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ORIGINAL PAPER

Metal-Free Catalytic Wet Oxidation: From Powder to Structured Catalyst Using N-Doped Carbon Nanotubes

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Abstract

This work shows a promising N-doped carbon catalyst for the oxidation of oxalic acid by catalytic wet oxidation, which is able to compete with the traditional noble metal and metal oxide catalysts used in the process. After preliminary studies conducted in batch mode, the catalytic performance of the metal-free carbon nanotubes, both in powder form and supported on a macrostructured carrier (a cordierite monolith), was evaluated under continuous operating conditions. The ability of the N-functionalities to promote activation and chemisorption of oxygen led not only to fast oxalic acid mineralization under batch mode (5 min of reaction to reach full mineralization), but also to good performance under continuous operation (more than 90% conversion of oxalic acid in the steady state, using the powder and around 55% using the catalyst immobilized on a honeycomb cordierite monolith).

Keywords Catalytic wet oxidation · Metal-free carbon catalyst · N-doped carbon nanotubes · Structured catalyst

1 Introduction

Wet oxidation (WO) is a well-established technology which is able to treat highly polluted industrial wastewater and sludge [1, 2], for instance resulting from refineries, pharmaceutical plants, pulp and paper industry. It uses oxygen to generate active species capable of oxidizing the organic compounds, preferentially into carbon dioxide and water, or alternatively into easily biodegradable by-products [3]. WO requires high temperatures (200–320 °C) and pressures (20–200 bar) to ensure solubility of oxygen and to promote fast mineralization and degradation [4, 5]. There are more than 200 industrial installations all over the world; however, WO still presents a high capital cost due to the expensive high-pressure equipment and construction materials required, in addition to the energy costs of operating at high temperature and pressure. The introduction of a catalyst can increase the process efficiency under less severe conditions (130–250 °C; 5–50 bar) [1, 6], affecting also positively the economics of the process. Commercial units of catalytic wet air oxidation (CWAO) employ homogeneous (as Cu, Fe) and heterogeneous noble metal (as Ru, Pd, Pt) catalysts [4, 5, 7]. Although noble metals or metal oxides can be used as catalysts in CWO, with good conversion ranges at moderate operating conditions, several drawbacks are usually pointed out for practical applications. The main disadvantage of homogeneous catalysts is the additional step required for recovery of the catalyst (by precipitation or other separation technique), which increases the operating costs. Supported metal catalysts are prone to leaching and deactivation phenomena, which not only affect the design of a clean technology but also represent additional operating costs [1, 8].

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In this context, metal-free carbon materials provide an interesting alternative to replace metal-based catalysts, eliminating the problem of deactivation and/or metal leaching. Novel nanocarbon materials with high external surface areas have been tested in CWO, including carbon nanotubes (CNTs) and fibres, carbon xerogels and graphene-based materials. In mesoporous carbons, the organic pollutants can easily diffuse trough the pores promoting faster degradation rates in comparison to microporous materials, as activated carbons [9]. The exceptional mechanical, electrical, and thermal properties of CNTs, allied to the recent large-scale production (and consequent lower cost and wider accessibility), allowed them to be investigated as potential catalysts for CWO [10–15]. Efforts were made to clarify the most suitable surface properties to enhance their catalytic activity, several improvements being achieved by doping the CNTs with nitrogen [12, 15–18]. The positive effect of N-functionalities on the CNTs was ascribed to the additional electrons provided, that increase the basicity of the surface, which is generally accepted to contribute not only to improve the performance of the catalysts in oxidation processes, but also to provide more stability in both acidic and alkaline media [19, 20].

In spite of the extensive investigation performed on the exploration of new heterogeneous catalysts for CWO, studies are mostly limited to catalysts in the powder form. CWO under batch operation results in a lower investment cost compared with the continuous mode. However, high labour costs are involved in reactor filling and cleaning steps. In this context and for large-scale wastewater treatment, reactors under continuous operation may be preferred. Furthermore, conventional and commercially available WO and CWO processes are usually performed in slurry reactors or packed-bed column reactors (fixed-bed reactors) operating in semi-batch or continuous mode [8, 21]. Bearing in mind a real scale application, the use of carbon materials in powder form in trickle-bed reactors can be a problem. Some drawbacks are associated with potential channelling, high-pressure drop, and decrease of the catalyst efficiency [22]. These problems can be overcome by using macrostructured supports, which can provide better control of the contact time of reactants and products with the catalyst, leading to a potential increase in the performance. Monolith carbon coated reactors can represent that alternative. Monoliths are typically characterized by long parallel channels separated by thin walls offering low-pressure drop, resistance to plugging, high mechanical strength, low axial dispersion, and high mass-transfer rates, due to their high void fraction and large geometric surface area [22–24]. For instance, the process NS-LC (a CWO unit commercialized by Nippon Shokubai, Japan) employed a Pt–Pd/TiO_2–ZrO_2 honeycomb catalyst (monolith reactor) to treat waste containing phenol, glucose, acetic acid, among others [7]. Nevertheless, studies reported on CWO using monolith reactors are still scarce, and were performed using metal-catalysts immobilized on monoliths (alumina coated cordierite monolith impregnated with copper salts [8] and copper oxide [25], lab-made monolith coated with Cu in γ-Al_2O_3/silicate [26], Pt/Al_2O_3 monolith [27], monolithic Cu/TiO_2 catalyst [28], noble metals as Au, Pd, Pt, Rh and Ru deposited on ceramic honeycomb [29], Pt, Ru and Ir coated Ti mesh monoliths [30–33]).

