On the role of Pd β-hydride in the reduction of nitrate over Pd based catalyst

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ABSTRACT

Two monometallic palladium catalysts supported on γ-Al_2O_3 were synthesized using different precursors, $Pd(AcAc)_2$ and $Pd(NO_3)_2$, while Pd-Cu/γ Al_2O_3 catalysts were prepared from those parent catalysts. The samples were tested for the elimination of nitrate and nitrite from aqueous solutions using hydrogen as a reductant in a standard batch reactor. Besides, the reduction of nitrate was carried out in a series of two reactors by an electrochemical cell mechanism. In this case, nitrate was reduced to nitrite by electrons supplied from the first reactor. The following reduction of nitrite was performed over the monometallic catalyst. Both the conversion and the selectivity to N_2 were higher than in the standard batch reactor. Monometallic samples prepared from $Pd(AcAc)_2$ showed an extremely high selectivity to the desired product. The catalysts were characterized by transmission electron microscopy (TEM), temperature programmed reduction (TPR) and H_2 chemisorption. Differences in particle size and β-hydride formation were observed for the different samples. The possible role of Pd β-hydride in the formation of overhydrogenated products is discussed.

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1. Introduction

In last years, nitrate concentration in ground water has been increasing in several parts of the world due to overusing of fertilizers [1]. Nitrate is harmful for human health because it is reduced to nitrite in the body. Nitrite is combined with hemoglobin in the blood leading to the so called "blue-baby syndrome" [2]. In addition, nitrite can be converted into carcinogenic nitrosamine [3].

Conventional physicochemical methods (ion exchange, reverse osmosis, electrodialysis) and biological denitrification processes (heterotrophic or autotrophic) for eliminating nitrate in water are complex and they have several economical and ecological disadvantages. The most promising technique for nitrate removal seems to be the catalytic hydrogenation over a solid catalyst. In this context, bimetallic palladium based supported catalysts have been extensively studied [4–15].

The global reaction scheme taking place over the supported catalysts is depicted in following scheme.
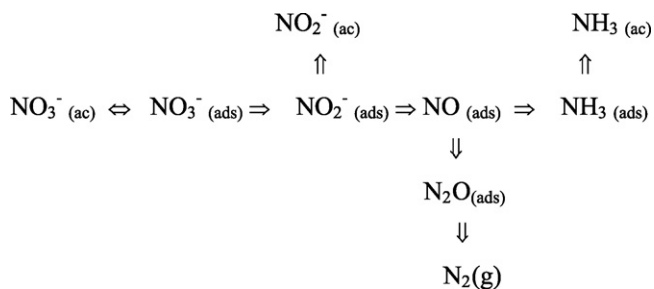
Pd is inactive for the reduction of nitrate to nitrite (the first step shown in Scheme 1), for this reason the addition of a promoter is necessary in order to transform nitrate into nitrite by a redox process. Copper [8,11–13,16,17], tin [1,11] and indium [1] have mostly been used as promoters. According to the reaction mechanism proposed by Wärna et al. [17], nitrates are reduced in a stepwise fashion, initially to nitrites over bimetallic sites, before migrating to monometallic sites where subsequent nitrite reduction takes place. For the case of Pd-Cu and Pt-Cu catalysts, previous studies [7,8,12] have demonstrated that nitrates might be reduced to nitrites on metallic copper according to a redox reaction, leading to the oxidation of copper species; subsequently, the role of the noble metal is to activate hydrogen and enable copper reduction. The activity of denitrification is acceptable, however, the formation of ammonia is not completely avoided. For example, Berndt et al. [18], when performing a batch catalytic test for reduction of $NaNO_3$ over Pd-Sn/Al_2O_3, reported a formation of 7 mg/l of ammonia, which corresponds to a 7% of selectivity towards NH_4^+, for a 99% level of conversion of nitrate.

More studies involving monometallic catalysts supported on semiconducting oxides (Pd/CeO_2 and Pd/TiO_2) have been developed [19,20]. In this study, it was suggested that support species (oxygen vacancies located at the metal-support interface) are directly involved in the nitrate reduction to nitrite. These catalysts are highly active, however, they exhibit high selectivity to ammonia, which was suggested to be due to the strong hydrogenation character of this type of catalyst.

