# Development of carbon materials as metal catalyst supports and metal-free catalysts for catalytic reduction of ions and advanced oxidation processes

## Desarrollo de materiales de carbono como soporte de catalizadores metálicos o catalizadores libres de metal para la reducción catalítica de iones o procesos de oxidación avanzada

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## Abstract

The versatility of carbon materials as metal supports as well as metal-free catalysts for environmental applications is presented, highlighting some of the work carried out at the Laboratory of Catalysis and Materials (LCM), which focuses on carbon materials and catalysis as its main research areas. Carbon materials with appropriate surface and textural properties to act as supports for the active phases or as catalysts on their own have been successfully developed for catalytic processes such as the catalytic reduction of ions and advanced oxidation processes.

## Resumen

El presente trabajo pretende destacar la versatilidad de los materiales de carbono tanto como soporte de catalizadores metálicos como catalizadores libres de metal para aplicaciones ambientales. Con este objetivo se presentan algunos de los trabajos realizados en el Laboratory of Catalysis and Materials (LCM), cuyas principales líneas de investigación se centran en la preparación de materiales de carbono y en la aplicación de los mismos en catálisis. Estos materiales de carbono, con propiedades superficiales y texturales adecuadas para actuar como soporte de las fases activas o como catalizadores en sí mismos, han sido aplicados con éxito en procesos catalíticos tales como la reducción catalítica de iones o procesos de oxidación avanzada.

## 1. Introduction

Carbon materials are currently used in heterogeneous catalysis both as supports or as catalysts on their own, due to their specific properties, namely: resistance to acid and basic media, possibility to tune their textural and surface properties, and easy recovery of precious metals by burning the carbon support [1, 2]. In particular, their use as metal-free catalysts is attracting a great deal of attention [2], being a good alternative to the traditional metal and metal oxide catalysts in several gas and liquid phase reactions [3].

Textural properties of the carbon materials can be tailored for specific applications by adequate preparation methods. The nature and concentration of the surface functional groups may be modified by appropriate thermal or chemical post-treatments. The presence of heteroatoms, such as oxygen, nitrogen and sulphur, bound to the edges of the graphene layers in the carbon material originates several surface functional groups. Such elements are either present in the starting material or become chemically bound to the structure during the preparation [4]. Oxygenated groups can be introduced onto the carbon materials surface by oxidative treatments, either in the gas or liquid phase [5], which can be selectively removed by thermal treatments under inert atmosphere. The introduction of heteroatoms on the carbon structure allows to control the electronic properties by introducing electron acceptors or donors, which can enhance $\pi$ bonding, leading to improved stability and electron transfer rate, and consequently, improved performance and durability of the catalysts during the processes [6, 7].

Carbon materials have demonstrated to be good supports for the catalytic reduction of ions over metallic catalysts in the presence of a reducing agent [8-13]. The presence of metals is mandatory for this reaction, but the carbon materials by themselves do not present any activity, their role being the promotion of a high metal dispersion. In contrast, it has been demonstrated that carbon materials are able to enhance the removal of organic pollutants as catalysts in catalytic wet air oxidation [14-16] and catalytic ozonation [17, 18] due to their outstanding textural and chemical properties. Therefore, here we describe some of the work carried out on the development of carbon materials with appropriate surface and textural properties to act as supports for the active phases or as catalysts on their own for catalytic processes such as the reduction of ions and advanced oxidation processes.

## 2. Carbon materials as catalyst supports

Carbon materials have a great potential as catalyst supports, especially when expensive noble metals are used, since a high metal loading and dispersion can be achieved. However, it is well known that the role of the support is not simply that of a carrier; the interaction between the active phase and the support can also affect the catalytic activity [19].

Catalytic reduction is a promising technology for water treatment, where the ions are reduced over metal catalysts in the presence of hydrogen without the formation of solid or liquid wastes. Metallic catalysts supported on carbon materials have been developed for the selective reduction of nitrate ions to nitrogen [8, 9, 20-23]; and more recently for the reduction of bromate to bromide [12, 13], showing significant advances in these catalytic processes using carbon materials as catalyst supports.

