

Nitrate Reduction of Brines from Water Desalination Plants Employing a Low Metallic Charge Pd, In Catalyst and Formic Acid as Reducing Agent

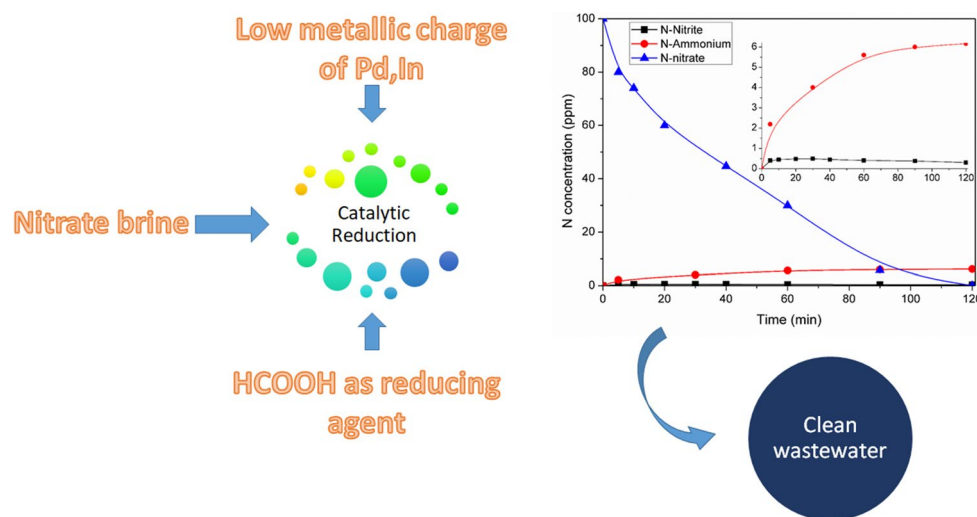
Fernanda M. Zoppas^{1,2}  · Andrea M. Bernardes² · E. E. Miró¹ · F. A. Marchesini¹

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Abstract

Brines from desalination plants lead to adverse environmental impact; therefore, their treatment by catalytic reduction has become a topic of increasing interest. This work aims to apply catalytic reduction to the treatment of water with high nitrate concentration, employing a low noble metal loading in the catalyst (Pd 1%, In 0.25%). Catalytic nitrate removal was evaluated under various conditions, e.g. at different pH values, by assessing the N₂ stripping effect, and by modifying the method of pH correction. A change on the final step of the synthesis was also evaluated as well as the reduction of the active phase by means of H₂ flux or by the reduction in the aqueous phase with hydrazine. The synthesis method through hydrazine reduction showed catalytic activity and selectivity comparable to those shown by the hydrogen-reduction method. It was found that activity and selectivity can be manipulated. The ratio between nitrate eliminated and Pd mass employed proved to be very high, and among the best ratios reported so far. The best conditions to obtain total nitrate conversion were obtained when the pH was controlled between 4 and 5. The stripping with N₂ to the reaction media resulted in lower selectivity to ammonium. The hydrazine-reduced catalyst characterization showed that the nanoparticles were well dispersed on the surface and had an indium: palladium surface ratio higher than that in the bulk, while the H₂-reduced catalyst had more Pd on the surface with lower dispersion.

Graphical Abstract



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Keywords Brine · Catalytic reduction · Low charge catalyst · Nitrate removal · Water treatment

1 Introduction

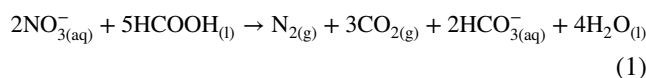
The contamination of water with high concentrations of nitrates is a worldwide problem. This pollution is related to the intensive use of fertilizers in agriculture, leachate from urban waste dump, untreated industrial wastewater [1, 2] and natural sources from the nitrogen cycle [3]. In wastewater treatment, the disposal of the saline effluent generated during membrane water desalination by electrodialysis (ED) or reverse osmosis (RO) is also an increasing problem, especially for the desalination of inland brackish water [4].

Among the different treatment methods, the catalytic reduction of nitrate is regarded as one of the most promising methods for water denitrification [5–11]. In this process, nitrates are reduced to gaseous nitrogen using a bimetallic catalyst and a reducing agent. The generally accepted mechanism for catalytic denitrification is the one that occurs in two steps: a first step, with the reduction of NO_3^- to NO_2^- by a promoter metal (i.e. Cu, In, Sn), and a second step, with the reduction of NO_2^- to N_2 or NH_4^+ , carried out by a noble metal like Pd, Rh, Ir or Pt [12, 13]. The most commonly used and studied reducing agent in this reaction is hydrogen.

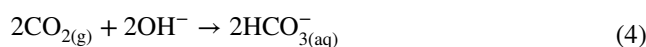
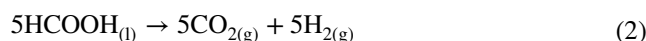
Hydrogen gas has at least two disadvantages in its use as reducing agent in aqueous media, i.e. it is difficult to control its concentration because it is poorly soluble in water, and its use is very dangerous to the operator. As an alternative to the use of hydrogen, formic acid (FA) has been proposed as reducing agent, due to its ability to decompose into H_2 and CO_2 [14] on the surface of several noble metals, including Pd [15]. In fact, FA decomposition has been studied as a way to store H_2 in a safe form and to this end some studies report FA dehydrogenation using Pd-based catalysts [16–18]. In our case, FA decomposition can provide in situ H_2 for nitrate reduction. The produced H_2 is dissociatively adsorbed over the Pd nanoparticles situated on the catalytic surface. The CO_2 formed acts as a pH controlling agent in the micro media around the active sites. In fact, for each mol of nitrate converted, 1 mol of hydroxide is produced, which must be neutralized in order to avoid the formation of undesired ammonia. Only a handful of studies have been reported in the literature using formic acid as reducing agent [14, 15, 19–21]. Most of them were performed employing high metallic loading catalysts, spending at least five times more noble metal than in the present work.

Prüsse and Vorlop [14] studied the effect of pH control using a Pd–Cu supported on alumina catalyst. Garron and Epron [19] reported total conversion of small amounts of nitrate (0.04 mmol/L) with alumina-supported Pd–Sn catalysts, when the stoichiometric relationship formic acid/nitrate ratio was used (Eq. 1). However, there is little

information about the behavior of catalytic reduction activity of large amounts of nitrate. High nitrate concentrations can be found in the tertiary treatment of water and wastewater treatment plants, such as electrodialysis, producing a concentrated stream. Concentrations of nitrate from electrodialysis are between 300 and 1600 mg/L [22, 23].



The decomposition of formic acid is proposed as serial reactions activated by the noble metal present in the catalyst, in which the FA is decomposed into CO_2 and H_2 (Eq. 2) on the surface of Pd [20]. The H_2 formed (Eq. 3) is dissociatively adsorbed over the noble metal which is near the bimetallic particle (Pd–In) and the nitrate is adsorbed and reduced to nitrite, which continues the reduction. The bicarbonates (Eq. 4) act as neutralizing agents in the reaction site where OH^- s are formed. Likewise, activity and selectivity are influenced by the pH [24].



