Nitrate Catalytic Reduction over Bimetallic Catalysts: Catalyst Optimization

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Abstract: The catalytic removal of nitrate (NO_3^-) in water using hydrogen as a reducing agent was studied using palladium-copper bimetallic catalysts in different supports. Commercial carbon nanotubes (CNTs), used as received and with different mechanical (CNT (BM 2h)) and chemical modifications (CNT (BM 4h)-N), titanium dioxide (TiO_2) and composite materials (TiO_2-CNT) were considered as main supports for the metallic phase. Different metal loadings were studied to synthesize an optimized catalyst with high NO_3^- conversion rate and considerable selectivity for N_2 formation. Among all the studied support materials, the milled carbon nanotubes (sample CNT (BM 2h) was the support that showed the most promising results using 1%Pd-1%Cu as metallic phases. The most active catalysts were 2.5%Pd-2.5%Cu and 5%Pd-2.5%Cu supported on CNT (BM 2h), achieving total conversion after a 120 min reaction with N_2 selectivity values of 62% and 60%, respectively. Reutilization experiments allowed us to conclude that these catalysts were stable during several reactions, in terms of NO_3^- conversion rate. However, the consecutive reuse of the catalyst leads to major changes concerning NH_4^+ selectivity values.

Keywords: catalytic reduction; nitrate removal; bimetallic catalysts; carbon nanotubes; titanium dioxide

1. Introduction

The excess of nitrate (NO_3^-) in water and wastewater is attributed to the use of fertilizers and to waste effluents from agricultural activities and certain industries. Most drinking water is produced from groundwater, and the contamination with NO_3^- can cause serious health risks when consumed (such as methemoglobinemia, cancer or hypertension). Legislation imposes a maximum admissible concentration for NO_3^- in drinking water of 50 mg/L (in the European Drinking Water Directive) and 25 mg/L is the guide level given by the World Health Organization [1–3].

NO_3^- is a stable and highly soluble ion with low potential for co-precipitation or adsorption, properties that hinder removal from water using conventional water treatment technologies. There are many physicochemical and biological processes used to perform its removal from water; however, most of them are not cost-effective or can be detrimental due to potential side effects on water quality [4–6].

The most favorable way to remove NO_3^- from water, from an ecological point of view, is to convert it into harmless gaseous nitrogen. Physicochemical treatments (ion exchange, reverse osmosis and electrodialysis) do not convert NO_3^- into harmless compounds; instead, they promote ion concentration which requires further treatment by a different technique or disposal afterwards [5–7]. Biological denitrification fulfills this requirement; however, the production of undesirable by-products,

such as nitrite (NO_2^-), can occur if the process is not fully achieved in addition to all the limitations of the process [1,8].

Catalytic reduction of NO_3^- appears as an interesting and economically reliable alternative for polluted water remediation. This process was described in 1989 by Vorlop et al. [1] and consists in the removal of NO_3^- through a selective heterogeneous catalytic hydrogenation to nitrogen. The main drawbacks of the process are the formation of nitrite as intermediate and ammonia (NH_4^+) as by-product, which is undesirable in drinking water. Limits for these species in drinking water, imposed by the European Drinking Water Directive, are relatively low: 0.1 mg/L for NO_2^- and 0.5 mg/L for NH_4^+. Another of the main advantages of this process is that the reaction is performed in mild conditions, room temperature and atmospheric pressure [9–14].

Over the past few years, several studies have been carried out to optimize the process of catalytic NO_3^- reduction, demonstrating that bimetallic catalysts are more efficient than monometallic ones. Bimetallic catalysts are composed of a noble metal, mainly Pd, Pt, Rh and Ru, and a transition metal such as Cu, Sn, Ag or In. Most used supports are alumina, silica, titanium dioxide and carbon materials [9,11,13,15]. Although the reaction mechanism is not yet fully understood, the most accepted one was proposed by Epron et al. [16], and it is assumed that the promoting metal is responsible for NO_3^- reduction through a redox reaction and the main function of the noble metal is to regenerate the promoting metal by means of spilled-over hydrogen (that is chemisorbed). Noble metals themselves do not present activity in NO_3^- reduction; however, they are very active for nitrite degradation (that is assumed to occur through the activated hydrogen) [4,16].

Activity and selectivity are strongly influenced by the reaction conditions, catalyst preparation, the way noble metal is promoted and the catalyst support. Palladium-copper (Pd-Cu) was identified as the most promising pair for catalytic nitrate reduction with increased N_2 selectivity. Catalytic properties of Pd-Cu were found to be sensitive to the ratio of the two metals, and there is a maximum for NO_3^- removal activity and N_2 selectivity for a defined Pd:Cu ratio that can differ according to the support used [1,10,14,17,18]. Therefore, adequate support plays an important role in the activity and selectivity of the catalyst [19–22].

Several studies focus on the application of different support materials in order to design active and selective catalysts for NO_3^- conversion; more recently, these studies have focused on the use of adequate supports that allow the integration of these catalysts in integrated processes for superior efficiency of the removal process [21,22]. Carbon materials bring together the most desired properties for the design of remarkable supports: high specific surface area, inertness and stability under reaction conditions, suitable mechanical properties, availability of methods to easily perform changes in their chemical and physical composition and their regenerative potential [23,24]. Carbon nanotubes (CNTs) stand out within this group due to several different properties of the material. In particular, since CNTs are a mesoporous material, consisting in an agglomeration of tubes, the active metal sites can concentrate in the external walls of the tubes, avoiding mass transfer limitations that are usually found, and promote metal dispersion [20,24,25].