We have studied in detail several mono and bimetallic catalysts supported on commercial activated carbon (ACo) in order to optimize their composition [8, 9], and then we have studied the activities and selectivities of the best catalysts, Pd-Cu and Pt-Cu, evaluating the effect of the support [10, 24]. Therefore, different carbon materials (activated carbons with different surface chemistries (AC1, AC2, AC3), multiwalled carbon nanotubes (CNT) and carbon xerogels (CXG)) were used as supports for the bimetallic catalysts [24]. Table 1 shows the main properties of these supports. Activated carbons present the highest BET surface areas and the CNTs present the lowest values and absence of micropores. The CXG sample has a mesopore surface area higher than the activated carbon samples. Among the activated carbons, no major differences in their textural properties were observed after oxidation with $HNO_3$ (AC1) or thermal treatments (AC2 and AC3 were obtained by thermally treating AC1 during 1 h at 700 ºC under $N_2$ or $H_2$ flow, respectively). The surface areas of the supported metal catalysts are not significantly different from the original supports.

Table 1. Textural characterization and $pH_{pzc}$ values of the supports. Adapted from [24] with permission from Springer.

Tabla 1. Caracterización textural y valores $pH_{PZC}$ de los soportes. Adaptado de [24] con permiso de Springer

| Sample | $S_{BET}$ (m²/g) | $S_{meso}$ (m²/g) | $V_{micro}$ (cm³/g) | $pH_{pzc}$ |
|---|---|---|---|---|
| ACo | 968 | 177 | 0.346 | 8.3 |
| AC1 | 886 | 162 | 0.322 | 3.1 |
| AC2 | 947 | 164 | 0.342 | 9.0 |
| AC3 | 1001 | 165 | 0.349 | 9.9 |
| CNT1 | 320 | 320 | 0 | 7.0 |
| CNT2 | 196 | 196 | 0 | 7.2 |
| CXG | 687 | 287 | 0.110 | 7.8 |

The amounts of CO and $CO_2$ released from the carbon supports during TPD experiments are shown in Figure 1. Among the activated carbon samples, it can be observed that sample AC1 (oxidised with $HNO_3$ 6 M) presents the highest amount of oxygen surface groups, containing a large amount of carboxylic acid groups and lactones, which confer acid properties to this sample. Some carboxylic anhydrides, phenol and carbonyl/quinone groups are also present [25, 26]. The thermally treated samples (AC2 and AC3) present a relatively low content of oxygen surface groups, since the $CO_2$ releasing groups (carboxylic acid groups, lactones, carboxylic anhydrides) have been completely removed and only some of the CO releasing groups still remain on the carbon surface at high temperatures. These groups can be carbonyl/quinones that have not been decomposed by the treatment at 700 ºC and pyrone groups, which have basic properties and decompose at high temperatures, conferring to these samples basic properties. Sample AC3 shows a lower amount of CO releasing groups than sample AC2 due to the treatment with hydrogen that leads to stable basic surfaces by forming C–H bonds, avoiding further adsorption of oxygen, whereas the thermal treatment under nitrogen leads to a carbon surface with reactive sites able of reincorporating oxygen when exposed to atmospheric air, leading to the formation of some of the previously removed groups. Carbon nanotube samples (CNT1 and CNT2 - commercial CNT with different proveniences) do

not have significant amounts of oxygenated surface groups and the carbon xerogel sample (CXG) presents only a few groups.
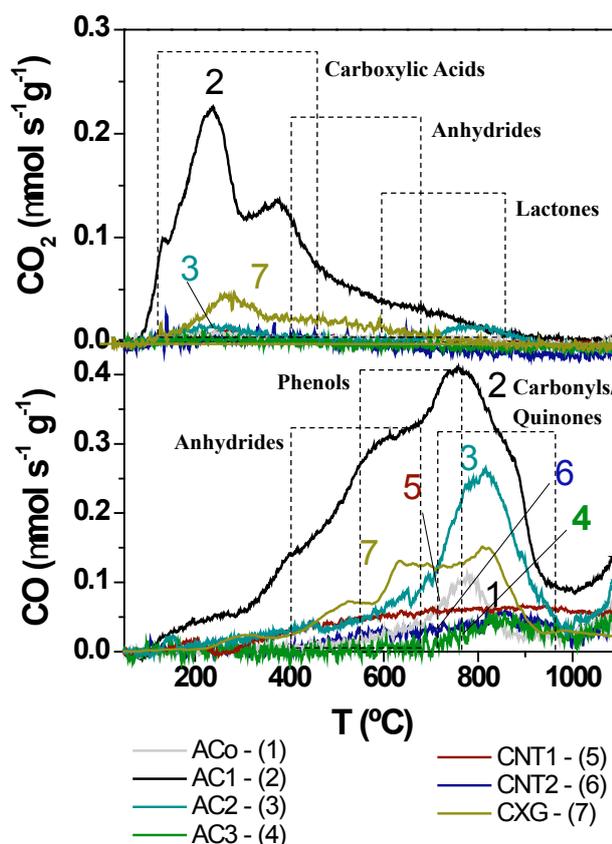