Though the exact origin of the reaction of formation of ammonia is not well established, undoubtedly it is related to the species which undergoes the redox conversion of nitrate to nitrite (promoter species for the bimetallic catalysts or a support site for the monometallic catalysts supported on CeO_2 or TiO_2).

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$$NO_2^-{}_{(ac)} \qquad\qquad NH_3{}_{(ac)}$$
$$\Uparrow \qquad\qquad\qquad \Uparrow$$
$$NO_3^-{}_{(ac)} \Leftrightarrow NO_3^-{}_{(ads)} \Rightarrow NO_2^-{}_{(ads)} \Rightarrow NO_{(ads)} \Rightarrow NH_3{}_{(ads)}$$
$$\Downarrow$$
$$N_2O_{(ads)}$$
$$\Downarrow$$
$$N_2(g)$$

Scheme 1. Probable mechanism for the reduction of nitrate.

In this context, the present work is focused on the study of monometallic Pd catalysts supported on γ-Al$_2$O$_3$ for the elimination of nitrate in water. In pursuing this, the reduction of nitrate to nitrite (the first step of the reaction) is carried out by a electrochemical cell mechanism with the couple Cu/Cu^{2+} located in an additional reactor. The following reduction of NO$_2^-$ is carried out in a classical batch reactor over monometallic palladium surface using H$_2$. Thus, this indirect reduction of nitrate technique excludes direct contact between palladium and promoter species.

In order to perform comparisons, the elimination of nitrate by reduction with H$_2$ is carried out over a modified copper catalysts, Pd-Cu/γ Al$_2$O$_3$, in a batch reactor.

2. Experimental

2.1. Catalysts preparation

Two methods were applied to prepare the monometallic Pd catalysts. For both cases, the support was γ-Al$_2$O$_3$ (Rhone-Poulenc, 210 m^2/g).

The first method was a wet impregnation of the support by means of a solution of Pd(C$_5$H$_7$O$_2$)$_2$ (palladium acetyl acetonate, 99%) in toluene. The solution was contacted with the support for 48 h, then the solid was filtered and calcined at 400 °C in air for 4 h. Finally, the catalyst was reduced for 2 h at 300 °C. This sample is named as PdA.

The second synthesis procedure was an incipient wetness impregnation with an aqueous solution of Pd(NO$_3$)$_2$ (Aldrich, 99%). The catalyst precursor was calcined for 4 h at 400 °C and then reduced in flowing H$_2$ for 2 h at 300 °C. This sample is named as PdN.

Two copper bimetallic samples were obtained by contacting the monometallic catalysts PdA and PdN, respectively, with aqueous solutions of Cu(NO$_3$)$_2$ (Aldrich, 99%). These samples are named as PdACu and PdNCu.

An additional monometallic sample was prepared from Pd(C$_5$H$_7$O$_2$)$_2$ employing a support with lower specific surface area: γ-Al$_2$O$_3$ with 80 m^2/g. This catalysts was named as PdA1.

2.2. Catalysts characterization

Pulse chemisorption measurements were carried out in a classical apparatus. Approximately, 100 mg were reduced in a 5 vol% H$_2$/Ar mixture at 573 K. Subsequently, an Ar flow was admitted to the reactor in order to purge the sample at the same temperature. Then, the catalyst was cooled down in Ar to room temperature. Afterwards pulses with a volume of 200 μl of a 5 vol% H$_2$/Ar mixture were admitted to the Ar flow. A TCD detector was employed to measure the amount of H$_2$ that saturates the Pd surface. The metal dispersion was calculated assuming a 1:1 chemisorption stoichiometry.

Characterization was also performed by transmission electron microscopy (TEM) analysis on a Jeol 100 CX2 (Tokyo, Japan).

Temperature programmed reduction (TPR) experiments were carried out in a conventional apparatus. The sample (approximately 200 mg) was previously calcined at 300 °C, and cooled down in Ar. After reaching room temperature, a Ar/H$_2$ mixture was admitted to the reactor and the sample was linearly heated to 500 °C. H$_2$ consumption and evolution were measured with a TCD detector as a function of the temperature.

