations have also limited the maximum NH_4^+ levels for drinking water to 0.5 mg/L (Della Rocca *et al.* 2007).

The removal of NO_3^- from water has been traditionally carried out by biological nitrification-denitrification which is a well-known, effective and cost-effective method. However, this method is not recommended for the treatment of drinking water because of the risk of biological

contamination. The application of other economically feasible, effective and environmentally friendly solutions is required. Other systems such as electroreduction can have drawbacks, such as the production of chlorates and perchlorates (Sánchez-Carretero *et al.* 2011). Some other technologies based on the reduction of NO_3^- and perchlorate such as advanced reduction processes have also been tested recently (Vellanki *et al.* 2013).

The catalytic reduction of NO_3^- is one of the more suitable technologies for the potabilization of ground water polluted with NO_3^- . The catalytic reduction of NO_3^- uses H_2 as reactant in the presence of a bimetallic catalyst containing a noble metal from group VIII, usually palladium, and a transition metal, usually copper, as catalytic promoter for the conversion of NO_3^- to N_2 (Hörold *et al.* 1993; Barabés & Sá 2011; Pizarro *et al.* 2015). The reported costs of NO_3^- catalytic reduction are in the same range as other technologies such as biological denitrification, reverse osmosis

and ionic exchange, and there are other advantages such as no brine production, innocuous end products, no biohazard risks, stability, and ease of fine-tuning and start-up, which have to be considered in the life cycle analysis comparison (Centi & Perathoner 2003). The main cost is the use of hydrogen that is used in very low concentration when the H_2 is limited in the reaction medium. The cost of this process decreases with the life of the catalyst; therefore the main objective is to obtain catalysts with high stability. Hence, NO_3^- can be converted selectively to N_2 using Pd and other metals as promoters under adequate operation conditions. Several works have studied the denitration process using monometallic Pd supported on SnO_2 (Gavagnin *et al.* 2002) and ZrO_2 (Marella *et al.* 2000), showing some advantages over traditional supports such as Al_2O_3 or SiO_2 . These conventional supports present narrow pores that allow the formation of an internal OH^- gradient that diminishes their activity and selectivity to N_2 , increasing the undesirable NH_4^+ production. The development of catalysts with a higher pore width (i.e. Pd/ SnO_2 , Pd/ ZrO_2) decreases the effect of alkalinity inside the pore system, causing a noticeable increase of the selectivity to N_2 compared with catalysts with narrow pores.

Previous works have reported low NH_4^+ selectivity using Al_2O_3 , activated carbon, TiO_2 , SiO_2 and SnO_2 as catalytic supports. The selectivity and activity greatly depends on the catalyst properties (active phase and surface charge) and the operation conditions, mainly pH, N:H ratio (liquid phase) and the competition between different species present in the feed stream. The catalytic supports also play an important role since they present significant differences in their surface charge, area, particle size, pore width and hydrophobicity. NH_4^+ selectivity is also reported as 5% to 10% using these supports (Hörold *et al.* 1993; Barrabés & Sá 2011; Pizarro *et al.* 2015). The interaction between Pd and the promoting metal such as Cu, In or Sn in bimetallic catalysts supported on inert materials is also more improbable than that present in reducible metal oxides where Pd nanoparticles are in full contact with the active supports such as SnO_2 (Gavagnin *et al.* 2002; Sá *et al.* 2007; Bošković *et al.* 2008; Guo *et al.* 2012), CeO_2 (Epron *et al.* 2002; Devadas *et al.* 2011; Kim *et al.* 2014; Lee *et al.* 2015) or TiO_2 (Gao *et al.* 2003; Sá & Anderson 2008; Zhang *et al.* 2008; Krawczyk *et al.* 2011; Chen *et al.* 2013; Kim *et al.* 2013, 2014).

The majority of studies (close to 75%) focused on the catalytic reduction of NO_3^- concluded that Pd is the most active phase to reduce NO_2^- . In addition, Pd is more selective to N_2 production than Rh, Ru or Pt catalysts (Hörold *et al.* 1993; Barrabés & Sá 2011). Studies on the use of other less toxic metals such as zero valent iron for NO_3^- reduction reported an undesirable high selectivity to NH_4^+ and iron leaching caused by its corrosion. Pd has demonstrated the highest stability so far and scarce leaching in the pH range for water potabilization. The aim of this work is to study and compare the catalytic reduction of NO_2^- and NO_3^- with H_2 as reducing agent using Pd catalysts supported on Al_2O_3 , SiO_2 and SnO_2 . The effect of the H_2 flow and the supplementation of CO_2 have also been evaluated. A novel Pd-In/ γ - Al_2O_3 catalyst has been also prepared and evaluated in terms of activity, selectivity to N_2 and stability treating NO_3^- bearing water.

MATERIALS AND METHODS

Catalyst preparation

Al_2O_3 Brockmann (Sigma Aldrich), SiO_2 (Scharlab), and SnO_2 (Sigma) were used as supports to prepare the monometallic catalysts tested in the batch experiments. Pd was incorporated in the oxides by wet impregnation of $PdCl_2$ (Sigma, 99.99%) dissolved in an acidic solution (0.1 M HCl) or Na_2PdCl_4 (Sigma, 99.99%) dissolved in water (1 mL/g of support). The bimetallic catalysts supported on Al_2O_3 or SiO_2 were co-impregnated using $PdCl_2$ (Sigma, 99.99%) (0.1 M HCl) with $InCl_3$ or $SnCl_4$ (liquid). The impregnated materials were dried overnight at 100 °C and calcined at 500 °C for 2 h. The resulting catalysts were reduced in H_2 atmosphere (35 NmL/min) at 100 °C for 1 h before the catalytic experiments. The Pd content in the monometallic catalyst was 5 wt%. Bimetallic catalysts were prepared with 5 wt% of Pd with a ratio Pd:Me 4:1 (w:w), where Me is Sn or In.

