

Review

Tuning CNT Properties for Metal-Free Environmental Catalytic Applications

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Abstract: The application of carbon nanotubes (CNTs) as metal-free catalysts is a novel approach for heterogeneous liquid phase catalytic systems. Textural and chemical modifications by liquid/gas phase or mechanical treatments, as well as solid state reactions, were successfully applied to obtain carbon nanotubes with different surface functionalities. Oxygen, nitrogen, and sulfur are the most common heteroatoms introduced on the carbon surface. This short-review highlights different routes used to develop metal-free carbon nanotube catalysts with enhanced properties for Advanced Oxidation Processes.

Keywords: carbon nanotubes; metal-free catalysts; oxygen surface groups; nitrogen-containing groups; sulfur surface functionalities; advanced oxidation processes

1. Introduction

The work published in 1991 by Ijima [1] boosted the interest by carbon nanotubes (CNTs) and since then they have been intensively studied due to their unusual mechanical, electronic, and thermal properties [2], allowing them to be currently used in a wide range of technological applications [3,4], including as catalysts or catalyst supports in the fields of renewable energy (storage and generation) and environmental technologies (oxidation/remediation/adsorption). In fact, CNTs have been intensively investigated as catalyst supports for those technologies, and less often as catalysts on their own, but recent advances in the development of reliable methods to tune their physicochemical properties by suitable thermal or chemical post-treatments provide a major asset for their use as catalysts in these applications [5,6]. Furthermore, the increasing role assumed by carbon nanomaterials in recent decades is intrinsically linked to the better understanding of the carbon surface chemistry, as a result of reliable methods of analysis.

In this review relevant methods for the chemical functionalization of CNTs will be presented, and their properties discussed, with emphasis on their use as catalysts in environmental metal-free processes. High efficiency, environmental compatibility, low energy consumption, and corrosion resistance are some of the advantages that nanocarbons offer compared with metal-based catalysts, in addition to high selectivity and long term stability under mild conditions in many catalytic processes [7].

2. Tuning Carbon Nanotube Properties

The performance of any catalyst depends on the availability of suitable active sites, capable of chemisorbing the reactants and forming surface intermediates of adequate strength. Therefore, the surface chemistry of CNTs plays an important role on the catalytic performance of CNTs for different applications [8]. The graphitic structure of the CNTs contains unsaturated carbon atoms at the edges of the graphene layers as well as defects on the basal plane. Both, contribute to the high

reactivity of the carbon surface with O-/N-/S-containing compounds, allowing the incorporation of different functionalities bound to the edge of the graphene layers, extending the application of the CNTs to a wide range of processes. Different heteroatoms can be successively attached to the CNT's surface like O, N, S, depending on the treatment performed. Figure 1 shows schematically the whole range of surface functionalities.

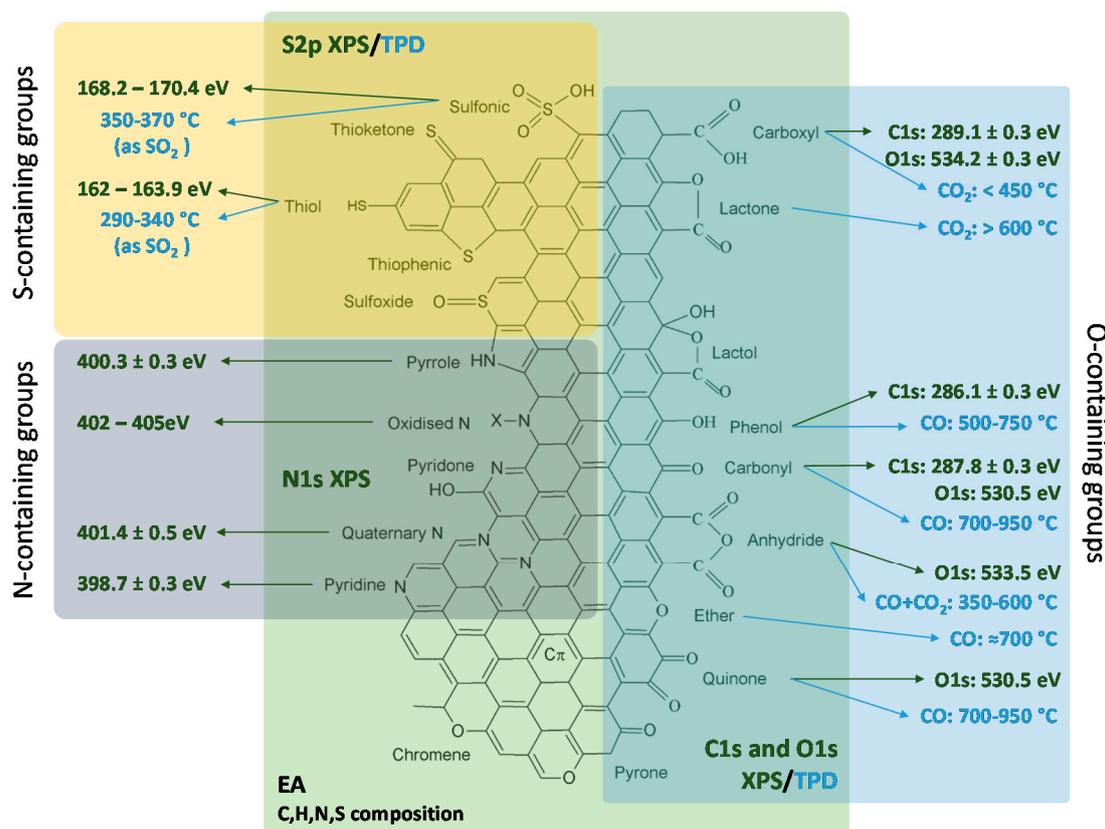


Figure 1. Oxygen, nitrogen and sulfur surface groups incorporated on carbon nanotubes (CNTs) by post-synthesis treatments, and techniques for their identification/quantification [9–17].

Several techniques are available to explore the chemical and structural properties of CNTs: scanning tunneling microscope (STM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), infrared (IR), and Raman spectroscopies, chemical titration methods, electron energy loss spectroscopy (EELS), temperature programmed desorption (TPD), thermogravimetry (TG), and point of zero charge (pH_{pzc}) [10,16,18,19]. Some techniques do not allow quantitative characterization, others require relatively large amounts of sample and are time consuming or difficult to implement as a routine analysis [16]. XPS and TPD techniques yield qualitative and quantitative information on individual functional groups on the carbon surface, with TPD being especially adequate for characterization of oxygen functional groups on carbon materials with extended porosity [10]. Nitrogen and sulfur can be properly quantified by elemental analysis (EA), while the nature of N-containing and S-containing groups is commonly identified by suitable deconvolution of the N1s and S2p XPS spectra. The nature of the functional surface groups and their characteristic binding energies (XPS) and/or temperature range of desorption in TPD analyses are also indicated in Figure 1.