Titanium dioxide possesses completely different properties from carbon materials, and its use as support is mainly based on the strong metal–support interaction effect (SMSI). In the case of TiO_2, as metal support for catalytic nitrate reduction, it was proposed that the oxide surface can participate in adsorption/reduction of nitrate to nitrite. Nitrate anions can adsorb on the exposed acid sites of the support, in close contact with metal particles, and would be reduced by excess electrons generated in the support after reduction. Even though titania-supported catalysts are very active, their selectivity towards N_2 formation is very low, and ammonia is usually produced in high concentrations [26–29].

Control of the desired N_2 selectivity towards obtaining the lowest values of NH_4^+ and NO_2^- remains a key issue in developing an optimized technology that can be commercialized and applied on a large-scale experiment [30]. Some studies focused on the application of NO_3^- catalytic reduction in continuous systems for water treatment. However, most of them focus on the integration of two

different technologies (catalytic reduction and ion exchange) in order to guarantee the efficiency of the process [30,31].

Process optimization is closely associated with the design of catalysts that promote reaction in an efficient and selective way. Thus, the objective of the present study is related to the synthesis of bimetallic catalysts with enhanced performance and stability to be used for efficient NO_3^- conversion processes. For this purpose, different materials, such as carbon nanotubes, titanium dioxide and composites of both materials will be considered as support. Physical and chemical modifications on the support will be performed to enhance the catalytic activity of the process and the selectivity for nitrogen. Palladium and copper bimetallic catalysts were used considering the high efficiency widely reported for this combination in catalytic reduction reactions. The content of each metal will be optimized to select the optimum composition and the best catalysts will be studied as to their stability over several catalytic reactions.

2. Materials and Methods

2.1. Bimetallic Catalyst Synthesis

Commercial multi-walled carbon nanotubes (CNTs) from Nanocyl 3100 (Sambreville, Belgium), and titanium dioxide (TiO_2) commercially obtained from Evonik Degussa Iberica SA (Barcelona, Spain), were used as support for the active metals.

Incipient wetness co-impregnation using aqueous solutions of the corresponding metal salts ($PdCl_2$ and $Cu(NO_3)_2 \cdot 3H_2O$) was performed in the selected supports. Different metal loadings were considered to optimize the ratio of the two metals. Thus, in the first stage, a content of 1 wt% for both promoter and noble metals was considered, and for the most active supports, a content of 5 wt% of palladium and 2.5 wt% of copper was adopted [17,32].

In order to modify the supports, physical and chemical changes were performed in the CNTs through a ball mill in Retsch MM200 equipment (Haan, Germany). Milled carbon nanotubes were obtained through milling of the as-received CNTs for 2 h using a frequency of 15 vibrations/s (CNT (BM 2h)) [33,34]. Carbon nanotubes doped with nitrogen (CNT (BM 4h)-N) were also synthesized through ball milling using melamine (99% Fluka, Buchs, Switzerland) as a nitrogen precursor. The material was milled for 4 h, with a frequency of 15 vibrations/s, and subsequently exposed to a thermal treatment at 600 °C under N_2 flow for 1 h. The contents of the nitrogen precursor and the conditions for the preparation of the materials were optimized in previous studies [34]. TiO_2 was used as commercially received.

Composite materials were prepared by mixing commercial TiO_2 and CNTs by means of a hydration–dehydration technique. First, as-received or modified CNTs were dispersed in water under ultrasonication for 30 min. Then, TiO_2 powder was added to the suspension, and the mixture was heated up to 80 °C and magnetically stirred until all the water was completely evaporated. The composite was dried overnight at 110 °C [35]. Composite materials were prepared using different proportions of each material to study the optimal composition of the material. The studied weight ratios of TiO_2:CNT were 20:80, 50:50 and 80:20.

After impregnation of both metals in the supports, samples were dried at 100 °C for 24 h, and then thermally treated at 200 °C, calcined under N_2 flow for 1 h and reduced under H_2 flow for 3 h [17,25].

2.2. Catalyst Characterization

Textural characterization of the synthesized catalysts and supports was performed through N_2 adsorption isotherms at −196 °C determined in a Quantachrome NOVA 4200e multistation (Davie, FL, United States) with previous sample degasification at 150 °C for 3 h.

Transmission electron microscopy (TEM) analyses were performed for selected catalysts in order to obtain information related to their structure. TEM micrographs were obtained using a transmission electron microscope with high-contrast JEOL JEM-1010 100 kV, (Tokyo, Japan).

High-resolution TEM micrographs were obtained using a JEOL 2100 microscope (Tokyo, Japan) equipped with a Probe-Corrected STEM-FEI Titan ChemiSTEM, FEG filament with an accelerating voltage of 200 kV and an EDX detector.

The nitrogen content of the doped support CNT (BM 4h)-N was determined by elemental analysis in a vario MICRO cube analyzer from Elemental GmbH (Kalkar, Germany).

2.3. Nitrate Catalytic Reduction Experiments

To study the performance of the synthesized catalysts, catalytic reduction experiments were conducted in a semi-batch reactor (ca. 1 L, designed and assembled in-house) equipped with a magnetic stirrer. In a typical run, 400 mg of catalyst was charged into the reactor containing 800 mL of a 30 mg/L of nitrate ($NaNO_3$ Sigma-Aldrich) solution in distilled water. This initial NO_3^- concentration, stipulated for the experiments conducted within the scope of this study, was selected taking into account a previous study related to the removal of a model organic compound (4-Nitrobenzaldehyde) by a catalytic ozonation process [36]. During this study, it was reported that a single ozonation process of the main molecule would lead to the formation of a large concentration of NO_3^- (around 30 mg/L).

The experiments were carried out at atmospheric pressure and ambient temperature with a stirring rate of 700 rpm. Hydrogen was used as a reducing agent and carbon dioxide as a pH buffer to maintain a constant pH value of approximately 5.5 (compatible value with drinking water parameters) and to help avoid NH_4^+ formation ($H_2 + CO_2$ (1:1), Q_{Total} = 200 Ncm^3/min).

