



Modification of carbon nanotubes by ball-milling to be used as ozonation catalysts



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ABSTRACT

The influence of ball-milling in the texture and surface chemistry of multi-walled carbon nanotubes (MWCNT) was studied in this work. Treatment times up to 360 min at constant frequency (15 vibrations/s) and frequencies from 10 to 20 vibrations/s during 30 min were used for the preparation of the modified samples. These were characterized by nitrogen adsorption at -196°C , temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The milled samples were used as catalysts for the ozonation of oxalic acid. The surface area of the MWCNT increases, whereas the particle size decreases with the ball-milling time until 240 min at 15 vibrations/s. The functionalization of MWCNT surface is not achieved by ball-milling under the conditions used. The catalytic performance of the ball-milled samples for oxalic acid mineralization increased significantly when compared to the unmilled MWCNT. Therefore, ball-milling is an effective and simple method to increase the surface area of commercial carbon nanotubes without significant changes of their structural properties, and, consequently, this method allows increasing their catalytic performance in ozonation processes.

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1. Introduction

Carbon nanotubes (CNTs) have shown promising potential for application in many engineering fields, due to their particular electronic and physical properties [1]. The morphology of the CNTs is important for specific applications. For some electronic or structural applications, long CNTs are required to be used as strong and conducting nanocables. However, for many other applications such as chemical or energy-storage, it is desirable to have short nanotubes with open tips to enhance the active surface area and facilitate diffusion and chemical reactions [2]. Several methods have been used to obtain short and opened CNTs, including acid treatment, ultrasonication, scanning tunnelling microscope nanostructuring, lithographic methods and ball-milling. Among them, ball-milling have attracted much attention as a promising way for modifying

carbon nanotubes, namely to adjust lengths and open the closed ends [2–4]. However, the surface properties of the CNTs can be dependent on the opening methods. By ball-milling, multiwalled carbon nanotubes (MWCNT) can be transformed into curved nanotubes [5], nanoparticles [6], short and open-tipped nanotubes [4], but also in amorphous as well as disrupted tubular structure when prolonged ball-milling is applied [2,7]. Tucho et al. [3] studied the effect of ball-milling intensity on morphology of MWCNT and observed that open and short MWCNT can be generated by tuning ball-milling intensity.

Catalytic ozonation is an innovative technology for the removal of organic pollutants in water and wastewater. Ozone preferentially attacks molecules containing unsaturated bonds, leading to the formation of saturated compounds such as aldehydes, ketones and carboxylic acids. Due to their low reactivity towards ozone, these compounds tend to accumulate in water. Therefore, ozonation by itself is not sufficient to achieve a high mineralization degree. To overcome this drawback, ozonation processes are being modified in order to increase their oxidizing capability. Heterogeneous catalytic ozonation, which is one of the most attractive alternatives, aims to enhance the removal of highly refractory compounds by the

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transformation of ozone into more reactive species and/or adsorption and reaction of the pollutants on the surface of the catalyst [8].

Carbon nanotubes have been appointed as a very promising material for catalytic applications [1]. The interest in the use of this material in ozonation processes has been increasing recently due to the good results observed [9–12]. Samples of commercial MWCNT and carbon nanotubes functionalized by oxidation both in liquid and gas phase have proved to efficiently perform as ozonation catalysts [9–11,13–16]. In this work, the influence of the milling time on the MWCNT properties (texture, morphology, structure and surface chemistry) was investigated. Milled samples were used as catalysts for the ozonation of oxalic acid, which is the most common final oxidation product of a vast number of organic compounds and is refractory to single ozonation [8,17]. Moreover, it is a quite simple molecule and, therefore, it was chosen as a model compound for more detailed studies. The results were compared with those obtained in the presence of the pristine MWCNT sample, previously reported [11].

2. Experimental

2.1. Preparation of materials

A commercial multi-walled carbon nanotube (MWCNT) sample (Nanocyl 3100) was used as starting material. According to the supplier, these nanotubes have an average diameter of 9.5 nm, an average length of 1.5 μm and carbon purity higher than 95%. In order to obtain the modified samples, the commercial carbon nanotubes were ball milled in a Retsch MM200 equipment under different milling conditions. Times up to 360 min at constant vibration frequency (15 vibrations/s) and vibration frequencies from 10 to 20 vibrations/s during 30 min were used for the preparation of the modified samples (identification of the samples: BM.X.Y, where X is the time in minutes and Y is the frequency in vibrations/s).