In addition to the surface chemistry characterization, textural properties, such as the specific surface area and pore size distribution, are required to evaluate the modifications promoted by the chemical treatments and to compare different carbon nanotubes, which will present significant differences depending on their provenience or synthesis method. Furthermore, specific surface

area (S_{BET}) is a critical parameter for applications in catalysis. Considering that CNTs present a non-microporous structure, their textural parameters (S_{BET} and pore volume) result from the free space in the CNT bundles, the accessibility to the tubes edges, the defects on the layers, and the alignment of the tubes [20].

Ball milling has attracted much attention as a promising method for modifying carbon nanotubes, namely to adjust their lengths and to open the closed ends [21–23], increasing their specific surface areas [23], by shortening and opening the nanotubes [23,24]. Although functionalization of the surface is not achieved by ball milling, the mechanical treatment by itself is able to tune the textural properties of the CNTs, which have a significant influence on their catalytic performance.

In the following sub-sections, different ways to incorporate heteroatoms on the CNT surface are separately presented for an easier discussion. However, it should be taken into consideration that the simultaneous functionalization of the surface often occurs, i.e., some treatments can incorporate O and S or O and N functional groups at the same time.

2.1. Oxygen-Containing Surface Groups

Different chemical and thermal treatments can be applied to CNTs in order to produce materials with oxygenated surface groups. The most common liquid-phase oxidation treatments include nitric acid, mixtures of sulfuric acid and nitric acid, hydrogen peroxide, and ozone. Although, liquid-phase functionalization of CNTs is easier, it requires filtration, washing and drying steps. Alternative gas-phase functionalization techniques involve oxidation with oxygen (usually diluted with nitrogen), ozone, carbon dioxide, oxidative plasmas or by means of nitric acid vapours, which can avoid the multi-step procedure of the liquid-phase functionalization [25–27].

Oxidation of CNTs is frequently performed using nitric acid as reagent; in addition, to removing amorphous carbon and metal impurities, abundant oxygenated groups are generated on the carbon surface [28]. Although a non-selective functionalization is achieved, the O-containing groups can be anchored on the defect sites of sidewall and open caps of CNTs or on the defect sites and edges [25]. Typically, liquid-phase oxidation can be performed in a Soxhlet extractor or just by boiling the CNTs in nitric acid. The extent of oxidation will depend on the method used, on the duration of the treatment, on the concentration of the acid used, and on the ratio CNT/oxidant [29,30]. Traditionally, CNTs are boiled in a 7 M HNO_3 solution for 3 h, as used in ref. [31], incorporating high amounts of O-containing groups: acidic oxygen groups include carboxylic acids, anhydrides, lactones and phenols, and carbonyls and quinones, as basic or neutral oxygen functional groups, which can be identified by deconvolution of the profiles of CO and CO_2 released during TPD analysis (Figure 2).

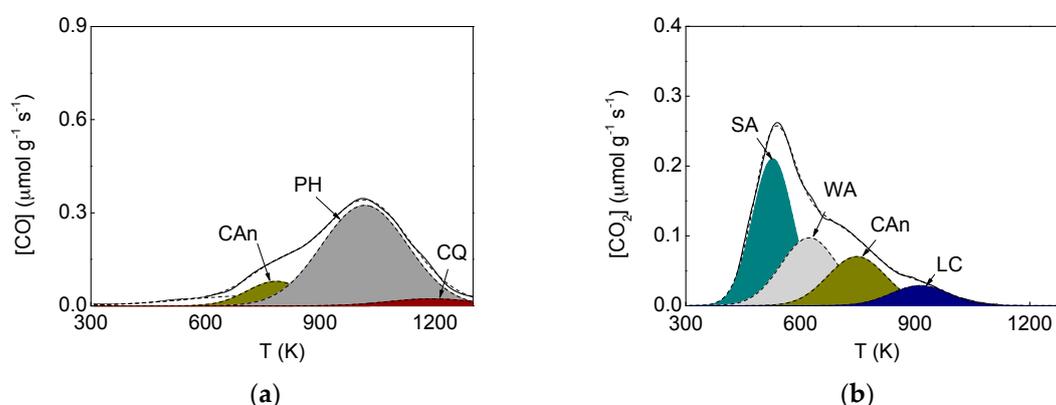


Figure 2. Deconvolution of temperature programmed desorption (TPD) profiles of commercial CNTs treated with a 7 M HNO_3 solution at boiling temperature: groups released as (a) CO and (b) CO_2 (PH—phenols; CAn—carboxylic anhydrides; CQ—carbonyl/quinones; LC—lactones; CAC—carboxylic acids; SA—strong acidic CAC; WA—weakly acidic CA) (adapted from [32]).

Severe degradation effects, especially loss of material, tube shortening as well as the formation of structural defects, usually occur during boiling in HNO_3 [33,34]. An alternative to the chemical functionalization of CNTs by refluxing with concentrated oxidants can be achieved using hydrothermal (HT) oxidation [35]. This methodology, firstly developed for carbon xerogels [36] and later extended to single walled carbon nanotubes [37] and multi walled carbon nanotubes [35], uses diluted concentrations of HNO_3 to control the amount of oxygenated functionalities created on the surface of CNTs. The method is quite effective, and the amount of oxygenated-surface groups (carboxylic acids, carboxylic anhydrides, phenols, carbonyl/quinones, and lactones) can be correlated with the HNO_3 concentration and temperature (Figure 3).

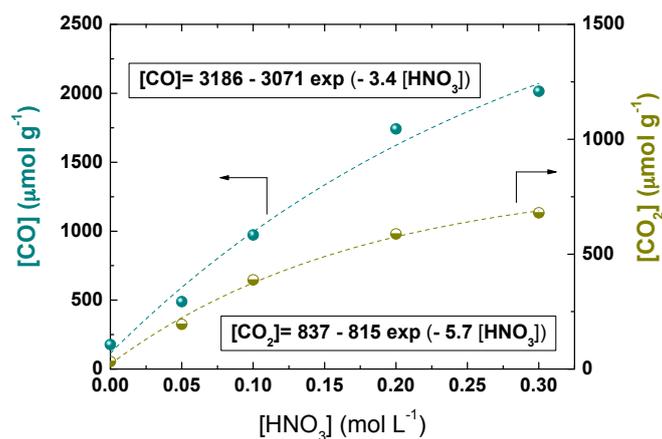


Figure 3. Evolution of the amounts of CO and CO_2 released from the surface of the hydrothermally treated CNTs (at 473 K) with HNO_3 concentration (adapted from [32]).