Another important factor concerning the selectivity of the catalysts is the way in which the active phase particles are distributed on the surface and the possibility of modifying them by means of less aggressive reduction methods. The use of reducing agents in the liquid phase, such as hydrazine (N_2H_4) for metal reduction is a relatively simple method [25, 26]. The use of hydrazine instead of $\text{H}_{2(\text{g})}$ at high temperature is preferred due to several factors such as the safety of carrying out a reaction in liquid phase and at room temperature, the simplicity of eliminating unutilized N_2H_4 from the solution by aeration, and the best dispersion results obtained with this reductant agent.

In this study, the reduction of large amounts of nitrate was evaluated to simulate a brine effluent and to test the efficiency of formic acid for the nitrate reduction reaction with a low metal charge catalyst, Pd, In (1:0.25) wt%, supported on alumina. Different reaction conditions were studied, like the effect of N_2 bubbling and of pH in the system in order to maximize the catalytic activity and to minimize the ammonium selectivity. This work also evaluated the use of catalysts produced by wet impregnation, with a variation of the final step of synthesis, i.e. the aqueous reduction with hydrazine instead of reduction with hydrogen. The fresh and used catalysts were characterized so as to know their physicochemical properties.

2 Experimental

2.1 Materials and Chemicals

The chemicals used were analytical grade and no purifications were made. Palladium(II) and Indium(III) were supplied by Sigma Aldrich as chloride and as oxide, respectively. Alumina was CK300 with 160 m²/g, 0.5 cm³/g pore volume. Hydrazine was provided by Merck (P.A.). Formic acid and KNO₃ were provided by Cicarelli and they were analytical grade. All aqueous solutions were made with deionized water purified with an Apema purifier system (0.20 μS/cm).

2.2 Catalysts Preparation

Alumina supported Pd–In catalysts were prepared by wet impregnation of the support. Palladium chloride (PdCl₂) and indium chloride (InCl₃) solutions were used to obtain the bimetallic catalyst [1]. A mass of support (Al₂O₃) was added to a container with water and a volume of concentrated solutions of Pd and In in order to obtain the wt% of the desired metal i.e. 1.00% Pd and 0.25% In. This metallic relationship was applied due to the fact that in previous experiments [6] it was found that by breaking this mass relation (4:1) the catalytic activity declines. The mixed slurry was stirred in a magnetic system and heated until total water evaporation. The residual solid was dried in an oven at 80 °C during 12 h. Finally, it was calcined in air for 4 h at 500 °C. In order to obtain the metallic form of the active phase, necessary for the nitrate reduction, the catalyst was reduced by two methods. In the first, a sample of the catalyst was reduced under hydrogen flow (H₂, INDURA, 99.998, 30 cc min⁻¹) at 450 °C, according to Marchesini et al. [6]. After that, the solid was ready to be used in the reaction. In the second method, another sample of catalyst was reduced by the wet method with hydrazine, i.e. a mass of calcined catalyst was reduced in aqueous media with hydrazine 0.2 M at 40 °C during 1 h. After this time, the dark grey solid was filtered and washed five times with deionized water. In the last step, before its evaluation in reaction, the wet solid was dried at 80 °C overnight. It is important to note that, despite its toxicity, hydrazine can be used in a safe manner if all safety precautions are taken for the operator, such as the use of personal protective equipment.

2.3 Catalyst Characterization

The catalysts were analyzed by temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO) and Dynamic H₂ Chemisorption, with a Micromeritics Auto-Chem II 2920. About 100 mg of catalyst were weighed out and each catalyst was subjected to TPR at a heating rate of

10 °C min and H₂/Ar (5% v/v) flow rate of 30 cm³/min. TPOs were performed at a heating rate of 10 °C/min and O₂/He flow (5% v/v) of 30 cm³/min. To perform pulse-chemisorption, about 100 mg of catalyst were used and those catalysts that were evaluated in reaction were simply heated to 150 °C. The fresh catalyst, on the other hand, was reduced as those which had been evaluated in reaction at 10 °C/min to 450 °C and held therein for 30 min; then cooled in Ar and the chemisorption was carried out at 150 °C to avoid βHPd formation. Dispersion was calculated according to [27] assuming that one hydrogen atom is adsorbed per palladium atom:

$$\%D = \frac{2PH_2}{x_m} \frac{VH_2}{m_{cat}} \frac{MPd}{RT} \quad (5)$$

where PH₂ is the hydrogen pressure (Pa); VH₂ is the volume adsorbed (mL); R = 8.314 J/K mol; T = 423 K; m_{cat} is the catalyst weight (g); MPd is the palladium molar weight (106.4 g/mol); and x_m is the palladium loading (wt%).

X-ray photoelectron spectroscopy (XPS) analyses were performed in a multi-technique system (SPECS) equipped with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with a pass energy of 30 eV and the Mg-KX-ray source was operated at 200 W. The samples were subjected to dehydration at 100 °C in Ar for 15 min in the pre-treatment chamber of the equipment and then to ultra-high vacuum (UHV) for 2 h prior to readings. The obtained spectra were processed using the CasaXPS software in order to estimate the relative proportions of the elements.

The SEM images were obtained using a Phenom World PRO X scanning electron microscope, equipped with an energy dispersive analytical system (EDX). Through ImageJ (free software, version 1.45), the size and distribution of particles were determined.

The XRD patterns of the catalysts 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 2θ = 10°–90° range.

2.4 Catalytic Nitrate Reduction

The reactions were performed in agreement with previous studies [6, 7]. In a typical experiment, a given amount of catalyst (200 mg) was charged in a spherical reactor containing 80.0 mL of deionized water. The reactor was purged with nitrogen gas prior to the addition of the catalyst in order to prevent its surface oxidation. The agitation was maintained at 800 rpm with magnetic stirring and the temperature was controlled at 25 °C. After that time, 100 N-ppm of nitrate (i.e. 443 mg/L NO₃⁻) were added to the reactor, as the initial concentration. In some experiments, the nitrogen flow was

maintained during the whole catalytic run. In addition, for the sake of comparison, a reaction was carried out using hydrogen as reducing agent, which was performed according to what was reported by Marchesini et al. [6].

The reducing agent, formic acid, was used in the molar ratio (see Eq. 1) $\text{HCOOH}:\text{NO}_3^-$ 5:2; the concentration of HCOOH in the reactor was 18×10^{-3} mol/L. Each reaction was monitored for 2 h, collecting samples at different times. The pH was controlled with minimal aliquots of a formic acid 0.4 M solution as reported by Prüsse and Vorlop [14] and the pH was measured using a pH electrode (Hanna HI021). The concentrations of NO_3^- , NO_2^- and NH_4^+ were determined using a spectrophotometer (Cole Parmer 1100) and colorimetric reagents, i.e. the Griess method for nitrites and nitrates (4500 NO_3^- A, from Standard Methods for Chemical Analysis of Water and Waste Water, SMWW) and the modified Berthelot method for ammonium (4500 NH_3 F). Formic acid concentration was detected by Total Organic Carbon with a TOC-L Shimadzu system and by Capillary electrophoresis (Wyn-CE, WynSep) using the 4140 Method from SMWW. Table 1 summarizes the reaction conditions used in each experiment.