Many organic compounds undergoing WO gradually degrade to low molecular weight compounds and, finally, to highly refractory short chain carboxylic acids. For instance, Devlin and Harris [34] studied WO of phenol and listed various oxidation products, including monobasic and dibasic acids, such as acetic acid, formic acid, glyoxalic acid and oxalic acid. Oxidation of these compounds is often the rate-controlling step during WO of an aqueous waste stream exhibiting very high chemical oxygen demand (COD) [35]. In particular, the WO of oxalic acid was found to require more severe conditions as compared to glyoxalic acid [36]. Therefore, oxalic acid was chosen as representative of short chain carboxylic acids and hard refractory compounds. The results reported in literature for non-catalytic WO of oxalic acid show that high temperatures (above 220 °C at 8 bar of pure O_2) are required to obtain 35% oxidation of this pollutant (500 mg L^{-1}) after 30 min in the absence of a catalyst [36]. The decrease of the COD of oxalic acid in aqueous solutions is also low (4%) in non-catalytic conditions at 245 °C, or even in the presence of a homogeneous $CuSO_4$ catalyst at a lower temperature (6% for 140 °C, 7 bar O_2) after 30 min [35]. Higher activities were found with a Pt/charcoal catalyst (30–60%, initial oxalic concentration of 5000 mg L^{-1}) for the same period of time under less severe conditions, 53 °C and atmospheric pressure [37], and ca. 90% of oxidation with a Pt/Al_2O_3 catalyst at 80 °C [38]. At 90 °C and at atmospheric pressure, 75% of oxalic acid degradation (for an initial concentration of 2000 mg L^{-1}) was obtained after 5 h of reaction with a Pt/ceria promoted alumina [39]. Extensive work has been carried out to replace the traditional noble metals and rare earth oxide-based catalysts by metal-free carbon-based catalysts; however, no studies were found in the literature where oxalic acid was considered as the main pollutant, apart from works published by our group, where N-doped CNTs [12, 16, 18, 40], carbon xerogels [3] and graphene based materials [41] have been investigated as metal-free alternatives.

In the present work, to the best of our knowledge, a metal-free carbon structured catalyst was tested for the first time in CWO, using oxalic acid as model compound. After the high catalytic performance obtained with N-doped CNTs (in powder form) for CWO experiments conducted in batch mode, and a reaction pathway exploratory study, the work was extended to studies in continuous CWO mode in a triphasic reactor using the same catalyst in powder and immobilized on a honeycomb cordierite monolith.

2 Experimental

2.1 Catalyst Preparation

The CNTs used in the present work were purchased from NANOCYL™ (NC3100 series). According to the manufacturer, NANOCYL® NC3100™ series are thin multiwalled carbon nanotubes produced via the Catalytic Chemical Vapor Deposition (CCVD) process and then purified up to 95% (wt). The CNTs are available as a solid black powder with a bulk density around 150 g L^{-1}, an average length of 1.5 µm and an average diameter of 9.5 nm. Henceforward, the as-received CNTs are referred as p-CNT.

2.1.1 N-Doping of Carbon Nanotubes

The p-CNTs were milled with melamine as N-precursor in grinding jars using zirconium oxide balls in a Retsch MM200 equipment without any gas flow or solvent, following a procedure described elsewhere [42]. Briefly, 1 g of 3:2 (weight ratio) mixture of p-CNT and melamine was mixed during 4 h at a constant vibration frequency of 15 vibrations/s. Milling conditions were selected according to the optimization reported by Soares et al. in a previous work [43]. Then, the resulting material was subjected to a thermal treatment under N_2 flow until 600 °C (at 10 °C min^{-1}) and kept at this temperature during 1 h (sample N@CNT).

2.1.2 Structured N@C Catalyst

Structured catalysts of metal-free N-doped CNTs were prepared with honeycomb cordierite monoliths, adapting a procedure developed by Ba et al. [44] for coating of silicon carbide foams.

