Nitrate removal by catalytic reduction with hydrogen

(Remoção de nitratos em águas por redução catalítica com hidrogénio)

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Preface

This PhD thesis was carried out at Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE/LCM, at the Department of Chemical Engineering, Faculty of Engineering of the University of Porto.

The thesis is divided in 10 chapters. Chapters 1 and 10 correspond to the introduction and main conclusions and suggestions for future work, respectively. The main core of the text (Chapters 2 to 9) is based on 8 scientific papers, 5 of which already published (August 2010) in refereed Journals, whereas the others are under review (1) or in the last phase of preparation to be submitted for publication (2).

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Chapter 2

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Chapter 9

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Abstract

The presence of nitrate in water is presently a common problem across Europe. The catalytic reduction of nitrate has been suggested in the literature as a promising method for its elimination, without the drawbacks of the conventional technologies. This process consists in the reduction of nitrate to nitrogen over bimetallic catalysts in the presence of a reducing agent. The main objective of this work was the study of the catalytic reduction of nitrate in water with hydrogen in a systematic way, evaluating several metal catalysts and their composition, preparation conditions and supports, focusing on the use of activated carbon as support, and clarifying some mechanistic aspects.

The first goal of this thesis was the evaluation of monometallic and bimetallic catalysts supported on activated carbon for nitrate and nitrite reduction, in order to select the most promising catalytic systems for further developments. It was observed that the monometallic catalysts supported on activated carbon were inactive or practically inactive for nitrate reduction but that they were active for nitrite reduction. The pairs Pd-Cu, Pt-Cu, Rh-Cu and Ir-Cu supported on activated carbon were studied in detail in order to establish their best formulation. It was shown that the efficiency of the catalysts is quite different depending on the copper content. The maximum activity was obtained for an atomic ratio noble metal/copper close to 1, which is indicative that the same amount of noble metal and promoter atoms is the best formulation to obtain a very active catalyst for this reaction. The selectivity to nitrogen increases with the atomic copper content up to 75%.

In addition to the type of supported metals, the reduction of nitrate is quite dependent on the preparation conditions (calcination and reduction temperatures). For the Pd-Cu and Pt-Cu bimetallic catalysts, it was observed that the activity decreases with the increase of calcination and reduction temperatures, whereas the effect on the selectivity is not uniform. The formation of alloys during the preparation of the catalysts is prejudicial for catalysts performance. The calcination at 200 ºC and reduction at 100 ºC seem to be the optimal temperatures to prepare the catalysts supported on activated carbon, when both activity and nitrogen selectivity are considered.

Physical mixtures of Pd and Cu or Pt and Cu monometallic catalysts perform similarly or even better than the corresponding bimetallic catalysts. This fact indicates that the initial presence of bimetallic sites on the catalysts for the reduction of nitrate is not mandatory; it is sufficient that both metals are present in the reaction

system. Nevertheless, the noble metal must be already supported and copper does not need to be in the metallic form. Based on these observations, a reaction mechanism considering that the nitrate reduction can occur in the presence of a bimetallic catalyst or a physical mixture of monometallic catalysts was proposed.

The surface chemistry of the support plays an important role in the catalyst activity and selectivity, being its influence more pronounced when Pt-Cu catalysts are used. Comparing the different carbon supports tested, basic samples and carbon nanotubes were the best, whereas carbon xerogels were the worst supports for this reaction.

Carbon nanotubes demonstrate to be a good support for this reaction. The results obtained show that the reduction of nitrate is quite different depending on the noble metal, the preparation conditions and the support used, as observed when activated carbon is used as support.

Several metals oxides, as well as metal oxides and activated carbon or carbon nanotubes composites, were also assessed as supports for nitrate reduction. It was observed that the support has an important effect on the catalytic performance and in some cases (ceria and titania) is involved in the reaction mechanism. Nevertheless, the supports are not active; the presence of one or two metals is mandatory to reduce nitrate. The results obtained show that titanium dioxide provides high activity for nitrate reduction and that the use of a composite with carbon nanotubes increases significantly the selectivity of the process to nitrogen. The catalysts supported on ceria are very selective to nitrogen and present the particularity of the monometallic to be more active than the bimetallic. Manganese oxides are not suitable supports for this reaction.

For all the preparation conditions tested, the Pd-Cu pair is the most selective in the transformation of nitrate into nitrogen. Selectivities to nitrogen as high as 82% and 76% were obtained with the 1%Pd-1%Cu bimetallic catalyst supported on carbon nanotubes and activated carbon, respectively. In some experiments, nitrate conversions near 100% were obtained, but in these cases the allowable ammonium values in drinking water were always exceeded.

Resumo

A presença de nitrato em água é actualmente um problema comum a toda a Europa. A redução catalítica de nitrato tem sido sugerida na literatura como um método promissor para a sua eliminação, sem os inconvenientes das tecnologias convencionais. Este processo consiste na redução de nitrato a azoto na presença de catalisadores bimetálicos e de um agente redutor. O principal objectivo deste trabalho foi estudar de uma forma sistemática a redução catalítica de nitrato em água com hidrogénio, avaliando-se vários catalisadores metálicos, nomeadamente a sua composição e condições de preparação e vários suportes, dando especial atenção ao uso de carvão activado como suporte, e esclarecer alguns aspectos do mecanismo da reacção.

O primeiro objectivo da tese foi avaliar catalisadores mono e bimetálicos suportados em carvão activado na redução de nitrato e nitrito, no sentido de seleccionar os sistemas catalíticos mais promissores. Observou-se que os catalisadores monometálicos suportados em carvão activado eram inactivos ou praticamente inactivos para a redução de nitrato, mas que eram activos para a redução de nitrito. Estudou-se em detalhe os pares Pd-Cu, Pt-Cu, Rh-Cu e Ir-Cu suportados em carvão activado com o objectivo de optimizar a sua formulação. Demonstrou-se que a eficiência dos catalisadores é bastante diferente, dependendo do teor de cobre. A actividade máxima foi obtida para a razão atómica metal nobre/cobre próxima de 1, indicando que a mesma quantidade atómica de metal nobre e de promotor é a melhor composição para obter um catalisador muito activo para esta reacção. A selectividade em azoto aumenta com o teor atómico de cobre até 75%.

Mostrou-se que, além do tipo de metais suportados, a redução do nitrato é bastante dependente das condições de preparação (temperaturas de calcinação e redução). Para os catalisadores bimetálicos Pd-Cu e Pt-Cu, observou-se que a actividade diminui com o aumento das temperaturas de calcinação e redução, mas que o efeito na selectividade não era uniforme. A formação de ligas durante a preparação dos catalisadores é prejudicial para o seu desempenho. Considerando a actividade e a selectividade em azoto, a calcinação a 200 ºC e redução a 100 ºC parecem ser as temperaturas óptimas para preparar os catalisadores suportados em carvão activado.

Verificou-se que misturas físicas de catalisadores monometálicos de Pd e Cu ou Pt e Cu apresentam um desempenho semelhante ou até melhor do que os

correspondentes catalisadores bimetálicos. Este facto indica que a presença inicial de sítios bimetálicos nos catalisadores não é obrigatória para a redução de nitrato, sendo suficiente que os metais estejam presentes no sistema reaccional. No entanto, o metal nobre tem de estar já suportado e o cobre não precisa estar na forma metálica. Com base nestas observações, foi proposto um mecanismo reaccional considerando que a redução de nitrato pode ocorrer na presença de um catalisador bimetálico ou de uma mistura física de catalisadores monometálicos.

Observou-se que a química superficial do suporte tem um papel importante na actividade catalítica e na selectividade, sendo a sua influência mais pronunciada quando são usados catalisadores de Pt-Cu. Comparando os diferentes suportes de carbono testados, concluiu-se que as amostras básicas e os nanotubos de carbono foram os melhores, enquanto que os xerogéis de carbono foram os piores suportes para esta reacção.

Os nanotubos de carbono demonstraram ser um bom suporte para esta reacção. Tal como observado quando o carvão activado foi usado como suporte, os resultados obtidos demonstraram que a redução do nitrato é bastante diferente, dependendo do metal nobre, das condições de preparação e do suporte utilizado.

Também foram avaliados como suporte para a redução de nitrato vários óxidos de metais, assim como óxidos de metais e compósitos de carvão activado ou de nanotubos de carbono. Observou-se que o suporte tem um papel importante no desempenho catalítico e que em alguns casos (cério e titânio) está envolvido no mecanismo reaccional. No entanto, os suportes sozinhos não são activos, a presença de um ou dois metais é obrigatória para a redução de nitrato. Os resultados obtidos mostraram que o dióxido de titânio é muito activo para redução de nitrato e que a utilização de um compósito com nanotubos de carbono aumenta significativamente a selectividade em azoto do processo. Os catalisadores suportados em cério são muito selectivos em azoto e apresentam a particularidade de o catalisador monometálico ser mais activo do que o bimetálico. Os óxidos de manganês não são suportes adequados para esta reacção.

O par Pd-Cu foi o catalisador mais selectivo na transformação de nitrato em azoto para todas as condições de preparação estudadas. Com o catalisador bimetálico 1%Pd-1%Cu suportado em nanotubos de carbono e carvão activado obtiveram-se selectividades em azoto de 82% e 76%, respectivamente. Obtiveram-se conversões em nitrato de 100% em alguns ensaios mas, nestes casos, o valor de amónia admissível em água para consumo humano foi sempre ultrapassado.

Résumé

La présence de nitrate dans l'eau est actuellement un problème commun à toute l'Europe. La réduction catalytique du nitrate a été décrite dans la littérature comme étant une méthode prometteuse pour leur élimination, sans présenter les inconvénients des technologies conventionnelles. Ce processus consiste en la réduction du nitrate en azote à travers de catalyseurs bimétalliques en présence d'un agent réducteur. L´objectif principal de ce travail était l'étude de la réduction catalytique du nitrate dans l'eau avec de l'hydrogène, évaluant plusieurs catalyseurs métalliques, nutament leur composition et conditions de préparation et les supports, en se concentrant sur l'utilisation de charbon actif comme support, et clarifier certains aspects de mécanisme.

Le premier objectif de cette thèse était l'évaluation de catalyseurs monométalliques et bimétalliques supporté sur charbon actif pour la réduction du nitrate et du nitrite, afin de choisir les systèmes les plus prometteurs de catalyseur pour de futurs développements.

Il a été observé que les catalyseurs monométalliques supporté sur charbon actif étaient inactifs ou quasi inactifs pour la réduction du nitrate, mais qu'ils étaient actifs pour la réduction du nitrite. Les paires Pd-Cu, Pt-Cu, Rh-Cu et Ir-Cu supporté sur charbon actif ont été étudiés en détail afin d'établir leur meilleure formulation. Il a été montré que l'efficacité des catalyseurs est très différente selon le taux de cuivre. L'activité maximale a été obtenue pour un rapport atomique métal noble/cuivre près de 1, ce qui indique que la même quantité d´atomes de métal noble et de promoteur est la meilleure formulation pour obtenir un catalyseur très actif pour cette réaction. La sélectivité à l'azote augmente avec la teneur en cuivre atomique jusqu'à 75%.

En plus du type de métal supporté, la réduction du nitrate est très dépendante des conditions de préparation (températures de calcination et de réduction). Pour les catalyseurs bimétalliques Pd-Cu et Pt-Cu, il a été constaté que l'activité diminue avec l'augmentation des températures de calcination et de réduction, cependant l'effet sur la sélectivité n'est pas uniforme. La formation d'alliages lors de la préparation des catalyseurs est préjudiciable aux performances des catalyseurs. La calcination à 200 ºC et la réduction à 100 ºC semblent être les températures optimales de préparation des catalyseurs supportés sur charbon actif, quand l'activité et la sélectivité d'azote sont considérées.

Les mélanges physiques de catalyseurs monométalliques de Pd et Cu ou Pt et Cu fonctionnent de manière semblable ou même mieux que les catalyseurs bimétalliques correspondants.

Cela indique que la présence initiale de sites bimétalliques sur les catalyseurs n'est pas obligatoire pour la réduction du nitrate; il suffit que les deux métaux soient présents dans le système réactionnel. Néanmoins, le métal noble doit déjà être supporté et le cuivre n'a pas besoin d'être sous forme métallique. Compte tenu de ces observations, un mécanisme de réaction a été proposé prenant en compte le fait que la réduction du nitrate peut se produire en présence d'un catalyseur bimétallique ou d'un mélange physique de catalyseurs monométalliques.

La chimie de surface du support a un rôle important dans l'activité du catalyseur et la sélectivité, étant son influence plus prononcée lorsque les catalyseurs Pt-Cu sont utilisés. Comparant les différents supports de carbone testés, les échantillons basiques et les nanotubes de carbone ont conduit aux meilleurs résultats, alors que les xérogels de carbone furent les pires supports pour cette réaction.

Les nanotubes de carbone ont démontré être un bon support pour cette réaction. Les résultats obtenus montent que la réduction du nitrate est très différente selon les métaux nobles, les conditions de préparations et le support utilisé tout comme il a été observé pour le charbon actif.

Plusieurs oxydes de métaux, ainsi que des oxydes métalliques et des composites comprenant du charbon actif ou des nanotubes de carbone, ont également été évaluées comme supports pour la réduction du nitrate. Il a été observé que le support joue un rôle important dans la performance catalytique et dans certains cas (oxyde de cérium et de titane) est impliquée dans le mécanisme réactionnel. Néanmoins, les supports ne sont pas actifs; la présence d'un ou de deux métaux est obligatoire afin de réduire le nitrate. Les résultats obtenus montrent que le dioxyde de titane permet d'obtenir une haute activité pour la réduction du nitrate et que l'utilisation d'un composite comprenant des nanotubes de carbone augmente de manière significative la sélectivité du processus à l'azote. Les catalyseurs supportés sur cérine sont très sélectifs à l'azote et présentent une particularité: le catalyseur monométallique est plus actif que le bimétallique. Les oxydes de manganèse ne sont pas de bons supports pour cette réaction.

Parmis toutes les conditions de préparation testées, la paire Pd-Cu est la plus sélective dans la transformation de nitrate en azote. Des sélectivités en azote de 82% et 76% ont été obtenus avec le catalyseur bimétallique 1%Pd-1%Cu supporté sur les nanotubes de carbone et sur le charbon actif, respectivement. Dans certaines expériences, des conversions du nitrate de près de 100% ont été obtenus, mais dans ces cas, les valeurs admissibles d'ammonium dans l'eau potable ont toujours été dépassées.

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Chapter I

1 Introduction

The first chapter of this thesis presents general considerations about water quality, focusing on the presence of nitrate. The impact in human health and environment is described. A summary of the existing legislation related to nitrate in Europe was included. An overview of the presence of nitrate in groundwater during the 2004-2007 period is provided. A short description of the available technologies for the removal of nitrate in water is presented, focusing on catalytic reduction. The possible nitrate reduction mechanisms, the type of catalysts used and factors that influence the process are reviewed. The role of the support on the process is emphasized, given special attention to the case of activated carbon. An overview of the results reported in the literature is also provided. Finally, the main objectives of this work and the thesis outline are presented.

1.1 Water: General considerations

Water is essential to sustain life, and a satisfactory (adequate, safe and accessible) supply must be available to all. Improving access to safe drinking-water can result in tangible benefits to health. Every effort should be made to achieve a drinking-water quality as safe as practicable [1].

Water is the most spread substance in the natural environment. Water exists in three states: liquid, solid and vapour. It forms oceans, seas, lakes, rivers and groundwater in the top layers of Earth's crust and soil cover. It is estimated that the Earth's hydrosphere contains a huge amount of water of about 1386 million cubic kilometres. However, 97.5% of this amount is saline water and only 2.5% is fresh water. The greater portion of the fresh water (68.7%) is in the form of ice and permanent snow cover in the Antarctic, the Arctic and mountainous regions. Next 30.1% are fresh groundwater. Only 0.26% of the total amount of freshwaters on the Earth is concentrated in lakes, reservoirs and river systems (Figure 1.1) [2].

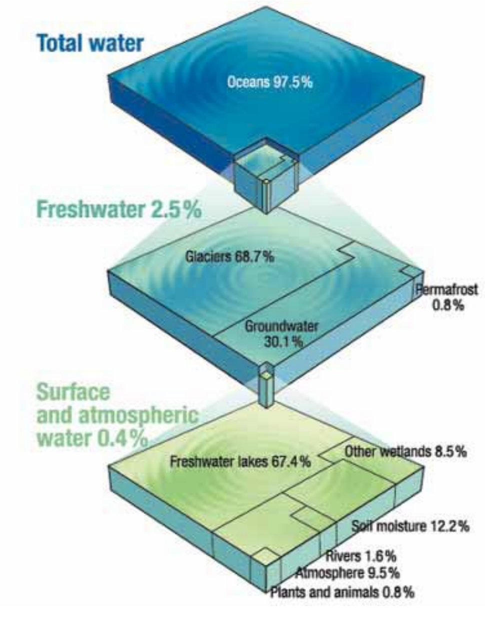

Figure 1.1 Global distribution of the world's water [2].

Until recently, focus on groundwater mainly concerned its use as drinking water. Nevertheless, groundwater is also an important resource for industry (e.g. cooling waters) and agriculture (irrigation) [3]. As can be seen in Figure 1.2, agriculture is the highest consumer of water (70%), followed by industry (20%) and domestic

(10%) [4]. Therefore, it has become increasingly obvious that groundwater should not only be viewed as a drinking water reservoir, but also protected for its environmental value. Since groundwater moves slowly through the subsurface, the impact of anthropogenic activities may last for a relatively long time, which means that pollution that occurred some decades ago (whether from agriculture, industry or other human activities) may still be threatening groundwater quality today and, in some cases, will continue to do so for several generations to come [3].

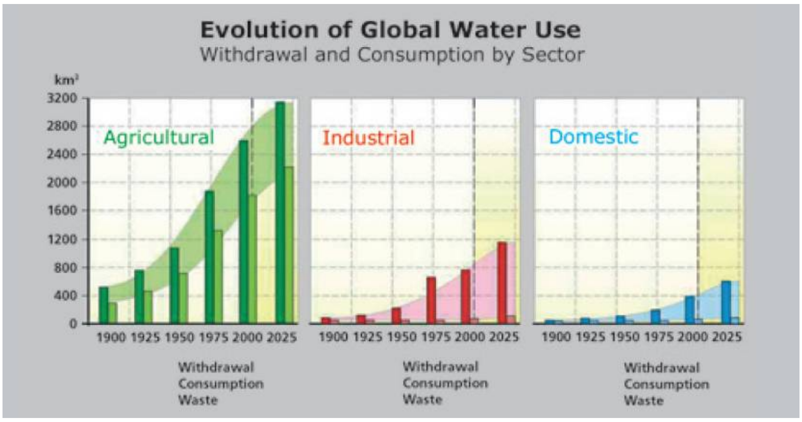

Figure 1.2 Groundwater utilization by sector [4].

Despite the progress in some fields, recent reports show that pollution from domestic, agricultural and industrial sources is still a major concern, either directly through discharges (effluents) or indirectly from the spreading of nitrogen fertilisers and pesticides or through leaching from old landfills or industrial sites (e.g. chlorinated hydrocarbons, heavy metals). For example, around one third of groundwater bodies in Europe currently exceed the nitrate guideline values [3].

Large inputs of nitrogen and phosphorus to water bodies (including rivers) can lead to eutrophication causing ecological changes. These result in a loss of plant and animal species and have negative impacts on the use of water for human consumption and other purposes. Eutrophication contributes to a number of water quality problems such as phytoplankton blooms, reduced recreational aesthetics, oxygen depletion, reduced transparency and fish kills. Some algal blooms produce toxins and also tastes and odours that threatens the use of this resource for human consumption in many places across Europe [5]. Figure 1.3 illustrates the many sources of pollution of the aquatic environment with nitrogen.

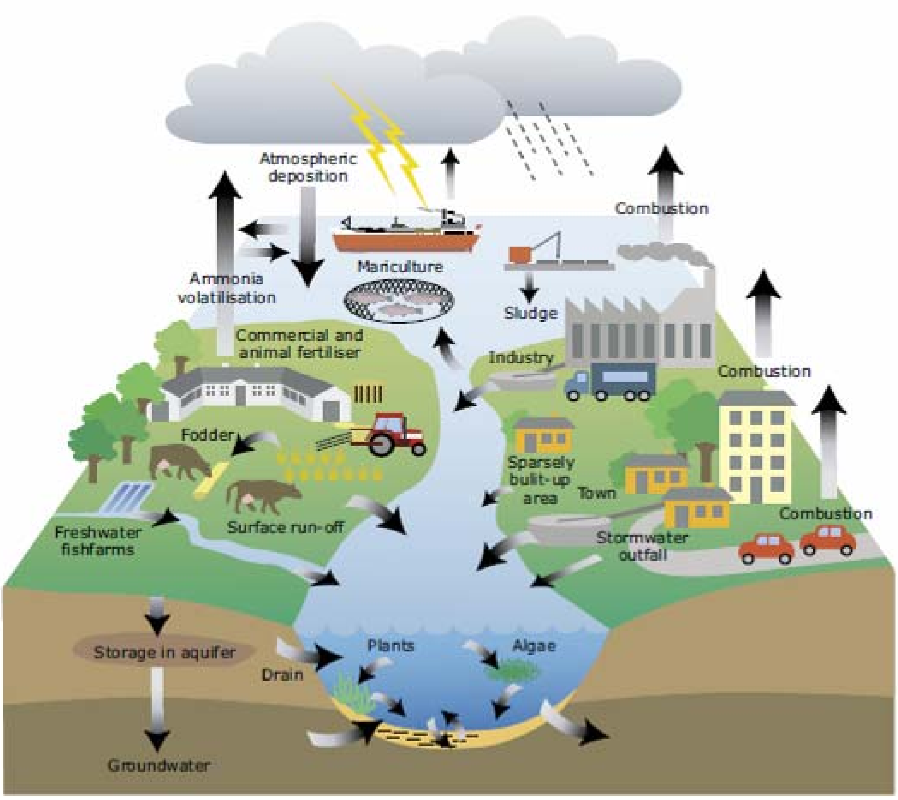

Figure 1.3 Sources of pollution of the aquatic environment with nitrogen [5].

1.2 Nitrate in drinking water

Nitrate may be occurring naturally, although its presence in drinking-water is frequently associated with contamination by excessive use of fertilizers, in combination with inappropriate farming practices and/or sewage disposal [1]. The use of nitrates in organic and chemical fertilisers in agriculture has been a major source of water pollution in Europe. Nitrate is highly soluble and the excess easily passes into the soil and into groundwater as well as being carried directly to surface waters in run-off and field drains [6]. As a result, levels of nitrate in many groundwater bodies and rivers throughout Europe have increased over the last 50 years. This affects the ecological quality of freshwater and coastal habitats, which has secondary effects on the recreational value and rural economy of the affected areas. Nitrate has now become a widespread contaminant in groundwater and surface water in many parts of Europe.

Nitrate is not directly toxic to humans, but in oxygen-free condition such as in the human gut it converts to nitrite. Nitrite can pass from the gut into the blood stream and bond to haemoglobin molecules - converting them to a form that cannot transport oxygen. In rare cases this has been found to cause a condition commonly known as “blue baby syndrome”. In addition, it is a precursor of the carcinogenic nitrosamines. Nitrate is a major problem for bottle-fed infants, in which the risk of methaemoglobinaemia (“blue-baby syndrome”) increases as the concentration of nitrate rises above 50 mg/L. The risk is increased by the presence of nitrite, which is a much more potent methaemoglobinaemic agent than nitrate. Nitrite has a similar action to nitrate, but is usually only found at very low concentrations [1]. For this reason quality standards have been set in Europe to safeguard the drinking water.

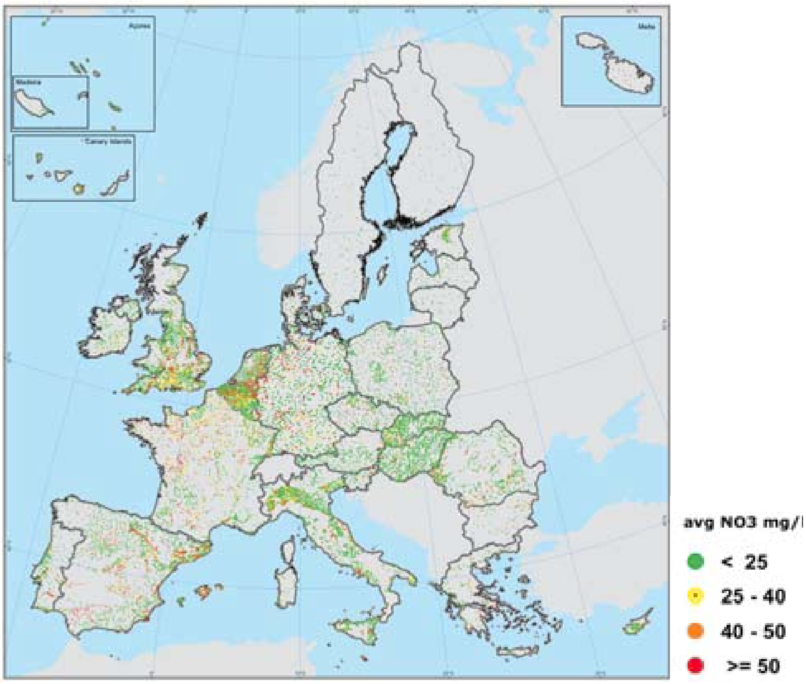

Figure 1.4 Average nitrate concentrations in groundwater (adapted from [7]).

Figure 1.4 shows the average nitrate concentrations in groundwater in Europe in the period 2004-2007. A recent report [8] shows the average nitrate concentrations in groundwater (Table 1.1) and surface water (Table 1.2) in the monitoring stations in EU 27 or EU 15 in this period.

Table 1.1 Nitrate concentration in groundwater [8].

	% of monitoring stations with average nitrate concentration in groundwater (mgNO$_3^-$/L)			
	< 25	25 - 40	40 - 50	> 50
EU 27	66%	13%	6%	15%
EU 15	62%	15%	6%	17%

Table 1.2 Nitrate concentration in surface water [8].

	% of monitoring stations with average nitrate concentration in surface water (mgNO$_3^-$/L)				
	< 2	2 - 10	10 - 40	40 - 50	> 50
EU27	21%	37%	36%	3%	3%
EU15	24%	30%	38%	4%	4%

1.3 Drinking water standards in Europe

Pure and clean water is vital to human health and well-being, as well as to natural ecosystems, so safeguarding water quality is one of the cornerstones of European environmental policy. An EU-wide approach is crucial to tackling problems of pollution, because water sources are not restricted within national boundaries. The Nitrates Directive (Council directive 91/676/EEC) is one of the earliest pieces of EU legislation aimed at controlling pollution and improving water quality [9].

The Nitrates Directive aims to control nitrogen pollution and requires Member States to identify groundwater that contain more than 50 mg/L nitrate or could contain more than 50 mg/L nitrate if preventative measures are not taken. In addition, the Drinking Water Directive (Directive 98/83/EC) sets the maximum allowable concentration for nitrate of 50 mg/L. It has been shown that drinking water in excess of the nitrate limit can result in adverse health effects, especially in infants less than two months of age. Groundwater is a very important source of drinking water in many countries and it is often used untreated, particularly from private wells. The Nitrates Directive sets a limit for the amount of livestock manure applied to land each year, including by the animals themselves, of 170 kg N per hectare.

The Nitrates Directive forms part of a comprehensive framework of EU legislation to protect the environment. The Nitrates Directive has close links with other EU policies concerning water, air, climate change and agriculture, and its implementation yields benefits in all these areas [7]:

- Reducing nitrates is an integral part of the EU Water Framework Directive (Directive 2000/60/EC) [10], which establishes a comprehensive, cross-border approach to water protection organised around river basin districts, with the aim of achieving good status for European bodies of water by 2015.

- The new Groundwater Directive (Directive 2006/118/EC) [11] confirms that nitrate concentrations must not exceed the trigger value of 50 mg/L.

- Air and soil quality: livestock management and farming cause, among other things, emissions of ammonia (NH_3), which have an impact on human health and on the environment, as they contribute to the acidification process in soil, eutrophication of water and ground-level ozone pollution, together with other pollutants (sulphur dioxide, nitrogen oxides, volatile organic compounds). The full implementation of the Nitrates Directive is expected to contribute to the reduction of ammonia emissions by 14% on 2000 levels by 2020, as measures limiting for example the amounts of fertiliser applied, have a positive impact on both nitrate losses towards water and ammonia emissions into the air [9].

- Climate change: All activities related to livestock and fertiliser management release nitrous oxide (N_2O) and methane (CH_4), greenhouse gasses with a global warming potential 310 and 21 times higher than CO_2, respectively. If fully implemented, the Nitrates Directive could cut for example N_2O emissions by 6% on 2000 levels by 2020 and contribute to climate change mitigation [9].

- The common agricultural policy (CAP) backs up the Nitrates Directive through direct support and rural development measures [9].

- The Urban Wastewater Directive (Council Directive 91/271/EEC) [12] sets standards for the collection and treatment of wastewater from homes and some industrial sectors.

1.4 Technologies to remove nitrate from water

The chemicals of greatest health concern in some natural waters are usually nitrate/nitrite, fluoride and arsenic. The removal of nitrate from drinking water is necessary in order to protect the environment and the human health. Their removal technologies are usually more complex and more expensive than those required for microbial control [1]. Nevertheless, the increasing pollution of natural sources of drinking water encourages the development of new emerging technologies and processes for water remediation.

Nitrate is a stable and highly soluble ion with low potential for co-precipitation or adsorption. These properties make it difficult to remove using conventional water treatment technologies [13]. Nitrate can be removed from water by physicochemical, biological and catalytic methods. The main disadvantage of the physicochemical treatments (ion exchange, reverse osmosis and electrodialysis) is the fact that nitrate is not converted into harmless compounds but only concentrated; then it must be treated afterwards or disposed of [13,14]. Among these methods, the capital and operating costs are the lowest for the ion-exchange process; nevertheless, it is very difficult and costly to dispose of large quantities of spent regenerant brine in noncoastal locations where natural evaporation is impossible. The most promising techniques for nitrate removal, without any occurrence of wastewater, are biological denitrification and catalytic denitrification by using noble metal catalysts. The biological denitrification process (either heterotrophic or autotrophic) is recognized as an useful method for the selective conversion of nitrate into harmless gaseous nitrogen for the treatment of municipal and industrial wastewater streams. However, this process has several disadvantages since it is difficult to handle and leads to the production of undesirable by-products [13]. The main reasons for the slow transfer of technology to drinking water treatment are concerns about possible bacterial contamination, the presence of residual organics in treated water and the possible increase in chlorine demand of purified water [13,14]. The reduction of nitrate by using hydrogen over a solid catalyst offers an alternative and economically advantageous process to biological treatment as a means of purifying drinking water streams. The main drawback of this process is the formation of ammonia as by-product, which is undesirable in drinking water [13,14].

An overview of the advantages and comparative characteristics of the technologies for water remediation after nitrate contamination is reported in Table 1.3.

Table 1.3 Comparison of the characteristics of technologies for water remediation after nitrate contamination [15].

	Technology			
Characteristic	**Ion exchange**	**Reverse osmosis**	**Biological denitrification**	**Catalytic reduction**
Fate of nitrate	Adsorbed and concentrated	Concentrated in a waste stream	Transformed to N_2	Transformed to N_2
Waste	Waste brine	Waste brine	Bacteria sludge	None
Chemical additives	Sodium chloride	Sulphuric acid and base	Ethanol and phosphoric acid	H_2
Percentage of efficiency in water purification	85–98%	75–80%	98%	98–100%
Flexibility in variable operations	Medium	Medium	Low	High
Energy use	Low	High	Medium	Low
Space requirements	Limited	Limited	High	Low
Movable	Yes	Yes	No	Yes
Manageability	Good	Good	Poor	Good
Type of operations	Periodic regeneration	Continuous	Continuous	Continuous
Sensitivity to deactivation	Medium	High	High	Medium
Automatic control	Simple	Simple	Complex	Simple
Start up time	Immediate	Immediate	Up to 1 month	Immediate
Monitoring required	Little	Little	Intensive	Medium
Selectivity of the process	Low	Low	High	High
Odors	No	No	Yes	No
Noise	Some	High	None	None
Indicative cost[a] (€/m^3)	0.15–0.25	0.4–0.6	0.2–0.3	0.25–0.55
Sensitivity of costs to scale-down	Medium	High	High	Low
Multipurpose use[b]	None	Depending on molecular size	Some[c]	Highly effective

[a] Estimated costs for a 1000 m^3/d process.

[b] Removal of pesticides and other halogenated compounds.

[c] Sensitivity to pesticides.

1.5 Catalytic reduction of nitrate

In 1989, Vorlop and Tacke [16] reported for the first time that nitrate could be reduced to nitrogen over bimetallic catalysts in the presence of a reducing agent. Nitrate reduction can be described by consecutive and parallel reactions where nitrate is reduced to nitrite, which is converted to nitrogen as main product and ammonium as undesired by-product, as illustrated in Figure 1.5 [17,18].

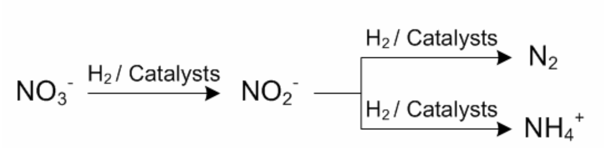

Figure 1.5 Scheme of nitrate reduction.

This reaction is a complex multistage process, once consists in consecutive and parallel reactions, in which the stable intermediates and products that take part or are supposed to take part are summarized in Table1.4 [19].

Table1.4 Nitrogen compounds involved in catalytic nitrate reduction [19].

Oxidation number	Formula	Name	Remarks
+5	NO_3^-	Nitrate	Substrate
+4	NO_2	Nitrogen dioxide	Possible intermediate
+3	NO_2^-	Nitrite	Known intermediate
+2	NO	Nitric oxide	Probable intermediate
+1	N_2O	Nitrous oxide	Known intermediate
0	N_2	Nitrogen	Known product
-1	NH_2OH	Hydroxylamine	Product at pH < 4
-2	N_2H_4	Hydrazine	No information
-3	NH_3/NH_4^+	Ammonia/Ammonium	Known product

To maintain the electroneutrality of the aqueous phase, consumed nitrates are replaced by hydroxide ions. Therefore, the catalytic activity and selectivity strongly depend on the pH value. In addition, the reduction of nitrate increases pH values up to 10, which is unacceptable for drinking water [20]. An efficient pH control is need during the reaction, as ammonium formation is strongly favoured under basic conditions [18,21]. The use of CO_2 in the gas feed allows to reduce the ammonia formation [22]. CO_2 is an ideal solution, because the CO_3^{2-}/HCO_3^- equilibrium has a buffer effect near a pH value of 5, which is compatible with drinking water quality [15].

Studies of nitrate reduction have demonstrated that bimetallic catalysts are more efficient in comparison to monometallic. The catalyst is usually composed of a noble metal, mainly Pd or Pt but also Ru or Rh, and a transition metal, such as Cu, Sn, Ag, Ni, Fe or In on different supports (alumina [19,23-31], silica [32-34], titania [35-39], activated carbon [17,40-44], niobia [45], hydrotalcite [46,47], ceria [48,49], tin oxide [22,50], polymers [51-54], zirconia, titania and alumina membranes [55]). Among them, Pd–Cu, Pd–Sn and Pt-Cu were the most studied catalysts and have been considered as the most actives and selectives for nitrate reduction, but are still inadequate in terms of selectivity towards nitrogen.

Preparation of these catalysts is typically carried out either by simultaneous co-impregnation of both metal salts on the support or by successive steps of metal salt addition. For either of these preparative methods it is virtually impossible to ensure the formation of only bimetallic particles [19]. An alternative approach for the preparation of bimetallic catalysts is the use of selective deposition methodology, in which the second metal salt is decomposed onto the first metal by a controlled reaction catalyzed by the pre-existing metal [26].

The following sections will described the most important features related with this process.

1.5.1 Reaction mechanism

Despite all the studies done so far there is still a lack of knowledge on how the mechanism may be. There are several factors that contribute to this: (i) *in situ* characterizations methods for heterogeneous catalysts are rare especially when the reaction is done in water phase; (ii) similar processes, which have been known for a long time and consequently are well studied, e.g. the catalytic hydration of nitrate to hydroxylamine under acidic conditions (DSM hydroxylamine process) or the electrochemical reduction of nitrate under acidic or alkaline conditions (known for >100 years), are without doubt similar, but not really comparable due to different catalysts and reaction conditions; (iii) the catalytic nitrate reduction is a relative new reaction first described about 20 years ago. So it is normal that most of the work done so far was devoted to the development and optimization of the catalysts than to a deeper understanding of the mechanism [19].

Prusse et al. [19] proposed that the nitrate reduction catalysts can be drawn as displayed in Figure 1.6, being the presence of monometallic and bimetallic sites necessary in the same catalyst. Even though, these authors do not distinguished the exact nature of the bimetallic ensembles and they do not have evidences that monometallic ensembles of the second metal are present in the catalyst. This is related to the fact that very few characterization data are available in the literature for nitrate reducing catalysts.

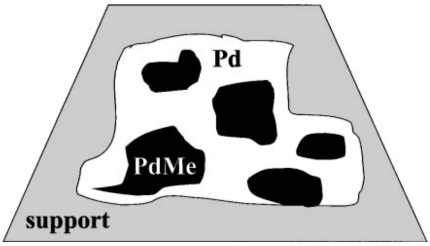

Figure 1.6 Scheme of nitrate reducing bimetallic catalysts [19].

According to them, nitrite adsorbs on monometallic palladium sites, where it is further converted to following N-containing intermediates as illustrated in Figure 1.7 a). Monometallic palladium catalysts exhibit no activity for nitrate reduction and due to that they concluded that nitrate does not adsorb on monometallic palladium sites. So, for nitrate reduction a second metal is needed. The second metal or the bimetallic ensemble enables nitrate adsorption (Figure 1.7 b)). After adsorption, nitrate is converted to the next intermediate, which probably will be nitrite, at these bimetallic ensembles. This can be achieved either by an electron transfer from the bimetallic ensemble to the adsorbed nitrate with a subsequent regeneration of the ensemble by the reductant or by the direct transfer of the reductant to nitrate.

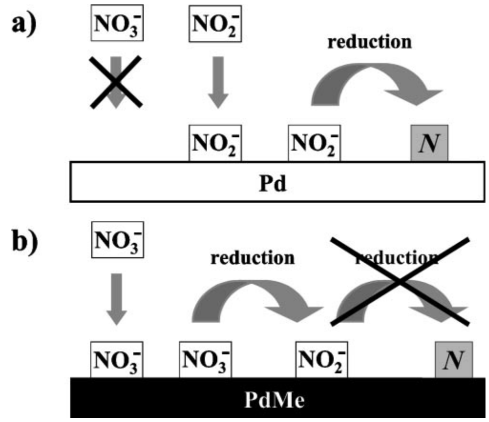

Figure 1.7 Schematic representation of adsorption and reduction steps of nitrogen-containing compounds at monometallic palladium and bimetallic sites. Me: Metal, N: reduced N-species [19].

These authors [19] assumed that after transformation of nitrate to nitrite on the bimetallic sites, no further reaction to following intermediates will occur at these sites (Figure 1.7 b)). So, nitrite will desorb or spillover from these sites and is re-adsorbed at monometallic palladium sites, where it is further reduced to the end-products. On the other hand, Pintar et al. [56] suggests that nitrite may also be converted on the surface of either Pd monometallic or Pd-Cu bimetallic sites.

According to Yoshinaga et al. [17], nitrite reduction has an important role in the nitrate reduction selectivity. Nitrate would be activated on Pd-Cu sites to form nitrite and nitrite reduction took place readily on both Pd and Pd-Cu sites. These authors [17] suggested that edge and corner sites of Pd in Pd microcrystallites possess high abilities for hydrogenation and these sites are probably favourable for deep hydrogenation of NO_2^-, forming NH_3. On the other hand, N_2 would be favourably formed on the terrace sites of the Pd crystallites, because these sites have mild hydrogenation abilities. If Cu atoms are deposited on the edge or corner sites of Pd in the Pd–Cu/AC (Figure 1.8), the edge or corner Pd sites, which are effective for NH_3 formation, will become inactive. Therefore, the selectivity to N_2 is enhanced by the addition of Cu. In the catalysts with high loadings of Cu, most of the Pd atoms will be isolated by the ensemble effect of Cu. The NO_2^- ions adsorbed on the active Pd are well separated from each other and its reduction form NH_3, because of the difficulty of the recombination of N atoms to N_2. They concluded that the changes on N_2 selectivity by addition of Cu are caused by the selective poisoning of nonselective sites at low loadings and by the isolation of Pd sites by the ensemble effect of Cu.

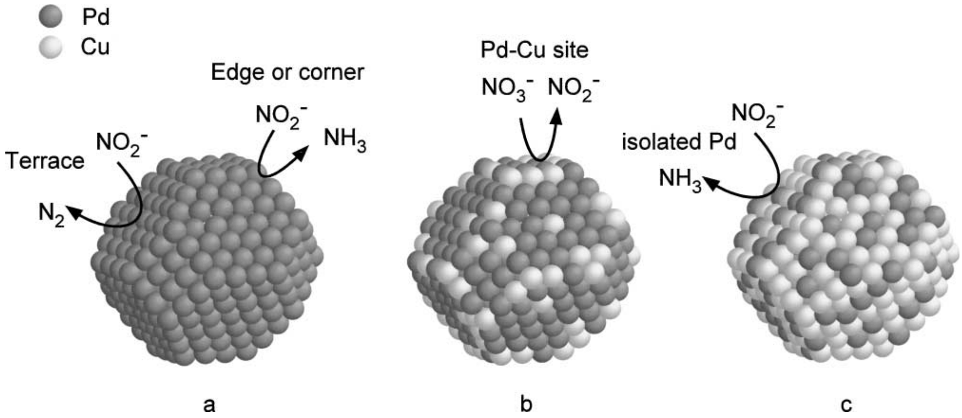

Figure 1.8 Proposed models of Pd and Pd–Cu particles: a) 5wt%Pd, b) 5 wt%Pd-0.6wt%Cu and c) 5wt%Pd-3wt%Cu [17].

Zhang et al. [57] reported that nitrate reduction is mainly assigned to the activation on the Pd-Cu bimetallic sites and the reduction of nitrite occur on the exposed palladium surface. Whereas the nitrite reduction strongly depends on the size of the exposed palladium, being the selectivity of nitrate hydrogenation greatly correlated to the size of Pd-Cu ensembles. The size dependent selective hydrogenation mechanism of nitrate can be described as in Figure 1.9, where nitrate is first activated on the Pd-Cu active sites to produce nitrite that was subsequently readsorbed on the exposed palladium sites for the formation of ammonium or nitrogen. The selectivity to ammonium and nitrogen is not similar on the surface of palladium with distinct size. They suggested that on the bimetallic ensembles with size below to 3.5 nm the exposed palladium particle becomes too small to adsorb and activate two N-containing species simultaneously for the formation of nitrogen. Since the formation of ammonium required only one N species, the size effect is not remarkable, and ammonium as by-product is always formed.

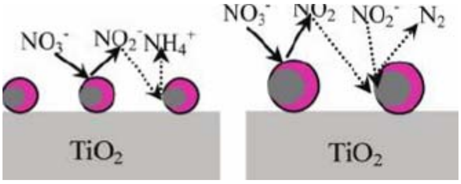

Figure 1.9 Selective hydrogenation mechanism of nitrate on the Pd-Cu/TiO_2 catalysts with different size of active phase: (left) < 3.5 nm; (right) > 3.5 nm. (●: Pd-Cu ensembles. ●: exposed palladium sites) [57].

The most accepted reaction mechanism for nitrate reduction (Figure 1.10 a)) was proposed by Epron et al. [58] and an additional step for the nitrite reduction (Figure 1.10 b)) was proposed by Barrabés et al. [41]. According to them, nitrate is reduced to nitrite by the promoter metal, and the role of the noble metal is to activate hydrogen, which reduces the promoter metal. The noble metal by itself does not present activity for nitrate reduction, but it is effective for nitrite reduction. The promoting role of Cu as the second metal is attributed to its ability to interact with "hard" O-centers of nitrate in contrast to Pd, which prefers "soft" N-centers of low-valence nitrogen oxides [59].

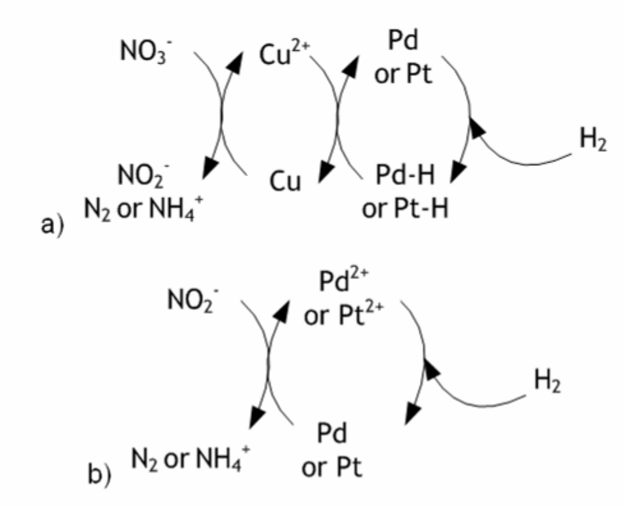

Figure 1.10 Generally accepted reaction mechanism for nitrate [58] (a) and nitrite [41] (b) reduction.

It is well established that the monometallic catalysts are generally inactive for nitrate reduction, a second metal being necessary to reduce nitrate to nitrite [16,19].

However, studies using monometallic catalysts supported on some metal oxides have been appearing and demonstrated that nitrate can be reduced in the presence of noble metals supported on those materials [22,36,48-50]. As mentioned before, when nitrate reduction occurs over bimetallic catalysts, it is generally accepted that nitrate is converted by a redox reaction on the promoter metal, whereas the role of the noble metal is to activate hydrogen, which reduces the promoter metal, completing the catalytic cycle [58]. When the monometallic catalyst is active, the mechanism involves partially reduced species of the support [36]. Epron et al. [48] proposed a mechanism (Figure 1.11) for the nitrate reduction in the presence of Pd/CeO_2. They suggested that nitrate reduction may occur by the interaction of oxygen atoms of nitrate with the oxygen vacancies created at the ceria surface upon the reduction treatment. Thus, nitrate reduction into nitrite would probably involve both vacancies located at metal-support interface and the noble metal.

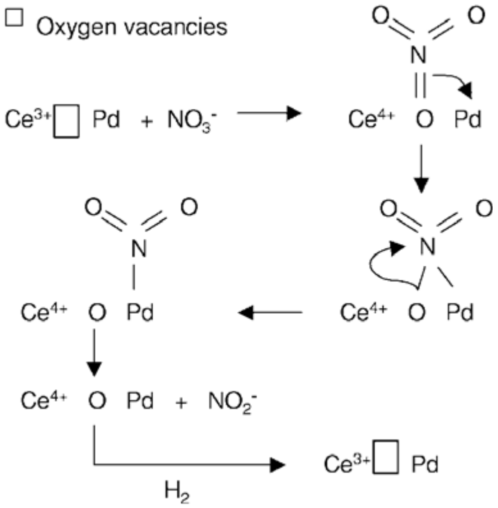

Figure 1.11 Schematic representation of nitrate reduction on a Pd/CeO_2 catalyst [48].

Only a small number of quantitative rate data concerning the catalytic nitrate reduction are published. Tacke and Vorlop [60] determined the kinetics of nitrate hydrogenation over a 5%Pd-1.25%Cu bimetallic catalyst. The measurements were performed in a slurry reactor at T = 10 ºC. They found that the reaction is of 0.7 order with respect to nitrate and independent of hydrogen partial pressure provided that this pressure is greater than about 1.0 bar. It is further reported that the observed rate per unit weight of catalyst is not affected by the catalyst amount. A detailed kinetic model of the catalytic nitrate reduction was derived by Pintar et al. [61], who observed that the rate of nitrate disappearance has been well described by a rate equation of the Langmuir-Hinshelwood type, which accounts for both noncompetitive and equilibrium nitrate and dissociative hydrogen adsorption steps as well as an irreversible bimolecular surface process that controls the overall reaction rate. The observed kinetics of nitrate reduction is not influenced by the presence of nitrites as intermediates in the process. Furthermore, the change in the pH value of aqueous solution during the reaction course has a minor influence on the nitrate disappearance rate. These authors also reported that the liquid-phase reduction of aqueous nitrate solutions over supported Pd-Cu bimetallic catalysts occur by a heterolytic electron transfer between adsorbed reactant species on different types of active sites. They also observed that when various nitrate salts where used as sources of nitrate ions the apparent surface reaction rate constant increases in the following order $K^+ < Na^+ < Ca^{2+} < Mg^{2+} < Al^{3+}$ and changes proportionally with the ionization potential of the cations present in the aqueous solution [21]. On the other hand, the nitrate disappearance rate as well as the nitrogen production yield decrease appreciably in the presence of hydrogencarbonate [21]. The apparent activation energy for the nitrate reduction on the Pd-Cu/GFC catalysts in the temperature range 25 - 35 ºC was found to be 42.2 kJ/mol [59], and a value of 47 kJ/mol was obtained when γ-Al_2O_3 was used as support [61].

1.5.2 Factors that influence the process

Many investigations have shown that the activity and selectivity of catalytic nitrate reduction are strongly influenced by several factors such as: the reaction conditions, the catalysts preparation, the way the noble metal is promoted, the type of catalyst supported and also by the support. This last factor will be discussed in section 1.6.

Horold et al. [18] reported that for an initial nitrate concentration of 100 mg/L, a nitrogen selectivity of 82% was found using Pd-Cu catalysts and that this value could be further increased by carrying out the reaction at lower hydrogen concentrations over a mixture of supported Pd-Cu and Pd catalysts.

It has been reported that nitrate reduction is influenced by the presence of other ions in water, probably due to a competitive adsorption of coexisting ions (SO_4^{2-}, CO_3^{2-}, HCO_3^-, etc) on the metallic active sites [21,47,62] led to the decrease of the catalytic activity and selectivity of nitrate. Wang et al. [63] reported that although Cu-Pd/activated carbon, with Cu/Pd molar ratio higher than 0.66, showed high activity, high selectivity for the formation of N_2 and N_2O (98%), and high durability for the reduction of 100 mg/L NO_3^- in distilled water, the catalytic performance decreased during the reduction of NO_3^- in groundwater, being the catalyst irreversibly deactivated during the reaction in groundwater. The organic species in the groundwater were responsible for the decrease in the catalytic performance and the irreversible catalyst deactivation. Chloride ion in the groundwater also caused the decrease in the activity and selectivity, but the effects of Cl^- were reversible. Sulphate ion and cations, including Mg^{2+}, Ca^{2+} and K^+, had little or no effect on the catalytic performance of Cu-Pd/activated carbon. Pintar et al. [21] reported that the permanent hardness of drinking water exhibits no inhibitive impact either on the extent of nitrate removal or on reaction selectivity. On the other hand, it was suggested that the presence of oxygen in the reducing gas stream feed has a remarkable improvement in the nitrogen selectivity of the process [64].

Prusse et al. [27] demonstrated that Pd-Sn and Pd-In catalysts can be much more suitable for an efficient nitrate reduction than Pd-Cu catalysts. They present a new concept by introducing formic acid as reducing agent instead of hydrogen, which is transformed *in situ* to H_2 and CO_2. The main advantage of formic acid compared to hydrogen is that hydroxide ions formed during nitrate reduction are neutralized *in situ* at the catalyst surface by the CO_2 formed by the decomposition of formic acid to maintain the electroneutrality of the process. The use of a mixture of H_2 and CO_2, where H_2 serves as the reductant and CO_2 as buffer, is useful to some extent, but it was found to be considerably less effective compared to the use of formic acid. Nevertheless, hydrogen is exclusively used as reductant in all laboratorial studies, which are more focused on a subsequent application of this process in a large scale [19].

The catalytic properties of bimetallic catalysts were found to be sensitive to the ratio of the two metals. Both the nitrate removal activity and selectivity have a maximum at a specific noble metal:promoter metal ratio, which can differ slightly with the support material and the preparation method used [18,19]. Epron et al. [58] demonstrated that the highest activity for the nitrate reduction is reached when 3%Pt-1%Cu and 1.7%Pd-0.5%Cu (wt%) supported on alumina are used. Sá et al. [25] reported that 2%Pd-0.6% Cu supported on alumina, which corresponds to an atomic ratio close to one, prepared by catalytic reduction presents the best performance for this reaction. Barrabés et al. [41], using activated carbon as a support, obtained 1%Pt-0.3%Cu and 1%Pd-1%Cu (wt%) as the optimal metal proportions. Matatov-Meytal and Sheintuch [65] found that 2%Pd-0.6%Cu (wt%) is the optimal content when activated cloth is used as a support. These studies demonstrate that the selection of the support is important in this process, since the catalysts activity and selectivity are affected by the interaction between the active phase and the support. In addition, all the conditions used during the preparation of the catalysts influence its catalytic performance; for that reason, for the same ratio of metals supported on the same material, different activities and selectivities can be found depending on the preparation conditions used.

Epron et al. [29] investigated the influence of oxidizing and reduction treatments, at ambient temperature or at 400 ºC, in a bimetallic Pt-Cu catalyst supported on alumina. They concluded that the catalytic activity for nitrate reduction in water is dependent on the Pt and Cu distribution on the catalyst surface, which is strongly affected by the pre-treatments. In a more recent work, Sá et al. [66] studied the influence of the reduction temperature in the performance of Pd-Cu catalysts supported on alumina, and they also observed significant changes in the catalytic activity. Gavagnin et al. [22] reported that ZrO_2 and SnO_2 can be used as supports for Pd-Cu in the nitrate reduction, and the activities and selectivities of the catalyst can be improved by decreasing the reduction temperature. Gao et al. [37] observed that Pd-Cu catalysts supported on titanium dioxide and treated at high temperatures (600 ºC) exhibit lower activity than non-thermally treated catalysts, probably because of the aggregation of active metal species caused by the high temperature treatment. It was also reported that the preparation method by catalytic reduction led to the most active catalysts compared to those resulting from classical methods such as co-impregnation or successive impregnation [58].

Several efforts have been carried out with the aim to overcome the main drawbacks of catalytic removal of nitrate and most of these efforts were more or less successful. Pintar et al. [24,67,68] studied the combination of an ion-exchange resin with a Pd-Cu/Al_2O_3 catalyst for the removal of nitrate. The integrated ion-exchange/catalytic process for nitrate removal from groundwater minimizes both the production of a secondary waste stream resulting from the conventional ion-exchange process, and the contamination of purified water with produced ammonium ions. The gradual deactivation of Pd-Cu/γ-Al_2O_3 bimetallic catalyst used in the integrated ion-exchange/catalytic process, in which a moderately concentrated aqueous NaCl solution is used as regenerant of the spent ion-exchange resin and as reaction medium, is due to catalyst surface deprotonation enhanced by the presence of chloride in the Helmholtz layer [69]. The disadvantage of the integrated ion-exchange/catalytic process is the enhanced production of ammonium ions observed during the hydrogenation of nitrate ions (stripped from the spent ion-exchange resin) in a “liquid-full” fixed-bed reactor packed with the Pd-Cu/γ-Al_2O_3 bimetallic catalyst [68]. To overcome this disadvantage, Pintar and Batista [67] proposed a novel scheme of integrated ion-exchange/catalytic process, which employs two separate reactor units. In the first reactor unit, selective reduction of nitrate to nitrite is carried out at high pH value (above 11.0) in the presence of Pd-Cu/γ-Al_2O_3 bimetallic catalyst, where up to 97% transformation of nitrate to nitrite was obtained, even at complete conversion of nitrate ions; being the rest in the form of ammonium ions. In the second reactor unit, selective reduction of nitrite to nitrogen takes place at low pH value (4.5) over a Pd//γ-Al_2O_3 monometallic catalyst. Comparing the scheme of integrated ion-exchange/catalytic process, in which the denitrification step was conducted in a single ‘‘liquid-full’’ reactor unit [68], with the scheme which employs two separate reactors, the production of ammonium ions was reduced by one order of magnitude [67]. Recently, Calvo et al. [70] optimised the nitrate reduction process, testing a two-step approach using a 0.25%Pd-0.25%Cu bimetallic catalyst and a Pd monometallic catalyst supported on activated carbon in a sequential arrangement, operating within the 6-7 pH range in the two steps. They observed that this two-step process does not improve nitrate conversion (around 80%), but increases significantly the selectivity to nitrogen, from 27% to 86%.

1.6 Catalysts supports

Several studies have been done in the last 20 years since the discovery of Pd-Cu as an active catalyst system for this reaction; however, the selectivities to nitrogen are still unsatisfactory. Many supports have been studied, such as alumina [19,23,30], zirconia, titania and alumina membranes [55], activated carbon [17,40], SnO_2 [22,50], TiO_2 [35-37], ceria [9] and SiO_2 [32], and it has been demonstrated that different supports significantly affect the catalytic activity and selectivity of the catalysts for nitrate reduction in addition to several other factors, such as: the reaction conditions, the catalysts preparation, the way the noble metal is promoted and the catalyst supported as reported in the previous section.

Several studies have demonstrated that monometallic catalysts are practically inactive for nitrate reduction and that some bimetallic catalysts are effective for this reaction [14,16,19]. However, monometallic Pd catalysts supported on SnO_2 [22], CeO_2 [48] and TiO_2 [36] were reported as showing some activity for nitrate reduction but rather low selectivity to nitrogen in comparison with bimetallic catalysts. These results suggest that the support plays an important role in nitrate reduction. Sá et al. [36] reported that Pd monometallic catalysts supported on TiO_2 are more active and present lower tendency for nitrite accumulation than the conventional bimetallic catalyst, although the concentration of ammonium produced was greater than the desired level. Shukla et al. [71] reported that a Fe/AC catalyst exhibits considerably activity and that the nitrogen selectivity is nearly 100%.

Constantinou et al. [64] reported that the catalytic performance of Pd-Cu catalysts supported on various mixed metal oxides, $MO_x/\gamma\text{-}Al_2O_3$ (MO_x = CeO_2, SrO, Mn_2O_3, Cr_2O_3, Y_2O_3 and TiO_2), varies significantly depending on the support. Yoshinaga et al. [17] observed that a Pd-Cu catalyst supported on activated carbon is slightly more active than that supported on silica, more active than on alumina, and is the most selective to nitrogen.

Maia et al. [45] observed that the performance of 2%Pd-0.5%Cu supported on Nb_2O_5 and on $\gamma\text{-}Al_2O_3$ was comparable in terms of activity and nitrogen selectivity, indicating that the activity is not related to any change of the support on the properties of the active metal.

The catalytic performance of the bimetallic catalysts can be adjusted by using different supports. Deganello et al. [72] selected pumice as support due to its electronic effects, which contributes to the high activity of palladium. Hydrotalcites as Pd-Cu support decrease the mass transfer limitations observed on Pd-Cu supported on alumina due to adsorption of nitrates in the interlayer of hydrotalcite. When this material is used as support, nitrates are forced to be located between the positively charged layers of the hydrotalcite and therefore close to the reductive active sites. The nitrates are reduced to nitrites that remain in the same position, and these are further reduced to nitrogen or in a much lower extent to ammonia. These final compounds due to their inadequate charge are released to the solution, reducing the problems related with diffusion limitations that strongly affect the selectivity of the reaction [73]. Roveda et al. [74] used Pd-Sn catalysts deposited on acrylic resins bearing carboxylic functional groups to control the selectivity of the catalysts, limiting ammonia formation due to the buffering ability of the $COOH/COO^-$ groups pending from the support surface which operate in proximity of the metals surface, where the catalytic reduction takes place. Recently, Xu et al. [75] studied the influence of the support properties on the catalytic performance of Pd-Cu/ZrO_2, suggesting that nitrate reduction can be optimized adjusting the properties of the support. Matatov-Meytal et al. [76] used glass fibers in the form of woven cloth as a new type of support. The possible role of tin oxides in the promotion of activity and selectivity of the catalysts was discussed by Gavanin et al. [22]. D'Arino et al. [50] reported that nitrate reduction depends on the nature of the metal (being Pd supported on SnO_2 much better than Pt) and on the morphology of the support (low surface area and large pore supports benefit the nitrogen selectivity).

Gasparicova et al. [77,78] studied Pd-Cu catalysts supported on cationic and anionic microporous ion exchange resins. They observed four times more activity for the anionic exchange resin supported catalyst [78]. This result was attributed to the high mobility of anions in the body of the swollen cationic resin. Despite the good results obtained with these resins as support, the activity was not higher than that obtained with inorganic supports. The difference in the activity between Pd-Cu catalysts supported on γ-Al_2O_3 and on the anionic exchange resin was attributed to diffusive effects, because the active sites are located inside in the polymeric resin, and on the outer surface in the inorganic support. Nevertheless, the resin supported catalysts present a better selectivity to N_2 [51].

Among several options, carbon materials were found to be good supports for this process, and this issue will be discussed below.

1.6.1 Activated carbon

Activated carbons are among the most common materials used in adsorption and catalysis. They are employed widely in both liquid and gaseous phases. This "universality" is due not only to their high surface areas and pore volumes, but also to the variety of surface chemical properties. Although for physical adsorption the porous structure is the most important feature, for chemical adsorption and catalysis the chemical surface plays an important role [79].

Carbon materials are finding an increasing number of applications in catalysis, either as supports, or as catalysts on their own, due to their specific characteristics, namely: (i) resistance to acid and basic media, (ii) possibility to control, up to certain limits, the porosity and surface chemistry, (iii) easy recovery of precious metals by support burning resulting in an economical benefit and in a low environmental impact and (iv) the cost of carbon supports is usually lower than the conventional supports such as alumina and silica [80,81].

Activated carbon presents an amorphous structure with high carbon content and hydrophobic surface properties. The surface of carbon materials is heterogeneous; it consists of faces of graphene sheets and of edges of such layers. The edge sites are much more reactive than the atoms in the interior of the graphene sheets, and chemisorbed foreign elements, in particular oxygen, are predominantly located on the edges [82]. Most of the commercial activated carbons have a surface area between 500 and 1500 m^2/g, being this area mainly constituted by micropores. Activated carbons are characterized by a ramified pore system (see Figure 1.12), with pores of various sizes [83].

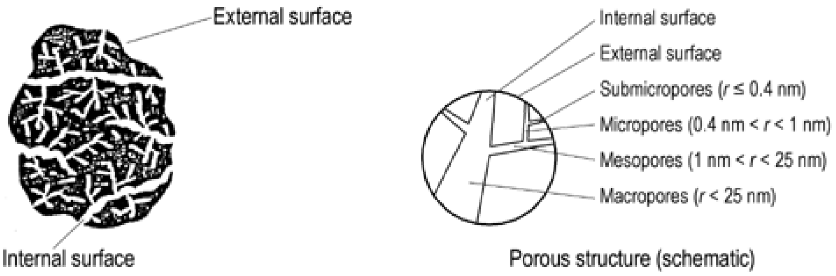

Figure 1.12 Schematic representation of activated carbon porosity [84].