**Figure 1 -** TPD profiles of carbon materials: $CO_2$ and CO evolutions (adapted from [24] with permission from Springer).

**Figura 1** - Perfiles de DTP de los materiales de carbono: evolución de $CO_2$ y CO (adaptado de [24] con permiso de Springer).

The surface chemistry of the support has an important role in the catalyst activity and selectivity during the nitrate reduction reaction. Figure 2 shows the results obtained with 2%Pd-Cu catalysts (wt.%), for which a nitrate conversion of 100% is always achieved, independently of the support; the time required to obtain this value being the main difference. When Pt-Cu catalysts are used this effect is much more marked [24]. Independently of the metals, catalysts supported on basic carbon materials and on carbon nanotubes (that present a neutral/basic character) are more active and selective for this reaction. TEM images revealed that the catalysts supported on AC1 and CXG present the largest metal particle sizes, showing that the surface groups of the support determine the metals dispersion. Thus, metal surface dispersion is promoted in supports without significant amounts of oxygenated surface groups, which could act as anchoring sites for the metal precursors, leading, under the condition used, to the agglomeration of the metal particles during the calcination/reduction step.

Carbon nanotubes revealed to be good supports not only due to their surface chemistry, which does not present significant amounts of surface groups, but also due to their high surface area and absence of microporosity. Therefore, this support was studied in detail. These studies demonstrate that the reduction of nitrate is quite different depending on the noble metal, the preparation conditions and the surface chemistry of the CNTs used as support [27]. The nitrogen selectivity experimentally obtained with

Pd-Cu catalysts supported on CNT is close to the maximum selectivity predicted by a mechanistic model developed for this catalytic system at the best operating conditions due to the absence of any mass transfer limitations [28].
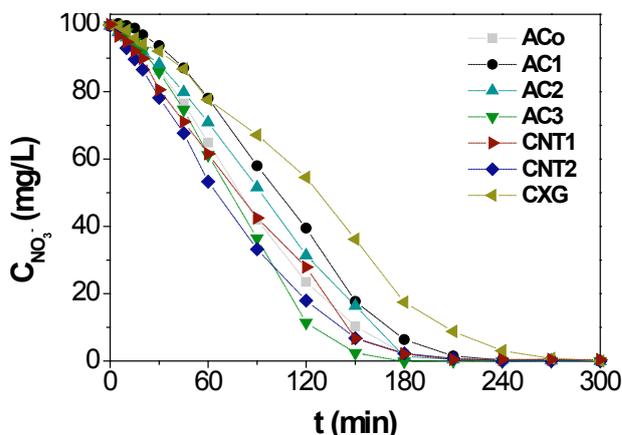


**Figure 2** - $NO_3^-$ concentration as a function of time during nitrate reduction in the presence of 2%Pd-1%Cu catalysts (adapted from [24] with permission from Springer).

**Figura 2** - Evolución de la concentración de $NO_3^-$ en función del tiempo durante la reducción de nitrato en presencia de los catalizadores 2%Pd-1%Cu (adaptado de [24] con permiso de Springer).

($C_{NO_3^-i}$ = 100 mg/L, catalyst = 0.5 g/L, pH = 5.5, $Q_{H2}$ = 100 Ncm³/min, $Q_{CO2}$ = 100 Ncm³/min, T = 25 °C).