Catalyst characterization methods

Room temperature powder X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance A25 diffractometer

with a Bragg Brentano configuration and a lineal detector Lynxeye (Bruker). The X-ray source was a copper long fine focus X-ray diffraction tube operating at 40 kV and 30 mA, with an angular step of 0.015° and a time per step of 0.1 s. Crystalline phases were identified by referencing the PDF 2014 database.

The porous structure of the catalyst was assessed from the -196°C N_2 adsorption-desorption isotherms, obtained in a Micromeritics ASAP 2020. The samples were previously outgassed at 160°C and 0.66 Pa for 16 h. The specific surface area was calculated from the BET method (S_{BET}). The particle size distribution of the metallic phase was determined by transmission electron microscopy (TEM) using a Phillips CM-200 microscope with a point of resolution of 2.8 \AA coupled with an energy dispersive EDAX X-ray spectrometer.

Catalytic reduction of nitrite and nitrate

The reduction experiments in batch mode were performed in batch glass reactors (0.6 L capacity) at 25°C and atmospheric pressure using 1.61 mM initial concentration of NO_2^- (NaNO_2 , Scharlau, 98%) or NO_3^- (NaNO_3 , Scharlau, 99%) with 1 g/L of catalyst. Internal and external mass transfer limitations were discarded after preliminary experiments where the effects of agitation (700 rpm), bubbling and particle size were checked. The reactor was placed in a thermostatic bath and the experiments were conducted under continuous H_2 or $\text{H}_2 + \text{CO}_2$ flow.

The catalyst was previously reduced at 100°C under H_2 flow (35 N mL/min) for 1 h and outgassed with N_2 for 30 min at ambient temperature. The temperature of the reactor was maintained at 25°C before and during the catalytic tests. The catalyst was placed inside the reactor with 450 mL of distilled water. The catalyst was maintained in this aqueous suspension under continuous stirring and bubbling H_2 or $\text{H}_2 + \text{CO}_2$ for 20 min prior to the catalytic test in order to favour the catalyst wetting. A H_2 gas flow of 15 N mL/min was used, which was reduced to 8 N mL/min when CO_2 was supplemented (8 N mL/min). Then, a concentrated solution containing (16.1 mM of NO_2^- (NaNO_2) or NO_3^- (NaNO_3) was fed to the catalytic reactor, reaching an initial concentration of 1.61 mM. Catalytic tests of 1 and 3 h were performed for NO_2^- and NO_3^- reduction,

respectively. Samples were withdrawn from the reactor and filtered through regenerated cellulose filters with a pore diameter of $0.45\text{ }\mu\text{m}$.

The stability of the catalysts was checked upon long-term continuous experiments (up to 500 h) carried out in a fixed-bed reactor (Pyrex glass, 30 cm length, 9 mm inner diameter). The catalysts were deposited on a porous glass support placed in the middle part of the reactor. The catalyst used consisted of 0.3 g of Pd-In/ Al_2O_3 synthesized according to the aforementioned method. An aqueous solution of 100 mg/L of NO_3^- was fed (0.5 mL/min) with H_2 and CO_2 at different flow rates (0.3–1.5 N mL/min) and fractions (3.75–100% H_2/CO_2 , v/v). Liquid samples were taken from the reactor at different times on stream.

Analytical methods

NO_3^- , NO_2^- , NH_4^+ and total nitrogen (N_T) were analyzed by colorimetric titration using Hach Lange reagents and a benchtop VIS spectrophotometer DR 3900TM with RFID (Hach Lange). The pH, electrical conductivity (EC) and temperature were analyzed using a Crison MM 40 equipment.

RESULTS AND DISCUSSION

Characterization of mono- and bimetallic catalysts

The XRD diffractograms of the Pd catalysts prepared by impregnation of PdCl_2 on SiO_2 , Al_2O_3 and SnO_2 are depicted in Figure 1(a)–1(c), respectively. The mean Pd particle size was measured using the Scherrer equation giving values of 14, 9 and 11 nm for Pd/ Al_2O_3 , Pd/ SiO_2 and Pd/ SnO_2 , respectively. The crystallinity of these catalysts samples resulted in 40%, 73% and 77%, respectively. Table 1 shows the BET area and the average pore diameter of these monometallic catalysts. A high increase of the pore width upon the impregnation stage was observed for Pd supported on Al_2O_3 probably due to the acidic nature of the PdCl_2 solution. Contrarily, pore size diminished when Pd was incorporated to SiO_2 , which seems to be related to pore system blockage. The effect of Pd incorporation on SnO_2 was negligible. A similar response was observed