The adsorptive properties of activated carbon are determined not only by its porous structure but also by its surface chemical properties. The presence of heteroatoms (O, N, H, Cl, S,…) bound to the edges of the graphene layers in the carbon material originates a variety of surface functional groups. These elements result either from the starting material or become chemically bonded to the structure during the preparation process [80]. Nitrogen groups are found when a nitrogen-containing precursor is used, or as a result of reactions with nitrogen-containing reagents [85]. Oxygenated groups are formed spontaneously by exposure of the carbon material to the ambient air. The concentration of these groups can be further increased by oxidative treatments, either in the gas (ozone, nitrous oxide, nitric oxide, carbon dioxide, oxygen, etc) or liquid (nitric acid, sodium hypochlorite, hydrogen peroxide, etc) phase [80,86]. Acidic groups include carboxylic acids and anhydrides, lactones or lactols, and phenols, while carbonyl and ether are neutral or may form basic structures, the nature of which is still open to debate, such as quinone, chromene, and pyrone groups [86]. On the other hand, the basicity on the π-electron density of the basal planes is considered to be weak [87]. Figure 1.13 summarizes the different oxygen and nitrogen functional groups that can be found on carbon surfaces.

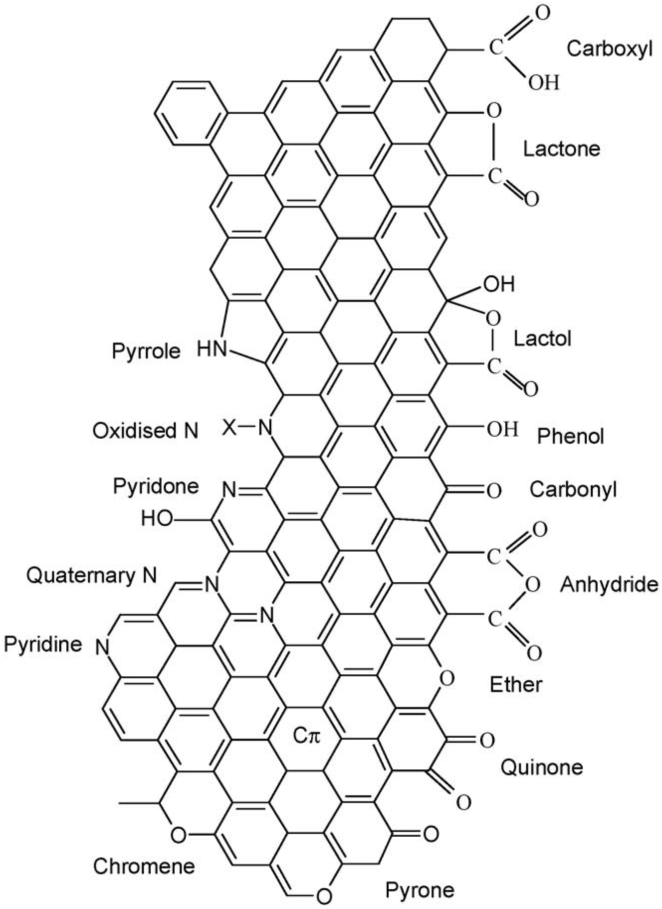

Figure 1.13 Nitrogen and oxygen surface groups on carbon [86].

Heat treatments may be used to selectively remove some of those groups formed, leading to an increase in the basicity of activated carbons. Figure 1.14 summarizes the temperature ranges corresponding to the evolution of CO and CO_2 upon decomposition of the various types of oxygenated functional groups.

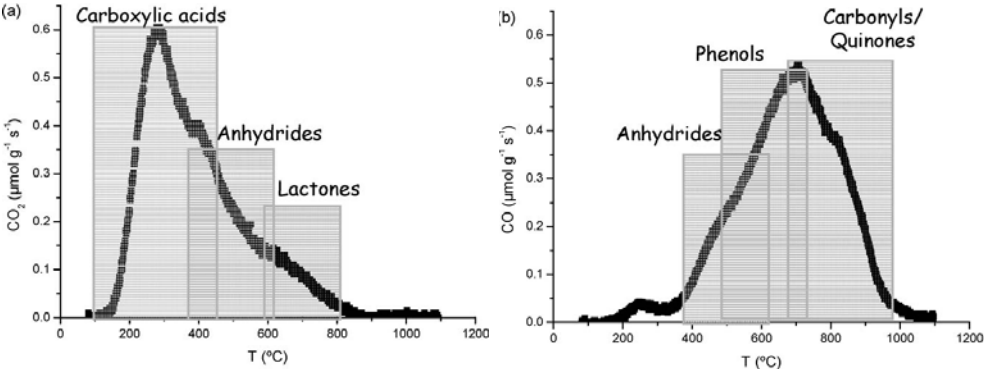

Figure 1.14 Temperature ranges corresponding to the evolution of (a) CO_2 and (b) CO upon decomposition of the various types of oxygenated functional groups [86].

Activated carbon can exhibit basic or acidic pH values in aqueous dispersions; the more acidic the dispersion, the higher the oxygen content. Carbons with acidic surface groups have cation exchange properties. Carbons with a low oxygen content exhibit basic surface properties and an anion exchange behaviour [88]. The carbon surface may have different amounts and types of oxygenated surface groups and consequently both negatively and positively charged surface sites may exist in aqueous solution, depending on the pH. At some pH (the isoelectric point, pH_{IEP}) the net overall surface charge will be zero; at pH> pH_{IEP} the carbon surface, covered by deprotonated carboxyl groups, will attract cations from solution; at pH < pH_{IEP} it will attract anions (see Figure 1.15). This means that when preparing a carbon-supported catalyst, the sites should be not only physically but also chemically accessible to the catalyst precursor.

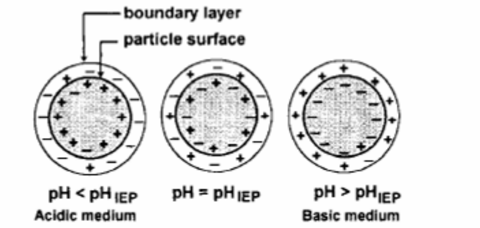

Figure 1.15 llustration of the amphoteric character of carbon materials [80].

The selection of the support is based on a series of desirable characteristics: inertness; stability under reaction and regeneration conditions; adequate mechanical properties; appropriate physical form for the given reactor; high surface area (which is usually, but not always, desirable); porosity and chemical nature [80]. Porous carbon materials constitute a very flexible set of supports for the preparation of heterogeneous catalysts. Their physical and chemical surface properties can easily be tailored to develop: a large surface area to disperse the active phases, the proper pore size distribution to facilitate the diffusion of reactants and products to and from the surface, and the acid–base character needed for obtaining the best performance. High surface area and a well-developed porosity are very important for achieving a high dispersion of the active phase in the catalyst. The presence of hereteoatms can affect the preparation of carbon-supported catalysts, as they confer to the carbon surface acid–base and hydrophilic character [89]. The presence of heteroatoms (mainly O, H and N) also introduces active sites on the carbon surface, and consequently the carbon surface is not as inert as it could be expected [80]. The presence of oxygenated groups on the carbon surface increases its hydrophilicity. When using incipient-wetness impregnation, electrostatic repulsions seem to be less important than other factors such as the hydrophilicity of the sample and the amount and distribution of oxygen-containing surface groups [90].

The relative inertness of the carbon surface is of paramount importance when carbon materials are going to be used as supports for hydrogenation catalysts. The carbon inertness facilitates interaction between metals and/or between metals and promoters, yielding more active and selective catalysts than those supported on other common supports [89].

The presence of oxygenated surface groups is beneficial in many aspects of the preparation, dispersion and activity of carbon-supported catalysts. However, considering that one of the main advantages of carbon supports in respect to conventional oxides like alumina and silica is the easy reducibility of the metal on the support, the presence of oxygenated groups would be detrimental. It should be realized that carbon materials are ideal supports for this type of study since, in contrast to alumina and silica, the carbon-active phase interaction is weak and the performance of the catalyst will basically governed by the chemical nature of the active phase; thus, the effect of adding other metals or promoters may be studied without the problem of undesirable effects with the support [89].

1.6.2 Carbon nanotubes

Carbon nanotubes (CNT) are seamless cylindrical graphitic nanofibers made of sp^2 carbon atoms. A carbon nanotube may consist of a single graphitic sheet [single-walled carbon nanotubes (SWCNT) as shown in Figure 1.16 a)] or multiple concentric graphitic sheets [multiwalled carbon nanotubes (MWCNT) as shown in Figure 1.16 b)] [91].

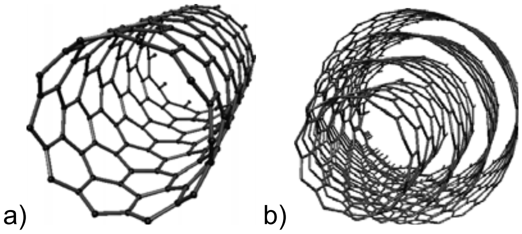

Figure 1.16 Some representative sp^2 carbon materials: (a) SWCNT; (b) MWCNT [91].

CNT form bundles, which are entangled together in the solid state giving rise to a highly complex network. Depending on the arrangement of the hexagon rings along the tubular surface, CNT may be either metallic or semiconducting, depending on the tube diameter and helicity [92].

Typical dimensions of MWCNT are: outer diameter, 2-20 nm, inner diameter, 1-3 nm, lengths - 1 μm. The intertubular distance is 340 pm, which is slightly larger than the interplanar distance in graphite. The total surface area of SWCNT range from 400 to 900 m^2/g, whereas for MWCNT values varying between 150 and 300 m^2/g are often reported [93].

Carbon nanotubes and nanofibers constitute a new family of support offering a good compromise between the advantages of activated carbon and high surface area graphite [93]. Indeed, CNT represent an interesting alternative to conventional supports for a number of reasons, including: (i) their high purity that eliminates self-poisoning; (ii) their impressive mechanical properties, high electrical conductivity and thermal stability; (iii) the high accessibility of the active phase and the absence of any microporosity, thus eliminating diffusion and intraparticle mass transfer limitations in the reactions medium; (iv) the possibility of macroscopic shaping of the support; (v) the possibility of tuning the specific metal–support interactions, which can directly affect the catalytic activity and selectivity; and (vi) the possibility of confinement effects in their inner cavity. Additionally, compared to conventional supports, CNT have a high flexibility for the dispersion of the active phase since it is possible to: (i) modulate their specific surface area or their internal diameter; (ii) easily functionalize chemically their surfaces; (iii) change their chemical composition; and (iv) deposit the catalytic phase either on their external surface or in their inner cavity [94].

1.6.3 Carbon supported catalysts

Activated carbon supported bimetallic catalysts have been shown to be very active and selective in the reduction of nitrate. For example, Wang et al. [95] reported that a 3.6%Pd-2.0%Cu(%wt) catalyst supported on hydrophobic activated carbon is a very active and selective catalyst for the reduction of nitrate in water. They observed that the activity and selectivity of the catalysts depended on the support used but they did not study the influence of the surface chemistry of the activated carbon.

Yoshinaga et al. [17] have investigated the influence of the support for the reduction of nitrate in water with hydrogen over supported Pd-Cu. They observed that activated carbon was superior in conversion, selectivity and insolubility of the metallic components to other supports like SiO_2, Al_2O_3 and ZrO_2, even when low pH values (2.3) were used. Sakamoto et al. [96] also observed that the activity and selectivity of $Cu_{0.63}$-Pd bimetallic clusters supported on activated carbon were superior than those observed for oxides such as TiO_2, Al_2O_3 and ZrO_2.

Matatov-Meytal and Sheintuch [65] reported that Pd-Cu catalysts supported on activated carbon cloth (Pd-Cu/ACC), prepared by selective deposition of Cu on pre-reduced Pd/ACC, showed high activity (92% conversion) and selectivity (ca 93%) in the reduction of nitrates to nitrogen. One reason for this performance of Pd-Cu/ACC catalysts may be related to the surface and pore size properties of this support, which has almost uniform micropores open directly to the outer surface. On the other hand, surface composition of the catalyst has a remarkable influence on the nitrate reduction. The results of the surface composition reveal a specific orientation for the Cu metal deposition on the core Pd crystallites, probably of Pd-Cu bimetallic islets and free Pd atoms [43].

1.7 Nitrate reduction: an overview

Table1.5 shows some of the results, as well as operation conditions used, reported in the literature for nitrate reduction. It can be observed that some catalysts present good performances. The majority of these studies were performed in batch or semi-batch equipments whereas only a few are reported using continuous reactors. Some values are not indicated in the table because that information was not available in the original reference.

Table1.5 Results, as well as operation conditions used, reported in the literature for the nitrate reduction.

Ref.	Catalyst (wt%)	Catalyst amount (g) or W/F (g_{cat} h/mmol)	Liquid amount (mL or mL/min)[b] and T(ºC)[a]	$C_{NO_3^-}i$ (mg/L)	Operation conditions	Gas flow rate (cm^3/min)		Final concentrations (mg/L)			Selectivities (%)		
						H_2	CO_2	$C_{NO_3^-}$ or $X_{NO_3^-}$ (%)	$C_{NO_2^-}$	$C_{NH_4^+}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
[17]	5%Pd-0.6%Cu/SiO_2	1	0.65 60 ºC pH=5.4	200	Continuous Reaction time = 6 h	1.4	-	95.5%			11.2	77.2	11.6
	Al_2O_3							45.7%			30.5	4.7	56.9
	ZrO_2							84.5%			14.6	45	40.4
	AC							97.1%			0.3	21.4	78.3
	5%Pd-3%Cu/AC							100%			0	81.7	18.3
[19]	5%Pd-1.25%Cu/ Al_2O_3	1-2g/L	500 10 ºC	100	Semi-batch	-	pH adjusted by 0.2 M HCl pH = 5	Activity 14 $mgNO_3^-$ /(h g_{cat})		2.3			
	5%Pd-Sn Ratio 1:1					0.83	pH = 9	Activity 58 $mgNO_3^-$ /(h g_{cat})	7.6	12.4			
[22]	5%Pd-1.5%Cu%/ ZrO_2	0.04	70	100	Semi-batch	120 H_2:CO_2 = 1/8		100%	0.3	8.1			
	SnO_2							100%	1.8	6			
[23]	4.4%Pd-1.21%Sn/ Al_2O_3	0.35	750	100	Semi-batch	90	90	100%	0	3.4			88
	5%Pd-1.25%Sn/ Al_2O_3							100%	0	6.8			77

Ref.	Catalyst (wt%)	Catalyst amount (g) or W/F (g_{cat} h/mmol)	Liquid amount (mL or mL/min)[b] and T(ºC)[a]	$C_{NO_3^-}$ i (mg/L)	Operation conditions	Gas flow rate (cm^3/min)		Final concentrations (mg/L)			Selectivities (%)		
						H_2	CO_2	$C_{NO_3^-}$ or $X_{NO_3^-}$ (%)	$C_{NO_2^-}$	$C_{NH_4^+}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
[27]	5%Pd-1%In/Al_2O_3	6.3	500 10 ºC	100	Continuous	50	0.2M HCl	54					50
							HCOOH = 5 mg/L	55					91
[32]	4.7%Pd-1.5%Sn/ Al_2O_3	0.064	100	100	Semi-batch	250 H_2:CO_2 = 1:1		75%					92.8
	SiO_2							75%					93.2
[41]	1%Pt-0.3%Cu/AC	1	1.2	60	Continuous	3	Without pH control	98%	-	-			100
	1%Pt-1%Cu/AC							75%	-	-			100
	1%Pd-1%Cu/AC						Final pH = 9	68%	20				
	1%Pd-0.3%Cu/AC							68%	12				
[42]	1.7 wt% $[Cu_2\text{-}Pd]_{cluster}$/AC	0.8-8.5		100	Continuous	3 H_2/He/CO_2 = 5/45/50		71.4%		<0.1	0.4	-	28.9
	4.4 wt% (Cu_2-Pd)/AC							74.2%		0.8	0.4	4.0	65.8

Ref.	**Catalyst (wt%)**	**Catalyst amount (g) or W/F** (g_{cat} h/mmol)	**Liquid amount (mL or mL/min)^b and T(ºC)^a**	$C_{NO_3^-}{}_i$ (mg/L)	**Operation conditions**	**Gas flow rate (cm^3/min)**		**Final concentrations (mg/L)**			**Selectivities (%)**		
						H_2	**CO_2**	$C_{NO_3^-}$ or $X_{NO_3^-}$ **(%)**	$C_{NO_2^-}$	$C_{NH_4^+}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
[43]	2%Pd/ACC	9.5	15	112	Continuous Reaction time = 6h	pH_2 = 6 bar		0%					
	2%Pd-0.28%Cu/ACC							52.2%			3.3	5.3	91.4
	2%Pd-0.59%Cu/ACC							91.6%			5.4	5.4	91.2
	2%Pd-1.2%Cu/ACC							77.8%			6.6	10.6	82.8
	2%Pd-1.8%Cu/ACC							60.4%			10.4	14.9	74.7
[45]	2%Pd-0.5%Cu/ Nb_2O_5	0.8	900	100	Semi-batch	50	50	100%		3.1			89
							Without pH control	47%		2.4			30
	2%$PdNb_2O_5$ + 0.5%Cu/Nb_2O_5						50	84%		6.0			79
	2%Pd-0.5%Cu/ γ-Al_2O_3						50	100%		3.9			87
[49]	CeO_2	0.5	1.2	60	Continuous			21			7	83	10
	0.2%Pt/CeO_2					3	-	93			0	54	46
	0.5%Pt/CeO_2							99			0	55	45
	0.5%Pt/CeO_2					3 H_2:CO_2		30			0	24	76
	1%Pt/CeO_2					3	-	99			0	100	0
	1%Pt/F-CeO_2 Prepared by combustion							90			0	21	79

Ref.	Catalyst (wt%)	Catalyst amount (g) or W/F (g_{cat} h/mmol)	Liquid amount (mL or mL/min)[b] and T(ºC)[a]	$C_{NO_3^-}i$ (mg/L)	Operation conditions	Gas flow rate (cm^3/min)		Final concentrations (mg/L)			Selectivities (%)		
						H_2	**CO_2**	$C_{NO_3^-}$ or $X_{NO_3^-}$ **(%)**	$C_{NO_2^-}$	$C_{NH_4^+}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
	Prepared by impregnation							50			0	34	66
[50]	5%Pd/SnO_2	0.04	70	100	Semi-batch	120 H_2:CO_2 = 1/8		100%		5.3			
						Without CO_2 Final pH =11.6		100%		17			
	5%Pt/SnO_2					120 H_2:CO_2 = 1/8		100%		14			
[51]	4%Pd-1Cu/Dowex 1*4	0.15	250	100	Semi-batch	64	Separate inlet of CO_2	43%			0	18	82
						H_2:N_2 = 64 43% H_2	Separate inlet of CO_2	52%			0	4	96
[52]	2%Pd-0.5%Cu /weak anionic exchange resin												
	Prepared by controlled surface reaction	1 mL	80	150	Batch	400	0.1M HCl pH=4-4.5	54%	0	0.6			
	Prepared by ion exhange							41%	5.2	0.4			

Ref.	**Catalyst (wt%)**	**Catalyst amount (g) or W/F** (g$_{cat}$ h/mmol)	**Liquid amount (mL or mL/min)^{b} and T(ºC)^{a}**	$C_{NO_3^-\,i}$ (mg/L)	**Operation conditions**	**Gas flow rate (cm^3/min)**		**Final concentrations (mg/L)**			**Selectivities (%)**		
						H_2	**CO_2**	$C_{NO_3^-}$ or $X_{NO_3^-}$ **(%)**	$C_{NO_2^-}$	$C_{NH_4^+}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
[58]	1.7%Pd-1%Cu/Al_2O_3	0.8	100 10 ºC	62	Batch	180	-	Activity 4e^{-5} mol/(min g$_{cat}$)				4	
	3%Pt-1%Cu/Al_2O_3							9e^{-5} mol/(min g$_{cat}$)gcat				4	
[63]	3.6%Pd-2%Cu/AC	0.5	0.084	100	continuous	3 H_2/He/CO_2 = 5/45/50		83%			0	2	61 (+37 N_2O)
				+ 50 mg Cl^- /L				55%			0	34	48 (+18 N_2O)
				+50 mg/L SO_4^{2-}				79			0	7	40 (+53 N_2O)
[64]	0.92%Pd-0.32%Cu/ Al_2O_3	4.0	200	100	Semi-batch	100	-						
						100% H_2	-	>90%			7.6	32.4	60.0
						70% H_2/30 %ar	-	>90%			3.5	6.0	90.5
				360		70% H_2/30 %ar	-	>90%			3.1	3.4	93.5

Ref.	Catalyst (wt%)	Catalyst amount (g) or W/F (g_{cat} h/mmol)	Liquid amount (mL or mL/min)[b] and T(ºC)[a]	$C_{NO_3^-}\,i$ (mg/L)	Operation conditions	Gas flow rate (cm^3/min)		Final concentrations (mg/L)			Selectivities (%)		
						H_2	CO_2	$C_{NO_3^-}$ or $X_{NO_3^-}$ (%)	$C_{NO_2^-}$	$C_{NH_4^+}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
[70]	0.25%Pd-0.25%Cu/AC	52		100	Continuous	50	Buffer solutions	77.3%			22.2	50.5	27.2
	0.5%Pd-0.5%Cu/AC							73.2%			28.8	29.3	41.9
	0.5%Pd-0.25%Cu/AC							82.5%			16.5	38.7	44.8
	0.5%Rh-0.5Cu/AC							61%			6	44	50
[73]	5.1%Pd-1.5%Cu/Al_2O_3	0.85	1000	90	Semi-batch	500	-	100%	3	19			
	4.9%Pd-1.5%Cu/ Mg/Al							100%	0	7			
[75]	5%Pd-1.25%Cu/ZrO_2	0.3	150	100	Semi-batch	60	0.2M HCl	100%	0	7			
[95]	3.6%Pd-2%Cu/AC	54-102 h^{-1}		100	Continuous	1.33 H_2:CO_2 = 50:50		100%	-	4.5	0	12	65
	3.6%Pd-2%Cu/ Al_2O_3								0	6.4	0	24	1

Ref.	**Catalyst (wt%)**	**Catalyst amount (g) or W/F** (g_{cat} h/mmol)	**Liquid amount (mL or mL/min)^b and T(ºC)^a**	$C_{NO_3^-}i$ (mg/L)	**Operation conditions**	**Gas flow rate (cm^3/min)**		**Final concentrations (mg/L)**			**Selectivities (%)**		
						H_2	**CO_2**	$C_{NO_3^-}$ or $X_{NO_3^-}$ **(%)**	$C_{NO_2^-}$	$C_{NH_4^+}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
[96]	1.0 wt% ($Cu_{0.63}$-Pd)/ AC	9.9	60 ºC	200	Continuous	3	3.5 mmol/h	100%			0	35	41
		3.2					- Final pH =10.5	93.6%			87.2	10.3	2.5
		1.8						86.1%			89.2	8.4	2.4
	1.0 wt% ($Cu_{0.63}$-Pd)/TiO_2	6.3						68.6%			56.3	27.0	16.7
	1.0 wt% ($Cu_{0.63}$-Pd)/ZrO_2	6.2						72.4%			69.8	21.3	8.9
	1.0 wt% ($Cu_{0.63}$-Pd)/Al_2O_3	5.9						65.0			72.3	27.7	0
[97]	0.3%Pd-0.5%Cu/ Fe-S	0.5	65 pH = 5.5	177	Semi-batch	Saturated with H_2		100%	1	38.1			5.6
[98]	1%Pd-0.3%Cu/ ACC	2.2	5	112	Continuous Reaction time = 6h	pH_2 = 6 bar	-	67.7%			1.9	3.2	
	2%Pd-0.6%Cu/ ACC							91.6%			3.4	5.4	

[a] g for batch and gcat h/mmol for continuous experiments.

[b] mL for batch and mL/min for continuous experiments.

1.8 Objectives and thesis outline

Removal of nitrate from drinking water is an important and developing area of research. There is still a need to further optimize the current treatment techniques and develop emerging processes for nitrate remediation. Therefore, the main objective of this work is the development of efficient and stable catalysts for nitrate removal in water by reduction with hydrogen. This work started with the assessment of several mono and bimetallic supported catalysts, being activated carbon used as the reference support. Subsequently, the preparation methods and the catalysts formulation were optimized. Activated carbons (chemically and thermally modified), carbon nanotubes and metal oxides were assessed as supports. Several metal catalysts supported on activated carbon were studied and characterized. The practical feasibility of the process was addressed, evaluating nitrate removal efficiency in polluted groundwater.

These studies were carried out in a semi-batch reactor (see Appendix A) at room temperature and atmospheric pressure. Preliminary studies (see Appendix B) were carried out in order to select the best operation conditions.

This thesis is organized in ten chapters. This introductory chapter is Chapter 1. The main core of this thesis is composed of Chapters 2 to 9.

Chapter 2 is dedicated to the assessment of the most promising metal phases supported on a commercial activated carbon.

Chapter 3 consists in the optimization of metals compositions, for the catalysts with the best performances, as determined in the previous chapter.

Chapter 4 describes the influence of calcination and reduction temperatures on the catalytic properties of Pd-Cu and Pt-Cu bimetallic catalysts supported on activated carbon.

Using the best preparations conditions reported in Chapter 4, Chapter 5 shows the results obtained using several physical mixtures with mono and bimetallic catalysts. In this chapter a reaction mechanism is proposed.

In Chapter 6, carbon materials with different chemistries and surface properties are explored as Pd-Cu and Pt-Cu supports.

Similar studies to those reported on Chapter 4 and 6 but using carbon nanotubes as support are discussed on Chapter 7.

Chapter 8 reports the effect of the support in the performance of Pd-Cu catalyst. Several metal oxides, activated carbon and carbon nanotubes as well as composites were assessed as support.

Chapter 9 shows the comparison between activated carbon and titanium dioxide as support for Pt-Sn bimetallic catalysts.

Finally, chapter 10 summarizes and integrates the main conclusions withdraw from this work. Some suggestions for further work are presented, taking also into account the preliminary results presented on Appendix C relative to the practical feasibility of this process.

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Chapter 2

2 Activated carbon supported metal catalysts for nitrate and nitrite reduction in water[1]

Ten monometallic and thirteen bimetallic catalysts supported on activated carbon were assessed, the former in the reduction of nitrate or nitrite and the latter in the nitrate reduction. Under the conditions used, nitrite was shown to be reduced by monometallic catalysts. With exception of Ru, only some of the bimetallic catalysts were able to reduce nitrate. Rh-Cu shows the highest conversion, but Pd-Cu is the most promising catalyst if selectivity into nitrogen is also considered.

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2.1 Introduction

The increasing pollution of natural sources of drinking water encourages the development of new emerging technologies and processes for water remediation. Nitrate concentrations in surface water and especially in groundwater have increased in many locations in the world. Nitrate anion is potentially harmful because it can be transformed into nitrite in the human body, which can cause blue baby syndrome, and it is also a precursor of the carcinogenic nitrosamines [1-4]. In addition, nitrates can originate eutrophization in rivers and lakes. The main sources of nitrates are the overuse of fertilisers in agriculture as well as the effluents from certain industries. Most of the nitrate salts are soluble in aqueous medium so that nitrate ions are easily spread over the groundwater sources [3]. For these reasons, the European Community limit values for nitrate, nitrite and ammonium concentrations in drinking water are 50, 0.5 and 0.5 mg/L, respectively, and for the discharge of wastewater are 50 and 10 mg/L for nitrate and ammonium concentrations, respectively.

Nitrates can be removed from water by physicochemical, biological and catalytic methods. The main disadvantage of the physicochemical treatments (ion exchange, reverse osmosis and electrodialysis) is the fact that nitrate is not converted into harmless compounds but only concentrated; then it must be treated afterwards or disposed of [3-5]. Biological denitrification is recognized as a useful method for the selective conversion of nitrate into harmless gaseous nitrogen. However, this process has several disadvantages since it is difficult to handle and leads to the production of undesirable by-products [1]. In addition, there are concerns about possible bacterial contamination, the presence of residual organics in the treated water and the possible increase in the chlorine demand of purified water [6].

The catalytic reduction of nitrate has been suggested in the literature as a promising method for nitrate removal from water without the drawbacks of the conventional methods [2,5-9]. This process was reported for the first time by Vorlop and Tacke [10] and consists in the reduction of nitrate anion to nitrogen over bimetallic catalysts in the presence of a reducing agent. Nitrite as intermediate and ammonium as by-product are considered the major limitations of this process [9,11]. Previous studies on the heterogeneous catalytic nitrate reduction have shown that bimetallic catalysts are much more efficient than the monometallic ones. The catalyst is usually composed of a noble metal, mainly Pd or Pt but also Ru, Rh or Ir, and a transition metal, such as Cu, Sn, Ag, Ni, Fe or In on different supports (alumina, silica, titania, activated carbon, polymers) [1-22]. Pd and Pt as noble metal and Cu and Sn as promoter metal were the most studied catalysts and have been considered as the most actives and selectives. Among them, Pd–Cu, Pd–Sn and Pt-Cu, seem to be the most effective for nitrate reduction, but are still inadequate in terms of selectivity towards nitrogen [4,5,7,9,16].

Carbon materials are finding an increasing number of applications in catalysis, either as supports for the active phases, or as catalysts on their own. They gather the desirable characteristics for a catalyst support: inertness; stability under reaction and regeneration conditions; adequate mechanical properties; possibility to adapt its physical form for a given reactor; high surface area and porosity [23]. In addition, it is possible to tailor both their texture and surface chemistry. The texture may be tailored to suit the specific application by adequate choice of the preparation procedure. In particular, it is possible to prepare carbons with different proportions of micro, meso and macropores. On the other hand, the nature and concentration of surface functional groups may be modified by suitable thermal or chemical post-treatments [23]. In water treatment processes, two additional advantages over inorganic supports must also be considered: activated carbon can play an additional important role as adsorbent since its effect in the adsorption of a vast range of micropollutants is well known; when used as a catalyst support for noble metals, as is the present case, the recovering of the metal just by burning the carbon material is very easy. This final advantage is of paramount importance to use this type of catalysts in industrial scale. Removal of nitrates from water is an important and developing area of research. Moreover, additional studies are still necessary to optimize the formulation of the catalysts and to get a better understanding about the influence of metals nature, in order to develop an effective catalytic process for purifying water streams. In this work, several metal catalysts supported on activated carbon were prepared, characterized and evaluated. Monometallic catalysts (Pt, Pd, Cu, Sn, Ru, Rh, Ni, Ir, Fe, and Zn) were considered for the study of the reduction of both nitrate and nitrite by hydrogen. Additionally, the bimetallic catalysts Pd-Cu, Pt-Cu, Rh-Cu, Ru-Cu, Pd-Ir, Pd-Sn, Pd-Fe, Pd-Ni, Pd-Zn, Ir-Cu, Rh-Sn, Pt-Sn and Pt-Fe, with 1%wt of each metal, were selected for the study of nitrate reduction. To the best of our knowledge, this is the first systematic study for testing a wide range of monometallic and bimetallic catalyst using activated carbon as a support for the nitrate and nitrite reduction in water. A similar study was reported by Horold et al [24], but only five monometallic and six bimetallic catalysts were tested, and using alumina as catalyst support in almost all cases. These screening tests represent the first step of a systematic investigation of metallic and bimetallic catalysts supported on activated carbon for nitrite and nitrate reduction, and were necessary to select the most promising catalytic systems for further developments.

2.2 Experimental

2.2.1 Preparation and characterization of the catalysts

The active metals were supported on a commercial activated carbon NORIT GAC 1240 PLUS (ACo) ground to a particle diameter between 0.1 and 0.3 mm. The catalysts were prepared by the incipient wetness method, and in the case of the bimetallic catalysts by co-impregnation, with aqueous solutions of the corresponding metal salts (H_2PtCl_6, $PdCl_2$, $Cu(NO_3)_2$, $SnCl_2$, $RhCl_3$, $RuCl_3$, $Ni(NO_3)_2$, $(NH_4)_3IrCl_6$, $Fe(NO_3)_3$, $ZnCl_2$). After that, the samples were dried at 100 ºC for 24 h, calcined under a nitrogen flow at 400 ºC for 1 h, and finally reduced at 400 ºC in hydrogen flow for 3 h. The contents of both noble and promoter metals were maintained constant at 1%wt.

Selected catalysts were characterized by H_2 chemisorption, N_2 adsorption at -196 ºC, temperature programme reduction (TPR) and X-ray diffraction (XRD). Metal dispersions were determined by chemisorption of H_2 at 30 ºC and atmospheric pressure in an Altamira Instruments AMI-200 apparatus, using the pulse method, and assuming a stoichiometric ratio of H_2/metal = 2. Pulses of 58 μL (from a calibrated loop) were successively injected in the carrier gas (25 Ncm^3/min of Ar), which passes through a catalyst bed (150 mg), until saturation of the catalyst surface. The non-adsorbed hydrogen is measured with an online thermal conductivity detector. The amount of H_2 corresponding to saturation was calculated by summing the differences between the amounts injected and detected at outlet. TPR experiments were carried out in the same equipment; the sample (150 mg) was heated at 5 ºC/min up to 600 ºC under a flow of 5% (v/v) H_2 diluted in He (total flow rate of 30 Ncm^3/min). The H_2 consumption was followed by mass spectrometry (Dymaxion 200 amu, Ametek).The textural characterization of the materials was based on the corresponding N_2 equilibrium adsorption isotherms, determined at -196 ºC with a Coulter Omnisorp 100 CX apparatus. XRD spectra of platinum and palladium catalysts were recorded in the range 2θ = 20–90º on a Philips X'Pert MPD diffractometer (Cu-Ka = 0.15406 nm). The average size of the metal particles was calculated from the half width of the diffraction peak using Scherrer equation.

The metallic dispersion and the average crystallite size of the monometallic catalysts that presented some activity are presented in Table 2.1. The results obtained by XRD, also presented in Table 2.1, are in agreement with those obtained by hydrogen chemisorption.

Table 2.1 Characterization of the monometallic catalysts.

Catalyst	**Dispersion (%)**	**Particle size (nm)**
1%Pt_ACo	19.9 (7.3)	6.0 (13.9)
1%Pd_ACo	3.2 (3.7)	36 (30)
1%Rh_ACo	15.2	7.1
1%Ir_ACo	50	2.2

The values in brackets were obtained by XRD

The characterization of the support is presented in Table 2.2. A sample with 2% of Pd and 1% of Cu (a total metal loading higher than all the samples tested in this work) was also characterized by N_2 adsorption at -196 ºC and the textural parameters remained almost unchanged compared to the unloaded activated carbon. Therefore, we assume that the surface area of the activated carbon supported metal catalysts is not significantly different from the original activated carbon.

Table 2.2 Textural characterization of the activated carbon (ACo).

S_{BET} (m^2/g)	S_{meso} [a] (m^2/g)	V_{micro} [a] (cm^3/g)	W_{01} [b] (cm^3/g)	W_{02} [b] (cm^3/g)	L_1 [c] (nm)
869	97	0.318	0.290	0.035	0.93

[a] Micropore volume (V_{micro}) and mesopore surface area (S_{meso}) were calculated by the t-method.

[b] A type IV deviation was noticed when the N_2 adsorption data was analysed by the Dubinin method; W_{01} and W_{02} are the micropore volumes associated to small and large micropores, respectively.

[c] Average small micropores width (assuming split-shaped geometry).

2.2.2 Catalysts evaluation

Kinetic experiments were carried out in a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure, and using hydrogen as reducing agent. Initially, 790 mL of deionised water and 400 mg of catalyst were fed into the reactor, the magnetic stirrer was adjusted to 700 rpm and the gas mixture of carbon dioxide and hydrogen (H_2+CO_2 (1:1), Q_{Total} = 200 Ncm^3/min) was passed through the reactor during 15 min to remove oxygen; CO_2 acts as pH buffer (pH = 5.5). After that period, 10 mL of a nitrate or nitrite solution, respectively prepared from $NaNO_3$ or $NaNO_2$, were added to the reactor, in order to obtain an initial NO_3^- or NO_2^- concentration equal to 100 mg/L. Preliminary studies were carried out varying the stirring rate and it was checked that under the selected conditions there was no external diffusion limitations.

Small samples were taken from the reactor for determination of nitrate, nitrite and ammonium concentrations after defined periods. Nitrate and nitrite ions were simultaneously determined by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was a Hamilton PRP-X100 column (150 mm x 4.1 mm) working at room temperature, under isocratic conditions. The mobile phase was a solution of 0.1 M $NaCl:CH_3OH$ (45:55). Ammonium ions were determined by potentiometry using a convenient selective electrode. pH values were also measured.

The selectivities of nitrite, ammonium and nitrogen were calculated as:

$$S_{NO_2^-} = \frac{n_{NO_2^-}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{2.1}$$

$$S_{NH_4^+} = \frac{n_{NH_4^+}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{2.2}$$

$$S_{N_2} = \frac{2 * n_{N_2}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{2.3}$$

where $n_{NO_3^-{}_i}$ is the initial amount of nitrate (mmol) and $n_{NO_3^-}$, $n_{NO_2^-}$, $n_{NH_4^+}$ and n_{N_2} are the amounts of the respective species (mmol) at time t (min). The amounts of nitrogen were calculated by a mole balance, assuming that the amount of NO_x produced is negligible [1,12].

2.3 Results and Discussion

2.3.1 Monometallic catalysts

The activity and selectivity of monometallic catalysts supported on activated carbon for the reduction of nitrates and nitrites were studied. A total of ten catalysts were evaluated, all containing 1%wt of metal. For comparatives purposes, the catalytic activity of the support, activated carbon (ACo), and the possibility of nitrate and nitrite reduction only in the presence of hydrogen (blank) were also checked. Figure 2.1 shows the evolution of nitrate concentration and, under the experimental conditions used, it can be observed that the monometallic catalysts are practically inactive for the reduction of nitrate. Only Ru presents some activity, being nitrate mainly converted into ammonium. The Fe catalyst is not completely inactive, since it presents a nitrate residual conversion of 3% after 5 h. This indicates that probably nitrate can be reduced on monometallic sites but the degradation rate is very low. These results are in line with the literature, where it is generally accepted that monometallic sites are inactive for nitrate reduction [3,5,25].

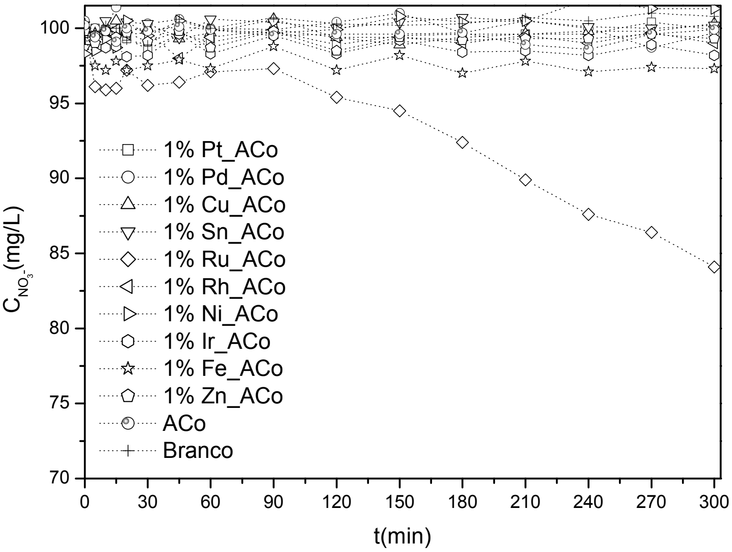

Figure 2.1 NO_3^- concentration as a function of time during nitrate reduction in the presence of monometallic catalysts ($C_{NO_3^- i}$ = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H_2} = 100 Ncm^3/min, Q_{CO_2} = 100 Ncm^3/min, T = 25 ºC).

No reduction of nitrate (Figure 2.1) or nitrite (Figure 2.2 a)) were achieved when the experiments were carried out using only the support or in the blank tests.

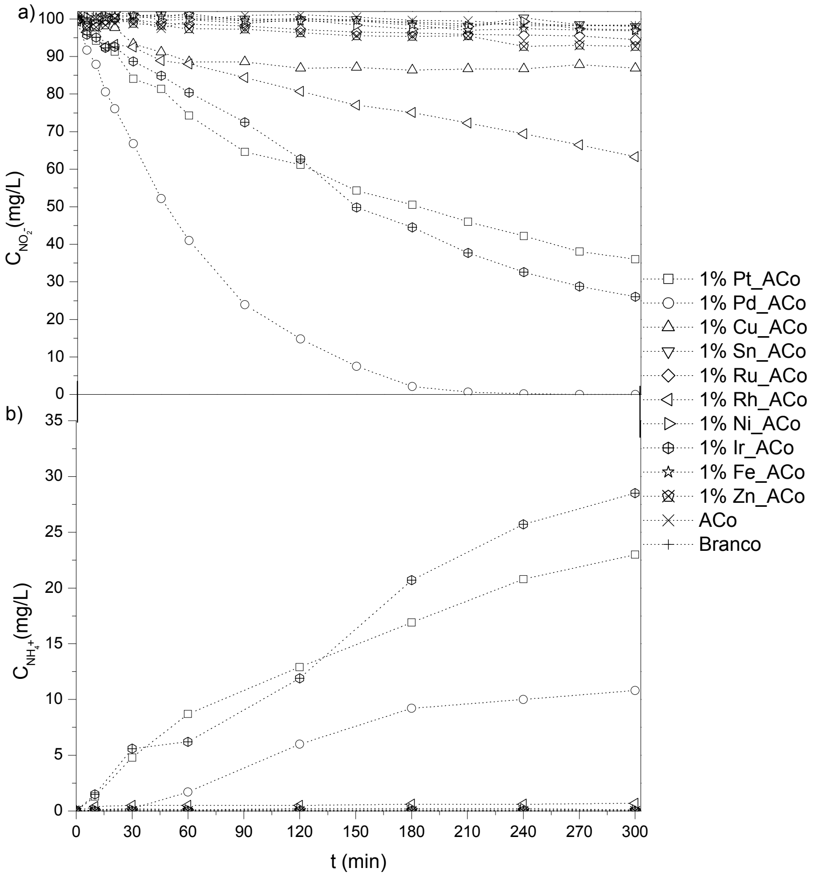

Figure 2.2 a) NO_2^- and b) NH_4^+ concentrations as a function of time during nitrite reduction in the presence of monometallic catalysts (C_{NO2^-i} = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

Figure 2.2 a) shows the results obtained for the reduction of nitrites over monometallic catalysts and Figure 2.2 b) presents the corresponding evolution of ammonium concentration during the reaction. Contrary to the reduction of nitrate, nitrite is rapidly reduced in the presence of some of the monometallic catalysts (Figure 2.2 a)). The conversions attained are quite different depending on the supported metal. The order of conversions in nitrite reduction is the following: Pd >>

Ir > Pt >> Rh >> Cu > Zn ≈ Ru, corresponding to values after 5 h of 100, 74, 64, 37, 13, 7 and 5%, respectively. On the other hand, Fe, Ni and Sn are practically inactive, at least under the experimental conditions studied. Copper presents some catalytic activity but the catalyst was completely deactivated after about 2 h. Significant concentrations of ammonium were measured only in the experiments with the three most active catalysts (Pd, Ir and Pt).

Figure 2.3 shows the evolution of nitrogen selectivities for the monometallic catalysts studied. As stated before, Pd is the most efficient metal for nitrite reduction; moreover, it is also more selective than Ir and Pt for the transformation of nitrite into nitrogen. These two catalysts give rise to a not very different nitrite conversion, but a lower ammonium formation is observed for the Pt catalyst (Figure 2.2 b)). In fact, Ir is the less selective towards nitrogen among the catalysts studied. For example, for a nitrite conversion of 50%, the selectivities into nitrogen are the following: ~95% for Pd, ~40% for Pt and ~10% for Ir. Cu and Zn catalysts present 100% selectivity into nitrogen from the beginning of the reaction but, as mentioned before, these catalysts are only marginally active. Ru and Rh catalysts show a similar trend in the selectivities; however, the conversion reached is much lower for Ru.

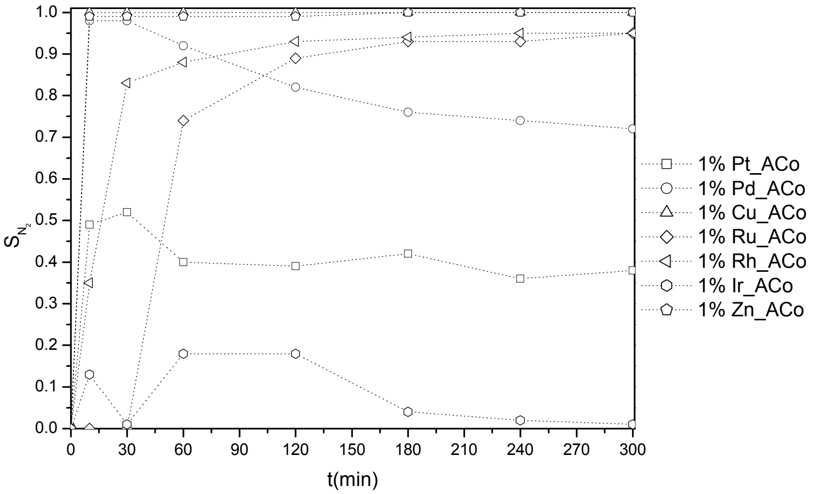

Figure 2.3 N_2 selectivities as a function of time during nitrite reduction in the presence of monometallic catalysts ($C_{NO_2^-\,i}$ = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

The results obtained are not in total agreement with those obtained by Horold et al. [24] in the screening of several metal catalysts for nitrite reduction. They observed that platinum supported on carbon was more active than palladium supported on alumina; iridium and rhodium catalysts supported on alumina reduced completely nitrite into ammonia; and only palladium was suitable for a selective nitrite reduction towards nitrogen. In the present work, it was observed that palladium is the most active catalyst, platinum and iridium present intermediate activities, but iridium is the most selective into ammonium, and rhodium is highly selective into nitrogen. The other catalysts tested are not suitable for practical purposes.

Considering that the same amount of metal was used in all the catalysts, their different performances should be related to the chemical nature of the metal and/or metallic surface area. It is assumed that the nitrite reduction involves the H_2 chemisorption on the metal in one of its mechanism steps [3,25]. Therefore, the results can be rationalized according to the Sabatier principle, which states that metals that form a medium-strength bond with hydrogen are expected to be particularly catalytically active. A qualitative assessment based on the classification of Bond [26] for the H_2 chemisorption on metals (nil for Sn and Zn, weak for Cu, moderate for the noble metals Rh, Pd, Pt and Ir, and strong for Ni, Ru and Fe), already points out for the expected good performance of the noble metals tested.

The metallic dispersion obtained (see Table 2.1) can be explained by the calcinations and reduction temperatures used. In spite of the different TPR profiles obtained for the catalysts tested (results not shown), for comparative purposes, all of them were calcined and reduced at the same temperature (400 ºC). This temperature may be too high to guarantee a good metal dispersion in some of the catalysts. Therefore, the low dispersions obtained seem to be caused by the high temperatures used in the preparation stage, and a trend in the increasing of the dispersion with the increasing of the melting point of the metal was observed. In order to have a quantitative justification for the nitrite reduction, the average activity obtained considering the first 4 h of reaction (expressed as mol of nitrite converted per hour and per mol of accessible metal atoms) as a function of the hydrogen chemisorption energy per atom, obtained from Norskov et al. [27] was calculated. These results (Table 2.3) shows that the maximum catalytic activity is achieved, as expected, at intermediate strength of chemisorptions (Pd, Pt, Ir and Rh); if the reactant is strongly adsorbed (e.g. Ni), the metal is inactive; and if it is weakly adsorbed (e.g. Cu) the catalytic activity is minimal.

Table 2.3 Activity for nitrite reduction over monometallic catalysts as a function of the hydrogen chemisorption energy per atom of metal.

Metal	**ΔE_H (eV)**	**Activity (mol NO_2^- converted/ (mol accessible metal)*h))**
Ni	-0.51	0
Pd	-0.38	441
Rh	-0.34	27
Pt	-0.33	76
Ir	-0.21	35
Cu	-0.05	≈ 0

2.3.2 Bimetallic catalysts

The monometallic Pd, Pt, Rh and Ir catalysts are not able to reduce nitrates; the presence of a second metal is mandatory to attain significant conversions. Most of the work in the area of catalytic nitrate reduction has been done using Pd-Cu bimetallic catalysts; also Pd-Sn and Pt-Cu on different supports, mainly alumina, have been considered [1-4,6-8,17-19]. A few investigations have been reported for other metallic pairs [15,20,22,28-31]. Therefore, we decided to study systematically the nitrate reduction in the presence of a larger set of bimetallic catalysts (Pd-Cu, Pt-Cu, Rh-Cu, Ru-Cu, Pd-Ir, Pd-Sn, Pd-Fe, Pd-Ni, Pd-Zn, Ir-Cu, Rh-Sn, Pt-Sn and Pt-Fe) supported on activated carbon, with 1%wt of each metal, in order to select the most promising systems. The nitrate conversions attained were used to characterize the catalysts efficiencies (Figure 2.4 a)). Figure 2.4 b) and c) show, respectively, the nitrite and ammonium formed during the reaction.

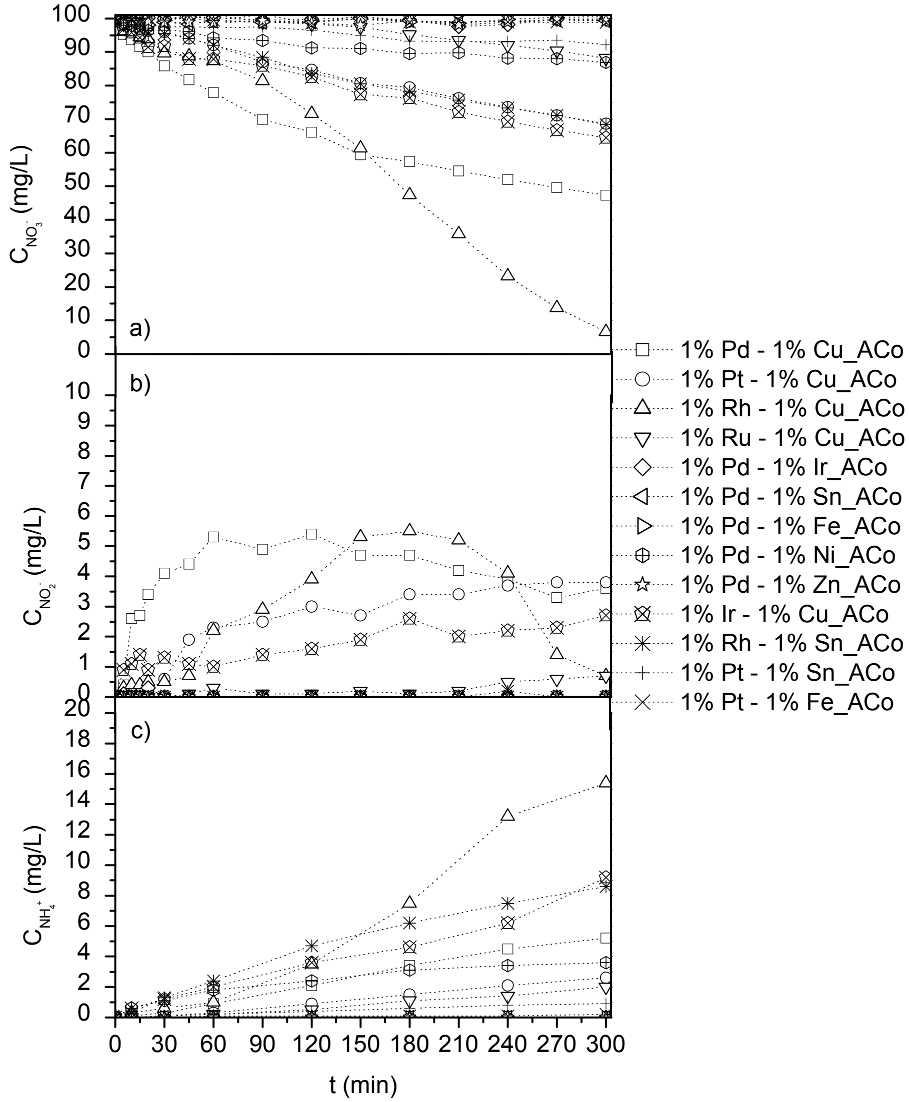

Figure 2.4 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of bimetallic catalysts ($C_{NO_3^- i}$ = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

The reduction of nitrate proceeds by a pathway involving consecutive and competitive reactions. Actually, the concentration of ammonium increases gradually with nitrate conversion for all the catalysts (Figure 2.4 c)). A similar trend is observed for the evolution of nitrogen. On the contrary, nitrite acts as an intermediate, since the respective concentration goes through a maximum (Figure 2.4 b)).

Figure 2.4 a) shows that the order of efficiencies for the nitrate reduction after 5 h of reaction in the presence of bimetallic catalysts is the following: Rh-Cu >> Pd-Cu >> Ir-Cu ≥ Pt-Cu ≈ Rh-Sn >> Pd-Ni > Ru-Cu ≥ Pt-Sn. Additionally, it is observed that the bimetallic catalysts Pd-Ir, Pd-Sn, Pd-Fe, Pd-Zn and Pt-Fe are inactive under the conditions used in this work, and they will not be further discussed. Several investigations have reported that Pd-Sn may be effective for this reaction [8,16,17,19]; this was not verified in our study, probably because higher contents and/or dispersions of the active phases would be necessary.

Figure 2.5 a) and b) show respectively the calculated ammonium and nitrogen selectivities as a function of time for the bimetallic catalysts studied.

The highest conversion of nitrate was obtained with the Rh-Cu catalyst, although for short reaction times (less than 2.5 h) the Pd-Cu catalyst was the most efficient. However, the Rh-Cu catalyst has the disadvantage of being only moderately selective towards nitrogen; additionally, significant amounts of ammonium are obtained. As mentioned before, the Pd-Cu catalyst is more efficient than the Pt-Cu catalyst, but ammonium and nitrogen selectivities are similar for both, at least for reaction times > 1 h (Figure 2.5 a) and b)). A similar behaviour in the reduction of nitrate was observed for Pt-Cu and Rh-Sn catalysts, being the corresponding efficiencies slightly lower than that associated to the Ir-Cu catalyst. However, Pt-Cu catalyst is much more selective towards nitrogen than Ir-Cu and Rh-Sn. The Ir-Cu and, principally, the Rh-Sn catalysts are highly selective into ammonium (an undesired by-product) in all the conversion range. For example, for a nitrate conversion of 30%, the selectivities into nitrogen of the Pd-Cu, Pt-Cu, Rh-Cu, Ir-Cu and Rh-Sn catalysts are, approximately, 55%, 55%, 40% 20% and 5%, respectively. The bimetallic Pd-Ni catalyst can promote the reduction of nitrate but the degradation rate is very slow; moreover, it presents an ammonium selectivity of almost 100%. Some activity was observed for the Ru-Cu catalyst, but the conversion only starts 90 min after the beginning of the reaction, which is a behaviour similar to the monometallic Ru catalyst (cf. Figure 2.1 a)). Finally, no nitrite was measured and a high selectivity towards nitrogen was determined for the Pt-Sn catalyst, but unfortunately the conversion of nitrate is not significant for practical application.

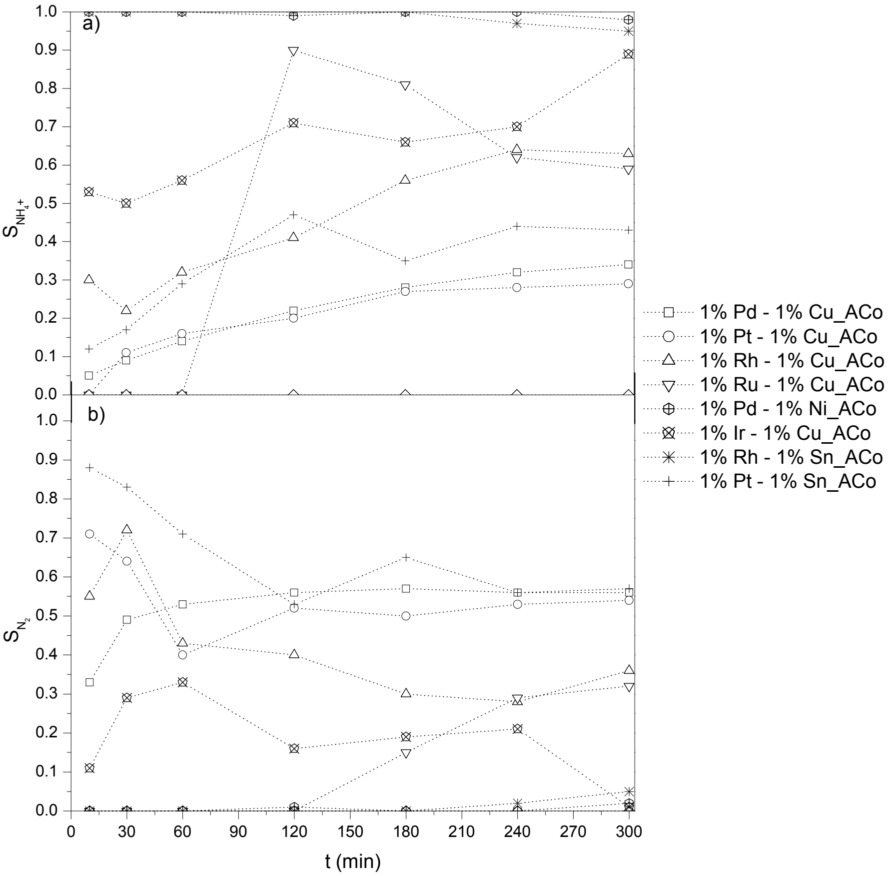

Figure 2.5 a) NH_4^+ and b) N_2 selectivities as a function of time during nitrate conversion in the presence of bimetallic catalysts ($C_{NO_3^- i}$ = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H_2} = 100 Ncm^3/min, Q_{CO_2} = 100 Ncm^3/min, T = 25 ºC).

Once again, the results obtained are not in total agreement with those obtained by Horold et al. [24], where alumina was used as support and only Pd was tested as noble metal. They observed a low nitrate removal and high ammonium formation when iron, cobalt or platinum were used as promoter metal; the Pd-Ni catalyst presented a high activity but reduced the nitrate quantitatively to ammonium; the Pd-Ag catalyst showed a comparable activity and considerable formation of ammonium; and the Pd-Cu catalyst had the highest activity and the lowest formation of ammonium. In the present study, it was observed that the Pd-Fe catalyst is inactive, the Pd-Ni catalyst reduces nitrate very slowly but also presents high ammonium selectivity, and Pd-Cu also presents a high selectivity into nitrogen.

An important feature is that among the Pd catalysts the combination with copper is the best, which is in line with the literature, followed by the catalyst with nickel, but in this case with a much lower activity. The Pd based bimetallic catalysts containing iridium, tin, iron or zinc are inactive, under the tested conditions. According to Gauthard et al. [15], the promoting effect of the second metal is related to their ability to reduce nitrate according to a redox reaction. Among the Pt catalysts tested, the combination with copper is the most efficient, followed by the Pt-Sn, which has only a residual activity. Considering the performance of the promoter metal, copper seems to be the most effective, which is in agreement with the literature [1,3,11,13], followed by tin. In addition, for the catalysts with tin, the highest conversion is obtained for that containing Rh.

2.4 Conclusions

To the best of our knowledge, this was the first time that an extensive evaluation of the most effective metallic catalysts supported on activated carbon for the reduction of nitrite and nitrate was carried out. According to the experimental results, the following main conclusions can be drawn:

1. The monometallic catalysts tested are inactive or practically inactive (Ru) for nitrate reduction.
2. Nitrite was shown to be reduced in the presence of monometallic catalysts, preferably Pd, although other noble metals such as Ir, Pt and Rh also presented significant activities, but they are generally less selective into nitrogen (the exception is Rh). A relationship between the activity for nitrite reduction over monometallic catalysts and the hydrogen chemisorption energy per atom was found.
3. Considering the bimetallic catalysts, the Rh-Cu catalyst shows the highest efficiency for nitrate reduction; however, a large amount of ammonium is produced. The Pd-Cu catalyst gives rise to higher conversions than Pt-Cu catalyst, although both catalysts present similar selectivities into nitrogen. The systems Pd-Ir, Pd-Sn, Pd-Fe, Pd-Zn and Pt-Fe are inactive for the reduction of nitrate, under the conditions studied.
4. Among the catalyst tested, activated carbon supported Pd-Cu catalyst is the most promising when both conversion and selectivity towards nitrogen are considered. However, considering that catalysts composition was not

optimised, also the pairs Rh-Cu, Pt-Cu and Ir-Cu supported on activated carbon are under further investigation.

Acknowledgments

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Chapter 3

3 Bimetallic catalysts supported on activated carbon for the nitrate reduction in water: optimization of catalysts composition[1]

The activities and selectivities of four pairs of bimetallic catalysts (Pd-Cu, Pt-Cu, Rh-Cu and Ir-Cu) supported on activated carbon were studied in order to optimize the metals composition for the reduction of nitrate in water with hydrogen. The catalytic tests were carried out in a semi-batch reactor, working at room temperature and pressure. The activity of the catalysts is quite different depending on the copper content. The maximum activity for the catalysts with 1% of the noble metal was obtained for 1%Rh-0.6%Cu, 1%Pd-0.6%Cu, 1%Pt-0.3%Cu and 1%Ir-0.3%Cu, with nitrate conversions after 5 h of reaction of 98%, 63%, 56%, and 55%, respectively. All these weight compositions correspond to an atomic ratio noble metal/copper close to 1. With the exception of the pair Ir-Cu, where the selectivity to ammonium is almost independent of the metals composition, for all the other cases it increases with the atomic copper content up to around 75%. The pair Rh-Cu was the most active among the bimetallic catalysts tested; however, significant amounts of ammonium are obtained. The nitrate conversions for the pairs Ir-Cu and Pt-Cu are similar but the former presents higher selectivities to ammonium. The pair Pd-Cu is the most selective in the transformation of nitrate to nitrogen.