Catalytic results are expressed as conversion X (%) and selectivity S (%), as defined in Eqs. (6) and (7).

$$X (\%) = \left[1 - \left(\frac{C}{C_0} \right) \right] \times 100 \quad (6)$$

$$S (\%) = \left[\frac{C_A}{(C_0 - C)} \right] \times 100 \quad (7)$$

where C_0 is N-ppm of nitrates at the beginning of the reduction process, C is N-ppm of nitrates at time t , and C_A is

Table 1 Reaction conditions, RC

Reaction	pH	N ₂ supply	pH correction	Reactive used for catalysts reduction
A	NC*	Yes	–	H ₂
B	5.0	Yes	FA	H ₂
C	5.0	–	FA	H ₂
D	3.0	–	FA	H ₂
E	7.5	–	FA	H ₂
C-hyd	5.0	–	FA	Hydrazine
D-hyd	3.0	–	FA	Hydrazine
F-hyd	4.0	–	FA	Hydrazine
G-hyd	5.0	–	–	Hydrazine
H-hyd	5.0	–	HCl	Hydrazine
I**	5.0	–	HCl	H ₂

**Using H₂ instead of formic acid

*NC pH not controlled; initial pH value 2.8

N-ppm of products (nitrites or ammonia) at time t . Nitrogen selectivity was calculated with Eq. (7).

ICP-MS (PerkinElmer, Optima 2100) was used to detect the dissolved Pd and In ions both after hydrazine treatment and nitrate reduction. Neither In nor Pd was detected in either case.

3 Results and Discussion

3.1 Characterization Results

The characterization results of fresh and used catalysts are presented below.

3.1.1 X-ray Diffraction

XRD patterns of Pd, In alumina supported catalysts are shown in Fig. 1. The catalysts prepared before reaction or fresh (only calcined), reduced with hydrazine and after reaction C-hyd show peaks corresponding to Al_2O_3 . Those peaks can be seen in all samples at 36.7° , 40.0° , 45.7° and 66.7° [28]. No signals corresponding to In_2O_3 or Pd^0 are detected in fresh and reduced samples. These results indicate that metal or oxide particles on Al_2O_3 are highly dispersed or, considering the low catalyst load, they are under the detection limit of the XRD system. The lightly signals at low angles in reduced and used samples are associated with Pd_2OCl_2 species, probably from the precursors salts. The presence of oxidized and reduced forms can be associated with the redox process in which the catalysts were involved. Around 52° the signal of indium oxide (PDF 6-416) is detected, which is in line with the redox process because this band increases its intensity in the used sample. At 39.2° there is a deformation at the characteristic peak of the alumina, which may be related to a contribution of the diffraction of In (110) (PDF 5-642) or could be associated with the diffraction peak of metallic Pd at 39.7° [29]. The data obtained with the H₂-reduced catalysts are similar (data not shown).

3.2 Surface Characterization: X-ray Photoelectron Spectroscopy

Table 2 shows the XPS characterization of fresh and used catalysts. The chemical states of elements and their relative proportions were determined. For comparison, Table 2 shows the results obtained for the fresh samples (after being reduced with H₂ and with hydrazine) and after reaction (as they were obtained after the reaction). In the reduced samples (1:0.25% H₂-reduced), the two components for Pd can be observed. The highest BE, which is directly associated with the higher oxidation states of Pd

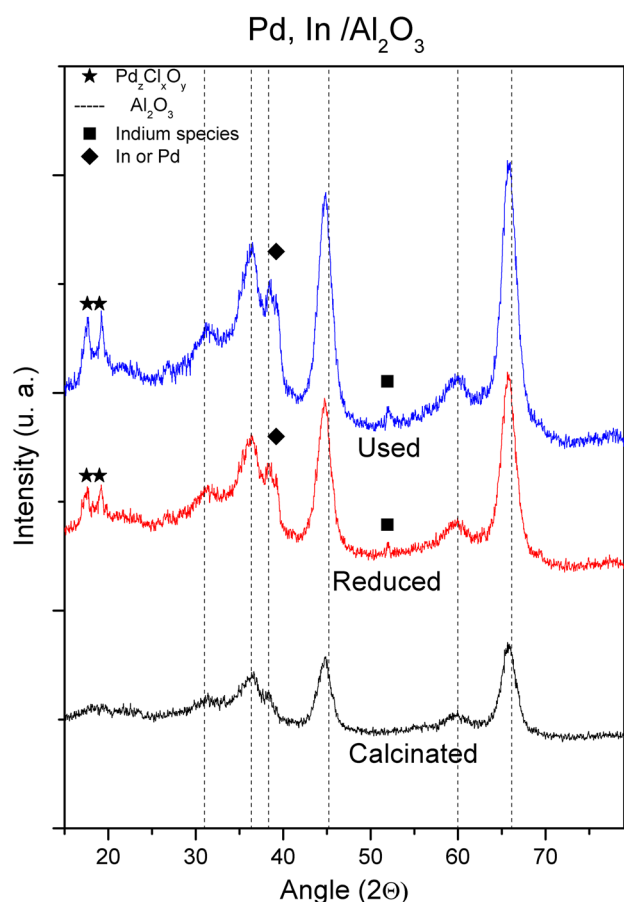


Fig. 1 XRD patterns of the alumina Pd, In 1:0, 25 wt% catalysts: calcined, reduced with hydrazine and used under reaction. Reaction conditions: pH 5

Table 2 Relative proportions determined by XPS of the Pd–In/Al₂O₃ catalyst: “1.00:0.25 H₂-reduced” (60 min at 450 °C with H₂ flow); “H₂” (Used to reduce nitrate with H₂ as a reducing agent), “1.00:0.25 hyd” (60 min at 40 °C, with hydrazine 0.2 M) A, B, C, D, and E (used to reduce nitrate with formic acid as a reducing agent)

	Pd–In/Al ₂ O ₃ catalyst	BE In 3d _{5/2} (eV)	Pd 3d _{5/2} (eV)	Pd/Al	In/Al	Pd/In _s ^a
Fresh catalysts	1.00:0.25. H ₂ -Reduced	444.6	335.2 (55%) 336.3 (45%)	0.0012	0.0009	1.33
	1.00:0.25. hyd-Reduced	444.1	334.1 (84%) 336.9 (16%)	0.0003	0.0027	0.11
Used in reactions	I	445.1 (92%) 443.5 (8%)	335.4 (59%) 337.1 (41%)	0.0025	0.0015	1.67
	A	444.7	334.8 (62%) 335.5 (38%)	0.0058	0.0009	6.44
	B	444.8	334.7 (79%) 336.3 (21%)	0.0035	0.0011	3.18
	C	444.5	334.4 (65%) 336.2 (35%)	0.0039	0.0015	2.60
	D	445.0	334.1 (81%) 336.2 (19%)	0.0025	0.0008	3.12
E	445.2	335.8 (100%)	0.0029	0.0009	3.22	

*Data: Pd/In bulk: 4.3 [33]

^aRatio between superficial Pd and In

(PdO 336.0 eV), and a second component with lower BE, associated with metallic Pd (BE Pd⁰ 335.2 eV), this latter component resulting in 55% of the total Pd 3d_{5/2}. In the sample reduced with hydrazine, the main component is metallic Pd (84%). It is important to highlight this difference because the hydrazine-reduced catalyst presented a higher content of metallic Pd, which is more active for nitrite elimination than the oxidized species.