The reaction lasted 5 h and samples were collected from the reactor with a syringe, at specific times, for quantification of nitrate, nitrite and ammonia. Species concentration was determined by ionic chromatography in a Metrohm 881 Compact IC Pro apparatus (Herisau, Switzerland), equipped with a Metrosep C4 cationic exchange column (250 mm × 4.0 mm) for quantification of ammonia and a Metrosep A Supp 7 anionic exchange column (250 mm × 4.0 mm) for quantification of nitrate and nitrite. Selectivities to nitrite, ammonium and nitrogen were calculated as described in [37]. Reutilization experiments were performed for the most active bimetallic catalyst to assess its durability. For these tests, the catalyst was recovered, after reaction, dried in an oven overnight and used again.

The catalytic experiments performed during the present work were performed in triplicate. The maximum error registered between experiments was 3%.

After each reaction, the solution was collected and inductively coupled plasma mass spectrometry analysis was performed to assess metal leaching. The analysis was performed in an ICP-OES ICAP 7400 THERMO (Waltham, MA, United States) equipped with a nebulizing system and using optical emission spectroscopy for detection, in order to determine the metal content on the samples. Measurements were done in triplicate and the mean value was the considered result. The quantification of metal present in the analyzed solution was quantified using calibration curves for each of the considered metals.

3. Results and Discussion

3.1. Catalyst Characterization

Table 1 presents the values of specific surface areas (S_{BET}), obtained using the Brunauer-Emmett-Teller method (BET) from nitrogen isothermal adsorption data, and pore volumes for all the supports and synthesized catalysts.

S_{BET} surface area values show that milling increases the specific surface area of carbon nanotubes by 12%. Titanium dioxide, as expected, presents a much lower surface area when compared with carbon nanotubes. Composite materials (TiO_2-CNT) present lower surface areas than those observed for the original carbon materials, which was expected since TiO_2 presents a much lower specific surface area.

Table 1. Textural properties of the synthesized bimetallic catalysts and supports.

	Sample	S_{BET} (m^2/g)	$V_{P \, p/p0=0.95}$ (cm^3/g)
Support	CNT	197	0.421
	CNT (BM 2h)	220	0.621
	CNT (BM 4h)-N	191	0.391
	TiO_2	50	0.130
	TiO_2-CNT (50:50)	122	0.276
	TiO_2-CNT (BM 2h) (50:50)	145	0.384
	TiO_2-CNT (80:20)	79	0.186
	TiO_2-CNT (20:80)	153	0.367
Catalyst	1% Pd-1% Cu/CNT	194	0.421
	1% Pd-1% Cu/CNT (BM 2h)	216	0.599
	1% Pd-1% Cu/CNT (BM 4h)-N	185	0.480
	1% Pd-1% Cu/TiO_2	46	0.143
	1% Pd-1% Cu/TiO_2-CNT (50:50)	118	0.283
	1% Pd-1% Cu/TiO_2-CNT (BM 2h) (50:50)	131	0.377
	1% Pd-1% Cu/TiO_2-CNT (20:80)	159	0.356
	1% Pd-1% Cu/TiO_2-CNT (80:20)	67	0.190
	5% Pd-2.5% Cu/CNT	182	0.403
	5% Pd-2.5% Cu/CNT (BM 2h)	203	0.574
	2.5% Pd-2.5% Cu/CNT (BM 2h)	220	0.609
	5% Pd-2.5% Cu/TiO_2	41	0.132
	5% Pd-2.5% Cu/TiO_2-CNT(50:50)	109	0.267
	5% Pd-5% Cu/CNT (BM 2h)	209	0.556

When the metallic phase is added, it is possible to observe that, independently of the support, specific surface area values do not change significantly for metal loadings of 1% of each metal [17]. However, when the amount of metal increases, a decay in the value of the specific surface area occurs, but it is still relatively low. Thus, surface area values of bimetallic catalysts are not significantly different from those recorded for the respective supports.

Regarding commercial titanium dioxide, the crystalline form consisted of 80% anatase and 20% rutile [38].

Figure 1 presents TEM micrographs of some of the synthesized catalysts. Results regarding metal particle size distribution of each catalyst are presented in the Supplementary Information (Figure S1).