The palladium and copper contents were determined by AAS.

2.3. Catalytic tests

2.3.1. Reduction of nitrite and nitrate in a standard batch experiment

The reduction of nitrite with H$_2$ was performed in a 200 ml pyrex reactor equipped with a magnetic Teflon stirrer, operating at atmospheric pressure. In a typical experiment, 50 ml of a 100 ppm NaNO$_2$ or NaNO$_3$ solution were put into the reactor. Subsequently, a pure H$_2$ stream was introduced into the vessel at a flow rate of 10 cm^3/min for purging of the liquid and gas phase of the reactor with. Approximately, 200 mg of the catalyst (average diameter lower than 50 μm, previously reduced) were introduced to the reactor, the gas flow was stopped, the reactor was closed and the stirring rate was fixed at 400 rpm. The reaction was considered to start at this moment. The reaction progress was followed by measuring the increase of pH, since for every mole of nitrate/nitrite converted to N$_2$ or NH$_4^+$, an increase of 1 mole of OH$^-$ is produced in order to maintain electroneutrality of the solution. The reaction was considered to be finished when no increase of pH was detected. Conversions, activities (calculated as mg of nitrate converted per min and per g of surface Pd) and selectivities to nitrite and ammonia were calculated.

NO$_3^-$, NO$_2^-$ and ammonia concentrations were determined by colorimetric analysis. Nitrate and nitrite concentrations were determined following the procedure detailed in the Standard Methods for the Examination of Water and Wastewater. Ammonium ions were also determined by a colorimetric technique (modified Berthelot method).

2.3.2. Reduction of nitrate over monometallic Pd/γAl$_2$O$_3$ catalysts (electrochemical cell device)

The device shown in Fig. 1 was employed for the elimination of nitrate in water over both monometallic PdA and PdN catalysts. It consists of two pyrex reactor, R1 and R2 connected by a saline
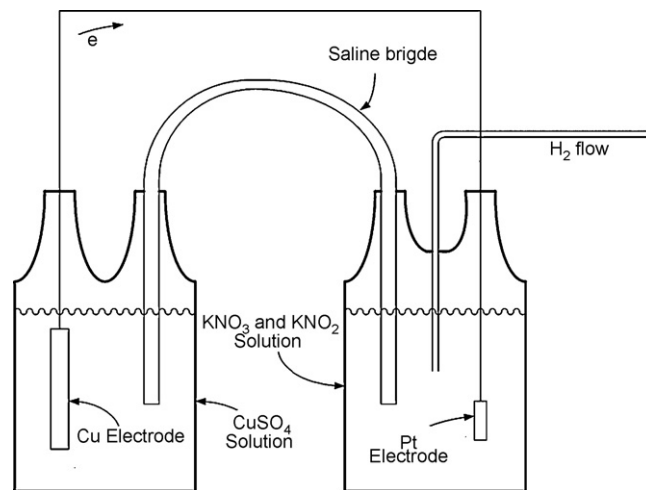
Fig. 1. Experimental device for testing Pd/γ-Al$_2$O$_3$ catalysts for the reduction of nitrate.

bridge. R1 contains a $CuSO_4$ solution and a Cu electrode (electrolytic copper), while R2 contains a NO_3^- solution (50 ml, 100 ppm of NO_3K) and a Pt electrode. In a typical run, R2 was filled with a nitrate solution and then H_2 started to flow (10 cm³/min) trough the solution. After 10 min of hydrogen purge, approximately 200 mg of catalysts (reduced *ex situ*) were added to R2. Finally, both electrodes were electrically connected and the reaction was considered to be started. The pH value was measured in both containers. The nitrate, nitrite and ammonia concentrations were measured after 6 h of reaction by colorimetric analysis.

3. Results and discussion

3.1. Catalysts preparation

In Table 1, the list of the catalysts, the concentration of Pd, as well as the noble metal dispersion is reported. The copper loading of all samples was approximately 0.30%.