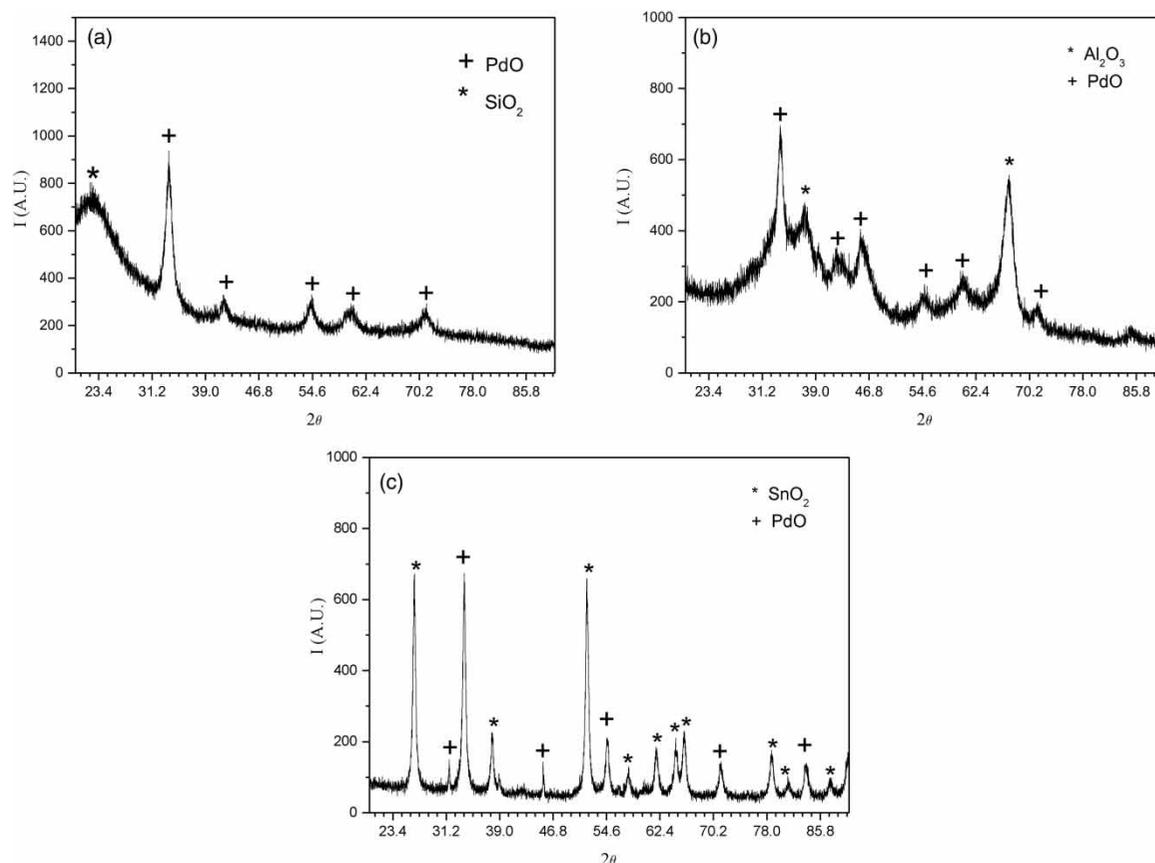


Figure 1 | XRD diffractograms of Pd/SiO₂ (a), Pd/Al₂O₃ (b), and Pd/SnO₂ (c).

Table 1 | Characterization of the monometallic catalysts

Support/ catalyst	BET surface area (m ² g ⁻¹)	External area (m ² g ⁻¹)	V _p ^a (cm ³ g ⁻¹)	D _p ^b (nm)
Al ₂ O ₃	145	149	0.27	2.4
SiO ₂	500	508	0.67	5.3
SnO ₂	30	28	0.19	18.0
Pd/Al ₂ O ₃	145	143	0.26	4.8
Pd/SiO ₂	497	513	0.62	3.9
Pd/SnO ₂	30	27	0.18	18.1

^aV_p (pore volume) Adsorption total volume of pores.

^bD_p (pore diameter) Adsorption average pore width (4 V/A by BET).

with the bimetallic catalysts (Table 2), but the effect of the impregnation was more severe in this case. The main difference with respect to the monometallic catalysts is the significant decrease in the BET surface area values obtained; this is because a high percentage of the metals are co-impregnated. The metal loads obtained are close to the

Table 2 | Characterization of the bimetallic catalysts tested and the catalytic activity in NO₃⁻ reduction

Catalyst	BET surface area (m ² g ⁻¹)	External area (m ² g ⁻¹)	V _p ^a (cm ³ g ⁻¹)	D _p ^b (nm)
Pd-Sn/Al ₂ O ₃	131	133	0.23	7.2
Pd-In/Al ₂ O ₃	122	120	0.22	6.1
Pd-Sn/SiO ₂	435	448	0.55	4.0
Pd-In/SiO ₂	420	434	0.54	5.1

^aV_p (pore volume) Adsorption total volume of pores.

^bD_p (pore diameter) Adsorption average pore width (4 V/A by BET).

expected nominal values, which indicates that the impregnation method proposed is highly effective.

TEM images of the monometallic catalysts are depicted in Figure 2. As can be observed in Figure 2(a) and 2(b), the high load of Pd achieved in the Al₂O₃ catalysts favoured the agglomeration of the Pd nanoparticles. The micrographs of Pd/SiO₂ (Figure 2(c) and 2(d)) and of Pd/SnO₂ (Figure 2(e)