Figure 1 shows that, generally, metals are well dispersed in the catalyst regardless of the support material used. Images obtained for the catalysts supported on CNTs and CNT (BM 2h) allow for noticing some relevant differences between the two supports. Figure 1A,D show a great entanglement of the tubes, which is characteristic of the original material. After the ball milling process, this entanglement was markedly reduced, due to damage during the process, leading to the formation of shorter CNTs (Figure 1B,E,G) [33]. This mechanical treatment allows for a significant increase in the specific surface area of the material, as is possible to see from the results presented in Table 1, which highly contributes to the good dispersion of the metallic phase of the material, which is possible to verify. Generally, for the catalyst supported on CNT-based supports, metal particle sizes are around 2 to 4 nm, and it is possible to notice a slight increase in the average size of metallic particles of catalysts with higher metal content (around 5–7 nm). The representative images of the catalyst supported on the composite material (Figure 1C,F) show a good mixture between the two materials and it is notorious that, for the catalysts supported on this material and on TiO_2, metal particles have larger dimensions when compared with carbon nanotube-based materials. For these materials, average metal particle sizes were of 14 to 20 nm [17]. Figure 2 shows the images obtained through High Resolution Transmission Electroscopy (HRTEM) for the catalysts with higher metallic percentages (5% Pd-2.5% Cu) supported on CNT (BM 2h) and TiO_2.
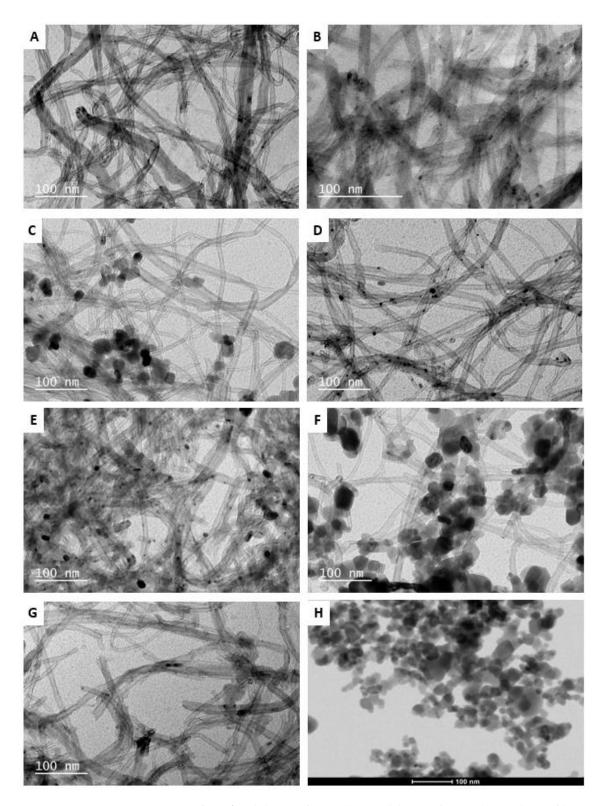
Figure 1. TEM micrographs of: (**A**) 1%Pd-1%Cu/CNT, (**B**) 1%Pd-1%Cu/CNT (BM 2h), (**C**) 1%Pd-1%Cu/TiO$_2$-CNT (50:50), (**D**) 5%Pd-2.5%Cu/CNT, (**E**) 5%Pd-2.5%Cu/CNT (BM 2h), (**F**) 5%Pd-2.5%Cu/TiO$_2$-CNT (50:50), (**G**) 2.5%Pd-2.5%Cu/CNT (BM 2h) and (**H**) 5%Pd-2.5%Cu/TiO$_2$.
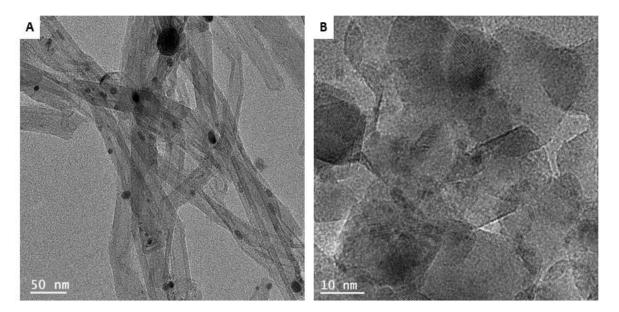
Figure 2. HRTEM micrographs of: (**A**) 5%Pd-2.5%Cu/CNT (BM 2h) and (**B**) 5%Pd-2.5%Cu/TiO$_2$.

Through the HRTEM images, it is possible to conclude that metal particles are on and inside the carbon nanotubes, which can be explained by the breaking of the tubes during the milling process of the original material, allowing the entrance of the metals into the tubes during the impregnation step. Additionally, EDX analysis (Figure S2) shows some overlap of the position of Cu and Pd, forming alloys on the support surface, and some areas where both metallic phases are present separately.

3.2. Catalytic Reduction Experiments

Synthesized catalysts were tested for their ability to reduce nitrates in water and selectivity for N$_2$ formation. In the first stage, the effect of each support was considered. The best performing support was then used to study the metal composition towards obtaining an optimized catalytic system for nitrate reduction.

3.2.1. Effect of the Support

Influence of the support on the activity and selectivity of the catalysts, during catalytic nitrate reduction, was studied under similar reaction conditions. Catalysts were prepared using the same metal amounts (1% (wt.) of each metal) on each different support material. Figure 3 presents the performance of the various catalysts, displaying nitrate conversion values, as well as the corresponding evolution of NO$_2^-$ and NH$_4^+$ concentrations. Figure 4 summarizes conversions of NO$_3^-$ and selectivities into NO$_2^-$, NH$_4^+$ and N$_2$ after 60 and 300 min of reaction.

The obtained results show that all the synthesized catalysts were able to achieve high nitrate conversion values (percentages higher than 98%) after 5 h of reaction. For the catalysts supported on carbon nanotubes, CNT, CNT (BM 2h) and CNT (BM 4h)-N, it is evident that nanotube milling was a key step towards obtaining a more active catalyst for NO$_3^-$ removal since this mechanism contributes to increasing the specific surface area of the material, allowing a good dispersion of the metallic phase, as can be seen through TEM micrographs presented in Figure 1. The catalyst 1% Pd-1% Cu/CNT, despite being able to achieve a conversion value of 98% (after 5 h of reaction), presented the lowest reaction rate of all the tested catalysts. Sample 1% Pd-1% Cu/CNT (BM 4h)-N proved to be slightly more active than the sample supported on CNTs, yet total reaction time was required to achieve a 99% conversion. However, when the CNT (BM 2h) sample is used as support, NO$_3^-$ was completely converted after 180 min of reaction. The selectivity values, obtained for each of the monitored species, observed in the milled support are very similar to the ones obtained for original CNTs. The increase in

