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Influence of sulfur on the structural, surface properties and photocatalytic activity of sulfated TiO_2

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ABSTRACT

TiO_2 materials were prepared by sol–gel method and then impregnated with sulfuric acid and calcined using different temperatures and atmosphere (air and nitrogen). Systematic variation of these two experimental parameters makes possible to modulate the amount of surface sulfur from the impregnation procedure. The best photocatalyst for liquid phenol degradation was obtained after calcination at 700 °C in air, while gas toluene degradation optimum performance is obtained by calcination at 700 °C in nitrogen from 500 °C. Structural analysis of these materials by XRD, micro-Raman spectroscopy and FE-SEM shows that once calcined at 700 °C the material was a well-crystallized, high surface area anatase structure in all cases. The surface characterization by FTIR and XPS confirms the presence of a higher amount of sulfur species and acidic OH groups in samples partially calcined in nitrogen, and a low XPS O/Ti-atomic ratio with the O 1s peak shifted to higher binding energies (1.8 vs. 2 ± 0.1 and 530.4 eV vs. 529.8 eV, respectively, against the reference materials) for samples calcined at 700 °C, temperature at which most of sulfate species have been evolved. The paper presents an attempt to correlate the contribution of the observed structural defects within the anatase sub-surface layers and surface acidity to the different photoactivity behaviour exhibited for phenol liquid phase and toluene gas phase photodegradation.

1. Introduction

The improvement and optimisation of TiO_2 as a photocatalyst is an important task for technical applications of heterogeneous photocatalysis in the future. In this sense, many investigations on the basic principles and enhancement of the photocatalytic activity either in the ultraviolet or visible have been carried out [1,2]. The activity of a TiO_2 powder depends on its bulk and surface properties. Regarding to the surface properties, the enhancement of acidity of the semiconductor is reported as a feasible way to enhance the photocatalytic activity of TiO_2. It is well known that WO_3 or MoO_3 increases the surface acid properties of TiO_2 improving at the same time the UV-photon efficiency by increasing the adsorption of the pollutant [3,4]. Incorporation of W^{6+}, up to ca. 20%, into the bulk of the anatase lattice promotes photoactivity in the visible due to generation of cation vacancies [5,6].

Moreover, the improvement of the final photocatalytic properties might be achieved by influencing those properties which control either the charge carrier dynamics (carrier generation, transfer and diffusion) or the surface catalytic process, which are the quality of the structure and the surface features.

It has been widely reported that sulfated TiO_2 could have interesting photocatalytic properties in certain reactions [7–9]. The improved efficiency of the sulfated materials might be due to a greater surface area as well as the larger fraction of anatase phase. However a combination of both effects, the increase of acid properties and the larger surface area with an appropriate structure cannot be excluded in principle. Deng et al. [10] concluded that the improved photocatalytic activity of sulfated TiO_2 should be grounded in a combining effect of the presence of sulfate on the catalyst surface and the increase in catalyst surface area. However, no significant effect of sulfation was found for sulfated rutile TiO_2. In this sense, previous works pointed out that acid treated TiO_2 might present an oxygen defective surface [11]. Therefore, it may be expected that sulfation pretreatment clearly leads to an oxygen deficient surface [12,13]. We concluded that anatase stabilization by sulfate ions up to 700 °C and the creation of bulk oxygen vacancies through a dehydroxylation process of the excess of adsorbed protons seems to be responsible for the generation of a highly defective material. The loss of the oxide ions from their surface and the small fraction of rutile phase would lead to clear enhancement in the UV-photocatalytic activity of these materials by the improvement of the charge separation and

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diffusion to the surface. Recently Rengifo-Herrera et al. have shown that N and S co-doped materials showed suitable photocatalytic activity under UV and visible illumination towards *Escherichia coli* inactivation [14]. They also argued that catalysts showed a varying degree of hydroxylation and particles sizes affecting to the trapping and transfer of the charge carriers and therefore to the semiconductor performance.

It is well known that sulfate groups are stable in the oxide structure during calcination up to 600 °C [15,16]. Indeed, we reported that the DTG curve of the sulfated TiO_2 showed a weight loss between 400 and 600 °C that could be due to the decomposition of strongly bonded sulfate species. The disappearance of surface sulfate would take place in three well-defined steps denoting the existence a three sulfate families probably with different acid strength [12,13]. In the present paper we have obtained different presulfated TiO_2 systems with tuned amount of residual surface sulfates which would allow tailoring the structural and surface feature of the catalysts. The residual surface sulfate was stabilized by changing the calcination atmosphere from air to nitrogen at two different temperatures. This way we assure the occurrence of a different surface situation in the final TiO_2 photocatalyst.