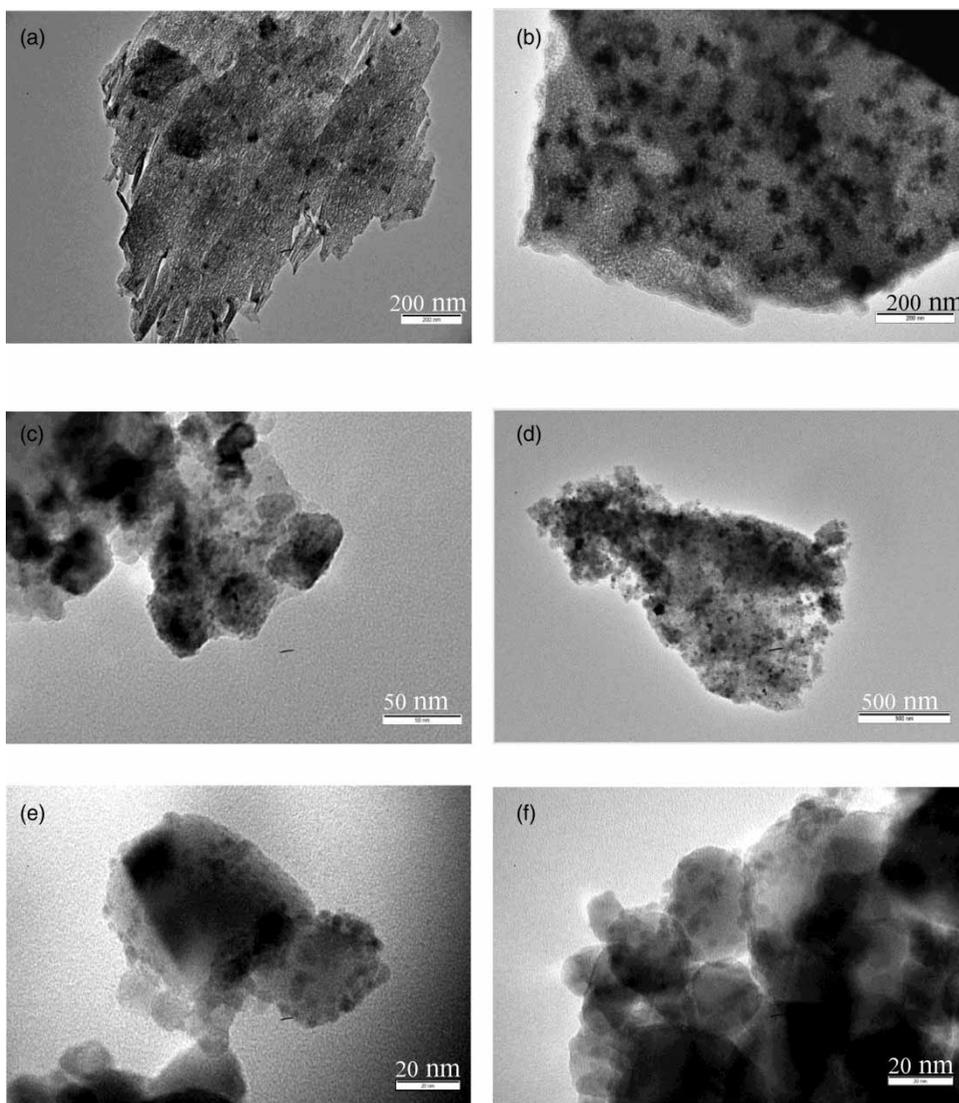


Figure 2 | TEM images of monometallic Pd catalysts on different supports: Al₂O₃ (a) and (b), SiO₂ (c) and (d) and SnO₂ (e) and (f).

and 2(f) show a high dispersion of the metallic active phase. The average nanoparticle diameters of the Pd nanoparticles calculated were 62, 20 and 5 nm for Pd-Al₂O₃, Pd/SiO₂ and Pd/SnO₂, respectively, following the procedure described elsewhere (Pizarro *et al.* 2014).

Catalytic reduction of nitrite using monometallic catalysts

Figure 3 shows the NH₄⁺ concentration observed at different NO₂⁻ conversion with monometallic catalysts impregnated with PdCl₂. The analysis of the selectivity to NH₄⁺ formation

revealed a broad response of the catalysts tested. The Pd/SiO₂ catalyst was especially attractive since a concentration of NH₄⁺ lower than 3.5 mg/L was obtained for a NO₂⁻ conversion close to 50%. This has been related to its small nanoparticle size, which favours the selectivity to N₂ (Matatov-Meytal *et al.* 2003). The use of Al₂O₃ and SnO₂ as supports led to NH₄⁺ concentrations of 7.0 and 8.5 mg/L, respectively, for a similar NO₂⁻ conversion value (50%).

The Pd/SnO₂ catalyst showed the highest reaction rates and conversion (70%), which reveals the positive impact of highly dispersed Pd nanoparticles (Figure 2). However, this catalyst led to an NH₄⁺ concentration higher than that

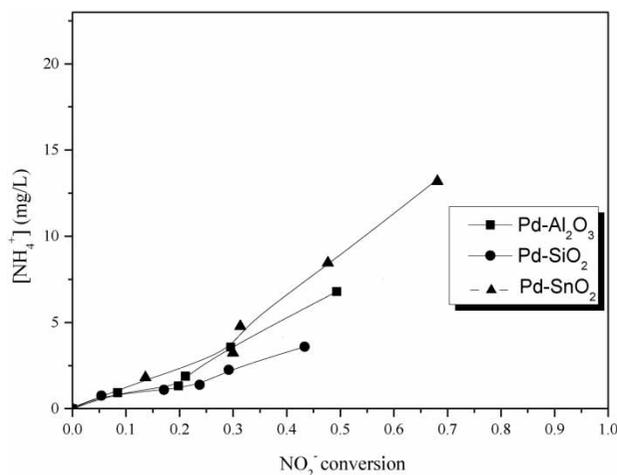


Figure 3 | NO_2^- reduction with monometallic Pd catalysts (25 °C, 1 atm, pH_0 6, $[\text{catalyst}]_0 = 1$ g/L, $[\text{NO}_2^-]_0 = 1.61$ mmol/L, $Q_{\text{H}_2} = 15$ N mL/min).

obtained using Pd/ Al_2O_3 and Pd/ SiO_2 catalysts. This fact could be related to the synergistic interaction between Pd and the SnO_2 reducible support.

Catalytic reduction of nitrite using bimetallic catalysts

The catalytic reduction of NO_2^- was also evaluated using bimetallic Pd-Sn and Pd-In catalysts supported on Al_2O_3 and SiO_2 . As can be observed in Figure 4(a), the addition of co-metals, especially In, increased the conversion extension up to 0.82. Figure 4(a) shows the NH_4^+ concentration produced with Pd-Sn/ Al_2O_3 and Pd-Sn/ SiO_2 catalysts. The conversion obtained with these catalysts exceeds the

values obtained with the monometallic catalysts supported on Al_2O_3 or SiO_2 . Previous works have reported that bimetallic catalysts favour the dispersion of the Pd metallic phase due to the strong interaction between Pd and the SnO_2 phase, expanding the active surface of Pd, especially when a co-impregnation method is used (Bošković *et al.* 2008; Pizarro *et al.* 2015).

The addition of Sn (Pd-Sn/ Al_2O_3) as co-metal also enhanced the selectivity to N_2 , reducing the NH_4^+ concentration from 6.7 to 3.6 mg/L at a NO_2^- conversion of 50%. Unlike the results observed with the monometallic catalysts, the use of SiO_2 in bimetallic catalysts produced more NH_4^+ than those supported in Al_2O_3 .

The results obtained in the catalytic reduction of NO_2^- with bimetallic Pd-In catalysts supported on Al_2O_3 and SiO_2 are shown in Figure 4(b). The presence of In led to a higher activity than that obtained with Sn doped catalysts. This enhancement of the catalytic activity seems to be related to a strong interaction between Pd and In_2O_3 phases that results in a close contact between the two active phases. The production of NH_4^+ with Pd-In catalysts yielded concentrations of 5.0 and 12.5 mg/L at a NO_2^- conversion of 50% with Pd-In/ Al_2O_3 and Pd-In/ SiO_2 , respectively.

