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Nitrogen-doped carbon xerogels as catalysts for advanced oxidation processes

R.P. Rocha, J. Restivo, J.P.S. Sousa, J.J.M. Órfão, M.F.R. Pereira, J.L. Figueiredo*

Laboratory of Catalysis and Materials - Associate Laboratory LSRE/LCM, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

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ABSTRACT

Nitrogen-doped carbon xerogels were tested as metal-free catalysts for the mineralization of oxalic acid by ozonation and by wet air oxidation. Oxalic acid was completely mineralized in less than 45 min in wet air oxidation, but complete conversion was never achieved with ozone. Some general trends were observed, and correlations between the catalytic activity and the surface chemistry of the carbon materials were established. In particular, the apparent reaction rate constants for both processes correlate with the concentration of surface nitrogen. The effect of N-doping is particularly effective in CWAO, the rate constants increasing by two orders of magnitude in comparison with the nitrogen-free material. With ozone, oxidation of oxalic acid may occur both in the liquid phase (homogeneous reaction) and on the catalyst surface, while wet air oxidation appears to proceed mainly on the carbon surface.

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1. Introduction

Advanced oxidation processes (AOPs) are a group of technologies designed to remove organic contaminants from water and wastewater by oxidation through reactions involving hydroxyl (or other highly reactive) radicals generated from different oxidants, such as oxygen (wet air oxidation), hydrogen peroxide (wet peroxide oxidation) and ozone (ozonation). These processes may be used upstream of conventional biological treatments to remove toxic or biologically non-degradable compounds, or downstream, as a polishing treatment.

Both homogeneous and heterogeneous catalysts, including supported metals and metal oxides, can be used to enhance the efficiency of these AOPs, and notably to decrease the severity of the operating conditions required in the case of wet air oxidation (200–320 °C and 20–200 bar) [1]. In addition, even if molecular ozone can be used for degradation of organic matter at room temperature and pressure in non-catalytic conditions, it presents low reactivity towards certain types of recalcitrant compounds and full mineralization cannot be achieved, a catalyst being then required to promote the generation of highly reactive radicals [2].

Homogeneous catalysts are usually avoided because they have to be separated from the treated effluent, while deactivation

phenomena, in particular leaching of active metals to the liquid phase, severely limit the efficiency of the heterogeneous catalytic processes. Using metal-free carbon materials as catalysts becomes an interesting option in this context, not only to avoid the lixiviation of metals, but also because carbon materials are stable both in acidic and alkaline media, and their texture and surface chemistry can be easily modified in order to provide adequate active sites for the reactions [3–6].

Activated carbons [2,7–11], carbon xerogels and ordered mesoporous carbons [12,13], carbon nanotubes [14–19] and other carbon materials [20–22] have been successfully used for the oxidation of organic compounds in catalytic wet air oxidation (CWAO), catalytic wet peroxide oxidation (CWPO) and catalytic ozonation.

A rewarding methodology consists in testing carbon materials with similar textural properties and different surface chemistries. Oxidation treatments in the liquid or gas phase can be used to introduce surface oxygenated groups such as carboxylic acids and anhydrides, lactones, phenol and carbonyl groups. Thermal treatments under inert atmosphere can then be used to remove selectively the most labile groups. By controlling the temperature and duration of the treatment, samples with different amounts of surface groups can be obtained, while keeping the textural properties essentially unchanged [23]. Most of the oxygenated groups are acidic; therefore, basic carbons can be obtained by heat treatments at high temperatures.

In general, some common features are observed when carbon materials are used as catalysts in the three AOPs mentioned: (i)

* Corresponding author.

E-mail address: jfig@fe.up.pt (J.L. Figueiredo).

oxidation of the organic compounds occurs both in the liquid phase (homogeneous reaction) and on the catalyst surface; (ii) free radical species are involved in the mechanism; (iii) basic carbons are generally the best catalysts. In particular, correlations between the catalytic activity and the surface chemistry of the carbon materials were established [15,24–26], showing that conversions increase with the pH at the point of zero charge (pH_{PZC}).

The presence of surface nitrogen groups is also extremely important for the catalytic applications of carbon materials. The additional electrons provided by nitrogen increase surface basicity. Moreover, electrons may be transferred from the surface to adsorbed oxygen, leading to the formation of highly reactive radicals in the presence of water [27]. Nitrogen groups can be formed by carbonization of nitrogen-containing precursors, or by reaction of the carbon material with a suitable nitrogen compound.

