TiO$_2$ nanotubes and CNT–TiO$_2$ hybrid materials for the photocatalytic oxidation of propene at low concentration

N. Bouazza [a], M. Ouzzine [a], M.A. Lillo-Ródenas [a,*], D. Eder [b], A. Linares-Solano [a]

[a] Grupo de Materiales Carbonosos y Medio Ambiente, Dpto. Química Inorgánica, Facultad de Ciencias, Universidad de Alicante, Ap. 99, E-03080, Alicante, Spain
[b] Department of Materials Science and Metallurgy, University of Cambridge, New Museums Site, Pembroke Street, Cambridge CB23QZ, UK

ARTICLE INFO

ABSTRACT

In this work, we investigated titanium dioxide (TiO$_2$) nanotubes and CNT–TiO$_2$ hybrid materials for the photocatalytic oxidation (PCO) of propene at low concentration (100 ppmv) in gaseous phase. The materials were prepared via sol–gel method using sacrificial multi-walled carbon nanotubes (CNT) as templates and subsequent heat treatments to obtain the desired crystalline phase (anatase, rutile or a mixture of both) and eventually to remove the carbon template. We also studied rutile nanotubes for the first time and demonstrate that the activity strongly depends on the crystalline composition, following rutile < anatase < anatase/rutile mixture. The enhanced activity of the anatase–rutile mixture is attributed to the decrease in the electron–hole pair recombination due to the multiphasic nature of the particles. The key result of this work is the exceptional performance of the CNT–TiO$_2$ hybrid, which yielded the highest observed photocatalytic activity. The improved performance is attributed to synergistic effects due to the hybrid nature of the material, resulting in small anatase crystalline sizes (CNT act as heat sinks) and a reduced electron–hole pair recombination rate (CNTs act as electron traps). These results demonstrate the great potential of hybrid materials and stimulate further research on CNT-inorganic hybrid materials in photocatalysis and related areas.

1. Introduction

In the last decade, the synthesis of nanostructured TiO$_2$ materials has received a great deal of attention. Three approaches have been reported for the preparation of TiO$_2$-nanotube materials: the hydrothermal synthesis [1–7], the anodic oxidation [8–11] and the template synthesis [12–17]. The advantage of the template-based synthesis route is the straightforward control over the morphology of the resulting TiO$_2$ nanotubes. For instance, the initial dimensions of carbon nanotubes (CNTs) determine both, diameter and length of the TiO$_2$ nanotubes, while the TiO$_2$ nanotube wall thickness depends on the type and initial concentration of the Ti precursor with respect to the CNTs [15]. The use of CNTs as a template was further significant as they can also support the tubular morphology of TiO$_2$ during the phase transformation from anatase to rutile, resulting in the first synthesis of pure rutile nanotubes [16]. A significant innovation was the addition of small amounts of benzyl alcohol as a linking agent, which enabled the use of pristine CNTs as templates without the need for covalent functionalisation [17].

The last few years have seen a boost in interest in TiO$_2$ nanotubes, due to their improved performance as photocatalysts in heterogeneous photocatalysis [2,7,11,18–22]. However, most of these studies have been devoted to photocatalysis in solution and only the work of Inagaki et al. deals with gaseous phase oxidation [22]. According to some authors, the advantages of TiO$_2$ nanotubes are solely based on their high surface areas [2,18,19,23]. Other authors showed that TiO$_2$ nanotubes contain a high amount of hydroxyl groups in comparison with TiO$_2$ in the form of powder [6,24]. In general, nanotubes have a particular advantage in the way they enable three-dimensional mechanically coherent structures, which provide ready gas and radiation access to the material [14]. For example, Macak et al. [20] demonstrated that TiO$_2$ nanotubes showed higher photocatalytic activity than P25, despite their smaller surface area. Eder et al. investigated anatase nanotubes, both pure and doped with iron ions, for the photocatalytic splitting of water and observed that – in contrast to the inactive P25 – the TiO$_2$ nanotubes did produce a significant amount of hydrogen [21]. Both authors related this improvement to the structure of the TiO$_2$ nanotubes, which favours short diffusion paths of the pollutant molecules and, in addition, also decreases the electron–hole pair recombination velocity.

Despite these promising studies, the photocatalytic performance of TiO$_2$ nanotubes is far from completely understood. One important question involves the phase composition of TiO$_2$, which

* Corresponding author. Tel.: +34 965 909350; fax: +34 965 903454.
E-mail address: mlillo@ua.es (M.A. Lillo-Ródenas).

has two main phases, anatase – typically formed upon synthesis – and rutile, the thermodynamically stable phase. Due to the synthesis conditions for rutile, which often require heat treatments at elevated temperatures (e.g. >600 °C), the crystal sizes in rutile are typically larger than in anatase, resulting in significantly smaller specific surface areas. The rutile nanotubes used in this work, however, have surface areas comparable with those of anatase nanotubes, and thus are ideal candidates for photocatalytic testing.