3.2. Catalysts characterization

The dispersion of PdA is quite high (approximately 50%). It was previously reported that the preparation of palladium supported catalysts on γ-Al_2O_3 following the wetness impregnation method with $Pd(AcAc)_2$, conducted to highly dispersed samples [21]. The palladium particle size of PdA was estimated from H_2 chemisorption results, following the procedure of Aben [22]. The calculated value was in the nanometric scale (1.6 nm). The PdA1 catalysts also showed a quite high metal dispersion (45%).

On the other hand, the sample prepared form the inorganic precursor, PdN, showed an extremely low dispersion of the noble metal. The calculated particle size from chemisorption data was approximately of 10 nm, which is much larger than the value found for the highly dispersed PdA catalyst.

Upon the addition of copper to PdA sample, a strong depletion of the amount of chemisorbed hydrogen was measured. The dispersion of PdACu was much lower than the one corresponding to the parent catalyst. This result indicates that at least certain fraction of the promoter is located at the surface of the palladium particles.

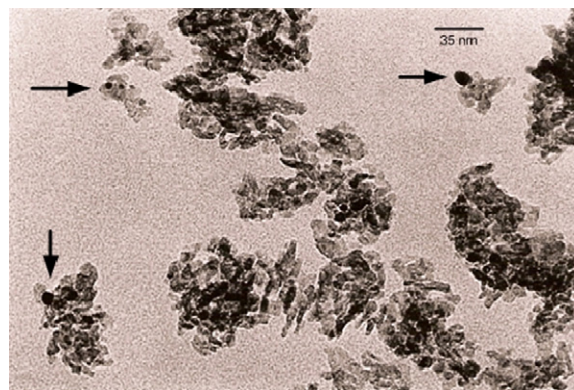The promotion of PdN with copper did not alter significantly the number of Pd exposed atoms.

The particle size distribution derived from TEM measurements indicated that the mean diameter was significantly much smaller for PdA (2 nm) than for PdN (100 nm). TEM observation revealed the occurrence of well separated crystalline palladium particles in the nanometric size range and a relative narrow particle size distribution for PdA. On the other hand, for PdN two types of particles were detected, with a mean diameter of 130 and 40 nm (see Fig. 2). The different preparation methods employed in the preparation of PdA and PdN would account for the morphological difference between these catalysts.

Besides, for PdN, the mean particle size determined by TEM was quite similar to the size calculated from H_2 chemisorption results.
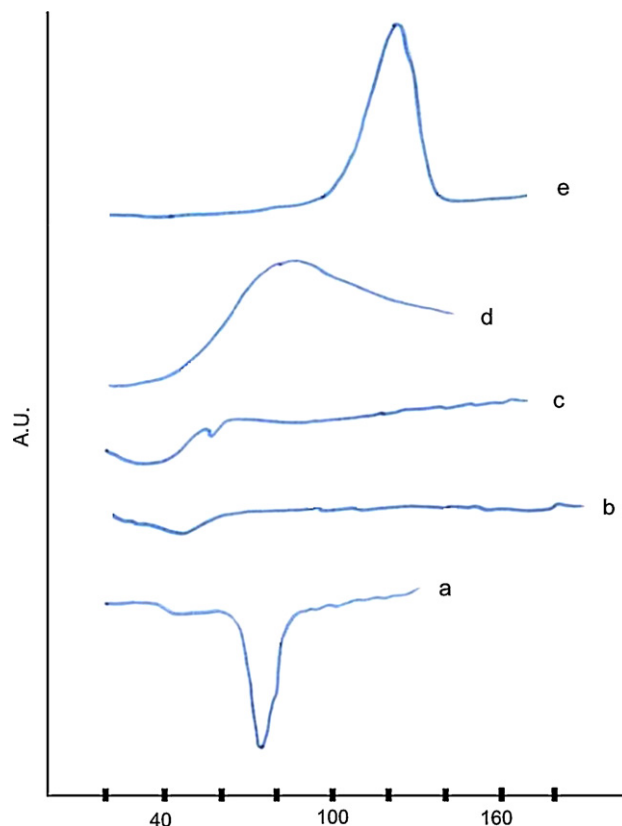

Fig. 2. TEM image for PdN catalyst.