Various types of carbon materials with incorporated nitrogen (carbon foams and fibers, carbon nanotubes and nanofibers, and activated carbons) have been tested in CWAO [14,28–30] and in catalytic ozonation [31,32]. Comparison of reported results is difficult, due to the wide differences in morphology, textural properties and amounts of impurities in these materials (for instance, activated carbons may contain significant amounts of transition metals, which may act as catalysts in AOPs). A more systematic approach is required in order to assess the effect of nitrogen on the performance of carbon materials in these AOPs. Carbon xerogels are interesting materials for this purpose, as they offer the possibility of tuning their textural properties by adequate selection of the synthesis parameters [33], and can be easily doped with nitrogen by incorporation of a nitrogen precursor during the synthesis [34,35]. Moreover, the synthesis does not involve contact with any transition metals.

Therefore, N-doped carbon xerogels were synthesized from resorcinol, formaldehyde and melamine or urea as nitrogen sources. In this way, carbon materials free from any transition metal contamination and with different nitrogen contents were obtained and subsequently tested as catalysts in the oxidation of oxalic acid by CWAO and ozonation.

2. Experimental

2.1. Materials

A series of nitrogen-doped carbon xerogels was prepared as described elsewhere [36]. In brief, a gel was prepared using resorcinol and formaldehyde, together with a nitrogen precursor, either urea or melamine. Before gelation, the pH of the solution was adjusted to the desired value (5.3, 6.0, or 6.9). Afterwards, the gels were carbonized at different temperatures under nitrogen flow (500, 700 or 900 °C). The materials prepared with urea were named CXU, and those prepared with melamine were named CXM, followed by the pH of the solution prior to gelation, and the carbonization temperature.

The carbon xerogel samples selected for the present work were CXM_6.9_700, CXM_6.9_900, and CXU_6.9_700, since they have relatively similar textural properties and different types and amounts of nitrogen surface groups. In addition, a carbon xerogel sample without nitrogen was prepared from resorcinol and formaldehyde at pH 6.9, and carbonized at 500 °C (CX_6.9_500).

2.2. Catalyst characterization

The textural characterization of the materials was based on the N_2 adsorption isotherms determined at -196 °C with a Quantachrome Nova 4200e apparatus. The nature and amounts of the surface oxygenated groups were determined by temperature

programmed desorption (TPD), carried out in an Altamira Instruments AMI-200 apparatus. The pH at the point of zero charge was measured by analysis of the pH change of NaCl solutions of different initial values of pH when exposed to a sample of the prepared materials. Elemental analysis was performed on a Carlo Erba instrument, model EA 1108. Additional details can be found in reference [36]. The XPS analysis of the CX samples after oxidation reactions was performed using a Kratos AXIS Ultra HSA, with VISION software for data acquisition and CASAXPS software for data analysis. The analysis was carried out with a monochromatic Al K α X-ray source (1486.7 eV), operating at 15 kV (90 W), in FAT mode (Fixed Analyser Transmission), with a pass energy of 40 eV for regions of interest and 80 eV for survey.

2.3. Experimental procedure

Oxalic acid was used as a model compound due to its refractory nature to direct oxidation by dissolved molecular ozone, and to its common presence as an accumulated final product in several processes of oxidation of organic pollutants [37].

Ozonation experiments were performed at room temperature and pressure in a stirred semi-batch tank reactor. A volume of 700 mL of solution was used, consisting of a 90 mg L $^{-1}$ solution of oxalic acid prepared with milliQ ultrapure water. Ozone generated from pure oxygen using a BMT 802X ozone generator was bubbled into the bulk of the solution using a diffusor (total flow rate = 150 cm 3 min $^{-1}$; ozone concentration = 50 g m $^{-3}$). Ozone in the gas phase was monitored using a BMT 964 ozone analyser. The powdered catalysts (100 mg, particle size between 0.1 and 0.3 mm) were introduced into the solution before starting gas flow admission and kept in suspension by stirring at 200 rpm. Blank (no catalyst) and adsorption (no ozone) tests were also performed. In the adsorption experiment, pure oxygen was kept flowing to maintain the mixing conditions of the ozonation tests. The ozonation reactions were carried out at the natural pH of the oxalic acid solution (around 3), no buffer being added. The homogeneous decomposition of ozone into hydroxyl radicals is not expected at this pH [37].