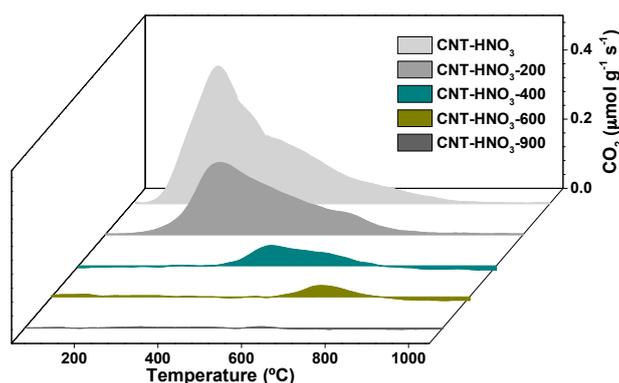
Comparing with the traditional oxidation (in 7 M solution of HNO_3 at boiling temperature) the hydrothermal functionalization of CNTs using a 0.3 M solution of HNO_3 at 200 °C can achieve a similar degree of functionalization, with the amount of oxygen-containing surface groups being even higher when compared with the traditional refluxing with HNO_3 [32] (Table 1). Oxidative treatments in the liquid-phase with hydrogen peroxide (H_2O_2) or ozone (O_3) have also been reported, but the degree of functionalization is lower [38]. While treatments with HNO_3 originate materials with large amounts of surface acidic groups, mainly carboxylic acids and, to a smaller extent, lactones, anhydrides, and phenol groups [15], H_2O_2 oxidation generates less acidic materials [39] (Table 1), whereas ozone treated CNTs in the liquid phase revealed slight functionalization [38]. In order to introduce mainly basic and neutral oxygenated groups on the surface (mainly phenol and carbonyl/quinone groups), CNTs can be oxidized in the gas phase with diluted oxygen (5% O_2 in N_2) at high temperatures (500 °C). In this case, it should be taken into consideration that O_2 leads to a significant increase of the specific surface area, while the oxidation with H_2O_2 does not promote drastic changes of the textural properties of the CNTs [26].

An alternative way to introduce basic or neutral oxygenated surface groups consists on performing thermal treatments under inert atmosphere at specific temperatures after oxidation with nitric acid, in order to selectively remove some of the groups previously introduced during oxidation. The large amount of oxygen containing groups incorporated on the CNTs by nitric acid oxidation, carboxylic acid groups (released below 450 °C), carboxylic anhydrides (evolved between 350 and 600 °C), lactones (released above 600 °C) as CO_2 during the TPD experiments, phenol (500–750 °C), and carbonyl/quinone groups (700–950 °C) released as CO, are successively removed with the thermal treatments. Thus, samples with different amounts of oxygen groups can be obtained, starting from the oxidized sample (CNT- HNO_3). Thus, the CNT- HNO_3 -200 sample presents a lower amount of carboxylic acids than CNT- HNO_3 . All the remaining carboxylic acids are practically removed, as well as a part of the anhydrides, when the thermal treatment is performed at 400 °C (CNT- HNO_3 -400).

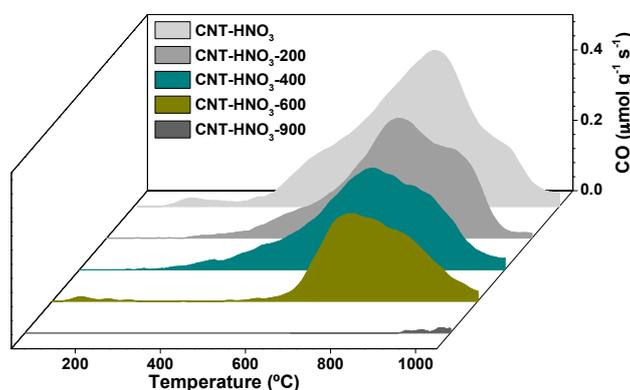
After treatment at 600 °C (CNT-HNO₃-600), the surface only contains phenol and carbonyl/quinone groups, and a small amount of lactones. Almost all the oxygen-containing surface groups are removed at 900 °C [26,38] (Figure 4). This approach has the advantage that the thermal treatments do not promote significant additional changes on the specific surface area of the CNTs [38], as can be seen in Table 1.

Table 1. Textural and chemical properties of modified commercial carbon nanotube (CNT) samples from the same supplier (Nanocyl NC3100).

Sample	S _{BET}	CO	CO ₂	Ref.
	(m ² ·g ⁻¹)	(μmol·g ⁻¹)	(μmol·g ⁻¹)	
Pristine CNTs	278	178	33	[32]
CNT-HNO ₃ 7M	—	1511	767	
CNT-HNO ₃ HT (0.3 M)	441	2015	680	
CNT-H ₂ O ₂	337	466	150	[26]
CNT-O ₂	508	1339	91	
CNT-O ₃ (liquid-phase)	333	503	298	[38]
CNT-HNO ₃ -200	408	1308	727	[38]
CNT-HNO ₃ -400	408	1205	113	
CNT-HNO ₃ -600	389	826	43	



(a)



(b)

Figure 4. Profiles of (a) CO₂ and (b) CO evolved in TPD of modified samples: nitric acid (CNT-HNO₃) and thermally treated samples (CNT-HNO₃-200, CNT-HNO₃-400, CNT-HNO₃-600, CNT-HNO₃-900) (adapted from [26,38]).

2.2. Nitrogen-Containing Surface Groups

The exceptional electronic properties and catalytic performances of N-doped carbon nanotubes are attracting much interest [11,25,40,41]. The incorporation of nitrogen atoms onto the carbon structure is relatively easy due to the similar sizes of the nitrogen and carbon atoms [42,43], providing additional electrons for the graphitic lattice [44]. Furthermore, nitrogen species are well anchored to the surface and, consequently, the drawbacks related to loss of active phase are unlikely to occur even under severe reaction conditions [45]. In-situ (during synthesis) or ex-situ (post-treatments) approaches are used to incorporate nitrogen onto the carbon structure [25]. Regarding post-treatments, the incorporation of nitrogen can be achieved either by treating the carbon materials with ammonia or using nitrogen-containing carbon precursors, such as urea, melamine, polyacrylonitriles, polyvinylpyridine, and quinoline-containing pitch [31,46,47]. Generally, the incorporation of pyridinic-like (N-6), pyrrolic-like (N-5), and graphitic-like (N-Q) structures enhances the basicity of the CNTs [10,11,48,49].