In the used samples (A–D; see reaction conditions in Table 1), two Pd components can also be observed and in all of them there is a decrease of the second component proportion, when compared with the H₂-reduced one. This is an important result, because it shows the redox mechanism in which the catalysts were involved. On the other side E presents one component for Pd, which corresponds to Pd^{δ+} forms [6].

Taking into account the Indium behavior over the surface of the catalysts, it can be seen that In presents only one component which is associated with metallic In. The catalyst surface is enriched with In (the Pd:In surface ratio is smaller than that corresponding to the bulk), and this effect is remarkable in the catalyst with H₂ as reducing agent (reaction I).

All catalysts used in reaction with formic acid showed an increase in ratio Pd/Al, suggesting that the surface is enriched with Pd, i.e. the bulk Pd (within the sample) migrates to the surface. The proportion Pd/In shows the same behavior. The particles probably suffer a re-dispersion as a result of exposure to the reaction medium, since the relationship of Pd/Al in the reduced sample are higher than fresh catalyst. In the hydrazine-reduced catalyst,

indium appears on the surface ten times more concentrated than that found in the H_2 -reduced catalyst. By observing the In/Al relation, it can be inferred that hydrazine rapidly reduces the metal, meaning that it does not migrate into the support.

3.2.1 Temperature-Programmed Experiments: TPO and TPR Characterization

Figure 2a shows the TPO profiles obtained with a flow of 5% O_2/Ar at $30\text{ cm}^3/\text{min}$. The calcined catalyst does not present O_2 consumption bands, which suggests that all the species present are in their maximum oxidation state. In all the catalysts used in the reaction, the presence of an oxidation band between 200 and 300 °C is observed, which can be attributed to the oxidation of In or Pd–In species found in the catalyst.

Figure 2b shows the TPR profiles obtained for the three reactions. They show desorption peaks at temperatures lower than 100 °C, which are associated with the decomposition of βHPd . The appearance of this band indicates the agglomeration of the palladium particles. Furthermore, it can be observed that the catalyst after reaction C has a reduction band between 300 and 450 °C, which may be associated with the reduction of In_2O_3 species which could appear by the redox process in which the catalyst participates [6, 7, 30, 31].

3.2.2 Dispersion of the Metallic Phase: H_2 Chemisorption

The dispersion of fresh and used Pd:In/ Al_2O_3 catalysts was obtained by the dynamic chemisorption of H_2 . The dispersion values are shown in Table 3. The fresh catalyst reduced

with hydrogen presents a low dispersion, typical of a simple preparation method, which implies the precipitation of the oxide phases on the support. It could be observed that the lack of control of the pH (Reaction A) promoted further deterioration of the catalyst structure, since it decreased its dispersion. For the catalyst in which the pH was controlled, and N_2 was used as a protective agent (Reaction B), the dispersion did not deteriorate very much. In the case of reaction C, the dispersion of the catalyst remained practically constant. This is a clear advantage over the reactions carried out with H_2 as the reducing agent since, in this case, a noticeable deterioration of the catalyst structure was observed [6]. In Table 3, it can clearly be observed that reaction C-hyd, which presented the best conversion of catalysts reduced with hydrazine, had the highest dispersion of all reactions evaluated. The difference of the dispersion values obtained in C and C-hyd certainly influences the production of ammonium during the nitrate reduction. High ammonium formation may be related to the arrangement and geometry of the metal particles in the catalytic surface. In this sense, although edge and corner sites of Pd microcrystals possess a high ability for hydrogenation, favoring the formation of NH_4^+ , nitrogen was formed on the terrace sites of Pd crystals with mild hydrogenation abilities [32]. The higher ammonium formation obtained in reaction C compared to C-hyd could be related to a high amount of edges and corner sites of Pd when it was less dispersed on the surface of the catalyst. When the catalyst was produced using the aqueous reduction method, i.e. with hydrazine, the dispersion was much greater than that of the fresh reduced hydrogen catalyst. Interestingly, this fact did not interfere in the high

Fig. 2 TPO and TPR experiments for (Pd 1%), In (0.25%)/ Al_2O_3 . **a** TPO results for the calcined catalyst, and after A, B and C reactions. **b** TPR results for the calcined catalyst and after A, B and C reactions

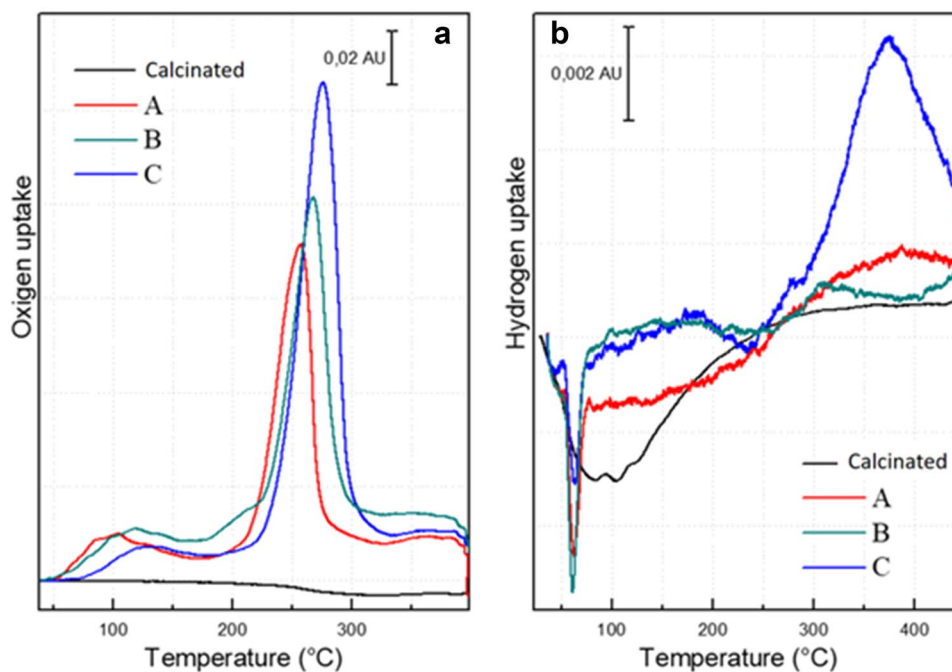


Table 3 Dispersion (%) values for fresh and used catalysts obtained by dynamic chemisorption of H₂

Sample	Dispersion
Fresh Pd, In/Al ₂ O ₃ (hyd)	35.3
Reaction C-hyd	39.4
Fresh Pd, In/Al ₂ O ₃ (H ₂)	8.9
Reaction A	3.8
Reaction B	7.8
Reaction C	8.1

conversion of nitrate obtained by reactions C and C-hyd. What can also be noticed is that the dispersion increased

slightly (about 11%) after contact with the reaction medium, while as regards the catalyst reduced with hydrogen, this value remained slightly lower.