ammonium concentration was very small over reaction time, contrary to what was verified with CNT (BM 2h), with a final concentration of 3.5 mg/L (selectivity of 42%), probably due to the lower nitrate removal rate using CNTs as support, while N_2 selectivity registered at the end of the reaction was 57%. To achieve a large metal dispersion and build catalysts with enhanced catalytic activity, large surface area and well-developed porosity are essential [33,39]. Ball milling applied to carbon nanotubes is used as a promising method to modify the material, namely, to adjust their lengths and to open closed ends, increasing the available specific surface area. Ball milling is highly effective in disentangling and shortening the CNTs by breaking up the tubes [40]. For this reason, the use of a milled support is able to obtain enhanced catalytic results. Soares et al. [41] reported that the ball mill technique applied on the carbon nanotubes promoted textural modifications, mainly related to the disentanglement of the tubes, which leads to a consequent increase in the specific surface area of the materials, and consequently enhances the activity of the catalyst; in this same work, milled carbon nanotubes were used as support for Pd and Pd-Cu complexes and applied for bromate conversion. Promising results were obtained for the modified carbon nanotubes, attributing their efficiency to the higher accessibility of the ionic species, present in water, to the support surface due to less entanglement of the tubes, which is a characteristic of the milled materials. Therefore, using milled carbon nanotubes as support for the metal phase decreases the mass transport limitations observed when original CNTs are used as support. These promising results obtained for CNT (BM 2h) samples are justified by HRTEM images present in Figure 2A, where it is possible to verify the good dispersion of the metallic nanoparticles that are deposited on the material surface and inside the tubes. The use of this support enhanced the catalytic activity, mainly in terms of reaction rate, achieving complete conversion in 180 min. Previous works, regarding bromate catalytic reduction in the presence of monometallic catalyst supported on modified carbon nanotubes, reported that the modifications performed on CNTs, through ball mill treatment, allowed an increase in the catalytic activity of the material, pointing to the increase in the specific surface area of the support and the disentangling of the tubes as the main causes for this result [34,41]. However, nitrite and ammonium concentrations at the end of the reaction are still a problem since their values are still above the imposed legal limits.
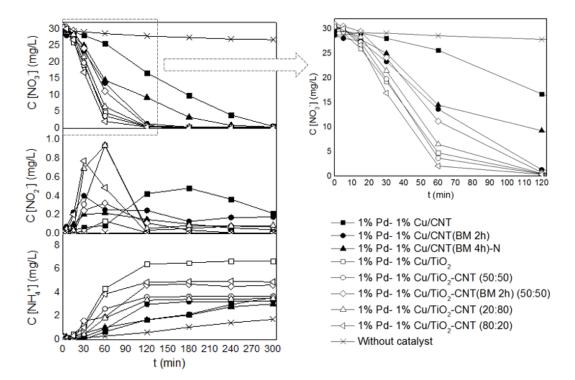

Figure 3. NO_3^-, NO_2^- and NH_4^+ concentrations as a function of time during nitrate reduction reactions in the presence of 1%Pd-1%Cu catalysts on different supports.
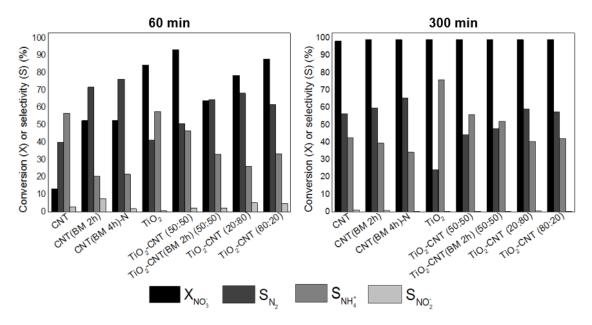
Figure 4. NO_3^- conversion and corresponding N_2, NH_4^+ and NO_2 selectivities after 60 and 300 min of reaction time for all the studied supports with a metal loading of 1% Pd and 1%Cu.

The catalyst support for nitrogen-doped carbon nanotubes (CNT (BM 4h)-N) achieved the most promising N_2 selectivity value at the end of the reaction (66%). However, despite the small improvement in NO_3^- conversion, compared to that recorded for the CNT-supported catalyst, complete conversion was achieved after 300 min. The incorporation of nitrogen heteroatoms in the carbon structure allows the support to be more electronegative, which in turn enables the anchorage and improved dispersion of the active metal phase that significantly contributes to enhancing the catalytic activity of the material [42,43]. Monometallic palladium catalysts supported in N-doped carbon nanotubes have been extensively studied over the past few years for electrochemical applications. Several works carried out in this area show that the use of N-doped carbon support strongly influences Pd distribution, which actively contributes to the good dispersion of the metal in the support [44–46]. From the accepted nitrate catalytic reduction mechanism, it is well known that a good metal dispersion is important to achieve an enhanced catalytic performance [47]. Pd centers are mainly responsible for NO_2^- reduction since it is reported that the catalytic activity of copper for this process is extremely low. Thus, the noble metal has increased importance in reaction selectivity since good metal dispersion promoted by the N-doped support could be a key step for the N_2 selectivity registered for the 1% Pd-1% Cu/CNT (BM 4h)-N catalyst.

It has been reported that Pd-Cu activity is higher when it is supported on carbon materials, instead of being supported on metal oxides such as TiO_2, Al_2O_3, SiO_2 and ZrO_2 [28]. However, in this study, one of the supports that presented the best performance for nitrate removal was TiO_2, reaching a nitrate conversion of 99% after 120 min of reaction. Selectivity to NO_2^- formation was very low, forming approximately 0.01 ppm, during almost all the reaction time, which constitutes a significant improvement when compared with the results obtained for CNT-based supports. Sá et al. [26] propose that the active sites of TiO_2 catalyst that are responsible for NO_3^- reduction are the same for NO_2^-, explaining the low concentration of this compound during the reaction time. However, this catalyst led to the formation of large concentrations of NH_4^+, around 6.7 mg/L, which corresponds to a selectivity of 76% after 300 min of reaction. Several studies have already reported this selectivity to NH_4^+ formation as the biggest disadvantage of using TiO_2 as support and it is attributed to the strong hydrogenation-promoting properties of $TiO_{2'}$ causing over-reduction [26,28,48].

