



Improving selectivity to dinitrogen using Palladium-Indium coated on activated carbon fibers: Preparation, characterization and application in water-phase nitrate reduction using formic acid as an alternative reductant source

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ABSTRACT

This work reports results on the preparation, characterization and application of activated carbon fibers as structured catalysts used in the decontamination of water containing nitrates. Activated carbon fibers were coated with Pd and In using sequential autocatalytic deposition. Besides, the efficiency of decontamination was evaluated when formic acid was used as a source of hydrogen. Different operating conditions were studied for conversion of nitrates to gaseous nitrogen in the aqueous phase, using Palladium and Indium as active phases. Concerning the selectivity to N₂ of the catalysts evaluated at the same conversion (10%), all catalysts showed selectivity to gaseous nitrogen greater than 99%, demonstrating the high potential of carbon fibers as a structured catalyst support to nitrate reduction. The surface characteristics of the bimetallic catalyst were investigated by temperature-programmed oxidation, temperature-programmed reduction, dynamic H₂ chemisorption, scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction showing that the metals were homogeneously distributed on the catalyst surface.

1. Introduction

Interest in the development of materials applied in water decontamination has increased in recent years. Particularly, in heterogeneous catalysis, there is great concern in using catalysts in structured substrates, and in the treatment of water contaminated with nitrates. Structured catalysts eliminate the need for recovery of the catalyst by some post-treatment process such as filtration, compared to powder catalysts. Among the removal techniques of nitrate-contaminated water, catalytic reduction is regarded as one of the most promising methods [1–6]. Nitrates in industrial wastewater can also be treated by membrane separation processes (MSP), like electrodialysis [7] or reverse osmosis. However, in these MSP, an effluent (the brine) was generated presenting high nitrate concentration [8], above 300 mg L⁻¹ of NO₃⁻ [9]. Activated carbons have interesting properties to act along these lines, such as porosity, chemical stability, high surface area, corrosion resistance, adsorption capacity, thermal resistance and electrical conductivity [10–12]. Within this group, activated carbon fibers (ACF) have additional properties. ACF can reduce the diffusion

limitations and the pressure drop in flow reactors by combining an open macrostructure with mechanical flexibility [1].

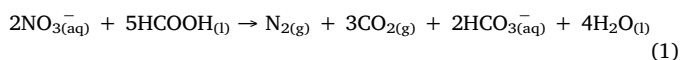
In catalytic reduction, nitrates are reduced to nitrogen using hydrogen or other reducing agents, but undesirable compounds such as ammonium and nitrite are also formed. For this reason, it is essential to control activity and selectivity so as to improve the effectiveness of this method [13]. The generally accepted mechanism for catalytic nitrate reduction is the one that occurs in two stages: first step the reduction of NO₃⁻ to NO₂⁻, and second step the reduction of NO₂⁻ to N₂ or NH₄⁺. Promoter metals M (ie., Cu, Sn, In) are required to initiate the nitrate reduction, but the reduction of nitrite and subsequent intermediates could be carried out by Pd. The most commonly used reducing agent in this reaction is gaseous hydrogen.

As an alternative to the use of hydrogen, formic acid (FA) has been proposed as reducing agent due to its ability to decompose into H₂ and CO₂ [14–16]. H₂ acts as reducing agent and CO₂ acts as buffering agent regulating the pH variation. The great advantage of this system is that CO₂ is generated exactly in the place where the reduction of NO₃⁻ produces OH⁻, favoring the neutralization. In fact, hydrogen is poorly

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soluble in water and it is necessary to employ large amounts to avoid the chemical limitation of the reaction and achieve the desired conversions. In addition, since H₂ is an important energy carrier, which has a great application in industry [17], it is interesting to look for cheaper alternatives for the catalytic reduction of nitrate. Another reason is the safety that an aqueous phase reducer can provide to the operator rather than the operation of gases with a latent risk of explosion. Then, formic acid emerges as a potential replacement. In the literature, several studies have been published which use formic acid as reducing agent in nitrate reduction [13,14,16,18–20] and also for hydrogen generation [21–24]. Prüsse and Vorlop [14] studied the catalytic reduction of nitrate with the addition of formic acid, using a Pd-Cu supported in alumina catalyst. Garron and Epron [18] reported total nitrate conversion with alumina-supported Pd-Sn catalysts when the stoichiometric formic acid: nitrate ratio was used (Eq. (1)). It should be noted that in their studies these authors used small amounts of nitrate, 4·10⁻⁵ mol L⁻¹ as initial NO₃⁻ concentration instead of 7.15·10⁻³ mol L⁻¹ as in the present study.



Most of these studies were accomplished using powder catalysts and in general catalysts with high metallic loading. However, there is relatively little information using this reducing agent in catalysts in structured catalysts. In this sense, carbon fibers attract attention due to both their ability to act as a good support for the active phases, such as Pd and In, and their capacity in the catalytic reduction of nitrates in the presence of H₂, already verified in a previous work [1]. To the best of our knowledge, there is no reported work using formic acid as a reducing agent and the carbon fibers as a catalyst support. This work wants to contribute knowledge in this area, to leverage future applications in water decontamination.

Previous studies also reported ACF as suitable supports for active phase Pd for nitrite reduction [25] and Pd-In for nitrate reduction [1] both using gaseous hydrogen as reducing agent. Yuranova et al. [26], used carbon fibers for the catalytic reduction of nitrates and bromates in water. They obtained 40% of nitrate conversion with the active phase of Pd 1% Cu 2% in continuous mode. In the semi-batch mode, a 35% nitrate conversion and total bromate conversion were obtained in 3 h of reaction, using H₂ as a reductant. But still, there is no information about the catalytic behavior when formic acid was used as reducing agent.

In a previous study [1], the efficiency of Pd (1.80%) In (0.90%)/ACF was verified in the catalytic reduction of nitrate using molecular hydrogen as reducing agent. In fact, good conversions of nitrate were obtained with different metallic loads of active phase using hydrogen. Now, formic acid was tested as reducing agent because of its promising characteristics cited above, in order to improve selectivity to N₂. To this end, ACF were used as supports for Pd-In active phases which were homogeneously deposited by a sequential autocatalytic deposition (SAD) technique to obtain active and selective catalysts deposited on a structured support. Then, the catalysts were tested in the nitrate reduction reaction using formic acid as reducing agent. We also investigated the mechanism by which the decomposition of the reducing agent occurs to provide H₂ for the catalytic reduction.

