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Carbon nanofibres as substrates for the preparation of TiO_2 nanostructured photocatalysts

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ABSTRACT

Carbon nanofibres from different origins have been used as substrates for the preparation of TiO_2/CNF hybrid materials and TiO_2 nanofibres. The influence of the CNFs on the final properties of the prepared materials is analysed. The results show that the crystallinity of the CNFs used is the parameter that most influences the quality of the TiO_2 deposition. CNFs with low-to-moderate crystallinities are suitable for preparing TiO_2/CNF materials with a uniform TiO_2 coating and with interesting properties: high surface areas, close to 400 m^2/g, and anatase phase. Additionally, TiO_2 nanofibres maintaining such anatase phase and an important surface area can be prepared from these uniform TiO_2/CNF hybrids by burning the CNFs. These TiO_2/CNF hybrid materials and TiO_2 nanofibres, having larger surface areas than similar materials prepared in a previous work using carbon nanotubes, are analysed as photocatalysts for the oxidation of propene at low concentration (100 ppmv) under UV light irradiation. The results show interesting photocatalytic activities (better for the hybrid materials than for the TiO_2 nanofibres), that can be further enhanced increasing the surface area and/or reaching a suitable anatase/rutile proportion.

1. Introduction

TiO_2 has been one of the most widely investigated and used materials over the past decades because it is nontoxic, easy to be made, inexpensive and chemically stable [1–3].

In recent years, TiO_2-based materials have attracted significant research attention due to their broad applications in the fields of water and air purification [4,5], hydrogen evolution [6], CO_2 photoreduction [7], dye sensitised solar cells [8] and sensor devices [9]. However, the large band gap in TiO_2 and high recombination rate of the photogenerated electron/hole pairs hinder further applications in industry [10].

In the field of photocatalysis, many efforts have been attempted to improve activity of TiO_2. One of the alternatives studied is based on immobilising TiO_2 on different substrate materials [6–9,11–21], which mostly include carbon materials [6–9,11,13–17], but also glass [12] or zeolites [20,21]. Among the different carbon materials studied, carbon nanotubes (CNTs) have been the preferred ones [6–9,14–17] due to their extraordinary mechanical and electronic properties and because they can be semiconducting [22].

In addition, CNTs have good adsorption capacity and uniform pore structure [23], which is an advantage for photocatalytic applications. These TiO_2/CNT hybrid materials have exhibited better photocatalytic performance than pure TiO_2 [6,14–16] due to two positive effect of the carbon nanotubes; (i) they provide a surface area that prevents charge recombination by trapping photo-excited electrons generated from TiO_2 [14] and (ii) they have conducting properties that help the transfer of electrons from TiO_2 to CNTs, enhancing the oxidative reactivity [14].

Thus, in a recent study [16] we have obtained promising photocatalytic activity for a TiO_2/CNT hybrid material prepared by sol–gel method, although its resulting specific surface area was low. To improve these results another nanostructured carbon material, with higher surface area, e.g. carbon nanofibres, has recently been investigated for the preparation of TiO_2-based materials, with positive results [17–19]. However, the influence of the properties of the CNFs on the resulting TiO_2/CNF hybrid materials was not investigated.

The present paper deals with the following objectives: (i) the preparation of TiO_2/CNF hybrid materials, paying attention to the properties of the CNFs used as substrates, mainly their structural order, porosity and surface chemistry, (ii) the preparation of high surface area TiO_2 nanofibres from the synthesised TiO_2/CNF hybrid materials, and (iii) an analysis of the photocatalytic application of the samples prepared in this study, evaluated by the photocatalytic

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oxidation (PCO) of propene under UV irradiation carried out in the gas phase at low concentration (100 ppmv).

2. Materials and methods

2.1. Carbon nanofibres

Three commercial carbon nanofibres (CNFs) have been selected to study their influence as substrates on the preparation of the TiO_2/CNF hybrids: Gun-ei (Gun-ei Chemical Ind. Co. Ltd., Japan), Pyrograph III (Pyrograph Products Inc., Cedarville, OH, USA) and GANF (Grupo Antolín Ingenieria, Spain). These CNF materials will be referred to as Gun-ei, Pyrograph and GANF.

Additionally, GANF and Gun-ei nanofibres were oxidised with nitric acid. For such surface oxidation, pristine GANF and Gun-ei CNFs were in contact with a nitric acid solution (HNO_3, 4 M) under stirring for 2 h at room temperature. The ratio CNF/nitric acid solution was 1 g of CNF for 20 ml of the acid solution. These acid-treated CNFs, named Gun-ei-ox and GANF-ox, were washed with deionised water until pH value being neutral and dried in an oven at 100 °C for 24 h.

2.2. Synthesis of TiO_2/CNF hybrids

Five TiO_2/CNF hybrids were prepared by sol–gel route using tetrabutyl titanate ($Ti(OBu)_4$) as follows [24]: firstly, the CNFs (Gun-ei, Pyrograph, GANF, Gun-ei-ox and GANF-ox) were dispersed into ethanol by ultrasonication for 15 min, previously to the addition of $Ti(OBu)_4$. Then, after strong stirring at room temperature for 1 h, a mixture of HCl and ethanol was added drop wise into the suspension; the mixture was continuously stirred for 1 h. Finally, the TiO_2/CNF materials were prepared by filtering and drying at 100 °C for 24 h. This procedure was repeated for eight times. A final heat treatment at 300 °C in a muffle was performed to induce crystallinity in the TiO_2 samples. The TiO_2/CNF hybrid materials are labelled using the CNF substrate name (as an example, TiO_2/Gun-ei).