3.2.3 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometer (EDS)

The SEM technique was used to see the morphology of the alumina catalysts produced with hydrazine reduction technique. With ImageJ software, distribution and particle size were calculated. Figure 3 shows the morphology of both a fresh alumina catalyst and a used alumina catalyst.

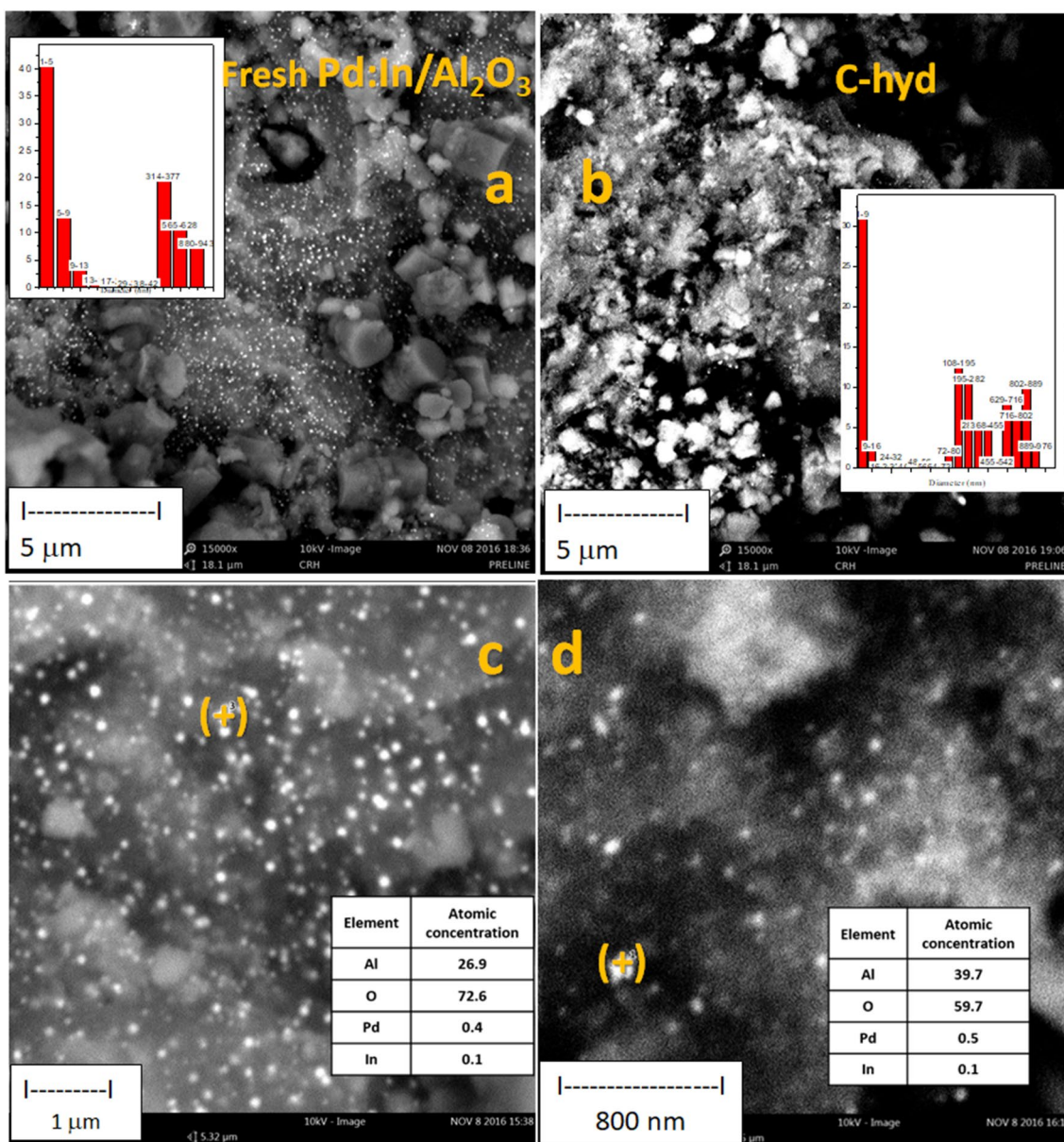


Fig. 3 SEM and EDS images of the alumina Pd, In 1:0.25 wt% catalysts: **a, c** fresh catalyst; **b, d** used in reaction C-hyd