In the present study, the reduction of large amounts of nitrate (100 N ppm NO₃⁻) was evaluated in order to simulate the nitrate concentration of membrane separation processes (MSP) brines. A lower concentration of nitrate (25 N ppm NO₃⁻) was also studied for comparison with a previous work [1]. The physicochemical characteristics of fresh and used catalysts were verified.

2. Experimental

2.1. Catalyst preparation

Commercial activated carbon felts (ACN 211-15, American Technical Trading, Inc.; area density: 180 g cm⁻², surface area: 1500 m² g⁻¹, thickness: 2.00 mm) were used. The bimetallic catalysts were prepared according to a previous study [1] by sequential autocatalytic deposition (SAD). The Pd felts were prepared in two steps. First, ACF surface was activated by deposition of catalytic Pd seed nuclei using a two-step SnCl₂/PdCl₂ procedure: substrates were immersed for 5 min in a 0.6·10⁻³ M solution of SnCl₂·2H₂O (pH 2) and then for another 5 min in a 0.1 M solution of PdCl₂ (pH 2). This activation step was repeated four times. Afterwards, the felts were immersed in the Pd plating bath (composition: PdCl₂ 2.5·10⁻³ M; NH₄OH 7.1 M, 80 mL L⁻¹; Na₂EDTA 25.3·10⁻³ M) at 50 °C using N₂H₄ 0.20 M as reducing agent for 90 min. The as-deposited samples were rinsed with deionized water several times. Then, the felts were immersed in the In plating bath, composed of In(NO₃)₃ with two concentrations: 3.0·10⁻³ M for catalysts with In 0.9% of loading and 6.0·10⁻⁴ M to 0.18% In of loading, and HCl (0.4 M) with the same reductant for 90 min at 50 °C and washed with deionized water several times. The proportion bath/felt was 10 ml·cm⁻² both in Pd and In autocatalytic deposition.

2.2. Catalytic nitrate reduction

The reactions were performed in agreement with literature results [2,25,27–29] in a spherical batch reactor of 250 ml with magnetic stirring and temperature controlling at 25 °C and atmospheric pressure. 80 ml of deionized water was added to the reactor, and then 200 mg of catalyst and an aliquot of concentrate nitrate solution (10,000 N ppm NO₃, KNO₃, P.A., Cicarelli) were added to the flask in order to obtain 25 or 100 N ppm NO₃ as initial concentration. The pH was monitored with a TPX1 pH-meter (Hanna Instruments).

Formic acid (85%, P.A., Cicarelli) was used as reducing agent, in a stoichiometric molar ratio HCOOH:NO₃ 5:2. Each reaction was monitored for 2 h, collecting samples at different times. The pH was controlled with minimal drops of formic acid 0.4 M solution, according to Prüsse et al., [13] and Prüsse and Vorlop [14]. The concentration of NO₃⁻, NO₂⁻ and NH₄⁺ were analyzed in the samples using a spectrophotometer (Cole Parmer 1100) and colorimetric reagents: the Griess method for nitrites and nitrates and the modified Berthelot method for ammonium. Formic acid concentration during the reaction was detected by Total Organic Carbon (TOC) with a TOC-L Shimadzu system and by Capillary Electrophoresis (CE) with a Wyn-CE instrument using the 4140 method from Standard methods for the examination of water and wastewater [30].

Experiments were performed using different initial nitrates concentrations (25 and 100 N ppm NO₃), pH (3, 5 and 7.5), initial formic acid concentrations (4.5, 18 and 72 mmol/L) and two catalyst compositions (1.8:0.9 and 1.8:0.18 Pd:In wt.%). The reactions are summarized in Table 1. The decomposition of formic acid was also evaluated in a blank test reaction with catalyst but without nitrates

Table 1
Reaction conditions.

Reaction	pH	Active phase	C ₀ ⁺ N-NO ₃ (ppm)	C ₀ HCOOH (mmol/L)
F	3.0	1.80% Pd, 0.90% In	25	4.5
G	3.0	1.80% Pd, 0.18% In	25	4.5
H	5.0	1.80% Pd, 0.90% In	25	4.5
I	7.5	1.80% Pd, 0.90% In	25	4.5
J	5.0	1.80% Pd, 0.90% In	25	18
K	5.0	1.80% Pd, 0.90% In	0	4.5
L	5.0	1.80% Pd, 0.90% In	100	18
M	5.0	1.80% Pd, 0.90% In	100	72

(reaction K).

The results of the catalytic reaction are expressed as conversion X (%) and selectivity S(%), defined by Eqs. (2) and (3).

$$X(\%) = \left[1 - \left(\frac{C}{C_0} \right) \right] \times 100 \quad (2)$$

$$S(\%) = \left[\frac{C_A}{(C_0 - C)} \right] \times 100 \quad (3)$$

where C_0 is N ppm of nitrates at the beginning of the reduction process, C is N ppm NO_3^- at time t , and C_A is N ppm of products (nitrites or ammonia) at time t . Nitrogen gases present in the products are nitrogen oxides and molecular nitrogen, but it has been demonstrated that nitrogen oxides concentration are negligible [13]; thus, selectivity to N_2 was calculated by $(100 - \text{SNO}_2^- - \text{SNH}_4^+)$ mass balance. SNO_2^- is the nitrite selectivity and SNH_4^+ is the ammonia selectivity, both calculated with Eq. (3).