On the other hand, for the case of PdA, palladium crystals size according to TEM measurements (2 nm) were larger than the one calculated from chemisorption results (1.6 nm), probably due to the fact that particles under 1 nm were not detected by TEM since they were under the detection limit of the technique.

No appreciable change in the size of the particles was detected upon the addition of copper.

The TPR profiles of the catalysts are shown in Fig. 3. Firstly, comparison between both monometallic will be performed. No consumption peaks were observed for these catalysts, due to the fact that PdO reduction is achieved at temperature bellow 20 °C [23–25]. PdN profile (Fig. 3a) showed a well defined negative peak centered at 75 °C. This peak is due to the hydrogen that evolves during the decomposition of the hydride phase. It is important to consider that palladium absorbs hydrogen to form Pd hydride even

Fig. 3. TPR profiles for PdN (a), PdA (b), PdNCu (c), PdACu (d) and Cu/Al_2O_3 (e) catalysts.

Table 1
Palladium loading, TEM particle size and H_2 chemisorption results for the studied catalyst

Sample	Pd (wt%)	Metal dispersion (%)	Particle size (Å)	H/Pd atomic ratio (TPR)
PdA	0.66	54	20	0.10
PdA1	0.98	45	–	0.12
PdACu	0.66	23	20	–
PdN	0.50	9	100	0.52
PdNCu	0.50	<9	100	–

at low hydrogen pressures and room temperatures [26]. In the present experimental conditions, hydrogen for the hydride phase is in the H_2/Ar carrier gas stream that contacts the sample at room temperature at the beginnings of the TPR experiments. The H:Pd atomic ratio (calculated from the amount of hydrogen evolved) is 0.52. Both, the hydride decomposition temperature (the maximum of the peak in Fig. 3, profile a) and the H:Pd ratio were similar to the values reported in the literature corresponding for Pd supported catalysts with particle size larger than 10 nm [27,28].

Fig. 3, profile b, shows the TPR corresponding to PdA. It can be observed that the peak corresponding to the β-hydride decomposition is quite broad (in the 20–60 °C range). The PdA1 sample (showing a low H:Pd ratio and a high metal dispersion) showed a profile (not shown in Fig. 3) similar to that corresponding to PdA. The H:Pd ratio of PdA and PdA1 (reported in Table 1) is much higher than for PdN. The fact that the noble metal is highly dispersed in these samples would account for this result. It is known that the tendency to form the hydride phase, as well as the decomposition temperature, decrease with increasing dispersion of Pd in supported catalysts [28–31]. For example, Bonarowska et al. [28] reported that for Pd-on-silica catalysts the H:Pd ratio decreases from about 0.5 to 0.03 as the dispersion increases from 4% to 55%. However, another interpretation is possible: during the preparation of samples PdA and PdA1, C atoms from the organic molecules used for making the catalyst (Pd(AcAc)₂) may form Pd carbide phases. Several authors [32–36] have reported the formation of PdC in supported Pd catalysts. It appears that the source of C is the organic precursors used to prepare the catalyst and/or the carbon containing chemicals (vinyl acetate, acetylene) used during those investigations. C in the Pd lattice may suppress the hydride formation. It is known that C in the Pd lattice suppresses the hydrogen absorption capacity to form the hydride phase.

The TPR profile corresponding to PdNCu is reported in Fig. 3c. A hydrogen consumption between 40 and 150 °C is observed, which would be due to the reduction of oxidic copper species. A relatively low desorption peak, centered at 75 °C is observed. This sharp and well-defined peak is assigned to the evolution of hydrogen from the hydride decomposition.

The profile corresponding to PdACu is shown in Fig. 3d. A broad consumption peak in the 60–150 °C range was observed. This consumption is assigned to the reduction of copper oxide species. In an additional experiment, a TPR experiment was carried out on a copper supported sample, Cu/γ-Al₂O₃ (profile e) with the same metal loading as PdACu and PdNCu. For monometallic copper sample a peak centered at 250 °C was observed, due to the reduction of supported copper oxide species. It is interesting to observe that the temperature reduction of supported copper species in PdCuA was diminished by the presence of palladium. This modification indicates that a close proximity between copper and palladium species was achieved.