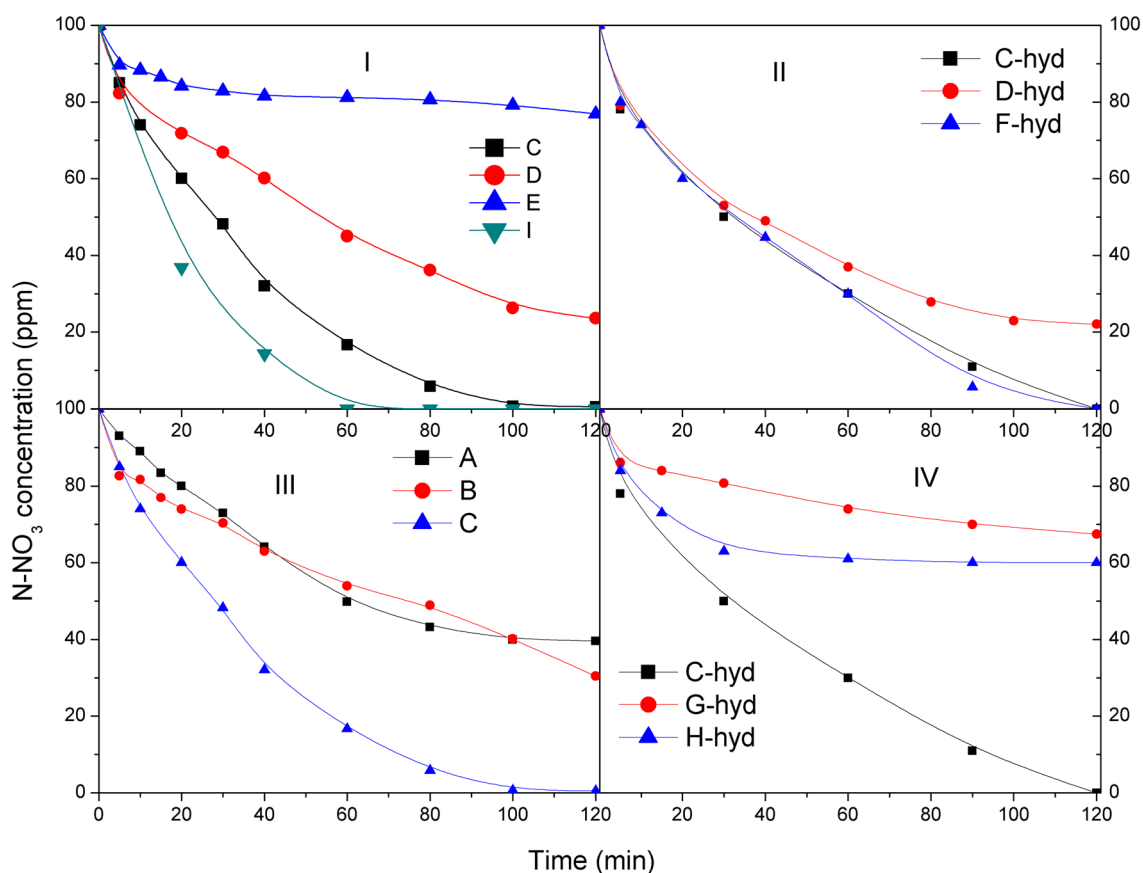


Fig. 4 Nitrate conversion (%) versus time (min) with a Pd (1.00%)-In (0.25%)/Al₂O₃ catalyst under different operational conditions: **I** pH influence using H₂-reduced catalysts; **II** pH influence using hydrazine

reduced catalysts; **III** Effect of N₂ bubbling during reaction; **IV** effect of pH corrector in nitrate reduction (see Table 1)

On the left side, images of SEM of Pd, In/Alumina fresh catalyst are shown, while the used samples are presented on the right side.

Concerning the fresh catalyst, Fig. 3a shows a uniform distribution of particles on the surface, in addition to the presence of agglomerates. By EDS analysis it could be observed that the agglomerates correspond to sites containing palladium and indium with atomic relation of four with a medium size of 1–5 nm (40%) (Fig. 3c). Other majority population of particles or agglomerates (not shown), with sizes between 300 and 900 nm, representing 35% of the population, are also counted.

In the used samples (Fig. 3b), the sizes of the particles are between 1 and 9 nm to around 30%, while 50% of the population forms aggregates with sizes between 100 and 800 nm. The smallest particles tend to aggregate, and the percentage of big particles increases. This behavior was verified before, using H₂ as a reducing agent, but this effect seems to be less extensive than in a previous work [6]. On the right side, Pd can be detected on the big particles, with different prismatic shapes and bimetallic particles are

found on the surface. The Pd:In relation remains constant and around five (Fig. 3d). The distribution of the particles remains homogeneous. The good surface particle distribution is an unexpected result, taking into account the simple preparation method employed in the catalyst synthesis, but corroborates the behavior observed by the H₂ chemisorption technique. Catalysts with low metal loading displayed a performance equal to, or higher than those reported in the literature for the same reaction. It is important to highlight the economic advantages associated with the production of a catalyst with low metallic loading.

3.3 Reaction Results

3.3.1 Nitrate Conversion

Figure 4 shows the results of the catalytic conversion of nitrates. Nitrite and ammonia production versus time are shown in Fig. 5. The results are organized in order to show the effects of the different conditions, trying to obtain those that yield better activity and selectivity.

Table 4 Rate of reaction, selectivity and conversions obtained in nitrate reduction with formic acid as reducing agent

Reaction	$-v^{\dagger}$ (ppm/min)	SN ₂ at equal conversion*	SN ₂ 120'	%X _{120'}	[NH ₄] _{120'}	[NO ₂] _{120'}
A	1.2	86.1	74.5	60.4	25.5	n. d.
B	3.4	99.9	82.0	69.6	18.0	n. d.
C	3.9	87.0	67.3	99.9	32.7	n. d.
D	3.4	99.6	99.5	76.4	0.3	0.1
E	1.6	69.6	93.0	23.2	6.9	0.1
C-hyd	3.8	76.0	88.2	100.0	11.7	0.1
D-hyd	3.8	86.5	93.1	78.9	6.8	0.1
F-hyd	4.0	89.6	93.6	100.0	6.1	0.3
G-hyd	1.5	94.3	98.9	34.0	0.8	0.3
H-hyd	2.7	94.3	98.6	40.0	0.8	0.6
I**	3.3	95.0	94.5	100	5.4	0.1

n. d. not detected

*Nitrate conversion of 23%

**Using H₂ instead of formic acid

v^{\dagger} Velocity of nitrate consumption calculated at 10% of conversion

3.3.2 Effect of pH

Figure 4.I shows that the best conversion reached by the H₂ reduced catalyst was at pH 5 (Reaction condition C). Then the lowest conversion was obtained at pH 7.5. It is known that the basic pH does not promote good nitrate conversion since, under these conditions, the alumina supported catalyst is negatively charged on the surface (the catalyst isoelectric point: 7.4), avoiding the approximation of negatively charged hydrated molecules such as NO₃⁻ and HCOO⁻. Another explanation could be that the OH-present in greater quantity at this pH value could act as inhibitor of the reaction due to its effect of blocking the active sites [33]. In the case of the hydrazine reduced catalyst (Fig. 4II), the best conversion was reached controlling at pH 4 and 5 (F-hyd and C-hyd) with very similar values. Then, it is possible to compare the effect of using a catalyst synthesized by reduction with hydrogen or with hydrazine. It can be noticed that comparable nitrate conversions resulted at pH 5 (C and C-hyd) and at pH 3 (D and D-hyd). These results express the similarity in catalytic activity in the reduction of nitrates shown by the two methods of synthesis evaluated.

3.3.3 Effect of N₂ Supply

When the pH was kept at five (Fig. 4III), it was possible to compare the influence of the N₂ supply over the reaction. Before the reaction started, N₂ was bubbled in the aqueous media in order to strip the oxygen dissolved or adsorbed over the catalyst surface. When the bubbling was maintained during the reaction, the nitrate conversion decreased

when compared with that obtained without N₂ supply, and the pH control only slightly favored the catalytic activity. The decrease in activity observed with N₂ supply during reaction may be caused by the stripping effect and the consequent partial loss of the hydrogen generated by the formic acid decomposition. The unreacted hydrogen left the reactor decreasing its availability for nitrate reduction. This effect was studied by Ding et al. [21]. They showed that the open system allows the partial escape of gases during the reaction, which makes the overall reaction less effective when compared to the closed system.

3.3.4 Effect of the pH Control Method

In Fig. 4IV, the effect of different pH correctors in reaction media can be observed. In the absence of a pH corrector (G-hyd), less catalytic activity was obtained among the three experiments compared. When hydrochloric acid was used as pH corrector (H-hyd), the reaction seemed to stop after around 30 min. This effect can be associated with the blocking of active sites due to a higher affinity for this acid than for HCOOH, avoiding the decomposition of the organic acid over the metallic particles [19]. Thus, formic acid proved to be more efficient than hydrochloric acid (C-hyd). This result was expected because formic acid, besides correcting the pH, provided excess reducing agent in the medium and corrected the increase of pH in the active site.