2.3. Catalysts characterization

The catalysts were analyzed by TPR (Temperature-Programmed Reduction), TPO (Temperature-Programmed Oxidation) and Dynamic H_2 Chemisorption, with a Micromeritics AutoChem II 2920. TPO analysis was performed with 100 mg of catalysts after the SAD preparation method, at a heating rate of $10^\circ\text{C min}^{-1}$ and an O_2/He (5% v/v) flow of $30\text{ cm}^3\text{ min}^{-1}$. After TPO, the samples were cooled in Argon flow until reaching the temperature of 45°C and then subjected to TPR at a heating rate of $10^\circ\text{C min}^{-1}$ and an H_2/Ar (5% v/v) flow of $30\text{ cm}^3\text{ min}^{-1}$. 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 to avoid formation of βHPd . Dispersion was calculated according to Bayley et al. [31] assuming that one hydrogen atom is adsorbed per palladium atom:

$$\%D = \frac{2\text{PH}_2 \text{ VH}_2 \text{ MPd}}{x_m \text{ m}_{\text{cat}} \text{ RT}} \quad (4)$$

where PH_2 is the hydrogen pressure (Pa); VH_2 is the volume adsorbed (mL); $R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$; $T = 423\text{ K}$; m_{cat} is the catalyst weight (g); MPd is the palladium molar weight (106.4 g mol^{-1}) and x_m is the palladium loading (wt.%).

The scanning electron microscopy (SEM) images were obtained using a Phenom World PRO X scanning electron microscope, equipped with an energy dispersive analytical system (EDS).

The X-Ray diffraction (XRD) patterns of the fibers were obtained with an XD-D1 Shimadzu instrument, using $\text{Cu K}\alpha$ radiation at 30 kV and 40 mA. The scan rate was 2° min^{-1} in the range $2\theta = 10\text{--}80^\circ$.

3. Results and discussion

3.1. ACF Catalysts applied on nitrate reduction

Fig. 1 shows the results of conversion of nitrates with two different initial concentrations, as well as the products of the reaction, both as a function of reaction time. Table 2 shows the initial velocities, selectivities and conversions obtained by catalysts in each reaction.

3.1.1. Reductant agent effects

Initially, the conversion obtained with formic acid was discussed in comparison with the data obtained with H_2 as reducing agent in a previous work. Compared with the hydrogen reductant, which obtained the total reduction of nitrates in 120 min, using the catalyst of Pd 1.8% In 0.9% [1], formic acid resulted less effective for nitrate conversion. It should be remarked that the high conversion results reported in the literature with formic acid are obtained with powdered catalysts with higher metallic charge, generally 5 wt.%.

Probably, in the case of formic acid, which is a larger molecule than gaseous hydrogen, the use of a support with little specific surface area would facilitate the superficial reaction. In the case of ACF, part of the active phase is in the inner surface. In this way, the inner surface active sites are inaccessible for the reducing agent, resulting in a decrease in the activity. In the case of a support with lower specific surface, i.e. alumina, in which the highest proportion of the active sites is over the outside surface, a better nitrate conversion can be observed.

Using low metal charges (Pd:In/Alumina or Silice 1:0.25 wt.%) and hydrogen as a reducing agent, Marchesini, Picard and Miró [3] reported conversions close to 100% and which showed lower selectivities to nitrogen than those achieved for the catalysts supported in ACF. As said before, alumina has a lower area than AFC; then, the superficial reaction could be favored in some way due to the following reasons: first, as HCOOH is an organic molecule with a coordination sphere bigger than H_2 . In this sense, probably there exists a steric impediment for it to reach the active site; second, as the porosity in AFC is very high, the metal active phase is more widely distributed and there are fewer active sites over the surface. Thus, the difference in these results could be due to the high specific surface area of the fibers, when compared to the alumina used by Prüsse and Vorlop [14]. After 20–30 min of reaction in the ACF catalysts, the reaction seems to decrease its activity. One possible justification for the loss of activity observed is the formation of βHPd on the Palladium superficial particles. This reaction is favored because when the H atom is formed on the surface, during formic acid decomposition, some of the H atoms never desorb and produce this stable β compound. As a result, the catalyst slowly loses its activity as the βHPd is formed [32]

3.1.2. Initial Formic acid and nitrate concentration effects

This paragraph discusses the conversion obtained by modifying the initial concentration of formic acid and nitrate. When the formic acid concentration was 4-fold stoichiometric (M), no improvement in conversion was observed in comparison with L, which had the stoichiometric concentration. On the contrary, in reaction L, a better conversion was reached. These results suggest that the system was already in a saturated condition of initial reagents that could be blocking the catalyst active sites at the beginning of the reaction, probably due to the βHPd formation, as described above. Thus, when the initial concentration of nitrate is lower (25 N ppm), the AF initial concentration has some influence on catalyst activity. If H is compared with J, the 4-fold increase in formic acid concentration causes a nitrate conversion improvement from 15.1% to 33.9%. In J, it is possible to emphasize the low ammonium formation, around 0.9 N ppm. However, when the initial nitrate concentration was 100 N ppm (L), this behavior (low ammonia production) was not repeated probably due to the saturation of the active sites.

3.1.3. pH influence

This section discusses the results for the different pH values tested, with formic acid as reducing agent. Nitrate conversions were 34.4%, 15.1% and 31.0% at pH 3.0 (F), 5.0 (H) and 7.5 (I), respectively. About the products generated in reaction, the presence of ammonium was not detected at pH 5 (H) and 3.0 (F) and about 0.1 N ppm of NH_4^+ at pH 7.5 (I) was found. The lack in the conversion observed at pH 5 is not in agreement with the tendency previously reported. At this pH, the ion formate is the main chemical form found in the aqueous media. Nevertheless, at this pH the ACF surface is positively charged ($\text{PZC}_{\text{ACF}} = 6.5$). Thus, all the negative ions dissolved in the reaction media (HCOO^- , NO_3^- , NO_2^-) are attracted electrostatically by the ACF surface. It is possible to assume that the active sites were sterically and chemical block by this ions avoiding the reaction, but some complementary studies are necessary in order to verify this assumption.

