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Visible-light driven TiO_2 photocatalysts from Ti-oxychloride precursors

P. Sampedro[a], G. Colón[b,*], M. Fernández-García[a,**]

[a] Instituto de Catálisis y Petroleoquímica, CSIC, Campus Cantoblanco, 28049 Madrid, Spain
[b] Instituto de Ciencia de Materiales de Sevilla, Centro Mixto CSIC-Universidad de Sevilla, C/Américo Vespucio, 49, 41092 Sevilla, Spain

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ABSTRACT

Series of nanosized anion-containing TiO_2-base materials with anatase-type structure were synthesized from N, Cl-containing precursors using two preparation methods, calcination and hydrotreatment. Samples were conditioned by a final calcination step in order to get free of surface anion impurities and their structural properties characterized by a combined X-ray diffraction (XRD), scanning (SEM) and transmission (TEM) microscopy, X-ray energy dispersive (XEDS), X-ray photoelectron (XPS), and diffuse reflectance infrared Fourier transform (DRIFTS) study. The structural characterization was used to interpret the UV–vis spectra. The resulting joint information allowed the rationalization of the photocatalytic activity observed for the visible-light-assisted liquid-phase degradation of phenol. We founded that maximization of photoactivity is not related with the net absorption power of our systems in the visible range but mostly driven by a combination of two characteristics; the adequate morphological properties and the presence of negatively charged N-containing species.

1. Introduction

Photocatalytic destruction of organic pollutants in the presence of TiO_2 appears as a viable decontamination process of widespread application, no matter the state (gas or liquid) or chemical nature of the process target [1,2]. TiO_2-anatase is a n-type semiconductor having a wide bandgap (3.0–3.4 eV depending on primary particle size and other properties) which necessitates UV light to create energy-rich electron–hole pairs upon absorption. All TiO_2-based technological applications aiming to use solar light as the energy source are thus limited and typically would need to optimize the handling of visible-light photons by the catalytic solid. This appears of prime importance and, furthermore, corresponds to an appealing challenge for the future generation of photocatalytic materials [3–6].

The pioneering work of Asahi et al. [7] highlighted the possibility of doping the TiO_2-anatase structure with anions to yield new, high-performance visible-light driven photocatalysts. After this report the use of N^{3-}, C^{4-}, S^{4-} or halides (F^-, Cl^-, Br^-, I^-), as doping agents has been subjected to intense research and summarized in several review articles [3,5,8,9]. Recently, several ways have been explored in order to improve and maximize the photo-activity of anion-doped titania systems and, among them, a fruitful one departs from the combination of nitrogen and halides. Reports concerning the use of N/F [10,11] and N/I [12] showed notable improvements over N-alone TiO_2-doped materials. Although essentially an open question, the improvement may come from the correct combination of the well-known N-impurity electronic levels located near the conduction band [13,14], either with the halide-modified conduction band [12] or with new color (F/F^+) centers [11]. In both cases, the visible-light absorption power is neatly enhanced. Additionally, in certain N-containing systems, the presence of a substantial amount of defects associated with the titania anion sublattice but with no direct correlation with the N-impurities creates empty electronic levels at about 2.0–2.5 eV from the upper part of the valence band [15,16], which may be strongly influenced by the presence of color centers detected in halide-containing materials. Apart from electronic matters, another point of importance in fluoride-doped systems concerns the surface acidity generated by the presence of surface anions [11].

In this work, we try to explore a novel N/Cl combination and develop a preparation process based on the precipitation of ammonium Ti-oxychlorides as initial solid precursors. This would allow to have a large doping N concentration in the precursor as well

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* Corresponding author.
** Corresponding author. Tel.: +34 91 585 4939; fax: +34 91 585 4760.
E-mail addresses: gcolon@icmse.csic.es (G. Colón), mfg@icp.csic.es (M. Fernández-García).

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as a variable Ti:Cl atomic ratio and to study the influence of these two parameters in the final structural and morphological features of the TiO_2 phase after calcination/hydrotreatment. Our main aim is to analyze the nature and amount of the impurity species and to correlate these with the photo-activity of the titania solids in the liquid-phase elimination of phenol. Materials are subjected to calcinations and/or hydrotreatment but a final, fixed calcination step was always applied in order to ensure the surface chemical uniformity of the samples. This is important as some doping surface species as chloride may change acid/base properties of the solid, may be leached from the surface during reaction (introducing uncertainties), and may drive to a lack of long-term stability. As detailed below, our systems will be essentially free of N, Cl surface adsorbed species which may be interfering in the interpretation of the results. The task to identify N, Cl-containing species is not easy as, for example, N–Ti–O, Ti–N–O (oxynitride), NO^+, N^-, N^{3-}, NH^-, or NH_x have been detected in the case of nitrogen-doped samples [3,5,7,8,13–15]. To this end, in this report we will describe the preparation and characterization of titania solids using a combination of XPS, Infrared (DRIFTS), SEM, TEM and XEDS. The joint analysis of the structural characterization and the electronic implications derived by UV–vis spectroscopy would be used to interpret photo-activity, highlighting key properties responsible for the enhancement of titania photo-activity in anion-doped TiO_2-based photocatalysts.