## 3. Carbon materials as metal-free catalysts

The use of CNT as metal-free catalysts is a novel approach that has been applied in heterogeneous liquid phase catalytic systems, in particular in advanced oxidation processes, as catalytic wet air oxidation (CWAO) and catalytic ozonation (COz). Briefly, wet air oxidation (WAO) is a technology that can play a major role as primary treatment for highly concentrated wastewaters that are refractory to biological treatments, operating at high reaction temperatures and pressures (200–320 °C and 20–200 bar), which can become milder in the presence of catalysts. Recent studies [14, 15] carried out in the LCM group demonstrate that carbon materials can be applied successfully as metal-free catalysts in CWAO, replacing the catalysts based on noble metals or metal oxides avoiding the leaching of the metals to the liquid

phase. COz is another promising technology for the treatment of organic pollutants, operating at room conditions. Single ozonation shows low reactivity towards specific types of recalcitrant compounds and usually leads to an incomplete degradation of the organic pollutants, but significant enhancements can be obtained in the presence of carbon materials [17]. In general, basic carbons are normally the best catalysts in these AOPs [15, 17].

Ball milling has attracted much attention as a promising method for modifying CNTs, namely to adjust their lengths and to open the closed ends, increasing their specific surface areas. Recently, we have studied the influence of ball-milling on the texture and surface properties of multi-walled carbon nanotubes to be used as catalysts for the ozonation of oxalic acid [18]. This was the pioneering work with ball milling in the LCM group. Different milling times at constant frequency and different frequencies during constant time were used for the preparation of the modified samples. It was observed that the surface area of the CNTs increases, whereas the particle size decreases with the ball-milling time until 240 min at 15 vibrations/s (see Figure 3), but the surface chemistry does not change.
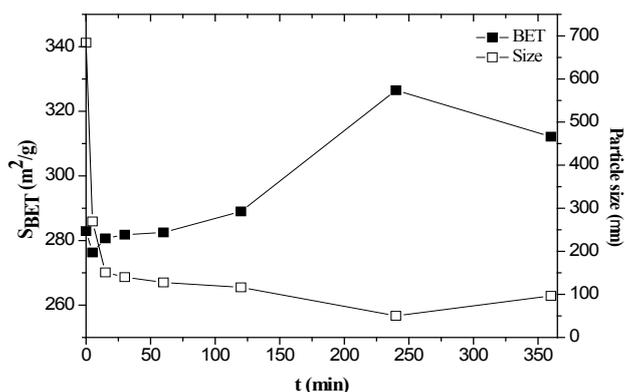


**Figure 3 –** Evolution of the surface area and mode of particle size distribution of CNT samples with the milling time, for the vibration frequency of 15 vibrations/s (Reprinted from [18] with permission from Elsevier).

**Figura 3 –** Evolución de la superficie y de la distribución de tamaño de partícula de las muestras de CNT con el tiempo de molienda, para una frecuencia de vibración de 15 vibraciones/s (Reimpreso de [18] con permiso de Elsevier).

a)



b)
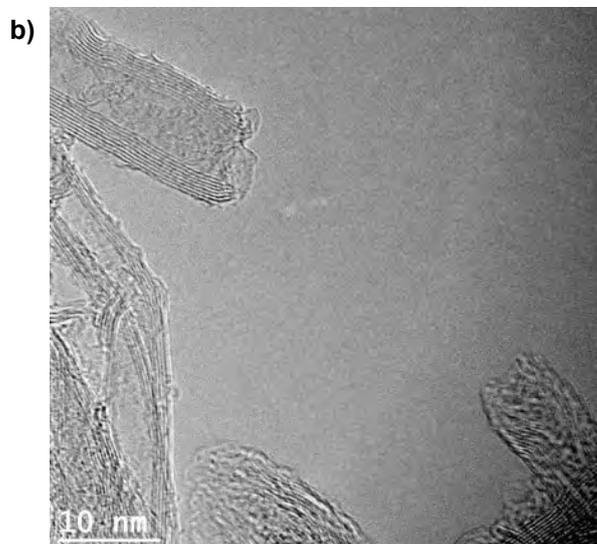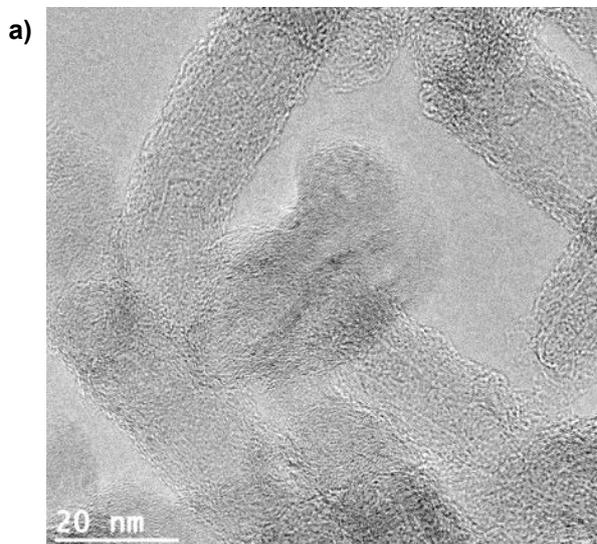