CWAO experiments with oxalic acid were performed in a 160 mL 316-SS high pressure batch reactor housing a glass liner (Parr Instruments, USA Mod. 4564). 50 mg of catalyst with a particle size between 0.2 and 0.3 mm were added to 75 mL of a 1000 mg L $^{-1}$ solution and placed into the reactor. The reactor was flushed with pure nitrogen till complete removal of oxygen, pressurized with 5 bar of nitrogen and then pre-heated up to the desired temperature (140 °C) under continuous stirring at 500 rpm in order to ensure proper mass transfer of oxygen in the liquid phase [12,38]. 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 oxygen partial pressure), this being considered time zero for the reaction. In addition, non-catalytic wet air oxidation (WAO) and adsorption experiments (absence of oxygen, 40 bar of N_2) were carried out.

Reutilization tests were carried out with the CX sample showing the best performance, in order to evaluate the stability of the catalyst in both processes. The catalyst was recovered at the end of each run, washed with distilled water and dried at 110 °C. It was then tested for a second time using fresh oxalic acid solutions. The same procedure was repeated before testing the sample in a third run. In order to obtain additional mechanistic information, both CWAO and catalytic ozonation experiments were performed with the best CX sample in the presence of the radical scavenger *tert*-butanol (*t*-BuOH) with a concentration ten times higher than oxalic acid.

Reproducibility tests showed relative errors lower than $\pm 5\%$.

Table 1

Relevant textural and chemical properties of the carbon xerogels tested in the catalytic ozonation and CWAO of oxalic acid.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	S_{meso} ($\text{m}^2 \text{g}^{-1}$)	N_{EA} (% wt.)	CO ($\mu\text{mol g}^{-1}$)	CO ₂ ($\mu\text{mol g}^{-1}$)	pH _{pzc}
CXM.6.9.700	287	0.10	35	4.0	454	489	7.1
CXM.6.9.900	331	0.07	156	3.6	395	169	7.6
CXU.6.9.700	461	0.12	122	2.9	1292	579	7.4
CX.6.9.500	486	0.10	174	–	1226	444	7.0

N_{EA} : Total nitrogen content determined by elemental analysis; CO: amount of CO released during TPD; CO₂: amount of CO₂ released during TPD; pH_{pzc}: pH at the point of zero charge.

2.4. Analytical techniques

Samples periodically withdrawn from the reactors were analysed by high performance liquid chromatography (HPLC) with a Hitachi Elite LaChrom system equipped with a Diode Array Detector (L-2450). In the ozonation experiments, the concentration of oxalic acid in solution was determined with an Alltech OA-1000 chromatography column using an isocratic 5 mM H₂SO₄ mobile phase at 0.5 mL min⁻¹. Quantification of the organic acid was made at 200 nm. A Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm) and a sulphuric acid solution (4 mM) at a flow rate of 0.6 mL min⁻¹ (as mobile phase) were used for the determination of oxalic acid concentration in the CWAO experiments. The quantification of oxalic acid was performed at $\lambda = 210$ nm, with a maximum relative standard deviation of $\pm 2\%$. The total organic carbon (TOC) was also determined using a Shimadzu TOC-5000A analyser.

3. Results and discussion

3.1. Characterization of carbon xerogel samples

The carbon xerogel samples used in the present work are described in Table 1, together with their relevant properties. More detailed characterization can be found elsewhere [36]. It is worth noting that the different parameters used in the preparation method (nitrogen precursor, pH, and carbonization temperature) resulted in carbon xerogels with different textural and surface chemical properties. The surface oxygenated groups were assessed by the amounts of CO and CO₂ released during the TPD experiments [23,39], which are shown in Table 1 together with the pH at the point of zero charge. XPS analysis revealed the presence of three nitrogen functionalities on the surface of the selected nitrogen-doped carbon xerogel samples: pyridine-like N atoms (N6, BE = 398.7 ± 0.3 eV), pyrrole-like N atoms (N5, BE = 400.3 ± 0.3 eV), and quaternary nitrogen (NQ, BE = 401.4 ± 0.5 eV). Due to the difficulty in distinguishing clearly the N5 and NQ components [30], we opted to give their total amount in Table 2. After ozonation, another peak appeared, corresponding to oxidized nitrogen (NX, BE = 402–405 eV).