Normally, all these methods implicate high energy consumption and multi-step procedures, which raise the catalyst manufacturing cost, limiting their practical applications. Recently, an easy to handle method to prepare N-doped carbon nanotubes [50] and also N-doped graphene oxide (GO) was developed [51], involving ball milling, followed by thermal treatment under N_2 up to $600\text{ }^\circ\text{C}$, avoiding the use of solvents and production of wastes. Incorporation of large amounts of N-groups (pyridine, N-6; pyrrole, N-5, and quaternary nitrogen, N-Q) is especially obtained using melamine as N-precursor by this method (see Figure 5).

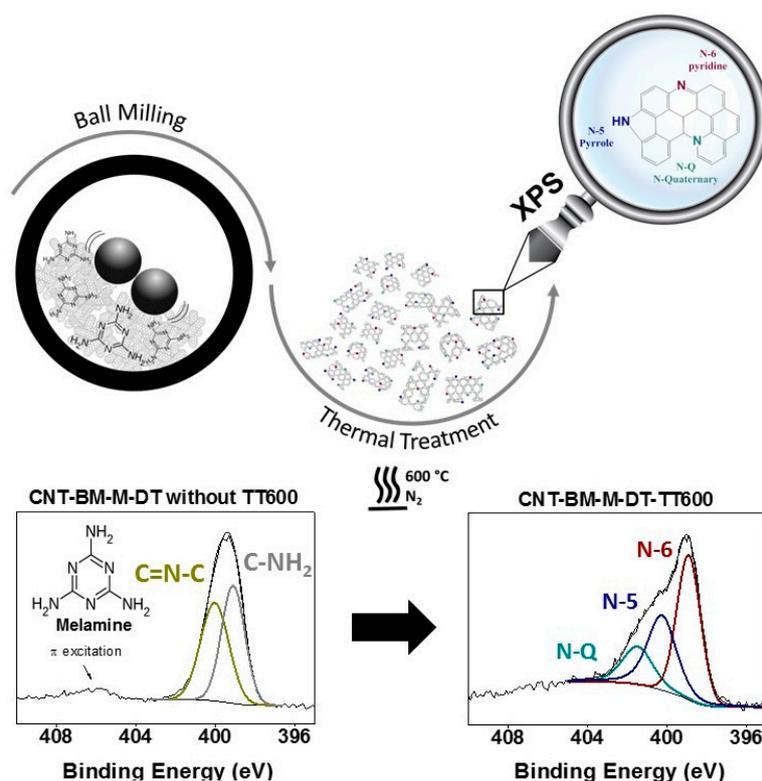


Figure 5. Illustration of the novel easy method to prepare N-doped carbon nanotubes by ball milling, with detailed N1s spectra evolution (adapted from [50,52]).

The thermal decomposition products of the N-precursor (melamine) 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. Furthermore, this method is easily scalable for practical applications, since the procedure does not require highly

specialized and expensive equipment. Another N-precursor (urea) was also studied in the same work; however, lower incorporation of N-groups was achieved.

Table 2 compares melamine and urea treated samples (CNT-BM-M and CNT-BM-U samples, respectively) using the ball milling approach, with a conventional hydrothermal treatment, where urea was used as N-precursor after the pre-oxidation of CNTs (CNT-NUT) [31]. The modified samples show differences regarding the surface area (S_{BET}) lower than $100 \text{ m}^2 \cdot \text{g}^{-1}$, comparing with the pristine CNTs. The addition/treatment with melamine/urea as N-precursor only slightly increases the oxygenated surface groups. On the contrary, significant amounts of nitrogen can be introduced on the surface of the CNTs, especially when melamine is used as 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.

Table 2. Textural and chemical properties of N-doped CNT samples using melamine and urea as N-precursor by ball milling approach or hydrothermal treatment.

Sample	S_{BET}	CO	CO ₂	N _{Content}	N-Functionalities	Ref.
	($\text{m}^2 \cdot \text{g}^{-1}$)	($\mu\text{mol} \cdot \text{g}^{-1}$)	($\mu\text{mol} \cdot \text{g}^{-1}$)	XPS/EA (wt. %)		
Pristine CNTs	291	200	23	n.d.	—	
CNT-BM-M	355	338	214	4.8/7.6	N-6/N-5/N-Q	[50]
CNT-BM-U	353	273	112	0.8/0.9	N-6/N-5/N-Q	
CNT-NUT	386	703	76	0.9/0.7	N-6/N-5	[31]

2.3. Sulfonic Acid Surface Groups

While the N-surface groups enhance the basicity of the carbon surface, CNTs can achieve strongly acidic properties by incorporation of sulfonic acid groups [38,53–56]. Oxidation with sulfuric acid or a mixture of sulfuric acid/nitric acid by hydrothermal methods is routinely used for such a purpose [12,13,53,55,57], incorporating mainly thiol (–SH) and sulfonic acid (–SO₃H) groups. Porous carbons functionalized with –SO₃H have been presented as environmental-friendly solid acid catalysts, and they are particularly important in reactions where typically liquid acids are used; however, they can be also beneficial for improved pollutant removal [12,13,38,55–57]. In addition to the use of H₂SO₄ as S-source, others sulfonating agents as benzenesulfonic acid (C₆H₅SO₃H), *p*-toluenesulfonic acid (PTSA, CH₃C₆H₄SO₃H), and “piranha” solution (H₂O₂–H₂SO₄) were proposed [29,57,58]. The methodology already presented for HNO₃ controlled functionalization of CNTs by hydrothermal treatment was adapted in a pioneer work to the use of H₂SO₄ (containing ammonium persulfate—(NH₄)₂S₂O₈) as an oxidizing agent [59].