The absence of a negative peak due to hydrogen evolution from the decomposition of a hydride phase may result to the large positive peak (between 60 and 150 °C due to hydrogen consumption) which completely masks any hydrogen evolution peak. It is also possible that in the presence of copper inside the palladium crystal inhibits the formation of hydride.

Summing up characterization results indicated that small palladium particles, with a low capacity to absorb hydrogen are present in PdA sample, while for PdN catalyst, palladium crystal are relatively larger and likely to form the β-hydride phase. For both PdACu and PdNCu samples, the presence of palladium increases the reduction of copper species suggesting a close proximity of copper and palladium.

Table 2
Catalytic results for the reduction of nitrite in a standard batch experiment

Sample	pH	X% NO_2^-	Activity[a]	S% NH_3
PdA	11	60	16	<1
PdA1	11	80	17	<1
PdACu	9	26	16	11
PdN	10	10	21	15
PdNCu	8	8	16	14

50 ml of a 100 ppm NO_2^- solution, 150 mg of catalyst, room temperature, 6 h of reaction time.
[a] Milligrams of nitrite converted per min and per g of surface Pd.

3.3. Catalytic results

3.3.1. Reduction of nitrate and nitrite in a standard batch experiment

Since in the present experimental conditions no buffering of the solution was carried out, the conversion of nitrite to nitrogen is accompanied by the formation of hydroxide ions in stoichiometric amounts to keep electroneutrality of the solution [19]. Concomitantly, the pH of the reaction media increased along with the reaction. Table 2 reports the pH value of the solution after 4 h of reaction time for all the catalysts. Since the increase of pH could be taken as a measurement of the conversion of nitrite, the amount of NO_2^- converted, at 4 h of reaction, was calculated from OH concentration. Besides, colorimetric measurements were carried out in order to determine the NO_2^- concentration. These results were quite similar to those calculated from pH.

Both, PdA and PdA1 presented a relatively high conversion for nitrite reduction at 6 h of reaction time. It is important to note that the catalysts remained active, even at high pH values. This fact shows that controlling pH is not a necessary experimental procedure for achieving high conversion under the present reaction conditions. The conversion of the catalyst prepared from Pd(AcAc)₂, PdA was higher than the corresponding to sample prepared from the inorganic precursor, PdN (see Table 2). The difference in the conversion level would be related with the lower dispersion of palladium in PdN than in PdA (as measured by H_2 chemisorption and TEM).

The conversion values corresponding to both bimetallic samples, PdNCu and PdACu, were markedly lower than the ones of the parent catalysts. The depletion of the conversion upon the addition of copper would be related to the dilution of the Pd surface by the promoter. The activity for the reduction of nitrite (expressed as moles of nitrite converted per mole of surface Pd) of PdACu is quite similar to the corresponding monometallic sample, PdA. Thus, this indicates that nitrite is being converted only on palladium sites, while bimetallic sites are inactive for nitrite activation. These results are in agreement with the assumption of Prusse and Vorlop [37] who have postulated that other sites than Pd ones are inactive for the reduction of nitrite. On the other hand, other authors have assumed that nitrite may also be converted in an unselective manner at bimetallic sites [7,10,11,38,39].

The selectivity towards ammonia at 6 h of reaction is reported in Table 2 for the monometallic and promoted samples. The lowest value was achieved over the PdA and PdA1 samples. These catalysts showed a selectivity to ammonia amongst the lowest ones which have been reported in the literature regarding the reduction of nitrite over mono or bimetallic Pd based catalysts. It is important to note that the high selectivity towards N_2 is achieved at high conversion levels (60% and 80%), showing that these catalysts should be considered as extremely high selective ones.

