TiO_2 nanotubes using carbon template materials for the photocatalytic oxidation of VOC at low concentration

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Introduction

TiO_2 has been one of the most widely investigated and used materials over the past decades [1], because it is nontoxic, easy to be made, inexpensive and chemically stable. In recent years, TiO_2-based nanomaterials have attracted significant research attention due to their broad applications in the fields of water and air purification [2]. However, one of the major factors that limits the efficiency of TiO_2 photocatalysis is the fast recombination of photo-generated electron/hole pairs, which releases energy in the form of unproductive heat or photons. Many efforts have been made to reduce charge recombination and enhance photocatalytic activity of TiO_2 [3]. Recently, synthesis of TiO_2-CNT composites to increase the photocatalytic efficiency of TiO_2 has attracted significant attention. Synthesis methods of TiO_2-CNT composites include sol-gel, chemical vapor deposition (CVD) and hydrothermal deposition, using carbon nanotubes as templates. In this work, we investigate the characteristics and the importance of the carbon nanofibres (CNF) to be used as templates for the preparation of TiO_2 nanotubes by sol-gel and evaluate the activity of these materials towards the photocatalytic oxidation (PCO) of volatile organic compounds (VOC) at low concentration (100 ppmv) in gaseous phase.

Experimental

We have tested three different commercial CNFs as templates: Gun-ei (Gun-ei Chemical Ind. CO. Ltd, Japan), Pyrograph III (Pyrograph, products, Inc., Cedarville, OH, USA) and GANF (Antolin Engineering Group, Spain). These carbon nanofibres have been deeply characterized to analyze their performance as supports.

The TiO_2/CNF composites were prepared by sol-gel using $Ti(OBu)_4$ as precursor. The decoration of the nanosized TiO_2 on CNFs was carried out as follows: firstly, the CNF 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 slowly dropped into the suspension; the mixture was continuously stirred for 1 h. Finally, by filtering and drying at 100 ºC for 24 h the TiO_2/CNF materials are prepared. This procedure was repeated several times.

To get 100% TiO_2 nanotubes from the TiO_2/CNF composites, CNFs are burned in air at different conditions.

The porous texture characterisation of the different materials was performed by nitrogen and carbon dioxide adsorption at -196ºC and 0ºC, respectively, using an Autosorb-6B apparatus from Quantachrome. The BET specific surface area and the total micropore volume (DR N_2) were assessed by N_2 adsorption at -196ºC and the narrow micropore volume (DR CO_2) was determined by CO_2 adsorption at 0ºC.

Temperature programmed desorption (TPD) experiments were carried out on the CNFs to characterize the surface chemistry of the materials used as templates by a DSC-TG equipment (TA Instruments, SDT 2960 Simultaneous) coupled to a mass spectrometer (Thermostar, Balzers). In these experiments 10 mg were heated up to 900ºC (heating 20ºC/min) under helium flow rate of 100 ml/min.

The crystalline structure of the CNF and the TiO_2/CNF composites was investigated by XRD analysis using a SEIFERT 2002 equipment and Cu Kα (1.54 Å) radiation. Transmission electron microscopy (TEM) was used to study the morphology of the photocatalysts, using INCA Energy TEM100 equipment from OXFORD instruments.

The experimental system used in propene PCO tests was designed in our laboratory. It consists of a quartz reactor where the photocatalyst bed is placed on quartz wool. An 8W 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 [4]. The weight of photocatalyst used in these experiments was selected to keep constant the weight of TiO_2 (0.11 g). The photocatalysts were used for the oxidation of propene at 100 ppmv in air at room temperature, 25 ºC. Different 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) coupled to the outlet of the reactor bed follows the evolution of the concentration of propene in the outlet gas.

Results and Discussion

Table 1 compiles the textural characteristics and the surface chemistry of the three CNFs tested to prepare the TiO_2/CNF composites. It can be seen that these samples are very different in terms of porosity and surface chemistry.

Table 1. Characterization of the CNFs.

Sample	S BET (m^2/g)	DR N_2 (cm^3/g)	DR CO_2 (cm^3/g)	CO (μmol/g)	CO_2 (μmol/g)
Gun-ei	493	0.23	0.25	1678	900
Pyrograph	44	0.02	0.00	344	340
GANF	178	0.06	0.03	548	409

Fig. 1 shows the XRD patterns of the three CNFs. The X-ray diffractogram of Gun-ei does not show peaks (or bands). X-ray diffraction of sample GANF results in sharper peaks than in the case of the Pyrograph III sample. This indicates the amorphous character of Gun-ei, whereas GANF presents a more ordered structure (with high graphitic character). Pyrograph crystallinity is intermediate [5].