Table 3 compares selected sulfonated CNTs from the literature. Direct functionalization with H₂SO₄ originates high incorporation of S-containing groups at low temperature (50 °C, [56]) or at high temperature (250 °C [53]); however, in the last case the authors did not show the textural modifications obtained after the treatment. Regarding the hydrothermal methodology, contrary to what was observed with HNO₃ (low acid concentration allowing similar functionalization as the conventional nitric acid boiling approach), the hydrothermal treatment of CNT with H₂SO₄ revealed a weak incorporation of S-containing groups on the surface [59]. The simultaneous use of H₂SO₄/HNO₃ led to higher incorporation of –SO₃H [56]; however, in this case a large amount of O-functionalities was also incorporated.

After an overview of the different possibilities for tuning the surface chemistry of the CNTs (Figure 6), the next section will emphasise the important role of these groups on some environmental processes catalysed by metal-free CNTs. The fine tuning allows a good distribution and arrangement of the heteroatoms in the graphitic lattice which is of a paramount importance concerning the catalytic behaviour of the CNTs.

Table 3. Textural and chemical properties of S-doped CNT samples from the literature.

Sample	S_{BET}	CO	CO ₂	SO ₂	Nature of S-Groups	Ref.
	(m ² ·g ⁻¹)	(μmol·g ⁻¹)	(μmol·g ⁻¹)	(μmol·g ⁻¹)		
CNT-H ₂ SO ₄	—	—	—	1900 ¹	-SO ₃ H ³	[53]
Pristine CNTs	326	187	33	—	—	
CNT-H ₂ SO ₄	294	381	195	579 ²	—	[56]
CNT-H ₂ SO ₄ /HNO ₃	394	2035	1394	203 ²	-SO ₃ H ⁴	
Pristine CNTs	315	187	31	—	—	
CNT-H ₂ SO ₄ HT (0.3 M) ^a	437	1312	471	81 ²	—	[59]
CNT-H ₂ SO ₄ HT (0.3 M) ^b	—	625	164	53 ²	-SO ₃ H	

^a With and ^b without ammonium persulfate during the sulfonation. ¹ Based on the uptake of ammonia during ammonia adsorption experiments; ² Determined by TPD; ³ Identified by FTIR; ⁴ Identified by XPS.

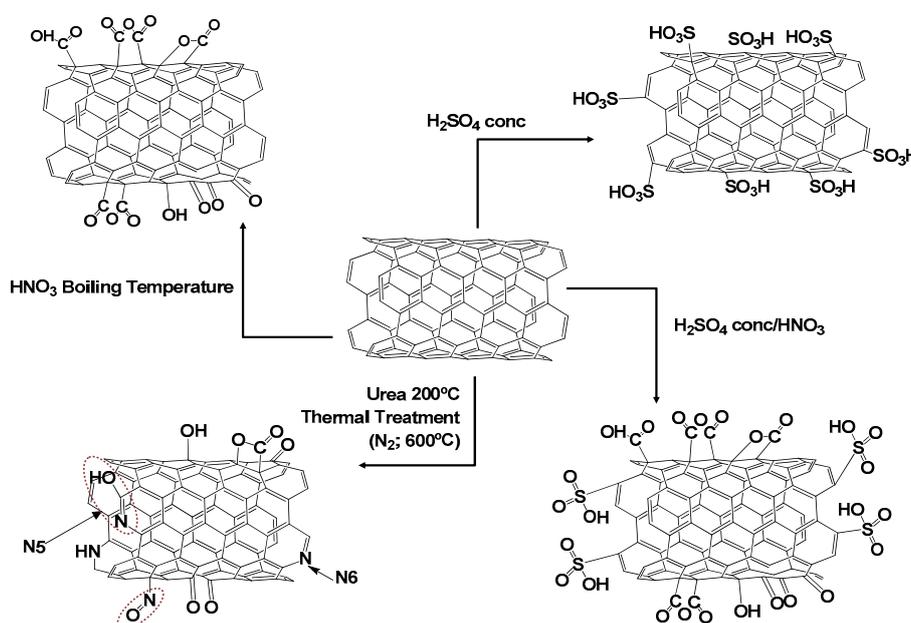


Figure 6. Schematic liquid-phase functionalization routes to incorporate different O, N and S heteroatoms onto the surface of CNTs. Reprinted from reference [56] with permission from Elsevier.

3. Environmental Catalytic Applications

Advanced oxidation processes (AOPs) are a group of environmental technologies developed to remove organic contaminants from water and to treat polluted wastewater by oxidation. Normally, the reactions involve highly reactive radicals generated from different oxidants, such as oxygen (wet air oxidation), hydrogen peroxide (wet peroxide oxidation) and ozone (ozonation).

Wet air oxidation (WAO) is a very attractive process that can play a major role as primary treatment for highly concentrated wastewaters that are refractory to biological treatments. The non-catalytic process operates at high temperatures (200–320 °C) and pressures (20–200 bar), but the process efficiency can be increased under less severe operating temperatures (130–250 °C) and pressures (5–50 bar) by using homogeneous or heterogeneous active catalysts [31]. The problems associated with the leaching of the metals to the liquid phase can be avoided by replacing the catalysts based on noble metals or metal oxides by metal-free carbon materials [60,61].

Catalytic Ozonation (COZ) is another promising technology for the treatment of organic pollutants, operating at room conditions. Significant enhancement of the non-catalytic process (single ozonation), that shows low reactivity towards specific types of recalcitrant compounds and usually leads to an incomplete degradation of the organic pollutants, can be obtained in the presence of carbon materials [26].

Thanks to their textural characteristics, mechanical resistance and chemical inertia, CNTs have already proved to be good candidates for these environmental control processes. CNTs are stable in both acidic and alkaline media, with the advantage of reducing, or even eliminating, diffusion limitations, due to their relatively high surface area and absence of microporosity.

In the last decade, metal-free CNTs were investigated as catalysts in Catalytic Wet Air Oxidation (CWAO) and COZ using selected model compounds. Oxalic acid and phenol are commonly selected as probe species, since they represent well a refractory short chain carboxylic acid end-product in AOPs (in the case of oxalic acid) [62–64] and a more complex molecule which is also an organic pollutant commonly found in industrial effluents (phenol) [38]. In some COZ cases, authors also studied antibiotics (as erythromycin [65] and sulfamethoxazole [66]), lipid regulators (as bezafibrate) [67], and herbicides (as atrazine) [68,69].

It is generally accepted that basic carbons are the best catalyst for both processes [10] and numerous works were carried out to clarify this issue. Although this is well accepted in literature for COZ, in the case of CWAO there is a controversy regarding the active sites on carbon nanotubes (i.e., sites of basic or acidic nature) required to achieve the best performance. The catalytic activity of nanocarbons successfully functionalized with different heteroatoms has been investigated in CWAO [31,38,52,56,70–73] and in COZ [26,51,56,67–69,74–78] by several authors. O-, N- and S-doped CNTs have been studied as catalysts in both processes. Table 4 summarizes CWAO and COZ works from the literature, where those surface groups were studied and their influence on the catalytic performance of the CNTs was evaluated.