**Figure 4 –** Representative HRTEM images of the pristine CNT sample (a) and after 240 minutes of milling at a vibration frequency of 15 vibrations/s (b).

**Figura 4 –** Imágenes representativas de HRTEM de la muestra CNT original (a) y de la misma muestra tras 240 minutos de molienda a una frecuencia de vibracion de 15 vibraciones/s (b).

The pristine CNT are formed by well-defined graphitic layers and is formed by several aggregates of tubes highly entangled, curved and twisted with each other (Figure 4a)). Ball-milling is highly effective in disentangling and shortening the CNT by breaking up the tubes and, due that, with the increase of the ball-milling time, the high entanglement is markedly reduced. Open tubes are present in the samples ball milled during 240 (Figure 4b)) or 360 min [18].

The catalytic performance of the ball-milled samples in COz increased significantly when compared to the unmilled CNTs, as shown is Figure 5. Through this work it was concluded that ball-milling is an effective and simple method to increase the surface area of CNTs without significant changes of their structural properties, allowing increased catalytic performance in the ozonation process.
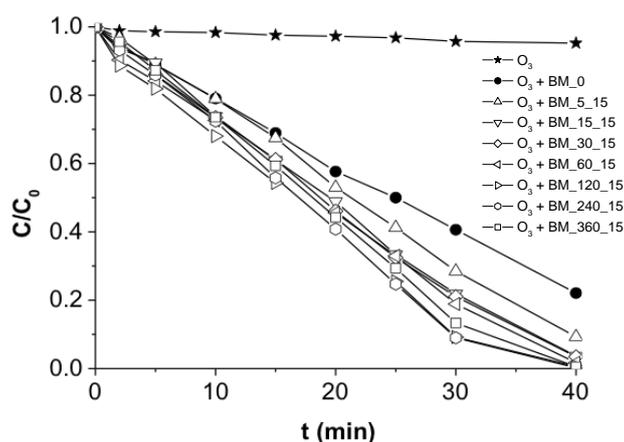


**Figure 5** – Evolution of the dimensionless concentration of oxalic acid during single ozonation ($O_3$) and in the presence of ball-milled CNT at different times and constant vibration rate (15) (Reprinted from [18] with permission from Elsevier).

**Figura 5** – Evolución de la concentración de ácido oxálico sin dimensiones durante la ozonización sola ($O_3$) y en presencia de CNT molino en diferentes tiempos y velocidad de vibración constante (15) (Reimpreso de [18] con permiso de Elsevier).

($C_0$ = 1 mM, CNT = 0.14 mg/L)

The development of metal-free carbon materials by tailoring textural and surface chemical properties can play an important role in the catalytic performance; in particular, N-doping was demonstrated to increase the activity of carbon catalysts in oxidation reactions [7, 15]. The main benefit of using N-doped carbons when compared to traditional catalysts (noble metals or metal oxides) is that the N-species are well anchored into the catalyst structure and, as a result, the drawbacks related to active phase sintering are improbable to occur even under severe reaction conditions [29]; in addition, there is improved stability and electron transfer rate, leading to a higher durability of the catalysts during the catalytic processes [6, 7].

Nitrogen doping of carbon materials can be attained in-situ during synthesis or ex-situ using appropriate post–treatments. In recent years, several routes have been tried to modify the carbon structure, in order to develop new functional materials with enhanced properties [30]. Normally, all these methods implicate high energy consumption and multi-step processes, which raise the catalyst manufacturing cost, limiting their practical applications. Recently, we have developed an easy to handle method to prepare N-doped carbon nanotubes [31] and also N-doped graphene oxide (GO) [32] by ball milling, followed by a thermal treatment under inert atmosphere, which avoids the use of solvents and production of wastes. Melamine and urea were used as nitrogen precursors and the procedure applied leads to the incorporation of large amounts of N-groups namely pyridine (N-6), pyrrole (N-5) and quaternary nitrogen (N-Q). The thermal decomposition products of the N-precursor lead to the incorporation of the N-functionalities onto the carbon surface due to the close contact between the precursor and the CNT as a result of the previous mechanical mixture performed by ball milling. The catalysts produced by this method can be easily scalable for practical applications, since their production does not require highly specialized and expensive equipment.