3.1.4. Effects of Pd:In ratio

The conversion of nitrate obtained using lower loading metallic

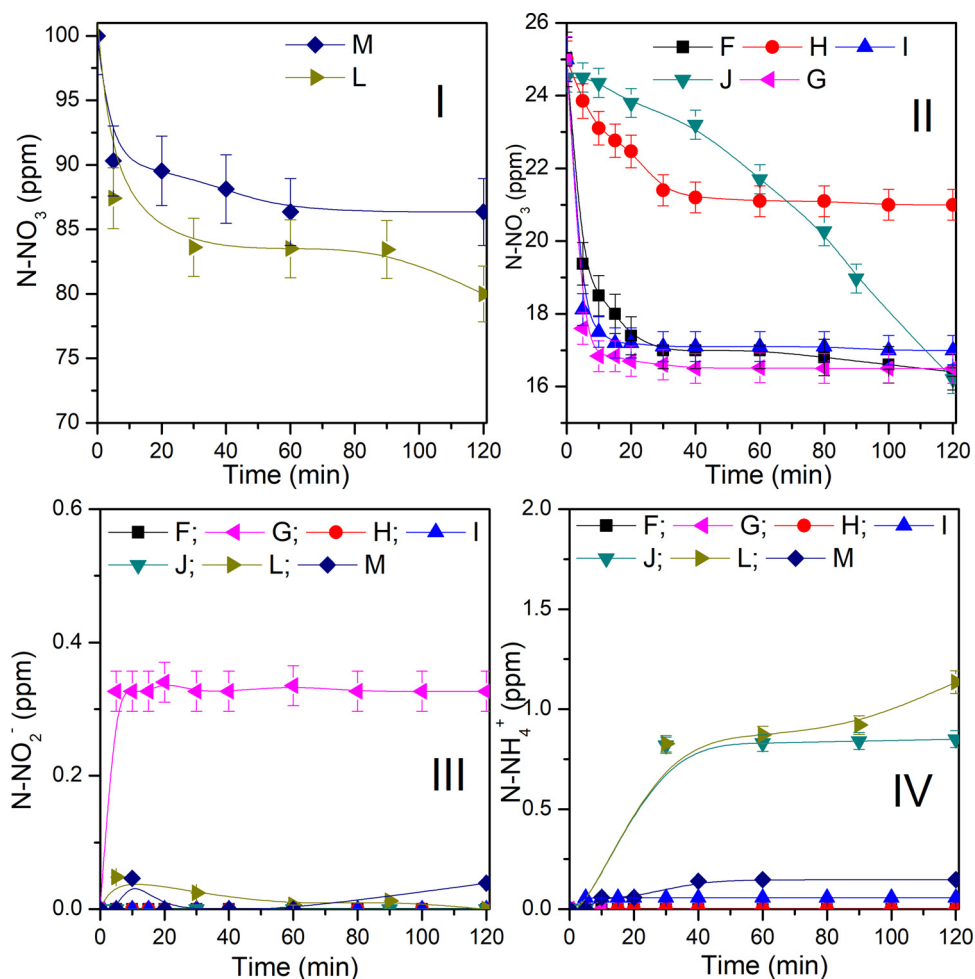


Fig. 1. Nitrate (I and II), Nitrite (III) and Ammonium (IV) concentration vs reaction time in different operational conditions (See Table 1).

catalyst can also be mentioned. The Pd:In 1.80:0.18 wt.% ACF was tested (G) with a Pd:In ratio equal to 10:1 at pH 3.0 and formic acid as reducing agent. These conditions were selected because they were the best for nitrate conversion (F) among the conditions tested. The nitrate conversion in reaction G was 32.0%, which is comparable with that of the F reaction. In this case, the nitrate conversion was similar to the one obtained using hydrogen as reducing agent in a previous publication [1]. This result is not in agreement with those reported by other authors. Prüsse and Vorlop [14] found significant differences in catalytic activity in nitrate conversion using different metal ratios of Pd (5%) and Cu as second metal, supported on alumina and using formic acid as reducing agent. Using the 10:1 ratio, the authors obtained the best nitrate reduction activity. This suggests that the difference in results may be due to the lower metal loading used in the catalysts of the present study and the type of support used. In the experiments performed in this work, no significant improvements were observed when using this

molar ratio of the metals in the catalyst preparation. About the reaction products, in reaction G the formation of approximately 0.3 N ppm of nitrite was detected. The presence of ammonium was not detected, which means a high selectivity to $N_2(g)$. As previously said, the low NH_4^+ formation is highly desirable in this process.

3.1.5. Other effects over the catalyst

About the activity results, the ones found in this work were better than the results reported by several studies in the literature, with lower ammonium formation. Prüsse and Vorlop [14], using an initial amount of nitrate of 100 mg L^{-1} and at similar catalytic activity levels, obtained higher selectivity to ammonium, if compared with the conditions studied in this work.

When FA is used as a reducing agent, less activity is observed than when $H_2(g)$ is the reducing agent [1], but FA provides good selectivity towards nitrogen, about 100%. Using a different catalyst support such

Table 2

Rate of reaction, selectivities, conversions and concentrations at 120 min of reaction, obtained in nitrate reduction with formic acid as reducing agent.

$[NO_3]$ Initial (ppm)	Reaction	$-v_i$ (ppm/min)	SN_2 10%	SN_2 120'	%X _{120'}	$[NH_4]$ 120'	$[NO_2]$ 120'	$[NO_3]$ 120'
25	F	1.1	100	100	34.4	n. d.	n. d.	16.2
	G	1.5	100	99.9	32.0	n. d.	0.3	16.6
	H	1.5	99.9	99.7	15.1	n. d.	n. d.	21.0
	I	1.5	100	99.9	31.0	0.1	n. d.	17.0
	J	0.1	99.9	99.2	33.9	0.9	n. d.	16.4
100	L	2.8	99.9	98.9	21.1	1.1	n. d.	80.0
	M	2.1	100	99.8	13.6	0.1	n. d.	86.3

as alumina [3,28,33,34], nitrate reduction achieves better conversions, but there is a certain loss in selectivity. On the other hand, ACFs achieve conversions close to those reported by other authors (see Table S1), but using higher initial concentrations of nitrates and lower metal loading in the catalyst. Those two things introduce an economic advantage, because a higher concentration of polluted water could be treated in a shorter time with a low catalyst production cost (due to the low metal loading).