3.2. Catalytic tests

3.2.1. Catalytic ozonation

The concentration profiles of oxalic acid during ozonation experiments using the selected samples of N-doped carbon xerogels are presented in Fig. 1a. Oxalic acid degradation during the

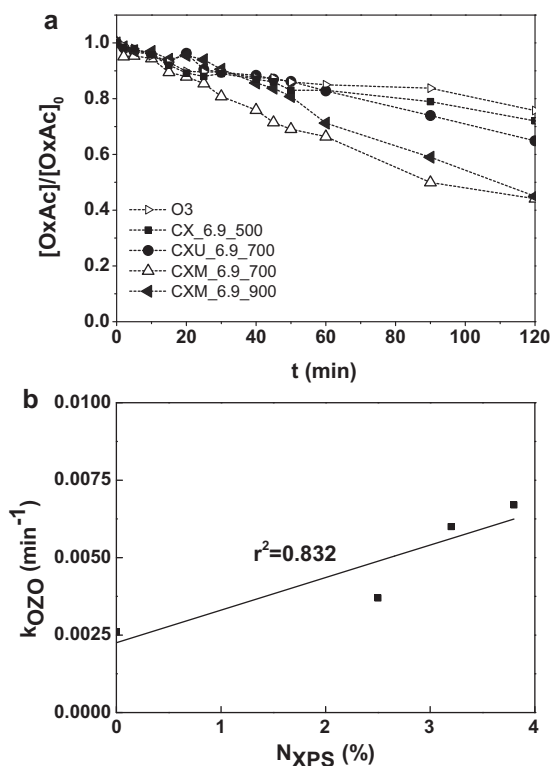


Fig. 1. (a) Evolution of the normalized oxalic acid concentration during catalytic ozonation experiments using N-doped carbon xerogels as catalysts; (b) Correlation between the first order apparent rate constant of oxalic acid removal by ozonation and the total amount of nitrogen determined by XPS.

catalytic ozonation process using carbon materials as catalysts is known to correlate well with the capacity of the materials to decompose ozone into more reactive species [15]. Thus, oxalic acid removal is a good indicator of the capacity of the materials to enhance the decomposition of dissolved molecular ozone. The HPLC separation method was calibrated for a series of carboxylic acids, including some possible by-products of oxalic acid degradation, but none were detected. So, the removal of oxalic acid corresponds to complete mineralization of the organic compound, as confirmed by measuring TOC values.

Fig. 1a shows that inclusion of a catalyst improves the removal of oxalic acid from solution when compared with the single ozonation experiment. The removal increased from 20% (without catalyst) to

Table 2

Apparent first-order reaction rate constants obtained using the N-doped CX samples in ozonation (k_{OZO}) and CWAO (k_{CWAO}) of oxalic acid, amounts of nitrogen-containing groups, and total oxygen contents determined by XPS.

Sample	k_{OZO} (min^{-1})	k_{CWAO} (min^{-1})	N6 (% wt.)	N5+NQ (% wt.)	O _{XPS} (%wt.)
CXM.6.9.700	0.0067	0.160	1.6	2.2	7.5
CXM.6.9.900	0.0060	0.125	1.4	1.9	6.0
CXU.6.9.700	0.0037	0.094	0.9	1.7	3.0
CX.6.9.500	0.0026	0.002	–	–	n.d.

around 55% with the best catalysts, after 120 min of reaction. The results show that carbon xerogels promote the formation of more reactive species from ozone, either in solution or on the surface of the catalyst [40]. Nevertheless, complete conversion of oxalic acid was never achieved up to the limit of the experiments (120 min). It is clear that these carbon xerogels do not perform as well as other carbon catalysts which have been previously tested in the same system: complete removal of oxalic acid was achieved after approximately 60 min of reaction with multi walled carbon nanotubes, using the same reaction system and operating conditions [15]; with activated carbons, the removal of oxalic acid was close to 70% after 120 min [37].

The apparent first-order reaction rate constants in ozonation (k_{O_3O}) of oxalic acid are listed in Table 2.

It is interesting to note that the performance of the catalysts is not significantly affected by the surface area (cf. Table 1). In fact, the sample which presents the largest surface area (sample CXU.6.9.700) performs worse than the remaining; while the sample with the smallest value of S_{BET} shows the best performance (sample CXM.6.9.700). In principle, the surface area should affect the amount of ozone decomposed [13,15,41–43], but in the present case the chemical properties are more important. A positive correlation was found between the first order reaction rate constant and the N content, as shown in Fig. 1b.