Table 4. Overview of Catalytic Wet Air Oxidation (CWAO) and Catalytic Ozonation (COZ) works from the literature studying different surface functionalities onto the CNTs.

Process(es)	Model Compound(s)	Type of Functionalities	Reference
CWAO	Oxalic Acid/Phenol	O-/S-containing groups	[38]
	Phenol	O-(S-) containing groups *	[71]
	Phenol	O-(S-) containing groups *	[72]
	Oxalic Acid	O-/N-containing groups	[31]
	Phenol	O-containing groups	[73]
	Phenol/Nitrobenzene/Aniline	O-containing groups	[79]
	Phenol	O-(S-) containing groups *	[80]
CWAO/COZ	Oxalic Acid	N-containing groups	[52]
	Oxalic Acid/Phenol	O-/N-/O-containing groups	[56]
COZ	Oxalic and Oxamic Acids	O-containing groups	[26]
	Sulfamethoxazole (antibiotic)	O-containing groups	[81]
	Indigo	O-containing groups	[75]
	Oxalic acid	O-containing groups	[76]
	Oxalic acid	O-containing groups	[77]
	Methyl orange dye	O-containing groups	[78]

* Authors only discussed the effect of oxygenated surface groups; however, they treated the samples with H₂SO₄ and, consequently, there are other surface groups.

Depending on the origin of the CNTs and their properties (single-walled/multi-walled, purity, length and diameter of tubes), pristine CNTs can present significant catalytic activity in both AOPs even without any functionalization [26,31,66,67], which is due to the presence of basic sites provided by the π -electron system of the basal planes (C π) [82]. Using undoped commercial CNTs from Nanocyl™, oxalic acid is completely oxidized in less than 30 min by CWAO [31] and in around 60 min by COZ [26]. Even without any functionalization, the performance of pristine CNTs can be improved using mechanical treatments [24,52], as ball milling. This treatment markedly reduces the entanglement of the CNTs, also leading to shorter CNTs by breaking up the tubes [24,50,83], and increasing their specific surface area. 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 was recently studied [24].

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, but the surface chemistry does not change. A higher amount of active sites is available due to the increase in surface area, increasing the reaction rate in comparison with the pristine and unmilled CNTs.

Despite the relative high catalytic activity of the raw CNTs in the oxidation of oxalic acid, the same is not always observed for the oxidation of other model compounds, such as phenol. Several post-treatments can promote a more substantial increase of the CNTs performance allowing them to be competitive with conventional catalysts.

It is well accepted that the rate of oxidation of the selected model compound depends on the chemical properties of the CNTs, in some cases being possible to find good correlations with the nature and amount of the surface functionalities. For instance, in reference [31], where various CNT samples obtained by different treatments (oxidation with HNO_3 , H_2O_2 , and O_2 ; treated with urea; and thermally treated at different temperatures to selectively remove surface groups) were tested as catalysts, the apparent first-order initial reaction rate constants of oxalic acid oxidation are dependent on the point of zero charge of the CNT samples (Figure 7a), while in reference [26] a similar correlation was found when the rate constant for the heterogeneous ozone decomposition using CNTs was normalized by the surface area (Figure 7b). Both works clearly show that basic carbon samples are better catalysts than acid samples.

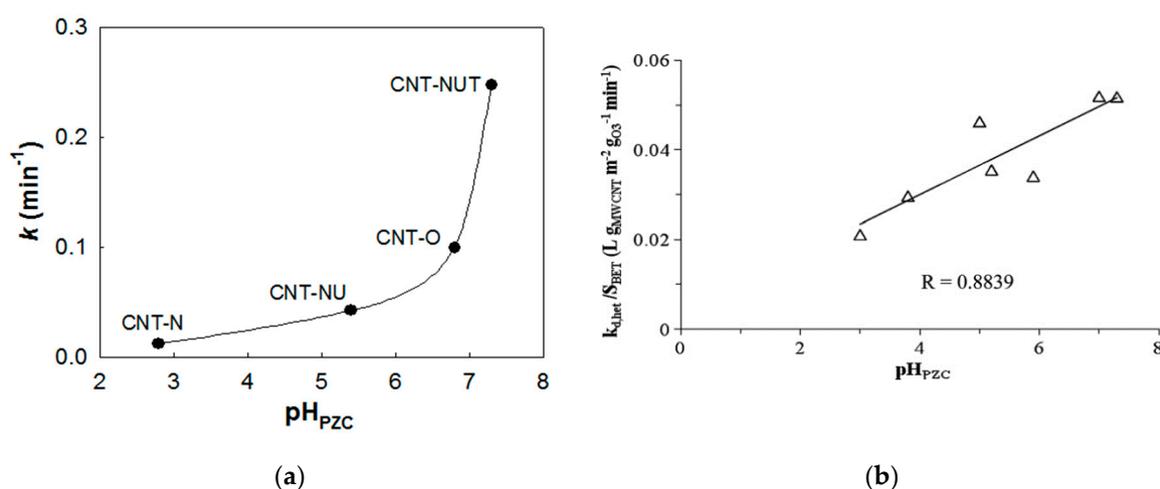


Figure 7. Enhancement of the catalytic activity by increasing the CNTs basicity in (a) CWAO: Apparent first-order initial reaction rate constants (k) of oxalic acid degradation vs. pH_{PZC} of CNTs [31] and (b) COZ: Normalized rate constants for heterogeneous ozone decomposition vs. pH_{PZC} of CNTs [26]. Reprinted from references [31] and [26] with permission from Elsevier.