The other monometallic sample, PdN, presented a selectivity to NH_3 higher than 20%. To explain the difference between the selectivity values of PdA and PdN (both prepared using the same alumina support) it should be considered that variation of the

preparation method affects both the catalytic activity and the selectivity of supported Pd catalysts [1]. The two preparation methods employed in the present work lead to quite different catalysts: (a) PdA and PdA1, with small palladium crystals for which the absorption of H_2 (β-hydride formation) is restricted, and (b) PdN for which noble metal particles are relatively bulky and without constraint on H_2 absorption. Thus, it could be speculated that the extremely low production of ammonia over PdA surface is in some way related to the nanometric palladium particle size in PdA. Which is the exact nature of the almost nule selectivity to ammonia over PdA is an open question. However, it could be speculated that if ammonia formation results from the over-hydrogenation of nitrite, the lack of hydrogen dissolved in the bulk of the palladium particles in PdA would minimizes the formation of NH_3. Still another interpretation is possible: intrinsic modification of the properties of metallic sites on small palladium particles would render the surface of PdA highly selective for the hydrogenation of nitrite to N_2. At this respect, it is interesting to comment that several works reported on the peculiar catalytic behaviour of palladium particles smaller than 3–5 nm [40,41] as catalysts for semihydrogenation reactions.

On the other hand, the relatively high selectivity to ammonia of PdN could be justified by the fact that this sample would present a marked hydrogenation character. Sá et al. [20] suggested that the high formation of ammonia in Pd/TiO_2 could be justified by the hydrogenation character of this catalyst giving rise to over-reduction.

Upon the introduction of copper, the amount of the ammonia formed at 4 h of reaction notably increased with respect to the corresponding monometallic sample. The selectivity to ammonia for PdACu is 14% and it is even higher for PdNCu. The notable increase in the selectivity to ammonia would be related to the dilution of Pd surface by promoter species. For the formation of the desired product, N_2, a combination of two surface N containing species has to take place. In contrast, ammonium formation occurs if the catalysts surface is covered with too many H species. The increase of the selectivity to ammonia due to the promotion of palladium has been previously reported for Pd-Cu, Pd, bimetallic catalysts.

The results of conversion of nitrate and the selectivities towards nitrite and ammonia at 4 h of reaction, are reported in Table 3 for PdACu and PdNCu.

The monometallic palladium catalysts were found to be inactive for the conversion of nitrate, as was previously reported [7,38]. When the reaction was performed over Cu/Al_2O_3, a minor amount of nitrate was converted and the reaction was stopped at 10–15 min.

The degradation of nitrate over PdACu was superior to that of PdNCu, probably due to a higher concentration of surface bimetallic sites in the former than in the latter sample. A release of nitrite into the solution was observed for both samples from 10 min of reaction time. The concentration of nitrite at 4 h of reaction was much higher for PdNCu than for PdACu. In the

reduction of nitrate over bimetallic catalysts, the further hydrogenation of nitrite to nitrogen or ammonia is performed on monometallic Pd (see results of Table 2, and ref. [12]). Thus, the low activity of the PdNCu sample for nitrite activation would be due to the low concentration of monometallic palladium sites at the surface of the catalysts. Finally, it could be concluded that the ratio between mono and bimetallic sites is not the optimal for the PdNCu catalyst. On the other hand, PdACu catalyst was relatively active for nitrite hydrogenation. This result is in agreement with that obtained for the reduction of nitrite.

Regarding ammonia formation (see Table 3), a 15% selectivity was measured over the PdACu catalyst, at a low conversion level (10%). This result indicates that PdACu is quite unselective to nitrogen, as was established for the reduction of nitrite. The PdNCu catalyst was also found to present a high selectivity to ammonia.

Summing up both bimetallic catalysts were not efficient for reducing nitrate to nitrogen, since the amount of nitrite released to the solution is high. Besides, nitrite is overhydrogenated to ammonia. Both characteristics would be related with the presence of a Pd surface diluted by copper atoms.

3.3.2. Reduction of nitrate over monometallic $Pd/\gamma Al_2O_3$ catalysts (electrochemical cell device depicted in Fig. 1)

It is important to recall that monometallic Pd catalysts are inactive for the reduction of nitrate, for this reason the addition of a promoter is necessary in order to transform nitrate into nitrite. In the present work, monometallic palladium catalysts are employed for reducing NO_3^- without promotion of the noble metal. In pursuing this, nitrate is reduced by an electrochemical cell mechanism in the reactors depicted in Fig. 1. In R1 the oxidation accomplished by the Cu^0/Cu^{2+} couple (copper electrode/copper sulfate solution) provides electrons for the nitrate reduction (nitrate solution in R2). The following catalytic conversion of nitrite was performed in R2 over palladium monometallic catalysts, PdA, PdA1 or PdN, using H_2 as the reductor. Thus, no second metal is employed in the formulation of the catalysts for the reduction of nitrate.