N-doped samples were obtained by ball milling the commercial multi-walled carbon nanotubes with the N-precursors, using the milling conditions optimized in a previous work [18], followed by a thermal treatment under $N_2$ flow until 600 ºC. The modified samples show small differences regarding the surface area ($S_{BET}$) (lower than 100 $m^2$ $g^{-1}$). The milling of the original CNTs leads to the largest increase of the surface area, while the incorporation of nitrogen originates samples with the lowest surface areas, as shown in Table 2. The addition of the N-precursor only slightly increases the oxygenated surface groups. On the contrary, significant amounts of nitrogen (between 0.2 and 4.8 %) can be introduced on the surface of the CNTs (see Table 2), especially when melamine was used as the N-source. The nature of the N-functionalities, identified by XPS, included pyridine -like N atoms (N-6), pyrrole-like N atoms (N-5), and quaternary nitrogen (N-Q), which are usually thermally stable on carbons.

In a subsequent work [16], it was demonstrated that this ball milling and solvent-free methodology is fairly adequate for the preparation of N-doped carbon materials with enhanced properties for the mineralization of organic pollutants in two distinct advanced oxidation processes: catalytic wet air oxidation and catalytic ozonation. Figure 6 shows that oxalic acid was completely mineralized in 5 min by CWAO and in 4 h by COz, under the operation conditions used.

**Table 2.** Textural and chemical properties of carbon nanotube samples adapted from [31] with permission from Elsevier.

**Tabla 2.** Textura y propiedades químicas de las muestras de nanotubos de carbono adaptado de [18] con permiso de Elsevier.

| Sample | $S_{BET}$ ($m^2$ $g^{-1}$) | $(CO)_{TPD}$ ($\mu$mol $g^{-1}$) | $(CO_2)_{TPD}$ ($\mu$mol $g^{-1}$) | $N_{XPS}$ (wt. %) |
|---|---|---|---|---|
| CNT-O | 291 | 200 | 23 | n.d. |
| CNT-BM | 391 | 173 | 44 | n.d. |
| CNT-BM-M-DT | 355 | 338 | 214 | 4.8 |
| CNT-BM-U-DT | 353 | 273 | 112 | 0.8 |

n.d. – not determined
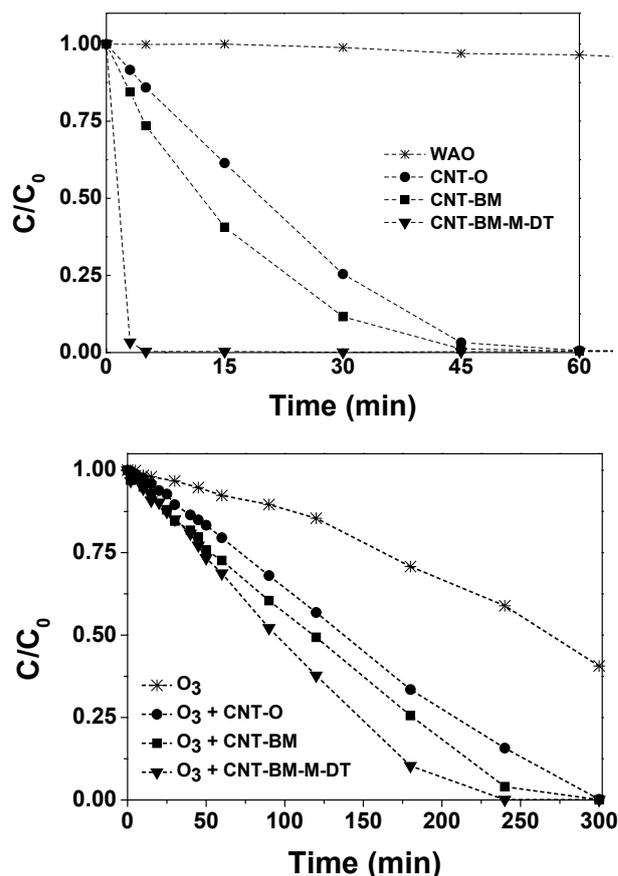
**Figure 6** - Evolution of the normalized oxalic acid concentrations: a) in CWAO (140 ºC and 40 bar of total pressure, 0.1 g of catalyst; Co =1000 mg/L) and b) in COz (room temperature, 0.05 g of catalyst; Co = 450 mg/L). (non-catalytic conditions (WAO), single ozonation ($O_3$), original (CNT-O), ball milled (CNT-BM) and sample doped with melamine (CNT-BM-M-DT) (adapted from [16] with permission from Elsevier).