2.3. Synthesis of TiO_2 nanofibres

The TiO_2 nanofibres were synthesised from the previously prepared TiO_2/CNF hybrids by burning out the CNFs. Thus, the TiO_2/CNF hybrids were placed in a muffle and heated at 10 °C/min rate up to 450–550 °C for 3 h to remove the carbon nanofibres. The TiO_2 nanofibres were labelled as NF-TiO_2 followed by the name of the nanofibre that was previously used as substrate. As an example, NF-TiO_2-Gun-ei corresponds to TiO_2 nanofibres that have been prepared from TiO_2/Gun-ei burning Gun-ei CNFs in air.

2.4. Characterisation of the samples

The carbon nanofibres, TiO_2/CNF hybrid materials and TiO_2 nanofibres were characterised as follows: (1) their porous texture was analysed by nitrogen and carbon dioxide adsorption at −196 °C and 0 °C, respectively, using an Autosorb-6B apparatus from Quantachrome. BET surface area (S_{BET}) was calculated applying the BET equation to N_2 adsorption data [25]. Total micropore volume (porosity below 2 nm width, referred to as DR N_2) was determined by application of the Dubinin–Radushkevich equation to the N_2 adsorption data [25]. The narrow micropore volume (porosity below 0.7 nm width, referred to as DR CO_2) was determined by the application of the Dubinin–Radushkevich equation to the CO_2 adsorption data [26,27]; (2) the surface chemistry of the CNFs was studied by temperature programmed desorption (TPD) experiments carried out over the CNFs using a DSC-TGA equipment (Simultaneous DSC-TGA SDT 2960, TA Instruments) coupled to a mass spectrometer (Thermostar, Balzers). In these experiments, 10 mg of sample were heated to 900 °C (heating rate 20 °C/min) under a helium flow rate of 100 ml/min; (3) the reactivity of the CNFs in air was analysed by thermogravimetric analysis (simultaneous DSC-TGA SDT 2960, TA Instruments), heating at 10 °C/min from room temperature to 900 °C; (4) their structures were characterised by powder X-ray diffraction (XRD). The XRD patterns were recorded using a SEIFERT 2002 equipment as well as a Bruker D8 Advance (40 kV/40 mA) with Cu Kα ($\alpha = 1.54$ Å) radiation. The scanning velocity was 2°/min and the 2θ range scanned ranged from 6° to 80°. The crystalline size of the different titanium dioxide crystalline phases was determined by the Scherrer formula, using a K factor of 0.93:

$$B = \frac{K\lambda}{\beta \, \cos\theta} \tag{1}$$

where B is the crystalline size (nm); λ the wavelength of the radiation used, which is 1.54056 Å for Cu; β the full width at half maximum intensity (FWHM); and θ is the angle for the XRD maximum peak. (5) The sample morphology was studied by scanning electronic microscopy (SEM) using JEOL JSM-840 and transmission electron microscopy (TEM) using INCA Energy TEM100 equipment from OXFORD Instruments. Thus, SEM and TEM of the hybrid samples were used, among others, to determine if a homogeneous TiO_2 covering has been obtained. The measurement and calculation of mean diameters of the hybrid materials and TiO_2 nanofibres was performed by the software analiSIS. (6) The TiO_2 content in the hybrid materials was determined by burning some portion of these samples in a muffle up to 900 °C and comparing the weight of the samples before and after such burning step.

2.5. Experimental conditions for propene oxidation at low concentration

The photocatalytic activities of TiO_2/CNFs and TiO_2 nanofibres were evaluated by photocatalytic oxidation (PCO) of propene, which is one of the major sources of both outdoor (it is involved in vehicle emissions and in many industrial applications, such as in petrochemical plants and foundry operations) as well as of indoor air pollution. So far, few studies have been reported on the photocatalytic oxidation of propene in gas phase using TiO_2 [16,28–30,32], despite the fact that it is one of the main components of tobacco smoke [28,31].

The experimental system used was designed in our laboratory. It consists of a quartz reactor provided by AFORA where the photocatalyst bed is placed on quartz wool. A Philips UV lamp is placed parallel to the quartz reactor, at around 1 cm. The UV lamp radiation peak appears at 257.7 nm (UV-C). The commercial reference of the lamp is TUV 8W FAM. The couple quartz reactor-lamp is surrounded by a cylinder covered by tinfoil. A scheme of this system is detailed elsewhere [32].

The weight of photocatalyst used in these experiments was 0.11 g for the TiO_2 nanofibres and, for comparison purposes, different TiO_2/CNF sample weights were used to maintain a constant 0.11 g mass of TiO_2.

These photocatalysts were used for the oxidation of propene at 100 ppmv in air at room temperature, 25 °C. Two flow rates of the propene stream, 30 and 60 ml/min (STP), were tested. These flow rates were controlled by automated mass flow-controllers (Brook Instruments). After suitable calibrations, a mass spectrometer (Balzers, Thermostar GSD 301 01) coupled to the outlet of the reactor bed follows the evolution of the concentration of propene in the outlet gas with time. The experiments were repeated at least