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3.1 Introduction

The presence of nitrates in water is presently a common problem across Europe. Nitrate anion is potentially harmful because it can be transformed into nitrite in the human body, which can cause blue baby syndrome, and it is also a precursor of the carcinogenic nitrosamines [1-4]. For these reasons, the European Community limit values for nitrate, nitrite and ammonium concentrations in drinking water are, respectively, 50, 0.5 and 0.5 mg/L. However, for the discharge of wastewater the limits are 50 and 10 mg/L for nitrate and ammonium concentrations, respectively. The catalytic reduction is one of the most promising alternatives for nitrates removal without the drawbacks of the conventional methods [2,5-9]. This process consists in the reduction of nitrate to nitrogen over metallic catalysts in the presence of a reducing agent [1]. Nitrite as intermediate and ammonium as by-product are considered the major limitations of this process [9,10]. Studies of nitrate reduction have demonstrated that bimetallic catalysts are more efficient in comparison to monometallic. The noble metals Pd or Pt combined with the transition metals Cu or Sn, on different supports (alumina [5,8-15], silica [14], titania [16,17], activated carbon [1,3,4,18,19], polymers [20,21]) have been extensively studied and have been considered as the most actives and selectives for the reduction of nitrates but are still inadequate in terms of selectivity towards nitrogen. Moreover, additional studies are still necessary, mainly to optimize the formulation of the catalysts in order to develop an effective catalytic process for purifying water streams.

The catalytic properties of Pd-Cu catalysts were found to be sensitive to the ratio of these two metals. Both the nitrate removal activity and selectivity have a maximum at a specific palladium copper ratio, which can differ slightly with the support material and the preparation method used [5,22]. Epron et al. [23] demonstrated that the highest activity for the nitrate reduction is reached when 3%Pt-1%Cu and 1.7%Pd-0.5%Cu (weight percent) supported on alumina are used. Barrabés et al. [3], using activated carbon as a support, obtained 1%Pt-0.3%Cu and 1%Pd-1%Cu (weight percent) as the optimal metal proportions. Matatov-Meytal and Sheintuch [18] found that the 2%Pd-0.6%Cu (weight percent) is the optimal content when activated cloth is used as a support. These studies demonstrate that the selection of the support is important in this process, since the catalysts activity and selectivity are affected by the interaction between the active phase and the support.

Carbon materials have been used for a long time in heterogeneous catalysis, because they can act directly as catalysts or, more important, they can satisfy most of the desirable properties required for a suitable support: inertness; stability under reaction and regeneration conditions; adequate mechanical properties; possibility to adapt their physical forms for a given reactor; and high surface area and porosity [24]. In addition, they allow easy recovery of the noble metals just by a simple burning process.

In a previous work [25] (see Chapter 2) it was found that Pd-Cu, Pt-Cu, Rh-Cu and Ir-Cu were the most promising systems for nitrate reduction with hydrogen using activated carbon as support. Therefore, in this work, those systems were studied in detail in order to establish their best formulation. Although several results on the area of catalytic nitrate reduction have been described in the literature, principally using Pd-Cu but also Pd-Sn and Pt-Cu catalysts [1-3,6,14], as far as we know, only a recent report from other group of authors was presented using Rh-Cu, but supported on alumina [26], and there are no additional studies using the pair Ir-Cu. Our main goal is to establish a relationship between the ratio noble metal/copper and the activity and selectivity of the catalysts supported on activated carbon for the reduction of nitrates to nitrogen. This study has the additional advantage of comparing in a systematic way four different pairs noble metal/Cu, using the same support and experimental conditions, which allows a comprehensive comparison of the different noble metals used.

3.2 Experimental

3.2.1 Catalysts preparation

The active metals were supported on a commercial activated carbon NORIT GAC 1240 PLUS (ACo) ground to a particle diameter between 0.1 and 0.3 mm. According to the supplier specifications, it is an acid washed granular activated carbon, produced by steam activation. It has a neutral pH and offers good properties for water applications. The catalysts were prepared by incipient wetness co-impregnation, from aqueous solutions of the corresponding metal salts (H_2PtCl_6, $PdCl_2$, $Cu(NO_3)_2$, $RhCl_3$, $(NH_4)_3IrCl_6$). The amount of noble metal was maintained constant at 1%wt and the Cu loadings tested for all systems were 0.1, 0.3, 0.6 or 1%wt. The composition corresponding to 2%wt of noble metal and 1%wt of Cu was also evaluated. In addition, for the pairs Pd-Cu and Rh-Cu the compositions 1%wt of noble metal and 2% or 5%wt of Cu were also tested. The samples were dried at 100 ºC for 24 h, calcined under a nitrogen flow at 400 ºC for 1 h, and finally reduced at 400 ºC in hydrogen flow for 3 h.

3.2.2 Catalysts characterization

Selected catalysts were characterized using different techniques: H_2 chemisorption, N_2 adsorption at -196 ºC, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The chemisorption of H_2 was carried out at 30 ºC and atmospheric pressure in an Altamira Instruments AMI-200 apparatus, using the pulse method. Pulses of 58 μL (from a calibrated loop) were successively injected in the carrier gas (25 Ncm^3/min of Ar), which passes through a catalyst bed (150 mg), until saturation of the catalyst surface. The non-adsorbed hydrogen is measured with an online thermal conductivity detector. The textural characterization of the materials was based on the corresponding N_2 adsorption isotherms, determined at -196 ºC with a Coulter Omnisorp 100 CX apparatus. BET surface areas (S_{BET}) were calculated, as well as the micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) according to the t-method. A type IV deviation was noticed when the N_2 adsorption data were analysed by the Dubinin method; the micropore volumes associated to small (W_{01}) and large micropores (W_{02}) were determined, as well as the average small micropores width (L_1). XRD spectra of the catalysts were recorded in the range 2θ = 20–90º on a Philips X'Pert MPD diffractometer (Cu-Ka = 0.15406 nm). TEM micrographs were obtained using a LEO 906E microscope operating with an accelerating voltage of 120 kV.

3.2.3 Catalysts evaluation

The catalytic tests were carried out in a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure, and using hydrogen as reducing agent. Initially, 790 mL of deionised water and 400 mg of catalyst were fed into the reactor, the magnetic stirrer was adjusted to 700 rpm and the gas mixture of carbon dioxide and hydrogen (H_2+CO_2 (1:1), flow rate = 200 Ncm^3/min) was passed through the reactor during 15 min to remove air; CO_2 acts as pH buffer (pH = 5.5). Then, 10 mL of a nitrate solution, prepared from $NaNO_3$, was added to the reactor, in order to obtain an initial NO_3^- concentration equal to 100 mg/L. Preliminary studies were carried out varying the stirring rate and it was checked that under the selected conditions used there was no external diffusional limitations.

Small samples were taken from the reactor for quantification of nitrate, nitrite and ammonium concentrations after defined periods. Nitrate and nitrite ions were simultaneously determined by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was a Hamilton PRP-X100 column (150 mm x 4.1 mm) working at room temperature, under isocratic conditions. The mobile phase was a solution of 0.1 M NaCl:CH_3OH (45:55). Ammonium ions were determined by potentiometry using a convenient selective electrode. pH values were also measured.

Selected experiments were carried out in duplicate and the results were founded to be reproducible with a maximum error of ca 2.5% relatively to the conversion average.

The selectivities (also named relative yields) into nitrite, ammonium and nitrogen were calculated as:

$$S_{NO_2^-} = \frac{n_{NO_2^-}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{3.1}$$

$$S_{NH_4^+} = \frac{n_{NH_4^+}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{3.2}$$

$$S_{N_2} = \frac{2 * n_{N_2}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{3.3}$$

where $n_{NO_3^-{}_i}$ is the initial amount of nitrate (mmol) and $n_{NO_3^-}$, $n_{NO_2^-}$, $n_{NH_4^+}$ and n_{N_2} are the amounts of the respective species (mmol) at time t (min). The amount of nitrogen was calculated by a mole balance, assuming that the amount of NO_x produced is negligible [1,27].

3.3 Results and Discussion

3.3.1 Catalysts characterization

3.3.1.1 Hydrogen chemisorption

From these experiments it was possible to obtain the metal dispersion for the monometallic catalyst (see Table 2.1 in chapter 2). For the bimetallic catalysts no hydrogen chemisorption was noticed, which may be an indication that some interaction exists between the noble metal and copper (forming an alloy) or/and copper is covering most of the noble metal strongly limiting hydrogen chemisorption.

3.3.1.2 Textural properties

Textural properties obtained from the N_2 adsorption isotherms at -196 ºC for the activated carbon and for the catalysts with 2% of Pd or Pt are presented in Table 3.1.

Table 3.1 Textural characterization of the activated carbon (ACo) and some of the catalysts.

Sample	**S_{BET} (m^2/g)**	**S_{meso} [a] (m^2/g)**	**V_{micro} [a] (cm^3/g)**	**W_{01} [b] (cm^3/g)**	**W_{02} [b] (cm^3/g)**	**L_1 [c] (nm)**
ACo	869	97	0.318	0.290	0.035	0.93
2%Pd-1%Cu_ACo	870	90	0.330	0.295	0.037	0.93
2%Pt-1%Cu_ACo	848	90	0.313	0.287	0.032	0.94

[a] Micropore volume (V_{micro}) and mesopore surface area (S_{meso}) calculated by the t-method.

[b] W_{01} and W_{02} are the micropore volumes associated to small and large micropores, respectively.

[c] Average small micropores width (assuming split-shaped geometry).

Table 3.1 shows that the BET surface area of the support is 869 m^2/g and it can be observed that for the samples 2%Pd-1%Cu and 2%Pt-1%Cu the textural parameters remained practically unchanged compared to the unloaded carbon. Therefore, it was assumed that the textural properties of the supported metal catalysts are not significantly different from those of the original activated carbon.

3.3.1.3 TEM

TEM micrographs were collected in order to get information about the metal particles size distributions.

Selected TEM micrographs of the Pd-Cu catalysts are shown in Figure 3.1. The metals are well dispersed on the support and the mode diameter (the most frequent value) is 3 nm for the catalyst 1%Pd-0.1%Cu, 5 nm for the catalysts 1%Pd-0.3 and 0.6%Cu and 4 nm for the remaining Pd-Cu samples. Although most of the particles diameter is in the range of 3 to 7 nm, some larger particles are also presented as can be seen in the micrographs. Barrabés et al. [3], varying the composition of Pd-Cu catalysts supported on a different type of activated carbon, did not observe significant differences in the metal particle sizes. Contrarily, Matatov-Meytal and Sheintuch [18] reported that an increasing in the Cu:Pd atomic ratio led to larger metal particles supported on an activated carbon cloth.

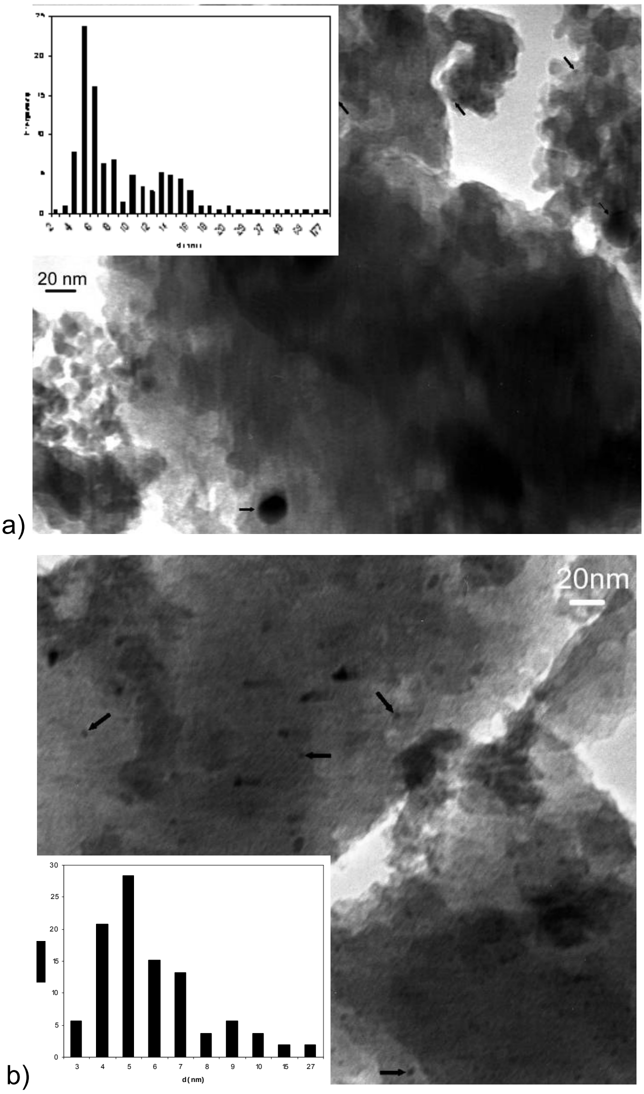
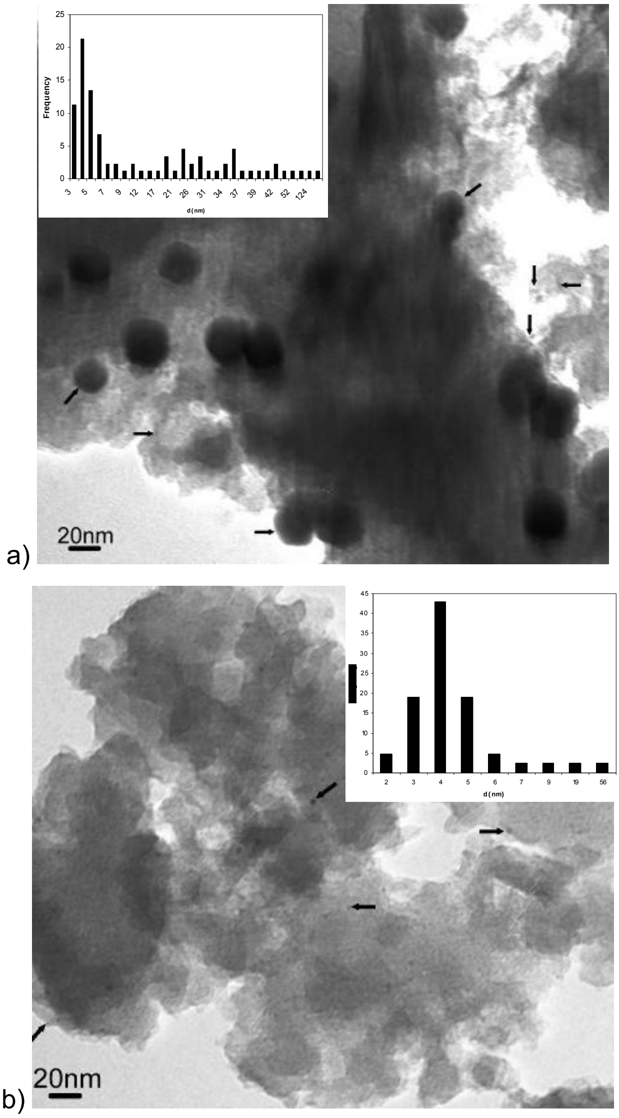


Figure 3.1 TEM micrographs of a) 1%Pd-0.3%Cu_ACo and b) 1%Pd-0.6%Cu_ACo catalysts.

For the pairs Pt-Cu, Rh-Cu and Ir-Cu, TEM micrographs were obtained for the most active catalysts and for the catalysts with higher amount of metals. TEM micrographs of the most active catalysts are shown in Figure 3.2.



c)

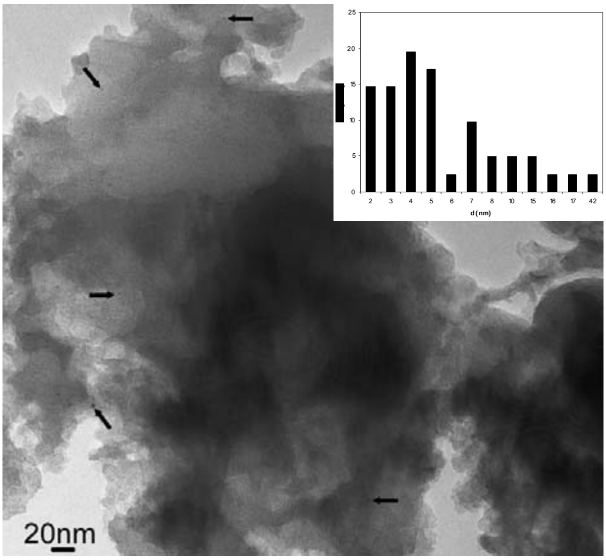


Figure 3.2 TEM micrographs of a) 1%Pt-0.3%Cu_ACo, b) 1%Rh-0.6%Cu_ACo and c) 1%Ir-0.3%Cu_ACo catalysts.

It can be observed that there are no significant differences in the metal particles sizes, despite the difference in the metals amount. In general, the metal particles are well dispersed. The pair Pt-Cu presents the largest particles, although the majority is in the range 4 - 6 nm. For the pairs Rh-Cu and Ir-Cu most of the particles have a diameter between 3 and 5 nm. With exception of the catalyst 2%Ir-1%Cu, which presents a mode diameter of 5 nm (results not shown), all the others catalysts present a mode diameter of 4 nm.

3.3.1.4 XRD

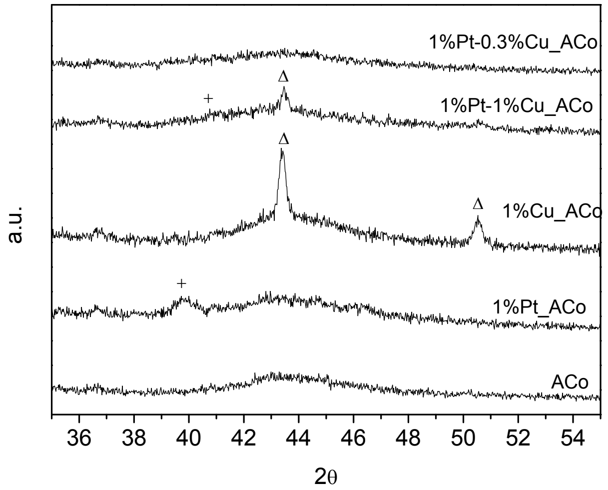


Figure 3.3 XRD spectra of bimetallic Pt-Cu and monometallic Pt and Cu catalysts. Copper (Δ), platinum (+).

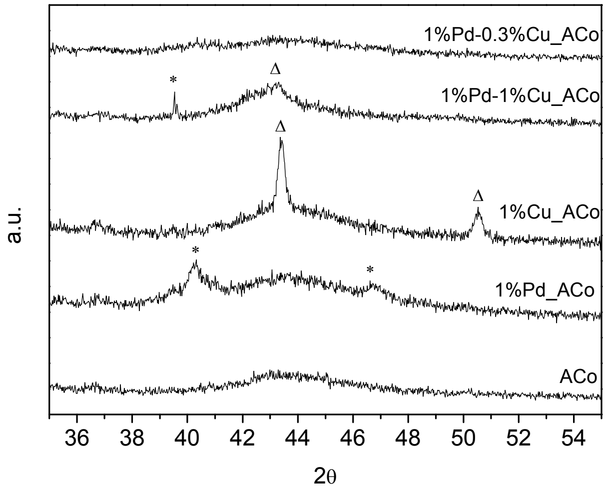


Figure 3.4 XRD spectra of bimetallic Pd-Cu and monometallic Pd and Cu catalysts. Copper (Δ), palladium (✶).

Selected catalysts were analyzed by XRD. XRD spectra of bimetallic catalysts (Figure 3.3 and Figure 3.4) do not show any intense peak of both metals, which could be due to the low amount of metal loaded or could be taken as an indication of a good metal dispersion on the support. TEM images support this last conclusion. The characteristic peaks of the metals can be observed in the XRD spectra of the monometallic catalysts. In addition, in the XRD spectra of the bimetallic catalysts, the peaks of Pd and Pt, when visible, are slightly displaced to the right, which could be indicative of the formation of alloys.

3.3.2 Catalytic activity and selectivity

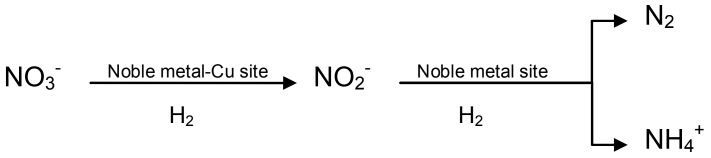
The four catalytic systems Pd-Cu, Pt-Cu, Rh-Cu and Ir-Cu were evaluated maintaining constant the content of noble metal at 1% wt and varying the copper content at 0.1, 0.3, 0.6 or 1%wt. The composition with 2%wt of noble metal and 1%wt of Cu was also checked for all the systems studied. For the pairs Pd-Cu and Rh-Cu the compositions with 1%wt of noble metal and 2% or 5%wt of Cu were also analyzed. It was found that the catalytic activity and the selectivities are quite different depending on the catalyst composition. All the monometallic catalysts tested are inactive for the nitrate reduction; therefore the presence of bimetallic catalyst is mandatory to reduce nitrate. Nitrite is a reaction intermediate; therefore, its concentration curves generally present a maximum at intermediate reaction times.

3.3.2.1 Pd-Cu catalysts

Figure 3.5 shows the results obtained for the reduction of nitrates over the Pd-Cu catalysts and presents the corresponding evolution of nitrite and ammonium concentrations.

For the catalysts with 1%Pd, there is an increase in the catalytic activity for nitrate reduction with the copper content up to 0.6%wt, which corresponds to an atomic ratio Pd/Cu close to 1, decreasing thereafter. The increase of palladium content to 2%, keeping the copper content at 1%, also increases the nitrate conversion. The order of nitrate conversions after 300 min is the following: 2%Pd-1%Cu > 1%Pd-0.6%Cu > 1%Pd-2%Cu > 1%Pd-1%Cu > 1%Pd-0.3%Cu > 1%Pd-5%Cu >> 1%Pd-0.1%Cu.

As expected, considering the well accepted reaction scheme:



the nitrite concentration goes through a maximum and the ammonium concentration increases with the nitrate conversion. The catalyst 2%Pd-1%Cu presents the highest nitrate conversion; compared to the other catalysts the maximum in the nitrite formation is obtained for shorter reaction times, which means that nitrite is more rapidly converted into ammonium and nitrogen. This is probably related to the content of palladium. Actually, considering that palladium is highly active for nitrite reduction [25] (see chapter 2), increasing its content increases the corresponding removal rate.

Matatov-Meytal and Sheintuch [18] reported that the composition of 2%Pd-0.6%Cu (Cu:Pd atomic ratio ≈ 0.5) is the optimal content when activated cloth was used as a support; nevertheless, this observation is not in agreement with the results obtained by Barrabés et al. [3], for the same metals supported on activated carbon, who have found the optimum composition of 1%Pd-1%Cu (Cu:Pd atomic ratio ≈ 1.7). However, they observed that more than a half of the converted nitrate was transformed into nitrite for this catalyst. Our results demonstrate that with this catalyst the concentrations of nitrite are lower than those obtained with the catalysts Pt-Cu (see section 3.3.2.2.). This is explained by the fact that palladium is more active than platinum for the nitrite reduction [25] (see chapter 2) and therefore the nitrite formed are more rapidly reduced.

Considering that there are no significant differences on the metal particles size supported on the activated carbon (Figure 3.1), the lost of activity with the increase of copper content above 0.6%wt cannot be explained by the increase of the particles size but probably by the atomic arrangement of the active particles on the surface of the catalysts.

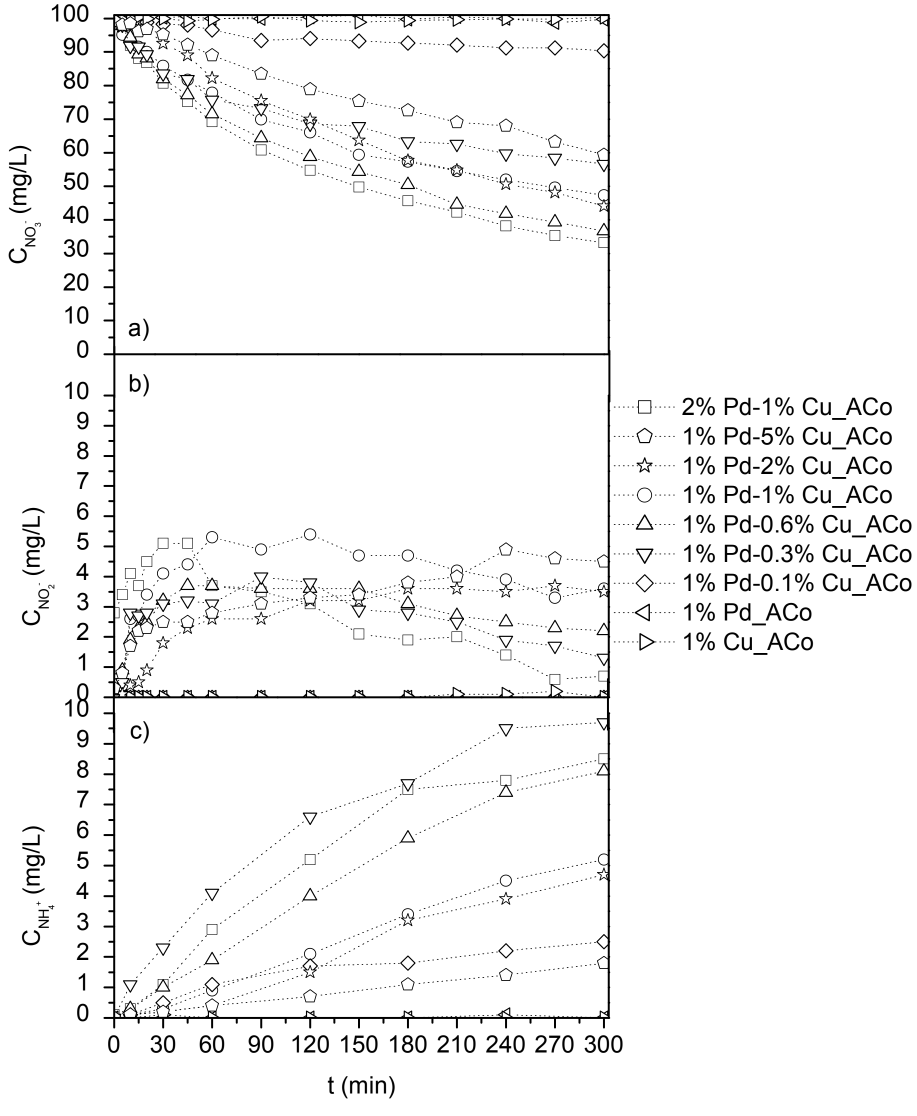


Figure 3.5 NO_3^-, NO_2^- and NH_4^+ concentrations as a function of time during nitrate reduction in the presence of Pd-Cu catalysts ($C_{NO_3^- i}$ = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

Table 3.2 shows that the selectivity to nitrogen has a tendency to increase with the increase of copper content. The most selective catalysts to nitrogen are the 1%Pd-5%Cu after 300 min of reaction and the 1%Pd-2%Cu for 20% of nitrate conversion. The catalyst is more active when the metals are in the same atomic proportion (1%Pd-0.6%Cu); however, the catalyst is more selective to nitrogen when the atomic copper content is higher than the atomic palladium content. Yoshinaga et al. [1], suggested that isolated Pd atoms are active sites for the ammonium formation. In fact Table 3.2 shows that ammonium selectivity increases with the relative amount of palladium content. Moreover, the catalyst 1%Pd-0.1%Cu is highly selective to ammonium, despite presenting small nitrate conversion (cf Figure 3.1). It can be concluded that the selectivity to nitrogen is highly dependent on the copper content. It is well established that nitrite reduction occurs mainly on the noble monometallic sites [5,23], and according to our results it can be considered that there are more isolated particles of the noble metal when the relative quantity of copper is lower. When the noble metal is present in higher amounts than copper, it is expected that the surface of free noble metal is also high and, as the noble metal is very active for hydrogenation reactions, the nitrite molecules are deeply hydrogenated (producing ammonium). When the atomic copper content is close or higher than 50% the noble metal and copper particles are probably not isolated but intercalated or superimposed favouring that the surface nitrogenated intermediates resulting from the nitrate hydrogenation can be combined producing nitrogen molecules instead of being deeply hydrogenated into ammonium.

Table 3.2 NO_3^- conversion and selectivities into NO_2^-, NH_4^+ and N_2 after 300 min of reaction and selectivities for 20% of nitrate conversion in the presence of Pd-Cu catalysts.

		t = 300 min				$X_{NO_3^-} = 20\%$		
Catalyst (wt%)	**Cu % atomic**	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Pd_ACo	0	0.00	-	-	-	-	-	-
1%Cu_ACo	100	0.00	-	-	-	-	-	-
2%Pd-1%Cu_ACo	45.6	0.67	0.01	0.44	0.55	0.35	0.22	0.43
1%Pd-5%Cu_ACo	89.3	0.40	0.15	0.15	0.70	0.22	0.12	0.66
1%Pd-2%Cu_ACo	77.0	0.56	0.08	0.29	0.62	0.19	0.10	0.71
1%Pd-1%Cu_ACo	62.6	0.52	0.09	0.34	0.56	0.35	0.13	0.52
1%Pd-0.6%Cu_ACo	50.1	0.63	0.05	0.44	0.52	0.23	0.19	0.58
1%Pd-0.3%Cu_ACo	33.4	0.44	0.04	0.74	0.22	0.18	0.52	0.30
1%Pd-0.1%Cu_ACo	14.3	0.09	0.00	0.96	0.04	-	-	-

3.3.2.2 Pt-Cu catalysts

Figure 3.6 shows the evolution of nitrate, nitrite and ammonium concentration in the presence of Pt-Cu catalysts. The catalytic activity and the selectivities are quite different depending on the Pt-Cu contents. For the catalysts with 1%Pt there is an increase in the nitrate conversion when copper contents increases until 0.3%, which corresponds to an atomic ratio noble metal/copper close to 1; then a decrease in the conversion was observed for higher amounts of Cu. The catalysts 2%Pt-1%Cu and 1%Pt-0.3%Cu present similar nitrate conversions. The order of nitrate conversions is the following: 1%Pt-0.3%Cu ≈ 2%Pt-1%Cu > 1%Pt-0.6%Cu > 1%Pt-1%Cu ≈ 1%Pt-0.1%Cu. The maximum activity obtained (Cu:Pt atomic ratio ≈ 1) is in agreement with the results reported for the same metals supported on activated carbon by Barrabés et al. [3] and supported on alumina by Epron et al. [23].

The nitrite concentration increases to a certain value, and, after 5 h, is generally higher than that obtained with the pairs Pd-Cu, Rh-Cu and Ir-Cu. This could be related to the fact that Pd and Ir are more active for the nitrite conversion [25] (see chapter 2) than the Pt. On the other hand, the nitrite concentration goes through a maximum in the case of Pd-Cu (cf. Figure 3.5) and Rh-Cu (cf. Figure 3.1) but in the case of Pt-Cu (cf. Figure 3.6) and Ir-Cu (cf. Figure 3.8) the nitrite concentration remains almost constant after a short reaction time.

Table 3.3 shows that the catalyst 1%Pt-1%Cu is the most selective to nitrogen and, for the catalysts with 1%Pt, the selectivity to ammonium decreases with the increase of copper content. This result is different from that obtained by Epron et al. [23], who observed the opposite performance for the same metals supported on alumina. In our opinion, if part of the noble metal is isolated, their atoms are active sites for ammonium formation and it explains the high ammonium selectivity observed for high Pt/Cu ratios as is the case of the catalyst 1%Pt-0.1%Cu. For the samples 1%Pd-1%Cu and 1%Pt-1%Cu the selectivity to nitrogen after 5 h is similar despite the lower nitrate conversion for the pair Pt-Cu.

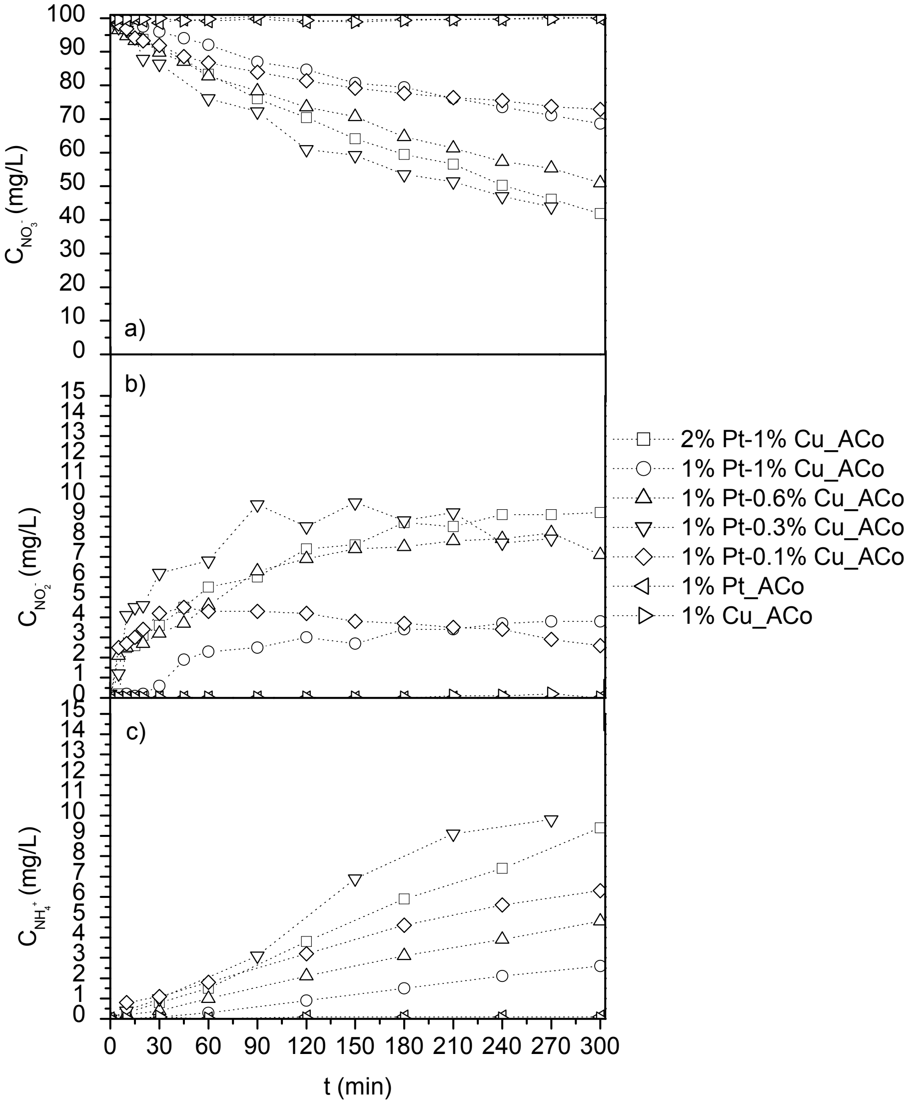


Figure 3.6 NO_3^-, NO_2^- and NH_4^+ concentrations as a function of time during nitrate reduction in the presence of Pt-Cu catalysts ($C_{NO_3^- i}$ = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

Table 3.3 NO_3^- conversion and selectivities into NO_2^-, NH_4^+ and N_2 after 300 min of reaction and selectivities for 20% of nitrate conversion in the presence of Pt-Cu catalysts.

		t = 300 min				$X_{NO_3^-}=20\%$		
Catalyst (wt%)	**Cu % atomic**	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Pt_ACo	0	0.00	-	-	-	-	-	-
1%Cu_ACo	100	0.00	-	-	-	-	-	-
2%Pt-1%Cu_ACo	60.6	0.58	0.21	0.56	0.23	0.42	0.34	0.24
1%Pt-1%Cu_ACo	75.4	0.31	0.17	0.29	0.54	0.23	0.27	0.50
1%Pt-0.6%Cu_ACo	64.8	0.48	0.20	0.34	0.46	0.38	0.23	0.39
1%Pt-0.3%Cu_ACo	47.9	0.56	0.19	0.51	0.30	0.56	0.34	0.10
1%Pt-0.1%Cu_ACo	23.5	0.27	0.13	0.79	0.08	0.28	0.63	0.09

3.3.2.3 Rh-Cu catalysts

Figure 3.7 shows the results for the catalysts containing Rh-Cu. In general, the extent of nitrate reduction is higher with these catalysts than with the other pairs studied. Even the catalyst with 1% Rh and just 0.1% of Cu is very active (X_{NO3^-} = 72%, after 300 min). All the other catalysts with 1%Rh present nitrate conversions between 90 and 98% after five hours of reaction, being the sample 1%Rh-0.6% the most active. The catalyst with 2%Rh-1%Cu provides the highest nitrate conversion. The catalyst 1%Rh-1%Cu presents a different performance compared to the other catalysts. For intermediate times, the nitrate conversion obtained with this catalyst is lower than with the others but, after 210 and 270 min becomes higher than those of samples 1%Rh-0.1%Cu and 1%Rh-0.3%Cu catalysts, respectively. This experiment was repeated and the observed behaviour was confirmed.

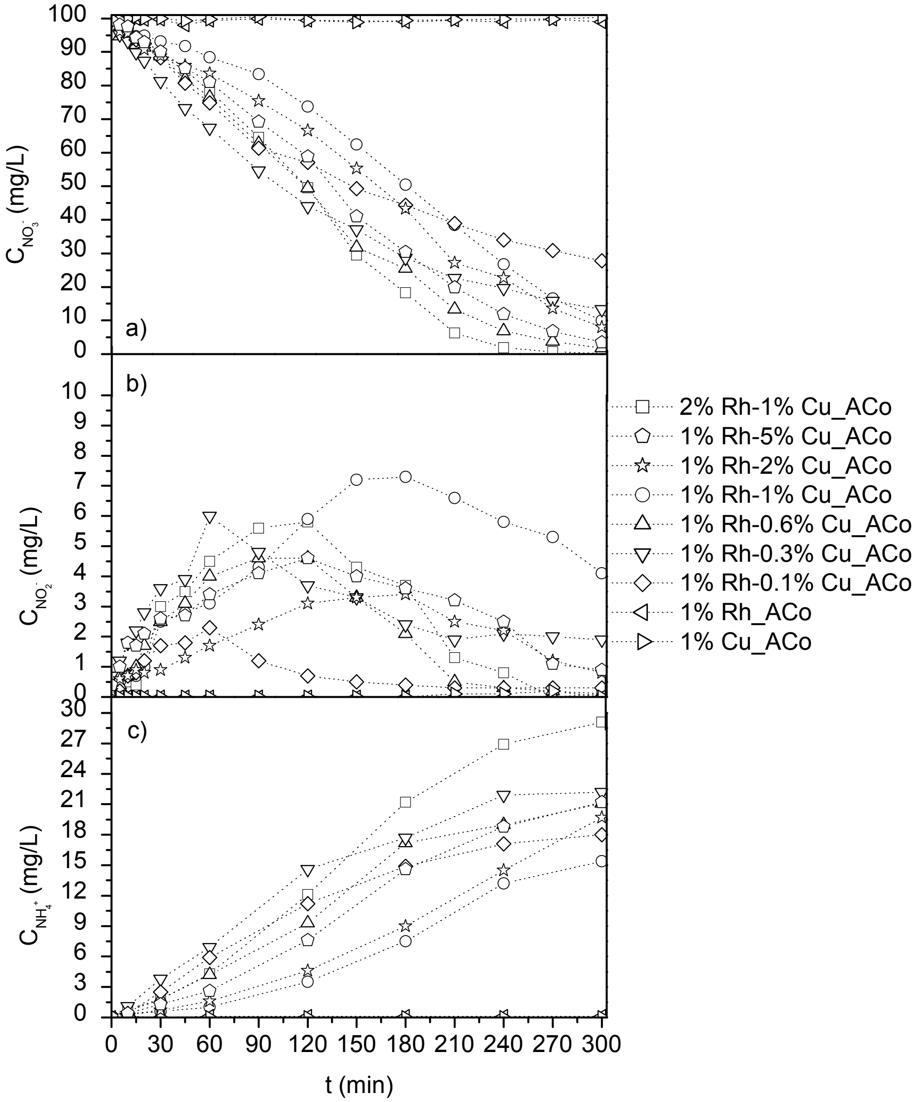


Figure 3.7 NO_3^-, NO_2^- and NH_4^+ concentrations as a function of time during nitrate reduction in the presence of Rh-Cu catalysts ($C_{NO_3^- i}$ = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

The Rh-Cu catalysts are the most active for the nitrate conversion among the catalysts tested, but unfortunately, they originate the highest ammonium concentration. Actually, in Table 3.4 it can be observed that the catalysts Rh-Cu are highly selective to ammonium. The lower selectivity to ammonium was obtained with the catalyst 1%Rh-1%Cu after 300 min of reaction and with the catalyst 1%Rh-2%Cu after 20% of nitrate conversion. As showed in Figure 3.7, the catalyst 1%Rh-0.6%Cu is more active than the catalyst 1%Rh-0.3%Cu; however, the latter is more selective to ammonium. Once again, it can be concluded that the selectivity to nitrogen is highly dependent on the copper content, and as well as observed for the catalysts Pd-Cu and Pt-Cu the highest selectivity to nitrogen is obtained for the catalysts with atomic copper contents higher than 50%. Also as in the previous systems, the highest activity in nitrate reduction is obtained for the catalyst with an atomic ratio noble metal/copper close to 1.

Table 3.4 NO_3^- conversion and selectivities into NO_2^-, NH_4^+ and N_2 after 300 min of reaction and selectivities for 20% of nitrate conversion in the presence of Rh-Cu catalysts.

			t = 300 min				$X_{NO_3^-} = 20\%$		
Catalyst (wt%)	**Cu % atomic**	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Rh_ACo	0	0.00	-	-	-	-	-	-
1%Cu_ACo	100	0.00	-	-	-	-	-	-
2%Rh-1%Cu_ACo	44.7	1.00	0.00	1.00	0.55	0.27	0.65	0.08
1%Rh-5%Cu_ACo	89.0	0.97	0.01	0.76	0.70	0.25	0.49	0.26
1%Rh-2%Cu_ACo	76.4	0.92	0.01	0.74	0.62	0.15	0.39	0.46
1%Rh-1%Cu_ACo	61.8	0.90	0.06	0.59	0.56	0.34	0.40	0.26
1%Rh-0.6%Cu_ACo	49.3	0.98	0.00	0.74	0.52	0.25	0.62	0.13
1%Rh-0.3%Cu_ACo	32.7	0.90	0.03	0.97	0.22	0.26	0.73	0.01
1%Rh-0.1%Cu_ACo	13.9	0.72	0.01	0.86	0.04	0.15	0.80	0.05

3.3.2.4 Ir-Cu catalysts

Figure 3.8 shows the results obtained for the reduction of nitrates over Ir-Cu catalysts as well as the corresponding evolution of nitrite and ammonium concentrations during the reaction. It is observed that the catalytic activity is quite different depending on the Ir-Cu content ratio. As observed for the Pt-Cu catalysts (Figure 3.6) the most active formulation for the Ir-Cu catalysts is that with 0.3% of

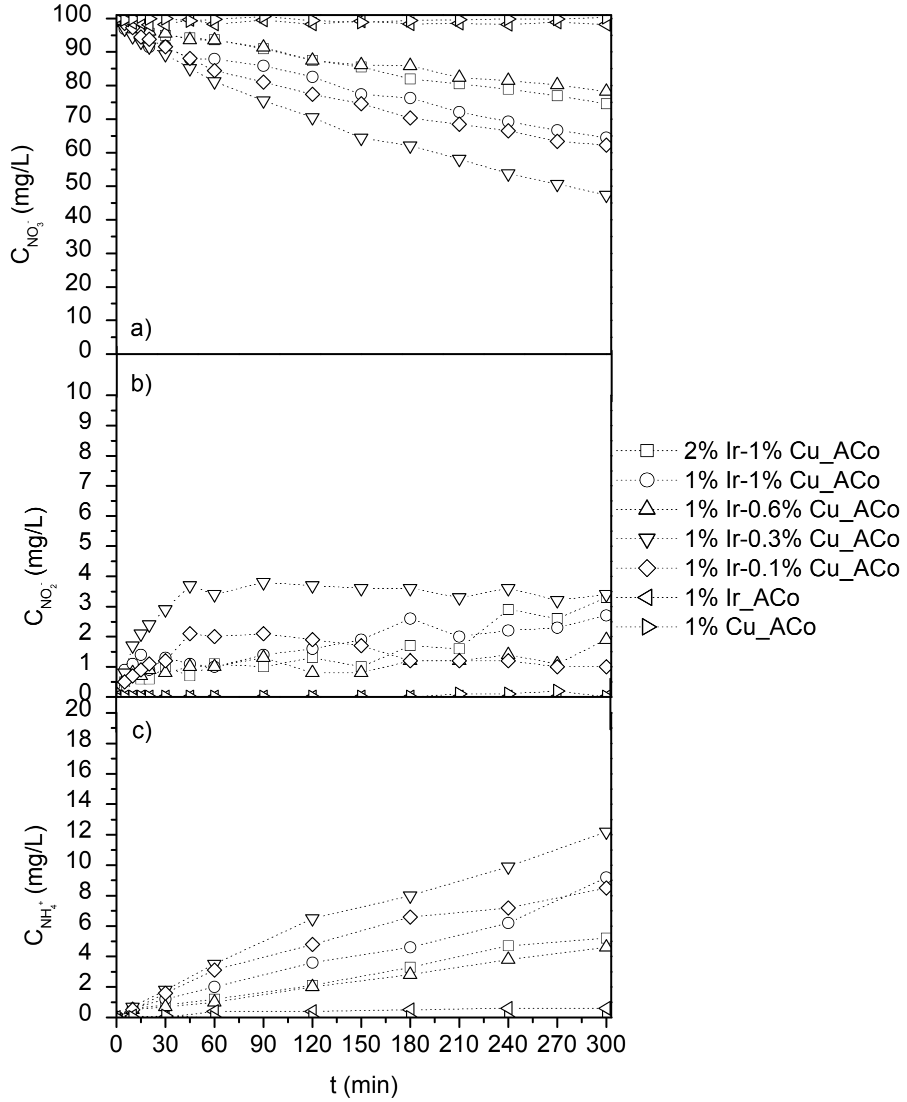


Figure 3.8 NO_3^-, NO_2^- and NH_4^+ concentrations as a function of time during nitrate reduction in the presence of Ir-Cu catalysts (C_{NO3^-i} = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

Cu, which corresponds to an atomic ratio noble metal/copper close to 1. However, in this case, a direct relationship with the metals content cannot be established, because the nitrate conversion obtained does not follow a tendency. The order of nitrate conversions is the following: 1%Ir-0.3%Cu > 1%Ir-0.1%Cu ≥ 1%Ir-1%Cu > 2%Ir-1%Cu ≥ 1%Ir-0.6%Cu. The monometallic catalyst with 1%Ir is practically inactive for the nitrate reduction, since a 2% conversion after 5 h was obtained but only nitrite was detected in the liquid mixture. Figure 3.8 shows that the concentration of nitrite increases as nitrate conversion increases only in the beginning of reaction and thereafter remains almost constant. On the other hand, the concentration of ammonium increases with the nitrate conversion and with reaction time. It was observed previously [25] (see chapter 2) that, after the palladium catalyst, the iridium catalyst is the most active for the nitrite conversion but it was the most selective to ammonium. Probably, this explains the higher NH_4^+ selectivities obtained with the iridium catalysts. Indeed, Table 3.5 shows that the Ir-Cu catalysts are highly selective to ammonium. The catalysts 1%Pt-0.3%Cu and 1%Ir-0.3%Cu (cf. Figure 3.6 and Figure 3.8, respectively) presents similar nitrate conversions after 5 h of reaction; however, it is possible to see in Table 3.5 that the catalyst with Ir is much more selective to ammonium than the catalyst with Pt (see also Table 3.3). It is interesting to note that only for the iridium-containing catalysts the selectivity to ammonium remains almost unchanged for different ratios noble metal/copper (cf. Figure 3.9).

Table 3.5 NO_3^- conversion and selectivities into NO_2^-, NH_4^+ and N_2 after 300 min of reaction and selectivities for 20% of nitrate conversion in the presence of Ir-Cu catalysts.

		t = 300 min				$X_{NO_3^-} = 20\%$		
Catalyst (wt%)	**Cu % atomic**	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Ir_ACo	0	0.02	0.00	1.00	0.00	-	-	-
1%Cu_ACo	100	0.00	-	-	-	-	-	-
2%Ir-1%Cu_ACo	60.2	0.25	0.18	0.73	0.09	0.20	0.79	0.09
1% Ir-1%Cu_ACo	75.2	0.35	0.10	0.89	0.01	0.13	0.69	0.18
1% Ir-0.6%Cu_ACo	64.5	0.22	0.11	0.72	0.17	0.12	0.71	0.17
1% Ir-0.3%Cu_ACo	47.6	0.55	0.09	0.81	0.10	0.25	0.66	0.09
1% Ir-0.1%Cu_ACo	23.2	0.38	0.04	0.78	0.18	0.14	0.72	0.14

3.3.2.5 Summary of the catalytic activity and selectivity results

Figure 3.9 summarizes the results obtained for nitrates conversion and selectivities to ammonium and nitrogen for all the catalysts tested as a function of atomic copper content.

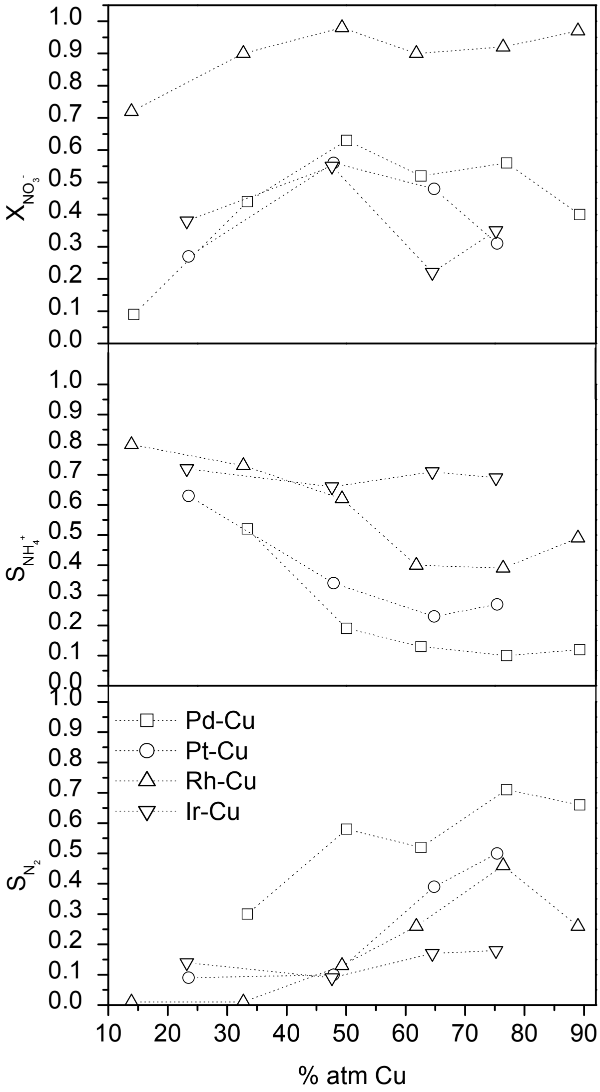


Figure 3.9 NO_3^- conversion after 5 h of reaction and NH_4^+ and N_2 selectivities at 20% of nitrate conversion as a function of % atomic of copper for the catalysts with 1%wt of noble metal.

The results compiled in this figure clearly indicate that both activity and selectivities are strongly affected by the type of metal pairs and also by the metals contents ratio. The Rh-Cu catalysts provide the highest nitrate conversions. For all pairs there is an increase in the nitrate conversion when copper contents increases: up to 0.3% for Pt-Cu and Ir-Cu catalysts and 0.6% for Pd-Cu and Rh-Cu catalysts, decreasing thereafter. These maxima in nitrate conversion correspond to an atomic ratio of noble metal/copper approximately equal to 1, indicating that the same amount of metal atoms is the best formulation to achieve a very active catalyst for this reaction. The selectivity to nitrogen increases with the atomic copper content, at least up to ca. 75% and it seems to decrease thereafter at least for Pd and Rh containing catalysts. The opposite is generally observed for the selectivity to ammonium, showing that with the increase of copper content the accessible surface of free noble metal, which is known to be very active for ammonium production, decreases. The Ir catalysts are the exception because their selectivity to ammonium is practically independent of the Cu content and always high. The pair Pd-Cu is the most selective in the transformation of nitrate to nitrogen compared to the pairs Pt-Cu and Rh-Cu, which presents similar nitrogen selectivities, and to the Ir-Cu pair.

All the catalyst tested in this work were calcined and reduced at 400 ºC. At this high temperature some alloy formation may occur. The XRD results and the fact that no hydrogen chemisorption was observed for the bimetallic catalysts, contrary to the monometallic catalysts, seem to support this observation. The possibility of alloy formation in the different catalytic systems could be responsible for the relatively low selectivity to nitrogen observed (the maximum obtained was around 70% for the Pd-Cu catalyst). Therefore, further studies on the influence of the calcination and reduction temperatures during catalysts preparation in the possibility of alloy formation and consequently in the selectivity to nitrogen are currently being carried out.

3.4 Conclusions

A detailed study on the influence of the metals composition of the bimetallic systems Pd-Cu, Pt-Cu, Ir-Cu and Rh-Cu supported on activated carbon as catalysts for the nitrate reduction with hydrogen in water was carried out. The pairs Ir-Cu and Rh-Cu were assessed for the first time.

The monometallic catalysts are inactive (Pd, Pt, Rh and Cu) or practically inactive (Ir) for the reduction of nitrate.

The activity of the catalysts is quite different depending on the copper content. For all the catalysts tested, the maximum activity was obtained for an atomic ratio noble metal/copper close to 1, which is indicative that the same amount of noble metal and promoter atoms is the best formulation to obtain a very active catalyst for this reaction.

Rh-Cu bimetallic catalysts are the most active among the catalysts tested, usually more than 90% of nitrate conversion being obtained after five hours of reaction. However, significant amounts of ammonium are obtained.

The pair Pd-Cu was the second most active system studied, reaching around 60% of nitrate conversion. Generally, the pairs Ir-Cu and Pt-Cu are less active and present similar nitrate conversions, but the former presents higher selectivities to ammonium.

There is a trend of the selectivity to nitrogen to increase with the increase of the atomic copper content up to 75%. This is valid for all the systems tested, with the exception of the pair Ir-Cu where the selectivity to ammonium is always high and practically independent of the metals composition.

The pair Pd-Cu is the most selective in the transformation of nitrate to nitrogen when compared to the other systems.

Acknowledgments

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Chapter 4

4 Pd-Cu/AC and Pt-Cu/AC catalysts for nitrate reduction with hydrogen: influence of calcination and reduction temperatures[1,2]

The influence of calcination and reduction temperatures on the catalytic properties of Pd-Cu and Pt-Cu bimetallic catalysts supported on activated carbon for the reduction of nitrates was studied. The catalysts were prepared using different calcination and reduction temperatures, and the respective activities and selectivities for the reduction of nitrates in water with hydrogen were assessed. It was found that the different preparation conditions lead to different catalytic performances. For both catalysts, the activity decreases by increasing calcination and reduction temperatures, whereas the effect on the selectivity is not uniform. For the 1%Pd-0.3%Cu (wt%) catalyst, the nitrate conversion after 5 h of reaction varies from 93% (sample calcined at 200 ºC and not reduced) to 25% (sample calcined and reduced at 400 ºC). The formation of alloys during the preparation of the catalysts is prejudicial for nitrate reduction. In all the preparation conditions tested the Pd-Cu pair is more selective for the transformation of nitrate into nitrogen. All the samples have been characterized by nitrogen adsorption at -196 ºC, CO adsorption microcalorimetry, TPR, XRD, XPS and TEM.

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[2] Selected catalysts were characterised by CO adsorption microcalorimetry in Laboratorio de Materiales Avanzados, Instituto Universitario de Materiales de Alicante - Departamento de Química Inorgánica, Universidad de Alicante.

4.1 Introduction

Nitrate concentrations in surface water, and especially in groundwater, have increased recently in many locations in the world, including Europe. The catalytic reduction with hydrogen has been suggested in the literature as a promising method for nitrate removal from water, without the drawbacks of the conventional methods [1,2]. This process was reported for the first time by Vorlop and Tacke [3], and consists in the reduction of nitrate to nitrogen over bimetallic catalysts in the presence of a reducing agent. The formation of nitrite as intermediate and ammonium as by-product is considered the main disadvantage of this process [2]. Previous studies on the heterogeneous catalytic nitrate reduction have shown that bimetallic catalysts are much more efficient than the monometallic ones. The catalyst is usually composed of a noble metal, mainly Pd or Pt but also Ru, Rh or Ir, and a promoter metal, such as Cu, Sn, Ag, Ni, Fe or In on different supports (alumina [4-10], silica [11-13], titania [14-16], activated carbon [17-24] (ref. 22 and 23 correspond to chapters 2 and 3), niobia [25], hydrotalcite [26,27], ceria [28,29], tin oxide [30,31], polymers [32-35]). Among them, Pd–Cu, Pd–Sn and Pt-Cu, seem to be the most effective, but are still inadequate in terms of selectivity to nitrogen [19,24]. The activity and selectivity of the bimetallic catalyst are highly dependent on the interaction between the metals, and this can be controlled by the preparation method, the nature of the promoter, the metal/promoter ratio and the operation conditions [36]. Alloying of metals may result in important changes in their activities and selectivities [9]. Segregation phenomena of the metal phases can occur during the preparation of the catalysts. The metal of lower energy of sublimation tends to migrate to the surface. However, this surface enrichment with one of the two metals depends on a large number of parameters, such as the interactions of the metal with the support and the preparation and activation methods [9]. The selection of the support is also important for this process, since it has been shown that the support may affect the catalytic activity and selectivity [36].

Epron et al. [9] investigated the influence of oxidizing and reduction treatments, at ambient temperature or at 400 ºC, in a bimetallic Pt-Cu catalyst supported on alumina. They concluded that the catalytic activity for nitrate reduction in water is dependent on the Pt and Cu distribution on the catalyst surface, which is strongly affected by the pre-treatments. In a more recent work, Sá et al. [37] studied the influence of the reduction temperature in the performance of a Pd-Cu catalysts supported on alumina, and they also observed significant changes in the catalytic activity. Gavagnin et al. [31] reported that ZrO_2 and SnO_2 can be used as supports for Pd-Cu in the nitrate reduction, and the activities and selectivities of the catalyst can be improved by decreasing the reduction temperature. Gao et al. [16] observed that Pd-Cu catalysts supported on titanium dioxide and treated at high temperatures (600 ºC) exhibit lower activity than non-thermally treated catalysts, probably because of the aggregation of active metal species caused by the high temperature treatment.

Activated carbons have been used in heterogeneous catalysis, both as catalysts on their own or as catalyst support. It has been proved that they have a great potential as catalyst support, especially for the expensive noble metals, since a high metal loading and dispersion can be achieved. Furthermore, the interaction between the active phase and the support can improve the catalytic activity [38]. In the present work, the influence of different calcination and reduction temperatures on the catalytic behaviour of activated carbon supported Pd-Cu and Pt-Cu bimetallic catalysts in the hydrogen-mediated reduction of nitrates in water has been studied.

4.2 Experimental

4.2.1 Catalysts preparation

The active metals were supported on a commercial activated carbon, NORIT GAC 1240 PLUS (ACo), ground to a particle diameter between 0.1 and 0.3 mm. The catalysts were prepared by incipient wetness co-impregnation, from aqueous solutions of the corresponding metal salts (H_2PtCl_6, $PdCl_2$, $Cu(NO_3)_2$). During the impregnation, the samples were placed in an ultrasonic bath. Then, the samples were dried at 100 ºC for 24 h. Different temperatures were selected for calcination (T_{Cal}) under a nitrogen flow for 1 h, and reduction (T_{Red}) under hydrogen flow for 3 h. No calcined and no reduced catalysts (N_{Cal} N_{Red}) were also studied; however, these samples could be considered calcined in air at 100 ºC, once they were dried in the oven during their preparation. The contents of noble and promoter metals were maintained constant at 1wt% and 0.3wt%, respectively. For the pair Pd-Cu the composition 2wt% of Pd and 1wt% of Cu was also checked.

4.2.2 Catalysts characterization

The catalysts were characterized using different techniques: N_2 adsorption at -196 ºC, temperature programme reduction (TPR), transmission electron microscopy (TEM), CO adsorption microcalorimetry, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

The textural characterization of the materials was based on the corresponding N_2 adsorption isotherms, determined at -196 ºC with a Coulter Omnisorp 100 CX apparatus. BET surface areas (S_{BET}) were calculated, as well as the micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) according to the t-method.

TPR experiments were carried out in a AMI-200 (Altamira Instruments) apparatus; the sample (150 mg) was heated at 5 ºC/min up to 600 ºC under a flow of 5% (v/v) H_2 diluted in He (total flow rate of 30 Ncm^3/min). The H_2 consumption was followed by a thermal conductivity detector (TCD) and by mass spectrometry (Dymaxion 200 amu, Ametek).

TEM analyses were obtained using a LEO 906E microscope operating at a 120 kV accelerating voltage.

Microcalorimetric measurements were performed at 25 ºC using a Setaram BT2.15D heat-flux calorimeter. The calorimeter was connected to a volumetric system employing a Baratron capacitance manometer for precision pressure measurement (±0.001 Torr). The maximum leak rate of the volumetric system (including the calorimetric cell) was 10^{-5} Torr/min in a system volume of approximately 60 cm^3. The catalysts (between 0.15 and 0.5 g) were calcined for 1 h and reduced for 3 h in a special cell with high purity helium and hydrogen (50 Ncm^3/min), respectively. After reduction, the sample was out-gassed at the reduction temperature for 15 min, and then purged at the same temperature for 1 h in high purity helium to remove any adsorbed hydrogen. Then, it was sealed in a Pyrex NMR tube and placed in a special calorimetric cell. When thermal equilibrium was reached, the capsule was broken, and small pulses of CO were introduced until saturation was achieved. The resulting heat response for each pulse was recorded as a function of time and integrated to determine the energy released. The differential heat (kJ/mol) was defined as the negative of the enthalpy change of adsorption per mole of gas adsorbed.

XRD spectra were recorded on a PANalytical X'Pert PRO diffractometer with Cu Kα radiation source (λ= 0.154 nm) and with a beam voltage of 50 kV and 40 mA of beam current. The data were collected in the 2θ range of 10º-90º with a scanning rate of 0.017 º/s.

XPS analyses were performed with a VG Scientific ESCALAB 200 A spectrometer using a nonmonochromatised Mg Kα radiation (1253.6 eV). The pressure in the analysis chamber was always lower than 1 × 10^{-7} Pa. The charging effects were corrected using the C1s peak, which was fixed on all samples at a binding energy (BE) of 285 eV. XPS data were fitted using the software XPSpeak.