2. Experimental

As previously reported [12], TiO_2 was prepared by a sol–gel method using titanium tetraisopropoxide (TIP) as precursor in isopropanol (3.9 ml TIP in 200 ml iPrOH). Hydrolysis of the isopropanol-TIP solution was achieved by adding certain volume of bidistilled water (TTIP:H_2O = 0.05). The precipitate was then filtered and dried at 120 °C overnight and divided in two portions. Sulfation of one of the batch was performed by dispersing the fresh dried powders in a H_2SO_4 1 M solution (50 ml/g) for 1 h. Then, the suspension was filtered off and the powder dried again at 120 °C overnight. Sulfated TiO_2 samples (hereafter, TS series) were calcined in flowing air at 650 and 700 °C for 2 h. Air flow was changed to N_2 atmosphere at different temperature (T_c = 500 and 600 °C) labelled hereafter by adding a number to the series label that indicates the temperature of calcination and the T_c temperature (i.e. TS650_Tc500 will mean samples calcined at 650 °C with N_2 atmosphere changing temperature at 500 °C). The thermal programme used in the calcinations is presented in Fig. 1.

BET surface area and porosity measurements were carried out by N_2 adsorption at 77 K using a Micromeritics 2000 instrument.

FTIR spectra were acquired using the transmission mode upon pellets of the studied powdered samples dispersed in KBr, using a Nicolet spectrometer (20SXB) with a DTGS detector, in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. The samples were uniformly ground in an agate mortar with KBr previously degasified at 400 °C.

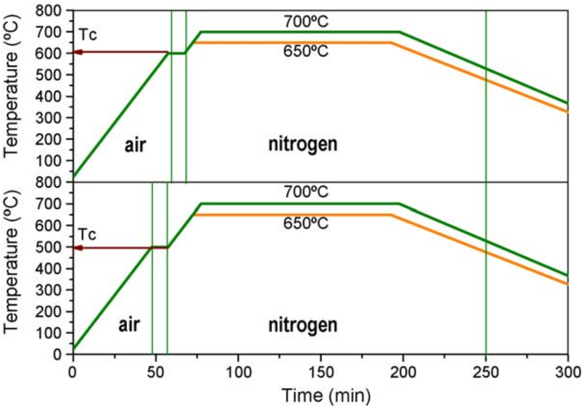

Fig. 1. Representation of the thermal programmes used.

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 (0.15406 nm). The line broadening (β_{hkl}) of X-ray diffraction peak corresponding to anatase phase planes was determined by deconvolution of the corresponding peak using a Voigt function. These values were incorporated into Williamson–Hall equation [17] for each sample according to the following expression:

$$\frac{\beta_{hkl}\cos\theta_{hkl}}{\lambda} = \frac{4\varepsilon\sin\theta_{hkl}}{\lambda} + \frac{1}{d}$$

where ε is the microstrain, d the crystallite size, λ the wavelength of the X-ray radiation 0.15406 nm and θ_{hkl} the diffracting angle.

Micro-Raman measurements were performed using a LabRAM Jobin Yvon spectrometer equipped with a microscope. Laser radiation (λ = 532 nm) was used as excitation source at 5 mW. All measurements were recorded under the same conditions (1 s of integration time and 30 accumulations) using a 100× magnification objective and a 125 μm pinhole.

The morphology of TS samples was followed by means of field emission-SEM (Hitachi S 4800). The samples were dispersed in ethanol using an ultrasonicator and dropped on a copper grid.

UV–vis spectra were recorded in the diffuse reflectance mode (R) and transformed to a magnitude proportional to the extinction coefficient (K) through the Kubelka–Munk function, $F(R_\infty)$. Samples were mixed with $BaSO_4$ that does not absorb in the UV–vis radiation range (white standard). Scans range was 240–800 nm.

XPS data were recorded on 4 mm × 4 mm pellets, 0.5 mm thick, prepared by slightly pressing the powdered materials which were outgassed in the prechamber of the instrument at 150 °C up to a pressure $< 2 \times 10^{-8}$ 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 using C(1s) as energy reference (284.6 eV). Surface chemical compositions were estimated from XP-spectra, by calculating the integral of each peak after subtraction of the "*S-shaped*" Shirley-type background using the appropriate experimental sensitivity factors [18].

Photocatalytic runs (2 h) of phenol oxidation using different catalysts (1 g/l) were performed in a batch reactor (250 ml) using a Osram Ultra-Vitalux lamp (300 W) with sunlike radiation spectrum and a main line in the UVA range at 365 nm. The intensity of the incident UVA light on the solution was measured with a PMA 2200 UVA photometer (Solar Light Co.) being ca. 105 W/m^2. In the oxidation tests, an oxygen flow was employed what produces a homogenous suspension of the catalyst in the solution. Before each experiment, the catalysts were settled in suspension with the reagent mixture for 15 min. The evolution of the initial phenol concentration (ca. 50 ppm) was followed through the evolution of the characteristic 270 nm band using a filtered aliquot ca. 2 ml of the suspension (Millipore Millex25 0.45 μm membrane filter). Total organic carbon was followed by means of a TOC analyzer (Shimadzu TOC VCPH).

Activity and selectivity for the gas phase photooxidation of toluene were tested in a continuous flow annular photoreactor (described elsewhere, Ref. [19]). The corresponding amount of catalyst was suspended in 1 ml of water, painted on a pyrex tube (cut-off at ca. 290 nm) and dried at RT. Thus, ca. 30 mg of photocatalyst is disposed as a thin layer coating on the pyrex tube showing an irregular thickness of ca. 40 μm. In any case, the reaction rates measured and reported were independent of the film thickness in the 20–60 μm range. The reacting mixture (100 ml/min) was prepared by injecting toluene (Panreac, spectroscopic grade) into a