First, the bare monoliths (8.3 mm × 32 mm, 400 channels per square inch) were thermally treated until 900 °C (10 °C min^{-1}) under air flow (100 cm^3 min^{-1}) and kept 1 h at the final temperature to remove impurities. 0.5 g of N@CNT were mixed in 50 mL of ultrapure Milli-Q water and placed in an ultrasound bath for 30 min to allow a good separation of the powder particles. 10 g of glucose, 14 g of citric acid and 14 g of ammonium carbonate were then dissolved in the solution in order to form a type of “glue” to promote the adherence of the CNTs to the monolith. The solution was kept under stirring overnight to ensure a good dispersion of the active phase. Afterwards, the honeycomb cordierite monolith was dipped into the suspension (using a dip rate of 3 cm min^{-1}) and kept immersed for 1 min. The excess of liquid was removed by compressed air, and the monolith dried by rotating around its own axis for 2 h under ambient temperature to favour the homogeneous deposition of the CNTs. A second immersion step was performed in the same way. The coated monolith was then thermally treated under air until 130 °C (at 10 °C min^{-1}) and kept 1 h at this temperature. The monolith was further treated in nitrogen at 450 °C (1 °C min^{-1}) for 2 h and at 900 °C (2 °C min^{-1}) for another 2 h in order to stabilize the coating so it can withstand the reaction conditions (N@CNT Coated Monolith).

2.2 Characterization Techniques

Pristine and N-doped CNTs were characterized to assess their main textural and surface properties and changes promoted by the chemical and thermal treatments applied. The textural characterization of the materials was based on the N_2 adsorption isotherms, determined at −196 °C in a Quantachrome NOVA 4200e multi-station apparatus. The bulk composition of the carbon samples was determined by Elemental Analysis (EA) carried out on a vario MICRO cube and a rapid OXY cube analysers from elemental GmbH. The carbon surface composition was analysed by X-ray photoelectron spectroscopy (XPS). Thermogravimetric analysis (TGA) was carried out using an STA 409 PC/4/H Luxx Netzsch thermal analyser. Additional details can be found elsewhere [40].

2.3 Experimental Procedure

2.3.1 Batch Mode

The catalytic assessment of powder carbon catalysts was carried out in a 160 mL 316-stainless steel high pressure batch reactor (Parr Instruments, USA Mod. 4564) with temperature and stirring controller (PARR 4842) (Fig. 1). A glass cylinder inside the reactor was used to prevent possible catalytic effects due to the reactor building material and in order to minimize corrosion problems [45]. A type J thermocouple in direct contact with the liquid solution is used to control the temperature inside the reactor. Gases are fed to the reactor by a high-pressure line, bubbling directly into the liquid phase. This allows a better dispersion of the gas phase in the liquid phase, reducing the mass transfer limitations at the gas–liquid interface. Liquid aliquots are recovered by a sampling line. The reactor is also equipped with a gas outlet line and a safety rupture disk.

The oxidation reaction depends on the concentration of oxygen in the liquid phase [46]. Therefore, the temperatures, pressures and the initial concentration of the model compound were selected after preliminary experiments and by taking into account the concentration of oxygen that is