Catalytic reduction of nitrate using monometallic catalysts

The catalytic reduction of NO_3^- using a monometallic Pd- SnO_2 catalyst was tested using two different salts as

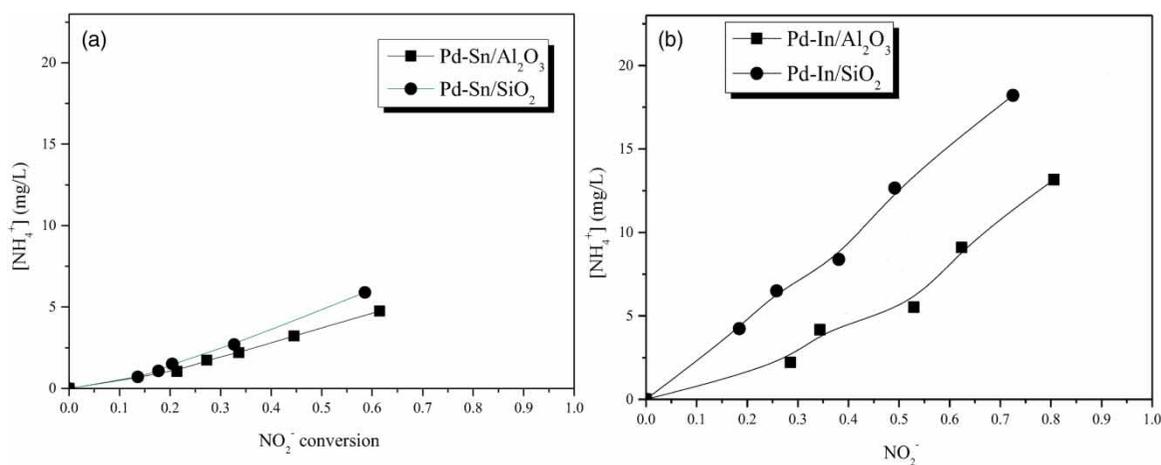


Figure 4 | NO_2^- reduction with bimetallic Pd catalysts supported on inert oxides; (a) catalysts based on Pd-Sn; (b) catalysts based on Pd-In (25 °C, 1 atm, pH_0 6, $[\text{catalyst}]_0 = 1$ g/L, $[\text{NO}_2^-]_0 = 1.61$ mmol/L, $Q_{\text{H}_2} = 15$ N mL/min).

precursors: PdCl₂ and Na₂PdCl₄ (Figure 5). First, the NO₃⁻ reduction was performed with H₂ as the only gas fed (Figure 5(a)). The conversion reached with the catalyst synthesized with PdCl₂ (90%) was higher than that synthesized with Na₂PdCl₄ (60%) while a slight difference was observed on the selectivity to NH₄⁺ at a similar NO₃⁻ conversion. Nitrite production was favoured with the catalyst impregnated with Na₂PdCl₄. Figure 5(b) shows the conversion of NO₃⁻ and the concentration of NH₄⁺ reached when feeding H₂:CO₂ (50%, v/v), where a significant enhancement in the catalytic performance was observed. The addition of CO₂ in the inlet gas led to a total NO₃⁻ conversion and decreased the selectivity to NH₄⁺ as a consequence of the

OH⁻ neutralization in the pore system. The use of PdCl₂ as salt precursor resulted in a higher catalytic activity and a high NO₃⁻ reduction rate due to the close interaction between Pd and the reducible support. In addition, NO₂⁻ accumulation in the reaction medium and the increase of the pH medium, were mitigated in the presence of CO₂.

Catalytic reduction of nitrate with bimetallic catalysts

The catalytic reduction of NO₃⁻ was also tested with Pd-Sn and Pd-In catalysts impregnated with PdCl₂ supported on Al₂O₃ and SiO₂ in absence and presence of CO₂. Figure 6(a) shows the NO₃⁻ conversion and the concentration of NO₂⁻

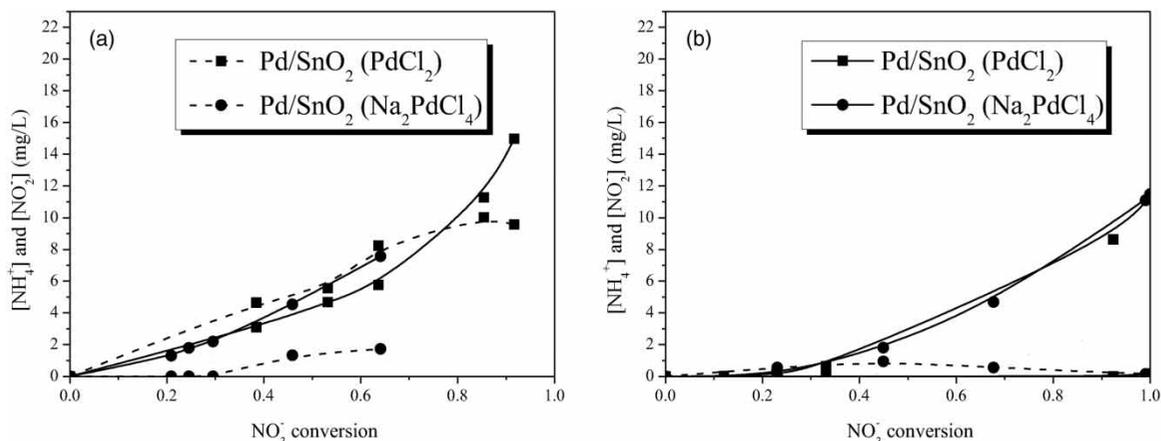


Figure 5 | NO₃⁻ reduction with monometallic Pd/SnO₂ catalyst synthesized with PdCl₂ and Na₂PdCl₄; (a) with H₂ and (b) with H₂ + CO₂ (25 °C, 1 atm, pH₀ 6, [catalyst]₀ = 1 g/L, [NO₃⁻]₀ = 1.61 mmol/L (100 mg/L), QH₂ = 15 Nml/min or QH₂ + CO₂ = 16 N ml/min). Dashed lines represent NO₂⁻ concentration.