**Figura 6** - Evolución de la concentracion de ácido oxálico: a) en CWAO (140 ºC y 40 bar de presión total, 0,1 g de catalizador; Co = 1000 mg/L) y b) en COz (temperatura ambiente, 0,05 g de catalizador; Co = 450 mg/L). (condiciones no catalíticas (WAO), ozonización ($O_3$), original (CNT-O), molida (CNT-BM) y la muestra dopada con melamina (CNT-BM-M-DT) (adaptado de [16] con permiso de Elsevier).
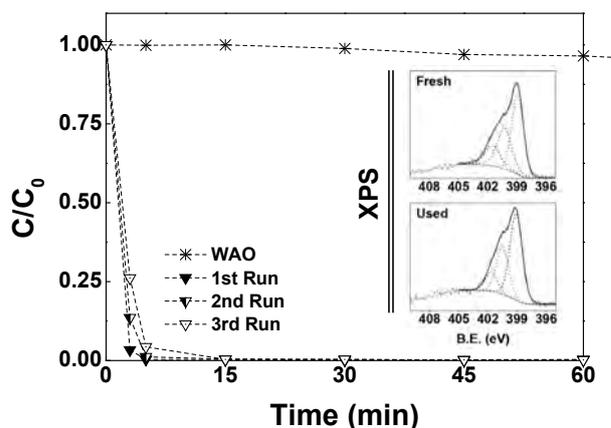


**Figure 7** - Cyclic experiments and N1s XPS spectra for the fresh CNT-MB-M-DT sample and after being used in CWAO of oxalic acid (adapted from [16] with permission from Elsevier).

**Figura 7** - Experimentos cíclicos y espectros de XPS N1s de la muestra CNT-MB-M-DT, antes y después de ser utilizada en la CWAO de ácido oxálico (adaptado de [16] con permiso de Elsevier).

Cyclic experiments using the same catalyst (CNT-BM-M-DT) with fresh solutions of oxalic acid show a slight deactivation of the catalyst during CWAO. Nevertheless, complete degradation of oxalic acid is observed in less than 15 min. This is frequently observed during consecutive runs of CWAO due to a slight oxidation of the carbon surface promoted by the operating conditions used. On the other hand, the N-groups introduced on the carbon surface showed to be stable, as can be seen in Figure 7, which shows that the N1s XPS spectra of this catalyst before and after being used in CWAO of oxalic acid present similar proportions of the N-functionalities (N-6, N-5 and N-Q groups).

The novel metal-free catalyst developed by this easy and simple one-step method demonstrated to be effective, confirming that this solvent-free ball milling methodology is quite adequate for the preparation of N-doped carbon materials with enhanced catalytic properties for the AOPs studied. Among the several types of carbon materials (activated carbons, carbon xerogels, ordered mesoporous carbons and carbon nanotubes) successfully tested in CWAO and in COz in the LCM [14, 15, 17, 33-35], the N-doped CNTs prepared by this ball milling method demonstrate to be those with the most outstanding catalytic performances. Therefore, we are currently focusing our interest on the development of the ball milling methodology to prepare carbon materials doped with different heteroatoms to be used as metal catalyst supports or as catalysts on their own for environmental applications.

## Conclusions

It was shown that carbon materials have a great potential as catalyst supports and also as catalysts on their own mainly due to their high versatility. Our recent studies demonstrated that the textural and chemical properties of carbon materials can be enhanced for environmental applications, namely catalytic reduction of ions and advanced oxidation processes.

## Acknowledgments

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