4.2.3 Catalysts evaluation

The catalytic tests were carried out in a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure, and using hydrogen as reducing agent. Initially, 790 mL of deionised water and 400 mg of catalyst were fed into the reactor, the magnetic stirrer was adjusted to 700 rpm and the gas mixture of hydrogen and carbon dioxide (1:1, flow rate = 200 Ncm^3/min) was passed through the reactor during 15 min to remove oxygen; CO_2 acts as pH buffer (pH = 5.5). After that period, 10 mL of a nitrate solution, prepared from $NaNO_3$, was added to the reactor, in order to obtain an initial NO_3^- concentration equal to 100 mg/L. Preliminary studies were carried out varying the stirring rate and it was checked that under the selected conditions there was no external diffusional limitations.

Small samples were taken from the reactor for determination of nitrate, nitrite and ammonium concentrations after defined periods. Nitrate and nitrite ions were simultaneously determined by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was a Hamilton PRP-X100 column (150 mm x 4.1 mm) working at room temperature under isocratic conditions. The mobile phase was a 0.1 M solution of NaCl:CH_3OH (45:55). Ammonium ions were determined by potentiometry using a convenient selective electrode. pH values were also measured.

The dissolved amounts of Pd, Pt and Cu were measured by atomic absorption spectroscopy, using the remaining solution after reaction tests. No leaching of Pd or Pt was detected at the end of the reaction, but in some experiments small amounts of dissolved Cu were observed in the solution. For example, for the catalyst 2%Pd-1%Cu_ACo a concentration of 0.327 mg/L of Cu was detected in the case of the sample N_{Cal} N_{Red}, corresponding to a leaching of 7%, which was the highest value measured; this value decreases to 0.6% for the catalyst T_{Cal}=400 ºC T_{Red}=400 ºC. On the contrary, in the case of Pt-Cu catalysts no dissolved Cu was measured for the sample N_{Cal} N_{Red}.

The selectivities of nitrite, ammonium and nitrogen were calculated as:

$$S_{NO_2^-} = \frac{n_{NO_2^-}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{4.1}$$

$$S_{NH_4^+} = \frac{n_{NH_4^+}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{4.2}$$

$$S_{N_2} = \frac{2 * n_{N_2}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{4.3}$$

where $n_{NO_3^-{}_i}$ is the initial amount of nitrate (mmol) and $n_{NO_3^-}$, $n_{NO_2^-}$, $n_{NH_4^+}$ and n_{N_2} are the amounts of the respective species (mmol) at time t (min). The amounts of nitrogen were calculated by a mole balance, assuming that the NO_x produced is negligible.

4.3 Results and Discussion

4.3.1 Catalysts characterization

4.3.1.1 Textural properties

Textural properties obtained from the N_2 adsorption isotherms at -196 ºC show that the support has a BET surface area of 869 m^2/g, a mesopore surface area of 97 m^2/g and a micropore volume of 0.32 cm^3/g. It was previously verified that the textural parameters remained almost unchanged compared to the unloaded carbon when higher metal loads were used in this same activated carbon as a support [23] (see chapter 3). Therefore, it is assumed that the textural properties of the supported metal catalysts are not significantly different from the original activated carbon.

4.3.1.2 TPR

The TPR profiles (not shown) of the monometallic catalysts show peaks at 190 ºC for Pd, 230 ºC for Cu and 200 ºC for Pt. The reduction peak at around 60 ºC relative to the decomposition of Pd β-hydride [31,39,40] was not observed, which may indicate that Pd is well dispersed on the support [41]. The Pd-Cu catalyst showed a single reduction peak at 150 ºC that can be assigned to the reduction of Cu oxides, promoted by the presence of the noble metal [32,39,41]. The decrease in the reduction temperature of supported copper in bimetallic catalysts induced by the presence of palladium indicates that a close proximity between copper and palladium species was achieved [41]. The TPR profile of the Pt-Cu catalyst is characterized by two peaks at 200 ºC and 400 ºC. The first one, located around that of the pure platinum catalyst, indicates the reduction of mixed Pt-Cu oxidized species where both metals are in close contact. The peak at higher temperatures could be attributed to the reduction of isolated copper species [6]. Supported CuO may be reduced at higher temperatures depending on the particle size and its interaction with the support [42]. It could be assumed that oxidized copper particles in the bimetallic catalyst are well dispersed and interact strongly with the support, which is the most probable explanation for their reduction at higher temperature than the monometallic copper particles [9].

4.3.1.3 TEM

TEM analyses were made in order to get information on the particle size distribution for all samples. TEM images and the corresponding histograms of the particle size distributions (Figure 4.1 to 3) revealed that the average particle size depends on the calcination/reduction conditions. In both series (Pd-Cu and Pt-Cu), the evolution of the particle size with the temperatures used during calcination/reduction presents a similar trend (Figure 4.1and Figure 4.3). No major differences were observed in the morphology of the catalysts neither calcined nor reduced; in fact, in this sample, no particles can be detected (Figure 4.3 a)), due to the fact that this catalyst was not heat treated and, consequently, no metal particles were generated, or the particles have a diameter lower than 2 nm (detection limit of the equipment used). For the catalysts T_{Cal}=200 ºC N_{Red} (Figure 4.1 a), Figure 4.2 and Figure 4.3 b)) only a few particles can be observed. In the case of 1%Pd-0.3%Cu_ACo T_{Cal}=200 ºC T_{Red}=100 ºC (Figure 4.1 b)) and 1%Pt-0.3%Cu_ACo T_{Cal}=200 ºC T_{Red}=100 ºC (Figure 4.3 c)) it is already possible to see a significant number of well defined particles. These observations suggest that metals are well dispersed on the support. From the particle size distributions it was observed that these catalysts mainly present particle sizes between 3 and 4 nm and only a few particles higher than 5 nm were detected in some of them. For the 1%Pd-0.3%Cu_ACo and 1%Pt-0.3%Cu_ACo catalysts with T_{Cal}=200 ºC T_{Red}=200 ºC and T_{Cal}=400 ºC T_{Red}=400 ºC, TEM analyses show the presence of not only small particles in the

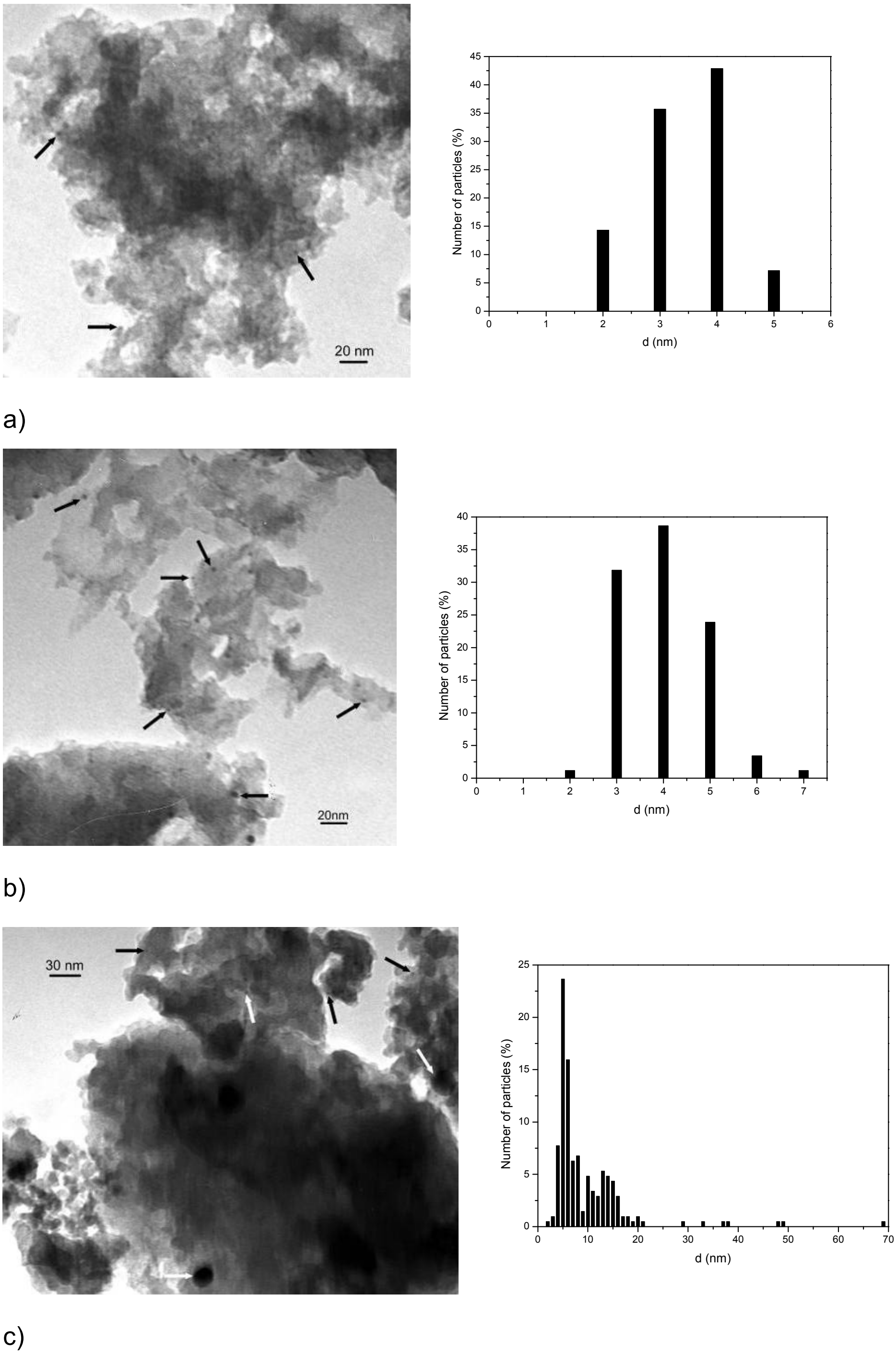


Figure 4.1 TEM micrographs and particles size distributions of 1%Pd-0.3%Cu_ACo catalysts: a) T_{Cal}=200 ºC N_{Red}, b) T_{Cal}=200 ºC T_{Red}=100 ºC and c) T_{Cal}=400 ºC T_{Red}=400 ºC.

range of 5-6 nm, but also many larger particles (see Figure 4.1 c), Figure 4.3 d) and e)).

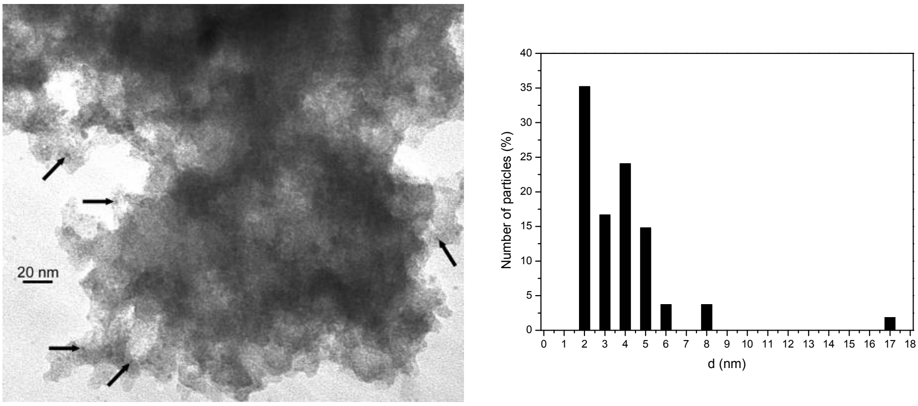
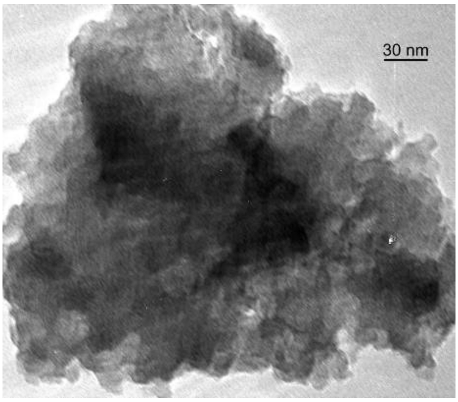
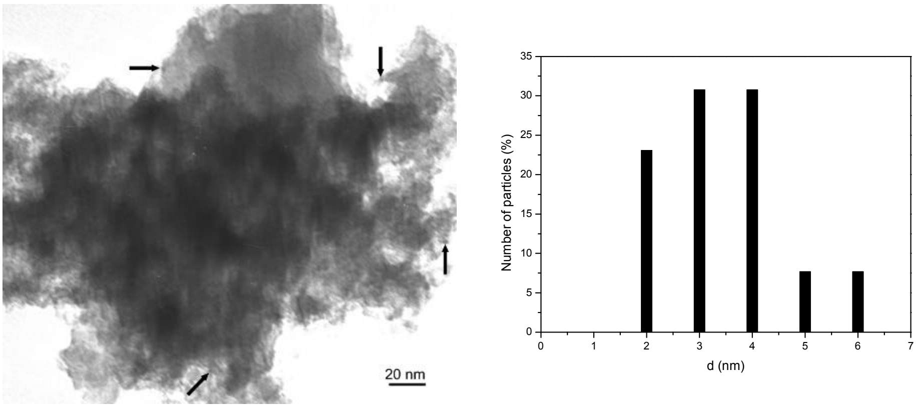


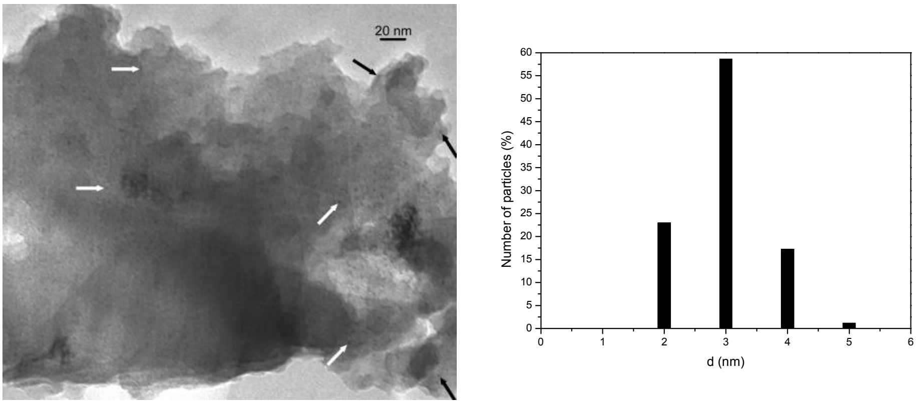
Figure 4.2 TEM micrograph and particles size distribution of the 2%Pd-1%Cu_ACo catalyst T_{Cal}=200 ºC N_{Red}.



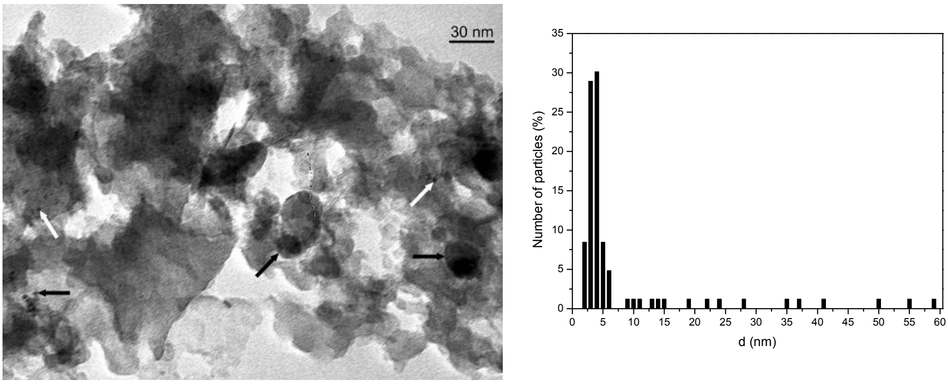
a)


20 nm
Number of particles (%)
d (nm)
0
5
10
15
20
25
30
35
0
1
2
3
4
5
6
7

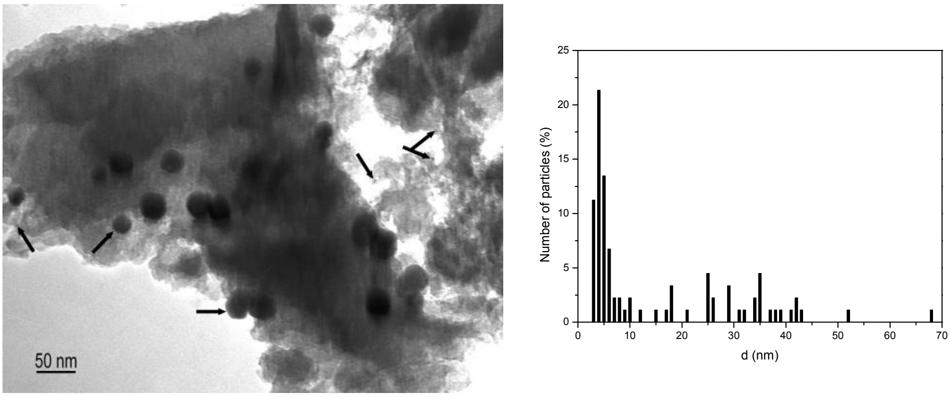
b)


20 nm
Number of particles (%)
d (nm)
0
5
10
15
20
25
30
35
40
45
50
55
60
0
1
2
3
4
5
6

c)


30 nm
Number of particles (%)
d (nm)
0
5
10
15
20
25
30
35
0
5
10
15
20
25
30
35
40
45
50
55
60

d)



e)

Figure 4.3 TEM micrographs and particles size distributions of 1%Pt-0.3%Cu_ACo catalysts: a) N_{Cal} N_{Red}, b) T_{Cal}=200 ºC N_{Red}, c) T_{Cal}=200 ºC T_{Red}=100 ºC, d) T_{Cal}=200 ºC T_{Red}=200 ºC and e) T_{Cal}=400 ºC T_{Red}=400 ºC.

From the TEM micrographs it can be concluded that calcination and reduction at different temperatures lead to significant changes in the average particle size. As can be seen in the histograms, an increase in the calcination and reduction temperatures causes an increase in the particle size of the crystallites. These results are in agreement with those reported by Gurrath et al. [40] and Ramos et al. [43] for Pd supported on activated carbons. These authors observed that reduction at higher temperatures originates a decrease in the dispersion, which should be attributed to an increase in the metallic particle size due to the migration of particles and sintering during the calcination and reduction steps [43]. Sepúlveda-Escribano et al. [44] observed the same effect for Pt supported on carbon blacks. The increase of the particle size can also be promoted by the thermal decomposition of the oxygenated surface groups initially present on the activated carbon surface. With the destruction of these groups, the fixed small metal particles (or the unreduced precursor) would become mobile on the surface and consequently would agglomerate to larger particles [44,45].

4.3.1.4 CO adsorption microcalorimetry

This technique can give information about the energetic interaction of CO with the different surface metals, which allows to assess the heterogeneity of the surface and the interaction between metals. Since CO hardly adsorb on copper [46], only

CO adsorption on either Pt or Pd was considered. Small doses of CO were contacted with the reduced catalysts and the differential heat of adsorption was measured as a function of the CO coverage.

Figure 4.4 shows the differential heat of CO adsorption at 25 ºC as a function of the coverage for the monometallic Pd and 1%Pd-0.3%Cu_ACo catalysts after different calcination/reduction treatments. For the monometallic catalyst, the initial heat is around 190 kJ/mol, and it strongly decreases with the CO coverage up to 40 µmol/g, where a pseudo+plateau was reached. The CO coverage was similar in the 1%Pd-0.3%Cu_ACo with T_{Cal}=200 ºC T_{Red}=100 ºC; therefore, Cu is not blocking the Pd sites where the CO is adsorbed. Moreover, the heat of adsorption profiles are roughly the same in both catalysts, so the energetic interaction of CO with Pd has not changed with the addition of Cu.

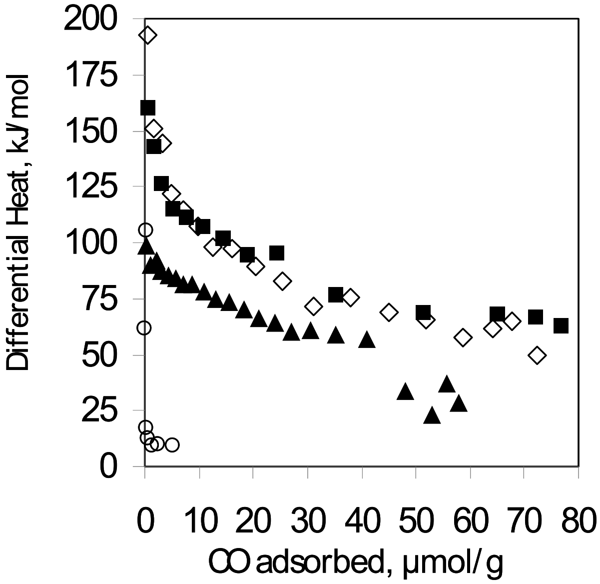


Figure 4.4 Differential heats of adsorption as a function of CO coverage at 25 ºC on the monometallic Pd_ACo (◊), on 1%Pd-0.3%Cu_ACo (T_{Cal}=200 ºC T_{Red}=100 ºC) (■); T_{Cal}=200 ºC T_{Red}=200 ºC (▲) and T_{cal} =400ºC T_{red} = 400ºC (o).

Different results are obtained with the 1%Pd-0.3%Cu_ACo catalyst using T_{Cal}=200 ºC T_{Red}=200 ºC. These changes in the profile show up important modifications in the Pd active sites by effect of the reduction temperature. The initial heat of adsorption is now 99 kJ/mol, and slightly decreases with the CO coverage; furthermore, the amount of CO adsorbed has also decreased with respect to its counterparts. The lower energetic interaction of CO with Pd active sites suggests that Cu is modifying Pd. These effects are even more clear after a calcination and reduction treatment at high temperature (T_{Cal}=400 ºC T_{Red}=400 ºC), where the lower energetic interaction of CO with Pd is also accompanied by a drastic decrease in the amount of CO adsorbed. Either the sintering of the Pd nanoparticles and/or, more likely, the dilution of surface Pd by Cu (large migration of Cu to surface positions after a high temperature reduction treatment), with possible PdCu alloy formation, may account for the observed behaviour. Earlier investigations [47] on the interaction of CO with Pd-Cu alloys have shown a decrease in the CO interaction with the amount of Cu. Fernández-Garcia et al. [48] and Anderson et al. [49] observed a decrease in the number of CO molecules bridging two or more Pd atoms, which are the most energetic sites for CO adsorption [50], when Cu was added, indicating a dilution of the surface Pd by Cu, which also correlates with the loss in the adsorption capacity.

The heat of CO adsorption profiles for the Pt catalysts are plotted in Figure 4.5. The low CO adsorption capacity of this catalyst complicates the analysis, since only few doses can be introduced. Nevertheless, the amount of CO adsorbed and the heat of adsorption on the bimetallic 1%Pt-0.3%Cu_ACo with T_{Cal}=200 ºC T_{Red}=200 ºC is lower than on the monometallic one in all the range of coverage. This effect, as in the Pd-Cu catalyst, would be most likely due to the formation of a Pt-Cu alloy. Copper in metallic state is diluting and interacting with the surface Pt atoms, thus decreasing the number of Pt active sites and their interaction with CO. Li et al. [51] found analogous results on Pt-Cu catalysts supported on SiO_2 for both, H_2 and CO adsorption.

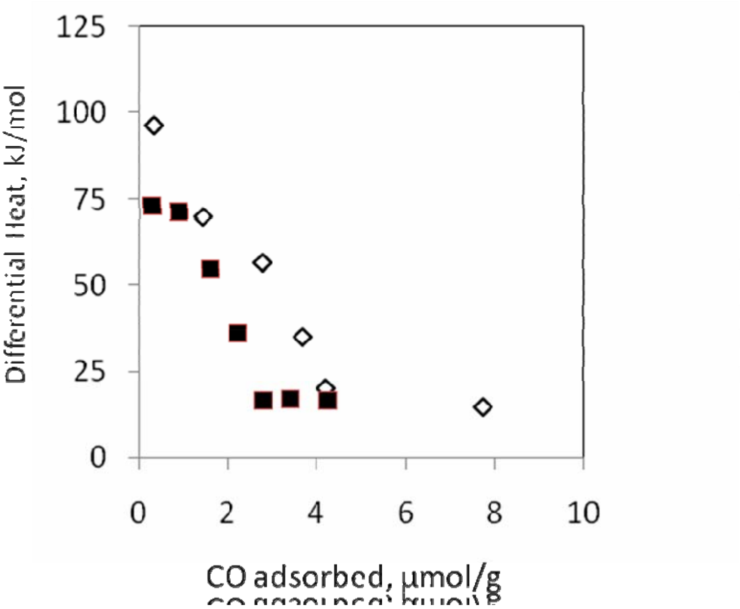
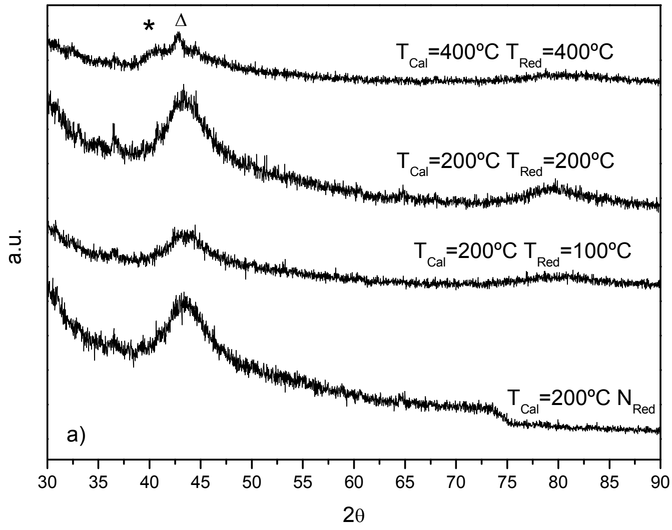


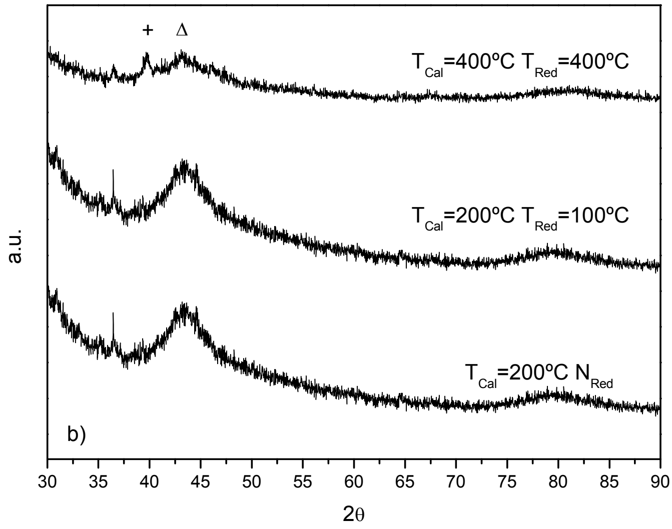
Figure 4.5 Differential heats of adsorption as a function of CO coverage at 25 ºC on the monometallic Pt_ACo (◊) and on 1%Pt-0.3%Cu_ACo T_{Cal}=200 ºC T_{Red}=200 ºC (■).

4.3.1.5 XRD

Figure 4.6 a) and b) show the X-ray diffraction spectra of the 1%Pd-0.3%Cu_ACo and 1%Pt-0.3%Cu_ACo catalysts, respectively, calcined and reduced at different temperatures. The X-ray diffraction spectra of the support (ACo) and of the monometallic catalysts (1%Pd_ACo, 1%Pt _ACo and 1%Cu_ACo) calcined and reduced at 400 ºC, are reported in Figure 4.6 c).

The XRD profile of the support (ACo) shows two broad peaks centered around 2θ = 24º and 44º, which are due to turbostratic carbon [52]. In 1%Pd-0.3%Cu_ACo and 1%Pt-0.3%Cu_ACo catalysts, the XRD spectra do not show any intense peak corresponding to the metals, which could be due to the low amount of metal loaded and, on the other hand, could be taken as an indication of a good metal dispersion on the support [31]. TEM observations support this last conclusion. Only in the XRD spectra of the bimetallic catalysts 1%Pd-0.3%Cu_ACo and 1%Pt-0.3%Cu_ACo with T_{Cal}=400 ºC T_{Red}=400 ºC significant peaks corresponding to the metals can be observed, this being indicative of the presence of larger particles than when the catalysts are treated at lower temperatures, and is in agreement with the TEM analyses. In addition, in these XRD spectra it can be observed that the Pd and Pt peaks are slightly displaced to the right, which is indicative of the formation of alloys [31,32], as confirmed by CO adsorption microcalorimetry.





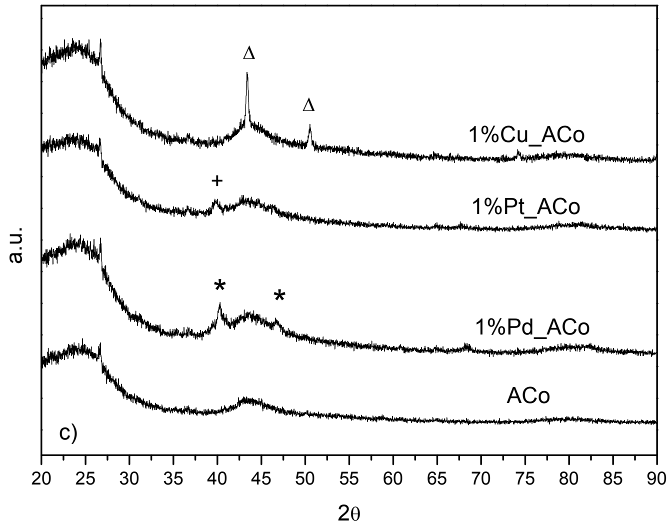


Figure 4.6 XRD spectra of a) 1%Pd-0.3%Cu_ACo, b) 1%Pt-0.3%Cu_ACo catalysts and c) monometallic catalysts T_{Cal}=400 ºC T_{Red}=400 ºC and support (ACo). Copper (□), platinum (+), palladium (*).

4.3.1.6 XPS

Concerning the XPS characterization, the objective was to estimate the relative abundance of the metals at the surface as a function of the calcination and reduction treatments. The information concerning their oxidation states must be considered with reserve because these experiments were not carried out in situ; therefore, some surface oxidation could result from the contact with air during sample manipulation. Besides the characterization by XPS of the fresh and the spent 1%Pd-0.3%Cu_ACo catalyst T_{Cal} = 200 ºC N_{Red}, an additional sample was prepared with the aim to understand the influence of the initial 15 min contact between the catalyst and hydrogen in water before starting reaction (addition of nitrate). The Pd 3d and Cu 2p spectra of the bimetallic samples were analysed and the binding energies of the Pd $3d_{5/2}$ and Cu $2p_{3/2}$ levels are reported in Table 4.1. The surface Pd/Cu atomic ratio, obtained by XPS, is also presented in Table 4.1.

Barrabés et al. [18] identified platinum, palladium and copper supported on activated carbon in the reduced form for the fresh catalysts, but for some of the used catalyst the metals were not only in the reduced but also in the oxidized form. According to the TPR profiles, it was expected that the heat treated catalysts were in the reduced form. However, in this work, the binding energies values found for copper and palladium are respectively characteristic of Cu^{2+} [53,54] and Pd^{2+} [55,56], i.e. of the oxidized form. Probably, this is due to the contact with air after the calcination and/or reduction and after reaction, which could oxidise the metals [39]. In addition, according to Yamamoto et al. [57], in the samples calcined at 200 ºC, the presence of copper prevents the reduction of Pd^{2+} to Pd^0 due to a preferential reduction of Cu^{2+} relatively to that of Pd^{2+} on the reduction sites of activated carbon, due to the lower redox potential of Cu^{2+} to Cu^+ (0.15V vs. Ag^+/AgCl) than that of Pd^{2+} to Pd^0 (0.92V). However, as can be seen in the next section, the contact with reaction media can change the surface of the catalysts, and although the metals are in the oxidized form they are reduced *in situ* during the kinetic experiments, where the catalysts are continuously in contact with hydrogen dissolved in water.

Table 4.1 XPS results for the 1%Pd-0.3%Cu_ACo catalysts.

Catalyst	**Cu 2p$_{3/2}$ (eV)**	**Pd 3d$_{5/2}$ (eV)**	$\frac{Pd}{Cu}(at.)XPS$
N_{Cal} N_{red}	934.2	337.5	1.15
T_{Cal} =200 ºC N_{Red}	934.1	337.5	1.09
T_{Cal} =200 ºC N_{Red} After 15min under hydrogen flow in water	935.8	337.1	0.48
T_{Cal} =200 ºC N_{Red} After 5h of reaction	935.1	337.9	0.26
T_{Cal} =200 ºC T_{Red} =100 ºC	935.1	337.6	1.50

The increase in the Pd/Cu ratio with increasing of the reduction temperature can be explained by Cu migration. Epron et al. [9] proposed Cu migration during the reduction of Pt-Cu catalysts. The migration was supposed to be towards the core of the bimetallic particles, leading to a surface enrichment with platinum, but also to a decrease in the amount of superficial copper. Moreover, according to Sá et al. [37], copper seems to migrate towards the support with the increase of the reduction temperature. These suggestions are consistent with our results.

Nevertheless, from the comparison between XPS results of the fresh and the spent catalyst T_{Cal}=200 ºC N_{Red}, significant differences were observed in their surface composition after 15 min of contact with hydrogen in water and after 5 h of reaction, where a low Pd/Cu ratio is obtained. Considering that the measurements of leached metals for this sample indicate that no palladium was detected and that the amount of dissolved copper is very low, the decrease of this ratio is not due to leaching of the metals. Yoshinaga et al. [17] have also found that when activated carbon is used as a support for this reaction the dissolved amounts of Pd and Cu were negligibly small. Therefore, the results can only be explained by the modification of the copper and palladium relative distribution on the catalyst surface. This surface modification may be induced by the contact with the reaction media, which allows an rearrangement of the metal phases [9]. The decrease of the Pd/Cu ratio could be due to the preferential migration of palladium towards the interior of the support [40] and/or the migration of copper to the surface of palladium during reaction.

As can be seen in Table 4.1 the atomic ratio between Pd and Cu obtained by XPS is lower than the theoretical (1.99). This is related with the fact that XPS is a surface technique and then only gives an estimative of the chemical composition of the uppermost surface layers (about 10-15 nm in depth).

4.3.2 Catalytic tests

The effect of calcination and reduction temperatures on the catalytic activity and selectivity during the reduction of nitrates was studied. The activities of 1%Pd-0.3%Cu_ACo and 1%Pt-0.3%Cu_ACo catalysts are shown in Figure 4.7 a) and Figure 4.8 a), respectively. Figure 4.7 and Figure 4.8 b) and c) show the corresponding evolution of nitrite and ammonium concentrations during the reaction.

As can be seen in Figure 4.7 and Figure 4.8 the reduction of nitrates is quite different depending on the supported metal and the calcination/reduction conditions. In general, for the two catalysts, the activity decreases by increasing the calcination and reduction temperatures. This effect is more pronounced for the pair Pd-Cu. For high calcination and reduction temperatures, the Pt-Cu catalysts are more active than the Pd-Cu catalysts. However, using a low reduction temperature or not carrying out the reduction step, the Pd-Cu catalysts are the most active. The order of activity for both catalysts is similar: T_{Cal} = 200 ºC N_{Red} > N_{Cal} N_{Red} > T_{Cal} = 200 ºC T_{Red} = 100 ºC > T_{Cal} = 200 ºC T_{Red} = 200 ºC > T_{Cal} = 400 ºC T_{Red} = 400 ºC, with nitrate conversion values after 5 h of 93, 85, 79, 35 and 25%, and 77, 73, 64, 57 and 53%, respectively for the Pd-Cu and the Pt-Cu catalysts. For

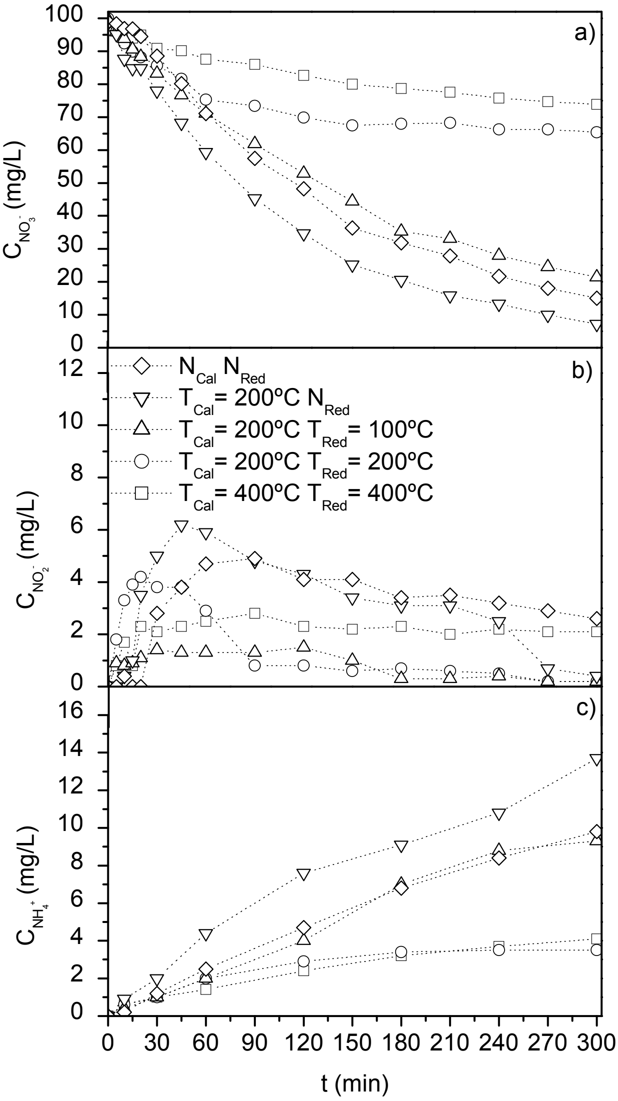


Figure 4.7 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of 1%Pd-0.3%Cu_ACo catalysts ($C_{NO_3^-i}$ = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

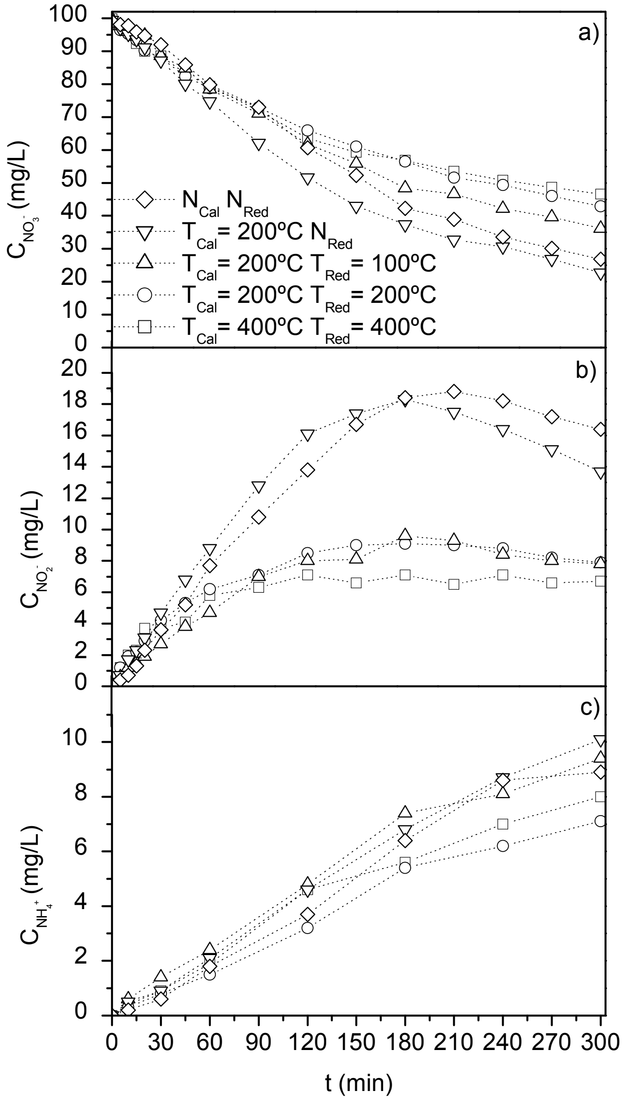


Figure 4.8 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of 1%Pt-0.3%Cu_ACo catalysts ($C_{NO_3^- i}$ = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H_2} = 100 Ncm^3/min, Q_{CO_2} = 100 Ncm^3/min, T = 25 ºC).

the 2%Pd-1%Cu_ACo catalyst the results are also similar; nevertheless, in this case, higher conversions are obtained. For example, 100% nitrate conversions were achieved for all the samples prepared at low temperatures (cf. Table 4.2), and for the best catalyst (T_{Cal} = 200 ºC N_{Red}) before 200 min of reaction. According to the TPR profiles, Pd-Cu and Pt-Cu bimetallic catalysts are reduced at around 150 ºC and 200 ºC, respectively. So, it was expected that the catalysts that have not been heat treated or have been treated at low temperatures were, after preparation, in the oxidized state. It is well assumed that the catalytic activity is related with several factors such as metals dispersion, preparation conditions, metals nature, type of support and, also, by the contact with hydrogen in water. In the next section, it will be demonstrated that the last factor plays an important role in the catalyst performance. This contact will originate some *in situ* reduction of the noble metal. Copper does not need to be in its reduced form in this catalytic system [9]. Epron et al. [9] studied the influence of oxidizing and reducing procedures on the activity of a Pt-Cu bimetallic catalyst supported on alumina, and they also observed that the poorest activity was achieved when the catalyst was oxidized and reduced at 400 ºC. They concluded that this lower activity results from the destruction of the interactions between copper and platinum, and a subsequent migration of copper towards the alumina support. Therefore, a surface enrichment with platinum was noticed, which eventually decreases the catalytic activity. In the present work, the results obtained by XPS confirm an increase of the Pd content on the surface of the catalyst with the increase of calcination and reduction temperatures.

The nitrite concentration goes through a maximum Figure 4.7 b) and Figure 4.8 b)) and the ammonium concentration increases with the nitrate conversion (Figure 4.7 c) and Figure 4.8 c)), according to the occurrence of consecutive/competitive reactions. The reduced catalysts give rise to similar nitrite concentrations which, particularly in the case of the Pt-Cu catalysts, are lower than the concentrations obtained with the non-reduced catalysts. This can be explained by the fact that for the catalysts only calcinated or not heat treated the active sites for nitrite reduction are not completely formed. As can be seen in the TEM micrographs, no or a limited number of particles were observed for these catalysts, indicating a good dispersion of the metals or, most probably, that the metal particles are still not completely formed after preparation (especially for the non heat treated sample). Therefore, in these conditions, the metal could not be very active for nitrite reduction. It is well assumed that nitrite reduction occurs principally on the monometallic sites of the noble metal [1,22] (ref. 22 corresponds to chapter 2).

Table 4.2 Nitrate conversions ($X_{NO_3^-}$) and nitrite, ammonium and nitrogen selectivities ($S_{NO_2^-}$, $S_{NH_4^+}$, S_{N_2}) of Pd-Cu and Pt-Cu catalysts after 5 h of reaction and nitrogen selectivity for 25% and 50% of nitrate conversion.

Catalyst (wt%)	**t = 300 min**				S_{N_2}	
	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$X_{NO_3^-}$	
					25%	**50%**
1%Pd-0.3%Cu_ACo						
N_{Cal} N_{Red}	0.85	0.04	0.40	0.56	0.46	0.58
T_{Cal} = 200 ºC N_{Red}	0.93	0.01	0.51	0.48	0.37	0.48
T_{Cal} = 200 ºC T_{Red} = 100 ºC	0.79	0.00	0.41	0.59	0.68	0.65
T_{Cal} = 200 ºC T_{Red} = 200 ºC	0.35	0.01	0.35	0.64	0.56	-
T_{Cal} = 400 ºC T_{Red} = 400 ºC	0.25	0.11	0.57	0.31	0.31	-
2%Pd-1%Cu_ACo						
N_{Cal} N_{Red}	1.00	0.00	0.39	0.61	0.49	0.51
T_{Cal} = 200 ºC N_{Red}	1.00	0.00	0.57	0.43	0.21	0.32
T_{Cal} = 200 ºC T_{Red} = 100 ºC	0.99	0.00	0.35	0.65	0.67	0.70
T_{Cal} = 200 ºC T_{Red} = 200 ºC	0.91	0.01	0.30	0.69	0.65	0.70
T_{Cal} = 400 ºC T_{Red} = 400 ºC	0.61	0.02	0.59	0.39	0.36	0.39
1%Pt-0.3%Cu_ACo						
N_{Cal} N_{Red}	0.73	0.31	0.42	0.27	0.17	0.19
T_{Cal} = 200 ºC N_{Red}	0.77	0.24	0.45	0.31	0.24	0.22
T_{Cal} = 200 ºC T_{Red} = 100 ºC	0.64	0.17	0.51	0.33	0.30	0.25
T_{Cal} = 200 ºC T_{Red} = 200 ºC	0.57	0.19	0.44	0.37	0.34	0.34
T_{Cal} = 400 ºC T_{Red} = 400 ºC	0.53	0.17	0.52	0.31	0.30	0.31

A similar trend is observed for ammonia, but in this case the highest concentrations were measured for the Pd-Cu catalysts, certainly because the conversions attained with for these catalysts are higher than in the presence of the Pt-Cu catalysts.

Considering that these catalysts have the same amount of metals, the different performances should be related to the metal dispersion and/or the nature of active sites. Calcination and reduction at high temperatures lead to a decrease of the nitrate conversion in comparison with the catalysts treated at low temperatures; this can be explained by the decrease of metal surface area due to sintering and/or alloying. Preparation of the catalysts at higher temperatures results in larger metal particles (see TEM results). Additionally, it was observed by CO adsorption microcalorimetry that heat treatments above 200 ºC lead to the formation of an alloy, thus decreasing the number of active sites able to reduce nitrate. Batista et al. [39] and Deganello et al. [58] observed similar performances for nitrate reduction using alloyed or non-alloyed Pd-Cu. On the contrary, our results clearly show that nitrate reduction is highly influenced by the preparation conditions, being the formation of alloys a severe limitation for this reaction. In order to obtain high activities, the metals must be in close contact but not alloyed.

The 2%Pd-1%Cu_ACo catalysts present nitrogen selectivities slightly higher than the 1%Pd-0.3%Cu_ACo catalysts. For the pairs Pd-Cu and Pt-Cu the highest nitrogen selectivities were observed for the catalysts T_{Cal} = 200 ºC T_{Red} = 200 ºC, being the catalysts T_{Cal} = 400 ºC T_{Red} = 400 ºC the most selective to ammonium. Nevertheless, for the Pt-Cu catalysts, the selectivities to nitrogen were not too different from sample to sample. As can be seen in Table 4.2, the catalysts corresponding to T_{Cal} = 400 ºC T_{Red} = 400 ºC present different nitrate conversions but similar high selectivities to ammonia. According to Sá et al. [37], the decrease in the nitrogen selectivity of the process with the increase of the reduction temperature, can be attributed to alloying of the metals. Yoshinaga et al. [17] suggested that a dilution of Pd takes place during alloying. This leads to an increment in the number of isolated Pd atoms, which are suggested to be active sites for the ammonium formation. In a recent work [23] (see chapter 3) it was demonstrated that the selectivity to ammonium is higher when the noble metal is isolated, because as the noble metal is very active for hydrogenation reactions the nitrite ions are deeply hydrogenated into ammonium. The pair Pd-Cu is more selective to nitrogen than the pair Pt-Cu. According to this work, the calcination temperature at 200 ºC and reduction temperature at 100 ºC have been selected as the optimal temperatures for the catalysts activation, in order to achieve reasonable activities and high selectivities to nitrogen. Higher temperatures led to substantial decrease in the catalytic activity probably due to alloy formation and/or sintering, and lower temperatures led to an increase in the catalytic activity but with lower selectivity to nitrogen.

In addition to the metal dispersion, a support promoting effect on the metals may also be considered, since activated carbon has a reducing character, and the contact with hydrogen in water must be consider as an important factor in the catalytic activity. To investigate the influence of passing a hydrogen flow during 15 min before the introduction of nitrates in water in the activity and in the oxidation state of the catalyst, the catalytic reduction of nitrates was performed under different conditions than that normally used. For that purpose, the catalyst (sample 1%Pd-0.3%Cu_ACo T_{Cal} = 200 ºC N_{Red}) was only introduced in the reactor together with the concentrated nitrate solution, i.e. after 15 min of flowing hydrogen. Figure 4.9 presents the evolution of nitrate concentration in this experiment.

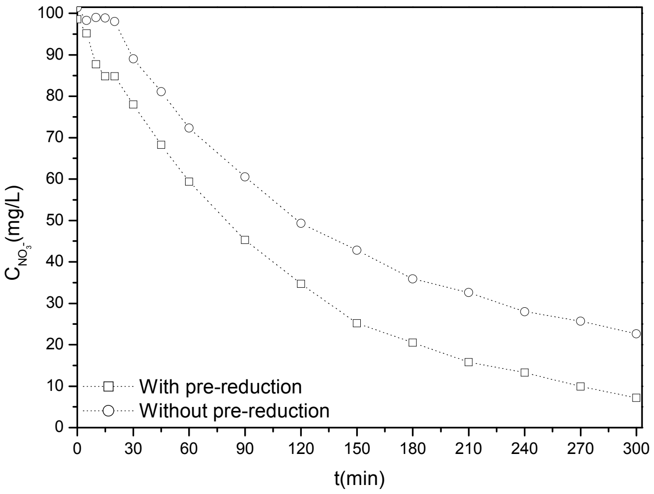


Figure 4.9 NO_3^- concentration as a function of time during nitrate reduction in the presence of 1%Pd-0.3%Cu_ACo catalysts with and without pre-reduction in water (C_{NO3^-i} = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

Figure 4.9 shows that, for the experiment without in situ pre-reduction, the reaction only begins after a period of about 20 min, and a displacement in the corresponding curve relative to that observed for the experiment with pre-reduction was noticed. This induction period can be explained by the time necessary to reduce the noble metal *in situ* with hydrogen and, probably, the presence of hydrogen in water allows a rearrangement of the metal phase, as it has been previously reported by Epron et al. [9]. To confirm this hypothesis, a XPS analysis of the catalyst was carried out after being in contact with hydrogen in water during 15 min. The XPS results (cf. Table 4.1) lead to the conclusion that the contact with hydrogen in water changes significantly the surface composition of the catalyst. A decrease of the metal surface ratio (Pd/Cu) is observed, probably due to a palladium migration towards the support and/or a migration of copper to the top of palladium. The results obtained permit to conclude that the noble metal can be reduced *in situ* by hydrogen in the presence of activated carbon (avoiding the *ex situ* reducing step).

An additional experiment was carried out to investigate the influence of the contact with dissolved hydrogen in water; the catalyst 1%Pd-0.3%Cu_ACo N_{Cal} N_{Red} was selected. After a first typical experiment, the catalyst was dried and used again under the same experimental conditions. The results obtained (not shown) demonstrated that in the second run the catalyst is initially more active than in the first experiment, but after 180 min the activity becomes slightly lower. Additionally, it was observed that the selectivity to nitrogen was similar in both experiments. Once again, these results may be interpreted considering that the noble metal was reduced *in situ* by hydrogen and, for that reason, the initial activity is higher in the second test.

4.4 Conclusions

The results obtained in this work show that the reduction of nitrate is quite different depending on the supported metal and the preparation conditions. For the catalysts tested, the activity decreases with the increase of calcination and reduction temperatures, whereas the effect on the selectivity is not uniform. The calcination and reduction at high temperatures are inadequate due to the formation of larger metal particles and/or alloys. The contact with hydrogen in water has an important effect on the catalytic activity. This contact allows an *in situ* reduction of the noble metal. Taking into consideration the selectivity to nitrogen, the performance of the catalysts is maximised at low calcination and reduction temperatures. The calcination at 200 ºC and reduction at 100 ºC seems to be the optimal temperatures to activate the catalysts, when both the activity and nitrogen selectivity are considered. For all the preparation conditions tested, the Pd-Cu pair is more selective in the transformation of nitrate into nitrogen.

Acknowledgments

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Chapter 5

5 Nitrate reduction with hydrogen in the presence of physical mixtures with mono and bimetallic catalysts and ions in solution[1]

Several physical mixtures with mono and bimetallic catalysts were tested in the catalytic nitrate reduction with hydrogen in order to minimize the selectivity to ammonium and to clarify the reaction mechanism. It was observed that the physical mixtures of Pd and Cu or Pt and Cu monometallic catalysts are similar or more active than the corresponding bimetallic catalysts. This fact indicates that the initial presence of bimetallic sites on the catalysts is not mandatory; it is sufficient that both metals are present in the reaction system. The mixtures with Pd catalysts are the most selective to nitrogen, being the mixtures with Rh catalysts the most selective to ammonium. The addition of a monometallic catalyst to a bimetallic catalyst does not decrease the accumulation of nitrite in solution neither the formation of ammonium. A mechanism is proposed considering that nitrate reduction can occur in the presence of a bimetallic catalyst or a physical mixture of monometallic catalysts.

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5.1 Introduction

Since the discovery by Vorlop and Tacke [1] of the reduction of nitrate towards nitrogen over bimetallic catalysts in the presence of a reducing agent, several studies [2-23] (ref. 21 corresponds to chapter 3) have been carried out to find better catalysts. Nitrate reduction can be described by consecutive and parallel reactions where nitrate is reduced to nitrite in the presence of H_2, which is converted to nitrogen as main product and ammonium as undesired by-product [24-26]. One of the advantages of this process is that there is no formation of solid or liquid wastes, but the drawback is the formation of nitrite and ammonium [27-31]. The permitted levels in drinking water are 0.5 mg/L for nitrite and ammonium and 50 mg/L for nitrate.

It was demonstrated that nitrate was reduced over bimetallic catalysts, containing a noble metal (Pd, Pt or Rh) and a promoter metal (Cu, Sn, In), while nitrite can be reduced with monometallic catalysts [24,32] (ref. 32 corresponds to chapter 2). According to the literature [33,34], nitrate is reduced to nitrite by the promoter metal, and the role of the noble metal is to activate the hydrogen, which reduces the promoter metal and nitrite. The noble metal by itself does not present activity for nitrate reduction, but is effective for nitrite reduction [32] (see chapter 2).

In addition to the preparation conditions, type of metals supported, corresponding atomic ratio, support material and operation conditions [24,35], which have shown to influence both the activity and selectivity of the catalyst, the nitrite reduction seems to play an important role in the nitrate reduction selectivity, as was pointed out by Yoshinaga et al. [25]. Nitrate would be activated on Pd-Cu sites to form nitrite, which reduction took place readily on both Pd and Pd-Cu sites. In a recent work [21] (see chapter 3), it was shown that the selectivity to ammonium is higher when the noble metal is isolated, because as the noble metal is very active for hydrogenation reactions, nitrite molecules are deeply hydrogenated into ammonium.

Horold et al. [26] observed that ammonium formation is reduced when Pd and Pd-Cu catalysts are combined. Yoshinaga et al. [25] showed that a physical mixture of 5%Pd and 3%Cu catalysts supported on activated carbon presented a nitrate conversion lower than the bimetallic catalyst with the same amount of metals, while the selectivity to nitrogen increased when the mixture was used. The results obtained by Pintar and co-authors [36,37] revealed that differently prepared bimetallic catalysts and the physical mixture containing Pd/Al_2O_3 and metallic copper particles exhibited very similar activities and that the Pd-Cu active sites that promote nitrate reduction were formed *in situ* by collision of particles.

The main goal of this work was to study in a systematic way mixtures of monometallic supported catalysts, bimetallic/monometallic supported catalysts and metallic ions in solution/monometallic supported catalysts and clarify the reaction mechanism. Several experiments with physical mixtures of bimetallic and monometallic catalysts where carried out with the aim of checking if the accumulation of nitrite in solution is suppressed and, consequently, the formation of ammonium. Once nitrite is converted in the presence of monometallic catalysts [32] (see chapter 2), it was expected that nitrite formed in the bimetallic catalyst during nitrate reduction were more rapidly reduced in the presence of a monometallic catalyst. Physical mixtures of monometallic catalysts and different combinations of metals in the liquid phase with or without monometallic supported catalysts were also studied.

5.2 Experimental

5.2.1 Catalysts preparation

A commercial activated carbon NORIT GAC 1240 Plus (ACo), with a BET surface area of 869 m^2/g [32] (see chapter 2), ground to a particle diameter between 0.1 and 0.3 mm, was used as support. The bimetallic catalysts (Pd-Cu, Pt-Cu, Rh-Cu) were obtained by incipient wetness co-impregnation and the monometallic catalysts by incipient wetness impregnation, using aqueous solutions of the corresponding metal salts ($PdCl_2$, H_2PtCl_6, $RhCl_3$, $Cu(NO_3)_2$). The amount of each metal was maintained constant at 1%wt. After impregnation, the samples were dried at 100 ºC for 24 h, heat treated under a nitrogen flow at 200 ºC for 1 h and finally reduced at 100 ºC under hydrogen flow for 3 h. According to a previous study [38] (see chapter 4), these calcination and reduction temperatures were the optimum preparation conditions, avoiding sintering and formation of alloys.

5.2.2 Catalysts characterization

The textural characterization of the support (ACo) was based on the N_2 adsorption isotherms determined at -196ºC as described elsewhere [32] (see chapter 2). TEM analyses were obtained using a LEO 906E microscope operating at a 120 kV accelerating voltage. A semi-quantitative elemental analysis of the catalysts was performed by SEM and energy dispersive X-ray spectroscopy (EDS) on a JEOL JSM 35 C / Noran Voyager system. The amounts of metals eventually leached during reaction were measured in a UNICAM 939/959 atomic absorption spectrometer (AAS), using the remaining solution after each reaction test.

5.2.3 Catalysts evaluation

Reduction of nitrate was performed using a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure. In all experiments, the reactor was filled with 790 mL of deionised water and 400 mg of catalyst; then the magnetic stirrer was adjusted to 700 rpm and the gas mixture of hydrogen and carbon dioxide (1:1, flow rate = 200 Ncm^3/min) was passed through the reactor during 15 min to remove air; CO_2 acts as pH buffer (pH = 5.5). After that period, 10 mL of a nitrate solution, prepared from $NaNO_3$, was added to the reactor, in order to obtain an initial NO_3^- concentration equal to 100 mg/L. In the experiments where the metals are in the liquid phase, the same metal amount that is present in 400 mg of the catalyst used in the solid phase was added to the reactor.

The concentrations of both nitrate and nitrite ions were followed by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was a Hamilton PRP-X100 column (150 mm x 4.1 mm) working at room temperature, under isocratic conditions. The mobile phase was a solution of 0.1 M $NaCl:CH_3OH$ (45:55). The concentration of ammonium ions were determined by potentiometry using a convenient selective electrode. pH values were also measured.

Catalysts performance was evaluated by calculating the nitrate conversion ($X_{NO_3^-}$) and the selectivities to nitrite ($S_{NO_2^-}$) and ammonium ($S_{NH_4^+}$) as:

$$X_{NO_3^-} = \frac{n_{NO_3^- i} - n_{NO_3^-}}{n_{NO_3^- i}} \tag{5.1}$$

$$S_{NO_2^-} = \frac{n_{NO_2^-}}{n_{NO_3^- i} - n_{NO_3^-}} \tag{5.2}$$

$$S_{NH_4^+} = \frac{n_{NH_4^+}}{n_{NO_3^- i} - n_{NO_3^-}} \tag{5.3}$$

where $n_{NO_3^-{}_i}$ is the initial amount of nitrate (mmol) and $n_{NO_3^-}$, $n_{NO_2^-}$ and $n_{NH_4^+}$ are the amounts of the respective species (mmol) at time t (min). The selectivity to nitrogen was calculated by difference.

5.3 Results and Discussion

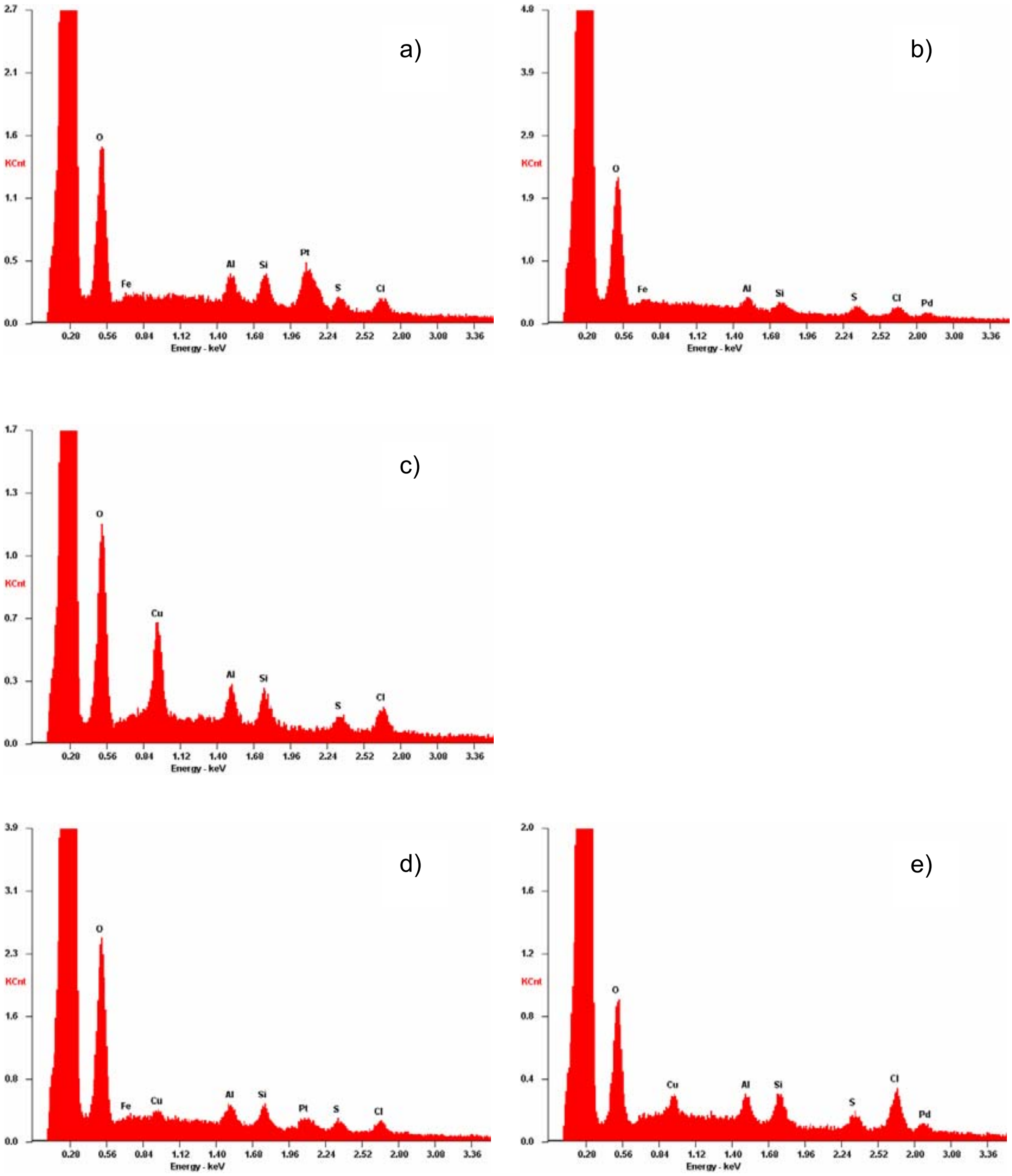
5.3.1 Catalysts characterization

TEM micrographs show that all the metals are well dispersed on the support. The average particle size of metallic phases is shown in Table 5.1.