Some other publications [71,72,80] have claimed that the carboxylic acid groups attached to the surface of CNTs promote their catalytic activity for the oxidation of phenol by the CWAO process. To clarify the controversy in the literature regarding the active sites of CNTs (i.e., sites of basic or acidic nature) required to achieve the best performance in CWAO, CNTs samples obtained by the oxidation of CNTs with HNO_3 , followed by thermal treatments for the selective removal of O-containing groups used in ref. [26], were tested in the CWAO of phenol [38]. The O-containing surface groups on the oxidized CNTs (carboxylic acids, phenols, anhydrides) contribute to the acidic character of the surface, and, simultaneously, decrease the catalytic activity for degradation of the tested pollutants [38]. Using the CNT samples treated with HNO_3 and subjected to thermal treatments as catalysts for degradation of oxalic acid and phenol by CWAO, it was observed that the conversion of these pollutants increases as the pH_{PZC} of the materials increase (Figure 8). In spite of this, in the same

work, CNTs modified with H_2SO_4 or $\text{HNO}_3/\text{H}_2\text{SO}_4$, which have a strong acidic character ($\text{pH}_{\text{pzc}} = 2.5$), showed an unexpected high activity for degradation of both model pollutants (Figure 8), although in the case of phenol only about 57% of TOC conversion was achieved. The performance of these strongly acidic materials was explained by the presence of S-containing surface groups [38] that may originate strong oxidant species in the liquid-phase, such as sulfate radicals, which are well known for their strong oxidizing potential [84]. Nevertheless, S-doped CNT samples were not stable during cyclic experiments and the catalytic activity is drastically reduced after the first run. Regarding the oxalic acid and phenol oxidation by COZ, S-treated CNT samples underperformed comparing to pristine CNTs [56].

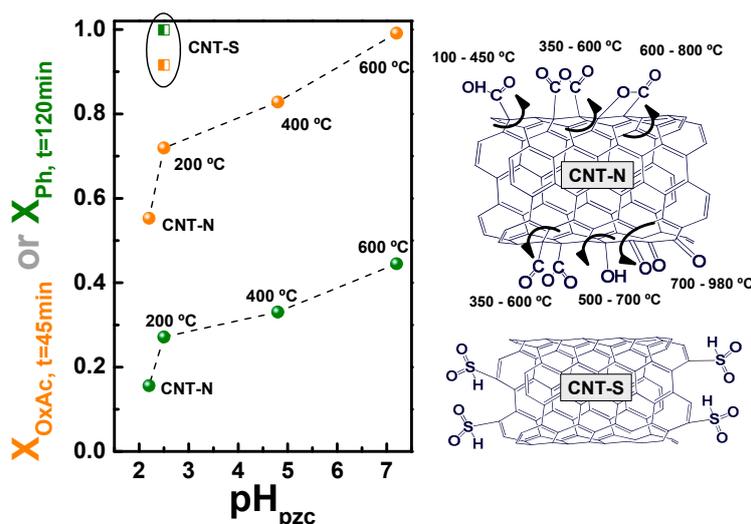


Figure 8. Influence of the surface chemistry on the catalytic performance of CNT: oxalic acid and phenol conversions obtained after 45 and 120 min of reaction, respectively, plotted against the pH_{pzc} of nitric acid and thermally treated samples and sulfuric treated samples. Reprinted from reference [38] with permission from Elsevier.

The modification of metal-free carbon materials by tailoring textural and surface chemical properties can play an important role in their catalytic performance; in particular, N-doping was demonstrated to increase the activity of carbon catalysts in oxidation reactions [11,31,51,52,56,85,86]. Regarding the use of N-doped CNTs in oxalic acid oxidation by CWAO, CNTs modified with nitric acid, urea and gas-phase thermal treatment showed the highest basic character and also the highest catalytic activity, but the performance is similar to that observed with the original CNTs after cyclic runs [31]. Also in the degradation of oxalic acid and phenol by COZ, only a slight increase of the catalytic performance was achieved using N-doped CNTs.

However, in a recent work [52], it was demonstrated that a ball milling and solvent-free methodology is fairly adequate for the preparation of N-doped carbon materials with enhanced properties for the mineralization of both organic pollutants in the two distinct processes, oxalic acid being completely mineralized in 5 min by CWAO and in 4 h by COZ. Furthermore, cyclic experiments showed low deactivation of the catalyst and high stability of the N-functionalities (mainly N-6, N-5, and N-Q groups) [52] (Figure 9). Moreover, catalytic experiments were performed using a lower catalyst loading (in the case of CWAO) and a higher initial concentration of the model pollutant (COZ). So far, those samples are the best metal-free carbon catalysts tested in both processes. Compared to traditional catalysts (noble metals or metal oxides), the N-species are well anchored into the catalyst structure and, as a result, the drawbacks related to loss of active phase are improbable to occur even under severe reaction conditions [45]; in addition, the stability and electron transfer rate are improved, leading to a higher durability of the catalysts during the catalytic processes [11,87].

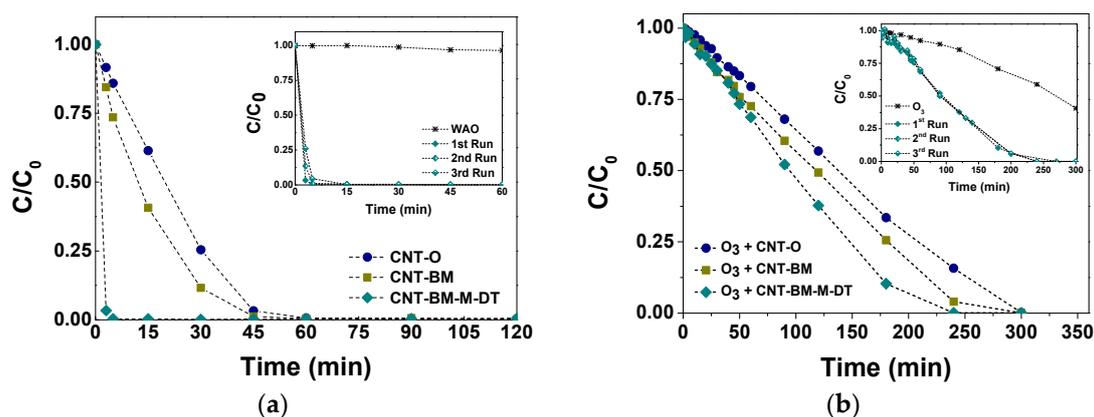


Figure 9. Evolution of the normalized oxalic acid concentrations: (a) in CWAO experiments ($T = 140\text{ }^{\circ}\text{C}$, $P_T = 40\text{ bar}$ ($P_{O_2} = 7\text{ bar}$), 0.1 g of catalyst; $[\text{Oxalic Acid}]_0 = 1000\text{ mg/L}$) and (b) in COZ (T_{Room} , 0.05 g of catalyst; $[\text{Oxalic Acid}]_0 = 450\text{ mg/L}$) and cyclic experiments inset using sample CNT-BM-M-DT. (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 [52]).