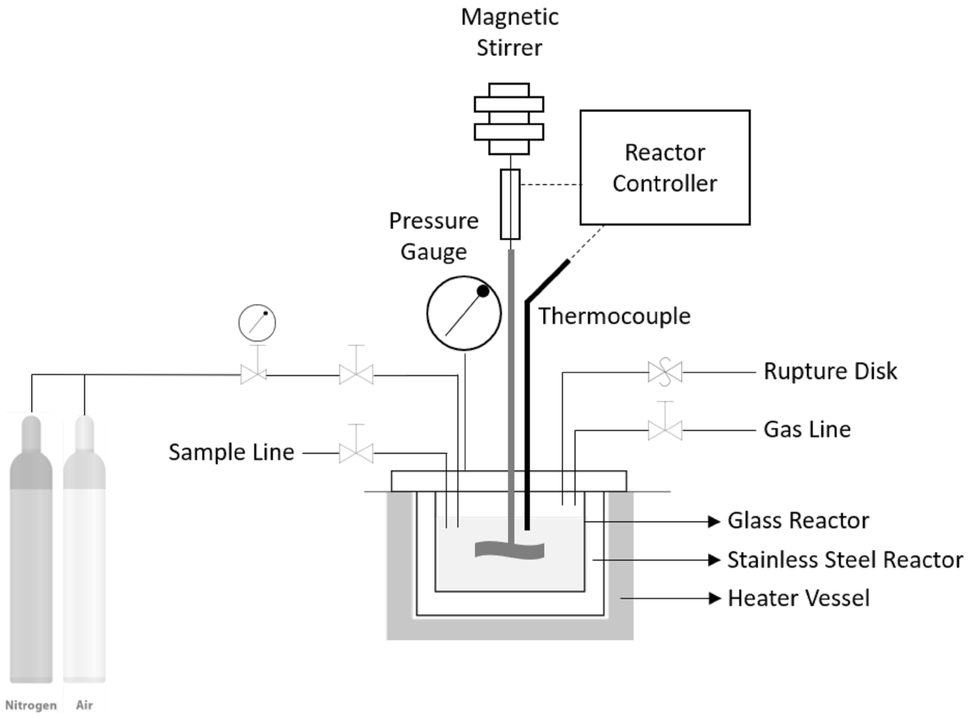

Fig. 1 Scheme of the batch reactor experimental set-up

dissolved in the liquid phase at the selected temperatures and pressures.

Catalytic wet air oxidation of oxalic acid was performed at 140 °C using an initial solution concentration of 1000 mg L^{-1}. Preliminary non-catalytic experiments showed that thermolysis of oxalic acid could occur above 180 °C, and that the availability of dissolved oxygen in solution might be compromised below 120 °C. Therefore, 140 °C and a total pressure of 40 bar were chosen to perform the WAO and CWAO studies. At this temperature, the oxygen partial pressure corresponds to 7 bar, considering the water vapour pressure at the selected temperature (3.6 bar) and the use of air as oxidant.

All experiments were performed under continuous stirring at 500 rpm in order to ensure proper mass transfer of air in the liquid phase [47, 48], and at natural pH (around 3 for oxalic acid).

Briefly, 75 mL of a 1000 mg L^{-1} oxalic acid solution and 0.05 g of catalyst were placed into the reactor. The reactor was flushed with pure nitrogen until the complete removal of oxygen, and then pressurized with 5 bar of nitrogen and pre-heated up to the desired temperature under continuous stirring. When the desired temperature was reached, pure air was injected to obtain a total pressure of 40 bar inside the reactor (corresponding to 7 bar of O_2 partial pressure), this being considered time zero for the reaction ($t = 0$ min). Reproducibility tests showed relative errors lower than ± 6%.

2.3.2 Continuous Mode

Continuous CWO experiments were carried out in a completely automated tubular reactor from Microactivity PID Eng&Tech equipped with a HPLC pump and a high-pressure liquid–gas separator (Fig. 2), working in down-flow. The tubular reactor has an internal diameter of 9 mm, an external diameter of 14.5 mm and a length of 305 mm. For the powder experiments, the catalysts tested were mixed with an inert material (0.06 g of catalyst and 2 g of carborundum), to ensure that the height of the catalyst bed was sufficient to allow a correct reading of the temperature by the thermocouple. For the monolith experiments, two monoliths (each with approximately 0.03 g of deposited material) were used. The catalysts were supported in quartz wool to guarantee that no clogging of the pipes occurred by dragging of the catalyst. The system was pre-heated under nitrogen flow (4 bar of pressure) until the desired temperature (140 °C). When the desired temperature was reached, nitrogen was replaced by oxygen, the pressure inside the reactor increased to the desired value (8 bar) and the model pollutant solution (1000 mg L^{-1} of oxalic acid) fed at 0.25 mL min^{-1}. The reactants were mixed and pre-heated outside the monolith. During the experiments, several liquid samples were collected to determine the evolution of the oxalic acid concentration. Reproducibility tests showed relative errors lower than ± 7%.