Table 5.1 Average particle size of metallic phases.

Catalyst	d (nm)
1%Pd_ACo	13
1%Pt_ACo	3
1%Cu_ACo	3
1%Rh_ACo	5
1%Pd-1%Cu_ACo	11
1%Pt-1%Cu_ACo	3
1%Rh-1%Cu_ACo	11

SEM/EDS provide information about the catalysts surface composition. Investigation of the external surface of fresh and used monometallic and bimetallic catalysts tested in the nitrate reduction was carried out in order to evaluate the influence of operation conditions on the catalysts surface composition. The EDS spectra (Figure 5.1 a), b) and c)) of fresh monometallic catalysts demonstrated the presence of the expected metals (Pt, Pd or Cu, respectively). In the case of the Pt-Cu and Pd-Cu bimetallic catalysts it can be observed, respectively in Figure 5.1 d) and f), the presence of the two metals. Finally, for physical mixtures of the monometallic catalysts after being used in the catalytic tests, SEM/EDS spectra (Figure 5.1 f) and g)) revealed both metals on the surface of the catalyst particles. This fact is indicative of the adsorption of the dissolved metals. It is well known that activated carbons are effective adsorbents for the removal of heavy metal ions from


a)
2.7
2.1
1.6
1.1
0.5
0.0
KCnt
O
Fe
Al
Si
Pt
S
Cl
0.20
0.56
0.84
1.12
1.40
1.68
1.96
2.24
2.52
2.80
3.08
3.36
Energy - keV
b)
4.8
3.9
2.9
1.9
1.0
0.0
KCnt
O
Fe
Al
Si
S
Cl
Pd
Energy - keV
c)
1.7
1.3
1.0
0.7
0.3
0.0
KCnt
O
Cu
Al
Si
S
Cl
Energy - keV
d)
3.9
3.1
2.3
1.6
0.8
0.0
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e)
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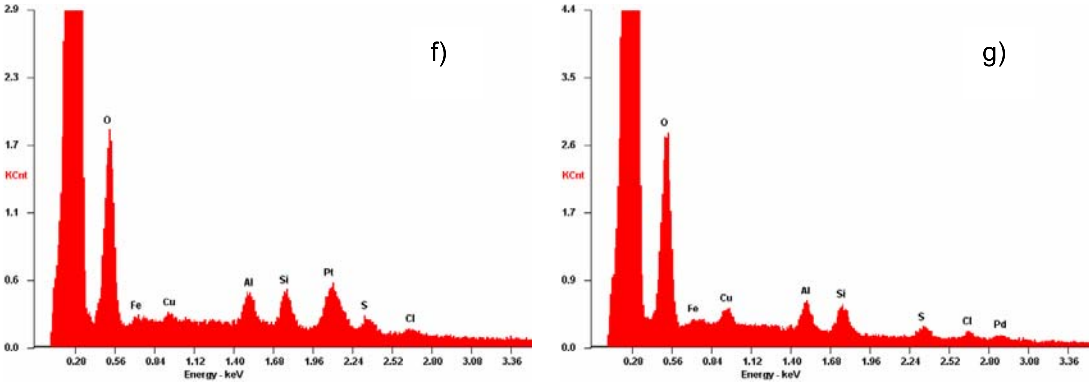

Figure 5.1 EDS spectra of the a) 1%Pt, b) 1%Pd, c) 1%Cu, d) 1%Pt-1%Cu, e) 1%Pd-1%Cu fresh catalysts and f) mixture 1%Pt+1%Cu and g) mixture 1%Pd+1%Cu after reaction tests.

aqueous phase [39]; then, it is expected that dissolved metals adsorb on the carbon surface. Activated carbons have several oxygen-containing surface groups (carboxyl, carbonyl, phenol, quinone and lactones) [40,41], which play an important role in the adsorption of metals. In order to check if there was any leaching of the metals initially supported on the activated carbon, the remaining solution after each reaction test was analyzed by atomic absorption spectroscopy. Pd or Pt were not detected, but in some experiments small amounts of Cu were measured. For example, in the experiment where the mixture of Pd and Cu monometallic catalysts was tested, a concentration of 0.042 mg/L of Cu was obtained, corresponding to a leaching of 0.8%. These observations indicate that activated carbon is a good support for the active phases [42] and a good adsorbent for the removal of metals from aqueous phases [39]; therefore, the amounts of dissolved metals are very low. Efremenko et al. [5] and Yoshinaga et al. [25] observed that the dissolved amounts of metals were negligible when activated carbon was used as support for this reaction. In addition, Calvo et al. [43], who tested Pd-Cu and Rh-Cu bimetallic catalysts prepared under similar conditions than those used in this work, observed that the leaching of the noble metals was always negligible, whereas copper leached in varying amounts. In the present work, it was observed by SEM/EDS that both metals (noble metal and copper) are present in the individual particles after using mixtures of monometallic catalysts in the catalytic tests, which, together with the observed leaching of copper by AAS, suggests that part of the leached copper is readsorbed on the carbon surface.

5.3.2 Catalytic tests

5.3.2.1 Pd-Cu catalysts

It is generally assumed that for activated carbon supported catalysts the presence of a noble metal and a promoter metal is required for nitrate reduction [24,32] (ref. 32 corresponds to chapter 2), which occurs on bimetallic sites [24,44]; however, as can be seen in Figure 5.2, the physical mixture of 1%Pd and 1%Cu presents a nitrate conversion after 5 h similar to the Pd-Cu bimetallic catalyst, but generally a better efficiency during the reaction. Pintar and co-authors [36,37] also revealed that differently prepared bimetallic catalysts and physical mixtures containing Pd/Al_2O_3 and metallic copper particles exhibited very similar activities, and according to them the Pd-Cu active sites that promote nitrate reduction were formed *in situ* by collision of particles. Yoshinaga et al. [25] observed that a physical mixture of 5%Pd/AC and 3%Cu/AC showed a nitrate conversion of 53%, while the bimetallic catalysts with the same amount of metals presented a conversion of 100%. According to these authors, the activity is related not only to the contact between the catalyst particles but also with hydrogen spillover through the catalysts particles. Maia et al. [12] observed that a physical mixture of Pd/Nb_2O_5 and Cu/Nb_2O_5 exhibited a different performance than the corresponding bimetallic catalyst (84% and 100% of nitrate conversion, respectively), proposing that the proximity between Pd and Cu is beneficial for the reaction. The results obtained show that nitrate reduction occurs providing that the metals are in close contact during reaction time, being the initial presence of bimetallic ensembles dispensable.

Figure 5.2 shows that physical mixtures of monometallic catalysts with the Pd-Cu bimetallic catalyst present not too much different performances, being the trend after 5 h of reaction the following: 1%Pd-1%Cu + 1%Pt ≈ 1%Pd-1%Cu + 1%Pd ≈ 1%Pd-1%Cu + 1%Rh > 1%Pd + 1%Cu ≈ 1%Pd-1%Cu > 1%Pd-1%Cu + 1%Cu. However, until t ≈ 200 min the mixture of 1%Pd-1%Cu + 1%Pd is the most efficient and until t ≈ 270 min the mixture of the monometallic Pd and Cu catalysts performs better than the Pd-Cu bimetallic catalyst. At the beginning of the experiment, the physical mixture 1%Pd-1%Cu + 1%Cu practically does not show any activity, which is probably responsible for the poorest performance after 5 h of reaction.

The concentration of nitrite in solution is very low in the physical mixture of Pd-Cu with Rh catalysts, but this mixture is the most selective to ammonium (see also Table 5.2). This could be related to the high selectivity of the Rh-Cu catalyst to ammonium [21] (see chapter 3). However, when Rh/AC is used in the nitrite reduction [32] (see chapter 2), this catalyst is very selective to nitrogen. Most probably, part of the copper from the Pd-Cu/ACo particles migrates to the Rh/ACo particles.

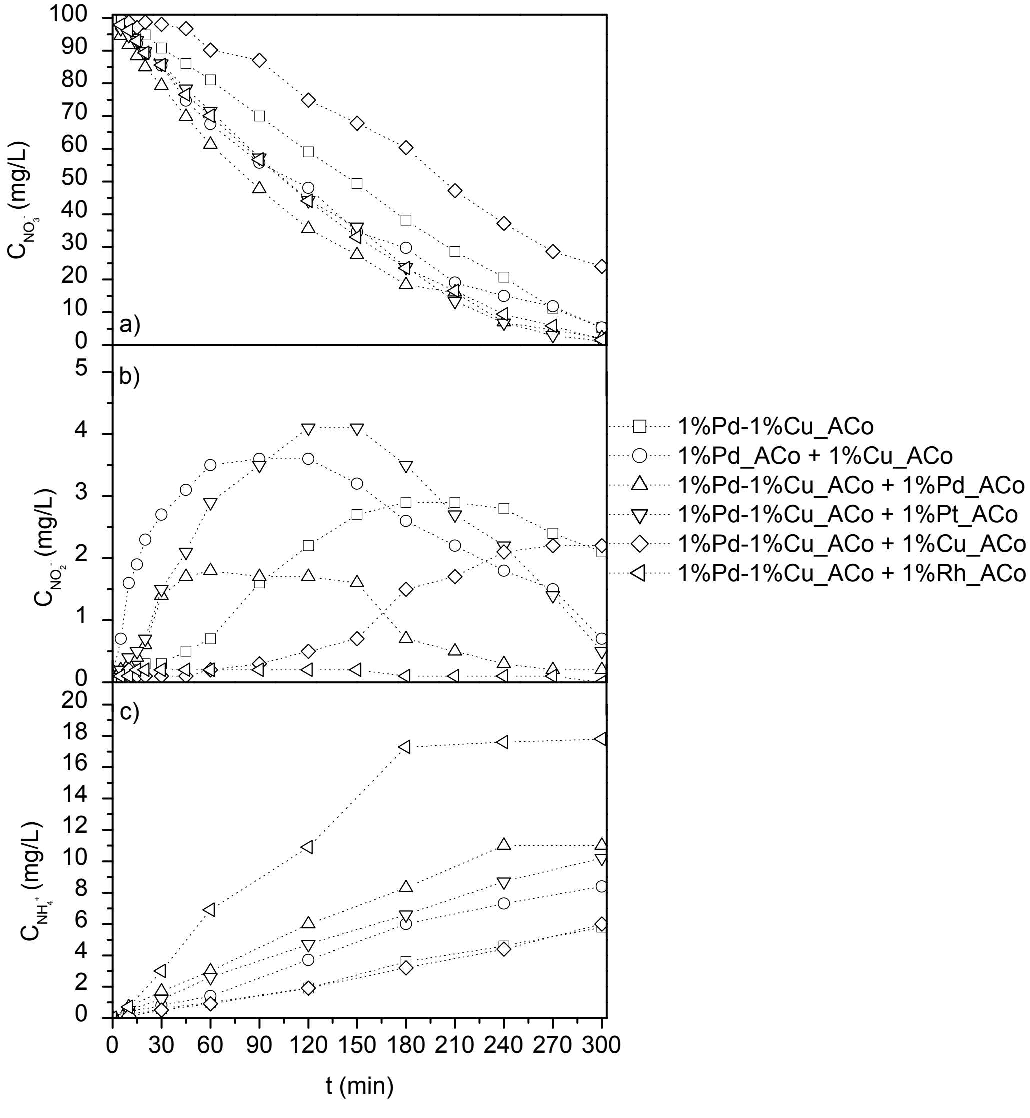

Figure 5.2 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of physical mixtures with Pd-Cu catalysts.

Initially, the concentration of nitrite accumulated in solution is higher in the mixture of the two monometallic catalysts than in the other combinations, but at the end of experiment that system presents a nitrite concentration lower than that observed in the bimetallic catalyst, probably due to the fact that palladium is very active for nitrite reaction [32] (see chapter 2) and is more accessible when the mixture is used.

Table 5.2 Nitrate conversions ($X_{NO_3^-}$) and nitrite, ammonium and nitrogen selectivities ($S_{NO_2^-}$, $S_{NH_4^+}$, S_{N_2}) of Pd-Cu catalysts after 5 h of reaction and for 50% of nitrate conversion.

	t = 300 min				**$X_{NO_3^-} = 50\%$**		
Catalyst	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Pd-1%Cu_ACo	0.95	0.03	0.21	0.76	0.06	0.19	0.75
1%Pd_ACo +1%Cu_ACo	0.95	0.01	0.30	0.69	0.09	0.24	0.67
1%Pd-1%Cu_ACo +1%Pd_ACo	0.98	0.00	0.39	0.61	0.05	0.30	0.65
%Pd-1%Cu_ACo +1%Cu_ACo	0.99	0.01	0.36	0.63	0.11	0.30	0.59
1%Pd-1%Cu_ACo +1%Cu_ACo	0.76	0.04	0.27	0.69	0.05	0.26	0.69
1%Pd-1%Cu_ACo +1%Rh_ACo	0.98	0.00	0.62	0.38	0.01	0.70	0.29

As mentioned before, for intermediate reaction times, the mixture 1%Pd-1% Cu + 1%Pd is slightly more efficient than the mixture 1%Pd-1% Cu + 1%Pt, but the nitrite concentration measured is lower, because Pd is more active for nitrite reduction than platinum [32] (see chapter 2). Contrarily to Horold et al. [26], who observed that ammonium formation is reduced when Pd and Pd-Cu catalysts supported on alumina are used, it is shown in the present work that the Pd-Cu bimetallic catalyst supported on activated carbon presents the lowest selectivity to ammonium, also being the most selective to nitrogen. Actually, Table 5.2 shows that the physical mixtures with Pt or Pd monometallic catalysts are more selective to ammonium than the bimetallic catalyst, which must be related to the high hydrogenation capacity of the noble metals, i.e. noble metals are more easily accessible in the monometallic catalysts and therefore the nitrite molecules are deeply hydrogenated into ammonium [21] (see chapter 3). The mixture of the two monometallic catalysts and the mixtures with the monometallic Cu catalyst have intermediate selectivities between the bimetallic catalyst and the mixture with the Pd or Pt catalysts. In the case of the mixture with copper, this occurs probably because copper is very selective towards nitrogen in the reduction of nitrite, as demonstrated in a previous work [32] (see chapter 2).

5.3.2.2 Pt-Cu catalysts

Unlike the observations in the experiments with the pairs Pd-Cu (section 5.3.2.1.) and Rh-Cu (to be presented in section 5.3.2.3.), in the experiments with the Pt-Cu system (Figure 5.3) there are more significant differences in activities and selectivities. The trend in nitrate conversion after 5 h of reaction is the following: 1%Pt-1%Cu + 1%Pd > 1%Pt-1%Cu + 1%Pt > 1%Pt-1%Cu + 1%Rh > 1%Pt + 1%Cu > 1%Pt-1%Cu > 1%Pt-1%Cu + 1%Cu. In this case, the addition of noble metal catalysts increases significantly the performance of the Pt-Cu bimetallic catalyst.

As observed for the mixture 1%Pd-1%Cu + 1%Cu (Figure 5.2), the mixture 1%Pt-1%Cu + 1%Cu practically does not show any activity in the beginning of the experiment. Most probably, some of the copper leached from the monometallic catalyst adsorbs on the bimetallic catalyst, increasing its copper contents. Therefore, the performance of this catalytic system is in agreement with the results obtained in a previous work [21] (see chapter 3), where it was found that increasing the copper content above 1% decreases the nitrate conversion. Once again, it is observed that the physical mixture of Pt and Cu monometallic catalysts is more efficient than the Pt-Cu bimetallic catalyst, suggesting, once more, that the initial presence of bimetallic sites is not mandatory, being enough that the metals become in close contact during reaction.

In the mixtures 1%Pt-1%Cu + 1%Pd or Pt the concentration of nitrite accumulated in solution goes through a maximum; as observed in the mixtures with the Pd-Cu system (Figure 5.2), the mixture with Rh presents the lowest nitrite concentration and the highest ammonium formation. Nitrite concentrations measured in the experiment with the mixture with the Pd monometallic catalyst are lower than those detected in the mixture with Pt, probably due to the fact that palladium is more active than platinum for nitrite reduction [32] (see chapter 2).

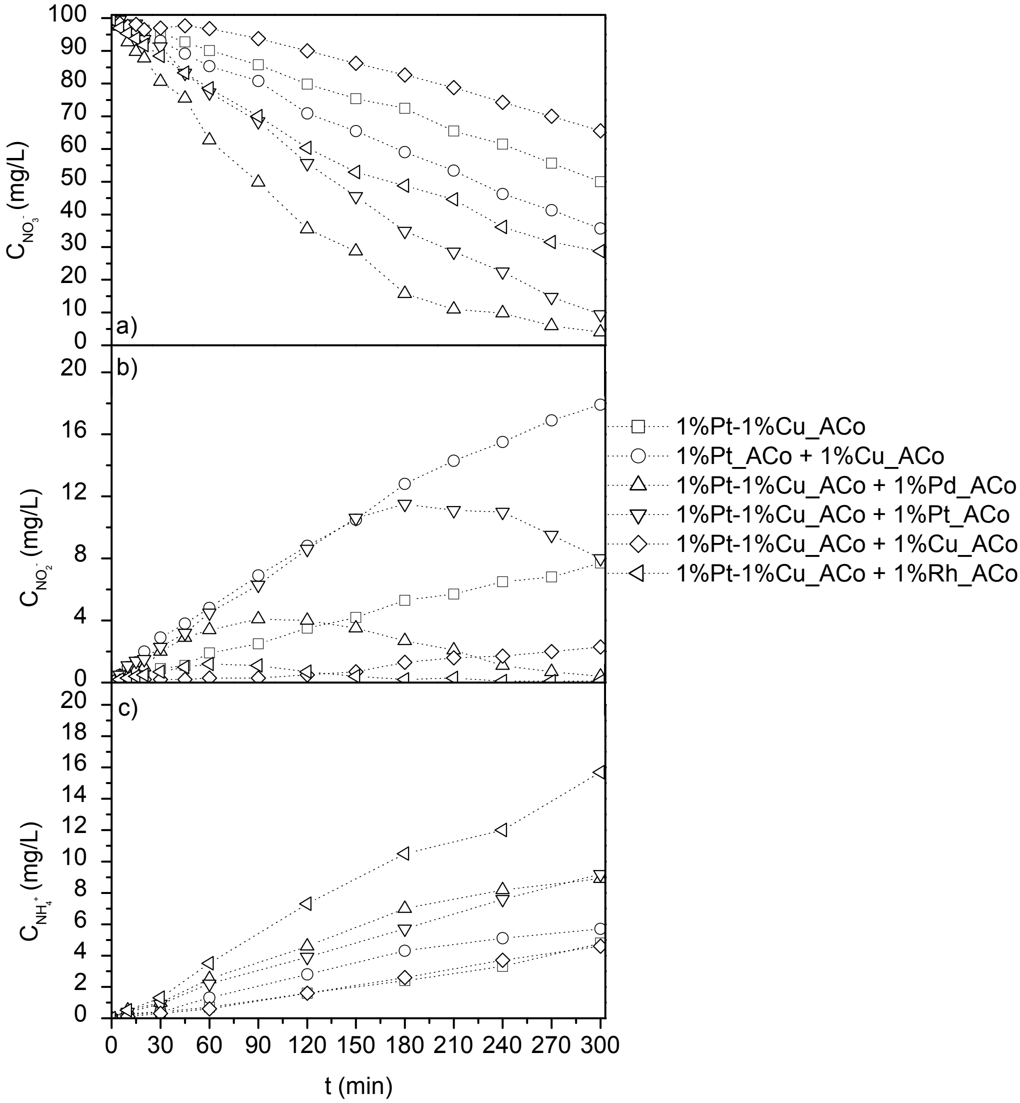

Figure 5.3 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of physical mixtures with Pt-Cu catalysts.

Concerning the selectivities, it can be observed in Table 5.3 that the mixture 1%Pt-1%Cu + 1%Pd is the most selective to nitrogen, being the mixture of monometallic catalysts and the mixture of the bimetallic system with the Rh monometallic catalyst the less selective. Moreover, the latter mixture is the most selective to ammonium. The addition of Pd monometallic catalyst to the Pt-Cu bimetallic catalyst increases significantly not only the conversion (from 50% to 96% after 5 h) but also the selectivity to nitrogen (from 45% to 67%). It can be concluded that a significant synergic effect occurs when the Pd catalyst is added to the Pt-Cu bimetallic catalyst. This effect is probably related to copper migration between particles, forming an additional Pd-Cu bimetallic catalyst *in situ*, and with the fact that palladium is very active for nitrite reduction with high selectivity to nitrogen [32] (see chapter 2).

Table 5.3 Nitrate conversions ($X_{NO_3^-}$) and nitrite, ammonium and nitrogen selectivities ($S_{NO_2^-}, S_{NH_4^+}, S_{N_2}$) of Pt-Cu catalysts after 5 h of reaction and for 50% of nitrate conversion.

	t = 300 min				$X_{NO_3^-} = 50\%$		
Catalyst	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Pt-1%Cu_ACo	0.50	0.21	0.34	0.45	0.21	0.34	0.45
1%Pt_ACo +1%Cu_ACo	0.64	0.38	0.31	0.31	0.40	0.34	0.26
1%Pt-1%Cu_ACo +1%Pd_ACo	0.96	0.01	0.32	0.67	0.10	0.24	0.66
1%Pt-1%Cu_ACo +1%Pt_ACo	0.91	0.12	0.35	0.53	0.25	0.31	0.44
1%Pt-1%Cu_ACo +1%Cu_ACo	0.34	0.09	0.46	0.45	-	-	-
1%Pt-1%Cu_ACo +1%Rh_ACo	0.71	0.00	0.76	0.24	0.01	0.71	0.28

5.3.2.3 Rh-Cu catalysts

With the exception of the Rh and Cu monometallic catalysts mixture, Figure 5.4 shows that nitrate conversions after 5 h are not too much different for all the physical mixtures tested, the following order being observed: 1%Rh-1%Cu > 1%Rh-1%Cu +1%Pd = 1%Rh-1%Cu +1%Cu > 1%Rh-1%Cu +1%Rh > 1%Rh-1%Cu +1%Pt >> 1%Rh + 1%Cu. Nevertheless, until about 180 min the trend in nitrate conversion is somewhat different: 1%Rh-1%Cu + 1%Pd > 1%Rh-1%Cu

+1%Rh > 1%Rh-1%Cu > 1%Rh-1%Cu +1%Pt > 1%Rh-1%Cu +1%Cu > 1%Rh + 1%Cu.

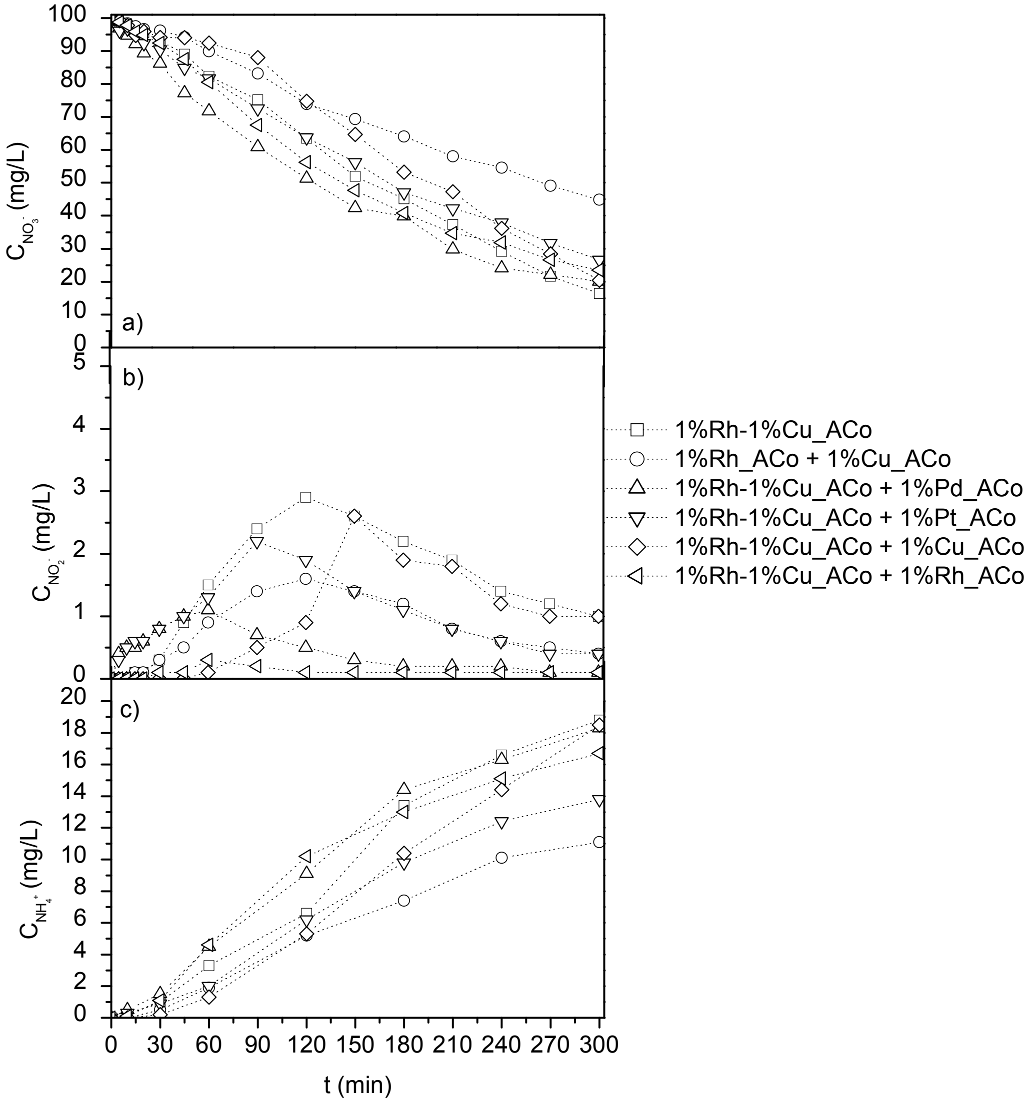

Figure 5.4 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of physical mixtures with Rh-Cu catalysts.

As observed for the mixtures with Pd-Cu and Pt-Cu bimetallic catalysts, the mixture with the monometallic Cu catalyst presents a low initial activity; however, comparatively, the activity increases significantly after 90 min of reaction in this case.

Nitrite concentrations accumulated in solution are generally lower than those measured in the previous combinations studied (Pd-Cu and Pt-Cu). This was already expected, since the mixtures 1%Pd-1%Cu + 1%Rh and 1%Pt-1%Cu + 1%Rh presented the lowest nitrite concentrations. Accordingly, the mixture 1%Rh-1%Cu + 1%Rh also shows the lowest level of nitrite concentrations. Nevertheless, as observed in the other combinations with rhodium, the concentration of ammonia formed is very high. Table 5.4 shows that the catalysts with Rh are very selective to ammonium.

Table 5.4 Nitrate conversions ($X_{NO_3^-}$) and nitrite, ammonium and nitrogen selectivities ($S_{NO_2^-}, S_{NH_4^+}, S_{N_2}$) of Rh-Cu catalysts after 5 h of reaction and for 50% of nitrate conversion.

	t = 300 min				$X_{NO_3^-} = 50\%$		
Catalyst	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Rh-1%Cu_ACo	0.84	0.01	0.77	0.22	0.06	0.80	0.14
1%Rh_ACo +1%Cu_ACo	0.55	0.01	0.69	0.30	0.02	0.73	0.25
1%Rh-1%Cu_ACo +1%Pd_ACo	0.80	0.00	0.80	0.20	0.01	0.67	0.32
1%Rh-1%Cu_ACo +1%Pt_ACo	0.73	0.01	0.65	0.34	0.04	0.63	0.33
1%Rh-1%Cu_ACo +1%Cu_ACo	0.80	0.02	0.80	0.18	0.04	0.77	0.19
1%Rh-1%Cu_ACo +1%Rh_ACo	0.76	0.00	0.75	0.25	0.00	0.78	0.22

In this system, the addition of monometallic catalysts to the Rh-Cu bimetallic catalyst decreases the nitrite concentration detected during the reaction time, increasing the nitrogen selectivities. Nevertheless, they are still very low.

5.3.2.4 Experiments with metals in the liquid phase

Physical mixtures of Pd and Cu or Pt and Cu monometallic catalysts present similar or higher efficiency than the correspondingly bimetallic catalysts. With the aim of clarifying the mechanism, some additional experiments with both metals in the liquid phase or with one monometallic catalyst and the other metal in the liquid phase were carried out. The following experiments were performed:

- 1%Pd+1%Cu: both metals are in the liquid phase; the same metal amounts that are present in 400 mg of the supported catalyst were used;

- 1%Pd+1%Cu+ACo: both metals are in the liquid phase and 400 mg of the support (ACo) was added to the reactor;

- 1%Pd_ACo+0.1% or 1%Cu: palladium is supported on activated carbon and copper is in the liquid phase;

- 1%Cu_ACo+1%Pd: copper is supported on activated carbon and palladium is in the liquid phase.

As can be seen in Figure 5.5, when both metals are in the liquid phase (1%Pd+1%Cu), even after adding the support (1%Pd+1%Cu+ACo), no significant reduction of nitrate is observed. The experiment where the support is added was carried out with the aim of verifying if the support by itself was able to promote the contact between the metals in a way that they could become active for this reaction; therefore, it may be concluded that this does not happen. The results obtained in the experiments where one metal is supported and the other is dissolved in solution clearly show that palladium must be supported, since in the experiment where palladium is not supported (1%Cu_ACo+1%Pd) no activity is observed too. On the other hand, copper does not need to be supported initially, because the experiment 1%Pd_ACo+1%Cu presents similar nitrate conversion after 5 h (95%) as that obtained with the Pd-Cu bimetallic catalyst and with the mixture of Pd and Cu monometallic catalysts (see Figure 5.5). The main difference is related to the ammonium formation. The experiment with 1%Pd_ACo+1%Cu leads to the highest ammonium formation, which must be related to the fact that palladium is very active for hydrogenation reactions, and the presence of noble metal sites on the surface promotes the over-reduction to ammonium. In the bimetallic catalysts the noble metal is less accessible (palladium and copper particles are probably intercalated or superimposed) than in the physical mixtures (here some bimetallic particles can

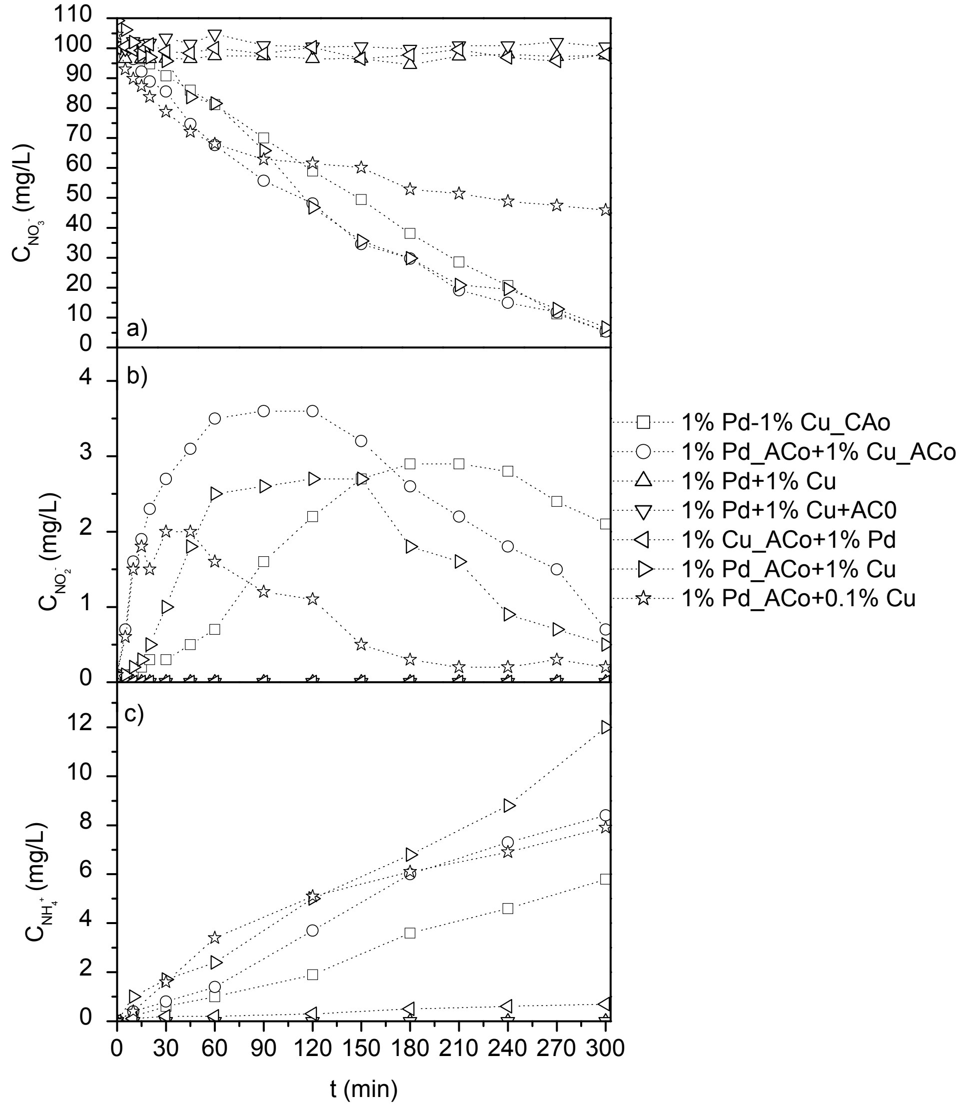

Figure 5.5 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of the Pd-Cu system with one or the two metals in the liquid phase.

also be present due to the adsorption of the leached copper) favouring the formation of nitrogen. In fact, in the experiment with 1%Pd_ACo+1%Cu the nitrogen selectivity is around 60% after 5 h of reaction, while in the experiment with the bimetallic catalyst is 76%. Even when a small amount of dissolved copper is used (1%Pd_ACo+0.1%Cu), it can be observed in Figure 5.5 that the conversion obtained after 5 h is 58% and the corresponding selectivity to nitrogen is 54%, which are relatively interesting values.

An additional experiment was carried out using the 1%Pd_ACo monometallic catalyst and copper in the liquid phase (the same metal amount that would be present in 400 mg of the 1%Cu monometallic catalyst was added to the reactor). After that, a second sequential reaction test was carried out without the addition of copper to the liquid in the reactor, and using the catalyst of the previous experiment, after being washed with distilled water and dried in the oven at 100 ºC. As can be seen in Figure 5.6, the results are similar in both experiments. The results obtained allow concluding that copper in the liquid phase is adsorbed on the carbon surface and, for that reason, the initially monometallic catalyst is very active for nitrate reduction. Actually, a bimetallic catalyst is produced under the reaction conditions used. In fact, after the first experiment, only 1.8% of the dissolved copper added to the reactor was measured by atomic absorption spectroscopy in the remaining solution.

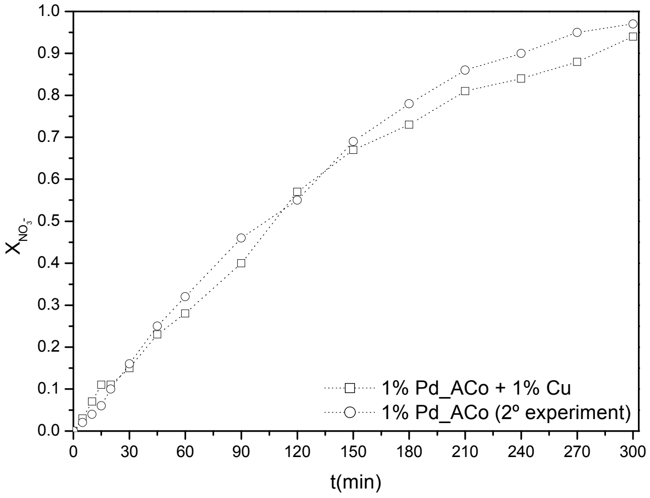

Figure 5.6 NO_3^- conversion as a function of time during nitrate reduction in the presence of 1%Pd catalyst and copper in liquid phase or copper ion adsorbed on the carbon surface (2nd experiment).

In our opinion, the good performance of the mixture of monometallic catalysts is due to the adsorption of the leached copper in the activated carbon producing a kind of bimetallic catalysts, which differs from the explanations previously proposed by Pintar and co-authors [36,37], for whom the Pd-Cu active sites were formed *in situ* by collision of particles and by Yoshinaga et al. [25], for whom the activity of the monometallic mixtures was due not only to the contact between the catalyst particles but also with hydrogen spillover through the catalysts particles.

5.3.2.5 Remarks on the mechanism

Based on the results obtained in this work, a mechanism was proposed considering that nitrate reduction can occur in the presence of a bimetallic catalyst or a physical mixture of monometallic catalysts. It is established that monometallic catalysts are generally inactive for nitrate reduction when activated carbon is used as support, a second metal being necessary to reduce nitrate to nitrite [1,32] (ref. 32 corresponds to chapter 2). For the physical mixtures of monometallic catalysts nitrate reduction could occur due to the *in situ* formation of bimetallic catalysts. SEM/EDS revealed that the individual support particles of physical mixtures of monometallic catalysts used in the catalytic tests present both metals; so the dissolved copper is able to adsorb on the surface of the activated carbon promoting the formation of bimetallic catalysts. From the results obtained using metals in the liquid phase (section 5.3.2.4), it can be said that the only constraint is that the noble metal must be already supported, most probably metal noble particles are required for this reaction, and copper does not need to be in the metallic form to be active [45]. Therefore, for all the situations where the catalysts were active, the general mechanism for nitrate reduction can be described as occurring in bimetallic catalysts. Figure 5.7 shows schematically the mechanism proposed, exemplified for the Pd-Cu pair. The role of the promoter metal is to reduce nitrate according to a redox reaction, leading to nitrite and to an oxidized form of the promoter metal, which is reduced by hydrogen adsorbed on the noble metal [34]. The noble metal by itself does not present activity for nitrate reduction, but is effective for nitrite reduction [32] (see chapter 2). Therefore, nitrite migrates from the promoter metal to palladium sites, where it is further reduced to the end-products (nitrogen or ammonium). When the reduction of nitrite occurs in the presence of a mixture containing noble monometallic catalysts the formation of ammonium is favoured due to the high hydrogenation capacity of noble metals (more accessible in this case than in the standard bimetallic catalysts), decreasing the selectivity of the process to nitrogen.

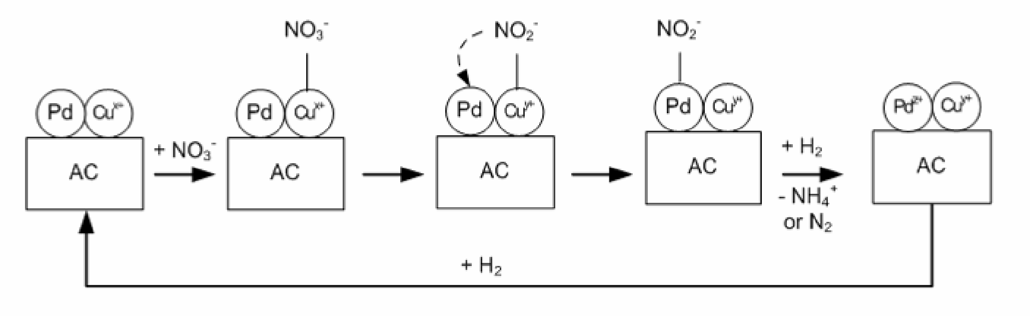

Figure 5.7 Scheme of reaction mechanism.

5.4 Conclusions

According to the experimental results, the following main conclusions can be drawn:

- The highest selectivity to nitrogen in this study (76%) was obtained with the 1%Pd-1%Cu bimetallic catalyst. In general, the mixtures involving the Pd-Cu bimetallic catalyst present the highest nitrate conversions and selectivities to nitrogen.
- When the Pd monometallic catalyst is added to the Pt-Cu bimetallic catalyst a strong synergic effect is observed, being this mixture the most selective to nitrogen among those involving the Pt-Cu pair.
- Physical mixtures of Pt and Cu or Pd and Cu monometallic catalysts are roughly as efficient as the corresponding bimetallic catalysts. This fact indicates that the presence of bimetallic sites in the initial catalyst is not mandatory to promote the reduction of nitrate; it is sufficient that the metals become in close contact during reaction.
- Activated carbon demonstrated to be a good support for this reaction. For the mixture of monometallic catalysts, it was able to promote the formation of *in situ* bimetallic catalysts due to the adsorption of the leached copper. The noble metal must be already supported, and copper does not need to be in the metallic form.
- A general mechanism involving bimetallic catalysts was proposed, which explains that nitrate reduction can occur in the presence of bimetallic catalysts or physical mixtures of monometallic catalysts.

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Chapter 6

6 Nitrate reduction catalyzed by Pd-Cu and Pt-Cu supported on different carbon materials[1]

The activities and selectivities of Pd-Cu and Pt-Cu bimetallic catalysts supported on different carbon materials (activated carbons with different surface chemistries, multiwalled carbon nanotubes and carbon xerogels) were studied in the catalytic reduction of nitrate in water. The surface chemistry of the support has an important role in the catalyst activity and selectivity, being its influence more pronounced when Pt-Cu catalysts are used. Generally, catalysts supported on basic carbon materials are more active and selective.

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[1] O.S.G.P. Soares, J.J.M. Órfão, M.F.R. Pereira, *Nitrate reduction catalyzed by Pd-Cu and Pt-Cu supported on different carbon materials.* Catal. Lett. in press (2010).

6.1 Introduction

Activated carbon is a widely used material in the industry. Water and wastewater treatment, namely as adsorbent of heavy metals and organic compounds, are the main applications [1]. Moreover, carbon materials have attracted a growing interest in heterogeneous catalysis, as catalysts on their own or as catalysts support, due to their specific characteristics, namely: (i) resistance to acid and basic media, (ii) possibility to control, up to certain limits, the porosity and surface chemistry and (iii) easy recovery of precious metals by support burning resulting in a low environmental impact [2,3]. Activated carbons have a great potential as catalyst support, especially when expensive noble metals are used, since a high metal loading and dispersion can be achieved. However, it is well documented that the role of the support is not merely that of a carrier; the interaction between the active phase and the support can also affect the catalytic activity [2].

Natural nitrate levels in groundwater are generally very low (typically < 10 mg/L), but concentrations higher than 50 mg/L are frequently observed in several parts of Europe. Nitrate concentration is increasing as a result of human activities such as: agriculture, industry, domestic effluents and emissions from combustion engines [4]. Nitrate is potentially harmful because it can be transformed into nitrite in the human body, which can cause blue baby syndrome; in addition, it is a precursor of the carcinogenic nitrosamines and can originate eutrophication in rivers and lakes. For these reasons, drinking water standards in Europe have been set. The maximum allowable concentration is 50 mg/L for nitrate and 0.5 mg/L for nitrite and ammonium.

The catalytic reduction of nitrate has been suggested in the literature as a promising method to remove nitrate from water. This process consists in the reduction of nitrate to nitrogen over bimetallic catalysts in the presence of a reducing agent [5]. The formation of ammonium as by-product is the critical problem of this process. Since the discovery by Vorlop and Tacke [5], several studies have been carried out using bimetallic catalysts, such as Pd-Cu [6-8], Pt-Cu [6,9], Pd-Sn [10-13] supported on different materials such as activated carbon [14-17] (ref. 15 and 16 correspond to chapters 2 and 3), cationic resin [18], alumina [19,20], titania [21,22], and other metal oxides [23-26]; however, the selectivities are not yet satisfactory. The activity and selectivity of the bimetallic catalysts in nitrate reduction have shown to be highly dependent on the preparation method, mode of noble metal promoting, metal-promoter ratio as well as the operation conditions. The selection of the support is also very important in this process, since the catalysts activity and selectivity can be affected by the interaction between the active phase and the support. Activated carbon supported bimetallic catalysts have been shown to be very active and selective in the reduction of nitrate [27-29]. For example, Wang et al. [27] reported that a 3.6%Pd-2.0%Cu(%wt) catalyst supported on hydrophobic activated carbon is a very active and selective catalyst for the reduction of nitrate in water. They observed that the activity and selectivity of the catalysts depended on the support used but they did not study the influence of the surface chemistry of the activated carbon. Sakamoto et al. [28] observed that the activity and selectivity of a $Cu_{0.63}$-Pd catalyst supported on activated carbon were higher than the same metallic phases supported on TiO_2, Al_2O_3 and ZrO_2.

The knowledge about the use of activated carbon as a support for the reduction of nitrates is not sufficient, particularly when compared to other supports like alumina. The variability of the activated carbon properties according to the original material is the main reason for that. In this work, the activities and selectivities of Pd-Cu and Pt-Cu bimetallic catalysts supported on different carbon materials (activated carbons with different surface chemistries, multiwalled carbon nanotubes and carbon xerogels) were studied. To the best of our knowledge, there are no studies on the influence of the surface chemistry of activated carbons used as support of the mentioned metallic phases in the nitrate reduction. Matatov-Meytal and Sheintuch [14] studied the relation between the surface composition of Pd-Cu catalysts supported on activated carbon cloths and their activity and selectivity. However, they only present surface composition results of high resolution scanning electron microscopy (HRSEM) and CO chemisorption.

Activated carbons with different surface chemistries, multiwalled carbon nanotubes and carbon xerogels were selected for the present work with the aim to study the influence of the surface characteristics of the carbon materials on the properties of the metal phases and, consequently, on the performance of the prepared catalysts for the nitrate reduction. In addition, carbon nanotubes and carbon xerogels were chosen due to their large mesoporosity, in contrast with the essentially microporous activated carbons, in order to avoid internal mass transfer limitations. It is expected that the use of these materials may increase the nitrogen selectivity, avoiding the overreduction of the intermediate nitrite into ammonium in the interior of the small pores.

6.2 Experimental

6.2.1 Catalysts preparation

A NORIT GAC 1240 PLUS commercial activated carbon (sample ACo), ground to a particle diameter between 0.1 and 0.3 mm, was used as the starting material for the preparation of samples with different surface chemical properties, but with no major differences in their textural properties, to be used as support. An acid material (sample AC1) was prepared by oxidation of ACo in liquid phase with HNO_3. Oxidation with HNO_3 was carried out in a 100 cm^3 Soxhlet extraction apparatus connected to a boiling flask and to a condenser. In each run, 100 cm^3 of HNO_3 6 M and 9 g of activated carbon were introduced into a 250 cm^3 Pyrex round-bottom flask and heated to boiling temperature with a heating mantle. The reflux was stopped after 3 h. Then, the activated carbon was washed with distilled water to neutral pH and dried at 110 ºC for 24 h. Sample AC1 was used as the starting material for the preparation of basic samples by thermal treatments. Samples AC2 and AC3 were obtained by heat treatment of AC1 during 1 h at 700 ºC under N_2 or H_2 flow, respectively. A commercial multiwalled carbon nanotubes sample Nanocyl-3100 (CNT1) and a sample prepared as described elsewhere [30] (CNT2) were also used as supports, as well as a carbon xerogel (CXG) with average pore diameter of 13 nm prepared as described elsewhere [31].

The catalysts were prepared by incipient wetness co-impregnation, from aqueous solutions of the corresponding metal salts ($PdCl_2$, H_2PtCl_6, $Cu(NO_3)_2$). After impregnation, the samples were dried at 110 ºC for 24 h. The contents of noble metal and copper were maintained constant at 2%Pd-1%Cu and 1%Pt-0.3%Cu (weight percent) which are among the best formulations for activated carbon supported catalysts, according to a previous study [15] (see chapter 3). These formulations correspond to similar atomic copper content. The Pd-Cu catalysts were heat treated under nitrogen flow at 200 ºC for 1 h and the Pt-Cu catalysts were heat treated under nitrogen flow at 200 ºC for 1 h and reduced at 100 ºC under hydrogen flow for 3 h. These preparation conditions were selected for the present work because they presented the best performances in previous studies [32] (see chapter 4), since it was observed that by increasing the calcination and reduction temperatures some alloying may occur, resulting in a decrease in the catalytic activity.

6.2.2 Catalysts characterization

Supports and catalysts were characterized using different techniques: N_2 adsorption at -196 ºC, transmission electron microscopy (TEM), temperature programmed desorption (TPD) and determination of pH_{pzc}.

The textural characterization of the materials was based on the corresponding N_2 adsorption isotherms, determined at -196 ºC with a Nova 4200e (Quantachrome Instruments) equipment. BET surface areas (S_{BET}) were calculated, as well as mesopore surface areas (S_{meso}) and micropore volumes (V_{micro}) according to the t-method.

TEM micrographs were obtained using a LEO 906E microscope operating with an accelerating voltage of 120 kV.

Temperature programmed desorption (TPD) spectra of CO and CO_2 were performed in an AMI-200 (Altamira Instruments) apparatus. In a typical experiment, 100 mg of the carbon material were submitted to a 5 ºC/min linear temperature rise up to 1100 ºC under helium at a flow rate of 25 Ncm^3/min. The amounts of CO (m/z = 28) and CO_2 (m/z = 44) released from the samples were followed with a mass spectrometer (Dymaxion 200 amu, Ametek). For CO_2, a calibration procedure between its signals at m/z = 44 and m/z = 28 was carried out in order to discount the influence of the m/z = 44 signal in the m/z = 28 during the TPD experiments.

The pH_{pzc} of carbon materials were determined by mixing 150 mg of each sample with 50 cm^3 of 0.01M NaCl solution with pH values adjusted between 2 and 12, by adding 0.1 M HCl or 0.1 M NaOH. The final pH was measured after 24 h of shaking at room temperature. The pH_{pzc} is the point were the curve pH_{final} *vs* $pH_{initial}$ crosses the line $pH_{initial} = pH_{final}$.

6.2.3 Catalysts evaluation

The reduction of nitrate tests were carried out in a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure, and using hydrogen as reducing agent. Initially, 790 mL of deionised water and 400 mg of catalyst were fed into the reactor, the magnetic stirrer was adjusted to 700 rpm and the gas mixture of hydrogen and carbon dioxide (1:1, flow rate = 200 Ncm^3/min) was passed through the reactor during 15 min to remove oxygen; CO_2 acts as pH buffer (pH = 5.5). After that period, 10 mL of a nitrate solution, prepared from $NaNO_3$, were added to the reactor, in order to obtain an initial NO_3^- concentration equal to 100 mg/L.

Small samples were taken from the reactor after defined periods for determination of nitrate, nitrite and ammonium concentrations. Nitrate and nitrite ions were simultaneously determined by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was a Hamilton PRP-X100 column (150 mm x 4.1 mm) working at room temperature, under isocratic conditions. The mobile phase was a solution of 0.1 M $NaCl:CH_3OH$ (45:55). Ammonium ions were determined by potentiometry using a convenient selective electrode. pH values were also measured.

The amounts of palladium, platinum and copper eventually lixiviated during reaction were measured in a UNICAM 939/959 atomic absorption spectrometer, using the remaining solution after each reaction test. No dissolution of Pd or Pt was detected, but in some experiments small amounts of dissolved Cu were measured. In the case of Pd-Cu catalysts a maximum leaching of 6.7% of copper was measured for the catalysts supported on samples AC2 and AC3, being lower than 1% for the other catalysts. In the case of Pt-Cu catalysts the value of dissolved Cu obtained was lower than 1% of the amount impregnated, for most of the samples, with the exception of the catalyst supported on sample CXG, which presented a leaching of 3.2%.

The selectivities to nitrite, ammonium and nitrogen were calculated as:

$$S_{NO_2^-} = \frac{n_{NO_2^-}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{6.1}$$

$$S_{NH_4^+} = \frac{n_{NH_4^+}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{6.2}$$

$$S_{N_2} = \frac{2 * n_{N_2}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{6.3}$$

where $n_{NO_3^-{}_i}$ is the initial amount of nitrate (mmol) and $n_{NO_3^-}$, $n_{NO_2^-}$, $n_{NH_4^+}$ and n_{N_2} are the amounts of the respective species (mmol) at time t (min). The amounts of nitrogen were calculated by a mole balance.

6.3 Results and Discussion

6.3.1 Catalysts characterization

6.3.1.1 Textural properties

Table 6.1 shows the textural properties of the supports tested. Activated carbons present the highest BET surface areas and the multiwalled carbon nanotubes present the lowest values and absence of micropores. The carbon xerogel presents a mesopore surface area higher than the activated carbon samples. As expected [33,34], no major differences in the textural properties of the activated carbons were observed after oxidation or thermal treatments. The slight decrease of the mesopore surface area and micropore volume for the sample oxidized with HNO_3 (AC1) may be due to the high amount of oxygen-containing groups on the surface of the activated carbon, which may partially block the access of N_2 molecules to the pores. The small increase in BET surface area and micropore volume in the heat treated samples (AC2 and AC3), relatively to the sample oxidized with HNO_3 (AC1), is related to the decomposition of the mentioned oxygen groups.

Table 6.1 Textural characterization and pH_{pzc} values of the supports used and metallic particle size mode of the 1%Pt-0.3%Cu catalysts.

Sample	S_{BET} (m^2/g)	S_{meso} (m^2/g)	V_{micro} (cm^3/g)	pH_{pzc}	d_M (nm)
ACo	968	177	0.346	8.3	2
AC1	886	162	0.322	3.1	15
AC2	947	164	0.342	9.0	3
AC3	1001	165	0.349	9.9	3
CNT1	320	320	0	7.0	2
CNT2	196	196	0	7.2	4
CXG	687	287	0.110	7.8	14

It was assumed that surface areas of the supported metal catalysts are not significantly different from the original supports, once the samples 2%Pd-1%Cu_ACo and 2%Pt-1%Cu_ACo (the last one with high metal loading than that used in this work) were analysed and it was observed that the textural parameters remained almost unchanged compared to the unloaded carbon [15] (see chapter 3). The same performance was observed for the carbon nanotubes supported catalysts.

6.3.1.2 TEM of catalysts

TEM analyses were made in order to get information on the metallic particle size distributions. Table 6.1 shows the particle size mode of the Pt-Cu catalysts. With exception of the catalysts supported on AC1 and CXG, which present a particle size distribution with a mode of 15 and 14 nm, respectively, all the other catalysts present a mode between 2 and 4 nm, which suggests that metals are well dispersed on the support.

In the case of the Pd-Cu catalysts, only a few particles were observed, probably due to the fact that these catalysts were only heat treated at 200 ºC (i.e. not completely reduced) and, consequently, only a few metal particles were generated, or the particles have a diameter lower than 2 nm (detection limit of the equipment used).

6.3.1.3 TPD of carbon supports

Figure 6.1 shows the TPD spectra (evolution of CO and CO_2) of the carbon supports. Comparing the TPD spectra of the activated carbon samples, it is obvious that the treatment with HNO_3 originates a large amount of oxygen-containing surface groups. Sample AC1 contains a large amount of carboxylic acid groups (released as CO_2 below 400 ºC), lactones (released as CO_2 around 650 ºC) and some carboxylic anhydrides (released as CO and CO_2 at around 550 ºC). Phenol groups (released as CO at around 700 ºC) and carbonyl/quinone groups (released as CO at around 850 ºC) are also present [33,34]. This sample has acid properties due to the high amount of oxygenated groups, most of them having acid characteristics.

The heat treatment of the acid sample at 700 ºC under N_2 flow (sample AC2) and H_2 flow (sample AC3) originates materials with quite low content of oxygen-containing groups. It can be observed in Figure 6.1 that the CO_2 releasing groups (carboxylic acids and anhydrides, lactones) have been completely removed and only some of the CO releasing groups at high temperatures still remain on the carbon surface, particularly in the case of sample AC2. These groups can be assigned to carbonyls and quinones that have not been decomposed by the treatment at 700 °C and pyrone groups, which have basic properties and decompose at high temperatures. These samples have basic properties, which are due to this type of oxygen-containing groups and mainly to the electron rich oxygen-free sites located on the carbon basal planes [35]. Heat treatments under inert atmosphere at high temperatures are effective to remove oxygen, but the resulting activated carbon has a surface with reactive sites capable of reincorporating oxygen, leading to the formation of some of the previously removed groups [36]. Treatments with hydrogen also remove oxygen groups but leave stable basic surfaces by forming C–H bonds, thus preventing further adsorption of oxygen. This is in agreement with the results obtained in this work, once the TPD spectrum of sample AC2 shows a higher amount of CO releasing groups than sample AC3.

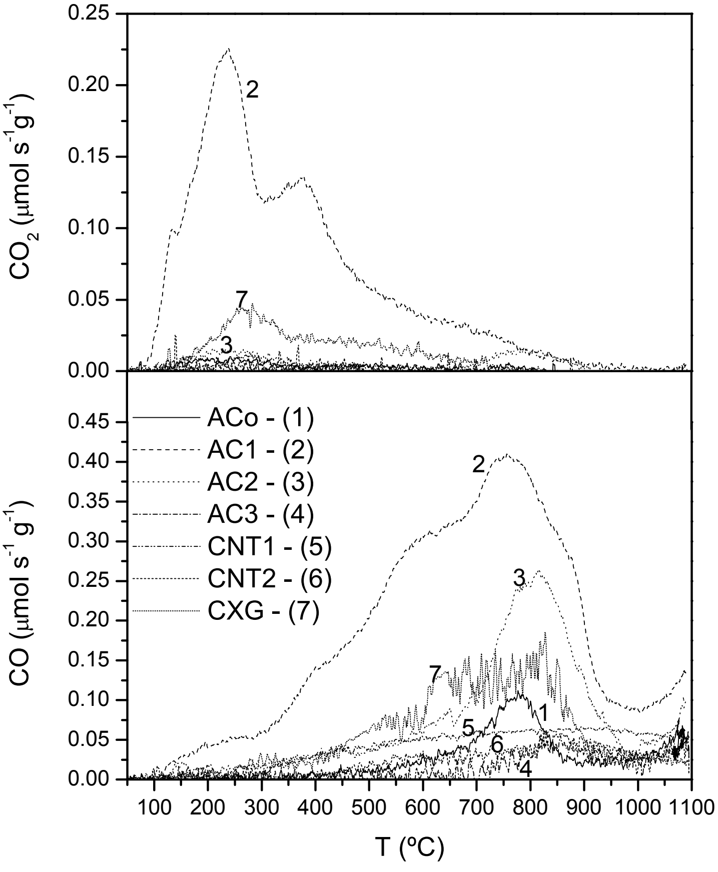

Figure 6.1 TPD spectra of carbon materials: CO_2 and CO evolutions.

Carbon nanotubes (samples CNT1 and CNT2) do not have significant amounts of oxygenated surface groups. On the other hand, the carbon xerogel sample (CXG) presents some oxygenated surface groups, with more CO_2 releasing groups than the heat treated activated carbons samples and the amount of CO releasing groups is between that of samples AC1 and AC2 and the remaining samples.

6.3.1.4 pH_{pzc} of the carbon materials

The values of the pH_{pzc} are shown in Table 6.1. The original activated carbon (ACo) presents slightly basic properties. Sample AC1 presents the lowest pH_{pzc} due to the introduction of several oxygenated functional groups with acid properties, namely carboxylic acids. As observed in the TPD profiles (Figure 6.1), the heat treatment at 700 ºC removes the acid groups from the surface; therefore, the pH_{pzc} values of samples AC2 and AC3 are higher than those of the ACo and AC1 samples. The sample AC3, which was heat treated under H_2 atmosphere, has the highest basic character. Carbon nanotubes (CNT1 and CNT2) present neutral characteristics and sample CXG presents slightly basic properties.

6.3.2 Catalytic tests

The influence of the support on the catalysts activity and selectivity during the reduction of nitrate was studied. The activities of 2%Pd-1%Cu and 1%Pt-0.3%Cu catalysts are shown in Figure 6.2 a) and Figure 6.3 a), respectively. Figure 6.2 b) and c) and Figure 6.3 b) and c) show the corresponding evolution of nitrite and ammonium concentrations during the reaction. Table 6.2 presents nitrate conversions and selectivities of the catalysts studied. Experiments using only the supports (blank tests) were carried out and it was observed that they do not show any activity for nitrate reduction, the presence of a noble metal and a promoter metal is mandatory to reduce nitrate. Pd, Pt and Cu monometallic catalysts supported on activated carbon are inactive [16] (see chapter 2).

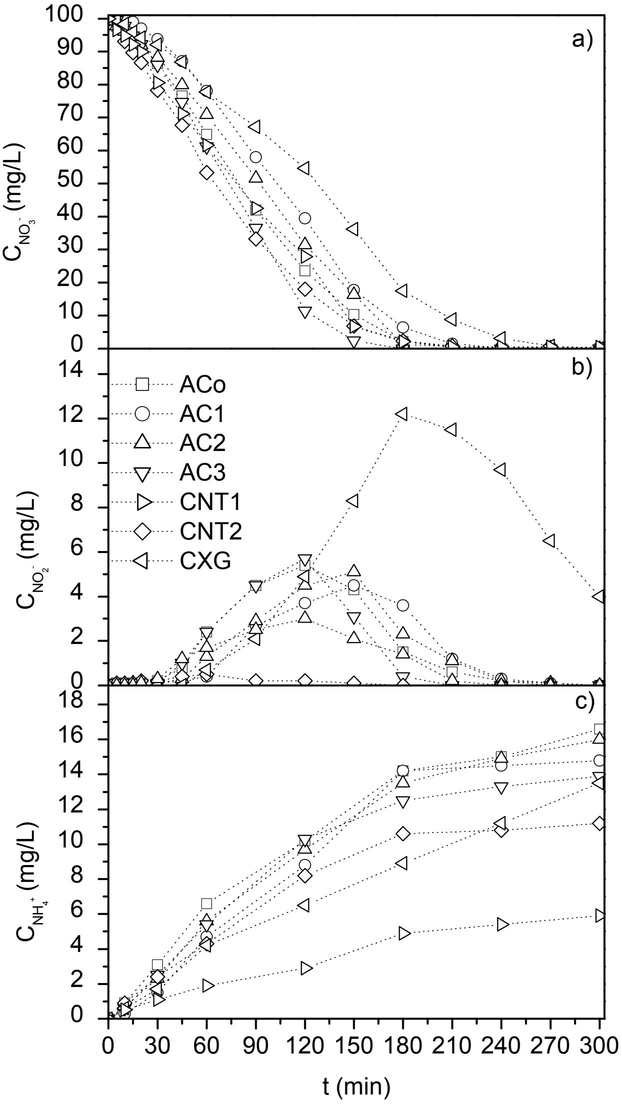

Figure 6.2 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of 2%Pd-1%Cu catalysts ($C_{NO_3^-{}_i}$ = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H_2} = 100 Ncm^3/min, Q_{CO_2} = 100 Ncm^3/min, T = 25 ºC).