Correlations with the pH_{pzc} or with the surface oxygen content were previously reported [15,37,44–47]. However, one should note that the changes in the pH at the point of zero charge are not very drastic in the present case, and thus its influence is probably not noticeable. Nevertheless, the effect of the nitrogen functionalities is quite significant. These groups contribute with electrons to the π -electron system, increasing the electron density on the surface of the material, which favours the reduction of ozone due to its electrophilic properties [15,36,48,49]. Furthermore, it has been suggested that ozone may attack pyrrolic groups on the carbon surface, yielding the hydroperoxide radical, which would lead to the formation of other highly reactive species which greatly contribute to increase the removal rate of oxalic acid during ozonation [43,50].

Further experiments were performed with *t*-BuOH as a radical scavenger using the most active sample as catalyst, in order to provide further insights into the reaction mechanism. *t*-BuOH is a well-known hydroxyl radical scavenger [51], reacting rapidly with hydroxyl radicals in the liquid phase [52]. The performance of the catalyst is shown in Fig. 2a, together with the corresponding adsorption experiment, using the same carbon xerogel sample.

It is clear that the extent of adsorption of oxalic acid on the catalyst is not significant when compared with the removals obtained during the catalytic ozonation experiments. A decrease in the removal of oxalic acid of approximately 15% after 120 min is observed when *t*-BuOH is used as a radical scavenger. Such behaviour suggests that the production of radicals in the liquid phase plays only a secondary role in the catalytic ozonation using N-containing carbon xerogels. Recycling experiments performed with the CXM.6.9.700 sample are presented in Fig. 2b. A slightly worse performance was observed when compared to the fresh sample; deactivation may be due to the oxidation of the carbon surface, as reported previously [15,42,48].

Post-reaction analysis of the CXM.6.9.700 sample by XPS (Fig. 3) showed a new peak, when compared with the fresh sample, with binding energy around 402.8 eV, which may be attributed to oxidized nitrogen species [27]. In addition, a large decrease was observed in the area of the N6 peak, corresponding to pyridine functionalities. In their work with ozone on activated carbons, Sánchez-Polo et al. observed that the surface pyridine groups were stable [43]. However, it is clear that the stability of the N6 group is lower in carbon xerogels. Nevertheless, rigorous quantification of the species found in the post-reaction samples was not

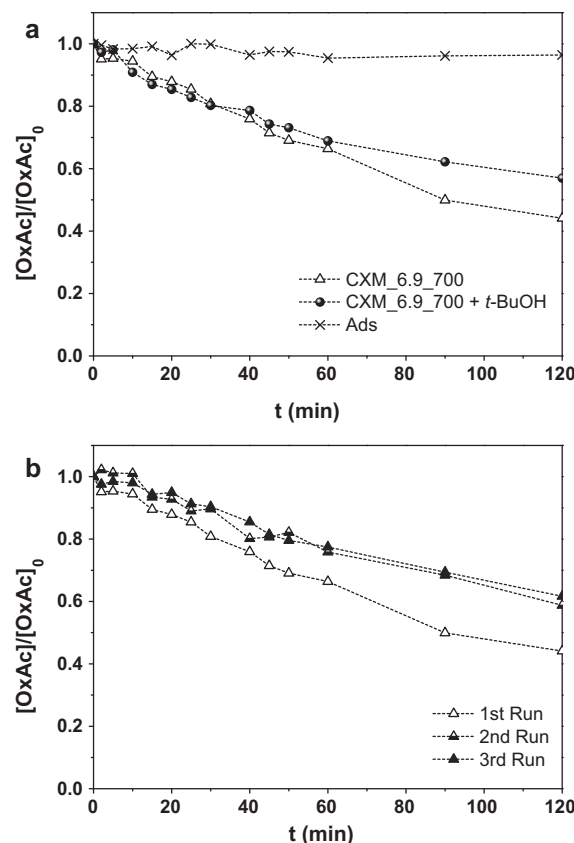


Fig. 2. (a) Evolution of the normalized oxalic acid concentration in catalytic ozonation experiments using the CXM.6.9.700 sample and in the presence of the radical scavenger *tert*-butanol (CXM.6.9.700 + *t*-BuOH), and in the adsorption experiment using CXM.6.9.700 under pure oxygen (Ads); (b) Evolution of the normalized oxalic acid concentration with CXM.6.9.700 in cyclic runs.

possible, due to the interference of the support used for XPS analysis of granulated samples, which did not form a uniform piece when mechanical pressure was applied.