Comparing formic acid (C) with hydrogen as the reducing agent (see Fig. 4I), both of them yielded total nitrate conversion. However, with H₂ nitrate was totally converted in about 70 min, whereas with formic acid the total conversion was

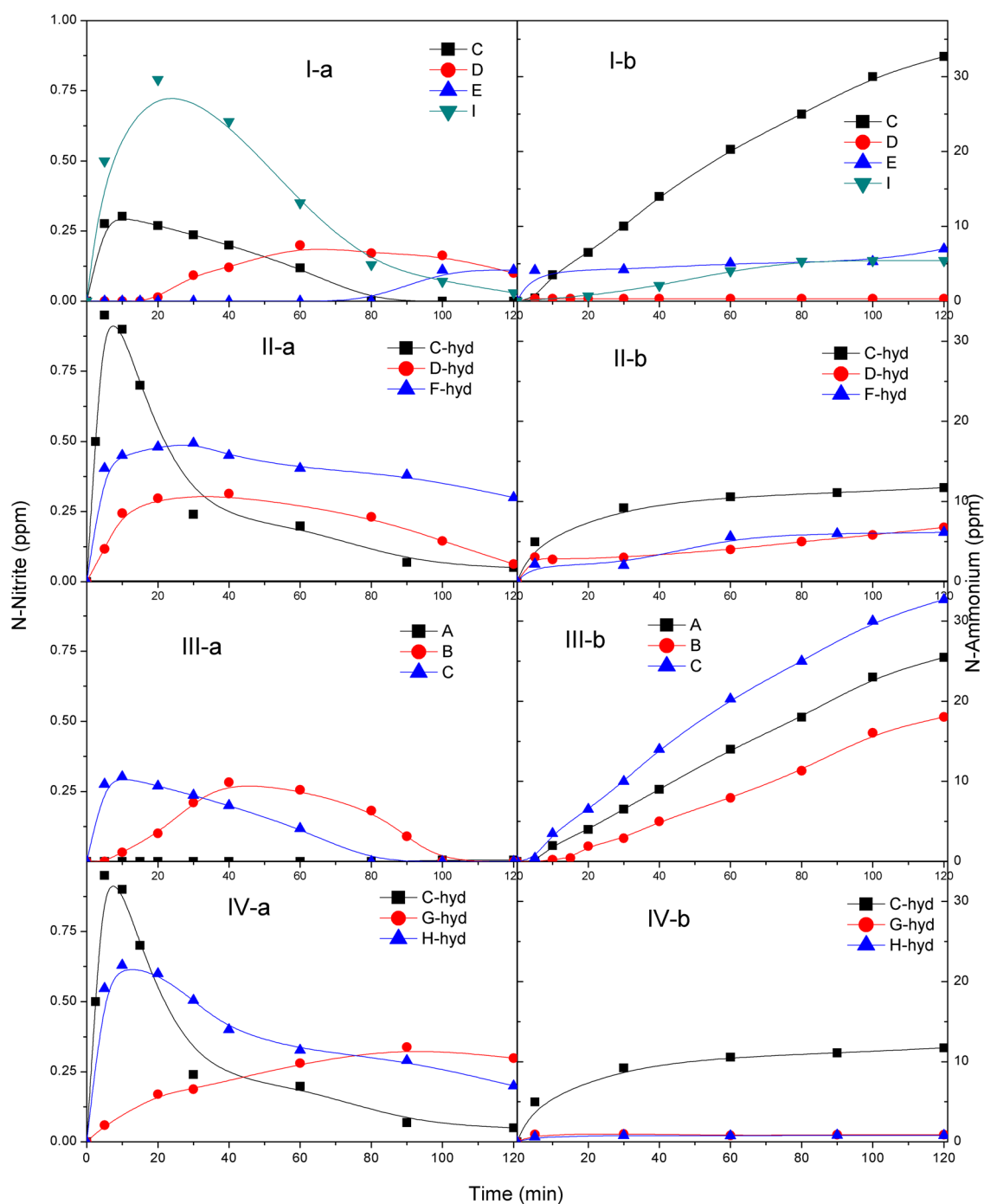


Fig. 5 Nitrite and ammonia production versus time (min) with a (Pd 1%), In (0.25%)/Al₂O₃ catalyst in different operational conditions (see Table 1)

achieved at 120 min. This is reasonable, because the formic acid molecule must adsorb and decompose to generate the H₂ necessary to react with nitrate molecule. Another factor to be considered is the steric hindrance, which prevented the FA molecules from adsorbing over the surface into adjacent metallic sites, which resulted in less hydrogen available.

3.3.5 Selectivity Effects

Garron and Epron [19], using a Pd–Sn supported on SiO₂ catalyst, controlled pH with FA and compared with the results obtained controlling pH with CO₂/H₂. They showed that FA in situ control produced a lower selectivity to NH₄⁺, ten times less than that obtained for H₂. Although the obtained NH₄⁺

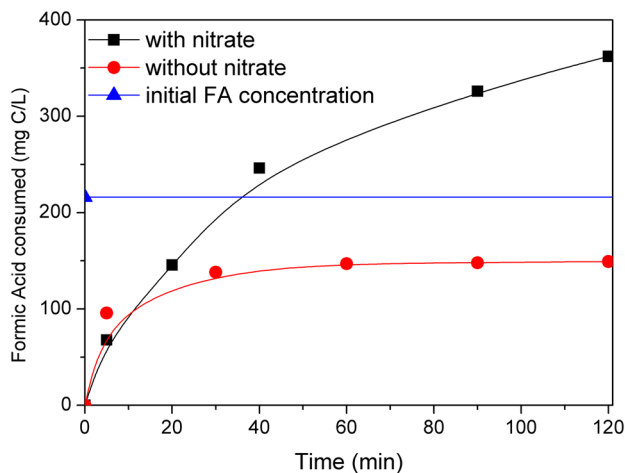


Fig. 6 Formic acid concentration in contact with the aqueous medium and catalyst: without nitrate and with high nitrate concentration

concentration was still above the permissible value, the next step of chlorination (for treating water) was to convert residual NH_4^+ into N_2 . Working with relations of $\text{FA}:\text{NO}_3^-$ 5:2, these authors achieved complete conversion of NO_3^- and elimination of the FA, good activity, and low formation of NH_4^+ . The same relationship was used in this study, allowing us to corroborate the high conversion of nitrates when the pH was controlled and the selectivity to NH_4^+ (Fig. 5) was low. In addition, it is important to mention that in this work the initial nitrates concentrations were about 180 times higher than the ones used in Garron and Epron's report.