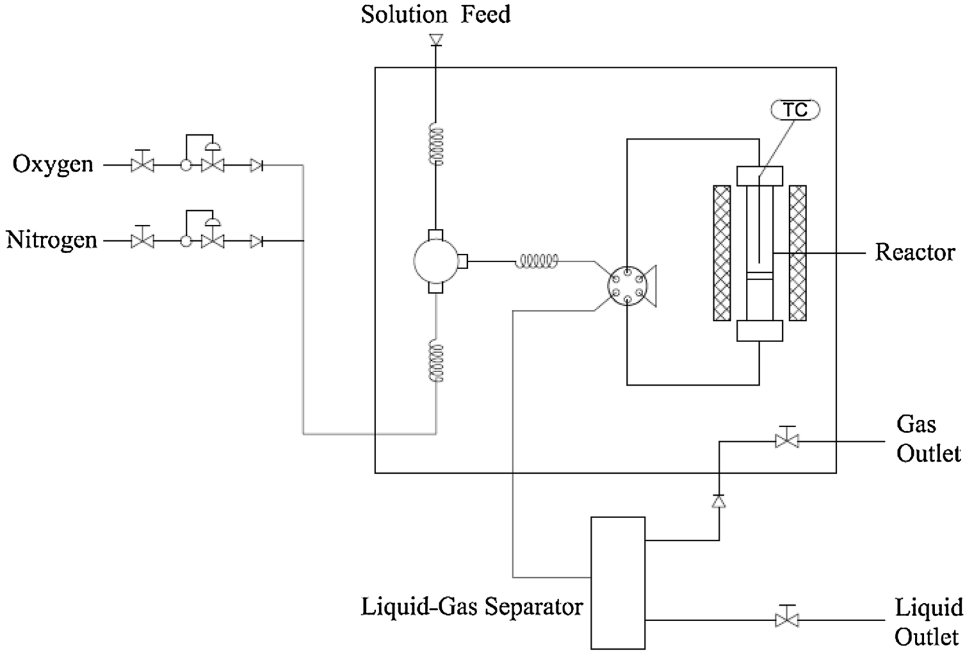

Fig. 2 Scheme of the continuous mode reactor experimental set-up

2.4 Analytical Techniques

Liquid aliquots were withdrawn from the batch and continuous reactors during reaction. The samples were analysed by high performance liquid chromatography (HPLC) with a Hitachi Elite LaChrom system equipped with a Diode Array Detector (L-2450). The determination of oxalic acid concentration was performed using an Alltech OA-1000 column (300 mm × 6.5 mm) and a H_2SO_4 solution (5 mmol L^{-1}) at a flow rate of 0.6 cm^3 min^{-1} (as mobile phase) at $\lambda = 200$ nm. Analyses were made using an injection volume of 15 µL. All solutions and standard compounds were prepared with ultrapure water with a resistivity of 18.2 mΩ at room temperature, obtained from a Milllipore Mili-Q system.

3 Results and Discussion

3.1 Materials Characterization—From Powder to Structured Catalyst

The relevant properties of the pristine and N-doped carbon nanotube samples used in the present work are described in Table 1. More detailed characterization can be found in our previous studies [40, 42], where an exhaustive characterization of the samples is presented and discussed. The procedure developed allows a large incorporation of nitrogen on the surface of CNTs (up to 4.8% of N determined by XPS), particularly as pyridinic and pyrrolic structures and in lower content some quaternary nitrogen, without significant changes of the BET surface area, or addition of O-functionalities, as confirmed by the low oxygen content determined by XPS. The mechanical treatment markedly reduced the entanglement of the CNTs, also leading to shorter CNT by breaking up the tubes, without affecting the tube diameters [43].

Figure 3 presents photos of the bare and coated monoliths. As can be seen by the dark colour of the coated monolith, a thin and uniform layer of the N@CNT sample can be achieved. The increase of the monolith weight suggested the immobilization of around 0.03 g of N@CNT+ “glue”. Furthermore, the coating is well attached to the support, with a weight loss lower than 1% after adhesion tests performed with ethanol and under sonication.

Table 1 Chemical and textural characterization of original and N-doped samples

Sample	S_{BET} (m^2 g^{-1})	Vp, $_{P/P_0=0.95}$ (cm^3 g^{-1})	N^{EA} (% wt)	N^{XPS} (% wt)	O^{XPS} (% wt)	$Volatiles^{TGA}$ (% wt)	Ash^{TGA} (% wt)
p-CNT	291	1.10	–	–	1.3	1.8	3.1
N@CNT	355	0.87	7.6	4.8	0.9	8.6	0.6

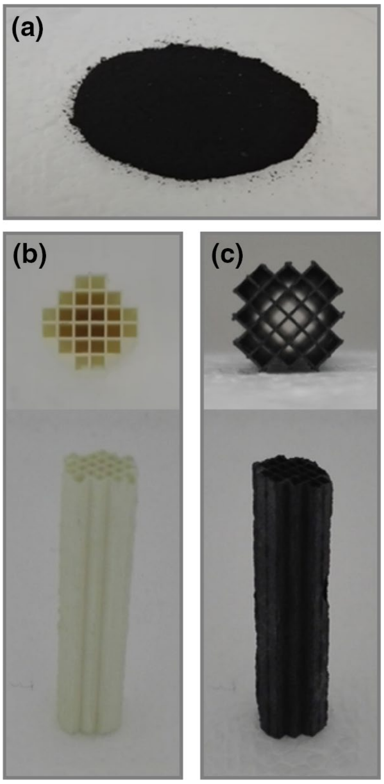

Fig. 3 Selected photographs of **a** N-doped carbon nanotubes in powder form, **b** bare cordierite monolith and **c** coated monolith with N-doped carbon nanotubes

