



Carbonized polyacrylonitrile fibers for the catalytic ozonation of oxalic acid



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ABSTRACT

Textile polyacrylonitrile (PAN) fibers, which contain nitrogen, were carbonized at different temperatures and activated during 10 h in order to assess their performance as ozonation catalysts in the oxalic acid degradation. The fiber carbonized at 800 °C shows the best performance due to its basic character and, mainly, the high concentration of nitrogen surface groups, particularly N-pyridinic (N6) groups. The carbonization of PAN fibers is a simple and effective method to prepare materials with good catalytic activity in ozonation processes.

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1. Introduction

Catalytic ozonation has emerged as a powerful treatment of water pollutants, even for refractory organic compounds. Carbon materials, such as activated carbon [1–15], carbon xerogels [16] and carbon nanotubes [17–22], have shown to be promising materials as ozonation catalysts. Some studies have reported that their textural properties and, mainly, the chemical surface properties play an important role in their performance as ozonation catalysts. In the case of the surface chemistry, it is well known that basic carbon materials favor the formation of hydroxyl radicals, which are species capable to quickly react with organic pollutants in solution [2,18]. Furthermore, the basicity of the carbon materials favors the adsorption of those organic compounds and their oxidation by surface reactions [2,4,18]. The basic character of the carbon materials is originated by a high density of π electrons on the basal planes. Therefore, this basicity could be promoted removing oxygenated electron-withdrawing groups and/or introducing some convenient functional groups, such as different nitrogenated groups (pyridines,

pyridones and pyrroles), which contribute to the increase of the electronic density on the material surface [23].

Nitrogen-containing groups can be introduced after preparation of carbon materials or during the material synthesis by several treatments. Among them, nitric acid oxidation, reaction of surface carboxyl groups with diamine compounds, and treatment at high temperatures with ammonia, ammonia-air, or ammonia-steam mixtures are commonly used [24]. Various types of carbon materials with incorporated nitrogen (carbon xerogels [25], carbon nanotubes [26] and activated carbons [27,28]) have been tested in catalytic ozonation. These studies have reported that the presence of nitrogenated groups on the surface of carbon materials improves their catalytic performance.

Adequate carbon materials having nitrogenated groups can be synthesized by carbonization of nitrogen-containing precursors, like polymers with nitrogen in their structure. This is the case of polyacrylonitrile (PAN) fibers, produced by polymerization from acrylonitrile and vinyl acetate monomers, which contain high amounts of nitrogen [29]. In this approach, chemical treatments for the introduction of nitrogenated groups are not required, decreasing the cost and time consumed for the synthesis of carbon materials enriched with nitrogen.

Therefore, this work aims to carbonize textile polyacrylonitrile fibers at different temperatures and expose them to 10 h of activation in order to test them as catalysts in the ozonation of oxalic

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acid, which is a common final oxidation product of several organic pollutants and is refractory to single ozonation.

2. Experimental

2.1. Preparation of materials

The materials to be used as ozonation catalysts were prepared from textile PAN fibers (FISIVON) supplied by FISIFE, Portugal, which were subsequently knitted in the facilities of the Technological Centre for the Textile and Clothing Industries of Portugal (CITEVE).

Pre-treatment of the fibers was carried out by heating 5 g of the original fibers up to 300 °C in a tubular reactor. A heating rate of 1 °C min⁻¹ under a constant air/N₂ flow of 85 cm³ min⁻¹ was used, and the final temperature was maintained for 2 h. The fibers were then carbonized by raising the temperature at 5 °C min⁻¹ up to the desired temperature (800, 850 or 900 °C), which was maintained for 1 h [30]. The study of the effect of the fiber activation in its performance as ozonation catalyst was carried out using the carbonized sample that presented the highest catalytic activity (i.e. carbonized at 800 °C). Thus, further activation was obtained by raising the temperature again at 15 °C min⁻¹ to 800 °C, but then switching the N₂ flow to a CO₂ flow for a specific time [29]. The reference given to each sample indicates carbon fiber (FI) as well as the respective carbonization temperature (800–900 °C) and activation time (0 or 10 h).

2.2. Characterization

The textural characterization of the materials, namely the Brunauer–Emmett–Teller (BET) surface area, was based on the N₂ adsorption isotherms, determined at –196 °C with a Quantachrome NOVA 4200e apparatus.

