Chemical Engineering Journal 293 (2016) 102–111

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Carbon nanofibers doped with nitrogen for the continuous catalytic ozonation of organic pollutants

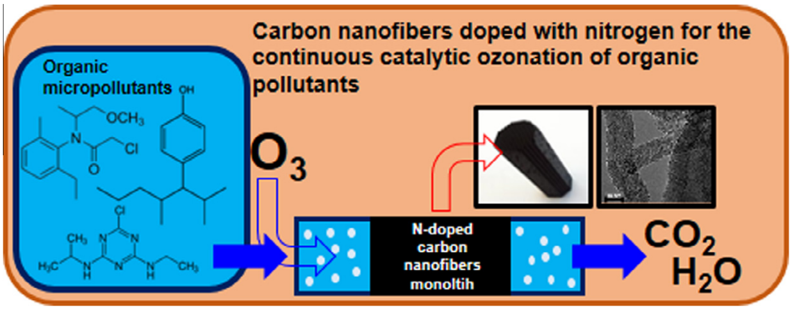
J. Restivo [a], E. Garcia-Bordejé [b], J.J.M. Órfão [a], M.F.R. Pereira [a],*

[a] Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE-LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465, Portugal
[b] Instituto de Carboquimica (ICB-C.S.I.C.), Miguel Luesma Castán 4, 50018 Zaragoza, Spain

HIGHLIGHTS

- Nitrogen-doped carbon nanofibers were prepared in powder and structured form.
- The role of nitrogen on the activity of the catalysts in ozonation was assessed.
- The degradation of model organic pollutants under continuous operation was investigated.
- The mineralization degree and the toxicity of the resulting effluents were evaluated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 October 2015
Received in revised form 7 February 2016
Accepted 17 February 2016
Available online 22 February 2016

Keywords:
Ozonation
Nitrogen-doped nanocarbons
Structured catalysts

ABSTRACT

Catalytic ozonation using carbon materials, in particular nanocarbons, has been appointed as an interesting alternative for the abatement of recalcitrant emerging organic pollutants. Efforts to achieve more efficient catalysts have been carried out, including carbon doping with heteroatoms. In this study, the effect of nitrogen doping of carbon nanofibers in their catalytic activity for the ozonation of organic pollutants was assessed. For this end, pristine and N-doped carbon nanofibers were prepared, both in powder and in structured forms. The former were tested in semi-batch ozonation experiments, while the latter were used in continuous ozonation experiments. It was observed that the presence of N-containing functionalities on the surface of the carbon nanofibers enhances their capability as catalysts for the studied reaction.

1. Introduction

Recent findings of the resistance of harmful products to conventional water treatments, as well as of the toxicity associated with the degradation products of these compounds, have led to a growing interest in the development of novel water treatment technologies that may efficiently remove recalcitrant emerging organic pollutants [1]. In particular, advanced oxidation processes such as catalytic ozonation have been shown to be an interesting method for the abatement of such pollutants [2–7].

Different materials have been used as catalysts for the ozonation process [8]. In particular, carbon materials such as activated carbons [9–11], multi-walled carbon nanotubes (MWCNTs) [12–16], carbon xerogels [17] and carbon nanofibers (CNFs) [18–21] have been shown to have the potential to be effective solutions.

The modification of the surface properties of carbon materials have been known to influence their catalytic properties [22,23]. In particular, the presence of surface heteroatoms, such as oxygen, sulfur and nitrogen, has been shown to significantly affect the

---

* Corresponding author.
E-mail address: fpereira@fe.up.pt (M.F.R. Pereira).

http://dx.doi.org/10.1016/j.cej.2016.02.055
1385-8947/

catalytic activity of carbon materials in catalytic ozonation [2,16,24–29].

The application of structured catalysts, in particular as honeycomb monoliths, has been appointed as an interesting alternative for the application of carbon materials as catalysts during the ozonation process [18–21].

In this work, a study of the influence of the presence of N-containing functionalities on the surface of CNFs was carried out. For this end, catalytic ozonation experiments were performed in semi-batch and continuous operation, using CNFs in powder form and in structured form, respectively. Oxalic acid and phenol were selected as model compounds, and further ahead atrazine, metolachlor and nonylphenol were used as model organic micropollutants.

2. Methods and materials

2.1. Preparation of catalysts

2.1.1. Powder carbon nanofibers

Carbon nanofibers in powder form were prepared using a 20% Ni on Al_2O_3 catalyst, which was previously reduced under H_2 at 550 °C. Carbon growth was carried out using a C_2H_6:H_2 (50:50) mixture at 600 °C. Nitrogen functionalities were introduced on the surface of the carbon nanofibers replacing H_2 by NH_3 during the growth phase. Both samples (without and with nitrogen, respectively CNF and N-CNF) were purified from the growth catalyst first under NaOH reflux at 80 °C for 4 h and later under HCl reflux at 100 °C for 4 h. After purification, less than 1 wt% residual catalyst remains on the carbon material.