The results support the idea that the enhanced catalytic ozonation with N-treated carbon xerogels is mostly due to the increase of the electronic density on the surface.

3.2.2. Catalytic wet air oxidation

Oxalic acid is poorly oxidized in the absence of a catalyst at 140 °C (WAO), and only 10% could be removed after 60 min with the undoped sample CX.6.9.500 (Fig. 4a). However, oxalic acid was completely degraded in less than 45 min in the presence of the N-doped carbon xerogels. In any case, oxalic acid is directly mineralized, because no by-products are detected by HPLC analysis and the TOC removal corresponds to the oxalic acid disappearance.

As shown in Table 1, the textural properties of the tested samples are not widely different, and no correlation was found between the catalytic activity and the surface area of these materials. The surface of the CX samples is essentially basic/neutral (pH_{pzc} between 7.0 and 7.6), indicating the absence of strong acidic groups. This observation is in agreement with the relevance that has been attributed to basic sites on the surface of carbon materials for CWAO [5], using carbon fibers enriched with nitrogen [28], activated carbon [7,53], and also carbon nanotubes [14,25].

The good catalytic performances obtained with the N-doped CXs in the degradation of oxalic acid by CWAO highlight the positive effect of the nitrogen groups. The amounts of surface nitrogen groups of the CXM and CXU samples, determined by XPS, are in the range of 2.6–3.8% (Table 2). Among the materials tested, the

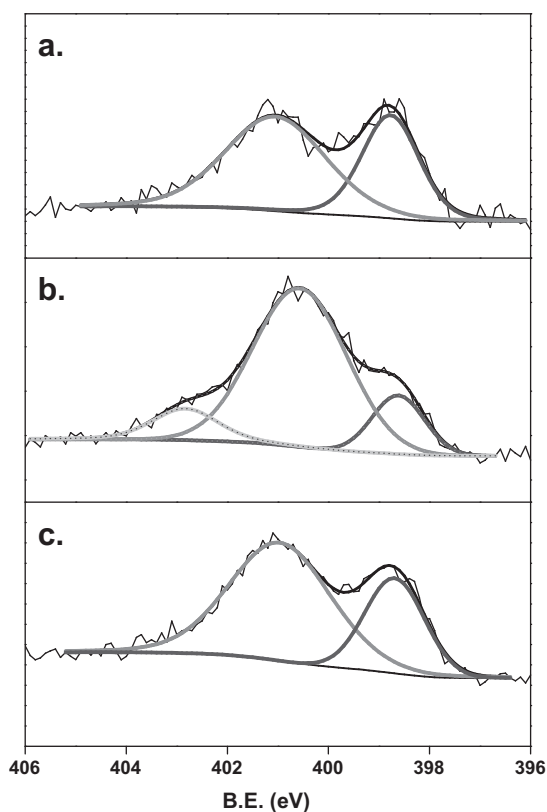


Fig. 3. N1s XPS spectra for the CXM.6.9.700 sample: (a) fresh (b) after catalytic ozonation; (c) after CWAO.

best performance was obtained with CXM.6.9.700, more than 90% of oxalic acid being converted in 15 min, while the conversions obtained with samples CXM.6.9.900 and CXU.6.9.700 were 85% and 76%, respectively.

The apparent reaction rate constants (k_{CWAO}) were determined assuming first-order kinetics (Table 2). According to the XPS results, the amount of nitrogen groups decreases as follows: CXM.6.9.700 > CXM.6.9.900 > CXU.6.9.700, which is exactly the sequence of the reaction rate constants. A strong positive correlation was observed between the apparent reaction rate constants and the total nitrogen contents determined by XPS, as shown in Fig. 4b.

In a previous work [28], a linear correlation was also found between the total organic carbon removal in aniline degradation by CWAO and the pyridinic-N group (N6) content of carbon fibers, indicating that the presence of these groups increases the catalytic efficiency. This was ascribed to the increased basicity of the carbon surface.