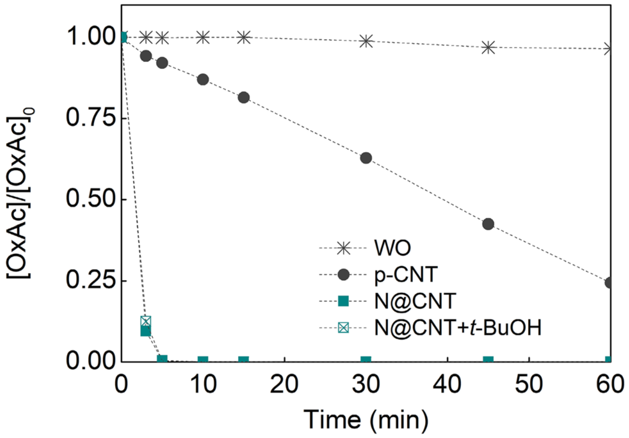

Fig. 4 Evolution of normalized oxalic acid concentration under non-catalytic conditions (WAO) and in catalytic experiments using pristine and N-doped carbon nanotubes in batch mode [T = 140 °C; P_T = 40 bar (7 bar of oxygen); 0.05 g of catalyst]

3.1.1 Catalytic Performance

In the present work, the catalytic activity of the CNT samples in powder form and deposited over cordierite monoliths was evaluated in the oxidation of oxalic acid by CWO in batch and continuous operating mode.

3.1.2 Catalytic Activity in Batch Mode

Oxalic acid is poorly oxidized under the operating conditions employed in the absence of a catalyst (Fig. 4, curve WO), demonstrating its refractory nature. The use of p-CNT and N@CNT samples significantly improves conversion of the acid; however, no complete oxalic acid oxidation could be achieved using the undoped CNTs. In contrast, the N@CNT sample requires only 5 min of reaction to reach complete oxidation of oxalic acid. No by-products were detected by HPLC, suggesting the selective mineralization of the acid into CO_2. The results obtained under inert atmosphere (adsorption experiment, not shown) were similar to those obtained in non-catalytic conditions. Therefore, in addition to the thermal stability of oxalic acid under the studied operating conditions, the contribution from adsorption to the removal rate can be neglected.

The tested carbon catalysts present strongly distinct surface natures, which directly affect the catalytic activity. The p-CNT sample, even without *N* heteroatoms or any supported metal, shows a reasonable ability to promote the oxidation of oxalic acid. In a previous work, where a higher catalyst load had been applied at the same operating conditions [12], the p-CNT allowed to reach full conversion of oxalic acid in 30 min. This catalytic activity can be explained by the presence of π electrons on the surface of the carbon material, which are known to be active sites for the formation of radicals [49]. However, an outstandingly better performance was achieved using the N-doped sample N@CNT. The N-functionalities on the CNTs provide extra delocalized electrons to the graphitic structure, being possible to promote the chemisorption [50] and activation of oxygen molecules [51].

It is generally accepted that the oxidizing ability of WO is based on the high solubility of oxygen at these severe conditions and the high temperature that increases the reaction rates and production of oxygen free radicals [4]. For many years, it has been accepted that the process involves a chain reaction mechanism in which oxygen and hydroxyl (HO·), hydroperoxyl (HO_2·), organic hydroperoxyl [4, 5], free radicals and oxyradicals [5] actively participate in the reaction. When catalysts are employed in the WO system, it is postulated that the catalyst plays three roles that enhance the wet oxidation process: oxygen activation, radical generation and organic oxidation. Since carbon materials have been introduced as catalysts in CWO, the most sophisticated kinetic studies take into account the heterogeneous nature of solid catalysed oxidation reactions involving adsorption of reactants, surface reaction and desorption of products [52].

In spite of all the studies already published regarding the use of carbon materials as catalysts in CWO, the reaction pathways involved in those reactions are still in doubt. Despite of their complexity, it is generally accepted that: (a) the reaction mechanisms involve free radicals; (b) basic carbons perform better than acidic ones; (c) oxidation of the organic compounds may occur both in the liquid phase (homogeneous reaction) and on the catalyst surface [53].

The difficulty in clarifying the mechanism is strictly related to the difficult identification and quantification of the radicals involved. In addition, it is also difficult to isolate potential active sites in order to assess their participation in the reaction pathway. Although numerous researchers have proposed that oxidation occurs mostly via free-radical chemical reactions, only a few have provided direct experimental evidence to support these claims. The severe operating conditions used, the instability of free-radicals and the experimental difficulties in determining the presence of such species in the reaction medium are some of the reasons that prevent their unequivocal identification [6]. Some studies provided indirect evidence of free radical reactions. The indirect method involves the use of compounds known to inhibit free-radical reactions, *tert*-butanol (*t*-BuOH) being the most common radical scavenger used. *t*-BuOH can scavenge the hydroxyl radicals in competition with other compounds in liquid phase [54, 55], decreasing the removal rate of these organic compounds [56, 57]. For phenol [58] and p-toluenesulphonic acid [56], it was found that the rate of oxidation decreased in the presence of the radical scavenger, indicating that a free-radical reaction was taking place.