A relation between the mass of metal used in catalysts and nitrate converted in catalytic reactions using FA as reducing agent is shown in Table S1, in Supplementary Material. In Table S1, it can be seen that results obtained in reaction M are comparable with those reported by Prüsse and Vorlop [14]. In addition, reactions F, G, I and J have a similar relation in mass of metal and nitrate converted than those used in the work of Garron and Epron [18]. Yuranova et al. [26], used carbon fibers for the catalytic reduction of nitrates and bromates in water. They obtained 40% of nitrate conversion with an active phase of Pd 1% Cu 2% in continuous mode. In the semibatch mode, a 35% nitrate conversion and total bromate conversion were obtained in 3 h of reaction, using H₂ as a reductant. In this sense, since the use of formic acid promoted similar conversions, studies with this reducing agent as a substitute could be encouraged. Thus, formic acid can be considered as a good possibility to act as a reductant in this reaction and an improvement is necessary in the reaction conditions in order to obtain higher conversions.

3.1.6. Selectivity improvement

At 10% conversion all catalysts had selectivities to N₂ higher than 99.2% which represents a superior selectivity to N₂ than the ones found in the literature at the same conversion level [1,14,18,34,35]. At 120 min, the selectivity remained higher than 98.9% to nitrogen gas, for all the conditions under study. It is then estimated that by improving the contact between the reductant agent and the metal loading, better conversions can be achieved. The same catalysts are not so selective to gaseous nitrogen production when gaseous hydrogen is used as reducing agent. At 120 min, with a 10:1 Pd:In molar proportion, 84% of selectivity to gas nitrogen was found; using 4:1 Pd:In 80% was obtained and with 2:1 Pd:In, 71% was found [1].

3.1.7. Formic acid decomposition mechanism

Fig. 2 shows an experiment in which two phenomena are explored: the influence of the presence of nitrates on FA decomposition and the effect of the contact between the catalyst and FA on nitrate reduction. It can be seen that during the first two hours of the experiment the amount of FA decomposed is very low (8%), and it increases after the

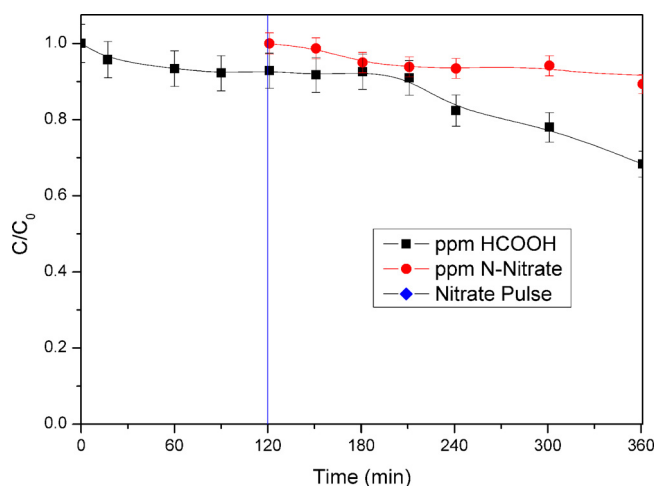


Fig. 2. Concentration of formic acid vs time in reaction K with a nitrate pulse of 100 N-ppm after 120 min.-.

addition of a nitrate pulse (33%). It is remarkable, that no significant changes in pH can be observed, so the FA is acting as pH regulator efficiently. On the other hand, the conversion of nitrate during the experiment is only 10%, which is lower than that shown in Fig. 1. These results suggest that nitrate promotes FA decomposition and, the prolonged exposure of the catalyst to the acid inhibits nitrate conversion, which is an effect that can also be observed in Fig. 1. As mentioned above, this finding could be associated with the formation of β HPd due to adsorption of atomic H in the Pd particles.

Thus, the decomposition of FA is affected by the presence of nitrate as shown by Choi et al., [19]. Prüsse and Vorlop [14] reported that if other reducible species are present in the aqueous medium, the adsorbed formate molecules on the catalyst surface act as reductants by transfer of hydrogen from the previous decomposition. In the absence of nitrate, the little decrease in the concentration of formic acid is indicative of the possibility that the reaction mechanism may be by donation of the hydrogen of the adsorbed formate on the catalyst surface and not by the decomposition of FA.

It is known that the catalytic performance also depends on the physicochemical properties of active metal and the support [36]. Besides, the decomposition of FA may be related to the number of available sites for adsorption on the catalyst surface. FA strongly adsorbs on palladium sites [14]. Possibly the amount of carbonates formed in the aqueous medium may also act to inhibit the nitrate molecules from approaching the catalyst surface. Since these two molecules have similar sizes and molecular structure, consequently they would also inhibit the adsorption of other formic acid molecules. This could also be an effect of the fibers high specific surface area and lower metal loading. When this result is compared to those of other studies, which obtained better conversions of nitrate with catalysts supported on alumina [14] and silica [18], with high metal load and low specific surface catalysts.

The behavior observed in Fig. 2 allows concluding that the mechanism of this reaction is hybrid, i.e., initially, the reduction of nitrate is due to the excess hydrogen when the formic acid is as a formate molecule on the catalyst surface. These formate molecules could form hydrogen, which would act as a reducing agent in the catalytic reduction of nitrate. After certain reaction time, the absence of these hydrogen molecules, which were consumed at the beginning, would boost the decomposition of FA.

The presence of FA at the end of the reactions was also detected by TOC (data not shown) and confirms the results obtained by CE. It was verified that when using the stoichiometric ratio, formic acid was not completely degraded during the reduction process. This limitation using ACFs in the process indicates the need for further research.

Choi et al., [19] reported that the decay rate of formic acid was slightly slower than the decay rate in the presence of nitrate, suggesting that the nitrate had a synergic effect in the decomposition of formic acid. This can be attributed to the consumption of H₂ by the reduction of nitrate on the surface of the catalyst and this consumption displaced chemical equilibrium towards FA decomposition.

3.2. Characterization results

In order to associate the physicochemical catalyst properties with the results of nitrate reduction, the catalysts were characterized before and after reaction.

The SEM technique was used to understand the morphology of the carbon fiber catalysts. Distribution and particle size were calculated with ImageJ software (free distribution). Fig. 3 shows the morphology of fresh and used carbon fiber catalysts.