Comparing with published results, the nitrogen containing CX samples seem to be competitive with carbon nanotubes (CNTs) doped with nitrogen, which also completely oxidize oxalic acid under similar operating conditions (140 °C, 40 bar) in less than 30 min [14]: assuming first-order kinetics, the apparent initial reaction rate constant determined for the catalyst with the best performance (a nitrogen-doped carbon nanotube sample with low amount of O-containing surface groups) was 0.247 min^{-1} . However, a higher catalyst loading was applied (2.67 g L^{-1}), while only 0.67 g L^{-1} of catalyst was used in the present case. Oxalic acid was also completely degraded in less than 60 min using CNTs without strongly acidic O-containing groups or CNTs with sulphonic acid groups [25], but the amount of catalyst used in these experiments was four times higher than in the present work (0.200 against 0.050 mg).

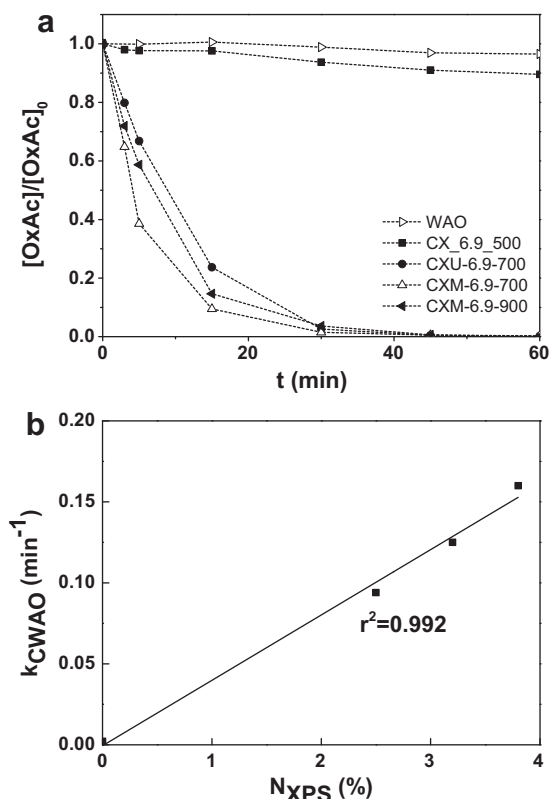


Fig. 4. (a) Evolution of the normalized oxalic acid concentration under non-catalytic conditions (WAO) and using the carbon xerogel samples as catalysts in CWAO; (b) Apparent first-order reaction rate constants (k_{CWAO}) vs. the total amount of nitrogen determined by XPS.

An experiment with the best catalyst (CXM.6.9.700) in the presence of the radical scavenger *t*-BuOH was also performed, in order to throw light on the reaction mechanism of oxalic acid degradation by CWAO. As mentioned above, *t*-BuOH can scavenge the hydroxyl radicals in liquid phase, decreasing the removal rate of the other compounds [54]. Even under severe conditions, as in CWAO experiments, the *t*-BuOH can scavenge the hydroxyl radicals in competition with other compounds [55].

As shown in Fig. 5a, the oxalic acid removed by adsorption after 60 min is less than 20%. Thus, it can be considered that most of the oxalic acid removal occurs by oxidation. The results obtained in the presence or absence of *t*-BuOH are identical, suggesting that hydroxyl radicals in the liquid phase are not needed, and that an alternative surface reaction mechanism is available for oxalic acid oxidation. Similar results were reported in a previous work [14].

In fact, the presence of nitrogen groups seems to favour the interaction of oxygen with the carbon surface [56]. The activation of oxygen by nitrogen groups to generate active oxygen species was reported in the case of an ammonia-treated activated carbon (AC) [29]. Such active oxygen species can react with adsorbed organic compounds leading to the oxidation of the organic pollutants. Nitrogen groups in AC with delocalized extra electrons were identified as the possible species responsible for the enhanced chemisorption [56] and activation of oxygen molecules [57].

A similar reaction pathway could be involved in oxalic acid degradation by CWAO. Oxygen and oxalic acid can be adsorbed on the carbon surface, oxygen being activated into reactive species that react with the adsorbed oxalic acid. Our results suggest that surface oxidation is the main mechanism for oxalic acid degradation in the presence of nitrogen-doped carbons.