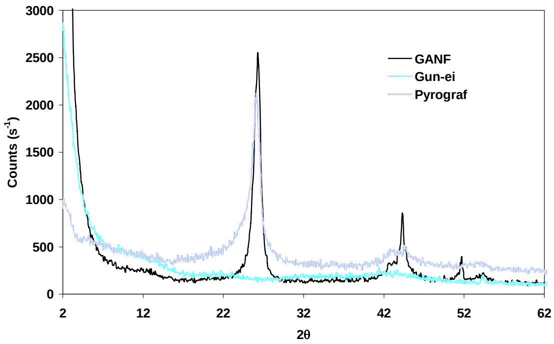

Fig.1. X-ray diffractograms of CNFs.

Regarding the TiO_2/CNF composites prepared using these CNFs, the samples were investigated with TEM (Figure 2a-2c).

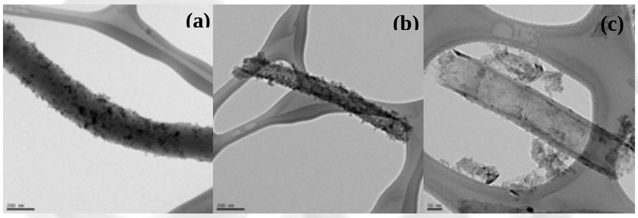

Fig. 2. TEM images of (a) TiO_2/Gun-ei; (b) TiO_2-Pyrograph; (c) TiO_2-GANF

Fig. 2a and 2b show that TiO_2 is homogeneously and densely spreaded on the surfaces of Gun-ei and Pyrograph. However, Fig. 2c shows that TiO_2 is not homogeneously supported on the surface of the GANF nanofibres which is the most crystalline CNF. These results indicate that amorphous CNF, or those not totally crystalline, are suitable supports for deposition of the TiO_2.

Removing the CNF from the samples TiO_2/Gun-ei and TiO_2/Pyrograph by a burning step in air TiO_2 nanotubes can be obtained (Fig. 3a and b). The TiO_2/GANF materials have not been studied since no uniform covering has been obtained.

For space reasons, the photocatalytic performance of the sample prepared from pyrograph CNF is summarized in Table 2. The results for propene conversion at 100 ppmv shows that TiO_2/Pyrograph is an active photocatalyst at the two flow rates studied (30 and 60 ml/min). The Pyrograph reference sample (which does not contain TiO_2) shows a negligible propene conversion, whereas the activity of TiO_2 nanotubes is noticeably, although lower than that of the composite TiO_2/Pyrograph. In the case of the materials prepared using Gun-Ei, the TiO_2 nanotubes show larger activities than those prepared using Pyrograph as template, and the activity of the hybrid TiO_2/Gun-Ei is larger than that of TiO_2 nanotubes prepared from Gun-Ei. The synergistic role of CNFs is based on charge transfer processes between CNFs and TiO_2 [6].

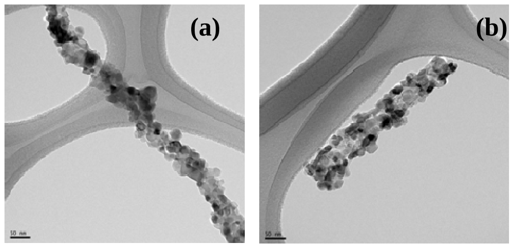

Fig. 3. Nanotubes of TiO_2 obtained from different CNF supports: a) Gun-ei and b) Pyrograph, after burning CNFs.

Table 2. Propene conversion.

Sample	Conversion at 30 ml/min	Conversion at 60 ml/min
Pyrograph	2	0
TiO_2/Pyrograph	42	21
TiO_2 NT (from Pyrograph template)	22	12

Conclusions

In this paper, we have successfully prepared TiO_2 nanoparticles homogeneously and densely supported on two CNFs having different crystallinity. CNF having amorphous and intermediate crystallinity CNFs can lead to TiO_2 nanotubes after burning in the CNF templates.

The photocatalytic activity results regarding propene conversion at low concentration (100 ppmv) have shown that the TiO_2 coated on carbon nanofibres presents a significant photocatalytic activity, being the composite materials the most interesting ones.

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