In fresh Pd:In 1.80:0.90 wt.% (Fig. 3-a and -f), a uniform distribution of particles on the surface (size smaller than 20 nm for around 70% of the particles) is observed in addition to the presence of clusters (size larger than 100 nm). The Pd particles are highly dispersed and well separated in the nanometric size range. Linear elemental mapping

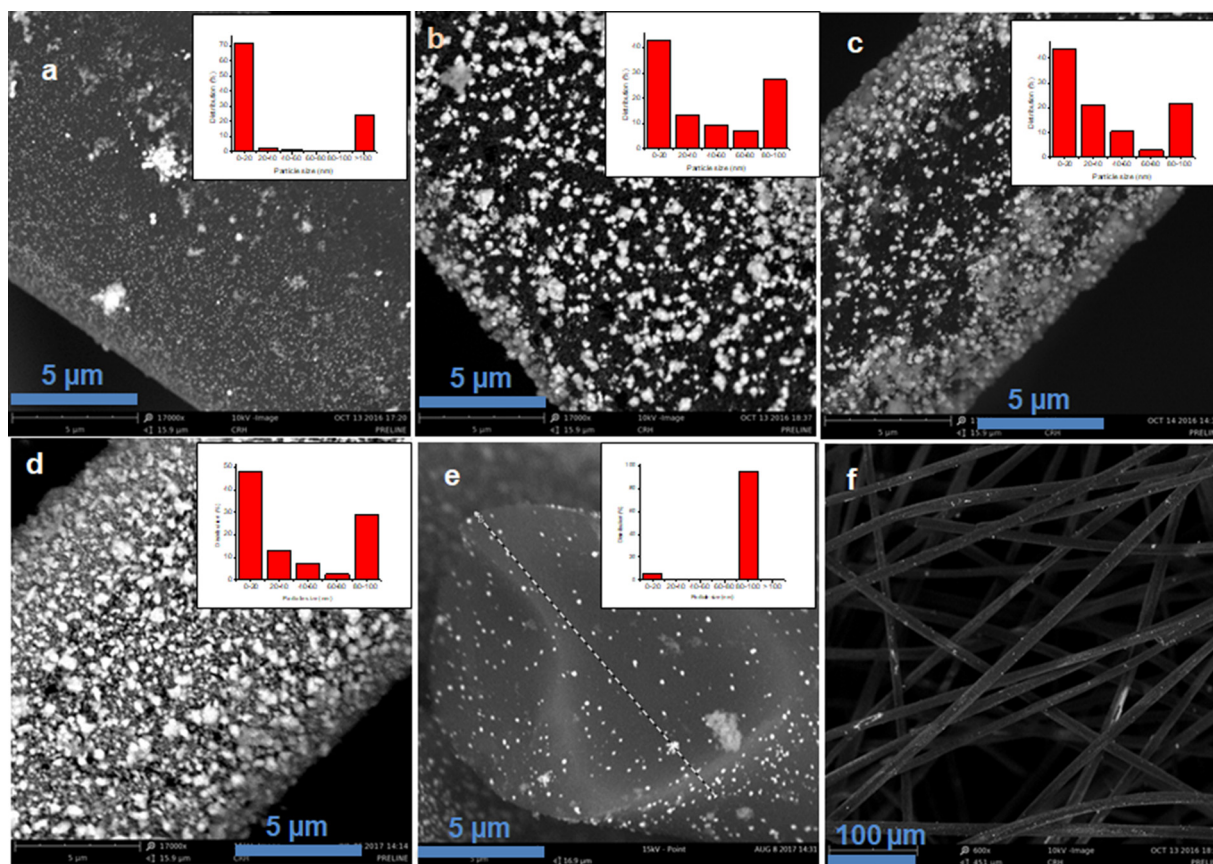


Fig. 3. a) Image of scanning electron microscopy of fresh Pd 1.80% In 0.90% catalyst. b) catalyst used in reaction H c) catalyst used in reaction M d) catalyst used in reaction with H₂ as reducing agent e) cut fiber of fresh Pd 1.80% In 0.90% catalyst; f) General view of Pd 1.80% In 0.90% catalyst.

(Figure S1) shows that the fiber is fully covered by the active phase, even in the visually dark parts where a partially uncovered fiber would be expected. After reaction with formic acid, the geometry of the particles on the surface is different (Fig. 3-b, -c and -d). The cube-shaped particles could be associated with the formation of indium oxide [37]. It is important to mention that even in the dark parts of the fibers, where it is not possible to visualize particles, Pd and In were detected by EDS, which indicates the formation of at least one monolayer during the synthesis process. A high formation of clusters (less than 50% of the particles are greater than 20 nm) can be observed if compared with the fresh fiber. This same behavior was observed in the nitrate reduction reaction when H₂ is used as reductant agent (Fig. 3-e).

In Figure S1, at point (+1) it can be seen that the elemental composition is Pd and Indium, in the ratio close to the molar ratio obtained by chemical analysis. This point represents the average surface composition, which corresponds to what is atomically impregnated (a ratio of 2:1 Pd:In). It can also be observed that there is a percentage of chlorine, possibly resulting from precursors used in the synthesis process. At point (+2) the signals for carbon and oxygen are the highest ones. At this point, the amount of indium is higher than the one of palladium. In the mapping, Pd, O and Cl can be identified as homogeneously distributed on the surface of the support. Indium is well distributed but appears in greater quantity in the clusters. On the other hand, the C signal appears uniformly distributed, but disappears where the clusters are located or they are hidden to detection by the In cluster.

Fig. 4 presents the results of EDS for the catalysts used in reactions H and M. Fig. 4-I shows three different proportions of the active phase. At point (+1), located in a cluster, the Pd:In ratio is higher than 8, which can confirm that palladium forms agglomerates during the reaction. At point (+2), the Pd:In ratio is 2, which corresponds to the bulk ratio. Point (+3) is located in a dark part, where the Pd:In ratio is 1: 1.

Therefore, it can be inferred that part of the metals are grouped during the reaction, but also that Pd and In are kept in equivalent proportions throughout the surface of the fiber.

In the catalyst used in reaction M (4-fold the stoichiometric amount of FA), it can be observed that the surface is more loaded with clusters than reaction H (stoichiometric amount of FA). At points (+1), (+2) and (+4) there is more Indium than palladium. This result confirms that the surface is enriched in indium, after contact with the reaction medium. This behavior was already observed in an earlier study, with the same support and active phase. After the reaction of nitrate hydrogenation, the surface was enriched with indium.

