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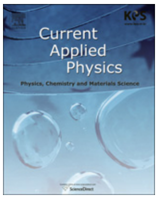

Correlation between carbon nanotube microstructure and their catalytic efficiency towards the p-coumaric acid degradation

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ABSTRACT

Pristine and annealed multi-walled C nanotubes are preliminarily tested as catalysts towards the degradation of p-coumaric acid with better performances than the widely used activated carbon. In order to clarify the origin of their different catalytic efficiency, the samples are analysed by means of high-resolution transmission electron microscopy, X-ray photoemission, reflection electron energy loss and micro-Raman spectroscopy. Chemical composition, mass density, bonding configurations and threefold- to fourfold-coordinated carbon bonding ratios are determined. The comparative discussion of the results obtained leads to attribute the higher catalytic activity of the pristine nanotubes to their larger sp^2/sp^3 carbon bonding fraction and greater amount of oxygen containing functional groups.

1. Introduction

Due to the continuous increase of fresh water demand for industrial and domestic activities, new technologies have been developed for the treatment and recycling of waste water. In particular, regarding the agro-industrial wastes, olive mill water (OMW) has been the object of recent interest [1]. The presence in OMW of high concentrations of polyphenols leads to a serious concern for its direct biological treatment. Among the manifold oxidation processes proposed for the abatement of bio-recalcitrant phenolic compounds present, the catalytic ones allow to work under milder oxidation conditions (i.e. pressure and temperature). In a recent paper it has shown that Multi-Walled Carbon nanotubes are very efficient catalysts in the case of the Catalytic Wet Air Oxidation (CWAO) of p-coumaric acid [2], with better performances than the widely used activated carbon [3].

A clear understanding of the structure and chemical composition of the MWCNTs could be a valuable help in clarifying the origin of CNT catalytic efficiency. In literature, the mainly relevant parameter taken into account is the overall O content [4]. Nevertheless, in the attempt to disclose the role of MWCNTs structure in the catalytic action, it is of fundamental importance the knowledge of the C bonding configurations present in the sample and the relation with the selected deposition parameters. In this respect, high-resolution transmission electron microscopy, X-ray photoemission, reflection electron energy loss and micro-Raman spectroscopies are powerful tools to perform a compositional analysis and also to investigate the relative bonding arrangements of C, O and other chemical species present in MWCNTs and coming from the preparation procedures.

The aim of the present work is to investigate the modification of the C content and the threefold/fourfold C coordination ratio as an effect of thermal annealing process, carried out in inert He environment at 1223 K in order to assess factors important for CNT catalytic efficiency. Moreover, we try to find the correlations between the C bonding configurations and the catalytic efficiency.

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2. Experimental section

Samples were synthesized by chemical vapour deposition over iron catalyst supported on alumina (Al_2O_3). Fe/Al_2O_3 catalyst with nominal metal of 29 wt% was prepared by wet impregnation method [5]. After calcinations in air at 750 °C, catalyst precursor was reduced at 500 °C in a quartz reactor located in a horizontal electric furnace. After 1 h of exposure to a 1:1 $H_2 + He$ flow, inlet at a rate of 120 cc/min, the temperature was raised to 600 °C and the helium was replaced by isobutane (i-C_4H_{10}) having care of keeping constant the total flow rate. Reaction was carried out for 2 h.

After synthesis, raw MWCNTs were treated with a 1 M solution of NaOH at 80 °C for Al_2O_3 support removal, while a solution at 37% of HCl at room temperature eliminated residual Fe-nanoparticles. A part of as purified sample (*p*-MWCNTs) was annealed in inert environment (helium) at 950 °C for 2 h. The treated sample portion is coded as *a*-MWCNTs. Further details concerning catalyst preparation and processing, synthesis reaction and MWCNT purification can be found elsewhere [5].

Morphological changes brought about by annealing process were investigated by high-resolution transmission electron microscopy (HRTEM). A JEOL JEM 2010 analytical electron microscope (LaB6 electron gun), operating at an accelerating voltage of 200 kV and equipped with a Gatan 794 Multi-Scan CCD camera for digital imaging, was used for HRTEM analysis. Nanotubes were dispersed in isopropyl alcohol for 2 min and deposited on standard TEM grid covered with holey carbon film. A large number (at least 70) of images for each sample were recorded on account of the possible lack of structural homogeneity.

Chemical composition and density of *p*-MWCNTs and *a*-MWCNTs were investigated by means of X-ray photoemission (XPS) and reflection electron energy loss (REELS) using a VG ESCALAB vacuum system. The Al K_α radiation (1486.6 eV) of a conventional twin anode Al/Mg was used as a source for the XPS measurements. Excited photoelectrons were analysed by means of a VG Scientific CLAM 100 hemispherical analyser. REELS measurements were carried out using a VG LEG61 electron gun. The primary electron energy was 2.0 keV; the incidence angle was always about 40° from the normal to the sample surface. The gun current was about 10 mA, while the pass energy of the analyser was set at 20 eV. The acceptance angle β of the analyser was approximately 3°. Under these conditions, the overall energy resolution, as determined from the shape (FWHM) of the elastic peak of REELS spectra, was approximately 0.6 eV. During measurements, the analysis-chamber pressure was in the 10^{-7} Pa range.