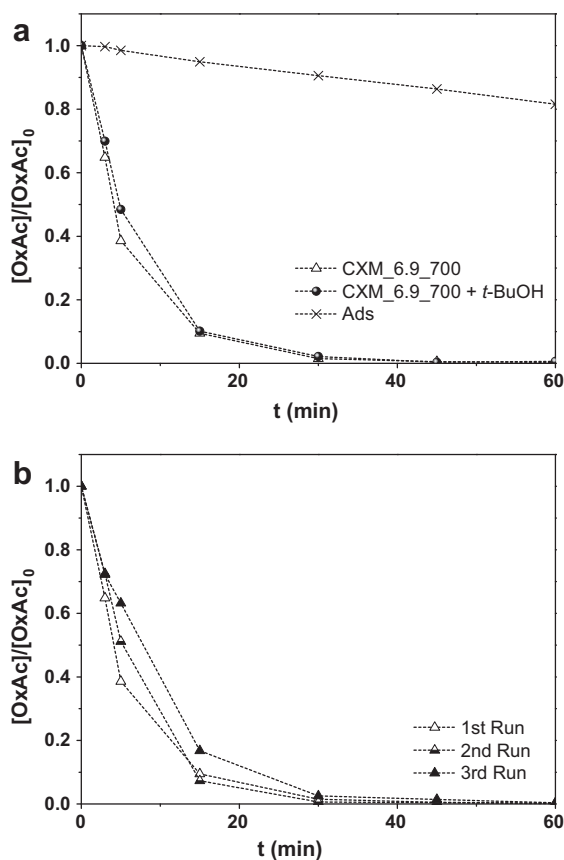


Fig. 5. (a) Evolution of the normalized oxalic acid concentration in CWAO experiments using the CXM.6.9.700 sample as catalyst and in the presence of the radical scavenger *tert*-butanol (CXM.6.9.700 + *t*-BuOH), and in the adsorption experiment using CXM.6.9.700 under pure nitrogen (Ads); (b) Evolution of the normalized oxalic acid concentration at 140 °C and 40 bar of total pressure for CWAO experiments with CXM.6.9.700 in cyclic runs.

In contrast with the results of the previous section (ozonation), XPS analysis of the CXM.6.9.700 sample after CWAO experiments did not reveal any significant alteration in the N1s spectrum (Fig. 3).

Cyclic experiments using sample CXM.6.9.700 were performed in order to assess the possible deactivation of the catalyst during CWAO. Fig. 5b shows that complete conversion of oxalic acid is obtained after 30 min of reaction in three successive runs. Very slight differences are observed in the course of the two first runs (about 90% of oxalic acid degradation in 15 min). However, the oxalic acid abatement in the same time was only 83% in the third run, which can be explained by changes in the surface chemistry of the carbon catalyst promoted by the oxidative conditions in the reactor. Indeed, using carbon nanotubes under similar operating conditions (140 °C and 40 bar of total pressure), we have observed that the pH_{pzc} decreased and the amount of CO_2 released by TPD increased upon successive utilization of the catalyst [14], indicating the formation of acidic groups on the surface, which have a negative influence on the catalytic activity of carbon materials for oxalic acid oxidation by CWAO [25].

4. Conclusions

Carbon xerogels prepared by the sol-gel process using melamine and urea as nitrogen precursors were tested as catalysts in the oxalic acid degradation by catalytic ozonation and by catalytic wet air oxidation. The selected samples have very small amounts of acidic surface groups (low amounts of CO_2 released in TPD), their pH_{pzc} being neutral or slightly basic, but they present

different types and amounts of nitrogen groups. The effect of these properties on the catalytic performance of the materials was evaluated.

In the ozonation experiments, despite the basic nature of their surface, the CXs underperformed when compared with other carbon based catalysts. In fact, complete conversion of oxalic acid was never achieved in the reaction times employed (120 min). However, a positive correlation was found between the removal rate and the surface nitrogen content.

Regarding the CWAO experiments, the N-doped CX samples showed high catalytic activity, oxalic acid being completely degraded in less than 45 min under the conditions tested. A strong positive correlation between the apparent reaction rate constant and the amount of nitrogen determined by XPS was also obtained. Therefore, N-doping improves the catalytic performance of the carbon xerogels in both liquid phase oxidation processes. However, the effect of nitrogen is much more evident in the case of CWAO, the rate constants increasing by two orders of magnitude in comparison with the nitrogen-free material. Moreover, experiments with a radical scavenger suggest that a surface reaction mechanism is the main pathway for the degradation of oxalic acid by CWAO.

Cyclic experiments showed a slight loss of performance, probably due to the oxidation of the carbon surface promoted by the operating conditions. This is more evident in the case of ozonation.

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