The TPO and TPR results of fresh and used catalysts can be observed in Fig. 5. TPO results are shown in Fig. 5-a and TPR in Fig. 5-b.

Fig. 5-a shows the TPOs obtained for the fresh fibers (CF) and for the fibers containing Pd and In, where PIFF is the fresh fiber, PIUF (J) is the used fiber in the reaction that produced the better conversion and PIUF (M) is the one which produced the poorest conversion. Upon comparison, the three TPO obtained for the catalysts show very similar oxidation regions. The fresh fiber (PIFF) shows the biggest area for the oxidation of Pd species (temperatures around 30–100 °C), and this area decreases for the used catalysts (PIUF (J)) and is the lowest for the catalyst which produced the minor conversion (PIUF (M)). This is in line with the idea of a catalyst suffering an oxidation process more quickly than the other. The second region of oxidation peaks probably corresponds to those more difficult oxidized particles, and here there is a clear difference between both catalysts. The one which has a better activity shows the highest band in the region with oxidation at smaller temperature. This suggests that the catalyst can oxidize and reduce more easily than the other, which could be the explanation for the different activities observed.

Next, TPR results of fresh and used catalysts (Fig. 5-b) are shown.

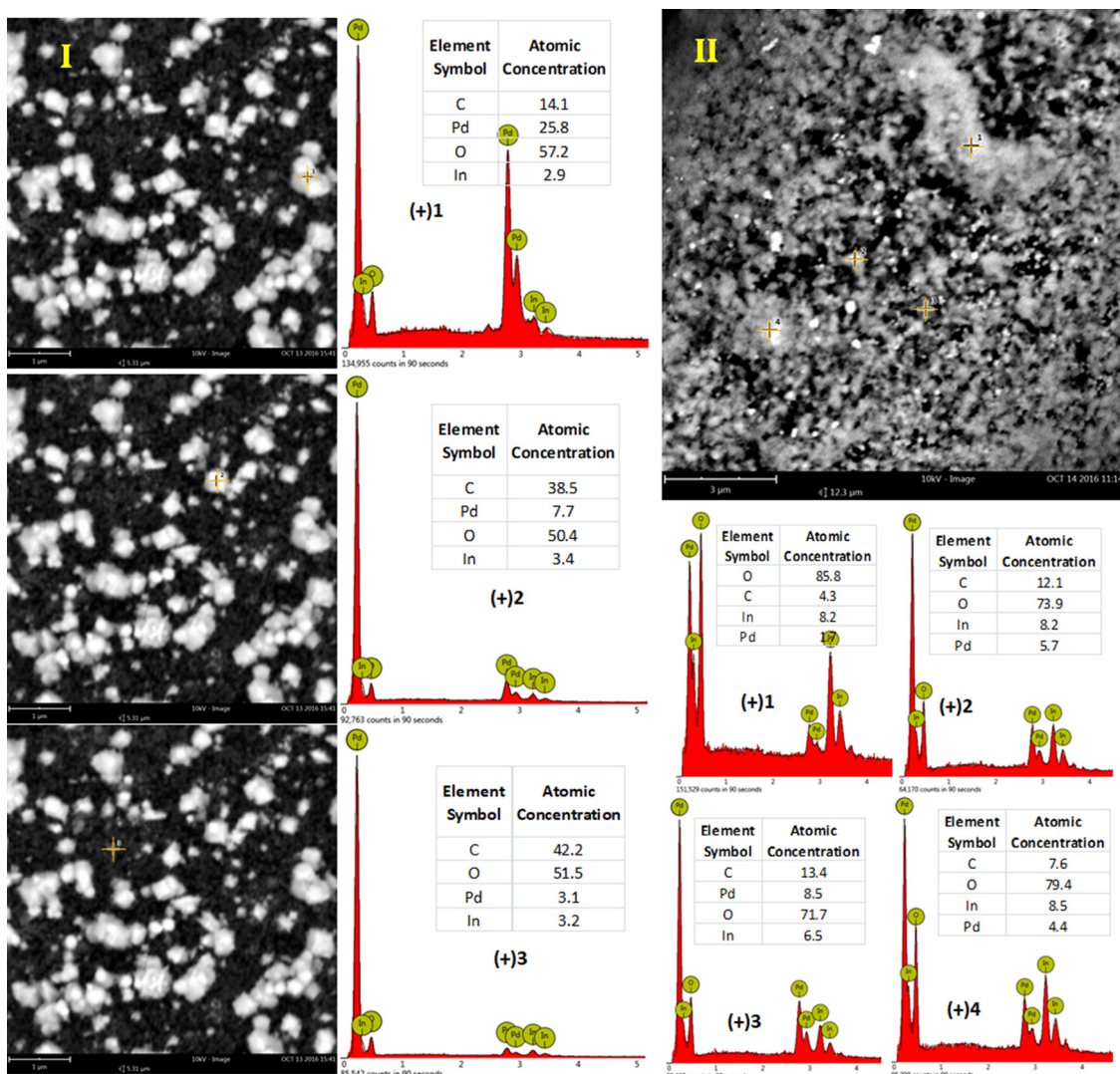


Fig. 4. EDS images of catalysts used in reaction H (I) and used in reaction M (II).

The TPR was carried out with the same sample after TPO analysis. As they were oxidized in the same extension, it would be expected that they would present similar responses to the reduction. But again, clearly, the one who shows the worst activity (PIUF (M)) has the most difficult reduction. In fact, its temperature of reduction occurs at a higher temperature than the other catalyst used on reaction. This is consistent with the impossibility to easily reload the active sites in order to proceed with the reduction reaction.

Table 3 presents the results of catalyst dispersion, obtained by

Table 3

Dispersion values for fresh and used catalysts obtained by Dynamic Chemisorption of H₂.