The surface chemistry of the prepared samples was characterized by temperature programmed desorption (TPD), in order to quantify the oxygenated groups [31], and by X-ray photoelectron spectroscopy (XPS). TPD analyses were performed in an AMI-200 (Altamira Instruments) apparatus. Helium was used as carrier gas (25 cm³ min⁻¹) and the temperature was programmed from room temperature to 1100 °C at a heating rate of 5 °C min⁻¹. The amounts of CO and CO₂ released from the samples were monitored with a Dymaxion mass spectrometer (Ametek Process Instruments). XPS analyses were performed in a Kratos AXIS Ultra HSA using 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.

Elemental analysis was performed in a Carlo Erba instrument, model EA 1108.

2.3. Kinetic experiments

The ozonation experiments were carried out in a laboratory scale reactor (ca. 1 L) equipped with agitation and a circulation jacket. Ozone was produced from pure oxygen in a BMT 802X ozone generator. The concentration of ozone in the gas phase was monitored with a BMT 964 ozone analyzer. Ozone leaving the reactor was removed in a series of gas washing bottles filled with potassium iodide (KI) solution. In each ozonation experiment the reactor was filled with 700 mL of a solution containing 1 mM of oxalic acid, at natural pH (approximately 3). Oxalic acid was purchased from Sigma–Aldrich. All solutions were prepared with ultrapure water with a resistivity of 18.2 m Ω cm at room temperature. In catalytic ozonation experiments, 100 mg of catalyst was introduced in the reactor. The experiments were performed at constant

Table 1
Textural properties of the prepared samples.

Sample	S _{BET} (m ² g ⁻¹)	V _{μpore} (cm ³ g ⁻¹)	S _{≠ μpore} (m ² g ⁻¹)
FI.800 °C.0 h	<0.5	–	–
FI.800 °C.10 h	117	0.050	20
FI.850 °C.0 h	<0.5	–	–
FI.900 °C.0 h	<0.5	–	–

gas flow rate (150 cm³ min⁻¹) and constant inlet ozone concentration (50 g m⁻³). The stirring rate was maintained constant at 200 rpm, in order to keep the reactor content perfectly mixed. For comparative purposes, adsorption experiments were performed in the same system, under identical conditions. All experiments were performed at room pressure and temperature. Samples for analysis were collected at selected times using a syringe and centrifuged. The experiments were carried out in duplicate and the maximum relative deviation obtained was 1%. The analytical measurements were also performed in duplicate with a maximum relative error of $\pm 0.5\%$. Concentration of oxalic acid was followed by HPLC, according to the procedure described in reference [18].

3. Results and discussion

3.1. Characterization of catalysts

The textural properties of the materials are shown in Table 1. The carbonized fibers have negligible surface areas regardless of the temperature used. However, activation has a strong impact on the textural properties. In fact, the activated sample presents a BET surface area of 117 m² g⁻¹.

XPS analysis was performed for all prepared materials in order to obtain additional information about the nature of the N bonding. According to the literature [30,32–34], the N1s XPS spectra can be decomposed in four peaks (1) at about 398 eV, attributed to pyridinic-N (N6); (2) between 400.0 and 400.9 eV, corresponding to pyrrolic-N or pyridone-N (N5); (3) in the range 401.4–401.7 eV, attributed to quaternary nitrogen (N-Q); and (4) between 402 and 403 eV, related to certain forms of oxidized nitrogen (N-X). However, in the XPS N1s spectra of all prepared samples only two peaks were found, as can be observed in Fig. 1. These peaks are associated to the presence of pyridinic groups (N6) and quaternary nitrogen (N-Q) on the fibers surface. The nitrogen contents obtained from the deconvolution of the XPS N1s spectra and from elemental analysis are presented in Table 2.

The original fiber has a large amount of nitrogen (24%) [30]. As expected, increasing the carbonization temperature, the bulk nitrogen amount (obtained from elemental analysis) decreases, as well as the total nitrogenated surface. Further activation also leads to a reduction of both bulk and surface nitrogen.

The amounts of CO and CO₂ released, obtained by integration of the areas under TPD profiles, the ratio CO/CO₂ and the mass percentage of oxygen (m_O%) on the surface of the carbon materials are shown in Table 2. For all the samples, the amount of CO-releasing groups is larger than the amount of groups which decompose into CO₂, indicating their basic character, which is in agreement with the respective pH_{pzc} values (between 7.2 and 8.5 for FI.800 °C.10 h and FI.850 °C.0 h, respectively), as reported in the literature [30]. As the temperatures used in the preparation of samples are higher or equal to 800 °C, the oxygenated surface groups present are mainly neutral and basic groups like carbonyls/quinones [31], which have a positive effect on the ozonation process [2,4,18]. The increase of carbonization temperatures or the activation lead to a decrease in the amount of CO-releasing groups.

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