The test reaction in this work is the photocatalytic oxidation of volatile organic compounds (VOC) at low concentration, a very important catalytic process, with the aim to reduce their harmful effects for human health and environment. Among the different VOCs, this work concentrates on propene, which is one of the major sources of both outdoor (involved in vehicle emissions and in many industrial applications, such as in petrochemical plants and foundry operations) as well as of indoor (one of the principal components of tobacco smoke) air pollution. So far, very few studies have been reported on the photocatalytic oxidation (PCO) of propene in gas phase using TiO_2 [25–28] and to the best of our knowledge the performance of TiO_2 nanotubes has not been explored at all for this application or, in general, for gaseous phase applications.

In this respect, the novelty of this work is a detailed investigation of various TiO_2 nanotubes, consisting of either pure anatase or rutile, or of a mixture of anatase and rutile, for the photocatalytic oxidation (PCO) of propene. Furthermore, this work compares the best results obtained previously with hybrid TiO_2 catalysts (containing activated carbon [26] or MCM-41 [27]) with CNT–TiO_2 hybrids, a very promising new class of functional materials [29], and investigates the beneficial role of CNTs in photocatalysis.

2. Experimental

2.1. Photocatalysts preparation

The TiO_2 nanotubes used in this work were synthesised via a sol–gel process using sacrificial CNT as templates. Multi-walled carbon nanotubes (CNTs) were prepared by a modified chemical vapor deposition (CVD) process, using ferrocene as the catalyst precursor and toluene as the feedstock. These reactants were vaporised into a hydrogen/argon atmosphere at 760 °C. The average outer diameter of the nanotubes was 70 nm and the length was between 20 and 30 μm, but can be controlled by adjusting various process parameters. Prior to their use as a template, amorphous carbon as well as residual iron catalyst particles were removed by annealing the as-grown CNTs in argon at 2000 °C for 5 h [29]. The synthesis of the CNT–TiO_2 hybrids and the TiO_2 nanotubes is described in detail elsewhere [14,16]. In summary, it involves (I) the deposition of a layer of TiO_2 synthesised by means of the sol–gel method on CNTs with the aid of benzyl alcohol as a linking agent, (II) heat treatment in argon to obtain the desired crystalline phases, e.g. anatase (350 °C), anatase–rutile mixture (550 °C) or rutile (700 °C), and (III) heat treatment in air at 520 °C to remove the CNT templates.

2.2. Characterisation techniques

The porosity characterisation of the TiO_2 nanotubes was performed by nitrogen adsorption at −196 °C, using an ASAP 2020 apparatus from Micromeritics. The specific surface area was measured by N_2 adsorption according to Brunauer–Emmett–Teller (BET).

X-ray powder diffraction was performed to characterise the phase composition and crystal structure of the photocatalysts,

using a SEIFERT 2002 equipment as well as a Bruker D8 Advance (40 kV/40 mA) with Cu Kα (1.54 Å) radiation. The scanning velocity was 2°/min, and the 2θ range scanned ranged from 2° to 80°. The percentages of anatase and rutile were determined by using the intensities of the strongest peaks for anatase and rutile following the equations [26]:

$$W_R \ (\%) = \frac{A_R}{0.8844 A_A + A_R} \times 100 \tag{1}$$

$$W_R \ (\%) + W_A \ (\%) = 100 \tag{2}$$

where W_A: composition percentage of anatase; W_R: composition percentage of rutile; A_A: integrated intensity of the maximum intensity peak of anatase (1 0 1); A_R: integrated intensity of the maximum intensity peak of rutile (1 1 0).

The crystalline sizes of the anatase and rutile phases were determined by the Scherrer formula, using a K factor of 0.93:

$$B = \frac{K\lambda}{\beta \cos\theta} \tag{3}$$

where B: crystalline size, in nm; λ: wavelength for the radiation used, which is 1.54056 Å for Cu; β: full width at half maximum intensity (FWHM); θ: angle for the XRD maximum peak.

The morphology of the samples was characterised by (i) scanning electron microscopy (SEM), using a JEOL 6340F FEG-SEM, and (ii) transmission electron microscopy (TEM) using INCA Energy TEM100 equipment from OXFORD instruments.

2.3. Experimental conditions for propene oxidation at low concentration

The experimental system used in propene PCO tests was designed in our laboratory. It consists of a quartz reactor (cut-off < 200 nm) where the photocatalyst bed is placed on quartz wool. The reactor is 50 mm height, its diameter is 20 mm and the quartz wool support height is around 10 mm. An 8 W 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 [26].

The weight of photocatalyst used in these experiments was 0.11 g for the TiO_2 nanotubes and, for comparison purposes, 0.16 g of the CNT–TiO_2 sample were used, maintaining a similar weight of TiO_2. The photocatalysts were used for the oxidation of propene at 100 ppm in air at room temperature, 25 °C.

Different flow rates of the propene stream, 7.5, 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 two times for checking reproducibility.

Propene conversion was calculated using the following expression:

$$\text{Propene conversion} \ (\%) = \frac{C_{\text{initial} \ C_3H_6} - C_{\text{stationary} \ C_3H_6}}{C_{\text{initial} \ C_3H_6}} \times 100$$

where $C_{\text{initial} \ C_3H_6}$ is the initial propene concentration, 100 ppmv, and $C_{\text{stationary} \ C_3H_6}$ is the stationary propene concentration in the photocatayst bed outlet gas when the UV is switched on.

The standard activity of different samples was determined by using the following equation:

$$\text{St. activity} = \frac{n}{m \cdot t}$$