2.1.2. Structured carbon nanofibers

A well attached layer of entangled CNFs was grown on the walls of cordierite monoliths as reported elsewhere [30]. In brief, cordierite monoliths (from Corning, 22 mm diameter, 60 mm length, 400 cpsi) were washcoated with alumina by a dip-coating method similar to the sol–gel coating described by Nijhuis et al. [31]. Nickel was deposited by adsorption from a pH-neutral nickel solution as described elsewhere [32]. To grow the CNFs, the Ni/alumina coated monolith was fitted in a quartz reactor by wrapping it in quartz band. The reduction of the calcined catalyst was carried out in a hydrogen atmosphere at 550 °C for 120 min (heating rate of 5 °C min^{-1}). The monolith was then heated (5 °C min^{-1}) to 600 °C. When this temperature was reached, 100 cm^3 (STP) min^{-1} of a C_2H_6:H_2 (50:50) gas mixture was fed. For N-doping of grown CNFs, H_2 was replaced by NH_3 in the gas feed [33]. The CNF growth was allowed to proceed for 2 h following up by cooling down under inert atmosphere.

2.2. Characterization of catalysts

The textural characterization of the prepared carbon nanofibers was carried out by N_2 physisorption at −196 °C using a Micromeritics ASAP 2020 apparatus, after outgassing for 4 h at 150 °C. The pore volume was calculated from the adsorbed amount at a relative pressure of 0.99. The specific surface area was calculated by the BET (Brunauer, Emmett and Teller) method in the relative pressure range 0.01–0.10 following the ASTM-4365 standard.

The nature of the N-containing functionalities introduced on the surface of the carbon nanofibers was characterized by XPS using a ESCAPlus Omnicrom equipped with a Mg Kα radiation source to excite the sample. Calibration of the instrument was performed with Ag 3d5/2 line at 368.27 eV. All measurements were performed under ultra-high vacuum better than 10^{-10} torr. Internal referencing of spectrometer energies was made using the C 1 s signal at 284.6 eV. The curve fitting of the spectra was performed using CASA XPS software after applying a Shirley baseline. For peak deconvolution, the full width at half maximum (FWHM) was fixed equal for all the peaks and with a maximum value of 2.5 eV.

SEM analysis was carried out with a microscope SEM EDX Hitachi S-3400 N with variable pressure up to 270 Pa and with an analyzer EDX Röntec XFlash of Si(Li). The samples were sputtered with gold previously to measurements. The images were obtained from the secondary electron signal.

HRTEM of was carried out using a FEI TECNAI F30 electron microscope equipped with Gatan Energy Filter and cold field emission gun (FEG) operated at 300 kV with 1.5 Å lattice resolution. TEM specimens were prepared by ultrasonic dispersion in ethanol and a drop of the suspension was applied to a holey carbon support grid.

Temperature programmed oxidation (TPO) was carried out in air using a SETARAM Setsys Evolution thermobalance under an air-flow of 100 cm^3 (STP) min^{-1} from room temperature to 800 °C at a heating rate of 10 °C min^{-1}.

2.3. Evaluation of catalysts

The prepared catalysts were evaluated in the catalytic ozonation of organic pollutants using two systems: a semi-batch system where the catalysts were used in powder form and a continuous ozonation system where the catalysts were used in their structured form. The powder samples are identified as CNF and N-CNF (without and with nitrogen, respectively), and the honeycomb monolith structured samples are identified as HM-CNF and HM-N-CNF (without and with nitrogen, respectively).

The selected organic pollutants included oxalic acid, phenol, atrazine (ATZ), metolachlor (MTLC) and nonylphenol (NLP).

The semi-batch ozonation experiments were carried out using a conventional stirred tank reactor. Ozone was produced from pure oxygen using a BMT 802N ozone generator, at 50 g m^{-3} (STP), and introduced into the reactor using a glass disperser at 150 cm^3 (STP) min^{-1}. A volume of 700 mL of solution containing the pollutants at the desired concentration was used, and the amount of powder catalyst used, when applicable, was 100 mg. The solution was kept homogeneously stirred using a magnetic stirrer at 200 rpm.

The continuous ozonation experiments were carried out using a bubble column containing an internal loop. Ozone was produced from pure oxygen using a BMT 802N ozone generator, at 50 g m^{-3} (STP), and introduced into the reactor using a glass disperser at the bottom of the bubble column at 20 cm^3 (STP) min^{-1}. The solution containing the selected pollutant was fed into the reaction system using a peristaltic pump at 12 mL min^{-1}, and the internal loop was kept flowing at all times at 60 mL min^{-1}. The structured catalysts were placed inside the bubble column, thus operating in a multiphase flow where the gas and liquid simultaneously contact with the solid phase. The reaction conditions were optimized to achieve homogeneous axial dispersion of the phases throughout the channels of the monoliths, and to allow the formation of Taylor flow, which is known to enhance the performance of such systems due to decreased mass transfer resistance [34].

The concentration of oxalic acid and other organic acids was followed using an Elite LaChrom HPLC coupled with a UV–vis detector. Separation was achieved using an Alltech OA-1000 chromatography column with a 5 mM H_2SO_4 mobile phase and detection was carried out at 200 nm. The concentrations of atrazine, metolachlor, nonylphenol and phenol were followed using an Elite LaChrom HPLC coupled with a DAD detector. Separation was achieved using a Lichrocart C18-RP Puroshper Star