To clarify the role of the free radicals on the mechanism of CWO using the N@CNT sample, this indirect method was applied. The oxidation of oxalic acid was evaluated in the presence of t-BuOH with a concentration ten times higher than the model pollutant (curve N@CNT + *t*-BuOH, Fig. 4). The results obtained in the presence or absence of *t*-BuOH are identical, suggesting that hydroxyl radicals in the liquid phase are not needed for oxalic acid degradation, and suggesting that an alternative surface reaction mechanism is taking place for oxidation of this organic compound.

In the presence of N-functionalities, particularly N-groups with delocalized extra electrons, such as the pyridinic group, an electron donation effect resulting from the unshared electron pair may enhance the adsorption of oxygen originating highly reactive oxygen species [59], without sacrificing the aromaticity of the molecule or the basal plane. 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, as schematically illustrated in Fig. 5.

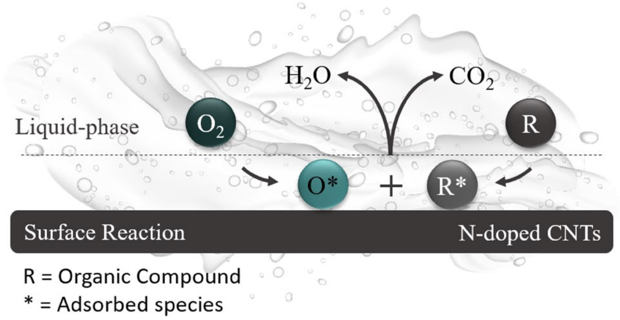

Fig. 5 Scheme of the reactions that might occur between the surface of CNTs and oxygen as oxidizing agent during CWO experiments

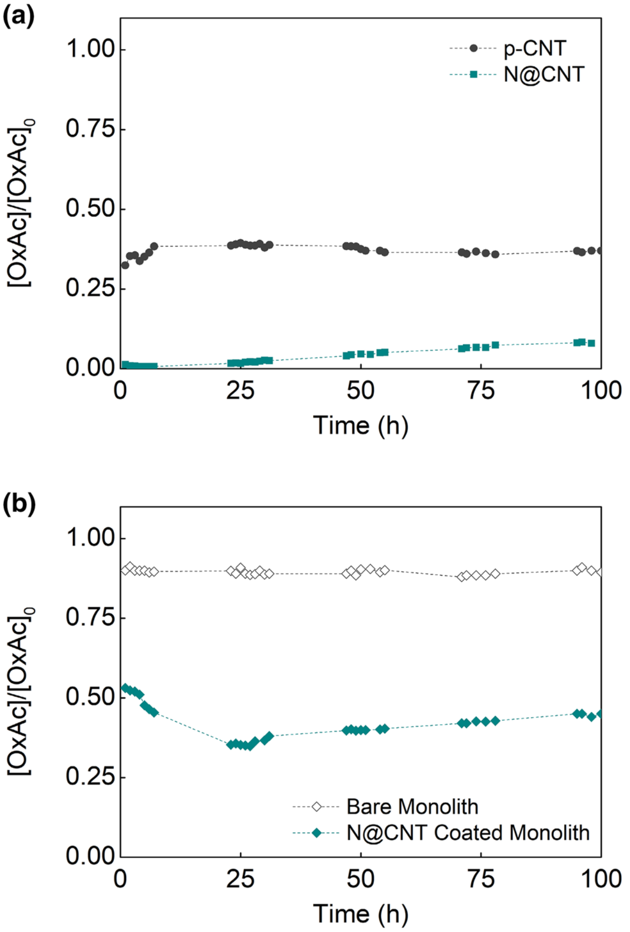

Fig. 6 Evolution of normalized oxalic acid concentration **a** using pristine and N-doped carbon nanotubes in powder form (0.06 g of catalyst) and **b** using bare monolith and N-doped carbon nanotubes coated monolith in continuous mode [T = 140 °C; P_{O_2} = 8 bar]

3.2 Catalytic Activity in Continuous Mode

The activity of the p-CNT and N@CNT catalysts was also studied in continuous CWO of oxalic acid (Fig. 6a). The experimental conditions in the continuous mode were slightly different from the batch experiments, particularly regarding the operating pressure (8 bar of pure oxygen instead of 40 bar of air, which corresponds to 7 bar of O_2 partial pressure in batch mode). This is not expected to have a large influence on the oxidation rate, small variations in the oxygen partial pressure were found to have a negligible influence in the oxidation reaction [15].