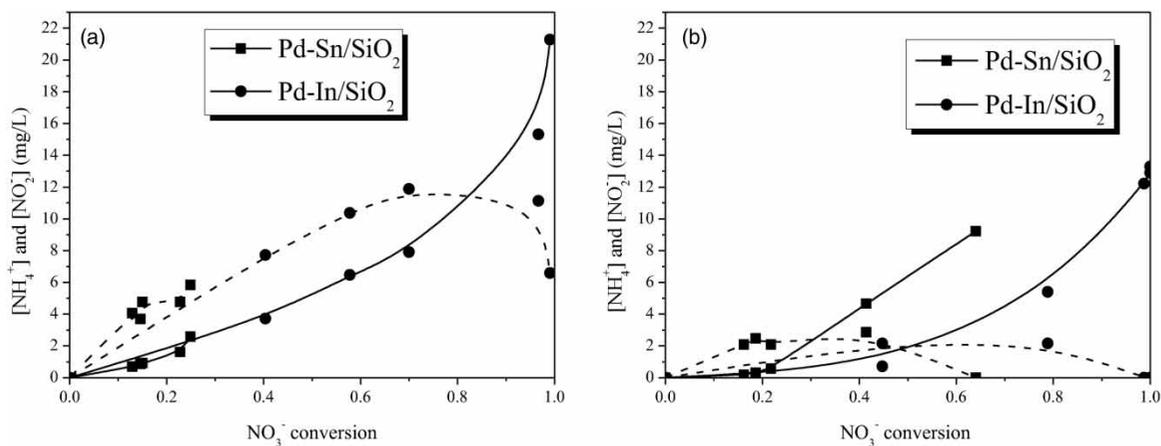


Figure 6 | NO₃⁻ reduction with Pd-Sn and Pd-In supported on SiO₂ (a) with H₂ and (b) with H₂ + CO₂ (25 °C, 1 atm, pH₀ 6, [catalyst]₀ = 1 g/L, [NO₃⁻]₀ = 1.61 mmol/L (100 mg/L), QH₂ = 15 Nml/min or QH₂ + CO₂ = 8 and 8 Nml/min). Dashed lines represent NO₂⁻ concentration.

and NH_4^+ , corresponding to the catalytic reduction of NO_3^- with Pd-Sn/SiO₂ and Pd-In/SiO₂ catalysts without pH buffering. The Pd-In catalyst yielded total conversion of NO_3^- in less than 3 h while the Pd-Sn catalyst reached less than 25% conversion. The latter was deactivated by the alkaline medium generated in the catalytic reaction studied.

The performance of these bimetallic Pd-Sn and Pd-In catalysts supported on SiO₂ was improved significantly when adding CO₂ to control the pH value between 5.0 and 5.5 in the reaction medium (Figure 6(b)). The NO_3^- conversion was significantly increased by supplementing CO₂, reaching a conversion of 65% with the Pd-Sn/SiO₂, and total conversion was achieved with the Pd-In/SiO₂ catalyst. The selectivity to NH_4^+ obtained with the latter clearly diminished, with concentrations from 21 to 14 mg/L and from 5 to less than 3 mg/L at a NO_3^- conversion of 100%

Table 3 | Selectivity to NH_4^+ (at different NO_3^- conversion values) and initial rates calculated in the catalytic reduction of NO_3^- with and without CO₂ addition

Catalyst	SNH_4^+ [H ₂] % (NO_3^- conversion)	SNH_4^+ [H ₂ + CO ₂] % (NO_3^- conversion)	Specific initial conversion rate ($\text{mmolNO}_3^- \text{ min}^{-1} \text{ g}_{\text{Pd}}^{-1}$)
Pd/SnO ₂	46 (91)	49 (100)	–
Pd/SnO ₂ (Na)	73 (91)	51 (100)	–
Pd-Sn/Al ₂ O ₃	74 (50)	56 (100)	0.74
Pd-In/Al ₂ O ₃	92 (100)	34 (100)	1.44
Pd-Sn/SiO ₂	48 (24)	64 (64)	0.50
Pd-In/SiO ₂	94 (100)	59 (100)	2.57

and 50%, respectively. The initial rate of NO_3^- reduction reached with the Pd-In/SiO₂ catalyst was fivefold higher than that of Pd-Sn/SiO₂ (Table 3).

NO_3^- conversion and selectivity to NH_4^+ was significantly improved when CO₂ was added using the Pd-Me bimetallic catalysts supported on Al₂O₃. Figure 7(a) shows the results obtained during the catalytic reduction of NO_3^- experiments with Pd-Sn/Al₂O₃ and Pd-In/Al₂O₃ in absence of CO₂. Bimetallic Pd-Sn/Al₂O₃ catalyst led to a higher conversion level (50%) than the Pd-Sn/SiO₂ catalyst (25%) showed in Figure 6(a). Pd-In/Al₂O₃ catalyst reached total conversion and a similar selectivity to NH_4^+ to that obtained with the Pd-In/SiO₂ catalyst (Figure 6(a)). NO_2^- is accumulated in the absence of a pH buffering source (Figure 6(a)), which is effectively transformed by the addition of CO₂ (Figure 6(b)).