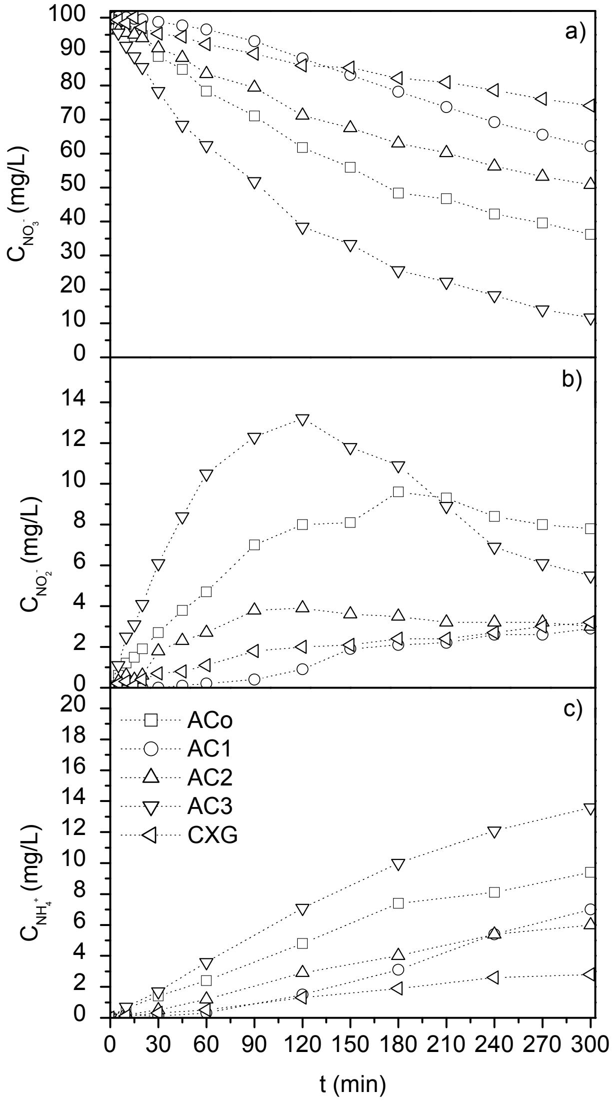

Figure 6.3 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of 1%Pt-0.3%Cu catalysts (C_{NO3^-i} = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

Wang et al. [27] reported that the activity and selectivity of a 3.6%Pd-2.0%Cu (%wt) catalyst supported on hydrophobic activated carbons with different provenience depend on the support used. Figure 6.2 and Figure 6.3 show that the surface chemistry of the activated carbon (see samples ACo to AC3) plays an important role in the performance of the catalysts for nitrate reduction, being its influence more pronounced when Pt-Cu catalysts are used. Generally, catalysts supported on basic carbon materials are more active. A nitrate conversion of 100% is always obtained when Pd-Cu catalysts are used, independently of the support; the main difference is related to the time necessary to obtain this value. The Pt-Cu catalysts present more marked distinct performances depending on the support used. The nitrate conversion after 5 h of reaction varies from 88% (sample supported on AC3) to 26% (sample supported on CXG).

Table 6.2 Nitrate conversions ($X_{NO_3^-}$) and nitrite, ammonium and nitrogen selectivities ($S_{NO_2^-}, S_{NH_4^+}, S_{N_2}$) of Pd-Cu and Pt-Cu catalysts after 5 h of reaction and selectivities for 50% nitrate conversion.

	t = 300 min				$X_{NO_3^-} = 50\%$		
Catalyst	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
2%Pd-1%Cu							
ACo	1.00	0.00	0.57	0.43	0.09	0.57	0.34
AC1	1.00	0.00	0.51	0.49	0.07	0.55	0.38
AC2	1.00	0.00	0.55	0.45	0.08	0.57	0.35
AC3	1.00	0.00	0.48	0.52	0.08	0.46	0.46
CNT1	1.00	0.00	0.20	0.80	0.06	0.16	0.78
CNT2	1.00	0.00	0.39	0.61	0.01	0.32	0.67
CXG	1.00	0.05	0.47	0.48	0.16	0.47	0.37
1%Pt-0.3%Cu							
ACo	0.64	0.16	0.51	0.33	0.25	0.49	0.26
AC1	0.38	0.10	0.63	0.27	-	-	-
AC2	0.49	0.08	0.42	0.50	-	-	-
AC3	0.88	0.08	0.53	0.39	0.33	0.36	0.31
CXG	0.26	0.17	0.37	0.46	-	-	-

When Pd-Cu catalysts are used the nitrite concentration accumulated in solution goes through a maximum and generally is inferior to the concentration obtained with Pt-Cu catalysts, disappearing completely before the 5 h of reaction (with the exception of sample CXG), which is related to the fact that palladium is very active for nitrite reduction [16] (see chapter 2). Figure 6.2 shows that the nitrite concentration measured during the reaction time and also the ammonium concentration formed after 5 h of reaction are lower in the catalysts supported on carbon nanotubes than in those supported on activated carbon. This fact must be related to the textural properties of the supports. Internal mass transfer limitations are avoided for carbon nanotubes, which are mesoporous materials, contrarily to activated carbons, which have an extensive microporosity. Nitrite is reduced on the carbon nanotubes surface, avoiding its overreduction into ammonium as may happen in the interior of the activated carbon micropores. Table 6.2 shows that the catalysts supported on carbon nanotubes are more selective to nitrogen than the catalysts supported on the other carbon materials.

The surface chemistry of the support influences the catalytic activity for the reduction of nitrate. This fact could be related to the size of the metallic particles, due to the different interactions of the precursors with the support during impregnation. Matatov-Meytal and Sheintuch [14] reported that changes in the surface of metallic particles supported on activated carbon cloths, namely the orientation of copper, influence the catalytic performance in nitrate hydrogenation. In this work, it was observed by TEM micrographs that the catalysts supported on AC1 and CXG present high metal particle sizes. The surface of sample AC1 has a lot of oxygen-containing groups and sample CXG, although in less extent, also presents some of these groups. Copper (as Cu^{2+}) is preferentially adsorbed on these groups [37], while palladium (as $PdCl_4^-$) [38] and platinum (as $PtCl_6^-$) [39] interact preferentially with the protonated sites. Due to the anchoring effect of the surface groups, the contact between Pd and Cu or Pt and Cu becomes difficult, which may justify the low activity observed for these catalysts. On the other hand, during the heat treatment used in the catalysts preparation step, bigger particles are formed. In the case of sample AC1, the increase of the particle sizes may be explained by the decomposition of the oxygenated surface groups on the support during the thermal treatment, which act as anchoring sites for the metal precursors; thus, the previously fixed small particles will become mobile on the surface of the support and agglomerate forming larger particles [40,41]. In the case of sample CXG, in addition to the mentioned effect of the oxygenated surface groups, the large particle size may also result from the different surface properties of this support.

The heat treated sample AC3 and the carbon nanotubes samples do not have a significant amount of oxygenated surface groups, which could act as anchoring sites for the metal precursors, promoting its surface dispersion. Then, the interaction between Cu and Pd or Cu and Pt may be significant because they are near. In a previous work [42] (this will be discussed in chapter 7) it was observed by TPR experiments that the interaction between copper and the activated carbon surface is higher in supports that present a lot of oxygen containing surface groups, and due to this interaction the contact with palladium or platinum is avoided. On the other hand, the heat treatments remove the major part of the functional groups created during the oxidation treatment and, for that reason, the activity observed for the catalysts supported on basic samples is higher than for the others. The catalyst supported on AC2 shows a lower activity than that supported on the other heat treated sample (AC3), but higher than the supported on AC1. This performance is related to the surface groups of the support, which determine the metals dispersion. As observed in Figure 6.1, sample AC2 still has some of the CO releasing groups at high temperatures, which may decrease the interaction between the metals.

It can be observed in Table 6.2 that the Pd-Cu catalysts are generally more selective to nitrogen than the Pt-Cu catalysts. Although the comparison of selectivities should only be made at the same conversion, it was observed that the selectivities do not change too much with the conversion (cf. in Table 6.2 the selectivities after 300 min and for 50% of conversion). In the case of Pd-Cu catalysts, when activated carbon is used as support, the basic sample AC3 provides the highest nitrogen selectivity, whereas the carbon nanotubes supported catalysts provide even higher nitrogen selectivities. For the Pt-Cu catalysts tested, the highest nitrogen selectivity was obtained for the basic sample AC2.

Despite the allowable ammonium values are exceeded, this work offers new possibilities in the development of the catalyst support to improve the activity and the selectivity of the process. Carbon materials show to be adequate supports for the catalysts used in the reduction of nitrate, particularly if the surface chemistry is tailored in order to obtain basic samples without oxygenated surface groups. The high catalytic performance observed for the catalysts supported on carbon nanotubes, in special its high selectivity to nitrogen, must be related not only to the surface chemistry of this support, which does not present a high amount of functional groups, but also to its high mesoporous surface area and absence of microporosity, which minimizes the internal mass transfers limitations and consequently the overreduction of nitrite to ammonium. The catalysts supported on carbon xerogel are not very promising catalysts for this reaction, at least under the preparation conditions used. This may be related with the surface characteristics of the carbon xerogels, which originated large metal particles sizes.

6.4 Conclusions

This work compares several carbon materials as bimetallic catalysts (Pd-Cu, Pt-Cu) support on the reduction of nitrate in water. The results obtained show that the surface chemistry of the support has an important role in the catalysts activity and selectivity, being its influence more pronounced when Pt-Cu catalysts are used. Generally, catalysts supported on basic carbon materials are more active.

Comparing the different supports under the conditions tested, basic samples and carbon nanotubes are the best, whereas carbon xerogels are the worst supports for this reaction; in part, this fact could be related to the size of the metallic particles due to the interaction with the support during impregnation.

Carbon materials show to be good catalysts supports for the reduction of nitrate. This work offers new possibilities in the development of the support to improve the activity and the selectivity of this process.

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Chapter 7

7 Pd-Cu and Pt-Cu catalysts supported on carbon nanotubes for nitrate reduction in water[1]

The influence of the preparation conditions on the performance of Pd-Cu and Pt-Cu supported on multiwalled carbon nanotubes for the reduction of nitrates was studied and compared with that obtained using a commercial activated carbon as support. Different preparation conditions lead to different catalytic activities and selectivities. Generally, the activity decreases by increasing the calcination and reduction temperatures for the catalysts supported on the original carbon nanotubes, where the nitrate conversion varies from 67% (non calcined and no reduced) to 15% (calcined and reduced at 200 ºC) for the pair Pd-Cu after 5 h of reaction; the inverse performance was observed for the catalysts supported on carbon nanotubes previously oxidised with HNO_3 and on this same sample heat treated at 400 ºC. The functional groups created during the oxidation treatment have a negative effect on the catalyst performance. For all the preparation conditions tested, the Pd-Cu pair is more selective to nitrogen than the pair Pt-Cu, 82% and 37% are the highest values obtained for each pair, respectively. Carbon nanotubes are demonstrated to be a good support for this reaction.

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[1] O.S.G.P. Soares, J.J.M. Órfão, M.F.R. Pereira, *Pd-Cu and Pt-Cu catalysts supported on carbon nanotubes for nitrate reduction in water.* Ind. Eng. Chem. Res. **49** (2010) 7183-7192.

7.1 Introduction

Carbon nanotubes (CNT) have attracted growing interest owing to their exceptional properties that make them suitable for many potential applications, such as polymer reinforcements for composites or advanced materials for energy storage, electronics and catalysis [1]. In catalytic applications, these conductive supports present clear differences compared to activated carbons, as shown in a recent theoretical study reporting the interaction of transition metal atoms with CNT and graphite [2]. It appears that carbon nanotubes present specific adsorption properties when compared to graphite or to activated carbon, mainly due to their peculiar morphology, the role of defects, opening/closing of the tubes, chemical purification or the presence of impurities [1]. An additional advantage of CNT is that they are usually applied as an agglomerate of tubes acting as a mesoporous material, with the metal active sites in the external walls of the tubes, avoiding the usual mass transfer limitations found in porous materials. The combination of all these properties makes CNT attractive and competitive catalyst supports by comparison with activated carbons. In particular, they could replace activated carbons in liquid-phase reactions as long as the properties of activated carbons are still difficult to control and their microporosity has often slowed down catalyst development [1]. However, high price and very low density are the main disadvantages for their practical use. The main advantages of CNT supports compared to activated carbon are: (i) the high purity of the material can avoid self-poisoning, (ii) the mesoporous nature of these supports can be of interest for liquid-phase reactions, thus reducing mass transfer limitations, and (iii) specific metal–support interactions exists, which can directly affect the catalytic activity and the selectivity [1]. As CNT are relatively inert supports, several studies have been conducted in order to find out which pre-treatment procedures are needed to achieve the optimal interaction between the support and the catalyst precursor [1]. The bare CNT does not possess a significant amount of functional groups and the anchoring sites for metals are mainly the surface defects [3]. For instance, some studies demonstrated that oxidative surface treatments of the supports improved the dispersion of the metallic phases [1,4].

In the present work, the use of multiwalled carbon nanotubes (MWCNT) as catalyst support for nitrate reduction in water was studied and the respective performance was compared to that of activated carbons (AC). To the best of our knowledge, there are no studies using CNT as a support in the scope of this reaction. The catalytic nitrate abatement process consists of the reduction of nitrate toward nitrogen over bimetallic catalysts (noble metal + promoter) in the presence of a reducing agent, such as hydrogen [5]. Nitrite as intermediate and ammonium as by-product are the main disadvantages of this process [6]. The activity and selectivity of the bimetallic catalyst is highly dependent on the preparation method, on the way the noble metal is promoted, on the metal/promoter ratio and on the operation conditions [7]. Moreover, alloying of metals may result in important changes in their activity and selectivity [8]. The selection of the support is also important for this process, since it was shown that the support affects the catalyst activity and selectivity [7,9-12].

In a previous work [13] (see chapter 3) it was found that 1%Pd-1%Cu and 1%Pt-0.3%Cu (weight percent) were the optimal formulations when the mentioned pairs supported on activated carbon were used. Therefore, these formulations were chosen for the present study. One of the most promising technologies for the reduction of nitrates in water is the use of nanostructured reactors, which are expected to minimize mass transfer limitations. Carbon nanotubes are among the best candidates for this scenario because they can be grown directly on the walls of those reactors. This study, where the use of carbon nanotubes as a catalyst support for this reaction is assessed, is the first step in a larger research area. Here, the main goal is to evaluate the influence of the surface chemistry of the MWCNT and of the preparation method (calcination and reduction temperatures) on the characteristics of the catalysts, including their catalytic performances.

7.2 Experimental Section

7.2.1 Catalyst preparation

The following supports were considered: a) a commercial multiwalled carbon nanotube sample Nanocyl-3100, as received (sample CNT), b) sample CNT after an oxidation treatment carried out to obtain a material with a high amount of oxygenated functional groups (sample CNT1), c) sample CNT1 after a heat treatment at 400 ºC under a nitrogen flow for 1 h to remove part of the acid groups (sample CNT2). The oxidation treatment was performed with 7 M HNO_3 at 130 ºC for 3 h. After that, the MWCNT were washed with distilled water to neutral pH, dried in an oven at 100 ºC for 24 h and then ground to obtain a powder. For comparative purposes, a commercial activated carbon NORIT GAC 1240 PLUS ground to a particle diameter between 0.1 and 0.3 mm (sample ACo) was also used as a support.

The catalysts were prepared by incipient wetness co-impregnation, from aqueous solutions of the corresponding metal salts (H_2PtCl_6, $PdCl_2$, $Cu(NO_3)_2$). After impregnation, the samples were dried at 100 ºC for 24 h. Different temperatures were selected for calcination (T_{Cal}) under nitrogen flow for 1 h and reduction (T_{Red}) under hydrogen flow for 3 h. No calcined and no reduced catalysts (N_{Cal} N_{Red}) were also studied; actually, these catalysts could be considered calcined in air at 100 ºC, once they were dried in the oven during their preparation. The catalysts supported on activated carbon were calcined under nitrogen flow at 200 ºC for 1 h and reduced at 100 ºC under hydrogen flow for 3 h. The contents of noble metal and copper were maintained constant at 1%Pd-1%Cu and 1%Pt-0.3%Cu (weight percent), which are the best formulations for the activated carbon supported catalysts, according to a previous study [13] (see chapter 3). Additionally, 1%Pd, 1%Pt and 1%Cu (weight %) monometallic catalysts were also prepared for comparison purposes in TPR analyses.

7.2.2 Catalyst characterization

Catalysts and supports were characterized using different techniques: N_2 adsorption at -196 ºC, temperature programmed reduction (TPR), transmission electron microscopy (TEM), temperature programmed desorption (TPD) and determination of pH_{pzc}.

The textural characterization of the materials was based on the corresponding N_2 adsorption isotherms, determined at -196 ºC with a Nova 4200e (Quantachrome Instruments) equipment or a Coulter Omnisorp 100CX apparatus. BET surface areas (S_{BET}) were calculated, as well as the mesopore surface area of sample ACo (S_{meso}) according to the t-method.

TPR experiments were carried out in order to determine the reduction temperature of the metals and to evaluate the effect of the pre-treatments and reaction conditions on the catalyst properties. An AMI-200 (Altamira Instruments) apparatus was used; the sample (150 mg) was heated at 5 ºC/min to 600 ºC under a flow of 5% (v/v) H_2 diluted with He (total flow rate of 30 Ncm^3/min). TPR analyses of selected Pd-Cu catalysts were also carried out after using them in the nitrate reduction, in order to evaluate the influence of reaction conditions in the TPR profile. In situ calcination was performed in selected samples before the TPR experiment, in order to evaluate the influence of the calcination step in the TPR profile. In these cases, each sample was heated to 200 or 400 ºC under nitrogen flow during 1 h, and then cooled to 30 ºC, before starting the TPR experiment. The H_2 consumption was followed by a thermal conductivity detector (TCD) and by mass spectrometry (Dymaxion 200 amu, Ametek).

Temperature programmed desorption (TPD) analyses were performed in the same equipment, in order to identify and quantify the amount of oxygen-containing surface groups of the supports. In a typical experiment, 100 mg sample was subjected to a 5 ºC/min linear temperature rise up to 1100 ºC under helium at a flow rate of 25 Ncm^3/min. The amounts of CO (m/z = 28) and CO_2 (m/z = 44) released from the samples were followed with a mass spectrometer. The calibration procedure allows quantification of the amount of each gas as well as subtraction the contribution of the signal of m/z = 44 in the m/z = 28 signal.

The pH_{pzc} was determined by mixing 150 mg of each sample with 50 cm^3 of 0.01 M NaCl solution with pH values adjusted between 2 and 12, by adding 0.1 M HCl or 0.1 M NaOH. The final pH was measured after 24 h of shaking at room temperature. The pH_{pzc} is the point where the curve pH_{final} *vs* $pH_{initial}$ crosses the line $pH_{initial} = pH_{final}$.

7.2.3 Catalyst evaluation

The reduction of nitrate was carried out in a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure, and using hydrogen as the reducing agent. Initially, 790 mL of deionised water and 400 mg of catalyst were fed into the reactor, the magnetic stirrer was adjusted to 700 rpm and the gas mixture of hydrogen and carbon dioxide (1:1, flow rate = 200 Ncm^3/min) was passed through the reactor during 15 min to remove oxygen; CO_2 acted as pH buffer (pH = 5.5). After that period, 10 mL of a nitrate solution, prepared from $NaNO_3$, was added to the reactor, in order to obtain an initial NO_3^- concentration equal to 100 mg/L.

Small samples were taken from the reactor for determination of nitrate, nitrite and ammonium concentrations after defined periods. Nitrate and nitrite ions were simultaneously determined by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was a Hamilton PRP-X100 column (150 mm x 4.1 mm) working at room temperature, under isocratic conditions. The mobile phase was a solution of 0.1 M $NaCl:CH_3OH$

(45:55). Ammonium ions were determined by potentiometry using a convenient selective electrode. pH values were also measured.

The amounts of Pd, Pt and Cu eventually lixiviated during reaction were measured using atomic absorption spectroscopy. No dissolution of Pd or Pt was detected at the end of the reaction but in some experiments small amounts of dissolved Cu were measured in the solution. In the case of Pd-Cu catalysts a maximum leaching of 4.6% of copper was measured, with the most common value obtained being lower than 1%. In the case of Pt-Cu catalysts no dissolved Cu was measured for most of the samples, and when detected the maximum value of leaching was 2.3%.

The selectivities into nitrite, ammonium and nitrogen were calculated as:

$$S_{NO_2^-} = \frac{n_{NO_2^-}}{n_{NO_3^-i} - n_{NO_3^-}} \qquad (7.1)$$

$$S_{NH_4^+} = \frac{n_{NH_4^+}}{n_{NO_3^-i} - n_{NO_3^-}} \qquad (7.2)$$

$$S_{N_2} = \frac{2 * n_{N_2}}{n_{NO_3^-i} - n_{NO_3^-}} \qquad (7.3)$$

where $n_{NO_3^-\,i}$ is the initial amount of nitrate (mmol) and $n_{NO_3^-}$, $n_{NO_2^-}$, $n_{NH_4^+}$ and n_{N_2} are the amounts of the respective species (mmol) at time t (min). The amount of nitrogen was calculated by a mole balance, assuming that the amount of NO_x produced is negligible [9,14].

7.3 Results and Discussion

7.3.1 Catalyst Characterization

7.3.1.1 Textural Properties

Textural properties obtained from the N_2 adsorption isotherms at -196 ºC are presented in Table 7.1. The activated carbon has a BET surface area of 869 m^2/g and the multiwalled carbon nanotubes present lower values (320, 439 and 458 m^2/g for CNT, CNT1 and CNT2, respectively), and the absence of micropores. The HNO_3 treatment increases the BET surface area, probably due to the opening of the MWCNT tips and to the damage in the walls caused by the oxidation treatment [15].

The subsequent N_2 heat treatment does not have a significant influence on the BET surface area.

Table 7.1 Textural characterization and pH_{pzc} values of the supports used.

Sample	S_{BET} (m^2/g)	S_{meso} (m^2/g)	pH_{pzc}
ACo	869	97	8.3
CNT	320	-	7.0
1%Pd-1%Cu_CNT	301	-	-
1%Pt-0.3%Cu_CNT	314	-	-
CNT1	439	-	3.0
1%Pd-1%Cu_CNT1	430	-	-
CNT2	458	-	3.8
1%Pt-0.3%Cu_CNT2	469	-	-

As can be seen in Table 7.1, the surface areas of the supported metal catalysts are not significantly different from the original supports. It the case of the catalysts supported on activated carbon, it was assumed that the surface areas of the supported metal catalysts are also not significantly different from that of the support, since one sample with 2%Pd-1%Cu_ACo (a total metal loading higher than the samples considered in this work) was analysed and it was observed that the textural parameters remained practically unchanged compared to the unloaded carbon.

7.3.1.2 TPR

TPR studies have been carried out for all the catalysts. As can been seen in Figure 7.1 and Figure 7.2 the position, width and intensity of the peaks depend on the pre-treatments of the supports.

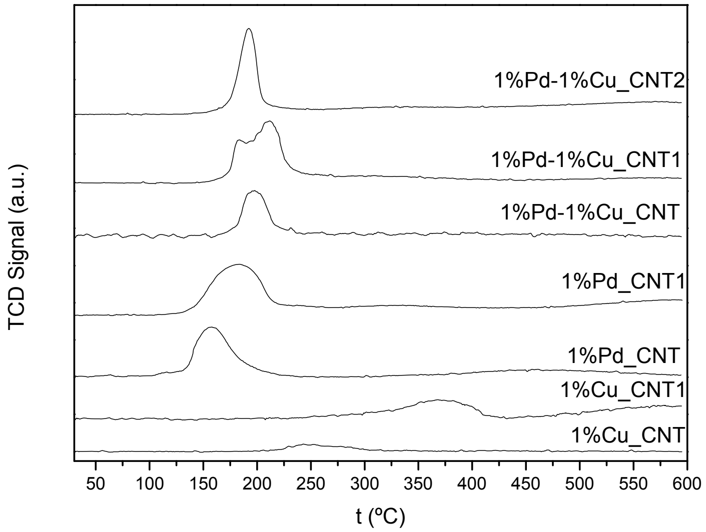


Figure 7.1 TPR profiles of fresh Pd, Cu and Pd-Cu catalysts.

Figure 7.1 shows that the reduction ranges of the Pd and Cu monometallic catalysts supported on the original carbon nanotubes are around 150 ºC and 250 ºC, respectively. From the TPR profile obtained it is not possible to distinguish the decomposition of Pd β-hydride, which presents a hydrogen desorption peak at about 60 ºC [16-21]. This may indicate that Pd is well dispersed on the support [22]. When CNT1 is used as a support the reduction peaks of both metals are displaced to the right, increasing the maximum reduction temperature to around 180 ºC and 370 ºC for Pd and Cu, respectively. Pure CuO can be expected to reduce around 240 ºC; supported CuO may be reduced at higher temperatures depending on the particle size and its interaction with the support [23]. For all the bimetallic catalysts, the reduction occurs around 200 ºC, which can be assigned to the reduction of Cu oxides promoted by the presence of Pd [16,17,22]. The decrease in the reduction temperature of supported copper in bimetallic catalysts indicates that a close proximity between copper and palladium species was achieved [22]. However, depending on the support, the features of the TPR profiles are distinct. The 1%Pd-1%Cu supported on the CNT and CNT2 present a well defined single peak, whereas the same metals supported on the CNT1 present a larger peak with a shoulder. This could be due to a higher interaction between copper and the oxygen surface groups formed during the oxidation treatment (mainly carboxylic acids).

Figure 7.2 shows the TPR profiles of Pt and Cu monometallic catalysts and of the Pt-Cu bimetallic catalysts. The 1%Pt monometallic catalyst and the 1%Pt-0.3%Cu bimetallic catalyst present a wide reduction peak around 125 - 225 ºC when supported on CNT, and a relatively well defined peak with a maximum around 225 ºC, with a shoulder at higher temperatures (up to 400 ºC), when supported on CNT1. The Pt-Cu bimetallic catalyst supported on CNT2 present a peak centered at 250 ºC with a shoulder at higher temperatures. Moreover, in the bimetallic catalysts, the reduction temperature, which is between those of platinum and copper monometallic catalyst, indicates an intimate contact between platinum and copper particles [8,24]. All the TPR profiles of the catalysts supported on CNT1 present a shoulder between 300 ºC and 400 ºC, which could be related to the interaction between the support and the metals since this shoulder is not detected in the TPR profile of the support CNT1 (not shown); on the contrary, the H_2 consumption observed at higher temperatures (> 400 ºC) is due to the support, since it is also present in the respective TPR profile.

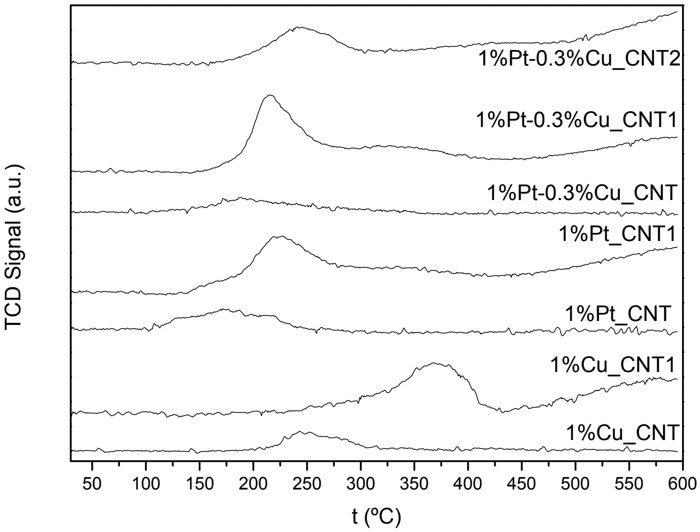


Figure 7.2 TPR profiles of fresh Pt, Cu and Pt-Cu catalysts.

In situ calcinations were performed before some TPR experiments, in order to determine its effect in the TPR profiles. Figure 7.3 shows that the Pd-Cu catalyst previously calcined at 200 ºC presents a reduction peak in the same range as the original catalyst (before reaction). The same effect is observed for the Pt-Cu catalyst (Figure 7.4), but when this catalyst was previously calcined at 400 ºC the TPR profile did not show any reduction peak. Therefore, the heat treatment at 400 ºC seems to be sufficient to reduce the metals, and a support promoter effect must also be considered. Sepúlveda-Escribano et al. [25] also observed that a heat treatment in helium at 400 ºC was able to reduce platinum species supported on carbon blacks.

Figure 7.3 also shows the TPR profiles of the Pd-Cu catalysts after being used in the catalytic reaction. For the catalysts supported on the original carbon nanotubes (Figure 7.3a)), it can be observed that the catalyst N_{Cal} N_{Red} does not show any intense reduction peak and the other catalysts present a reduction peak at around 130 ºC, which is a much lower value than that observed for the same catalyst before the reaction; moreover, the intensity of these peaks is also much smaller than the original peak. The catalysts supported on the sample CNT1 (Figure 7.3 b)) present a similar behaviour, but in this case the reduction temperature is only slightly lower than that observed in the catalyst before reaction, with exception of the catalyst T_{Cal} = 400 ºC T_{Red} = 400 ºC, which presents a small peak at 225 ºC; the different behaviour of this sample could be related to the formation of an alloy, in accordance with the high temperature used during its preparation [26] (see chapter 4). The decrease of the intensity of the reduction peaks could result from the fact that the catalysts were reduced not only before the reaction, during the calcination and reduction treatments, but also during the kinetic experiments, where the catalysts are continuously in contact with dissolved hydrogen in water.

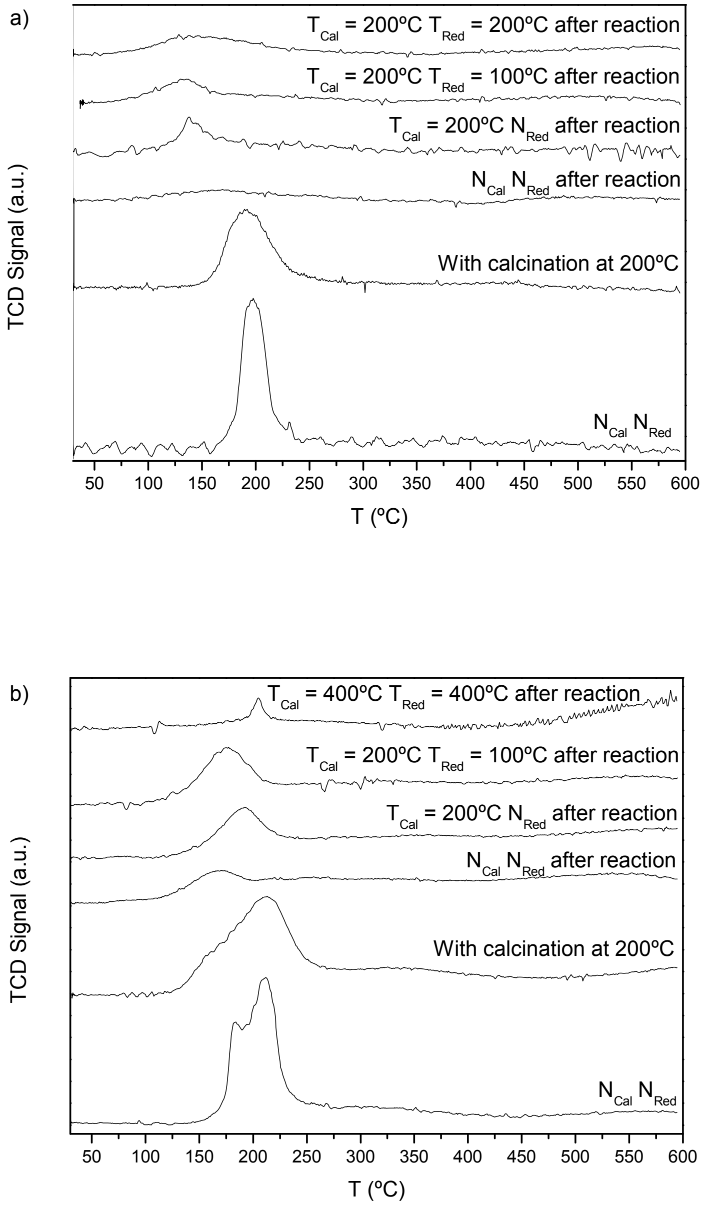


Figure 7.3 TPR profiles of a) Pd-Cu_CNT and b) Pd-Cu_CNT1 catalysts before and after reaction and with in situ calcinations at 200 ºC.

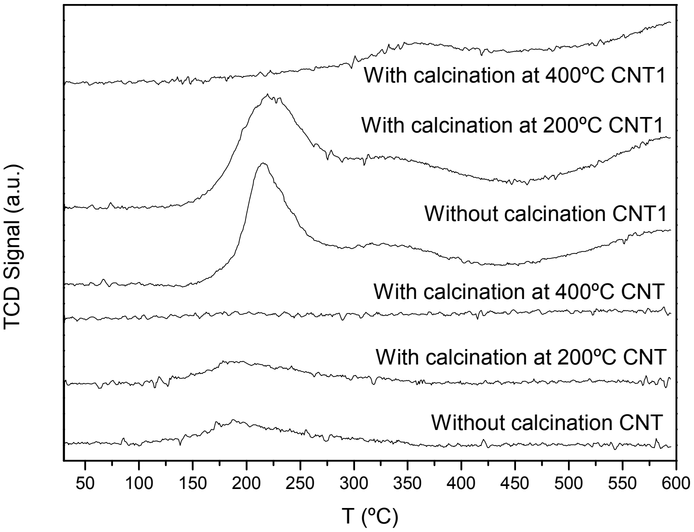


Figure 7.4 TPR profiles of Pt-Cu catalysts supported on CNT and CNT1 samples without and with in situ calcinations at 200 or 400 ºC.

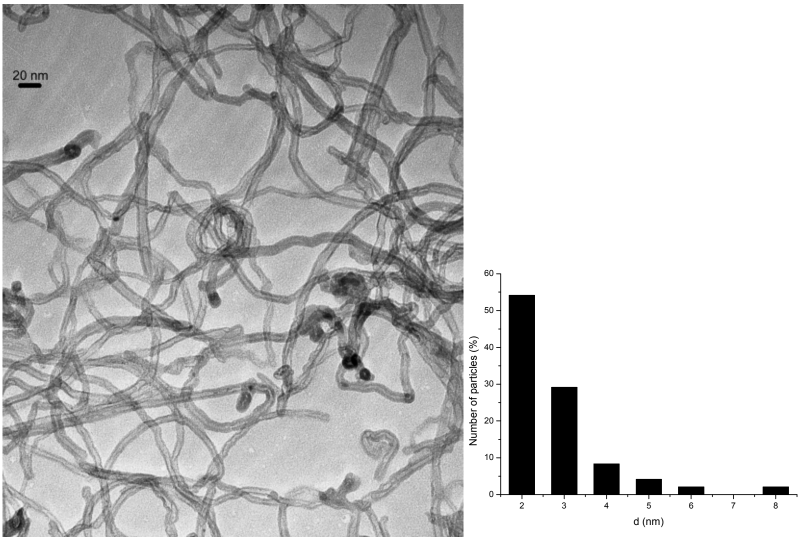
7.3.1.3 TEM

TEM analyses (Figure 7.5) were made in order to get information on the particle size distributions of the samples and on the possible morphology changes of the MWCNT after the oxidation treatment. Figure 5 shows that the oxidation with HNO_3 leads to considerable changes in the MWCNT morphology, since their walls seem to be highly damaged (see Figure 7.5 c)).

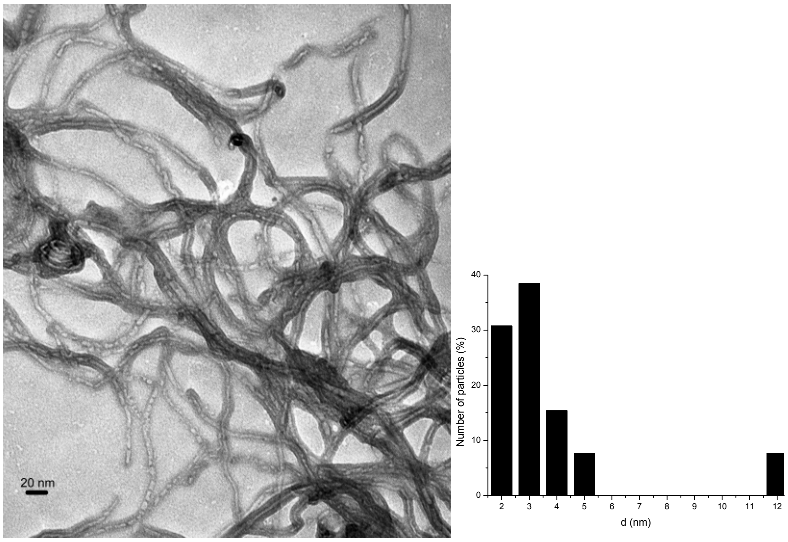
TEM analyses show that the Pd-Cu catalysts supported on CNT present a particle size distribution with a mode of 2 nm. This value moves to 3 nm for the catalysts supported on CNT1, although a lot of particles around 2 nm were also found.

TEM analyses of the Pt-Cu catalysts (Figure 7.6) shows that highly dispersed metallic particles were also obtained over all the samples, and the particle size distribution presents a mode of 3 nm.

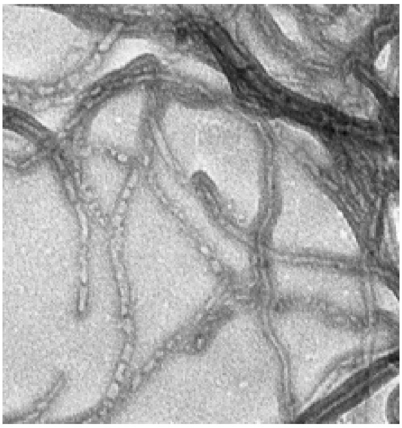
For the Pt-Cu catalysts supported on the oxidised support a slight increase of the particle sizes, with an average of 3 – 5 nm, was observed. This increase can be attributed to the thermal decomposition of the functional groups formed during the oxidative treatment, which act as anchoring sites for the metal precursors; thus the previously fixed small particles will become mobile on the surface of the support and agglomerate forming larger particles [25,27].



a)



b)



c)

Figure 7.5 TEM micrographs of a) 1%Pd-1%Cu_CNT, b) 1%Pd-1%Cu_CNT1 catalysts after calcination (200 ºC) and reduction (100 ºC) and c) magnification of image b).

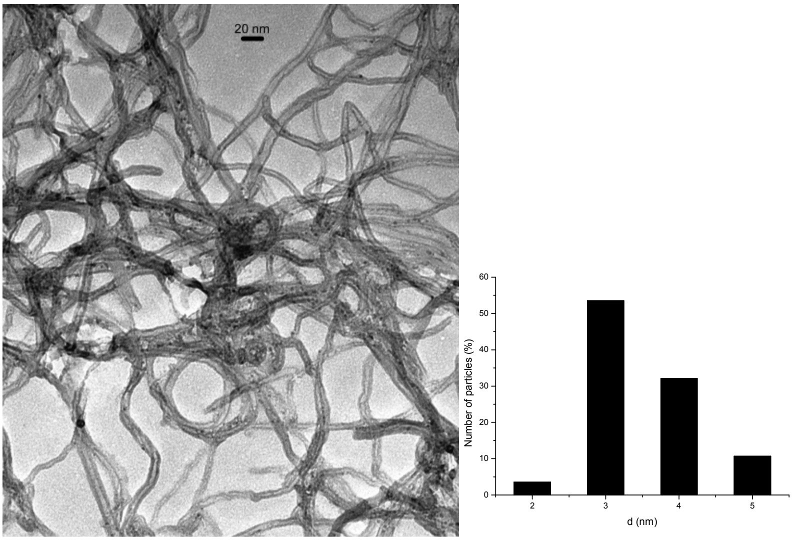


Figure 7.6 TEM micrograph of the 1%Pt-0.3%Cu_CNT catalyst after calcination (200 ºC) and reduction (100 ºC).

TEM analyses of the catalysts supported on the activated carbon show that the catalyst 1%Pd-1%Cu_ACo presents an average particle size of 13 nm and a mode of 11 nm, although very small particles between 3 and 6 nm were also observed. On the other hand, the catalyst 1%Pt-0.3%Cu_ACo presents an average particle size of 3 nm.

7.3.1.4 TPD

One of the objectives of this work is to study the influence of the surface chemical characteristics of the MWCNT on the properties of the metal phases and, consequently, on the performance of the prepared catalysts. For that purpose, a sample treated with HNO_3 (CNT1) and sample CNT1 heat treated under N_2 at 400 ºC (CNT2) were prepared. Oxidation with HNO_3 is known to generate acid materials and to keep almost unchanged the textural parameters of activated carbon samples [28]. In the present case, an increase of 37% in the surface area was observed, as discussed in section 7.3.1.1. It has been shown that treatment with HNO_3 mainly leads to the formation of carboxylic acid groups, but also to the formation of lactones, anhydrides, phenols, carbonyls and quinones [28].

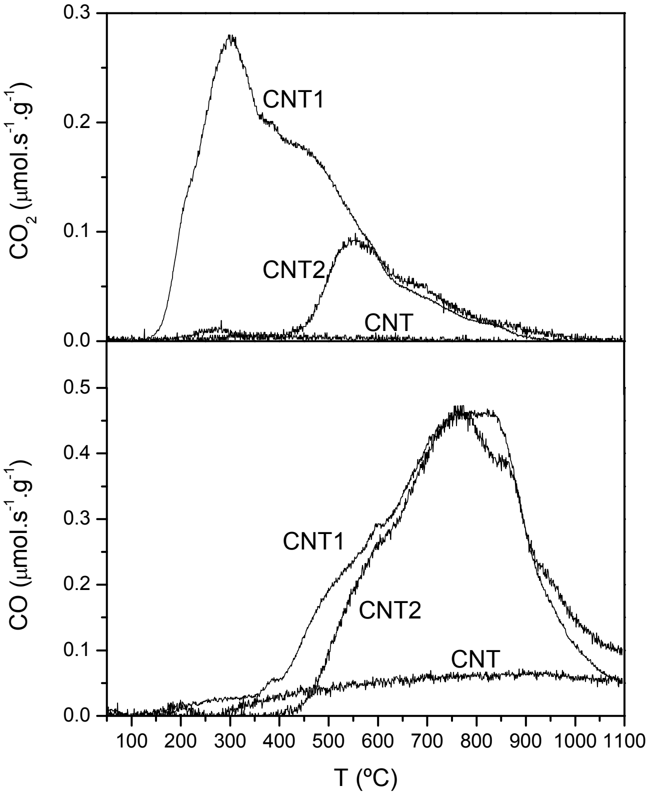


Figure 7.7 CO_2 and CO evolution by TPD in samples CNT, CNT1 and CNT2.

Figure 7.7 shows that the original CNT does not have significant amounts of oxygenated surface groups. A considerable increase in the amount of oxygen-containing surface groups, evidenced by the increase of the CO and CO_2 evolved, is observed after the nitric acid treatment (sample CNT1). This sample contains a large amount of carboxylic acid groups (released as CO_2 below 450 ºC), lactones (released as CO_2 around 630 ºC) and some carboxylic anhydrides (released as CO and CO_2 at around 580 ºC) [15]. Phenol and carbonyl/quinone groups are also present (released as CO at high temperatures) [15]. These results are similar to those observed for activated carbons oxidised with nitric acid [28,29]. After the heat treatment at 400 ºC under N_2 flow (sample CNT2), it can be observed that the CO_2 releasing groups below 450 ºC have been almost completely removed and most of the CO releasing groups still remain on the surface. This indicates that almost all the carboxylic acid groups and a few carboxylic anhydrides were removed during the preparation of sample CNT2.

7.3.1.5 pHpzc

The values of the pH_{pzc} are shown in Table 7.1. The original samples of carbon nanotubes (CNT) and the activated carbon (ACo) present neutral and slightly basic properties, respectively. The sample CNT1 presents the lowest pH_{pzc} due to the introduction of several oxygenated functional groups, namely carboxylic acids. As observed in the TPD profiles (Figure 7.7), the heat treatment under N_2 flow at 400 ºC removes part of the acid groups from the surface; therefore, the pH_{pzc} of the sample CNT2 is slightly higher than that of CNT1.

7.3.2 Catalytic Tests

The influence of the support and the effects of calcination and reduction temperatures on the catalyst activity and selectivity during the reduction of nitrate were studied. The activities of 1%Pd-1%Cu and 1%Pt-0.3%Cu catalysts are obtained from Figure 7.8 and Figure 7.9 a), respectively. Figure 7.8 b) and c) and Figure 7.9 b) and c) show the corresponding evolutions of nitrite and ammonium concentrations during the reaction. Table 7.2 and Table 7.3 present some of the values of conversion and selectivities.

7.3.2.1 Pd-Cu Catalysts

Figure 7.8 a) and Table 7.2 show that when the original MWCNT is used as a support (sample CNT) there are no significant differences in the conversion of nitrate, except for catalyst calcined and reduced at 200 ºC. Almost all nitrate conversion curves are very similar, although the catalysts had been prepared under different conditions; the mentioned exception corresponds to a rather low nitrate conversion and suggests that the reduction temperature of 200 ºC has a negative effect on the catalytic performance. This observation is in agreement with the results of Gurrath et al. [19], who showed that reduction temperatures of palladium catalysts supported on activated carbon above around 150 ºC had a negative effect in the apparent metal dispersion obtained by CO chemisorption. In addition, the high temperatures used in the preparation of these catalysts may change the appropriate Pd-Cu interaction, probably as a result of the formation of alloys [26].

Figure 7.8 b) shows that the amount of nitrite accumulated is very low when CNT are used as a support. It can be observed that the catalyst CNT T_{Cal} = 200 ºC T_{Red} = 200 ºC is the most selective to ammonium (Table 7.2) and the catalyst CNT T_{Cal} = 200 ºC N_{Red} is the most selective to nitrogen (Table 7.2), presenting a value of 82%, after 5 h of reaction.

When functionalized carbon nanotubes (CNT1) are used as a support, it can be observed that the activity is much lower than that obtained with the catalysts supporting the original nanotubes, with exception of the catalysts CNT1 T_{Cal} = 200 ºC T_{Red} = 200 ºC and T_{Cal} = 400 ºC T_{Red} = 400 ºC, which present a nitrate conversion similar to that observed for the original carbon nanotubes calcined and reduced at low temperatures. In the case of CNT1 as support, the activity is influenced by the different temperatures used in the catalyst preparation. The catalyst CNT1 N_{Cal} N_{Red} only presents a residual activity (X_{NO3^-} = 15% after 5 h of reaction), while the catalyst CNT1 T_{Cal} = 200 ºC T_{Red} = 200 ºC shows the highest activity for this support (X_{NO3^-} = 68%, after 5 h of reaction). The catalyst activity increases by increasing the calcination and reduction temperatures until 200 ºC, with a slightly decrease thereafter. This can be related to the fact that in the catalysts only calcined or not heat treated the active sites could not be completely formed; probably the metal is still in its salt form after preparation. To understand this explanation, it is important to notice that the reductive power of the carbon materials decreases with increasing surface oxidation [25]. In addition, as observed in the TPR profiles the interaction between copper and the oxygen-containing

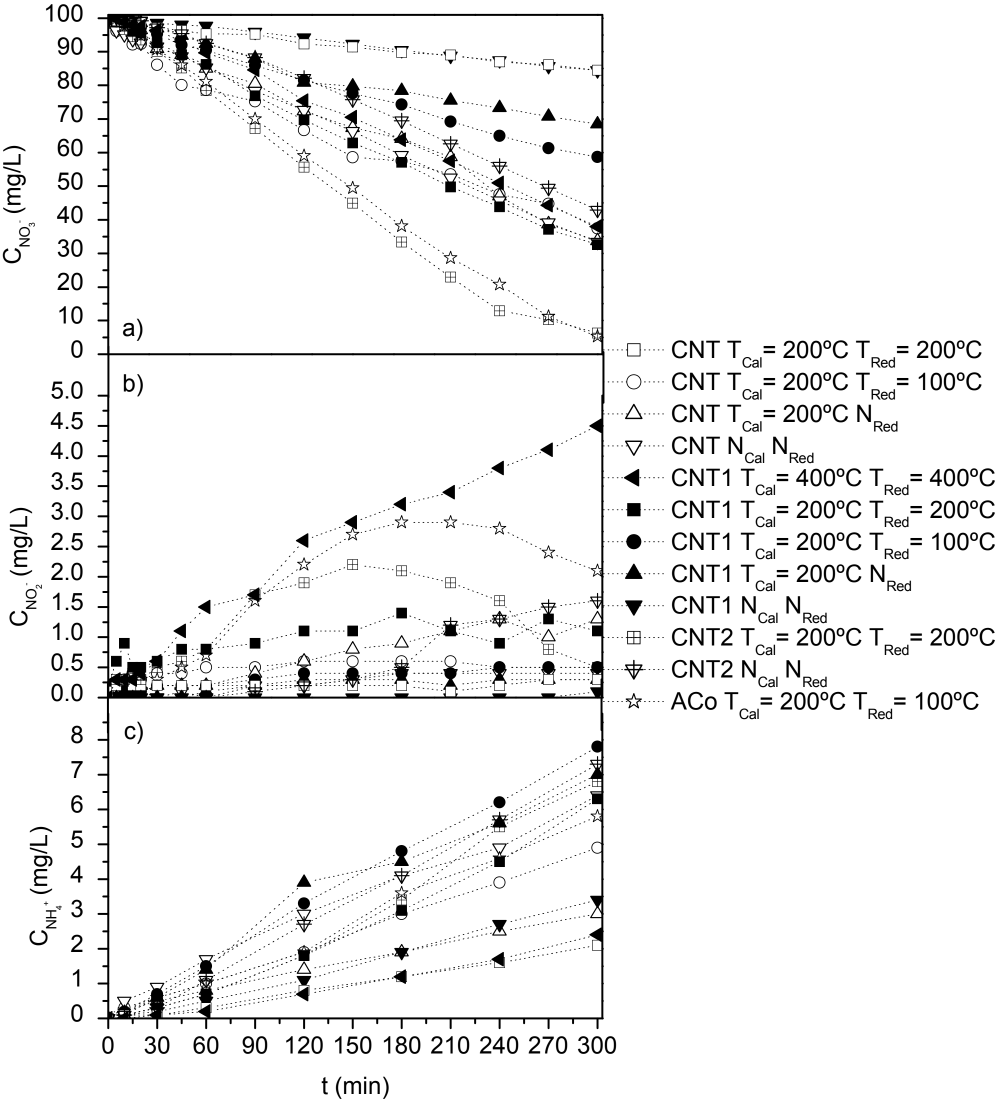


Figure 7.8 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of 1%Pd-1%Cu catalysts ($C_{NO_3^- i}$ = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

surface groups is higher, avoiding the close contact with palladium. Therefore, the support CNT1, which has a lot of oxygen containing surface groups, must be heat treated at temperatures as high as 200 ºC for the metal to be in its active form and/or to promote the connection between the metals. These results are in agreement with the TPR observations, where reduction peaks larger and displaced to high temperatures are observed for CNT1 compared to CNT catalysts. In addition, the heat treatments remove part of the functional groups created during the functionalization (mainly carboxylic acid groups) and for that reason the conversion obtained with the catalysts CNT1 T_{Cal} = 200 ºC T_{Red} = 200 ºC and T_{Cal} = 400 ºC T_{Red} = 400 ºC is similar to that observed for the catalysts supported on the original carbon nanotubes. Although the catalysts treated at low temperatures do not present a high nitrate conversion, they originate a relatively high amount of ammonia and a very low amount of nitrite. In fact, they are very selective to ammonia (Table 7.2). The increase of the calcination and reduction temperatures decreases significantly the selectivity to ammonium. The catalyst CNT1 T_{Cal} = 400 ºC T_{Red} = 400 ºC is the less selective to ammonium, but presents the highest concentration of accumulated nitrite. This could be related to the fact that the increase of the calcination and reduction temperatures promotes the sintering of the metals [19] and/or the formation of alloys [26] (see chapter 4), with some Pd dilution at the surface (enrichment of copper) being expected, which is prejudicial to the process since Pd atoms are the active centers for nitrite reduction [9,30] (ref. 30 corresponds to chapter 2).

For the catalysts supported on CNT2, the nitrate conversion also increases after calcination and reduction at 200 ºC. This catalyst presents a higher activity than those prepared under the same conditions on the other two supports. This could be related to the fact that the support CNT2 was heat treated at 400 ºC under a N_2 flow and, as observed in the TPD profile (Figure 7.7), most of the carboxylic acids were removed, favouring the nitrate conversion, as discussed below.

For comparative purposes, an experiment with a 1%Pd-1%Cu catalysts with T_{Cal} = 200 ºC T_{Red} = 100 ºC supported on activated carbon was also carried out. It was observed (Figure 7.8) that this catalyst is more active than the corresponding catalysts supported on the original nanotubes, showing a conversion of 95% after 5 h of reaction. The high formation of nitrite observed for this catalyst, is due to its high activity; however, the concentration of nitrite in solution goes through a maximum, which is due to the fact that palladium is very active for its reduction [30] (see chapter 2), being rapidly converted into ammonia or nitrogen. When carbon nanotubes are used as support, the concentration of nitrite remains almost constant during the experiments, with the exception of the catalysts CNT1 T_{Cal} = 400 ºC T_{Red} = 400 ºC and CNT2 T_{Cal} = 200 ºC T_{Red} = 200 ºC.

Moreover, the surface chemistry of the support also seems to influence the activity for the reduction of nitrate. The sample CNT does not have a significant amount of oxygen surface groups, which could act as anchoring sites for the metal precursors promoting its surface dispersion, and then it is possible that the interaction between Cu and Pd is higher because they are near. Therefore, the catalysts prepared on CNT at low and intermediate temperatures are more active than the catalysts treated at high temperatures, since once the metals are not anchored to the oxygen surface groups they can easily form agglomerates by heat treatment at high temperatures, which is prejudicial for the reaction. The best condition for nitrate reduction is when those metals are in contact but not in the form of an alloy [26] (see chapter 4).

The surface of the sample CNT1 has a lot of oxygen-containing groups and copper (as Cu^{2+}) is preferentially adsorbed in these groups [31], while palladium (as $PdCl_4^-$) interacts with the protonated sites [32]. Due to the anchoring effect of the surface groups, the contact between Pd and Cu becomes difficult, which may justify the low activity observed when these catalysts are heat treated at low temperatures after impregnation. With the increase of calcination and reduction temperatures, some of the mentioned groups are decomposed and, as a consequence, there is an enhanced connection between Cu and Pd, which justifies the increase of the activity. The optimum temperature seems to be around 200 ºC, because if the temperature is too high some alloying may occur [26], originating a decrease in the nitrate conversion, as shown for the catalyst CNT1 T_{Cal} = 400 ºC T_{Red} = 400 ºC.

Concerning the selectivities to nitrogen, it can be observed in Table 7.2 that the catalysts supported on CNT, activated carbon and CNT2 as well as on CNT1 T_{Cal} = 200 ºC T_{Red} = 200 ºC and T_{Cal} = 400 ºC T_{Red} = 400 ºC are more selective than those prepared on CNT1 and heat treated at low temperatures. Although the comparison of selectivities should only be made at the same conversion, it was observed for all the catalysts that, after a stabilization period of about 1 h of reaction, the selectivities remained practically constant and did not change with the conversion (cf. in Table 7.2 the selectivities after 300 min and for 50% of conversion). Therefore, it seems acceptable to compare the selectivities calculated at 50% conversion (for most of the samples) with the selectivities after 5 h of reaction (for the catalysts that did not allow reaching that conversion). The catalyst

Table 7.2 Nitrate conversions ($X_{NO_3^-}$) and nitrite, ammonium and nitrogen selectivities ($S_{NO_2^-}, S_{NH_4^+}, S_{N_2}$) of Pd-Cu catalysts after 5 h of reaction and selectivities for 50% nitrate conversion.

		t = 300 min			$X_{NO_3^-} = 50\%$		
Catalyst[#]	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Pd-1%Cu_ACo							
T_{Cal} = 200 ºC T_{Red} = 100 ºC	0.95	0.03	0.21	0.76	0.06	0.18	0.75
1%Pd-1%Cu_CNT							
N_{Cal} N_{Red}	0.67	0.01	0.33	0.66	0.01	0.32	0.67
T_{Cal} = 200 ºC N_{Red}	0.66	0.03	0.15	0.82	0.03	0.16	0.81
T_{Cal} = 200 ºC T_{Red} = 100 ºC	0.62	0.01	0.27	0.72	0.02	0.25	0.73
T_{Cal} = 200 ºC T_{Red} = 200 ºC	0.15	0.02	0.46	0.52	-	-	-
1%Pd-1%Cu_CNT1							
N_{Cal} N_{Red}	0.15	0.00	0.78	0.22	-	-	-
T_{Cal} = 200 ºC N_{Red}	0.31	0.01	0.77	0.22	-	-	-
T_{Cal} = 200 ºC T_{Red} = 100 ºC	0.41	0.02	0.65	0.33	-	-	-
T_{Cal} = 200 ºC T_{Red} = 200 ºC	0.68	0.02	0.32	0.66	0.02	0.28	0.70
T_{Cal} = 400 ºC T_{Red} = 400 ºC	0.62	0.10	0.13	0.77	0.10	0.12	0.78
1%Pd-1%Cu_CNT2							
N_{Cal} N_{Red}	0.57	0.04	0.44	0.52	0.04	0.44	0.52
T_{Cal} = 200 ºC T_{Red} = 200 ºC	0.94	0.01	0.25	0.74	0.05	0.16	0.79

[#] T_{Cal}: calcination temperature, T_{Red}: reduction temperature, N_{Cal}: non calcined, N_{Red}: non reduced

supported on CNT T_{Cal} = 200 ºC N_{Red} is the most selective to nitrogen (S_{N2} = 82% after 5 h of reaction). This performance can be related to the surface chemistry of the support. CNT is a material that does not present a high amount of functional groups on its surface, and mainly surface defects can be considered as anchoring sites for the metals. The oxidation treatment with HNO_3 was carried out in order to introduce some surface oxygenated functional groups, with the aim to enhance the interaction between the support and the catalyst precursor. However, the results obtained shows that the oxygenated groups created during the oxidation step have a negative effect on nitrate reduction, decreasing the nitrate conversion and the selectivity to nitrogen. Nevertheless, as observed in the TEM micrographs (Figure 7.5) this treatment can also originate a structural modification, which reduces the metal dispersion and, in this way, decreases the activity and, more significantly, the selectivity to nitrogen. Considering that sample CNT2 also presents high selectivities to nitrogen, it can be concluded that the carboxylic acid groups, which exist in significant amounts only in the CNT1 supported catalysts treated at low temperatures, are mainly responsible for the low selectivity to nitrogen. This effect may result from their role in anchoring the metal precursors, avoiding the close contact between Pd and Cu.

7.3.2.2 Pt-Cu Catalysts

Figure 7.9 a) and Table 7.3 show that the reduction of nitrate is quite different depending on the preparation conditions for the Pt-Cu catalysts. For the catalysts supported on the original carbon nanotubes (CNT) the activity decreases by increasing the reduction temperature, with the following order of activity: T_{Cal} = 200 ºC N_{Red} >> T_{Cal} = 200 ºC T_{Red} = 100 ºC >> T_{Cal} = 200 ºC T_{Red} = 200 ºC, with conversion values after 5 h of 97, 68 and 35%, respectively. Figure 7.9 b) shows that the reduced catalysts give rise to similar nitrite concentrations, which are much lower that those obtained with the non-reduced catalysts; however, in the latter case the nitrite concentration goes through a well defined maximum with only 4 mg/L after 5 h of reaction. This can be explained by the fact that the active sites for nitrite reduction are not completely formed in the non-reduced catalysts. Accordingly, no particles were observed in TEM analysis, indicating that the noble metal is probably still in its salt form. It is well assumed that nitrite reduction occurs principally on noble monometallic sites [33,34]. Therefore, in these conditions, the catalyst could not be very active for nitrite reduction. The ammonium concentration significantly increases with the nitrate conversion (Figure 7.9 c)), particularly in the case of the non-reduced catalyst. Once again, this could be related to the fact that the active sites are not completely formed, with this catalyst being less selective to nitrogen. These results are in line with those obtained using activated carbon as a support [26] (see chapter 4).

