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WO_3-modified TiO_2 nanotubes for photocatalytic elimination of methylethylketone under UVA and solar light irradiation

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ABSTRACT

We report on the synthesis, the characterizations and the photocatalytic activity of WO_3/TiO_2 nanotubes for methylethylketone (MEK) elimination under both UVA and simulated-solar light irradiations. TiO_2 nanotubes (TiNTs) were synthetized using the hydrothermal method in a concentrated 10 M NaOH solution heated at 130 °C during 48 h, post-impregnated with tungstate salt and finally calcined. The photocatalytic efficiency for both UVA and solar light irradiation strongly depends on the WO_3 content, ranging from 4 to 51 wt.%. The different photocatalytic activities were analysed, in terms of initial and stabilized activities and deactivation phenomena. Complementary post-tests characterizations (TGA and XPS) aiming at the establishment of correlations between WO_3 content, surface composition, surface species and the photocatalytic activity and deactivation are discussed.

1. Introduction

TiO_2-based nanomaterials are well-studied and commonly used materials for liquid and gas-phase photocatalytic applications [1,2]. Since the discovery of carbon nanotubes [3], intensive researches of one-dimensional nanostructures such as nanotubes, nanorods, nanowires, nanobelts, *etc.* of inorganic materials have attracted great attention because they offer interesting potential for use in various applications [4]. Amongst them, there have been significant efforts to elaborate controlled TiO_2-based nanotubes. Currently developed methods for elaborating TiO_2 nanotubes include electrochemical anodic oxidation [5–8], assisted-template methods [9,10], and sol–gel processes [11,12]. However, these nanotubes generally have large diameters and their walls are composed of nanoparticles. Kasuga et al. [13] revealed that *via* a simple hydrothermal treatment of crystalline TiO_2 particles with NaOH aqueous solution, high quality TiO_2 nanotubes (TiNTs) with uniform diameters around 10 nm could be obtained. These nanotubes are not constituted of nanoparticles but are grown through the bending and rolling of titanate nanosheets [14–16]. However, the exact formation mechanism and the phase nature of TiO_2 nanotubes prepared by hydrothermal method is still under debate. The nanoscale 1D-layered titanate structures obtained by this simple hydrothermal synthesis have attracted much attention since they offer a larger surface area available in comparison to nanoparticles and to TiO_2 nanotubes obtained from the template and electrochemical anodization methods. Moreover, they provide channels for enhanced electron transfer thus limiting photogenerated charge recombinations [13,17]. The combination of these properties should have determinant roles in photocatalytic reactions, in addition to the fact that the hydrothermal technique is a simple and cost-effective method for large scale production of TiO_2 nanotubes.

Nowadays, one of the challenges in photocatalysis is to build up photocatalytic processes working with solar light as a clean and renewable energy source. However, the large band gap value (around 3.1–3.2 eV) of TiO_2 nanotubes, resulting in low absorption of solar light, is a serious drawback for these applications. Thus, to keep advantages of the unique properties of this 1D-layered TiO_2 morphology for visible light activation, several strategies could be explored. Up to now, amongst them, one can note fluor, nitrogen and carbon doping [18–20] but also coupling with a narrow gap semiconductor like CdS, ZnS and WO_3, yielding heterojunction formation [21–27].

In the present study, WO_3-modified TiNT samples with different WO_3 contents were prepared by post-impregnation of TiNT obtained *via* hydrothermal synthesis, followed by a final calcination step. Their photocatalytic properties were evaluated towards UV-A and simulated-solar light degradation of methylethylketone (MEK). Electronic microscopies, surface area and porosity measurements, UV–vis, TGA, zetametry and XPS characterizations were performed

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on the as-prepared samples, whereas complementary TGA and XPS analyses were carried out after photocatalytic tests. The contribution of WO_3 in terms of visible light activation (in addition to UV-A activation) and of heterojunction formation was discussed and on-stream deactivation behaviour was also explained.

2. Experimental

2.1. Synthesis of WO_3/TiNT catalysts

Typically, high aspect ratio TiNTs were synthetized by hydrothermal treatment of 3 g of TiO_2 powder in 180 ml of concentrated 10 M NaOH solution at 130 °C for 48 h. After hydrothermal treatment, the white powder obtained was vacuum-filtered, washed with 1 M HCl solution and distilled water until neutral pH, followed by overnight drying at 100 °C. Post-synthesis modifications with WO_3 were performed by classical impregnation with ammonium paratungstate salt. Starting from 1 g of the prepared TiNT catalyst, 0.047 mg, 0.098 mg, 0.214 mg and 0.530 mg of $(NH_4)_{10}W_{12}O_{40}\cdot 5H_2O$ salt was added and completed with 10 ml of distilled water, magnetically stirred until evaporation of the solvent and dried overnight at 100 °C. A final calcination step for 3 h at 350 °C was performed to yield theoretically 4, 9, 18 and 51 wt.% of WO_3/TiNT, respectively.

2.2. Characterizations of WO_3/TiNT catalysts

The surface area measurements were performed on ASAP2010 Micromeritics porosimeter using N_2 as an adsorbant at liquid N_2 temperature. Before each measurement, the sample was outgassed overnight at 250 °C. Surface areas were calculated from the N_2 adsorption isotherms using the BET method (S_{BET}). The micropore surface areas were calculated using the *t*-plot method and the pore size distribution was obtained using the B.J.H. method during the desorption branch [28]. A detailed study of the method, concerning the correctness of the different parameters used, has been published elsewhere [29].