The results obtained with the Pd-Sn/Al₂O₃ and Pd-In/Al₂O₃ catalysts without and with CO₂ in the gas feed are depicted in Figure 7(a) and 7(b), respectively. A total NO_3^- conversion was achieved with both catalysts when CO₂ was added, the Pd-In catalyst being less selective to NH_4^+ , reaching a concentration of 7.5 mg/L in the final effluent (Figure 7(b)). The initial rate of NO_3^- reduction reached by the Pd-In/Al₂O₃ catalyst was twice the observed with the Pd-Sn/Al₂O₃ catalyst (Table 3). Again, the pH control by adding CO₂ was an effective strategy to diminish the production of NO_2^- and NH_4^+ . These results indicate that the bimetallic catalysts supported on Al₂O₃ are the most appropriate for the reduction of NO_3^- ; the Pd-In/Al₂O₃ catalyst

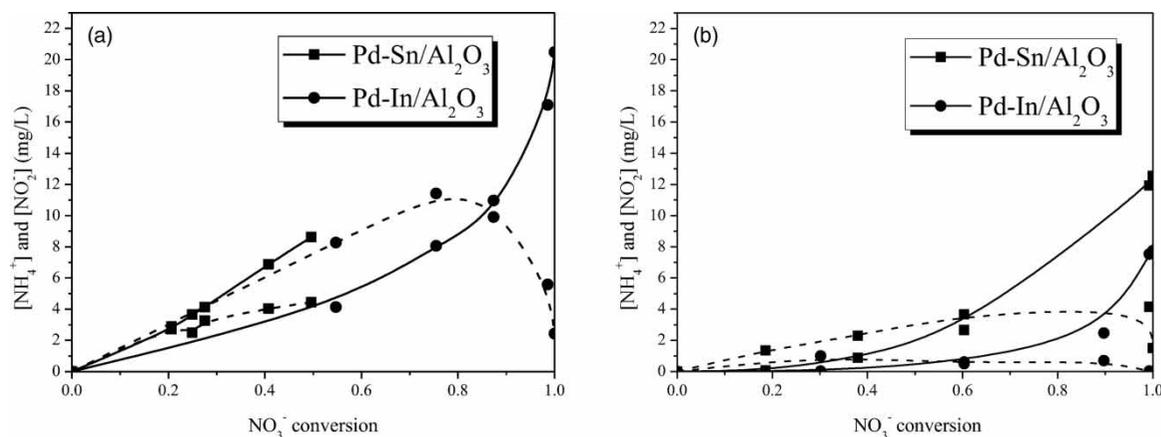


Figure 7 | NO_3^- reduction with Pd-Sn and Pd-In supported on Al₂O₃ (a) with H₂ and (b) with H₂ + CO₂ (25 °C, 1 atm, pH₀ 6, [catalyst]₀ = 1 g/L, [NO_3^-]₀ = 1.61 mmol/L (100 mg/L), QH₂ = 15 N mL/min or QH₂ + CO₂ = 8 and 8 N mL/min). Dashed lines represent NO_2^- concentration.

was selected for the next experiments. The wider pores of Al_2O_3 than that observed for SiO_2 could present a positive effect on the neutralization of OH^- when CO_2 is supplemented.

Influence of H_2 flow on the catalytic activity

It has been reported that the H:N ratio in the gas feed can have a decisive influence on the selectivity to N_2 obtained during the catalytic reduction of NO_3^- (Hörold *et al.* 1993). With the aim of analyzing the influence of the amount of H_2 present in the reaction medium, the H_2 flow was varied from 0.3 to 8.0 N mL/min maintaining a CO_2 gas flow of 8.0 N mL/min with the Pd-In/ Al_2O_3 catalyst. Figure 8(a) shows the concentration of NH_4^+ obtained at different NO_3^- conversions. The amount of NH_4^+ produced with the lowest H_2 flow rate (0.3 N mL/min) was 0.33 mg/L of NH_4^+ (selectivity to NH_4^+ of 2.7%) for a NO_3^- conversion

of 55%, reaching the legal limits established by the environmental legislation. This result improves those obtained under H_2 and CO_2 saturation as reflected in Table 3. This shows that selectivity towards NH_4^+ can be effectively diminished by controlling the H:N ratio in the gas feed. High values of NO_3^- conversion (around 80%) were reached at increasing H_2 flows (4.0 and 8.0 N mL/min).

The availability of chemisorbed hydrogen promotes the formation of NH_4^+ from NO_2^- (Ebbesen *et al.* 2008). This fact determines the selectivity when different relative concentrations of $\text{NO}_3^-/\text{NO}_2^-$ are treated, different sizes of Pd nanoparticles are used or the solubility of H_2 is modified by changing the operation conditions.

Stability of the Pd-In/ Al_2O_3 catalyst

The stability of the Pd-based catalysts has been scarcely studied, showing high and constant activities treating