2.2. Characterization of materials

The texture, morphology and surface chemistry of the samples were characterized by nitrogen adsorption, particle size distribution, transmission electron microscopy (TEM), temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS).

The textural characterization of the samples was based on the N_2 adsorption isotherms, determined at -196°C in a Quantachrome NOVA 4200e multistation apparatus. Samples were previously degassed at 150°C for 3 h.

The particle size distributions were measured in a Coulter LS 230 equipment.

High Resolution Transmission Electron Microscopy (HRTEM) measurements were performed on a JEOL2010F instrument; with 0.19 nm spatial resolution at Scherzer defocus conditions.

The surface chemistry was characterized by temperature programmed desorption (TPD) analysis. CO and CO_2 TPD profiles were obtained with a fully automated AMI 300 Catalyst characterization apparatus (Altamira Instruments) connected to a Dycor Dymaxion Mass Spectrometer. Each sample (0.100 g) was heated up to 1100°C at $5^\circ\text{C}/\text{min}$ using a constant flow rate of helium equal to $25\text{ cm}^3(\text{STP})/\text{min}$. For quantification of the CO and CO_2 released during the analyses, calibration of these gases was carried out at the end of each experiment.

The XPS analyses were performed using a Kratos AXIS Ultra HSA, with VISION software for data acquisition and CASAXPS software for data treatment. The analyses were carried out with a monochromatic Al $\text{K}\alpha$ X-ray source (1486.7 eV), operating at 15 kV (90 W),

in FAT (Fixed Analyser Transmission) mode, with a pass energy of 40 eV for regions ROI and 80 eV for survey. Data acquisition was performed at a pressure lower than 10^{-6} Pa, and a charge neutralization system was used. Modelling of the spectra was performed using the XPSPEAK4.1 program, in which the peaks were fitted with a Gaussian-Lorentzian function using a Shirley type background subtraction.

2.3. Catalytic tests

The ozonation experiments were carried out in a laboratory-scale reactor (ca. 1 L) equipped with stirring and a recirculation 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 analyser. Ozone leaving the reactor was removed in a series of gas-washing bottles filled with potassium iodide (KI) solution.

In each experiment the reactor was filled with 700 mL of oxalic acid solution with a concentration of 1 mM, at the natural pH (around 3). The solution was prepared from ultrapure water obtained in a Milli-Q Millipore system. In the catalytic ozonation experiments, 100 mg of MWCNT were introduced in the reactor. The experiments were performed at constant flow rate ($150\text{ cm}^3(\text{STP})/\text{min}$) and constant inlet ozone concentration ($50\text{ g}/\text{m}^3(\text{STP})$). The agitation was maintained constant at 200 rpm. Some experiments were performed in duplicate and the average deviations were lower than $\pm 2\%$.

For comparative purposes, both adsorption on selected samples and ozonation experiments in their absence (single ozonation) were performed in the same system, under identical experimental conditions.

Samples were collected using a syringe at selected times and centrifuged for further analysis. The concentration of oxalic acid was followed by HPLC using a Hitachi Elite LaChrom HPLC equipped with a diode array detector. The stationary phase was a BIO-RAD Aminex HPX 87H (300 mm \times 7.8 mm) working at room temperature. Analyses were carried out under isocratic elution with a solution of H_2SO_4 4 mM at a flow rate of 0.6 mL/min. The retention time for oxalic acid was 7.2 min and the wavelength of 210 nm was used for quantitative measurements. Six point calibration curves (0.05–1 mM) were considered. Linear responses were obtained in this range. The R^2 value of calibration line was 0.99989, the limit of quantification (LOQ) was 0.0097 mM and the limit of detection (LOD) was 0.00096 mM.

3. Results and discussion

3.1. Materials characterization

Fig. 1A shows that the pristine MWCNT are formed by well-defined graphitic layers. This sample is formed by several aggregates of tubes highly entangled, curved and twisted with each other (data not shown). This high entanglement was markedly reduced after ball-milling. Fig. 1B shows the evidences of CNT damage due to the ball-milling treatment, which gradually lead to shortened CNT with the increase of the ball-milling time by breaking up the tubes. Similar results were reported in the literature [18,19]. In addition, to clearly show that the ball-milling process is highly effective in disentangling and shortening MWCNT, TEM characterization demonstrate that open MWCNT are present in the samples obtained using high milling times (240 and 360 min).

The evolution of the surface area and particle size of the MWCNT samples with the ball-milling time, for the vibration frequency of 15 vibrations/s, is represented in Fig. 2. The surface area remains practically constant (within the experimental error) until 60 min,

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