



Influence of iron leaching and oxidizing agent employed on solar photodegradation of phenol over nanostructured iron-doped titania catalysts

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ABSTRACT

Iron-doped TiO₂ catalysts with two different iron contents (0.7 and 3.5 wt.%) as well as the corresponding undoped system, prepared by a combined sol–gel/microemulsion method and calcined at 600 °C, have been examined with respect to their behaviour for photocatalytic degradation of aqueous phenol with H₂O₂ under solar light. The activity results are complemented with structural/morphological and electronic characterization analysis achieved by XRD, TEM, Raman, S_{BET}, UV–vis DRS and XPS techniques. A detrimental effect of the presence of iron on the photoactivity is detected for the sample with 0.7 wt.% iron. In contrast, some activity enhancement is produced for the sample with highest iron loading. Such irregular catalytic behaviour with respect to iron loading is analyzed on the basis of the presence of additional catalytic contributions from new photoactive species. These are created as a consequence of surface modifications produced under reaction conditions related to the existence of phenomena of iron leaching from the catalysts. Differences in the specific nanostructure present in each case can also play a role on explaining the differences observed in the photoactivity. Finally, an analysis of the photoactivity as a function of the oxidizing agent employed, either H₂O₂ or oxygen from air, is also performed.

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1. Introduction

Polycrystalline titanium dioxide presents unique properties as heterogeneous photocatalyst considering its good stability in aqueous environment under ambient pressure and temperature condition [1,2]. However, its photocatalytic efficiency can be limited by stabilization of the charge photocarriers in the bulk of the material, by fast electron–hole recombination either at the bulk or at the surface of the oxide or by its relatively large band gap which limits light absorption in the visible region [1–6]. Among strategies aimed to enhance such properties, in particular extending light absorption to the visible region, it is common to employ methods based on doping the titania catalyst with transition metal cations [7–10]. Fe³⁺ is considered among most interesting dopants in this sense since it originates a localized narrow band above the valence band of titania which makes the catalyst sensitive to visible absorption [11,12]. However, the catalytic role of the Fe³⁺ dopant during photooxidation processes remains controversial [8–10,13–15]. Thus, discrepancies appear with respect to its role in enhancing electron/hole recombination properties since the

presence of iron in the catalyst formulation has been reported to be detrimental to the photoactivity in a great number of cases [10,13]. In turn, the photoactivity of iron-doped titania under visible light can be limited because the oxidizing power and mobility of holes in the Fe³⁺-derived localized narrow band can be lower than that of holes in the valence band of TiO₂ [11].

In any case, optimum photocatalytic properties have been apparently achieved in an important number of cases upon homogeneous doping at a relatively low level around 0.5–1 at.%, at which the distance between dopant cations in the titania lattice could optimize dynamical characteristics of the recombination process [1,3,10]. However, doping above such optimum level typically results detrimental to the photoactivity [10,15–17]. In turn, the specific reaction conditions (solution pH or type of oxidant employed) can strongly affect the photocatalytic properties of titania-based materials [10,18,19]. In this sense, it is generally concluded that the use of H₂O₂ as oxidizing agent can significantly enhance, as compared with dissolved oxygen, the UV- or visible-photoassisted contaminants oxidation rate [18,20–22], in spite of its possible hydroxyl radical scavenger role [18,23,24]. Other interrelated aspects that could affect the photoactivity concern modifications of the surface properties induced by doping as well as the possibility that species originated from iron lixivates can participate in the reaction mechanism [11,12,17,25–28].