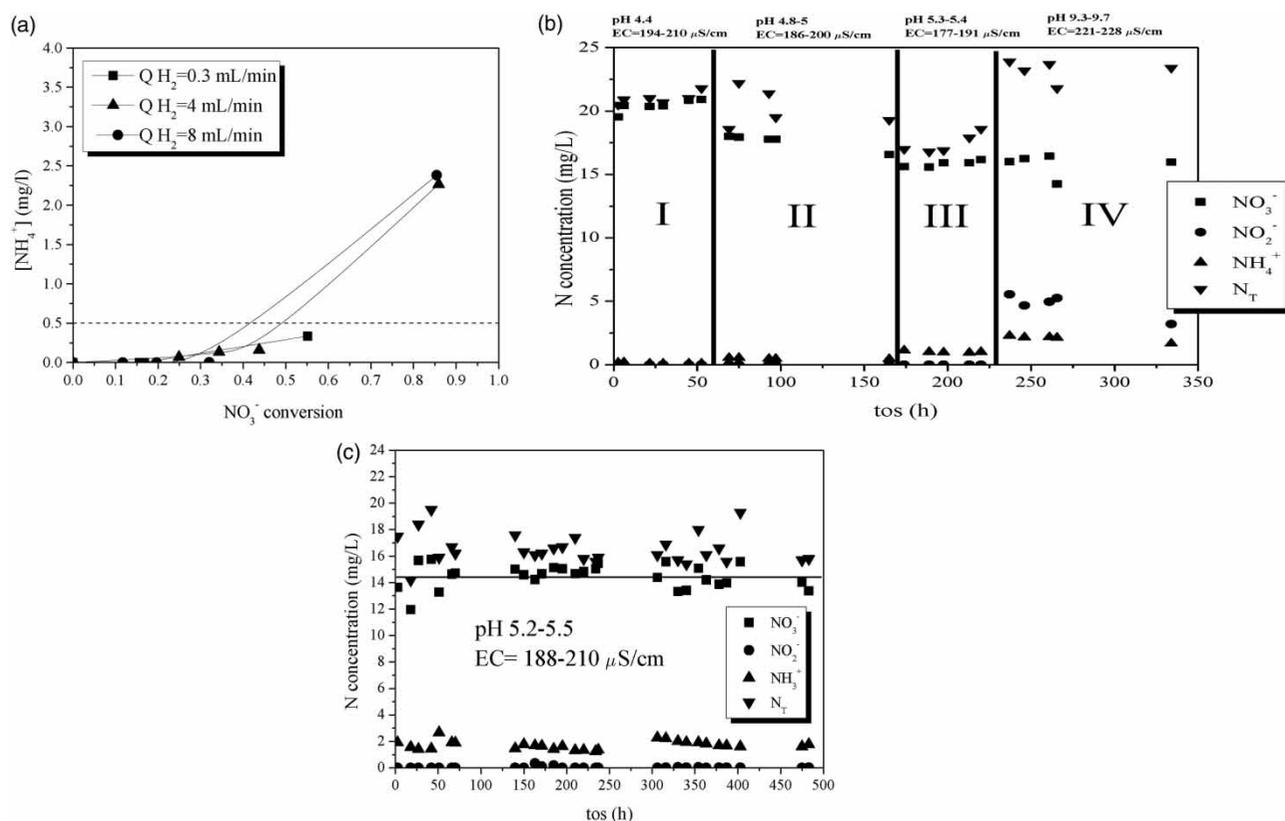


Figure 8 | (a) NO_3^- reduction with Pd-In/ Al_2O_3 with different gas flows (25 °C, 1 atm, pH_0 6, $[\text{catalyst}]_0 = 1$ g/L, $[\text{NO}_3^-]_0 = 1.61$ mmol/L (100 mg/L), $Q_{\text{H}_2} = 0.3, 4$ and 8 N mL/min or $Q_{\text{CO}_2} = 8$ N mL/min). (b) Long-term NO_3^- reduction test with Pd-In/ Al_2O_3 (25 °C, 1 atm, pH_0 6, $W_{\text{cat}} = 0.3$ g, $[\text{NO}_3^-]_0 = 1.61$ mmol/L (100 mg/L), different $Q_{\text{H}_2}/Q_{\text{CO}_2}$ in each stage). (c) Long-term NO_3^- reduction test with Pd-In/ Al_2O_3 (25 °C, 1 atm, pH_0 6, $W_{\text{cat}} = 0.3$ g, $[\text{NO}_3^-]_0 = 1.61$ mmol/L (100 mg/L), $Q_{\text{H}_2} = 0.75$ N mL/min or $Q_{\text{CO}_2} = 0.75$ N mL/min).

synthetic NO_3^- -polluted waters (Wang et al. 2009). The influence of the amount or relative fraction of the gases fed has been also analyzed during long-term stability tests. Other long-term experiments with Pd-In catalysts using different experimental conditions such as powdered Pd/ Al_2O_3 catalysts, H_2 or formic acid as reducing agents and lower temperatures have been conducted in previous studies (Prüsse et al. 2000; Chaplin et al. 2007, 2009).

The Pd-In/ Al_2O_3 was used in a fixed-bed reactor varying the gas flow and the proportion of H_2 to CO_2 . Four different gas mixtures were evaluated, stages I–IV (Figure 8(b)). A gas composition of 0.3 N mL/min of H_2 diluted in 8 N mL/min of CO_2 (3.6% H_2) was fed during stage I. This experiment lasted for more than 50 h, detecting a very low amount of NH_4^+ in the resulting effluent (0.2 mg/L) but reaching a low NO_3^- conversion of around 11%. Higher NO_3^- conversions (28%) were obtained when the CO_2 flow was reduced to 1.2 N mL (25% H_2) where no more than 0.5 mg/L of NH_4^+ was detected. The addition of a higher amount of H_2 (0.75 N mL/min), keeping the relative H_2 : CO_2 fraction constant (50%), also led to an increase of NO_3^- conversion up to 32% and an NH_4^+ concentration of around 1.0 mg/L. During the last stage H_2 was fed solely to the reactor at a flow rate of 1.5 N mL/min. The catalytic activity showed a significant increase of the NO_3^- conversion by 31–37% with respect to the previous experimental stages. Nevertheless, the selectivity to NH_4^+ increased, detecting 2.0 mg/L in the discharge due to the increase of the pH values from 4–5 to around 9 (Figure 8(b)). Decreasing H_2 feed flow values reduces the production of NH_4^+ dramatically, and the pH of the resulting effluents are leveled to neutral values.

Finally, a catalytic test was performed under the same conditions evaluated in stage III to analyze the stability of the catalyst (Figure 8(c)). The space-time used was 6.21 $\text{kg}_{\text{cat}}\cdot\text{h}/\text{mol}$. The results showed herein demonstrate that the Pd-In/ Al_2O_3 catalyst was stable during 500 h on stream. The conversion values were maintained between 30% and 42% with a production of NH_4^+ between 1.6 and 2.2 mg/L during the whole experiment. The pH values directly depend on the amount of CO_2 added, concluding that values lower than 5.5 are optimal for the catalytic reaction. The concentration of H_2 is one of the main limiting

steps that determines the N:H ratio in this process which can be fine-tuned in future applications.

CONCLUSIONS

The activity and selectivity to N_2 of monometallic Pd catalysts used for NO_2^- removal in water have been evaluated with SnO_2 , Al_2O_3 and SiO_2 as supports, respectively. The use of bimetallic Pd-Sn and Pd-In catalysts improved the NO_2^- conversion, especially with the Pd-In catalysts where the metallic phases showed a strong interaction. Pd-In catalysts showed high activity in the NO_3^- reduction, leading to low NH_4^+ concentration effluents. The Pd-In/ Al_2O_3 prepared in this work has shown promising stability (more than 20 days in continuous operation) and a high selectivity to N_2 . The addition of CO_2 in the gas feed as buffering agent and the limitation of H_2 dose are effective to control NH_4^+ formation, and offer an efficient strategy to ensure a long-term operation satisfying drinking water quality standards.

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