Besides all the research studies already published regarding the kind of functionalities on CNTs that allow high activity and stability of metal-free CNTs on CWAO and COZ, the reaction pathways involved in those reactions are still in doubt. Despite their complexity, it is generally accepted that: (a) the reaction mechanisms involve free radicals; (b) basic carbons are the best catalysts; and (c) oxidation of the organic compounds may occur both in the liquid phase (homogenous reaction) and on the catalyst surface [10]. Figure 10 schematically illustrates these possible reaction pathways.

Clarification of the mechanism involved in the CWAO and COZ processes has been attempted in some works, by using radical scavengers. For instance, a CWAO experiment using pristine commercial CNTs was performed in the presence of *tert*-butanol with a concentration ten times higher than that of oxalic acid [31]. The obtained results were very similar to those obtained in the absence of the radical scavenger, suggesting that hydroxyl radicals in solution were not the relevant species involved in the oxidation mechanism, and that oxalic acid oxidation should be mainly promoted by active oxygen species on the CNT surface produced from the decomposition of oxygen. When other N-doped carbon materials were tested in CWAO (carbon xerogels [85] and graphene based materials [51]) similar evidences were observed, suggesting again that hydroxyl radicals in solution are not in fact the main species involved in the oxidation mechanism, and that oxalic acid conversion by CWAO can occur by means of surface active species produced from the decomposition of oxygen. The enhanced catalytic activity observed in the presence of N-functionalities seems to result from the interaction of oxygen with the carbon surface [88]. N-groups with delocalized extra electrons were identified as the possible species responsible for the enhanced chemisorption [88] and activation of oxygen molecules [89]. Such active oxygen species can react with adsorbed organic compounds leading to the oxidation of the organic pollutants. Therefore, in the presence of N-functionalities on the carbon surface, hydroxyl radicals in the liquid phase may not be required, suggesting that the oxidation reaction can occur by an alternative surface reaction mechanism, possibly as described above [51].

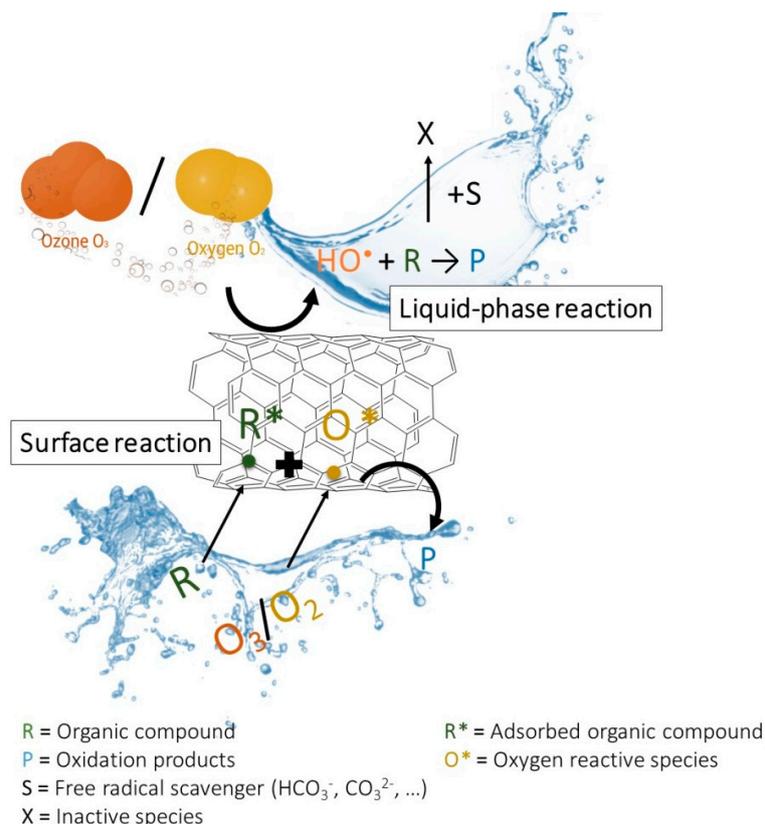


Figure 10. Scheme of the reactions that might occur between the surface of CNTs and the oxidative agents (O_2 or O_3) during CWAO and COZ experiments (adapted from [10]).

In the case of COZ, experiments performed using CNTs in the presence of *tert*-butanol suggested that $\bullet\text{OH}$ should participate in the oxalic acid removal [76], since it was found that the presence of *tert*-butanol decreases the degradation efficiency of oxalic acid comparatively to the presence of only CNTs. A similar conclusion was defended in reference [26], ozonation of oxalic acid in the presence of CNTs occurring both on the surface and in solution. In the presence of N-doped carbons, the addition of *tert*-butanol into the reaction medium also leads to a slight decrease in oxalic acid removal, suggesting that the production of radicals in the liquid phase plays a secondary role in the catalytic ozonation [85].

In the presence of S-doped CNTs a different reaction pathway may be involved [56]. In an attempt to clarify the reaction mechanism involved in COZ and CWAO with the S-modified samples, experiments were done using sodium persulfate with an equivalent S molar concentration of the carbon samples as a source of sulfate radicals. The experiments performed showed different mechanisms in both processes. While in CWAO the thermal activation of sulfate radicals occurs (by decomposition of the S-containing surface groups, $-\text{SO}_3\text{H}$) and the reaction mechanism involves sulfate radicals in solution; in COZ, the species resulting from the decomposition of S-containing groups are not active.

4. Conclusions

The present work discloses the potentialities of carbon nanotubes as metal free catalysts in liquid phase oxidation reactions for water treatment, with special emphasis in CWAO and COZ. Their performance can be substantially enhanced by tailoring the textural and chemical properties with appropriate thermal or chemical post-treatments. N-doped carbon materials prepared by a ball milling method were shown to be the most promising carbon catalysts for these reactions.

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Abbreviations

The following abbreviations are used in this manuscript:

AOPs	Advanced oxidation processes
CNT	Carbon Nanotube
COZ	Catalytic Ozonation
CWAO	Catalytic Wet Air Oxiation
EELS	Electron Energy Loss Spectroscopy
HT	Hydrothermal
IR	Infrared Spectroscopie
N-	Nitrogen
N-5	Pyrrolic-like group
N-6	Pyridinic-like group
N-Q	Graphitic-like group
O-	Oxygen
pHpzc	Point of Zero Charge
S-	Sulfur
STM	Scanning Tunneling Microscope
TEM	Transmission Electron Microscopy
TG	Thermogravimetry
TPD	Temperature Programmed Desorption
WAO	Wet Air Oxidation
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

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