2. Experimental

In order to vary the Ti:Cl ratio of our precursor solids within the 1:1 to 1:6 ratio, we prepared the corresponding Ti-isopropoxide:HCl mixtures in isopropanol. The so-formed Ti:Cl complexes were stirred in a water/isopropanol (1:10) mixture for 4 h and subsequently precipitated with an ammonia solution corresponding to a NH_3:Ti ratio of 3. Solids were filtered and washed with distilled water, dried at 383 K and finally subjected to hydro- and/or calcinations treatments. Calcined samples were subjected to a heating ramp of 2 K/min up to 723 K in a (20%) O_2/N_2 atmosphere. The hydrotreated set of samples were obtained by placing the solid precursor together with 1 M NH_3 solution (30 ml/g of precursor) in a Teflon-lined reactor at 120 °C for a period between 3 and 24 h. These materials were subsequently filtered and dried at 383 K and calcined at 723 K following the above-mentioned recipe. A blank is obtained using a similar procedure but without HCl and ammonia in the preparation and precipitation steps of the precursor solid. Samples are described by an initial set of letters (B blank; TC1 and TC6 for samples prepared with Ti:Cl ratios of, respectively, 1:1 and 1:6) followed by another set describing the treatment (no letter for calcinations; HT for hydrotreatment). Table 1 summarizes the sample labels and corresponding treatment details, and gives their main physico-chemical characteristics.

Table 1
Main synthesis details and physico-chemical characteristics of samples

Sample	S_{BET} ($m^2\,g^{-1}$)	Particle size (nm)
B	107.4	10.4
B-HT3	117.9	10.7
B-2HT3	101.2	13.1
B-HT6	143.1	11.7
B-HT24	120.1	12.3
TC1	104.9	11.9
TC1-HT3	123.9	11.8
TC1-2HT3	135.3	11.5
TC1-HT6	94.2	14.7
TC1-HT24	78.6	16.0
TC6	110.0	12.0
TC6-HT3	153.3	10.7
TC6-2HT3	141.4	10.8
TC6-HT6	93.2	14.9
TC6-HT24	90.0	15.3

X-ray diffraction (XRD) patterns were obtained using a Siemens D-501 diffractometer with Ni filter and graphite monochromator. The X-ray source was Cu Kα radiation. From the line broadening of corresponding X-ray diffraction peaks, according to the Scherrer equation (peaks were fitted by using a Voigt function).

$$D = \frac{\lambda 180}{\pi \cos \theta L}$$

where L is the line width at medium height, λ the wavelength of the X-ray radiation 0.15406 nm and θ is the diffracting angle.

XPS data were recorded on 4 mm × 4 mm pellets, 0.5-mm thick, prepared by gently pressing the powdered materials which were outgassed in the prechamber of the instrument at 150 °C up to a pressure below 2×10^{-8} Torr to remove chemisorbed water from their surfaces. The Leibold-Heraeus LHS10 spectrometer main chamber, working at a pressure $< 2 \times 10^{-9}$ Torr, was equipped with an EA-200 MCD hemispherical electron analyzer with a dual X-ray source working with Al Kα ($h\nu = 1486.6$ eV) at 120 W, 30 mA. C 1s was used as energy reference (284.6 eV).

Diffuse reflectance infrared spectra (DRIFTS) were taken in Bruker Equinox 55 FTIR spectrometer fitted with an MCT detector. The spectra consisted of 400 accumulations with a total of 5 min acquisition time, using a 4-cm^{-1} resolution. UV–vis diffuse reflectance spectroscopy experiments were performed with a Shimadzu UV2100 apparatus with a nominal resolution of ca. 5 nm using $BaSO_4$ as reference.

Scanning electron microscopy (SEM) pictures were taken on a JEOL JSM-5400 scanning electron microscope equipped with an energy dispersive X-rays analysis (XEDS) Link system for qualitative chemical analysis. Fractured samples were deposited on copper supports and covered by a thin film of gold.

Selected samples were also studied by transmission electron microscopy (TEM) using a Philips CM200 instrument. The microscope was equipped with a top-entry holder and ion pumping system, operating at an accelerating voltage of 200 kV and giving a nominal structural resolution of 0.21 nm. Samples were prepared by dipping a 3-mm holey carbon grid into ultrasonic dispersion of the oxide powder in ethanol

Photocatalytic runs (2 h) of phenol oxidation over the different catalysts (1 g/l) were performed in a Pyrex immersion well reactor (450 ml) using a metal halide 250 W lamp (Sylvania, metalarc HIS; exhibiting spectral lines above 390 nm, with main emission between 450–550 nm). In the oxidation tests, an oxygen flow was used to produce a homogenous suspension of the catalyst in the solution. Before each photo-experiment, the catalysts were settled in suspension with the reagent mixture for 15 min in the dark. The evolution of the initial phenol concentration (ca. 50 ppm in water) was followed by UV–vis spectrometry through the evolution of its characteristic 270 nm band, using a filtered aliquot ca. 2 ml of the suspension (Millipore Millex25 0.45-μm membrane filter). The degradation rates were calculated from the slopes of the conversion plots at the first 15 min of reaction, and assuming linear time dependence. The regression coefficients for such fittings are in all cases higher than 0.998.

3. Results and discussion

Under the experimental conditions of the study, the photodegradation of phenol displays a linear time dependence, with rate constants presented in Fig. 1. A linear time dependence is char-