Considering the results related to specific surface areas of the supports, displayed in Table 1, TiO_2 presents a relatively low surface area when compared with CNT samples (50 and 197 m^2/g, respectively). However, this support appears to be more promising due to the high availability

of active centers. This mechanism happens with NO_3^- adsorbed at the exposed Lewis acid sites (oxygen vacancies) of the support by electrostatic interaction. These electrons may be located on Ti^{3+} centers. This is the reason why the catalytic reduction of the nitrate process occurs so quickly since the material's surface is also available for NO_3^- anion adsorption, unlike what happens with carbon supports where the presence of a promoter metal is mandatory for nitrate adsorption [17]. Ammonia formation is favored due to the high reaction rate that occurs in the available adsorption spots.

Sá et al. [26] reported that a monometallic catalyst with palladium supported on titanium dioxide was active in the catalytic nitrate reduction. In the present work, in addition to palladium, active copper centers are also available for nitrate adsorption, which may assist the reaction rate.

Taking into account the efficient conversion results obtained with the TiO_2 support and the promising selectivities obtained with the catalysts supported in CNTs, composite materials were synthesized in order to take advantage of the favorable characteristics of both materials, considering, for this purpose, different proportions of the two materials [17,44]. The NO_3^- conversion results obtained for composite materials verify the potential of these materials with an almost complete conversion of nitrate present in solution after 180 min of reaction. CNTs and CNT (BM 2h) were both used in the synthesis of the composite materials (for a material proportion of 50:50) to ascertain whether the use of a milled material could benefit the catalytic activity of the composite (samples 1% Pd-1%Cu /TiO$_2$-CNT and 1% Pd-1% Cu/TiO$_2$-CNT (BM 2h)). The conversion results display a significant decrease in the reaction rate for the TiO$_2$-CNT (BM 2h) support. However, in terms of NO_3^- conversion and N_2 selectivity, these catalysts behave in a very similar way, as the milled catalyst only slightly contributes to increasing the selectivity for N_2.

Comparing the selectivity values obtained for the composite materials, it is possible to conclude that the use of these hybrid materials as supports leads to a significant improvement in ammonia selectivity when compared with the results obtained with the TiO_2 support. Moreover, N_2 selectivity increases for the supports that have a higher percentage of CNTs in their composition. Similar results were previously reported by Silva et al. [28]. However, regarding nitrate conversion values, in this work, the highest conversion values were obtained by the catalysts with a lower amount of carbon nanotubes in their constitution (20 and 50%). Our results show that the most efficient composite material for NO_3^- reduction into N_2 was 1%Pd- 1%Cu/CNT-TiO$_2$ (50:50).

Figure 4 presents the conversion values and respective selectivities, for each of the synthesized catalysts, for a reaction time of 60 min and 300 min. This picture allows a better comparison of the efficiencies obtained for all the catalysts since, generally, all of them proved to be very active for NO_3^- reduction, achieving conversions very close to 100% after 5 h of reaction.

The obtained results allowed us to attribute the best catalytic results (in terms of NO_3^- conversion) to the TiO_2 and TiO_2-CNT(50:50) supports. However, as already discussed, the N_2 selectivity was significantly compromised during the reaction, when these supports were used, and carbon nanotube-based supports showed better commitment in terms of NO_3^- conversion efficiency and N_2 selectivity. Generally, for all the tested supports, selectivity for NO_2^- formation, after 300 min, remaining in percentages below 1%.

3.2.2. Optimization of Metal Loadings

Although the support has a significant impact on the activity of the catalyst, namely in the selectivities, the metallic phase of the material is mainly responsible for all the reaction mechanisms, as the optimization of the catalyst with respect to the amounts of the metal phase is important. To optimize the synthesized catalysts, different metal loadings were tested to study their influence on catalytic activity and selectivity during nitrate reduction. Considering the previous studies performed with different support materials, to continue the study, the ones that revealed the best compromise between activity and selectivity were selected, considering, also, the methodology adopted for their synthesis. Thus, the supports selected were CNT (BM 2h), TiO$_2$ and TiO$_2$-CNT (50:50).

Figure 5 presents the nitrate concentration and respective evolution of NO_2^- and NH_4^+ concentrations during their reduction over the catalysts prepared. Figure 6 displays the corresponding selectivities after 60 and 300 min of reaction.
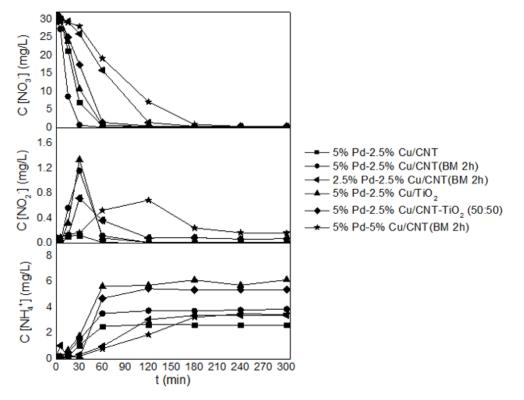

Figure 5. NO_3^-, NO_2^- and NH_4^+ concentrations as a function of time during nitrate reduction in the presence of catalysts with different metal loadings of Pd-Cu.
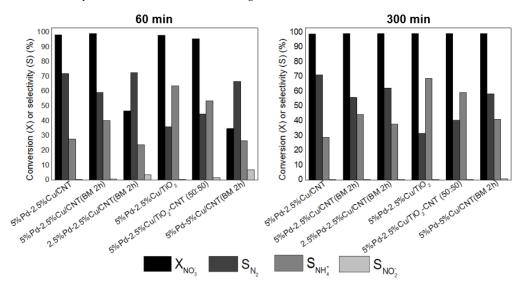

Figure 6. NO_3^- conversion and selectivities (in %) into N_2, NH_4^+ and NO_2 after 60 and 300 min of reaction.