Sample	Dispersion (± St. Deviation)
Fresh Pd 1.80% In 0.90%	60.0 ± 1.8
Reaction J	38.7 ± 1.2
Reaction M	14.1 ± 0.4

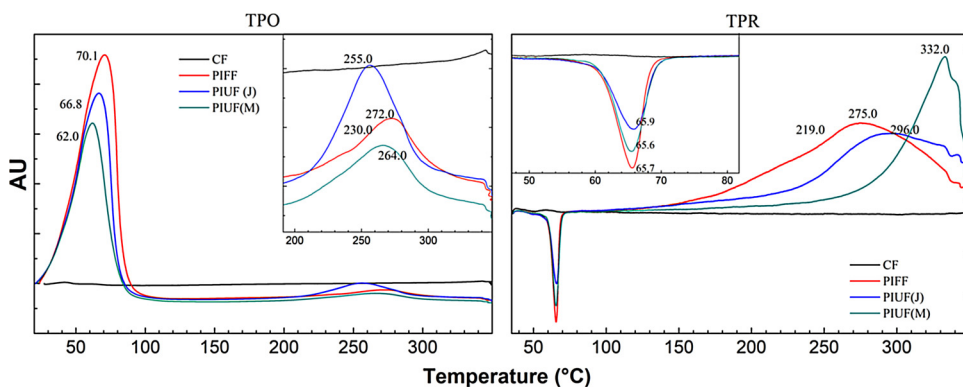


Fig. 5. 5-a Temperature Oxidation Programmed assay. CF, clean fiber; PIFF, PdIn Fresh Fiber; PIUF(J) PdIn Used Fiber with reaction J; PIUF(M) PdIn Used Fiber with reaction M. 5-b Temperature Reduction Programmed assay. CF, clean fiber; PIFF, PdIn Fresh Fiber; PIUF(J) PdIn Used Fiber with reaction J; PIUF(M) PdIn Used Fiber with reaction M.

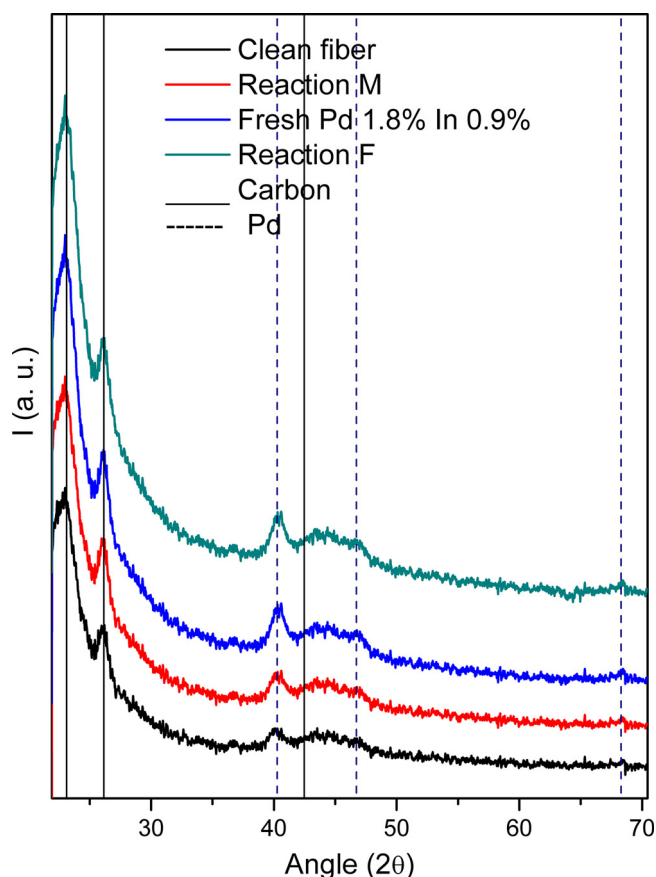


Fig. 6. XRD of catalysts. (---) carbon signals. (—) metallic Pd signals.

dynamic H_2 chemisorption. As expected, the fibers exhibit high dispersion. Autocatalytic deposition promotes better distributed particles on the surface of the substrate. Dispersion decreases drastically (loss of dispersion of 75%) in the worst conversion result (reaction M). In the case of reaction J, the drop in the dispersion is around 35%, pointing out changes on the surface after contact with the reaction medium, but these are less drastic when compared to reaction M.

Finally, Fig. 6 shows XRD results in fresh and used catalysts.

Fig. 6 shows the spectra corresponding to the support (clean fiber), and to the fresh and used catalysts. Since all used catalysts show similar spectra, only those used in F and M reactions are shown. Once all used catalysts obtained similar spectra, F and M reactions are shown in Fig. 6. The main signals of the carbon support can be seen at a low angle. The signals at angles of 22.3° and 25.7° are related to the structure of the carbon fiber [38]. On the other hand, since the fiber is constituted by a partially amorphous material, a background in the 20° – 30° region is observed. While PdO signals are not detected, metallic palladium diffractions can be seen at 40.1° , 46.7° and 68.1° [39]. The signal of metallic palladium at 82.1° does not appear, probably due to the low metal loading and its high dispersion. For all catalysts, the metallic Indium reflection signals are not clearly distinguished, since the Pd peak at 46.7° is more intense than the Indium signal. After reaction, the formation of clusters on the surface of the fibers was observed by SEM microscopy, which should favor the observation of the crystal reflections by XRD. However, no signals of In_2O_3 are detected at the characteristic angles of 32.7° , 45.6° , 57.2° and 58.2° [38].

4. Conclusions

ACF coated with Pd and In were prepared, characterized and applied in the catalytic reduction of nitrate. The catalysts are effective in nitrate reduction using formic acid as a hydrogen source. All catalysts

showed selectivity to gas N_2 close to 100% under the conditions studied. Despite this high selectivity, conversions still need to be improved. The catalyst structure changes after reaction in all cases and further experiments with used catalysts are needed in order to determine if these changes are due to the strong adsorption of some of the reactants or intermediates of the reaction or due to permanent changes of the catalytic surface.

The proposed mechanism, i.e. nitrate reduction using formic acid, consists of two steps: first, the nitrate reduction occurs due to hydrogen generated through formate molecules on the catalyst surface; second, by hydrogen generated by decomposition of formic acid in the absence of hydrogen produced in the first stage.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jece.2018.07.015>.

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