Structural characterization was done by powder X-ray diffraction (XRD) measurements, carried out with a D8 Advance Bruker diffractometer, using a Cu Kα radiation source in a $\theta/2\theta$ mode, with a duration scan of 0.5 s and a small step scan (0.04° 2θ).

Thermogravimetric analysis (TGA) was performed using a Q500 TA Instrument thermoanalyzer. Each sample was placed in a platinum crucible and heated from room temperature to 900 °C at a rate of 10 °C/min, using a 20% (v/v) O_2/N_2 mixture at a flow rate of 25 ml/min.

X-ray photoelectron spectroscopy (XPS) surface characterizations were performed using a Multilab 2000 (Thermo) apparatus equipped with an Al Kα (1487) source (pass energy of 20 eV). All of the spectra were decomposed assuming several contributions, each having a Doniach–Sunjic shape [30] and a Shirley background subtraction [31]. The tungsten-to-titanium (W/Ti) surface atomic ratios were calculated using the sensitivity factors, as determined by Scofield [32]. The subtraction of the energy shift due to electrostatic charging was determined using the contamination carbon C1s band at 284.6 eV as a reference.

Scanning electron microscopy (SEM) was performed using a JEOL XL 30 FEG microscope working at 10–20 kV.

Transmission electron microscopy (TEM) was performed on a Topcon 002B microscope working with 200 kV and a point-to-point resolution of 0.17 nm. The sample was sonically dispersed in an ethanol solution before a drop of this solution was deposited onto a copper grid covered by a holey carbon membrane for observation.

Isoelectrical point (IEP) measurements were carried out on a Malvern ZetaSizer with automatic titration.

UV–vis absorption spectra of the materials were recorded on a Cary 100 Scan UV/vis spectrophotometer from Varian equipped with a DRA-CA-301 *Labsphere* diffuse reflectance cell.

2.3. Experimental photocatalytic device and procedure

The photocatalytic reaction was carried out in a 300-mm long cylindrical concentric tubular Pyrex reactor composed of two coaxial tubes 4 mm apart, between which the reactant mixture passes through. Detailed descriptions of the photocatalytic reactor and device can be found elsewhere [33,34]. Photocatalytic material (400 mg) was evenly coated on the internal side of the 35-mm diameter external tube by evaporating a catalyst containing aqueous slurry to dryness. The catalyst-coated reactor was then dried at 110 °C for 1 h in air. MEK (Sigma–Aldrich, 99%) and water were fed at ambient temperature and atmospheric pressure by bubbling air through two saturators, then mixed with additional air (using Brooks 5850 massflow controllers) to obtain the required MEK–water–air ratios with a constant total air flow of 350 cm^3/min. The MEK content was set at 400 ppm in flowing air. The relative humidity was set at 50%, with 100% of relative humidity defined as the saturated vapour pressure of water at 25 °C, corresponding to about 24 Torr, that is, about 3% relative to the total atmospheric pressure. No pretreatment of the photocatalysts has been carried out prior to photocatalytic experiments. Before the photocatalytic reaction, the catalyst was first exposed to the polluted air stream with no illumination until dark-adsorption equilibrium was reached. Afterward, illumination was switched on. Illumination was provided by a commercially available 8-W UV-A (45.3 W/m^2) black light tube (Philips) with a spectral peak centred around 365 nm (Fig. 1a) or by a 8-W day light tube (Philips) (Fig. 1b) located inside the inner tube of the reactor. One may mention that the daylight, considered here as being simulated-solar light, was composed in terms of irradiance power of 42.5 W/m^2 of visible light and of 0.7 W/m^2 of UV-A (*i.e.* of 1.6%).

The reaction products were analysed on-line every 2 min by a thermal conductivity detector on a micro-gas chromatograph (Agilant microCG R3000), allowing detection and quantification of MEK, water, CO_2, and organic byproducts on Stabilwax, PLOT Q, OV1 and MS-5A columns.

The efficiency of the depollution process was expressed in terms of MEK conversion, of CO_2 selectivity and yield, as well as of carbon deficit, and calculated as follows:

$$\text{Conversion}\quad(\%) = \frac{[\text{MEK}]_{\text{in}} - [\text{MEK}]_{\text{out}}}{[\text{MEK}]_{\text{in}}} \times 100$$

$$S_{CO_2}\,(\%) = \left[\frac{[CO_2]_{\text{out}}}{[\text{MEK}]_{\text{in}} - [\text{MEK}]_{\text{out}}} \times \frac{1}{4}\right] \times 100$$

CO_2 yield (%) is defined as : (S_{CO_2} × Conversion)/100.

The carbon deficit (expressed in ppm) is defined as the amount of carbon remaining adsorbed or deposited on the catalyst surface and is expressed as

$$\text{C deficit}\,(\text{ppm}) = [\text{MEK}]_{\text{in}} - [\text{MEK}]_{\text{out}} - \sum \frac{1}{\alpha_j}[\text{Products}]_{j,\ \text{gas phase}}$$

where $[\text{Products}]_j$ is the concentration of each j carbonaceous compound in the gas phase and α_j is the stoichiometry factor of the j compound.

Carbon deficit yield (%) is defined as :

$(1 - S_{CO_2} \times \text{Conversion}) \times 100.$