Generally, through the results obtained for the catalysts with different metal loadings, it is possible to conclude that there is an optimal formulation of both metals, which allows for achieving high NO_3^- conversion. As described in several works, the catalytic properties of Pd-Cu are sensitive to the ratio of the two metals [10,32,49,50]. Both the nitrate removal activity and N_2 selectivity have a maximum at a specific Pd:Cu ratio that may change depending on the support used.

Concerning the combinations studied in this work and using CNT (BM 2h) material as the main support, the 5% Pd-2.5% Cu sample proved to be most efficient for NO_3^- conversion. This catalyst allowed full NO_3^- conversion after 60 min of reaction with N_2 selectivity of 60%. Additionally, the catalyst 2.5% Pd-2.5% Cu showed promising results regarding N_2 selectivity (62% at the end of the reaction time), but it presented a slower conversion rate when compared with 5% Pd-2.5% Cu. However, when metal loadings were increased to 5% of both metals (5% Pd-5% Cu/CNT (BM 2h) catalyst), the nitrate conversion rate strongly decreased, requiring 300 min of reaction time to perform complete NO_3^- removal efficiently.

As already reported in several works, the activity of the catalyst may be associated with the different locations of the active phases. The accepted reaction mechanism of nitrate reduction over bimetallic catalysts proposes that these are reduced into nitrite on Pd-Cu ensembles which, in turn, are converted in Pd centers [13]. Yoshinaga et al. [51] reported that not all palladium centers have the same reducing capacity, attributing a superior hydrogenation capacity to the Pd centers located in the edges and corners of the microcrystals of Pd which are more capable of converting NO_2^- into NH_4^+. Moreover, Pd centers located on the terraces of Pd microcrystals are more selective for N_2 formation. Generally, a higher content of Cu in the catalyst would enhance NO_3^- catalytic reduction. Nevertheless, increasing the copper content can lead to a possible deposition of Cu in the entire surface of Pd microcrystals, separating Pd active centers and consequently separating NO_2^- molecules adsorbed on the active centers leading, preferentially, to NH_4^+ formation due to the difficulty in recombining the N atoms to form N_2. Thus, for the specific case of the 5% Pd-5% Cu/CNT (BM 2h) catalyst, the low catalytic results obtained may be explained by an interference due to an excess of copper nanoparticles.

Al Bahri et al. [13] studied the influence of each metal content, for nitrate removal efficiency, using activated carbon as support. Their results showed that for a fixed copper amount of 2.5%, the palladium content that allowed the best results was 5% in terms of nitrate removal (around 90% after 8 h of reaction) and selectivity for N_2 formation [13].

In the present work, the most promising catalyst for NO_3^- conversion was 5% Pd-2.5% Cu/CNT (BM 2h), which achieved complete nitrate removal in 60 min of reaction. The ammonia produced stabilized around 3.8 mg/L, corresponding to a selectivity of 44%. The N_2 selectivity was 56%. The same proportion was applied in the unmodified support (sample 5% Pd-2.5% Cu/CNT) and a total NO_3^- conversion was achieved after 120 min of reaction with N_2 selectivity values of about 60%, which are very similar to the ones obtained with the milled support.

The most promising metal loading (5% Pd-2.5% Cu) was also studied for the TiO_2 and TiO_2-CNT (50:50) supports, considering the promising results obtained in the previous section. For 5% Pd-2.5% Cu/TiO_2, the total nitrate conversion was achieved after 120 min of reaction; however, obtained selectivity values were very unsatisfactory, presenting around 69% selectivity for NH_4^+ formation, corresponding to a concentration of about 6 mg/L. For the composite, maximum NO_3^- conversion was also achieved after 120 min of reaction with a corresponding NH_4^+ selectivity of 59 %. This ammonia concentration was lower when compared with the 5% Pd-2.5% Cu/TiO_2 catalyst; however, there is no significant advantage to applying this catalyst in NO_3^- catalytic reductions since CNT- and CNT (BM 2h)-supported catalysts achieved more interesting conversion and selectivity values.

The kinetic constants, for the conversion reactions carried out with 1% Pd-1% Cu/CNT, 5% Pd-2.5%Cu/CNT (BM 2h) and 2.5%Pd-2.5%Cu/CNT (BM 2h), were calculated. A first-order kinetic model was considered to fit the experimental data. Table 2 represents the kinetic constants obtained for each of the considered catalysts. As it is possible to see through the obtained values, the reaction rate for NO_3^- conversion using 5% Pd-2.5% Cu/CNT (BM 2h) is about 40 times greater than that recorded for 1% Pd-1% Cu/CNT. For 2.5% Pd-2.5% Cu/CNT (BM 2h), the increase in the reaction rate was smaller (about four times the value obtained for 1% Pd-1% Cu/CNT).

Table 2. Apparent first-order rate constant values for NO_3^- degradation for the selected catalysts.

Catalyst	$k \times 10^3$ (min^{-1})
1% Pd-1% Cu/CNT	2.2
5% Pd-2.5% Cu/CNT (BM 2h)	86.7
2.5% Pd-2.5% Cu/CNT (BM 2h)	8.6

3.2.3. Reutilization Experiments

Taking into account the obtained results, and having in mind the real application of the developed catalysts, 5% Pd-2.5% Cu/CNT (BM 2h) and 2.5% Pd-2.5% Cu/CNT (BM 2h) samples were selected to perform reutilization tests. These catalysts were chosen to carry out more exhaustive tests considering the conversion and N_2 selectivities achieved in the previous experiments.

Reutilization tests, shown in Figure 7, allowed us to conclude that both catalysts were stable and active during five reuses, without compromising the total NO_3^- conversion. However, the selectivity of the process in the presence of both catalysts experienced a major change with the successive runs, as NH_4^+ selectivity values gradually increase with the successive reuses. After five cycles, NH_4^+ concentration in solution was approximately 6 mg/L, with corresponding NH_4^+ selectivity values of 68% for 2.5% Pd-2.5% Cu/CNT (BM 2h) and 71% for 5% Pd-2.5% Cu/CNT (BM 2h).