In a previous experiment, the reduction of nitrate to nitrite, employing this experimental device, was carried out in the absence of catalyst in R2. The redox conversion of nitrate into nitrite (100 ppm) by electrons provided by the copper couple was carried out in approximately in 10–20 min, which is considered to be a short time of reaction. It is important to comment that this result was not quite reproducible, probably due to surface fouling of the electrodes.

In Table 3, the conversion values of NO_3^- (measured at 4 h of reaction) over PdA, PdA1 and PdN performed in the experimental device depicted in Fig. 1 are reported. The conversion level of monometallic catalysts in R2 were quite high. The same trend was observed for the catalysts prepared form $Pd(NO_3)_2$. The reason for the high conversion achieved over monometallic catalysts would be that nitrate are converted to nitrite by the electrochemical cell reaction faster than by the catalytic reaction over supported copper species. The reduction of NO_3^- to NO_2^- is known to be the rate-determining step. This was verified by electrochemical experiments which showed the first electron transfer to be rate determining [42]. However, it is important to comment that the reproducibility of the result was not quite good, probably due to the above commented facts regarding the loss of activity of the electrodes.

Regarding the undesired formation of ammonia, the concentration of this product was extremely low (concentration in the limit of the detection technique) after 4 h of reaction over the catalysts prepared from $Pd(AcAc)_2$, PdA and PdA1. The high selectivity to N_2 corresponding to these samples would be related to the high concentration of surface palladium sites available for

Table 3

Reduction of nitrate over bimetallic sample (standard batch experiment) and over monometallic catalyst (electrochemical experiment)

Sample	X% NO_3^-	%S NO_2^-	%S NH_3
PdA	65	0	<1
PdA1	75	0	<1
PdACu	10	60	15
PdN	11	0	5
PdNCu	5	80	<1

Conversion, and selectivity towards nitrite ammonia. 50 ml of a 100 ppm de NO_3^- solution, 150 mg of catalyst, room temperature, 6 h of reaction time.

the reduction of nitrite. Still, another interpretation is possible: the incapability of palladium crystals to dissolve hydrogen (β-hydride) would restrict the concentration of hydrogenation species, controlling in this way overhydrogenation reactions.

The experimental device (Fig. 1) could be considered a too complicated one in the context of a possible technological applications. However, the extremely high selectivity of PdA and PdA1 towards N_2, in the nitrate reduction reaction is a significant finding, because it offers opportunities for the design of mono-metallic catalysts based on palladium with the objective of improving the nitrogen selectivity.

PdN was also active, however, from the point of view of selectivity it could be not considered a selective catalysts: the formation of ammonia, though lower than in the case of the standard batch experiment, is higher than in the case of PdA. Over-reduction of nitrite could not be avoided over PdN. The higher selectivity to ammonia of PdN by comparison with PdA would be in some way related to the difference in particle size for both cases. Thus, the absence of promoter species is not the only condition to achieve low formation of ammonia.

4. Conclusion

It is possible to reduce nitrate, in aqueous phase, to N_2 over an unpromoted Pd/γ-Al$_2$O$_3$ prepared from Pd(AcAc)$_2$, achieving a high activity and an optimal selectivity to N_2. This result is attained by performing the reaction of reduction of NO_3^- to NO_2^- by an electrochemical cell mechanism; subsequently, the reduction of nitrite to N_2 takes place on Pd/γ-Al$_2$O$_3$. The high selectivity to N_2 over the monometallic sample is due to the fact that no dilution of the palladium surface by the promoter species exist. Besides, nano palladium particles, for which the formation of β-hydride phase is restricted, are highly selective to N_2 due to the suppression of overhydrogenation reactions.

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