The crystalline arrangement of MWCNTs was also investigated by micro-Raman spectroscopy (MRS). A Coherent Innova 70Ar^+ laser operating at 2.41 eV (514.5 nm) was used as an excitation source for the MRS investigation of the crystalline arrangement. Spectra were recorded in air at RT using an Olympus BX40 microscope coupled to a Jobin Yvon Raman or U-1000 double monochromator (0.15 cm^{-1} resolution) and to a Hamamatsu R943-02 photomultiplier operating in photon-counting mode.

The 800–3350 cm^{-1} spectral range was investigated. A high-grade single-crystal diamond sample (1332.5 cm^{-1}) was initially used for wavenumber calibration. Light was focused onto the sample to a spot of 2 μm in diameter through the 50× microscope objective lens. The choice of a low laser-power (3 mW at the sample surface, resulting in a power density less than 10^5 W/cm^2) prevented local heating of the samples. Several different locations were sampled in order to reliably describe the bulk of each specimen, on account of the possible lack of structural homogeneity. An acquisition time of 30 s was used to improve the signal-to-noise ratio. For each sample, pre-scans with lower power density and shorter acquisition time were initially carried out to check the reproducibility and to rule out the occurrence of thermal effects, as evidenced by band-shift and/or relative-intensity variation.

After normalization, all the spectra collected were analysed carrying out a deconvolution procedure using lorentzian bands, superimposed to a constant background. The wavenumber position, width (FWHM) and intensity of the bands were chosen by a least-square best-fit method. The graphitization indexes I_G/I_D, $I_{G'}/I_G$ and $I_{G'}/I_D$ (defined below in the Raman section) were calculated as integrated intensity ratios.

CWAO of p-coumaric acid (PCA) was carried out in an autoclave (Parr model 4560) at 80 °C, in air, at a pressure of 2 MPa. PCA aqueous solution with a concentration 4.5 mM, corresponding to the maximum solubility of PCA in water at 25 °C, was used. The amount of catalyst (p-CNTs or t-CNTs) is 0.5 g. The residence time was fixed at 5 h. Further experimental details on CWAO of PCA can be found elsewhere [2]. The catalyst efficiency toward the removal of the organic carbon was evaluated by measuring the total organic carbon (TOC) content in the solution by means of a TOC analyser (Shimadzu 5050).

3. Results and discussion

3.1. HRTEM and XPS analysis

Fig. 1 shows the results of TEM analysis on the pristine sample. No appreciable difference in morphology of the samples is introduced after thermal treatment. Highly entangled (5 μm long) carbon filaments are observed at low magnifications. The nanotubes have external diameters between 5 nm and 20 nm. Higher magnification images show that their walls consist mainly of smooth graphene-layers.

Fig. 2 displays the C 1s, O 1s and Fe 2p high-resolution XPS spectra of all the samples. The core line of C 1s peak is located at 284.5 ± 0.1 eV, as in the case of the C bulk material [5]. The C 1s photoelectron peak of the pristine sample is located at the same energy value of the annealed one while its width slightly increases after the annealing. This behaviour suggests an increase of a material structural disorder. The O 1s structure exhibits two distinct components centred at about 530.2 ± 0.1 eV and 531.9 ± 0.1 eV, ascribed to C–O and O–H bonds, respectively. The characteristic components $2p_{3/2}$ and $2p_{1/2}$, located respectively at 710 ± 0.1 eV and 725 ± 0.1 eV, are detected in the Fe 2p structure and attributed to the oxide iron phase [6]. From the area of the above peaks, by using proper sensitivity factors [5], the concentration of each element can be inferred.

The estimated percentage of the chemical species are: 91.1% C, 6.3% O, 2.6% Fe for the pristine sample and 88.0% C, 8.9% O, 3.1% Fe for the annealed one. After carbon, oxygen is the most abundant chemical species in both the samples. Moreover, traces of iron are detected and their presence is explained considering that Fe-nanoparticles may have been encapsulated by carbonaceous layers or sucked into the tube channel during MWCNT extrusion, thus escaping to the post-growth purification step [2,7]. The presence of oxygen in the case of *p*-MWCNTs is mainly due to the presence of carbonyl groups (–C=O) anchored on the surface, as demonstrated by Temperature Programmed Desorption (TPD) analysis carried out on the pristine sample [2]. The analysis indeed shows a sharp CO peak at ≈930 °C arising from the decomposition of carbonyl/quinone groups [8]. However it cannot be ruled out that a contribution is also given by carbon encapsulated Fe_2O_3 nanoparticles, formerly detected [7] within the purified reaction products.

After the annealing at 950 °C, some changes in the chemical composition of the MWCNTs occur. The diminishing of the atomic concentration of C in *a*-MWCNTs (88% *vs* 91%) is consistent with the elimination of the carbonyl functionalities upon heating treatment.