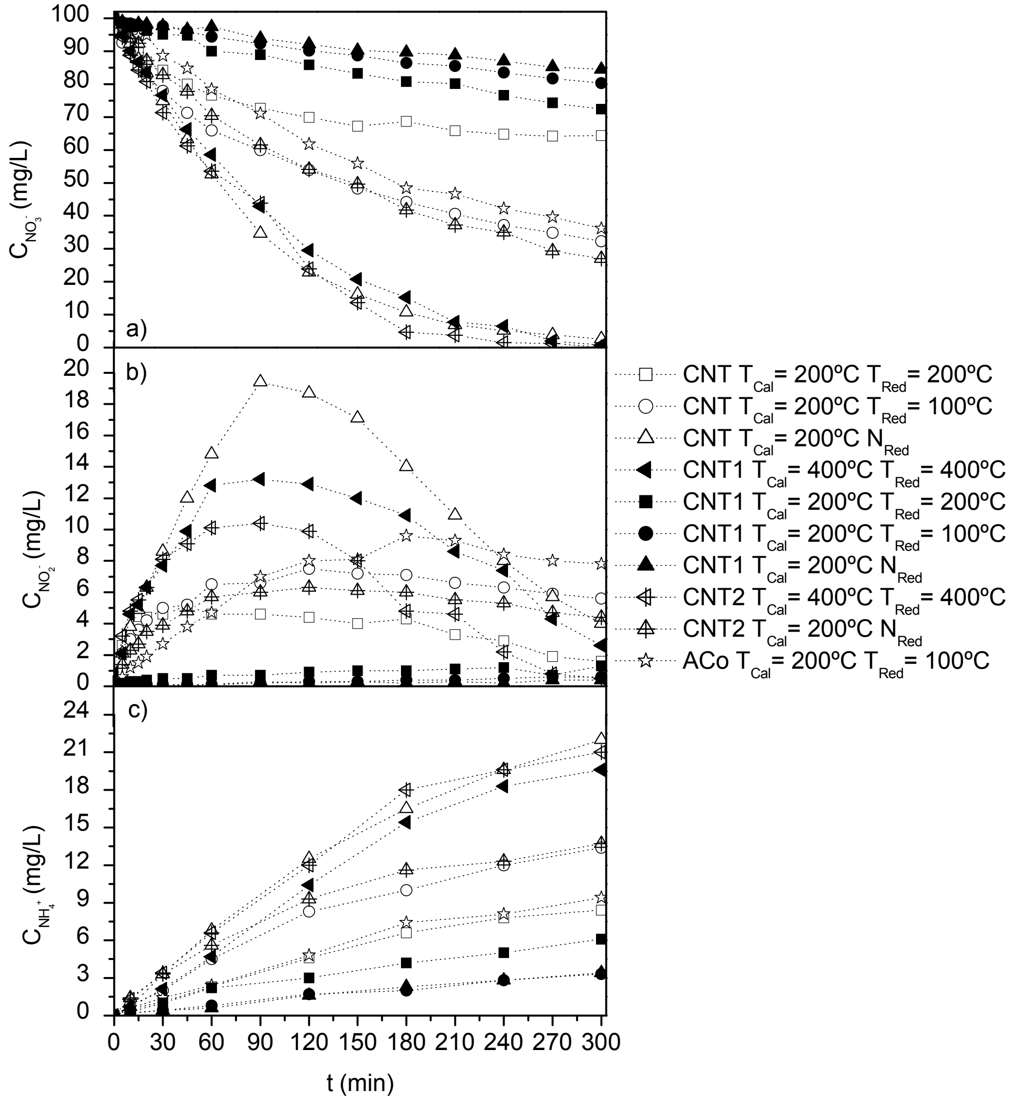


Figure 7.9 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of 1%Pt-0.3%Cu catalysts (C_{NO3^-i} = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

When functionalized carbon nanotubes are used as support (CNT1), it can be observed in Figure 7.9 a) that the respective catalysts present a very low activity, with the exception of catalyst CNT1 T_{Cal} = 400 ºC T_{Red} = 400 ºC, which is very active

(X_{NO3^-} = 99% after 5 h of reaction), and that the order of activity is inverse to that observed for the original carbon nanotubes (CNT). For the Pt-Cu catalysts supported on CNT1 and CNT2 the nitrate conversion increases with the increase of the calcination and reduction temperatures, with the catalyst CNT2 T_{Cal} = 400 ºC T_{Red} = 400 ºC being the most active (X_{NO3^-} = 100% after 5 h of reaction). This could be related to the fact that the heat treatment removes part of the functional groups created during the oxidative treatment with HNO_3 and the reduction temperature used is higher than the reduction temperature observed in the TPR profile (cf. Figure 7.7). However, these catalysts are more selective to ammonium than to nitrogen (see Table 7.3), with the catalyst CNT1 T_{Cal} = 200 ºC T_{Red} = 100 ºC being the most selective to nitrogen (S_{N2} = 37% after 5 h of reaction). This performance is similar to that observed for the Pd-Cu catalysts also supported on the functionalized carbon nanotubes, with the difference that the Pt-Cu catalysts are more active for the reduction of nitrate and less selective to nitrogen. The explanation for the negative impact of the acid carboxylic groups on the performance of the Pt-Cu catalysts was already given before for the Pd-Cu catalysts.

Figure 7.9 shows that the catalyst supported on activated carbon presents a nitrate conversion slightly lower than that observed for the catalyst supported on CNT with T_{Cal} = 200 ºC T_{Red} = 100 ºC. However, as observed for the Pd-Cu catalysts supported on the activated carbon, the nitrite accumulated after 5 hours of reaction is higher in the catalyst supported on the activated carbon, suggesting that mass transfer limitations may play a role in the process. It is also relevant to notice that the selectivity to nitrogen is higher in the catalyst supported on the activated carbon (see Table 7.3).

The results obtained demonstrate that the Pd-Cu catalysts are much more selective for the transformation of nitrate into nitrogen than the Pt-Cu catalysts, independently of the support used.

Table 7.3 Nitrate conversions ($X_{NO_3^-}$) and nitrite, ammonium and nitrogen selectivities ($S_{NO_2^-}$, $S_{NH_4^+}$, S_{N_2}) of of Pt-Cu catalysts after 5 h of reaction and for 50% of nitrate conversion.

	t = 300 min				$X_{NO_3^-}=50\%$		
Catalyst[#]	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Pt-0.3%Cu_ACo							
T_{Cal} = 200 ºC T_{Red} = 100 ºC	0.64	0.17	0.51	0.33	0.25	0.49	0.25
1%Pt-0.3%Cu_CNT							
T_{Cal} = 200 ºC N_{Red}	0.97	0.05	0.78	0.17	0.40	0.50	0.10
T_{Cal} = 200 ºC T_{Red} = 100 ºC	0.68	0.11	0.68	0.21	0.20	0.62	0.18
T_{Cal} = 200 ºC T_{Red} = 200 ºC	0.35	0.06	0.83	0.11	-	-	-
1%Pt-0.3%Cu_CNT1							
T_{Cal} = 200 ºC N_{Red}	0.15	0.04	0.77	0.19	-	-	-
T_{Cal} = 200 ºC T_{Red} = 100 ºC	0.19	0.04	0.59	0.37	-	-	-
T_{Cal} = 200 ºC T_{Red} = 200 ºC	0.28	0.07	0.75	0.18	-	-	-
T_{Cal} = 400 ºC T_{Red} = 400 ºC	0.99	0.04	0.67	0.29	0.34	0.43	0.23
1%Pt-0.3%Cu_CNT2							
T_{Cal} = 200 ºC N_{Red}	0.73	0.08	0.65	0.27	0.16	0.69	0.15
T_{Cal} = 400 ºC T_{Red} = 400 ºC	1.00	0.01	0.72	0.27	0.23	0.52	0.25

[#] T_{Cal}: calcination temperature, T_{Red}: reduction temperature, N_{Cal}: non calcined, N_{Red}: non reduced

7.4 Conclusions

This work presents for the first time detailed data on the use of carbon nanotubes as catalyst supports for the reduction of nitrate in water. The results obtained for the systems Pd-Cu and Pt-Cu show that the reduction of nitrate is quite different depending on the noble metal, the preparation conditions and the support used. The calcination and reduction temperatures significantly affect the activity of the catalysts prepared. Generally, when original carbon nanotubes are used as a support, the activity decreases with the increase of calcination and reduction temperatures; the opposite is observed for carbon nanotubes previously oxidised with HNO_3 or heat treated at 400 ºC under N_2 flow rate. The use of catalysts supported on functionalized carbon nanotubes has a negative effect in nitrate reduction, unless when they are calcined and reduced at 200 ºC (for the pair Pd-Cu) and at 400 ºC (for the pair Pt-Cu). The Pd-Cu catalysts, although less active, are more selective to nitrogen than the corresponding Pt-Cu catalysts.

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Chapter 8

8 Nitrate reduction in water catalyzed by Pd-Cu on different supports[1]

The influence of the support in the performance of Pd monometallic and Pd-Cu bimetallic catalysts for the reduction of nitrate was studied. Several metal oxides, as well as metal oxides supported on activated carbon or carbon nanotubes, were assessed as supports. The catalysts were prepared and tested under the same operation conditions. It was observed that the support plays an important role in the catalytic performance and in some cases is involved in the reaction mechanism. Under the conditions tested, the Pd-Cu catalyst supported on titanium dioxide and on the composite containing carbon nanotubes and titanium dioxide present the highest conversions, while the catalysts supported on ceria materials are the most selective to nitrogen.

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8.1 Introduction

Nitrate is a potentially harmful compound to human health because it can be converted into nitrites in human body and may cause various diseases: blue baby syndrome, cancer or hypertension. The increase of pollution in natural sources of drinking water requires the development of technologies for water remediation. Since the discovery of Pd-Cu [1] as an effective catalyst for the reduction of nitrate, several studies using bimetallic catalysts, composed by a noble metal (Pd, Pt or Rh) and a promoter metal (Cu, Sn or In) supported on different materials [2-15] (ref. 15 corresponds to chapter 3) have been carried out. It is well known that monometallic catalysts supported on activated carbon are inactive for nitrate reduction [16] (see chapter 2). However, studies using monometallic catalysts supported on some metal oxides have been appearing and demonstrated that nitrate can be reduced in the presence of noble metals supported on those materials [17-21]. When nitrate reduction occurs over bimetallic catalysts, it is generally accepted that nitrate is converted into nitrite by a redox reaction on the promoter metal, whereas the role of the noble metal is to activate hydrogen, which reduces the promoter metal, completing the catalytic cycle [22]. The noble metal is active for nitrite reduction. In the case of monometallic catalysts, the initial step (nitrate reduction to nitrite) is believed to be catalysed by sites on the partially reduced support [23]. High nitrate conversions are obtained in the presence of several catalysts, but also high ammonium and nitrite selectivities, which are the undesirable by-products of this process.

Many supports have been reported in literature, such as alumina [24-26], zirconia, titania and alumina membranes [27], activated carbon [16,28], SnO_2 [18,21], TiO_2 [4,23], ceria [19] and SiO_2 [29], and it has been demonstrated that different supports significantly affect the catalytic activity and selectivity of the catalysts for nitrate reduction in addition to several other factors, such as: the reaction conditions, the catalysts preparation, the way the noble metal is promoted and the catalyst supported [15,23,29-32]. Constantinou et al. [33] reported that the catalytic performance of Pd-Cu catalysts supported on various mixed metal oxides, $MO_x/\gamma\text{-}Al_2O_3$ (MO_x = CeO_2, SrO, Mn_2O_3, Cr_2O_3, Y_2O_3 and TiO_2), varies significantly depending on the support. Yoshinaga et al. [34] observed that Pd-Cu catalysts supported on activated carbon are very selective to nitrogen, and its activity is slightly higher or higher than those supported on silica or alumina, respectively. Recently, we reported that the surface chemistry of carbon materials has a remarkable effect in nitrate reduction [35] (see chapter 6) and that the support may have an important role in this reaction due to its possible involvement in the reaction mechanism [36] (this will be discussed in chapter 9). Nevertheless, more information about the role of the support in the catalysts activity and selectivity is needed.

In this study, the catalytic activity of Pd monometallic and Pd-Cu bimetallic catalysts supported on different materials was assessed under the same experimental conditions. Several metal oxides, as well as metal oxides supported on activated carbon or carbon nanotubes, were considered as support of the mono and bimetallic phases. The results obtained were compared with those obtained when activated carbon and carbon nanotubes were used as support. The main goal of this work is to select the most promising supports for nitrate reduction. Until now, there are no studies using manganese oxides, activated carbon and ceria or manganese composites and carbon nanotubes and titanium dioxide composites as support.

8.2 Experimental

8.2.1 Catalysts preparation

The following commercial materials were used as support: activated carbon (NORIT GAC 1240 PLUS) (sample ACo), multiwalled carbon nanotubes (Nanocyl-3100) (sample CNT), cerium(IV) oxide (Fluka) (sample CeO_2), manganese(IV) oxide (Sigma-Aldrich) (sample MnO_2), titanium dioxide (P25 Degussa) (sample TiO_2), γ–alumina (Degussa) (sample Al_2O_3), silica (Saint Gobain NorPro Corporation) (sample SiO_2). Some synthesised materials prepared as described elsewhere were also used as support: cerium oxide [37] (sample Ce-O), cryptomelane (sample K-OMS-2) [38], activated carbon and cerium oxide composite (sample AC-Ce) [37], activated carbon and manganese oxide composite (sample AC-Mn) [37] and carbon nanotubes and titanium dioxide composite (sample CNT-TiO_2) [39]. All the supports were ground before use ($d_p < 0.1$ mm).

The monometallic catalysts were prepared by incipient wetness impregnation and the bimetallic catalysts by incipient wetness co-impregnation, from aqueous solutions of the corresponding metal salts ($PdCl_2$, $Cu(NO_3)_2$). After impregnation, the samples were dried at 100 ºC for 24 h. The contents of noble metal and copper were fixed at 1%Pd-1%Cu and 1%Pd (weight percent). The catalysts were heat treated under nitrogen flow at 200 ºC for 1 h and reduced at 200 ºC under hydrogen flow for 3 h.

8.2.2 Catalysts characterization

The catalysts were characterized using different techniques: N_2 adsorption at -196 ºC, temperature programmed reduction (TPR) and transmission electron microscopy (TEM).

The textural characterization of the materials was based on the corresponding N_2 adsorption isotherms, determined at -196 ºC with a Nova 4200e (Quantachrome Instruments) equipment. BET surface areas (S_{BET}) were calculated, as well as mesopore surface areas (S_{meso}) and micropore volumes (V_{micro}) according to the t-method.

TPR experiments were carried out in an AMI-200 (Altamira Instruments) apparatus; the sample (150 mg) was heated at 5 ºC/min up to 600 ºC under a flow of 5% (v/v) H_2 diluted with He (total flow rate of 30 Ncm^3/min). The H_2 consumption was followed by a thermal conductivity detector (TCD) and by mass spectrometry (Dymaxion 200 amu, Ametek).

TEM micrographs were obtained using a LEO 906E microscope operating with an accelerating voltage of 120 kV.

8.2.3 Catalysts evaluation

The reduction of nitrate was carried out in a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure, and using hydrogen as reducing agent. Initially, 790 mL of deionised water and 400 mg of catalyst were fed into the reactor, the magnetic stirrer was adjusted to 700 rpm and the gas mixture of hydrogen and carbon dioxide (1:1, flow rate = 200 Ncm^3/min) was passed through the reactor during 15 min to remove oxygen; CO_2 acts as pH buffer (pH = 5.5). After that period, 10 mL of a nitrate solution, prepared from $NaNO_3$, were added to the reactor, in order to obtain an initial NO_3^- concentration equal to 100 mg/L.

Small samples were taken from the reactor for determination of nitrate, nitrite and ammonium concentrations after defined periods. Nitrate and nitrite ions were simultaneously determined by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was a Hamilton PRP-X100 column (150 mm x 4.1 mm) working at room temperature, under isocratic conditions. The mobile phase was a solution of 0.1 M NaCl:CH_3OH (45:55). Ammonium ions were determined by potentiometry using a convenient selective electrode. pH values were also measured.

The amounts of palladium and copper eventually leached during reaction were measured in a UNICAM 939/959 atomic absorption spectrometer, using the remaining solution after each reaction test.

The selectivities to nitrite, ammonium and nitrogen were calculated as:

$$S_{NO_2^-} = \frac{n_{NO_2^-}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{8.1}$$

$$S_{NH_4^+} = \frac{n_{NH_4^+}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{8.2}$$

$$S_{N_2} = \frac{2 * n_{N_2}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \tag{8.3}$$

where $n_{NO_3^-{}_i}$ is the initial amount of nitrate (mmol) and $n_{NO_3^-}$, $n_{NO_2^-}$, $n_{NH_4^+}$ and n_{N_2} are the amounts of the respective species (mmol) at time t (min). The amounts of nitrogen were calculated by a mole balance.

8.3 Results and Discussion

8.3.1 Catalysts characterization

8.3.1.1 Textural properties

Textural properties obtained from the N_2 adsorption isotherms at -196 ºC for the supports are listed in Table 8.1. The activated carbon (ACo) has the highest BET surface area and is a microporous support. The CeO_2 and MnO_2 supports present the lowest BET surface areas. The composite samples present surface areas much lower than the observed in the original carbon materials, which was expected considering the low surface areas of the oxides used. From our previous experience [15] (see chapter 3), the textural parameters of the catalysts remain practically unchanged compared to the unloaded supports.

Table 8.1 Textural characterization of the supports and copper leaching of the Pd-Cu catalysts.

Sample	S_{BET} (m^2/g)	S_{meso} (m^2/g)	V_{micro} (cm^3/g)	wt% carbon material	%Cu leaching
ACo	968	177	0.346	-	0
CNT	320	320	0	-	0
CeO_2	20	20	0	-	56.4
MnO_2	7	7	0	-	2.5
TiO_2	50	50	0	-	0
Ce-O	121	121	0	-	32.0
K-OMS-2	71	71	0	-	0.1
Al_2O_3	196	196	0	-	34.5
SiO_2	164	164	0	-	0
AC-Ce	240	156	0.042	40	18.1
AC-Mn	269	88	0.094	35	2.2
CNT-TiO_2	131	131	0	14	15.9

8.3.1.2 TPR

The TPR profiles of the Pd-Cu catalysts are shown in Figure 8.1. Only the comparison among bimetallic catalysts was carried out. It can be observed that the position, width and intensity of the peaks depend on the support. The reduction ranges of the Pd and Cu monometallic catalysts are around 150 ºC and 250 ºC, respectively [40,41] (ref. 40 corresponds to chapter 7). The reduction peak at around 60 ºC relative to the decomposition of Pd β-hydride [42,43] was not observed, which may indicate that Pd is well dispersed on the support [44]. Almost all the bimetallic catalysts present a reduction peak in the range 140 - 200 ºC, which can be assigned to the reduction of Cu oxides promoted by the presence of Pd [42,44]. The exception is the catalyst supported on K-OMS-2, which presents a peak at 256 ºC. The decrease in the reduction temperature of supported copper in bimetallic catalysts induced by the presence of palladium indicates that a close contact between copper and palladium species was achieved [44]. Nevertheless, depending on the support, the features of the TPR profiles are distinct. The typical profile of CeO_2 is characterized by two asymmetrical and broad peaks at around 455 and 912 ºC, which are assigned to the surface and bulk reductions, respectively [45]. The catalysts supported on ceria materials present a reduction peak below 200 ºC and also other peak at around 350 ºC. The first peak at lower temperature may be attributed to the Pd–Cu sites, while the other may be assigned to the reduction peaks characteristic of the support, which are displaced to lower temperatures due to the presence of Pd [19].

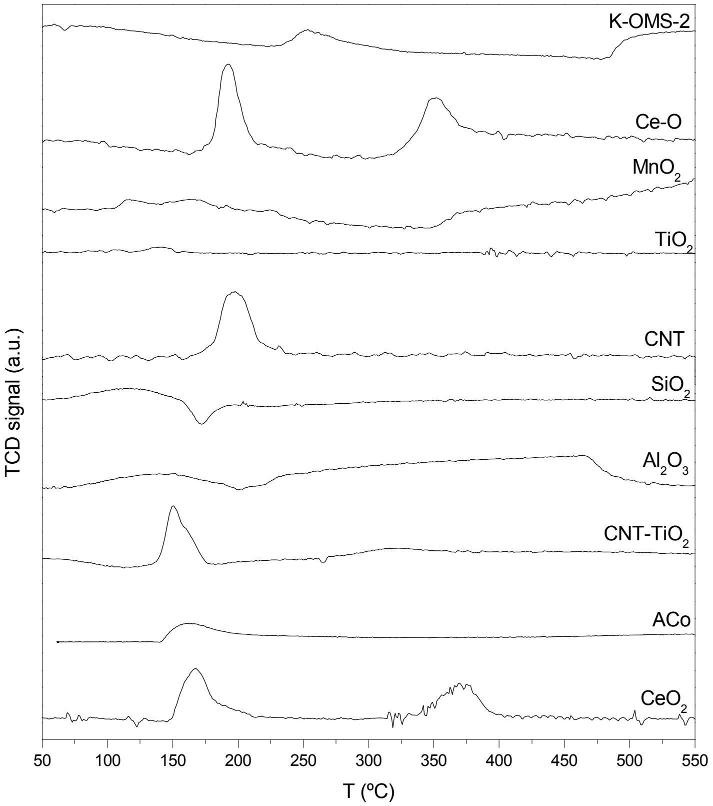


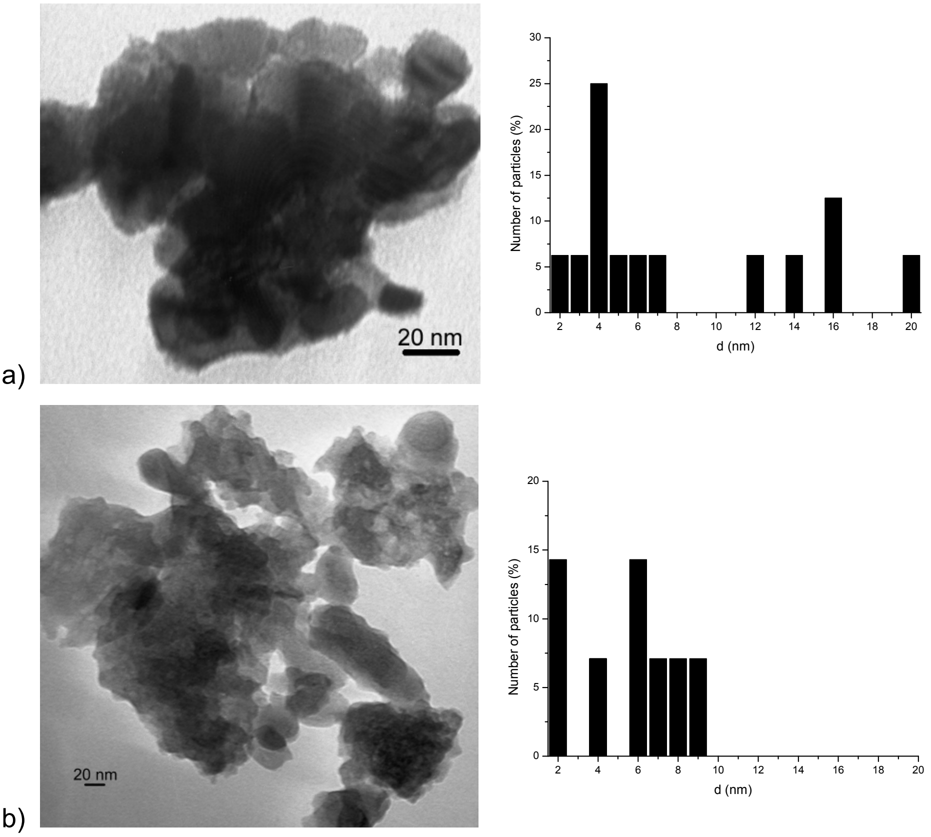
Figure 8.1 TPR profiles of the bimetallic catalyst.

The TPR profile of the catalysts supported on manganese oxides does not show intense peaks. It is generally accepted that the presence of noble metals affects the reduction profile of the metal oxides. The addition of noble metals increase the reducibility of the support [46]. This could be due to the fact that noble metals catalyse the reduction of MnO_x by hydrogen spillover during TPR experiment or by increasing the mobility of the lattice oxygen [47]. It is also generally accepted, in

Cu-Mn catalysts, that copper has a promoting effect on the reduction of manganese ions and that the reduction of copper ions is also promoted by the presence of manganese ions [48]. The peak observed at 256 ºC in the Pd-Cu catalyst supported on K-OMS-2 could be due to the reduction of Mn^{4+} to Mn^{3+} [49].

8.3.1.3 TEM

Selected catalysts were characterised by TEM in order to evaluate the particle size distributions. Figure 8.2 shows that the catalysts supported on ACo, CeO_2 and CNT-TiO_2 present very small particles; the corresponding modes are 6 nm for the former and 4 nm for the remaining. The catalyst supported on TiO_2 presents larger particles, with a mode of 18 nm.



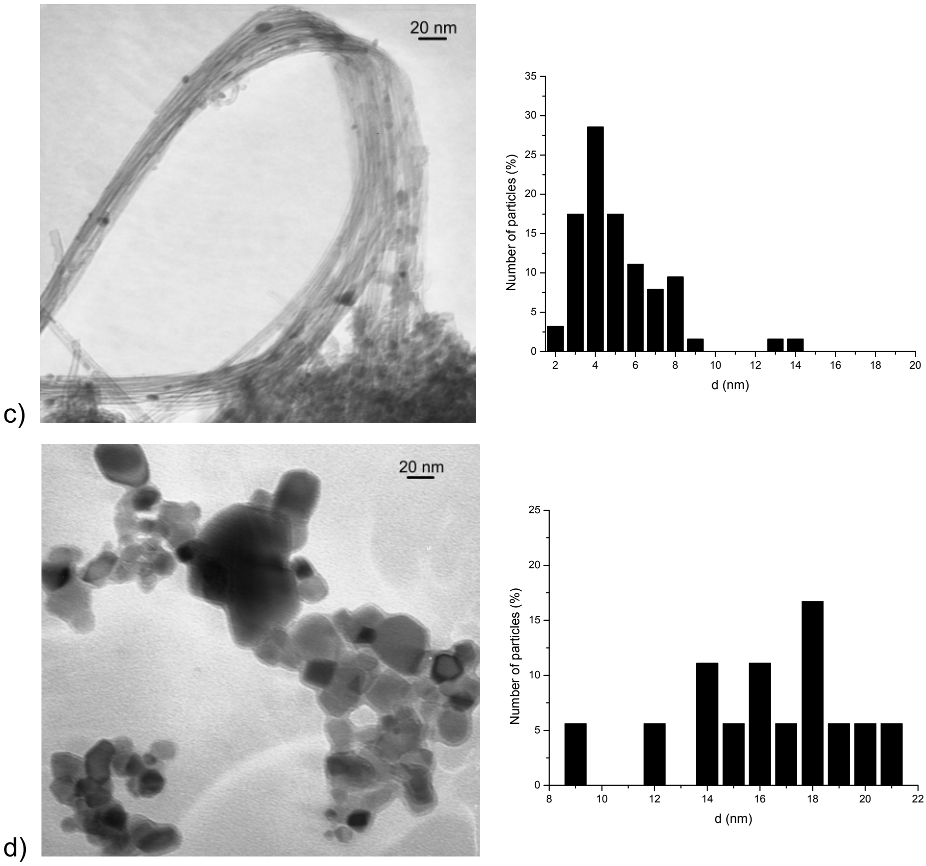


Figure 8.2 TEM micrographs of Pd-Cu catalysts supported on a) CeO_2, b) ACo, c) CNT-TiO_2 and d) TiO_2.

8.3.1.4 Metal leaching

Considering the practical application of these catalysts in water treatment, it is important to find catalysts not only active for nitrate reduction but also stable, without loss of metals in order to avoid the increase of effluent toxicity. Therefore, after each reaction test, the amounts of metals leached were measured. No dissolution of Pd was detected in all the experiments (within the experimental error), whereas Cu leached in varying amounts depending on the support used, as is summarised in Table 8.1. The leaching of Cu was significantly higher when CeO_2, Ce-O and Al_2O_3 were used as support and no dissolution was observed in the case of ACo, CNT, TiO_2 and SiO_2. Yoshinaga et al. [34] also reported that the dissolved amounts of Pd and Cu are negligible when activated carbon is used as support but higher amounts were measured when SiO_2 or Al_2O_3 are used.

The amounts of dissolved Mn were not quantified, but during the determination of ammonium, which implies an increase of the pH value, the formation of a brown precipitate was observed. Despite the low dissolution of Pd and Cu in the catalysts supported on Mn materials, the formation of this precipitate indicates that these catalysts are not suitable for practical applications.

8.3.2 Catalytic tests

The influence of the support on the catalysts activity and selectivity during the reduction of nitrate was studied. The catalysts were prepared similarly and using the same metal amounts. The activities of monometallic and bimetallic catalysts are shown in Figure 8.3 a) and Figure 8.4 a), respectively. Figure 8.3 b) and c) and Figure 8.4 b) and c) show the corresponding evolution of nitrite and ammonium concentrations during the reaction. Nitrate conversions and selectivities are summarised in Table 8.2.

Figure 8.3 shows that nitrate is reduced on the presence of monometallic catalysts supported on CeO_2 and TiO_2. When palladium is supported on MnO_2 there is no reduction of nitrate. Previously, it was observed that when activated carbon is used as support the monometallic Pd catalyst is not active for nitrate reduction [16] (see chapter 3), and the Pd monometallic catalyst supported on Al_2O_3 can reduce nitrate but the degradation rate is very low [50]. Epron et al. [19] observed that Pd/CeO_2 is active for this reaction and that this catalyst was very selective to ammonium; however, when a H_2/CO_2 mixture is used the nitrate reduction is inhibited due to CO_2 poisoning. In a recent work [17] the poisoning effect of CO_2 was also demonstrated for a Pt monometallic catalyst supported on ceria, leading to a decrease in nitrate conversion from 99% to 30%. Nevertheless, the introduction of CO_2 increases the nitrogen selectivity from 45% to 76%. Nitrate reduction occurs due to a promoting effect of the support, namely by the interaction of the oxygen atoms of nitrate with the oxygen vacancies on ceria [19].

Sá et al. [23] also reported that palladium supported on titanium dioxide is active for this reaction. According to them, nitrate is adsorbed at exposed Lewis acid sites (oxygen vacancies) of the support by electrostatic interactions. The electrons associated with the reduction process may be located for example on Ti^{3+} centres. Nevertheless, Pd catalysts supported on TiO_2 have very low nitrogen selectivities, which can be justified by the strong hydrogenation character of this type of catalysts, causing over-reduction [23].

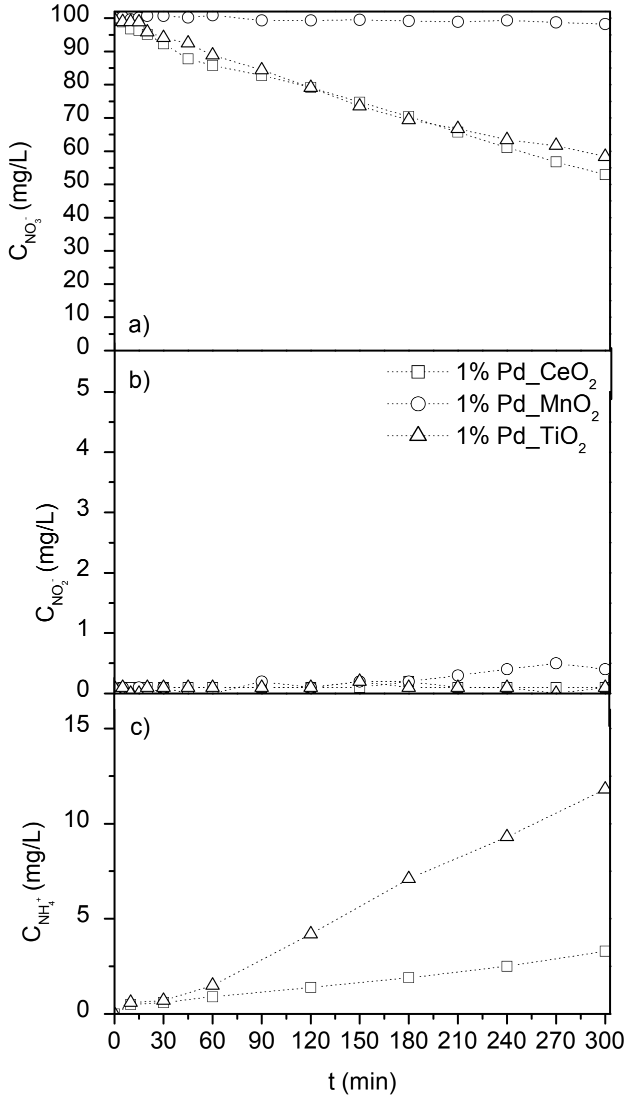


Figure 8.3 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of 1%Pd monometallic catalysts (C_{NO3^-i} = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

It was expected that Pd monometallic catalysts supported on MnO_2 were also active for nitrate reduction, once manganese has the ability to form oxides with different oxidation states. Nevertheless, the results obtained in this work clearly show that manganese oxides are not able to promote the reduction of nitrate. Actually, the nitrate conversion obtained for this catalyst after 5 h of reaction is only 2%.

Figure 8.4 shows that the support plays an important role in nitrate reduction. The nitrate conversion varies from 0% for the catalyst supported on K-OMS-2 to 100% for the catalysts supported on TiO_2 or CNT-TiO_2. The addition of copper to the monometallic Pd catalyst supported on TiO_2 increases significantly the nitrate conversion after 5 h (from 42 to 100%). This addition also increases the selectivity to nitrogen from 2% to 17% after 5 h of reaction (see Table 8.2). When the composite CNT-TiO_2 is used as support, the nitrogen selectivity (66%) increases significantly compared to the catalyst supported on TiO_2 (17%) or even on CNT (52%). The comparison of selectivities was generally made after 300 min of reaction, because it was observed that after a period of stabilization of about 30 - 60 min of reaction, the selectivity values remain practically constant and did not change with conversion (see in Table 8.2, the selectivities after 300 min and for 50% conversion). The exceptions were the catalysts supported on TiO_2, which present a high variation with conversion. In these cases, the nitrogen selectivity decreases continuously. This is probably related to the high hydrogenation capacity of this type of catalysts, producing higher amounts of ammonium. For the most active catalysts the selectivities were also compared at 50% conversion (Table 8.2). It can be concluded that nitrogen selectivities for the catalysts supported on TiO_2 and CNT-TiO_2 are similar (68% and 70%, respectively), and in the case of TiO_2 is much higher than that observed after 300 min of reaction.

The addition of copper to the catalyst supported on manganese oxide does not increase the nitrate conversion. As mentioned above, the Pd monometallic catalyst is not active for nitrate reduction but some activity was expected for the Pd-Cu bimetallic catalyst. This unexpected result is probably related to the formation of Mn-Cu mixed oxides (hopcalite), which under the calcination and reduction temperatures used in this work (200 ºC) present an amorphous form [49]. It is generally accepted that nitrate is adsorbed on the promoter metal on bimetallic ensembles [26], but in this case, probably due the formation of the Mn-Cu mixed oxide, Cu is not able to interact with nitrate and no activity is observed. On the other hand, when the composite AC-Mn is used as support, the nitrate conversion is slightly lower than that observed for ACo (59% and 66% after 5 h, respectively). This is indicative that in the composite copper is preferentially supported on the activated carbon, being available to reduce nitrate.

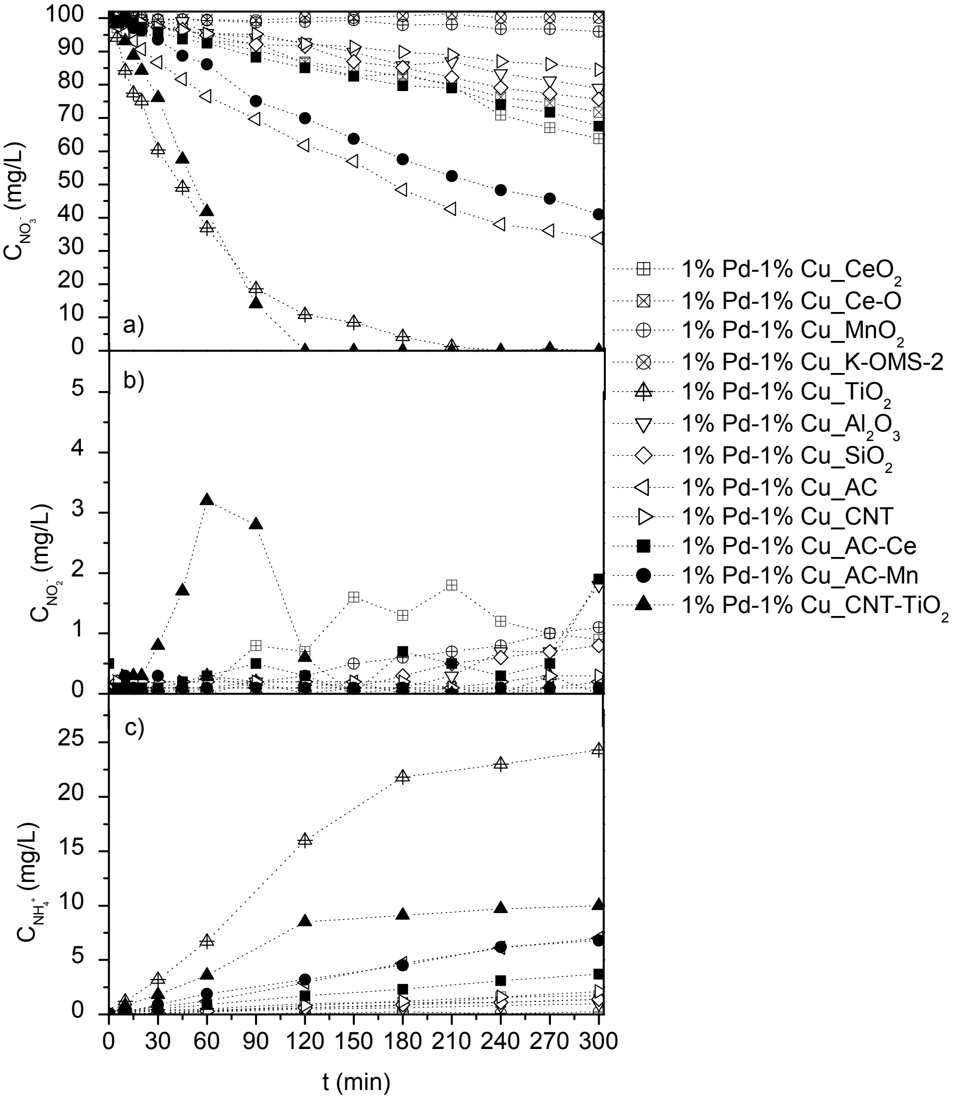


Figure 8.4 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of 1%Pd-1%Cu bimetallic catalysts (C_{NO3^-i} = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC).

Table 8.2. Nitrate conversions ($X_{NO_3^-}$) and nitrite, ammonium and nitrogen selectivities ($S_{NO_2^-}, S_{NH_4^+}, S_{N_2}$) of mono and bimetallic catalysts after 5 h of reaction and selectivities for 50% of nitrate conversion.

	t = 300 min				$X_{NO_3^-} = 50\%$		
Catalyst	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Pd							
CeO_2	0.47	0.00	0.24	0.76	-	-	-
MnO_2	0.02	-	-	-	-	-	-
TiO_2	0.42	0.00	0.98	0.02	-	-	-
1%Pd-1%Cu							
CeO_2	0.37	0.03	0.16	0.81	-	-	-
Ce-O	0.28	0.00	0.18	0.82	-	-	-
MnO_2	0.05	0.31	0.16	0.53	-	-	-
K-OMS-2	0.00	-	-	-	-	-	-
TiO_2	1.00	0.00	0.83	0.17	0.00	0.32	0.68
Al_2O_3	0.21	0.11	0.17	0.72	-	-	-
SiO_2	0.24	0.05	0.21	0.74	-	-	-
AC	0.66	0.00	0.37	0.63	0.00	0.32	0.68
CNT	0.15	0.02	0.46	0.52	-	-	-
AC-Ce	0.33	0.07	0.39	0.54	-	-	-
AC-Mn	0.59	0.00	0.40	0.60	0.00	0.41	0.59
CNT-TiO_2	1.00	0.00	0.34	0.66	0.06	0.24	0.70

The bimetallic catalysts supported on Ce-O and CeO_2 present lower activity than the monometallic catalyst supported on CeO_2; nevertheless, they are very selective to nitrogen. The decrease in the activity could result from the competition between the support and copper for nitrate adsorption, being the promoting effect of the support apparently higher than that of copper. The slight increase in the nitrogen selectivity may be explained by the formation of bimetallic particles, which are known to be more selective to nitrogen than the noble metal particles. In previous studies [15] (see chapter 3), it was shown that when the noble metal is present in higher amounts than the promoting metal, the ammonium selectivity increases with the relative amount of noble metal available on the surface. It is well established that nitrite reduction occurs mainly on the noble metal sites [26], and Yoshinaga et al. [34] suggested that isolated Pd atoms are active sites for ammonium formation. Therefore, it can be concluded that when only the noble metal is present, the number of noble metal surface sites available is higher and, as the noble metal is very active for hydrogenation reactions, the nitrite molecules would be deeply hydrogenated, producing ammonium.

Alumina is one of the most studied supports for this reaction [22,29,51,52], and it was expected that the catalysts supported on alumina would present one of the highest nitrate conversions; however, the nitrate conversion obtained is relatively low (21% after 5 h). Nevertheless, these results are in line with those obtained by Gao et al. [4], who reported that Pd-Cu catalyst supported on TiO_2 was much more active than supported on Al_2O_3 (55% and 7% nitrate conversion, respectively). Yoshinaga et al. [34] reported that the catalysts supported on activated carbon are more or slightly more active than those supported on Al_2O_3 or SiO_2, respectively. A higher activity and a lower production of ammonium were observed when Pd-Cu is supported on hydrotalcite compared to alumina [53]. The catalysts supported on SiO_2 and Al_2O_3 present similar nitrate conversions after 5 h (24% and 21%, respectively) and nitrogen selectivities (74% and 72%). The values of nitrate conversion are much inferior to that observed with ACo as support (66%). Garron et al. [29] observed that Pd-Sn catalysts supported on silica are more selective to nitrogen but less active than those supported on alumina. Nevertheless, in addition to the promoting effect of the different supports, these different performances can be related to the preparation conditions of the catalysts. Under the conditions used in this work, nitrate conversions for the catalysts supported on SiO_2, Al_2O_3 or CNT are very low. This can be related to the calcination and reduction temperatures selected to prepare the catalysts. In previous works [40,54] (see chapters 7 and 4), it was observed that the nitrate conversion increases by decreasing the calcination and reduction temperatures when carbon nanotubes and activated carbons are used as support for this process. For example, when the Pd-Cu catalyst supported on carbon nanotubes is calcined at 200 ºC and reduced at 100 ºC, the nitrate conversion is 62% and the nitrogen selectivity is 72% after 5 h of reaction, values higher than 15% and 52%, respectively, obtained in this work for the same catalyst calcined and reduced at 200 ºC. Nevertheless, the aim of this work is to evaluate the catalysts under the same conditions, although they were not optimised for all the supports tested. The temperatures were chosen after analysing the TPR profiles and observing that at 200 ºC all the supported metals are reduced. Certainly, the catalytic activity and selectivity of this process can be improved optimising the calcination and reduction temperatures for the most promising supports tested.

The concentrations of nitrite detected in solution during the reduction of nitrate are very low for all the catalysts studied. Most of the catalysts give rise to concentrations lower than 0.5 mg/L. For short reaction times the composite CNT-TiO_2 shows the highest nitrite concentration measured, which is rapidly reduced by increasing the reaction time, confirming that nitrite is an intermediate species.

The ammonium concentration increases with nitrate conversion (see Figure 8.4). The bimetallic catalyst supported on TiO_2 presents the highest ammonium concentration followed by the composite CNT-TiO_2.

It was found that the BET surface area does not have a significant effect on the catalysts activity, once catalysts with significantly different surface areas present similar nitrate conversions. The different catalytic performances should be related to the chemical nature of the support, which may interact with nitrate, promoting its reduction. However, the supports by it are not active; the presence of one or two metals is mandatory to reduce nitrate. It is well established that the monometallic catalysts are generally inactive for nitrate reduction, a second metal being necessary to reduce nitrate to nitrite [1,26]. The role of the promoter metal is to reduce nitrate according to a redox reaction leading to nitrite intermediates and to an oxidised form of the promoter metal, which is regenerated to a reduced form by hydrogen adsorbed and dissociated on the noble metal [22]. When the monometallic catalyst is active, the mechanism involves partially reduced species of the support [23], as was the case of cerium and titanium oxides in the present work. Constatinou et al. [33], when studding the catalytic performance of Pd-Cu catalysts supported on various mixed metal oxides of type $MO_x/\gamma\text{-}Al_2O_3$ (MO_x = CeO_2, SrO, Mn_2O_3, Cr_2O_3, Y_2O_3 and TiO_2), also observed that the chemical composition of the support influences the nitrate conversion and the selectivity. According to them, CeO_2, Mn_2O_3 and Cr_2O_3 are the best supports for nitrate conversion but also present the highest selectivities to ammonium, being $TiO_2/\gamma\text{-}Al_2O_3$ the most selective to nitrogen. On the contrary, the results obtained in this work clearly show that both the monometallic and the bimetallic catalysts supported on TiO_2 present the lowest nitrogen selectivity, being the catalysts supported on CeO_2 the most selective to nitrogen.

8.4 Conclusions

The present work reports the influence of the support in nitrate reduction. The support plays an important role in the catalytic performance. The results obtained show that titanium dioxide provides high activity for nitrate reduction and that the use of a composite with carbon nanotubes increases significantly the selectivity of the process to nitrogen. The catalysts supported on ceria are very selective to nitrogen and present the particularity of the monometallic to be more active than the bimetallic. Manganese oxides are not suitable supports for this reaction. Activated carbon demonstrated to be a good support with intermediate activity and nitrogen selectivity. The activities of this process can be improved, optimizing the preparation conditions for the most promising supported catalysts.

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Chapter 9

9 Pt-Sn catalysts for nitrate reduction in water: activated carbon and titania as supports[1,2]

The effect of the support (activated carbon or titanium dioxide) on the catalytic activity and selectivity to nitrogen of Pt-Sn catalysts in nitrate reduction was studied. The effects of the preparation conditions and the Pt:Sn atomic ratio were also evaluated. It was observed that the support plays an important role in nitrate reduction and that different preparation conditions lead to different catalytic activities and selectivities. Generally, the catalysts supported on activated carbon were less active but more selective to nitrogen than those supported on titanium dioxide. The monometallic Pt catalyst is active for nitrate reduction only when supported on titanium dioxide, which is explained by the involvement of the support in the reaction mechanism.

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[2] All the catalysts used in this chapter were prepared and characterized in Laboratorio de Materiales Avanzados, Instituto Universitario de Materiales de Alicante - Departamento de Química Inorgánica, Universidad de Alicante.

9.1 Introduction

The removal of nitrate is an important and developing area of research due to the increase of pollution in natural sources of drinking water. Nitrate is a potentially harmful compound to human health because it can be converted into nitrites in human body and may cause various diseases: blue baby syndrome, cancer or hypertension [1-3]. The European community has limited the level of nitrate in drinking water to 50 mg/L. The catalytic removal of nitrate in water consists in the reduction of nitrate to nitrogen over bimetallic catalysts, composed by a noble metal (Pd or Pt) and a promoter metal (Cu, Sn, etc.) supported on different materials, in the presence of a reducing agent [3-5]. Nitrite as intermediate and ammonium as by-product are the major limitations of this process.

Many studies have been done in the last 20 years since the discovery of Pd-Cu as an active catalyst system for this reaction [4]; however, the selectivities to nitrogen are still unsatisfactory. Several studies have demonstrated that monometallic catalysts are practically inactive for nitrate reduction and that some bimetallic catalysts are effective for this reaction [3-7] (ref. 7 corresponds to chapter 2). However, monometallic Pd catalysts supported on SnO_2 [8], CeO_2 [9] and TiO_2 [10] were reported as showing some activity for nitrate reduction. Generally, a second metal is necessary to promote the reduction of nitrate, while the noble metal by itself does not present activity for this reaction, but it is effective for nitrite reduction. In the reaction mechanism proposed [6] nitrate is converted by a redox reaction with copper, whereas the role of the noble metal is to activate hydrogen, which reduces copper, completing the catalytic cycle. In the case of monometallic catalysts, the initial step is believed to be catalysed by sites on the partially reduced support [10].

Many investigations have shown that the activity and selectivity of catalytic nitrate reduction are strongly influenced by several factors such as the reaction conditions, the catalysts preparation, the way the noble metal is promoted and the catalyst support [10-17] (ref. 16 corresponds to chapter 3). Many supports have been studied, such as alumina [3,18,19], zirconia, titania and alumina membranes [20], activated carbon [7,16,17,21] (ref. 7 and 16 correspond to chapters 2 and 3), SnO_2 [8,11], TiO_2 [1,10,22], ceria [9] and SiO_2 [13], and it has been demonstrated that the different supports significantly affect the catalytic activity and selectivity of the catalysts for the nitrate reduction.

Activated carbon and titanium dioxide have proven to be suitable supports for this reaction, and they were selected for this study. Activated carbon has been widely used in heterogeneous catalysis due to its particular features, and it has some advantages as catalyst support. It is relatively inexpensive, possess a high surface area, allow easy recovery of supported metal by simple combustion of the support and show chemical inertness both in acidic and basic media [23]. This inertness makes it also very useful when it is used as support for bimetallic catalysts, as it favours the interaction between both metallic phases.

On the other hand, titanium dioxide possesses completely different properties. Its use as catalyst support is mainly based on the possibility of strongly interact with supported metals after reduction treatments (strong-metal support effect, SMSI), which modifies the catalytic behavior of the metallic phase. In the case of TiO_2 supported catalysts for nitrates reduction in water, it has been proposed that the oxide surface can participate in the first step of the reaction, namely the adsorption/reduction of nitrates to nitrites [10,22]. Thus, nitrate anions would be adsorbed on exposed acid sites of the support, which are supposed to be in close vicinity of the metal particles, and would be reduced by excess electrons generated in the support after the reduction treatment (SMSI effect). Although these titania-supported catalysts were very active in nitrate reduction, their selectivity towards nitrogen was poor, and ammonia was produced due to over-reduction. Thus, although they result in a very promising system, new catalyst preparation strategies are needed in order to develop active and selective catalysts.

In this work, the effect of the support (activated carbon or titanium dioxide) on the performance of Pt-Sn catalysts with different Pt:Sn atomic ratios was investigated for the nitrate reduction, taking in consideration both the catalytic activity and the selectivity. To the best of our knowledge, this is the first study testing Pt-Sn catalysts using titanium dioxide or activated carbon as a supports for the nitrate reduction. Several Pt-Sn catalysts with different preparation conditions and different atomic ratios were tested under the same experimental conditions with the main goal at analyzing the influence of the support in this reaction.

9.2 Experimental

9.2.1 Catalysts preparation

Activated carbon Nuchar RGC 30, from Mead-Westvaco Corp., with a BET surface area of 1535 m^2/g and a particle size between 0.1-0.3 mm, was used as support. The monometallic Pt/AC catalyst was prepared by incipient wetness impregnation with an aqueous solution of H_2PtCl_6 (Alfa Aesar). The bimetallic Pt-Sn/AC catalysts were prepared by incipient wetness co-impregnation with aqueous solutions of H_2PtCl_6 (Alfa Aesar) and $SnCl_2{\cdot}2H_2O$ (Sigma Aldrich). The prepared catalysts were dried at room temperature for 12 h and finally dried at 120 ºC overnight. A series of catalysts was prepared with a nominal Pt content of 1 wt% and a Pt:Sn atomic ratio of 1:0, 4:1, 2:1, 4:3 and 1:1. Additionally, two more samples were prepared with constant Pt:Sn atomic ratio (1:1) and higher total metal content (2.5wt%Pt and 5wt%Pt).

Degussa P25 (60% anatase, 40% rutile), with a BET surface area of 50 m^2/g and particle size of about 100 nm, was used as the TiO_2 support. The $PtSn/TiO_2$ catalysts were prepared by a co-impregnation method. The support was first calcined in air at 500 ºC for 5 h and then impregnated with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (Johnson Matthey), with the appropriate concentration to achieve a Pt content of 2wt%, and $SnCl_2{\cdot}2H_2O$ (Aldrich). Catalysts with nominal Pt:Sn atomic ratios of 4:1, 3:1, 2:1 and 1:2 were prepared. The slurry was stirred for 12 h and the excess of solvent was removed by heating at 90 ºC under vacuum in a rotary evaporator. Finally, the catalysts were dried at 110 ºC for 24 h.

9.2.2 Catalysts characterization

The catalysts were characterized using different techniques: N_2 adsorption/desorption at -196 ºC, temperature programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS). Additionally, the TiO_2-supported catalysts have been characterized by *in situ* IR spectroscopy of adsorbed CO, after different thermal treatments, and the results have been reported elsewhere [24].

N_2 adsorption/desorption isotherms were performed in a home-made fully automated manometric equipment. Before the adsorption experiment, samples were submitted to an out-gassing treatment at 250 ºC during 4 h at a base pressure of 10^{-3} Pa.

TPR experiments were carried out in a U-shape quartz reactor using a 5% H_2/He gas flow rate of 50 Ncm^3/min and about 100 mg of catalysts. Hydrogen evolution was monitored by on-line mass spectrometry.

XPS analyses of the TiO_2-supported Pt-Sn catalysts have been already reported elsewhere [24]. For the carbon-supported Pt-Sn catalysts, XPS measurements were recorded with a Physical Electronics 5700 instrument provided with a hemispherical electron analyzer, the band-pass energy being 29.35 eV. The Mg Kα X-ray excitation source ($h\nu$ = 1253.6 eV) was at a power of 300 W. The pressure in the analysis chamber was maintained below 1.3×10^{-7} Pa during data acquisition. The binding energies (BE) were obtained with ± 0.1 eV accuracy and charge compensation was done with the adventitious C1s peak at 248.8 eV. Before the XPS measurements samples were pre-treated ex-situ and then placed in micro-centrifuge tubes containing 1 mL of cyclohexane under flowing helium, to avoid contact with air. Tubes with samples were kept at 4 ºC. Finally, the sample was placed in the system pre-chamber, where the impregnating cyclohexane was removed.

9.2.3 Catalysts evaluation

The reduction of nitrate was carried out in a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure, and using hydrogen as reducing agent. Initially, 790 mL of deionised water and 400 mg of catalyst were fed into the reactor, the magnetic stirrer was adjusted to 700 rpm and the gas mixture of carbon dioxide and hydrogen (H_2 + CO_2 (1:1), flow rate = 200 Ncm^3/min) was passed through the reactor during 15 min to remove oxygen; CO_2 acts as pH buffer (pH = 5.5). After that period, 10 mL of a nitrate solution, prepared from $NaNO_3$, were added, in order to obtain an initial NO_3^- concentration equal to 100 mg/L. Preliminary studies were carried out varying the stirring rate and it was checked that under the selected conditions there was no external diffusional limitations. Before the catalytic experiments, Pt-Sn catalysts were submitted to different thermal/reduction treatments: calcination at 200 ºC or 400 ºC – 500 ºC under a He flow (100 Ncm^3/min) for 1 h followed by a reduction treatment at 200 ºC or 400 ºC – 500 ºC under a H_2 flow (100 Ncm^{3}min) for 1 h. Non-calcined/non-reduced samples were also tested. Small samples were taken from the reactor for determination of nitrate, nitrite and ammonium concentrations after defined periods. Nitrate and nitrite ions were simultaneously determined by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was a Hamilton PRP-X100 column (150 mm x 4.1 mm) working at room temperature, under isocratic conditions. The mobile phase was a solution of 0.1 M NaCl:CH_3OH (45:55). Ammonium ions were determined by potentiometry using a convenient selective electrode. pH values were also measured.

The selectivities to nitrite and ammonium were calculated as:

$$S_{NO_2^-} = \frac{n_{NO_2^-}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \qquad (9.1)$$

$$S_{NH_4^+} = \frac{n_{NH_4^+}}{n_{NO_3^-{}_i} - n_{NO_3^-}} \qquad (9.2)$$

where $n_{NO_3^-{}_i}$ is the initial amount of nitrate (mmol) and $n_{NO_3^-}$, $n_{NO_2^-}$ and $n_{NH_4^+}$ are the amounts of the respective species (mmol) at time t (min). The selectivity to nitrogen was calculated by difference.

9.3 Results and Discussion

9.3.1 Catalysts characterization

9.3.1.1 Textural properties

N_2 adsorption/desorption measurements at -196 ºC for the original supports show a Type II isotherm, characteristic of a non-porous sample, for the TiO_2 support, whereas a combination of Type I and Type IV isotherm is obtained for the RGC-30 activated carbon, characteristic of a material that combines both micro and mesoporosity. Incorporation of the different metal species (either Pt and/or Sn) produces no changes in the textural properties of both supports. Only the catalyst containing 5wt%Pt and 5wt%Sn supported on activated carbon (5Pt-Sn/AC) exhibits a certain decrease in the specific surface area from 1540 m^2/g to 1322 m^2/g, due to the partial blocking of the microporosity after metal incorporation.

9.3.1.2 TPR

TPR studies have been carried out on Pt-Sn catalysts supported on activated carbon, previously submitted to a thermal treatment in He at 400 ºC. The monometallic Pt/AC catalyst shows no hydrogen consumption peaks in the temperature range studied, thus confirming the reduction of Pt during the thermal treatment in He. Bimetallic samples containing only 1wt%Pt exhibit broad hydrogen consumption peaks going from 177 ºC to 442 ºC (see Figure 9.1). However, the small metal content in these samples makes it difficult the identification of the

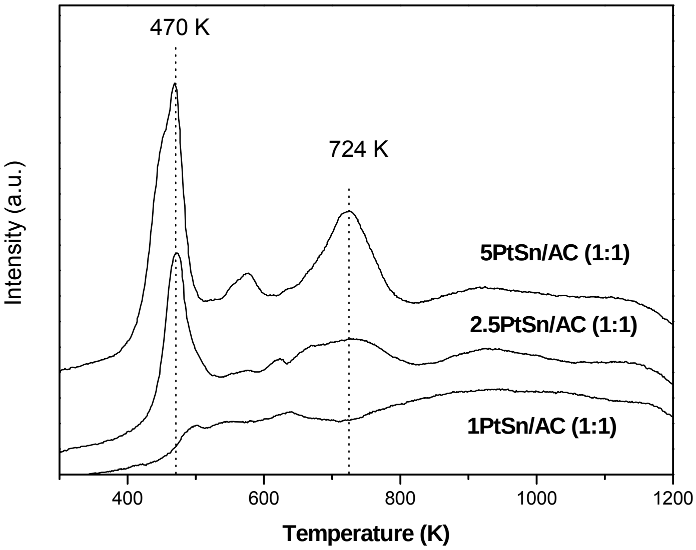

Figure 9.1 TPR profiles of different Pt-Sn/AC catalysts with a Pt:Sn (1:1) atomic ratio and a total Pt content of 1wt%, 2.5wt% and 5wt%.

different reduction peaks and, consequently, the determination of the different reduction processes taking place in the catalyst surface. The incorporation of a larger metal content (2.5wt%Pt or 5wt%Pt) allows to clearly discern well-defined reduction processes that must be attributed to the reduction of either Pt and/or Sn species. In this sense, both catalysts with a high metal content, 2.5Pt-Sn/AC (1:1) and 5Pt-Sn/AC (1:1), exhibit a first reduction peak centred at 470 K which is accompanied by a shoulder at lower temperatures (176 ºC), in the case of the sample with 5wt%Pt. These reduction processes at low temperature must be attributed to the reduction of oxidized platinum species to the metallic state [25]. In both cases there is an additional contribution at higher temperatures (451 ºC), this contribution being clearer for the sample with 5wt%, which must involve the reduction of SnO_x species in close contact with Pt to metallic Sn. The presence of metallic Sn after a reduction treatment at high temperature opens the possibility for Pt_xSn_y alloys formation. Bimetallic catalyst with 5wt%Pt exhibits an additional peak at 302 ºC, thus showing the presence of different SnO_x surface species when using high metal loadings. Based on these results, 200 ºC and 400 ºC have been selected as reduction temperatures for the subsequent characterization and reaction analysis. Whereas after reduction at low temperature only metallic Pt and oxidized Sn are expected, after a reduction treatment at high temperature both metallic Pt and Sn would be present, with the possibility of alloy formation.

9.3.1.3 XPS

XPS analysis of the Pt-Sn/TiO_2 catalyst has been previously reported [24]. Briefly, it shows the presence of metallic Pt after a reduction treatment either at low (200 ºC) or high (400 ºC) temperature [24]. Only the non-reduced catalysts exhibit partially oxidized Pt species (binding energy ~ 72.5 - 72.7 eV), most probably chlorinated platinum species. Concerning the Sn $3d_{5/2}$ level, XPS spectra show the presence of different oxidized species for the catalysts non-reduced and reduced at low temperature (binding energy ~ 486.2 eV - 487.0 eV). However, an increase in the reduction temperature 500 ºC gives rise to a new band at lower values (~ 484.8 eV - 485.2 eV), which is unambiguously attributed to metallic Sn. Therefore, the surface composition of the bimetallic catalysts reduced at 200 ºC and 500 ºC differs considerably. Whereas platinum is in the metallic state after both reduction treatments, tin is in oxidized state when catalysts are reduced at low temperature (200 ºC), and in both oxidized and metallic state after reduction at high temperature (500 ºC). The presence of metallic Sn after a high temperature reduction treatment opens the possibility for the existence of Pt-Sn alloy formation in these systems. In this sense, FTIR results of adsorbed CO show a red shift of the linearly adsorbed CO band (from 2082 cm^{-1} to 2072 cm^{-1}) after an increase in the reduction temperature to 500 ºC. Compared to the monometallic Pt/TiO_2 catalyst, incorporation of Sn produces a shift of this band to lower wavenumbers, which must be attributed to geometric and/or electronic effects. Concerning the effect of the reduction treatment, bimetallic samples reduced at 500 ºC experience, in addition to the aforementioned shift to lower frequencies of the linearly bonded CO band, a large decrease in the CO bands intensity. This loss in adsorption capacity can be attributed to the migration of partially reduced titania particles (SMSI effect) and metallic Sn to the platinum surface, in accordance with XPS data. Furthermore, the observed red shift can be explained by a close interaction between Pt and Sn, with a certain proportion of Pt-Sn alloy formation.

Concerning the Pt-Sn/AC catalysts, the XPS analysis has been carried out on sample 1%Pt-Sn/AC (1:1), after being subjected to different pre-treatments.

Table 9.1 reports the results obtained in terms of binding energies of platinum and tin species and surface composition.

Table 9.1 XPS characterization of catalyst 1%Pt-Sn/AC (1:1) after different thermal treatments.

	N_{Cal} N_{Red}	T_{Cal} = 200 ºC T_{Red} = 200 ºC	T_{Cal} = 400 ºC T_{Red} = 200 ºC	T_{Cal} = 400 ºC T_{Red} = 400 ºC
BE Pt $4f_{7/2}$ (eV)	71.9	71.5	71.5	71.8
BE Sn $3d_{5/2}$ (eV)	487.2	487.3	487.6	486.4
%Pt atomic	0.09	0.04	0.05	0.03
%Sn atomic	0.31	0.16	0.31	0.09
Pt/Sn atomic	0.29	0.25	0.16	0.33

Results in Table 9.1 show that platinum are already in a reduced state in the catalyst which has not been submitted to any pre-treatment. This fact has been previously observed in carbon supported Pt-Sn catalysts prepared from H_2PtCl_6 and $SnCl_2$, and it is assigned to two independent processes. On one hand, Pt^{IV} in the platinum precursor is reduced by carbon to both Pt^0 and Pt^{II} upon impregnation with an aqueous solution of H_2PtCl_6 [26]. On the other hand, also the oxidation of Sn^{II} species in the tin precursor to Sn^{IV} can be accomplished by the reduction of Pt^{IV} to Pt^0 [27]. In fact, the binding energy in the Pt $4f_{7/2}$ level for the monometallic Pt/AC catalyst (not shown in Table 9.1) is 72.1 eV, and it is shifted to lower values as the amount of tin increases while keeping 1wt%Pt, which demonstrates the reducing effect of Sn^{II} in the precursor. TPR experiments have shown that there is hydrogen consumption at around 197 ºC, which has been assigned to the reduction of oxidized Pt species, the amount of hydrogen consumed increasing with the metal content. The TPR peak at this region for catalyst 1%Pt-Sn/AC (1:1) shows a low amount of hydrogen consumed, what can be explained on the basis of the low total amount of platinum which, as shown by XPS measurements, is already in a reduced state.