Both the p-CNT and N@CNT catalysts showed high activity for the oxidation of oxalic acid in continuous operation (Fig. 6a); however, the activity of the N-doped sample is significantly higher, achieving more than 90% conversion of oxalic acid in the steady state, compared to around 60% removal with p-CNT. Once again, this shows the positive effect of the N-functionalities on the activity of the carbon nanotubes. No byproducts were detected by HPLC, showing the selective conversion of oxalic acid to CO_2. The catalysts presented high stability, maintaining the conversions mentioned for 100 h of reaction, which is important when considering a real scale application. Comparing the N-doped catalysts in batch and continuous modes, and considering that the contact time between the contaminated effluent and the catalyst in continuous mode is around 6 min, it may be concluded that the performance of the continuous reaction is lower (92% conversion in the steady state) compared to complete removal in batch mode. This can be due to several factors, such as mass transfer limitations, preferential flow paths, as well as the inefficient wetting of the catalyst in the continuous mode reactor [60], which lead to a lower performance.

The N-doped catalyst was incorporated in a cordierite monolith to overcome some of the drawbacks related to the utilization of powdered catalysts in real scale applications. Figure 6b shows the results obtained with the structured catalyst. An experiment with a bare monolith (without incorporation of the active phase, but submitted to a thermal treatment at 900 °C to remove impurities) was also performed to assess the influence of the honeycomb cordierite monolith in the conversions obtained. The removal of oxalic acid is low in the presence of the bare monolith; however, using the N@CNT coated monolith, an oxalic acid removal around 55% in the steady state was achieved. This conversion was significantly lower than that obtained with N@CNT in powder form. This result can be ascribed to two main reasons: (1) not all of the material incorporated on the monolith consists of N@CNT—i.e. the material resulting from the binding solution used is also present in the monolith and, therefore, the available carbon material is not the same in the powder and in the structured catalyst; (2) the higher temperature used in the last thermal treatment of the monolith (900 °C compared to a final treatment at 600 °C for the powdered catalyst) can remove part of the N-functionalities [40], decreasing the activity of the catalyst. However, if this last treatment is performed at 600 °C, the performance of the monolithic catalyst becomes unstable, with the oxalic acid conversion decreasing significantly and the TOC value increasing to values higher than those of the initial solution ($1000\ \mathrm{mg\ L^{-1}}$ of oxalic acid) (results not shown), which may result from the release of carbon material that was not fully stabilized by the heat treatment during synthesis.

Both N@CNT in powder and N@CNT coated monoliths seem to suffer some deactivation during the reaction. This can be explained by an effect commonly observed when carbon materials are used in CWO, which may introduce some acidic groups on the surface, which are known to have a negative effect on the catalytic performance of carbon materials in this reaction [12, 18]. However, it is important to note that the catalyst after reaction can be almost completely regenerated by a simple thermal treatment, as shown in one of our previous studies [15].

Further optimization of the monolith (temperature of the final thermal treatment and the amount of active phase and of the other compounds in the impregnation solution) is being carried out to increase its performance for CWO reactions. Nevertheless, high activities were obtained considering that only a small amount of catalyst was used (around 60 mg) for a fairly high amount of oxalic acid ($1000\ \mathrm{mg\ L^{-1}}$), achieving a normalized oxalic acid removal per gram of material incorporated, in the steady state, of approximately $9100\ \mathrm{mg_{oxalic\ acid}\ L^{-1}\ g_{material\ incorporated}}^{-1}$.

To the best of our knowledge, no other studies on the application of monoliths coated with functionalized carbon nanotubes for the oxidation of organic compounds by CWO have been published. In addition, taking into account the promising results obtained, this work will be the first step in a larger research effort to improve the performance of such structured catalysts. Fluidodynamic characterization of the system using the coated monoliths will be carried out and investigated in future works to access the best operating parameters, including the optimization of hydraulic regime inside the monoliths channels.

4 Conclusions

Looking for alternatives to replace noble metals and metal oxide catalysts, traditionally used in the CWO process, the present work discloses the potentialities of N-doped carbon nanotubes as metal-free catalysts in oxalic acid oxidation. The presence of nitrogen groups on the carbon surface leads to the fast removal of oxalic acid under batch mode, but also proved to be able to oxidize the model pollutant under continuous operation. A coated macroscopic support (a cordierite monolith) was prepared and also tested as an alternative to overcome the drawbacks of using catalysts in powder form in industrial applications. Around 55% of conversion of oxalic acid was obtained in the steady state, in spite of the low content of the carbon material immobilized onto the monolith.

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