Figure 7. NO_3^- conversion and corresponding N_2, NO_2^- and NH_4^+ selectivities after 60 and 300 min of reaction time regarding reutilization experiments performed using 2.5% Pd-2.5% Cu/CNT (BM 2h) and 5% Pd-2.5% Cu/CNT (BM 2h) catalysts.

Analysis of metal content in treated solutions, in the presence of tested catalysts, was performed to evaluate the catalyst leaching and, in this way, verify the physical stability of the bimetallic catalysts. These experiments were performed for the after-reaction solutions for each of the studied catalysts, as well as for the solutions obtained after catalyst reuse experiments. The results obtained can be consulted in the Supplementary Information (Figures S3 and S4).

Generally, the catalysts were revealed to be rather stable during reaction since no significant leaching was measured for either metal in the treated solution. The percentages of leached metal were below 1% for most of the catalysts, which represented concentrations of leached metal below the legal limits allowed in drinking water. However, the obtained results allowed us to conclude that catalysts supported on TiO_2 and composite materials presented higher leaching of the metallic phase in the treated solution when compared with the catalysts supported in CNTs. In the case of composite material supports, higher concentrations of leached metal were recorded when a higher amount of TiO_2 is present. Soares et al. [17] reported in a previous study that Pd-Cu was less stable when supported on metal oxides, such as CeO_2, Ce-O and Al_2O_3, during nitrate reduction. However, TiO_2 and TiO_2-CNT supports did not present a significant metal dissolution after reaction. Additionally, the concentration of Cu leached after reaction depends, not only on the support used, but also on the proportion of the two metals present in the catalyst. The materials that presented the highest concentrations of Cu leached after reaction corresponds to the catalysts with different metal proportions, the 5% Pd-2.5% Cu/CNT (BM 2h), 5% Pd-2.5% Cu/TiO_2 and 5% Pd-2.5% Cu/TiO_2-CNT (50:50) samples. Maximum leaching percentage was achieved for the 5%Pd-2.5%Cu/TiO_2 catalyst (2.1%).

The results regarding metal leaching during cycle experiments show that there is a continuous metal leaching during catalyst reuse but at very low concentrations. The leaching of the metallic phase during the cycle experiments could be related to the results presented in Figure 7 regarding the selectivity values for N_2 and NH_4^+. The obtained results suggest that the catalyst may suffer some modifications, after the reaction, due to the leaching of the metallic phase, although in low concentrations, which can lead to modifications in the configuration of the mono- and/or bimetallic centers of the material that are closely related to the conversion and selectivity values. For both tested catalysts, the maximum concentration of leached metal was registered for the 5% Pd-2.5% Cu/CNT (BM 2h) catalyst, and it was 0.06 mg of Pd/L.

TEM analyses were performed for the after-reaction catalysts (catalysts collected after five uses) in order to ascertain if it would be possible to see any structural modification of the catalysts (Figure 8), but it is not possible to conclude whether the metallic phase of the catalysts suffers any modification. The average metal particle size obtained for the after-reaction catalysts are very similar to what has been registered for the fresh catalysts, being another factor that proves the good stability of the catalysts since it does not suffer major changes during reaction.
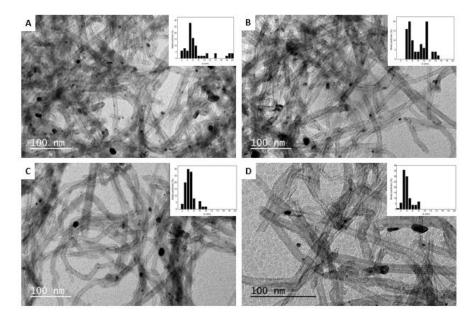

Figure 8. TEM micrographs for the most efficient catalysts before and after reaction: (**A**) 5% Pd-2.5% Cu/CNT (BM 2h)_fresh, (**B**) 5% Pd-2.5% Cu/CNT (BM 2h)_after reaction, (**C**) 2.5% Pd-2.5% Cu/CNT (BM 2h)_fresh and (**D**) 2.5% Pd-2.5% Cu/CNT (BM 2h)_after reaction.

4. Conclusions

Bimetallic catalysts, consisting in Pd-Cu ensembles, synthesized on different supports and with different metal loadings, were studied during NO_3^- catalytic reductions of a simulated ion solution. The results allowed us to conclude that the support plays a key role in the reaction rate and selectivity of the process. Chemical and textural modifications performed on commercial carbon nanotubes allowed us to achieve interesting NO_3^- conversion values and N_2 selectivity. For a metal loading of 1% Pd and 1% Cu, the samples TiO_2, CNT (BM 2h) and TiO_2-CNT (50:50) proved to be the most active supports for NO_3^- conversion. However, in terms of the selectivity of the process, TiO_2 and TiO_2-CNT (50:50) supports lead to the formation of higher concentrations of NH_4^+, while the CNT (BM 2h) sample achieved N_2 selectivity of around 60% after 300 min of reaction. The milling of CNTs proved to be a key step to obtain more active catalysts for NO_3^- without compromising their N_2 selectivity.

For the most efficient supports, different metal loadings were studied and the combinations of 2.5% Pd-2.5% Cu and 5% Pd-2.5% Cu showed the most promising results regarding selectivity to N_2 formation and NO_3^- conversion, respectively. The reutilization tests showed that the structure of the catalyst might be slightly compromised over several uses, leading to significant differences regarding the obtained catalyst selectivities, but the catalysts remained very active in terms of NO_3^- conversion, allowing complete NO_3^- conversions even after several reutilizations.

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