XPS results on the chemical state of tin species in the catalyst after the different pre-treatments are very significant. Thus, tin is in an oxidized state (binding energy around 487.3 eV), likely forming chlorinated species, in the untreated sample and in samples reduced at 473 K. Unfortunately, XPS cannot discriminate between Sn^{II}

and Sn^{IV}. When the catalysts is reduced at 400 ºC the Sn $3d_{5/2}$ peak is shifted to lower binding energy values (486.4 eV), which indicates the presence of metallic tin. This opens the possibility to the formation of Pt_xSn_y alloy phases, as noted previously for the titania-supported catalysts.

Finally, the evolution of the surface atomic concentration of platinum and tin, as well as that of the Pt-Sn atomic ratio, indicates a surface modification with the thermal treatments. Thus, the surface platinum concentration tends to decrease when increasing the severity of the treatment. The trend is similar for tin species, although the calcination treatment at 400 ºC previous to the reduction treatment at 200 ºC produces a surface enrichment with tin species, which may cover to some extent the platinum surface. Finally, there is a large decrease in the surface concentration of tin after reduction at 400 ºC, which is related to the, at least, partial reduction of oxidized tin species to metallic tin.

9.3.2 Catalytic tests

The influence of the support on the catalysts activity and selectivity during the reduction of nitrates was studied. The effects of the calcination and reduction treatments at different temperatures and of the Pt-Sn atomic ratios were also evaluated.

9.3.2.1 Effect of pre-treatment conditions

9.3.2.1.1 Pt-Sn catalysts supported on TiO_2

The 2%Pt-Sn/TiO_2 (1:2) catalyst was chosen to evaluate the effect of the pre-treatment conditions in the nitrate reduction process. Table 9.2 summarizes the results obtained. The untreated sample (non-calcined and non-reduced) shows a very low nitrate conversion (8%). This sample, which has not been subjected to any calcination or reduction step, was tested because previous studies on activated carbon supported Pd-Cu and Pt-Cu catalysts have shown that under these initial conditions, bimetallic catalysts can exhibit an improved catalytic performance [28] (see chapter 4). The fact that the N_{cal} N_{Red} Pt-Sn/TiO_2 sample was almost inactive indicates that a reduction step is needed for these systems to achieve a minimum activity. The heat treated samples (calcined and reduced) present similar nitrate conversion (24% and 21%), independently of the selected temperatures. Gao et al. [1] observed that Pd-Cu catalysts supported on titanium dioxide and treated at high temperatures (600 ºC) exhibit lower activity than non-thermally treated catalysts, probably because of the aggregation of active metal species caused by the high temperature treatment. However, our results show that in the case of the Pt-Sn system, the activity is marginal for the non-treated catalyst. Catalysts with other Pt-Sn atomic ratios were tested (results not shown), and the results allowed to confirm that the untreated catalysts are practically inactive under the experimental conditions used.

Table 9.2 Catalytic performance of 2%Pt-Sn/TiO_2 (1:2) for nitrate reduction after 5 h of reaction and selectivities for 8% and 20% of nitrate conversion.

				$X_{NO_3^-}=8\%$			$X_{NO_3^-}=20\%$		
Catalyst (2%Pt-Sn/TiO$_2$ (1:2))	$X_{NO_3^-}$	$C_{NO_2^-f}$ (mg/L)	$C_{NH_4^+f}$ (mg/L)	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
N_{Cal} N_{Red}	0.08	0.4	1.2	0.07	0.52	0.41	-	-	-
T_{Cal} = 400 ºC T_{Red} = 200 ºC	0.24	5.6	1.6	0.31	0.23	0.46	0.38	0.14	0.48
T_{Cal} = 500 ºC T_{Red} = 500 ºC	0.21	3.8	3.4	0.25	0.57	0.18	0.28	0.54	0.18

Sá et al. [22] observed by FTIR analyses that nitrate adsorption on Pd/TiO_2 increased with the reduction temperature. It was suggested [10] that Lewis acid sites on TiO_2 (unsaturated surface Ti^{3+} sites), produced from the removal of surface oxygen during the reduction process, and whose abundance increases with the reduction temperature, are possible adsorption sites for nitrate and nitrite. Actually, the reduction of the coordination number of titanium leads to a positive charging of the surface (presence of oxygen vacancies), which makes those sites favourable for the adsorption of anionic species.

Concerning the heat treated samples, the main differences obtained are related with selectivity. Experimental results show a detrimental decrease in the selectivity to nitrogen after a reduction treatment at high temperatures, these differences remaining independently of the conversion level. The different selectivity obtained could result from a different disposition of the metal species on the surface of the support. By in situ IR spectroscopy of adsorbed CO, the presence of a Pt-Sn alloy in the catalyst after reduction at high temperature was observed, although a fraction of platinum remained in a non-alloyed state [24]. It can be assumed that the formation of alloys upon the reduction at high temperature is detrimental for the efficiency of the catalyst in the selective reduction of nitrate to nitrogen. Epron et al. [12] observed that the activity of Pt-Cu catalysts supported on alumina in the nitrate reduction process also decreased after a thermal treatment at high temperatures (400 ºC), and this was attributed to the weakening of the interactions between copper and platinum, a migration of copper towards the support being observed.

9.3.2.1.2 Pt-Sn catalysts supported on AC

The catalyst with a Pt-Sn atomic ratio of 1:1 was selected to study the influence of the different thermal treatments when using activated carbon as a support. Table 9.3 shows that the Pt-Sn bimetallic catalyst supported on activated carbon was hardly active for nitrate reduction after all the pre-treatments used. Selectivity to nitrogen is relatively high, with low formation of nitrite and ammonium. It has been previously observed for a different activated carbon-supported Pt-Cu bimetallic catalysts treated at different temperatures that the nitrate reduction efficiency decreases with the increase of calcination and reduction temperatures [28] (see chapter 4). However, this effect is not evident in the Pt-Sn system studied in this work, probably because the nitrate conversions are very low. The highest nitrate conversion is observed for the sample which has been submitted to a calcination treatment at 400 ºC and subsequently reduced at 200 ºC.

Table 9.3 Catalytic performance of 1%Pt-Sn/AC (1:1) for nitrate reduction after 5 h of reaction and selectivities for 10% of nitrate conversion.

				$X_{NO_3^-} = 10\%$		
Catalyst (1%Pt-Sn/AC (1:1))	$X_{NO_3^-}$	$C_{NO_2^- f}$ (mg/L)	$C_{NH_4^+ f}$ (mg/L)	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
N_{Cal} N_{Red}	0.10	0.2	0.3	0.00	0.08	0.92
T_{Cal} = 200 ºC T_{Red} = 200 ºC	0.12	0.2	1.8	0.03	0.50	0.47
T_{Cal} = 400 ºC T_{Red} = 200 ºC	0.17	0.2	1.0	0.02	0.07	0.91
T_{Cal} = 400 ºC T_{Red} = 400 ºC	0.11	0.3	1.5	0.02	0.35	0.63

From the aforementioned results it is clear that Pt-Sn systems exhibit an improved catalytic behaviour in terms of activity and selectivity after a calcination treatment at 400 ºC followed by a reduction treatment at 200 ºC, independently of the selected support (either TiO_2 or activated carbon). For this reason and in order to avoid the formation of alloys (according to XPS and FTIR studies) and to try to obtain high nitrate conversions and nitrogen selectivities, these experimental conditions were selected for the subsequent analysis of the effect of the Pt:Sn atomic ratio.

9.3.2.2 3.2.2Effect of Pt-Sn atomic ratio

9.3.2.2.1 Pt-Sn catalysts supported on TiO_2

The activities of Pt-Sn/TiO_2 catalysts for nitrate conversion are shown in Figure 9.2 a) in terms of nitrate concentration versus reaction time. Figure 9.2 b) and c) show the corresponding evolutions of nitrite and ammonium concentrations during the reaction. The selectivities to nitrite, ammonium and nitrogen are reported in Figure 9.3.

The atomic ratio of the metals has an important role in the activity and selectivity of the catalysts [1,3,16,17,29] (ref. 16 corresponds to chapter 3). Figure 9.2 shows that the order of activity for the Pt-Sn catalysts supported on titanium dioxide is the following: 3:1 > 2:1 ≈ 4:1 > 1:0 >> 1:2. The best catalyst found corresponds to a Pt-Sn atomic ratio of 3:1, which allows to obtain a nitrate conversion of 76% after 5 h of reaction. The catalyst with the highest tin content (1:2) provides the lower nitrate reduction, probably due to the covering of platinum by tin, as confirmed by XPS measurements [24]. These XPS analyses confirmed a large decrease in the Pt:Sn atomic ratio for the catalyst with an excess of Sn (1:2), independently of the reduction treatment applied. Gao et al. [1] found for Pd-Cu catalysts supported on TiO_2 that the optimum ratio is 2:1 for a total metal content of 3wt%. Nitrite concentration decreases with the increase of the Pt:Sn ratio in the bimetallic catalysts; this is likely related to the fact that when the noble metal is present in a larger proportion than tin, it can be expected that the amount of noble metal sites available on the catalyst surface must be larger, which leads to a faster reduction of nitrite formed by the reaction of nitrate with hydrogen, particularly considering that platinum is very active for this reaction [7] (see chapter 2).

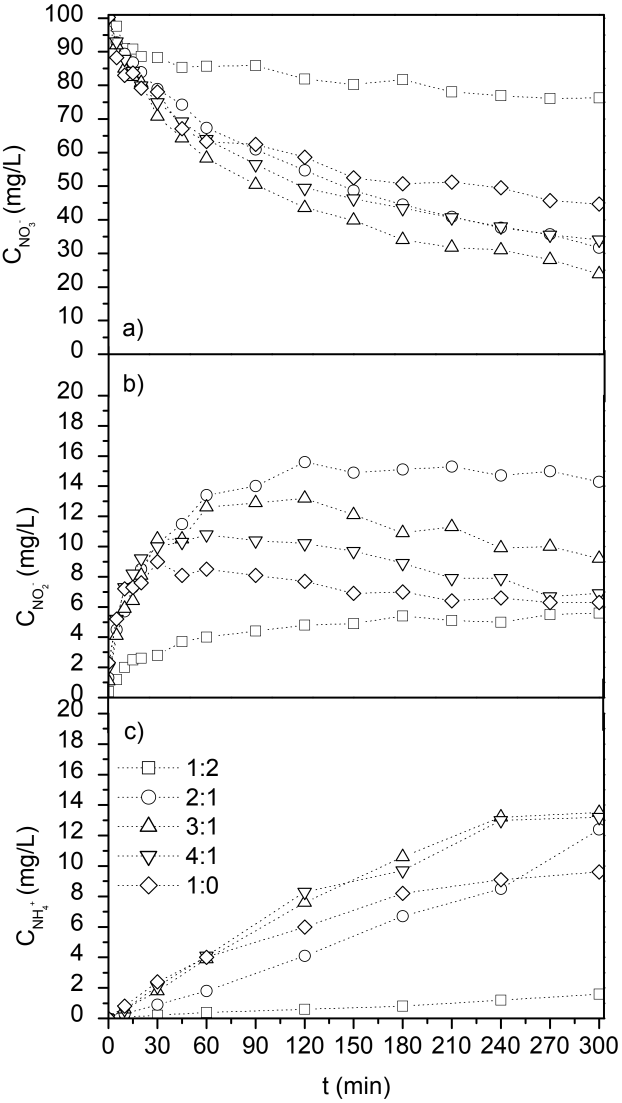

Figure 9.2 a) NO_3^-, b) NO_2^- and c) NH_4^+ concentrations as a function of time during nitrate reduction in the presence of Pt-Sn/TiO_2 catalysts.

It is well established that the monometallic catalysts are in general inactive for nitrate reduction, the presence of a second metal being mandatory to reduce nitrate to nitrite [3,4,6]. However, results in Figure 9.2 a) show that that the monometallic Pt/TiO_2 catalyst is active in this reaction. In fact, this catalyst presents a reasonably high nitrate conversion (55% after 5 h of reaction), with a relatively low nitrite formation compared with most of the bimetallic catalysts. Sá et al. [10] also observed a similar trend when Pd/TiO_2 was used in nitrate reduction. This performance can be related to the important role of partially reducible oxides as support of catalysts for this reaction. In the accepted reaction mechanism it is assumed that the promoting metal reduces nitrate by a redox reaction and the role of the noble metal is to reduce the promoting metal through activated hydrogen [6]. In the case of monometallic catalysts, the role of the promoting metal is replaced by partially reduced species on the support [10].

It can be observed in Figure 9.3 that the TiO_2 supported catalysts are not very selective to nitrogen. This can be related to their strong hydrogenation activity, causing over-reduction [10]. The catalyst with the highest tin content (1:2) presents the lowest ammonium selectivity, whereas all other catalysts, with a larger Pt:Sn ratio, present selectivities to ammonium higher than 60% after 5h of reaction. This can be explained by the distribution of the metals on the surface. In previous studies [16] (see chapter 3) it was shown that when the noble metal is present in higher amounts than the promoting metal, the ammonium selectivity increases with the relative amount of noble metal available on the surface. It is well established that nitrite reduction occurs mainly on the noble metal sites [3], and Yoshinaga et al. [17] suggested that isolated Pd atoms are active sites for ammonium formation. Therefore, it can be concluded that when the noble metal is present in higher amounts than the promoter metal, the number of noble metal surface sites available would be also higher and, as the noble metal is very active for hydrogenation reactions, the nitrite molecules would be deeply hydrogenated (producing ammonium).

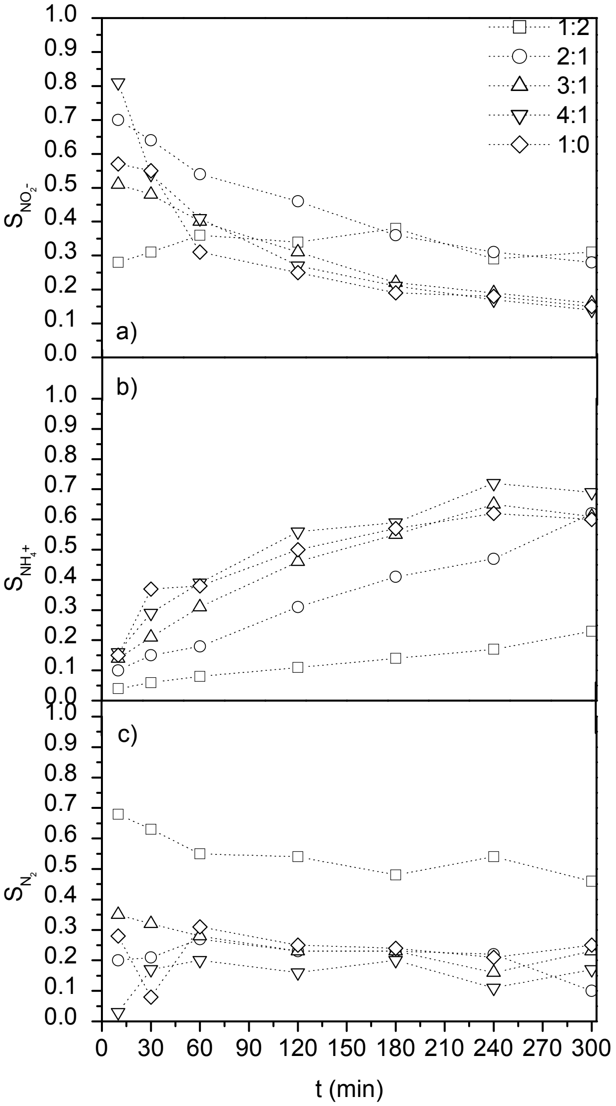

Figure 9.3 a) NO_2^-, b) NH_4^+ and c) N_2 selectivities as a function of time during nitrate reduction in the presence of Pt-Sn/TiO_2 catalysts.

9.3.2.2.2 Pt-Sn catalysts supported on AC

Table 9.4 shows that the Pt-Sn catalysts supported on activated carbon are not very active for nitrate reduction; however, they are very selective to nitrogen, with the exception of catalysts with large metal content (2.5wt%Pt and 5wt%Pt).

Nevertheless, due to the low activity, it can be concluded that Pt-Sn supported on activated carbon is not a very promising system for the reaction under study. As expected, the monometallic Pt catalyst supported on activated carbon is practically inactive for nitrate reduction. The presence of a second metal is mandatory to obtain significant nitrate conversion, as shown in previous studies [4,7] (ref. 7 corresponds to chapter 2).

Table 9.4 Catalytic performance of 1%Pt-Sn/AC T_{Cal} = 200 ºC T_{Red} = 200 ºC for nitrate reduction after 5 h of reaction and selectivities for 10% of nitrate conversion.

				$X_{NO_3^-} = 10\%$		
Catalyst	$X_{NO_3^-}$	$C_{NO_2^- f}$ (mg/L)	$C_{NH_4^+ f}$ (mg/L)	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1:0	0.03	0.1	0.2	-	-	-
4:1	0.12	0.1	1.1	0.02	0.35	0.63
2:1	0.15	0.0	1.6	0.00	0.18	0.82
4:3	0.12	0.1	1.3	0.01	0.39	0.60
1:1	0.17	0.2	1.0	0.02	0.07	0.91
1:1 (2.5wt%)	0.15	0.3	2.6	0.04	0.50	0.46
1:1 (5wt%)	0.21	1.1	3.0	0.14	0.42	0.44

9.3.2.3 Comparison of the supports

It has been found that the different preparation conditions lead to different catalytic activities and selectivities, independently of the support used; however, these effects are more pronounced when titanium dioxide is used. It can be concluded that the support also plays an important role in nitrate reduction. Generally, catalysts supported on activated carbon were less active and more selective to nitrogen than those supported on titanium dioxide. These different performances can be assigned to different compositions and arrangements of the catalyst surface due to the pre-treatment conditions, which can also depend on the support used and/or to the possible influence of the support in the reaction mechanism. Experiments using only the supports (activated carbon or titanium dioxide) were carried out and it was observed that these supports do not show any activity for nitrate reduction; the additional presence of one or two metals is necessary to observe nitrate reduction over titanium dioxide and activated carbon, respectively.

The Pt monometallic catalyst supported on titanium dioxide is active for nitrate reduction, but the same metal supported on activated carbon does not show activity. This performance could be related to the support. It is well established that the monometallic catalysts are generally inactive for nitrate reduction, a second metal being necessary to reduce nitrate to nitrite [3,4,6]. The role of the promoter metal is to reduce nitrate according to a redox reaction leading to nitrite intermediates or to nitrogen or ammonium and to an oxidised form of the promoter metal, which is regenerated to the reduced form by hydrogen adsorbed and dissociated on the noble metal [6]. When the monometallic catalyst is used, the mechanism involves partially reduced species of the support [10]. According to Sá and Anderson [22], the monometallic catalyst supported on TiO_2 is active because nitrate seems to be adsorbed at Lewis acid sites following exchange with OH^-, being reduced by the electron enriched titania species, possibly Ti_4O_7 formed by hydrogen spillover, and leading to the formation of nitrites. Based on our results and on the mechanism proposed by Sá and Anderson [22], when titanium dioxide is used as a support, a modified mechanism is proposed considering the presence of a noble metal (Figure 9.4), once it was observed that the support by itself does not show any activity for nitrate reduction and, thus, that the presence of metals is mandatory. Nitrate adsorption can occur not only on the surface of the support, but also on tin in the case of the bimetallic catalyst, as it has been observed that the bimetallic catalysts present higher activity than the monometallic one. When activated carbon is used as a support the reduction of nitrates only occurs in the presence of bimetallic catalysts (Figure 9.5), with nitrate adsorption taking place on tin sites on the bimetallic ensembles. Despite the possibility of activated carbon acting as a reducing agent, it is not able to promote the adsorption and reduction of nitrate to nitrite. The reduction of nitrate to nitrite could be achieved by an electron transfer from the bimetallic ensemble to the adsorbed nitrate, with the subsequent regeneration of the ensemble by the reductant or by the direct transfer of the reductant to the nitrate [3]. This mechanism is not fully established and more studies are necessary to understand the nitrate reduction reaction when activated carbon is used as a support. When bimetallic catalysts supported on titanium dioxide were used, nitrate reduction can follow both Figure 9.4 and Figure 9.5.

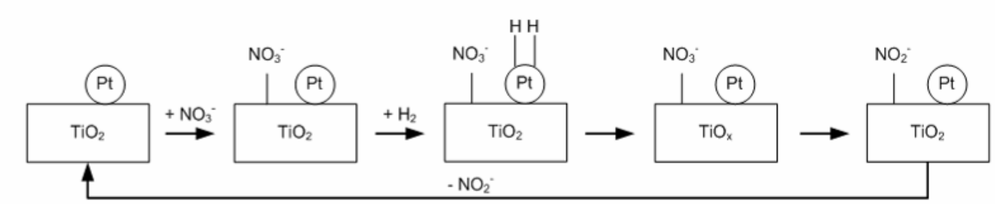

Figure 9.4 Nitrate reduction mechanism when titanium dioxide is used as a support.

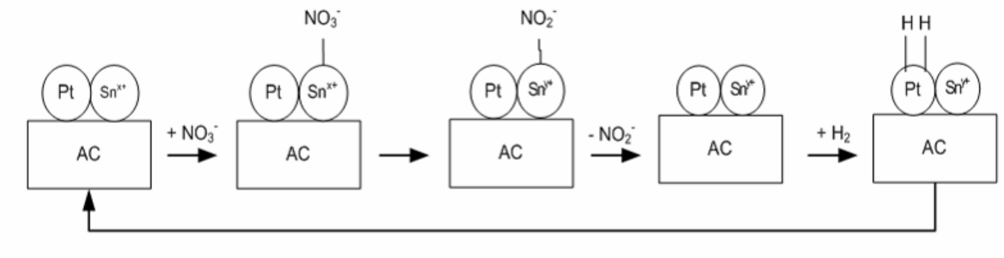

Figure 9.5 Nitrate reduction mechanism when activated carbon is used as a support.

9.4 Conclusions

The effect of the support, activated carbon or titanium dioxide, on the performance of Pt-Sn catalysts with different Pt:Sn atomic ratios was investigated. It was observed that the support can play an important role in nitrate reduction. Generally, the catalysts supported on activated carbon were less active and more selective to nitrogen than those supported on titanium dioxide. The Pt monometallic catalyst supported on TiO_2 is active for nitrate reduction but the catalyst supported on activated carbon does not show activity, which is explained by the involvement of the support in the reaction mechanism.

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Chapter 10

10 Conclusions and future work

The final chapter of this thesis presents a general overview of the main results, along with the most relevant conclusions. Finally, some ideas for future work are suggested.

10.1 Motivation

The increasing pollution of natural sources of drinking water encourages the development of new emerging technologies and processes for water remediation. The presence of nitrate in water is presently a common problem across Europe. Nitrate anion is potentially harmful because it can be transformed into nitrite in the human body, which can cause blue baby syndrome, and it is also a precursor of the carcinogenic nitrosamines. In addition, nitrates can originate eutrophization in rivers and lakes. The main sources of nitrate are the overuse of fertilisers in agriculture as well as the effluents from certain industries. Most of the nitrate salts are soluble in aqueous medium, so nitrate ions are easily spread over groundwater sources.

Nitrate can be removed from water by physicochemical, biological and catalytic methods. The main disadvantage of the physicochemical treatments (ion exchange, reverse osmosis and electrodialysis) is the fact that nitrate is not converted into harmless compounds but only concentrated; then it must be treated afterwards or disposed of. Biological denitrification is recognized as a useful method for the selective conversion of nitrate into harmless gaseous nitrogen. However, this process has several disadvantages, since it is difficult to handle and leads to the production of undesirable by-products. In addition, there are concerns about possible bacterial contamination, the presence of residual organics in the treated water and the possible increase in the chlorine demand of purified water.

The catalytic reduction of nitrate has been suggested in the literature as a promising method of nitrate removal, without the drawbacks of the conventional methods. This process consists in the reduction of nitrate to nitrogen over bimetallic catalysts in the presence of a reducing agent. Nitrite as intermediate and ammonium as by-product are considered the major limitations of this process. It has been shown that the activity and selectivity of catalytic nitrate reduction are strongly influenced by several factors such as: the reaction conditions, the catalysts preparation, the catalyst supported and also by the support.

Carbon materials have been used for a long time in heterogeneous catalysis, because they can act directly as catalysts or, more important, they can satisfy most of the desirable properties required for a suitable support: inertness; stability under reaction and regeneration conditions; adequate mechanical properties; possibility to adapt their physical forms for a given reactor; and high surface area and porosity. It is well documented that the role of the support is not merely that of a carrier; the interaction between the active phase and the support can also affect the catalytic activity.

10.2 Main conclusions

The main objective of this work was the study of the catalytic reduction of nitrate in water with hydrogen in a systematic way, focusing on the use of activated carbon as support. Several metal catalysts and their composition, preparation conditions and supports were evaluated and some mechanistic aspects were clarified. Activated carbons (chemically and thermally modified), carbon nanotubes and metal oxides were assessed as supports. Several metal catalysts were prepared, characterized and tested in this process.

The first goal of this thesis was the study of monometallic and bimetallic catalysts supported on activated carbon for nitrate and nitrite reduction in order to select the most promising catalytic systems for further developments. It was observed that the monometallic catalysts supported on activated carbon are inactive (Pt, Pd, Cu, Sn, Rh, Ni, Ir, Fe, Zn) or practically inactive (Ru) for nitrate reduction. Nitrite is reduced in the presence of monometallic catalysts, preferably Pd, although other noble metals such as Ir, Pt and Rh also present significant activities, but, with the exception of Rh, they are less selective to nitrogen. The Rh-Cu catalyst shows the highest efficiency for nitrate reduction, among the bimetallic catalysts tested; however, a large amount of ammonium is produced. The Pd-Cu catalyst presents higher conversions than the Pt-Cu catalyst, although both catalysts present similar selectivities into nitrogen. The systems Pd-Ir, Pd-Sn, Pd-Fe, Pd-Zn and Pt-Fe are inactive for the reduction of nitrate, under the conditions studied.

The activated carbon supported Pd-Cu catalyst is the most promising, among the catalyst tested, when both conversion and selectivity to nitrogen are considered. However, the pairs Rh-Cu, Pt-Cu and Ir-Cu supported on activated carbon were also studied in detail in order to establish their best formulation. The activity of the catalysts is quite different depending on the copper content. The maximum activity was obtained for an atomic ratio noble metal/copper close to 1. There is a trend of the selectivity to nitrogen, increasing with the atomic copper content up to 75%. This is valid for all the systems tested, with the exception of the pair Ir-Cu where the selectivity to ammonium is always high and practically independent of metals composition. It was concluded that the selectivity to nitrogen is highly dependent on the copper content. When the atomic copper content is close or higher than 50%, the noble metal and copper particles are probably not isolated but intercalated or superimposed favouring that the surface nitrogenated intermediates, resulting from the nitrate hydrogenation, can be combined producing nitrogen molecules instead of being deeply hydrogenated into ammonium. The pair Rh-Cu was the most active among the bimetallic catalysts tested; however, significant amounts of ammonium were obtained. The nitrate conversions for the pairs Ir-Cu and Pt-Cu are similar but the former presents higher selectivities to ammonium. The pair Pd-Cu was the second most active system studied and is the most selective in the conversion of nitrate to nitrogen.

The results obtained showed that in addition to the type of supported metals, the reduction of nitrate is quite dependent on the preparation conditions (calcination and reduction temperatures). For the activated carbon supported Pd-Cu and Pt-Cu bimetallic catalysts tested, the activity decreases with the increase of calcination and reduction temperatures, whereas the effect on the selectivity is not uniform. The calcination and reduction at high temperatures are inadequate due to the formation of larger metal particles and/or alloys. In addition, the contact with hydrogen in water has an important effect on the catalytic activity. This contact allows the *in situ* reduction of the noble metal and, for that reason, the catalysts not heat treated were active; nevertheless, this occurs due to the important role of the activated carbon, which increases the reducibility of the noble metal supported. The calcination at 200 ºC and reduction at 100 ºC seem to be the optimal temperatures to prepare the catalysts, when both activity and nitrogen selectivity are considered. Once again, for all the preparation conditions tested, the Pd-Cu pair is more selective for the conversion of nitrate to nitrogen.

In order to clarify the reaction mechanism, several mixtures of monometallic/monometallic activated carbon supported catalysts, bimetallic/monometallic supported catalysts and metallic ions in solution/monometallic supported catalysts were studied in a systematic way. For this study, Pd-Cu, Pt-Cu and Rh-Cu as well as the corresponding monometallic catalysts were tested, using the best preparation conditions previously obtained. It was established that the monometallic catalysts are generally inactive for nitrate reduction, a second metal being necessary to reduce nitrate to nitrite. The role of the promoter metal is to reduce nitrate according to a redox reaction, leading to nitrite intermediates or to nitrogen or ammonium and to an oxidized form of the promoter metal, which is reduced by hydrogen adsorbed on the noble metal. In this work, it was observed that physical mixtures of Pd and Cu or Pt and Cu monometallic catalysts perform similarly or even better than the corresponding bimetallic catalysts. This fact indicates that the initial presence of bimetallic sites on the catalysts is not mandatory; it is sufficient that both metals are present in the reaction system. Nevertheless, the noble metal must be supported but copper does not need to be supported initially, actually, the experiment with Pd monometallic catalysts and copper in liquid phase presents similar nitrate conversion as that obtained with the Pd-Cu bimetallic catalyst and with the mixture of Pd and Cu monometallic catalysts. Based on the results obtained in this work, a mechanism was proposed considering that the nitrate reduction can occur in the presence of a bimetallic catalyst or a physical mixture of monometallic catalysts, considering that bimetallic catalysts are formed *in situ* due to the adsorption of the leached copper on the carbon surface. Copper does not need to be in the metal form to be active. The only constraint is that the noble metal must be already supported, and most probably metal noble particles are required for this reaction.

Activated carbon demonstrated to be a good support for this reaction, where its role is to promote a high dispersion of metals. This support (activated carbon) by itself does not present any activity for nitrate reduction.

The highest selectivity to nitrogen in this study (76%) was obtained with the 1%Pd-1%Cu bimetallic catalyst supported on activated carbon. The mixtures with the Pd-Cu bimetallic catalysts present the highest nitrate conversions and selectivities to nitrogen. When the Pd monometallic catalyst is added to the Pt-Cu bimetallic catalyst a strong synergic effect was observed, being this mixture the most selective to nitrogen among those involving the Pt-Cu pair. The mixtures with Pd catalysts are the most selective to nitrogen, being the mixtures with Rh catalysts the most selective to ammonium.

One of the main purposes of this work was the development of catalysts for the nitrate reduction, focusing on the use of carbon materials as support. Starting from the best preparations conditions, Pd-Cu and Pt-Cu bimetallic catalysts, with similar atomic copper content, supported on different carbon materials (activated carbons with different surface chemistries, multiwalled carbon nanotubes and carbon xerogels) were prepared, characterized and tested in the process. Activated carbons with different surface chemistries were selected to study the influence of the surface characteristics of the carbon materials on the properties of the metal phases and, consequently, on the performance of the prepared catalysts for the nitrate reduction. In addition, carbon nanotubes and carbon xerogels were chosen due to their large mesoporosity, in contrast with the essentially microporous activated carbons, which may be important in order to avoid internal mass transfer limitations. The surface chemistry of the support plays an important role in the catalyst activity and selectivity, being its influence more pronounced when Pt-Cu catalysts are used. Generally, catalysts supported on basic carbon materials are more active and selective. Comparing the different supports under the conditions tested, basic samples and carbon nanotubes were the best, whereas carbon xerogels were the worst supports for this reaction. The high catalytic performance observed for the catalysts supported on carbon nanotubes, in special its high selectivity to nitrogen, must be related not only to the surface chemistry of this support, which does not present a high amount of functional groups, but also to its high mesoporous surface area and absence of microporosity, which minimizes the internal mass transfer limitations, and consequently the over-reduction of nitrite to ammonium. The catalysts supported on carbon xerogel were not very promising for this reaction, at least under the preparation conditions used. This may be related to the surface characteristics of the carbon xerogels, which originated large metal particle sizes.

The use of carbon nanotubes as catalyst supports for the reduction of nitrate in water were assessed, using 1%Pd-1%Cu and 1%Pt-0.3%Cu (%wt), which were the optimum formulations when the mentioned pairs supported on activated carbon were used. The influence of the surface chemistry of the CNT and of the preparation method (calcination and reduction temperatures) in the characteristics of the catalysts, including their catalytic performances was evaluated. The results obtained when carbon nanotubes are used as support were similar to those obtained with activated carbon. It was observed that the performance for the reduction of nitrate is quite different depending on the noble metal, the preparation conditions and the support used. The calcination and reduction temperatures significantly affect the activity of the catalysts prepared. Generally, when original carbon nanotubes are used as support, the activity decreases with the increase of calcination and reduction temperatures; the opposite is observed for carbon nanotubes previously oxidised with HNO_3 or heat treated at 400 ºC under nitrogen flow. The use of catalysts supported on functionalized carbon nanotubes has a negative effect in nitrate reduction, unless when they are calcined and reduced at 200 ºC (for the pair Pd-Cu) or at 400 ºC (for the pair Pt-Cu). For comparative purposes, experiments with 1%Pd-1%Cu and 1%Pt-0.3%Cu catalysts, prepared at T_{Cal} = 200 ºC and T_{Red} = 100 ºC, supported on activated carbon, were also carried out. It was observed that these catalysts were more active or slightly lower, respectively, than the corresponding catalysts supported on the original nanotubes. The nitrite accumulated after 5 h of reaction is higher in the catalysts supported on the activated carbon, suggesting that mass transfer limitations may play a role in the process. The results obtained demonstrate that Pd-Cu catalysts, although less active, are much more selective to nitrogen than the corresponding Pt-Cu catalysts, independently of the support used, being 82% and 37% the highest values obtained for each pair, respectively. Generally, carbon nanotubes demonstrate to be a good support for the metal phases that catalyze the reaction.

In order to select other promising supports, the catalytic activity of Pd monometallic and Pd-Cu bimetallic catalysts supported on different materials was assessed under the same experimental conditions. It was observed that the support plays an important role in the catalytic performance and, in some cases, is involved in the reaction mechanism. Nevertheless, the supports by itself are not active; the presence of one or two metals is mandatory to reduce nitrate. It is well established that the monometallic catalysts are generally inactive for nitrate reduction, a second metal being necessary to reduce nitrate to nitrite. The role of the promoter metal is to reduce nitrate according to a redox reaction leading to nitrite intermediates and to an oxidised form of the promoter metal, which is regenerated to a reduced form by hydrogen adsorbed and dissociated on the noble metal. When the monometallic catalyst is active, the mechanism involves partially reduced species of the support, as was the case of cerium and titanium oxides. The results obtained show that the bimetallic catalyst supported on titanium dioxide provides high activity for nitrate reduction and that the use of a composite with carbon nanotubes increases significantly the selectivity of the process to nitrogen. The catalysts supported on ceria are very selective to nitrogen and present the particularity of the monometallic to be more active than the bimetallic. Manganese oxides are not suitable supports for this reaction. Activated carbon demonstrated to be a satisfactory support, with intermediate activity and nitrogen selectivity.

Several Pt-Sn catalysts with different preparation conditions and different atomic ratios were tested under the same experimental conditions with the main goal to analyze the influence of the support in this reaction. Once again, it was observed that the support can play an important role in nitrate reduction and that different preparation conditions lead to different catalytic activities and selectivities. Generally, the catalysts supported on activated carbon were less active and more selective to nitrogen than those supported on titanium dioxide. The Pt monometallic catalyst supported on TiO_2 is active for nitrate reduction, but the catalyst supported on activated carbon does not show any activity, which is explained by the involvement of the support in the reaction mechanism.

In summary, the catalytic reduction of nitrate in water demonstrated to be an effective method to remove nitrate, which is very influenced by the metal phases, preparation method and support. High nitrate conversion can be obtained for an atomic ratio noble metal/copper close to 1 and using a calcination temperature of 200 ºC and reduction at 100 ºC, preferably using Pd-Cu catalysts supported on basic carbon materials or carbon nanotubes. In addition to high nitrate conversions for the pair Pd-Cu, nitrogen selectivities of 76% and 82% were respectively obtained when activated carbon or carbon nanotubes were used as support. Additionally, the composite containing carbon nanotubes and titanium dioxide demonstrates to be a promising support for this process, since high nitrate conversions and interesting nitrogen selectivities were obtained with the pair Pd-Cu. Nevertheless, ammonium concentrations obtained after 5 h were always higher than the allowable values in drinking water.

10.3 Suggestions for future work

Catalytic reduction of nitrate in water has been denoted as a promising method but its nitrogen selectivity remains challenging and more fundamental work should be carried out for further insights.

It was observed that some carbon materials were adequate supports for this reaction and that the surface chemistry and also the textural properties have an important role in the catalysts performance. In order to improve the activity and the selectivity of the process, new supports should be tailored to obtain basic samples with high mesoporous surface area and absence of microporosity, which minimize the internal mass transfer limitations.

The good results achieved with ceria materials and the composite with carbon nanotubes and titanium dioxide should be explored, taking into account the involvement of the support in the reaction mechanism. The catalysts formulation and also the preparation conditions (calcination and reduction temperatures) for each support should be optimised. Also the composition of the composite should be optimised.

A kinetic study using the most promising systems should be carried out, since only a few studies are available in the literature.

Preliminary studies of nitrate reduction by hydrogen over a Pd-Cu catalyst supported on carbon nanotubes (see Appendix C) were carried out to evaluate the influence of the most common inorganic ions (Cl^-, SO_4^{2-}, PO_4^{3-}) and natural organic matter (NOM) present in groundwater. Some differences were observed in the catalyst performances, depending on the groundwater composition. Since the mentioned inorganic ions and NOM are often present in natural waters, further research is necessary in order to minimize their negative effects on the catalysts performance.

Regarding the practical application of this process, continuous experiment in column should be carried out. For that purpose two different conditions should be explored. Taking into account the good results obtained with carbon nanotubes, nanostructured reactors, where carbon nanotubes can be grown directly on the walls, should be considered in order to minimize mass transfer limitations. On the other hand, considering the results obtained with the physical mixtures, experiments using two columns in series with different configurations would be of great interest.

The main focus of this work was the drinking water treatment; nevertheless, this process could be also promising for waste water treatment. It was observed that high nitrate conversion can be achieved and in this case the selectivity of the process is not as restrictive as in the case of drinking water.

Appendices

Appendix A. Operation conditions

Appendix A.1 Schematic representation of the experimental set-up

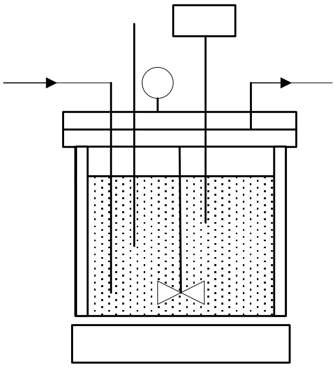

Figure A.1 Representation of the experimental set-up used for the nitrate reduction experiments.

Standard operation conditions:

- $C_{NO_3^-\,i}$ = 100 mg/L,
- pH = 5.5,
- Catalyst amount = 0.5 g/L,
- Q_{H2} = 100 Ncm^3/min,
- Q_{CO2} = 100 Ncm^3/min,
- Stirring rate = 700 rpm,
- T = 25 ºC
- P = 1bar.

Appendix B. Preliminary studies

Appendix B.1 Reaction conditions

Preliminary studies were carried out in order to select the most appropriate reaction conditions. Several parameters, namely catalyst amount, stirring rate, catalyst particle size, reaction temperature and hydrogen flow rate, were checked. The 1%Pd-0.3%Cu_ACo, 2%Pd-1%Cu_ACo or 1%Pt-0.3%Cu_ACo (T_{Cal}=400ºC T_{Red}=400ºC) catalysts were selected for these studies. The following standard conditions were used in the experiments, being only changed one parameter at each time: $C_{NO3^- i}$ = 100 mg/L, pH = 5.5, Catalyst amount = 0.5 g/L, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, Stirring rate = 700 rpm, T = 25 ºC, P = 1bar.

Appendix B.1.1 Catalyst amount

Experiments varying the 1%Pt-0.3%Cu_ACo catalyst amount (200, 300 and 400 mg) were carried out. It was observed that the nitrate conversion increases with the catalyst amount, but the experiment with 400 mg of catalyst presents only a small increase (X_{N03^-}=56%) relatively to the experiment with 300 mg (X_{N03^-}=52%). Therefore, 400 mg of catalysts, which corresponds to 0.5 g/L, was selected for standard experiments.

Appendix B.1.2 Stirring rate

Several experiments altering the stirring rate were carried out, using a catalyst (1%Pt-0.3%Cu_ACo) amount of 400 mg. It was observed that for a stirring rate lower than 600 rpm the distribution of the catalysts in the reactor was not uniform and that the experiments with 700 rpm and 800 rpm present similar results. It was concluded that above 700 rpm there are no external mass transfer limitations, being this stirring rate value used in all experiments.

Appendix B.1.3 Particle size

Experiments changing the particle sizes were also carried out and it was observed that the nitrate conversion increases with the decreasing of the particle size, which indicates the presence of internal mass transfer limitations. However, the selectivities obtained were not too different. As an example, Table B.1 presents the results obtained for the catalyst 2%Pd-1%Cu_ACo with two different size ranges.

Table B.1 NO_3^- conversion and selectivities to NO_2^-, NH_4^+ and N_2 after 300 min of reaction in the presence of 2%Pd-1%Cu_ACo catalysts with different particle sizes.

2%Pd-1%Cu_ACo	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
0.1 < d < 0.3mm	0.67	0.01	0.44	0.55
d < 0.1 mm	0.83	0.00	0.51	0.48

The range between 0.1 and 0.3 mm was selected, considering the preparation conditions of the catalysts. Moreover, it should be noticed that all the catalysts tested in this work have the same particle size, so the effect of internal mass transfer limitations is the same in all of them.

Appendix B.1.4 Reaction temperature

The influence of reaction temperature was evaluated in the range 15 – 35ºC in the presence of the 1%Pd-0.3%Cu_ACo catalyst.

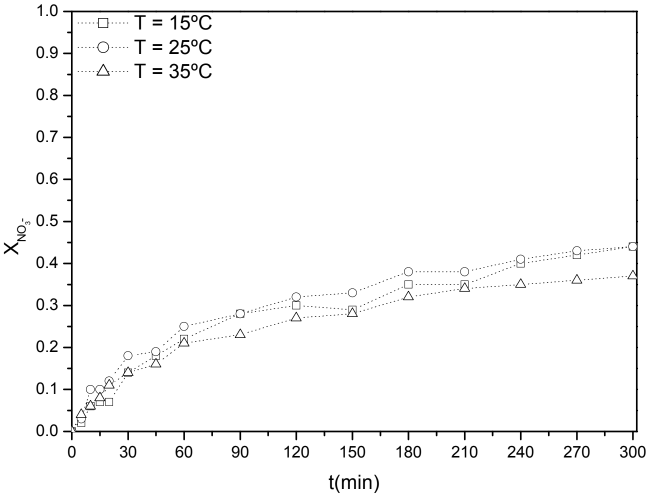

Figure B.2 Influence of reaction temperature in the performance of the 1%Pd-0.3%Cu_ACo catalyst.

As can be seen in Figure B.2, the nitrate conversion is similar in the experiments at 15 ºC and 25 ºC, being slightly lower in the experiment at higher temperature, which could be related with the hydrogen solubility. The experiment at 15 ºC presents the highest nitrogen selectivity. The temperature of 25 ºC was selected for further studies in order to work near the room temperature.

Appendix B.1.4 Hydrogen flow rate

Hydrogen was used as reducing agent, being its influence evaluated in two different conditions. First, the influence of flow rate was evaluated. Figure B.3 shows that nitrate conversions are similar in the range 50 - 150 Ncm^3/min, but decrease significantly for lower flow rates. The nitrogen selectivities were practically the same for the three experiments at higher flow rates. Taking into account these results and in order to facilitate a high dispersion of catalyst particles in the reactor a flow rate of 100 Ncm^3/min was selected.

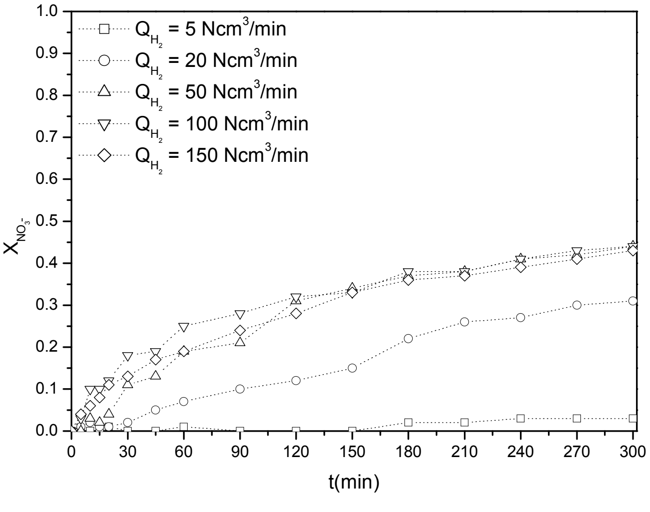

Figure B.3 Influence of hydrogen flow rate in the performance of the 1%Pd-0.3%Cu_ACo catalyst.

In addition, the influence of flowing hydrogen in the solution during 15 min before starting the reaction, i.e. before adding the nitrate solution, was also assessed.

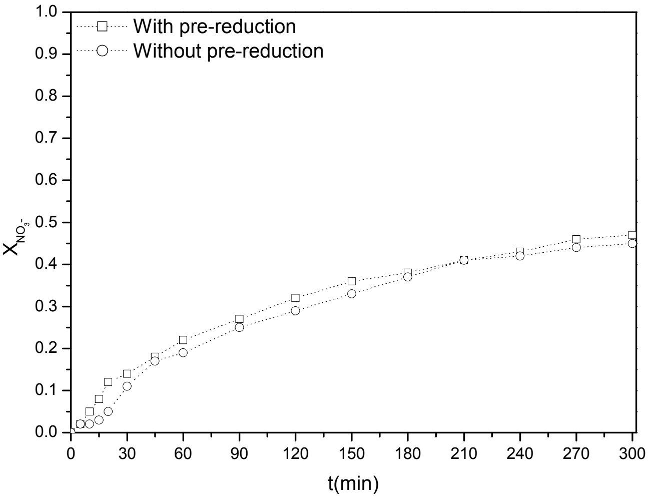

Figure B.4 Influence of hydrogen flowing before reaction in the performance of the 1%Pd-0.3%Cu_ACo catalyst.

Figure B.4 shows that nitrate reduction is slightly lower in the experiment without the 15 min period of hydrogen flowing (i.e. without pre-reduction) before adding the nitrate solution. It was also observed that for short reaction times the catalyst practically do not show any activity. This fact indicates that this period is needed to saturate the solution with hydrogen.

Appendix B.2 Catalysts preparation method

Preliminary studies were carried out in order to select the most appropriate method to prepare the catalysts. Several catalysts were prepared using different methodologies: by co-impregnation and by sequential impregnation changing the order of the metals, with or without intermediate calcinations.

Appendix B.2.1 Catalysts impregnation

All the catalysts were prepared by the incipient wetness impregnation method, using aqueous solutions of the corresponding metal salts. All the metal salts were dissolved in distilled water with the exception of $PdCl_2$, which was dissolved in a HCl solution.

The catalysts impregnation was carried out in a conical flask connected to a vacuum pump. Normally, 1 g of the support was introduced into a 100 cm^3 conical flask and placed in an ultrasonic batch under vacuum during 30 min to remove air from the activated carbon pores. After that period, 2.2 cm^3 (which is the volume previously determined to completely wet the support) of the aqueous solution of the metal precursor was added dropwise, using a peristaltic pump, with a concentration calculated in order to obtain the desirable metals amounts in the catalyst. The maturation and drying phases continued during more 90 min with the system stirred under vacuum in the ultrasonic bath. After that, the samples were dried at 100 ºC for 24 h and stored in a desiccator. Finally the catalysts were calcined under nitrogen and reduced under hydrogen flow.

When co-impregnation was performed, the two metals were added to the support at the same time using the procedure described above.

In sequential impregnation the support was impregnated with one metal and dried at 100 ºC for 24 h before adding the other metal using the same procedure. When an intermediate calcination was performed, catalysts were calcined under nitrogen flow for 1 h between impregnations.

Catalysts were calcined under nitrogen flow at selected temperatures for 1 h and reduced under hydrogen flow at selected temperatures for 3 h, with a flow rate of 50 Ncm^3/min. A nitrogen flow was used during heating and cooling, using a ramp of 10 ºC/min and 30 ºC/min, respectively.

Appendix B.2.2 Influence of preparation methodologies

Preliminary studies were carried out varying the preparation methodology; several catalysts were prepared by co-impregnation and by sequential impregnation changing the order of the metals, with or without intermediate calcinations. It was observed that there are some differences in the nitrate conversion between co-impregnation and sequential impregnation and that the worst results were obtained when the catalysts were prepared by sequential impregnation with intermediate calcination. However, these effects depend on the calcination and reduction temperature used. If high temperatures are used in the preparation of the catalysts, these effects are more pronounced. If low temperatures are used there are no significant differences between the different methods. Generally, for the pair Pd-Cu, the co-impregnation method and the sequential impregnation when Cu is impregnated first present similar nitrogen selectivities, which are higher than those obtained when Pd is impregnated first. For the pair Pt-Cu there are no significant differences in the nitrogen selectivity among the different procedures. So, in order to make easier the preparation of the catalysts, the co-impregnation method was selected.

Figures B.2.1. B.2.2 and B.2.3 show the results obtained for the catalysts 1%Pd-0.3%Cu_ACo calcined and reduced at 400 ºC, 2%Pd-1%Cu_ACo only calcined at 200 ºC and 1%Pt-0.3%Cu_ACo calcined at 200 ºC and reduced at 100 ºC, as examples.

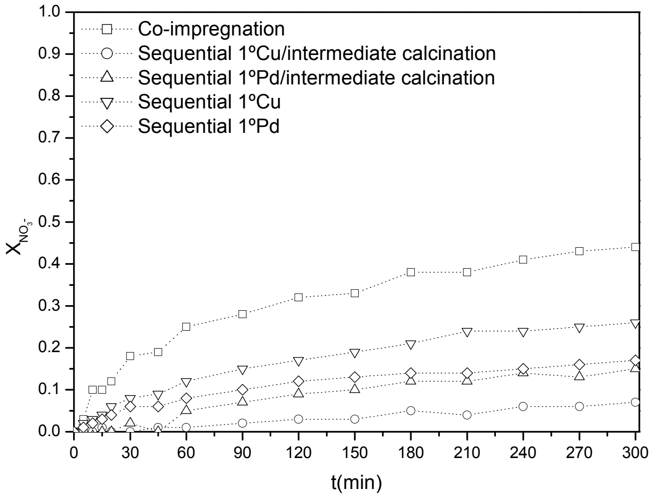

Figure B.2.1 Influence of impregnation method in the performance of 1%Pd-0.3%Cu_ACo catalyst (T_{Cal} =400 ºC T_{Red}=400 ºC).

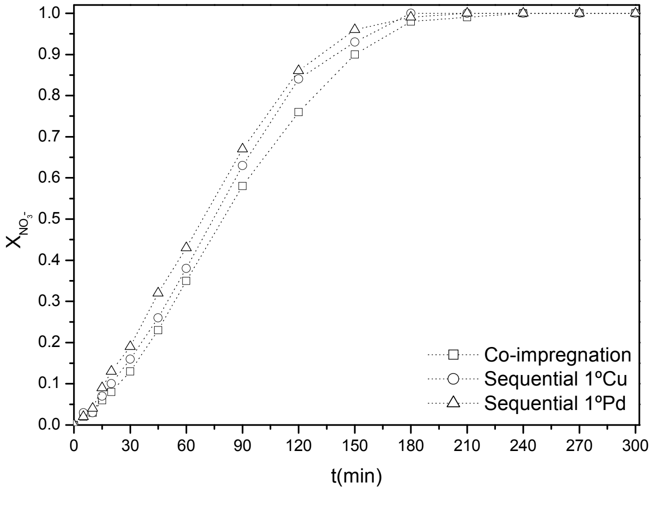

Figure B.2.2 Influence of impregnation method in the performance of 2%Pd-1%Cu_ACo catalyst (T_{Cal} =200 ºC N_{Red}).

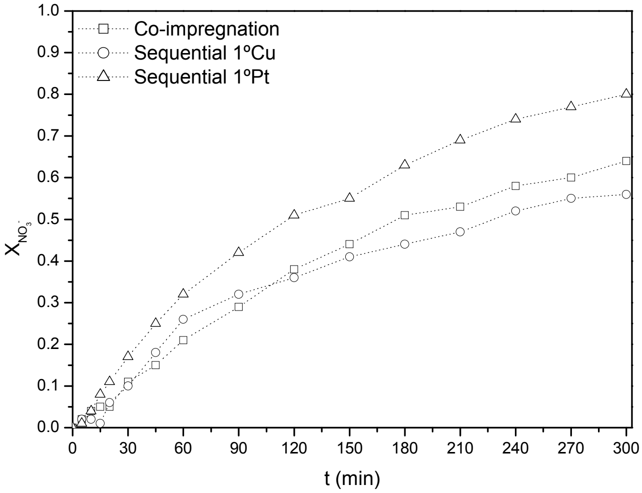

Figure B.2.3 Influence of impregnation method in the performance of 1%Pt-0.3%Cu_ACo catalyst (T_{Cal} =200 ºC T_{Red}=100 ºC).

Appendix C. Influence of inorganic and organic matter in nitrate reduction in water by hydrogen

It has been reported that nitrate reduction is influenced by the presence of other ions in water, probably due to a competitive adsorption on the metallic active sites [1-3]; on the other hand, it was suggested that the presence of oxygen has a positive influence in the selectivity of the process [4]. The objective of this study is to evaluate the influence of the most common inorganic ions (Cl^-, SO_4^{2-}, PO_4^{3-}) and natural organic matter (NOM) present in groundwater in nitrate reduction by hydrogen over a Pd-Cu catalyst supported on carbon nanotubes. A simulated groundwater (SG) and a groundwater obtained from a well (RG) in Gaia, Portugal, were also used to evaluate the catalyst performance.

In order to investigate the influence of the anions Cl^- (20 mg Cl^-/L from NaCl), SO_4^{2-} (30 mg SO_4^{2-}/L from Na_2SO_4) and PO_4^{3-} (1.3 mg PO_4^{3-}/L from HNa_2O_4P) and natural organic matter (5 mg C/L from humic acid), these species were dissolved in water, separately or mixed. The concentrations indicated represent the typical highest values measured in groundwater in Portugal. The concentration of nitrate was adjusted to 100 mg/L. The composition of the sample RG is listed in Table C.1. In addition, a simulated groundwater (SRG) was also prepared dissolving the same concentrations of anions and TOC present in the real groundwater (RG).

Table C.1 Composition of groundwater RG.

Component	Concentration (mg/L)
NO_3^-	139.8
NO_2^-	0.06
NH_4^+	0.9
Cl^-	70.2
SO_4^{2-}	59.7
PO_4^{3-}	<0.21
TOC*	1.2
Conductivity	608 μS/cm

* Total organic carbon

The catalytic tests were performed under the conditions normally used in previous studies: Catalyst = 0.5 g/L, pH = 5.5, Q_{H2} = 100 Ncm^3/min, Q_{CO2} = 100 Ncm^3/min, T = 25 ºC.

The 1%Pd-1%Cu/CNT catalyst, heat treated under nitrogen flow at 200 ºC for 1 h and reduced at 100 ºC under hydrogen flow for 3 h, was selected for this study, because it presents one of the best performances according to a previous work [5] (see chapter 7).

Nitrate conversions are shown in Figure C.1 a). Figure C.1 b) and c) show the corresponding evolution of nitrite and ammonium concentrations during the reaction. Nitrate conversions and selectivities obtained for all the samples studied are summarized inTable C.2.

As can be seen in Figure C.1, there are some differences in the catalyst performances depending on the groundwater composition, which must be related to its different characteristics. With exception of the sample that contains SO_4^{2-} all the other components in water have a negative influence in the nitrate reduction and nitrogen selectivity. Under the conditions used in this work, it was observed that the presence of SO_4^{2-} slightly increases nitrate conversion, which is in agreement with the results previously reported by Pintar et al. [1]. The nitrate conversion after 5 h decreases from 64% to 54% when Cl^- or organic matter are present and to 47% in the case of PO_4^{3-}. Wang et al. [6] reported that the presence of Cl^- decreases the nitrate conversion and the selectivity of the process, while the presence of SO_4^{2-} had no effect on the catalytic performance of Pd-Cu supported on activated carbon. The decrease observed in the nitrate conversion when humic acid is present are in agreement with the results reported by Chaplin et al [3]. However, they observed a smaller amount of nitrite than in the experiment without humic acid, contrary to the results obtained in this study. As can be seen in Figure C.1, the highest nitrite and ammonium concentrations were obtained in this experiment (considering the tests where the influence of ions was studied separately).

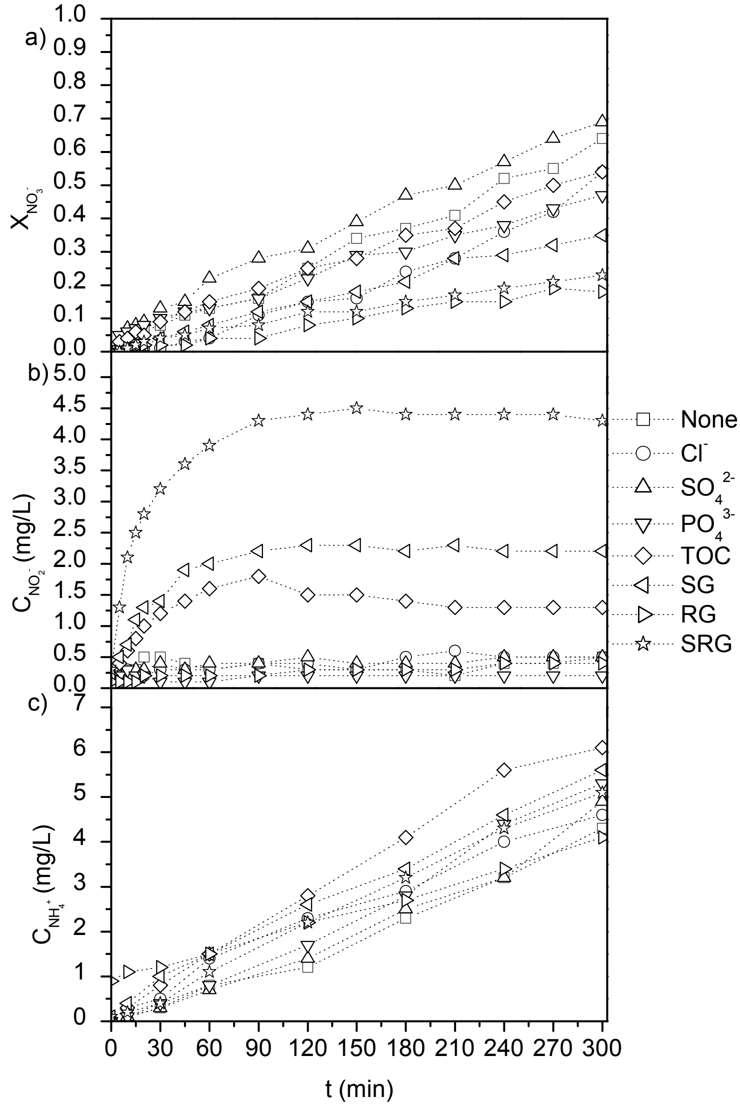

Figure C.1 NO_3^- conversions (a) and NO_2^- (b) and NH_4^+ (c) concentrations as a function of time during nitrate reduction.

Table C.2 Nitrate conversions ($X_{NO_3^-}$) and nitrite, ammonium and nitrogen selectivities ($S_{NO_2^-}$, $S_{NH_4^+}$, S_{N_2})after 5 h of reaction and selectivities for 50% nitrate conversion.

	t = 300 min				$X_{NO_3^-} = 50\%$		
Condition	$X_{NO_3^-}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
None	0.64	0.01	0.23	0.76	0.01	0.21	0.78
Cl^- = 20mg/L	0.54	0.01	0.29	0.70	0.01	0.31	0.68
SO_4^{2-} = 30mg/L	0.69	0.01	0.24	0.75	0.01	0.19	0.80
PO_4^{3-} = 1.3mg/L	0.47	0.01	0.38	0.61	-	-	-
TOC = 5mg/L	0.54	0.03	0.39	0.58	0.04	0.41	0.55
SG	0.35	0.08	0.55	0.37	-	-	-
RG	0.18	0.03	0.42	0.55	-	-	-
SRG	0.23	0.19	0.54	0.27	-	-	-

The catalyst performance is more affected when all the components are present. Nitrate conversion is higher in the experiment using deionised water than in the experiments with simulated and real groundwater. Table C.2 shows that the nitrogen selectivity also decreases from 76% to 37%, 55% and 27% for SG, RG and SRG, respectively. Although RG and SRG samples have the same amount of contaminants, the performance of the catalyst is different during nitrate reduction. These results must be related to the fact that RG (a real groundwater) has several additional ions, which were not quantified, that probably have influence in the process.

The decrease in the rate of nitrate reduction where other ions are present can be ascribed to the competitive adsorption of the different ions for the active metallic sites [1-3] or to a partial deactivation of the catalyst due to some of the ions present in water [7]. Actually, Wang et al. [6] reported that the presence of organic species causes the deactivation of Pd-Cu catalysts supported on activated carbon.

The process is adequate to remove nitrate/nitrite from water but is not adequate to remove the other species considered in the study, once it was observed that their concentrations remain practically unchanged after 5 h of reaction. Since they are often present in natural waters, further research is necessary in order to minimize their negative effects.

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