3.3.6 Nitrite Production

In Fig. 5I(a)–IV(a) it can be observed that nitrite formation has the typical behavior of an intermediate product, being formed and then consumed over time. At different pH values [Fig. 5I(a), II(a)] the maximum nitrite concentration found during the reaction was 0.3 ppm in H_2 -reduced catalysts and 0.9 ppm with hydrazine-reduced ones, both at pH 5. However, at the end of the reaction, nitrites were almost totally consumed in both cases. In reactions with N_2 supply, nitrite was totally consumed at the end of the reaction in all the cases shown in Fig. 5III(a). In Fig. 5IV(a) it can be seen that, either when the pH was not controlled or was controlled with HCl, nitrite was not entirely consumed after 120 min of reaction (G-hyd, H-hyd). In fact, here it is also possible to see that the best option for pH control is the addition of small amounts of formic acid. Besides, all the hydrogen formed during formic acid decomposition is not available for nitrate reduction, because some amount is stripped from water [20]; thus, the admixture of formic acid aliquots not only controls the pH, but also provides an additional reducing agent to complete the reaction.

3.3.7 Ammonia Production

In Fig. 5I(b) it can be observed that the quantity of ammonium formed during the reaction with the best conversion (C) of H_2 -reduced catalyst was about 32 ppm, whereas Fig. 5II(b) shows that when hydrazine was used during the synthesis, at pH 5 (higher catalytic activity), the ammonium formation was lower (10 ppm); this would express an advantage of the aqueous reduction method in relation to the H_2 reduction method. Nevertheless, in both cases, the values were above the limit for drinking water (0.5 ppm). The same behavior did not occur at pH 3 because D did not generate NH_4^+ , even when comparable conversions of NO_3^- were obtained. The effect of using nitrogen gas in the medium promoted the decrease of NH_4^+ formation [see Fig. 5III(b)], possibly due to the drag effect of hydrogen on the surface of the catalyst, avoiding over-reduction of NO_2^- . In Fig. 5IV(b) it can be noticed that when using HCl as pH corrector, the amount of ammonium generated was minimal. The same behavior was observed in G-hyd, in the absence of pH correction. These results show that there is a compromise between activity and selectivity when choosing the operating conditions.

3.3.8 Kinetic Aspects

Table 4 shows the nitrate consumption velocities (v) calculated at 10% of nitrate conversion in order to determine which catalyst resulted more active before the reaction media produced some effect over their structure. The higher reaction velocities correspond to reactions C, C-hyd, F-hyd, D-hyd, B, and D, having similar values. Among them C, C-hyd and F-hyd reached total conversion after 120 min of reaction. These results indicate that while the effect of low pH (pH 3) and N_2 bubbling did not affect the nitrate consumption during the start of the reaction, they impacted negatively during the increasing time-on-stream. On the other hand, high pH (pH 7.5), absence of pH control, and pH control with HCl, negatively affected both reaction velocity at 10% of conversion and nitrate consumption at the end of the reaction (120 min). Thus, in terms of catalytic activity for nitrate conversion, pH 5 was the convenient value, and the use of hydrazine was preferred for the synthesis instead of hydrogen, due to its simplicity, low cost and safe operation. Among the conditions where total conversion was obtained, F-hyd presented lower selectivity to ammonium.

The same table shows that at the same nitrate conversion (23%), reaction B presented the highest selectivity to N_2 , 99.9%. This may be related to the effect of nitrogen gas bubbling in the reaction medium. The second more selective condition was D (99.6%), operated at pH 3. Moreover, considering that in this case the production of ammonium at the end of the reaction was much lower than that obtained in

B, this would be a good choice for an optimal compromise between nitrogen selectivity versus nitrate conversion.

3.3.9 Formic Acid Decomposition

Figure 6 shows the results obtained for the consumption of HCOOH in the presence of the catalyst, with and without nitrates. Through TOC and CE techniques it was verified that formic acid decomposes in the presence of the catalyst (Fig. 6). In the presence of the catalyst and nitrate, total decomposition was achieved in approximately 35 min of reaction. If formic acid had not been added to the medium to pH correction, the reaction would have been finished in approximately 35 min, with the total consumption of the initial concentration of FA. This behavior has already been observed in open systems, with Pd-based catalysts [21]. The amount added during the nitrate reduction allowed the reaction to continue until its complete conversion. In the absence of nitrate, the concentration of formic acid stabilized at about 30% of its initial concentration after 60 min. This could indicate that the surface of the catalyst would be saturated with formate molecules and byproducts of its degradation, such as CO₂ in chemical equilibrium with the carbonate, acting as a barrier for the approximation of new formic acid/formate molecules on the surface of the catalyst. In the presence of nitrate this does not happen in the same way. As the degradation products are being consumed, they open spaces for new formic acid/formate molecules to approach and adsorb on the surface of the catalyst. Then, it can also be suggested that the presence of nitrate accelerates the decomposition of formic acid, once it begins to be consumed during the reaction. This behavior is in agreement with the results reported by Choi et al. [20]. In the Supplementary Material (Table S1) we have included information which shows that the ratio between the amounts of nitrate reduced in our study and the Pd employed is higher as compared with other values reported in the literature, using formic acid as reducing agent. This is a remarkable economic advantage. In order to analyze the intrinsic activity, the turnover frequency (TOF) values were obtained by dividing the reaction rates by the number of exposed palladium sites per gram of catalyst (calculated by H₂ chemisorption analysis) [34]. The TOF value calculated at 10% of conversion was 0.003 min⁻¹ for the reaction using the reduced in aqueous phase catalyst (C-hyd) and 0.009 min⁻¹ for the H₂-reduced catalyst (C). This difference in values is related to the dispersion of each catalyst. In order to compare with literature results, the TOF value calculated from the specific activity reported by Prusse and Vorlop [14] was 0.0009 mol NO₃ per mol of superficial Pd per minute, about ten times less than C-hyd TOF and C TOF if we express them in these units (0.011 and 0.009 mol NO₃ per mol of superficial Pd per minute, respectively).

4 Conclusions

Catalytic reduction proves to be a viable technique for treating nitrate brine. The control of pH in the process is essential since it directly influences the catalytic activity and the selectivity to ammonium, which is an undesirable product. Formic acid is shown to be an interesting alternative to replace hydrogen gas as reducing agent, providing H₂ in a more controlled way avoiding over reduction and the increase in selectivity to ammonia.

With respect to the change in the final step of the synthesis, the hydrazine reduced catalysts are equally applicable as well as the catalysts reduced with H₂. However, hydrazine reduction presents an economic and operational advantage, being the most attractive method to be used in the catalytic removal of nitrate brines.

Since it is technically feasible to use low metal charge catalysts to treat high concentrations of nitrate, it is also very important to reach a compromise between nitrogen selectivity versus nitrate conversion. Considering this question, the best conditions obtained were at low pH, with N₂ bubbling, and correction with formic acid. The next step could be the employment of structured catalysts so that this method can be effectively part of the brine treatment systems in the future.

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Affiliations

Fernanda M. Zoppas^{1,2}  · Andrea M. Bernardes² · E. E. Miró¹ · F. A. Marchesini¹

✉ F. A. Marchesini
albana@fiq.unl.edu.ar

¹ Instituto de Investigaciones en Catálisis y Petroquímica (FIQ, UNL-CONICET), Santa Fe, Argentina

² Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e de Materiais (PPGE3M-UFRGS), Porto Alegre, Brazil