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With respect to this latter, we have proposed in a recent work the involvement of iron species leached under reaction conditions from iron-doped titania in the mechanism of solar contaminants photodegradation employing oxygen as oxidant under semi-pilot plant conditions [27]. A similar study has been performed when H_2O_2 is employed as oxidant over nanostructured anatase TiO_2 (crystal size between about 10 and 12 nm, as obtained when using calcination at 450°C as final preparation step) systems of this kind, also indicating an important role of such leached iron species [17]. The present work aims to extend the latter analysis, employing H_2O_2 as oxidant, to more crystalline catalysts (obtained by calcination at 600°C) in order to explore whether the mechanism involving iron leached species could still prevail in the presence of more crystallized and likely more stable iron oxide and titania entities, and considering also the effects of crystallinity on phenol photooxidation activity [22,27–30]. In this respect, it must be noted that our previous results comparing samples calcined at 450°C (anatase) and 600°C (mixed anatase–rutile) when using O_2 (from air) as oxidant showed a generally higher photoactivity for the latter despite their appreciably lower specific surface area [27]. Within this context, pure titania and iron-doped titania catalysts prepared by sol–gel/microemulsion method and (as final preparation step) calcined at 600°C have been tested for phenol photodegradation with H_2O_2 under solar light irradiation in a pilot plant system. Information achieved by employing different structural and electronic characterization techniques (XRD, TEM, Raman, S_{BET} , as well as UV–vis and XPS spectroscopies) has been employed to complement the discussion of the catalytic activity results.

2. Experimental

Iron-doped photocatalysts were prepared using a combined sol–gel/microemulsion preparation method. Titanium-tetraisopropoxide was added to a reverse microemulsion in which the aqueous phase contains a solution of iron (III) nitrate nonahydrate; this was dispersed in *n*-heptane, using Triton X-100 (Aldrich) as surfactant and 1-hexanol as cosurfactant [3,15,27]. The resulting mixture was stirred for 24 h, centrifuged and decanted, and the obtained solid was rinsed with methanol and dried at room temperature for 12 h. Then, it was calcined for 2 h at 600°C under air atmosphere. Nominal iron amounts employed (0.7 and 3.5 wt.%, corresponding to ca. 1 and 5 at.%, respectively) were similar (within experimental error) to experimental contents determined by ICP-OES chemical analysis. Reference undoped TiO_2 was prepared by using the same method. Hereafter, the catalysts will be referred to as 600-T0, 600-T1 and 600-T5; the nomenclature is the same as employed in our previous report [27] and reflects the calcination temperature employed for the preparation (prefix) and the iron at.% loading of the catalysts (suffix).

Powder XRD patterns were obtained with a Siemens D-500 apparatus using nickel-filtered $\text{Cu K}\alpha$ radiation operating at 40 kV and 40 mA, with a 0.04° step size and accumulating a total of 5 s per point. Crystal size analysis was made by employing the Scherrer equation. The phase contents of a determinate catalyst were calculated from the integrated intensities of anatase (101) and rutile (110) peaks, employing a method reported elsewhere [31]. High resolution transmission electron microscopy (TEM) images were obtained with a JEOL JEM 2100F UHR electron microscope. Specimens were prepared by depositing particles of the catalysts to be investigated from acetone dispersions onto a copper grid supporting a perforated carbon film. Particle size distribution for estimation of average size has been performed by taking into account more than one hundred particles from the multiple TEM images made. Raman data were acquired using a Renishaw dispersive system 1000, equipped with a single monochromator, a holographic notch filter, and a cooled TCD; the catalysts

were excited using the 514 nm emission line of an Ar laser. The diffuse reflectance absorption spectra of the photocatalysts were recorded with a UV–Visible Varian 2300 apparatus. Nitrogen adsorption–desorption isotherms (for determination of specific surface areas, as examined by the BET method) were measured at -196°C in a Micromeritics Tristar automatic apparatus on catalysts previously outgassed overnight at 140°C to a vacuum of $<10^{-4}$ Pa to ensure a dry clean surface free from any loosely held adsorbed species. X-ray photoelectron spectroscopy (XPS) studies were performed with a VG Escalab 200R spectrometer employing an $\text{Mg K}\alpha$ (1253.6 eV) X-ray source. The catalyst was first placed in a copper holder mounted on a sample-rod in the pre-treatment chamber of the spectrometer and then outgassed at room temperature for 1 h before being transferred to the analysis chamber. The desired region of the spectrum was then scanned a number of times in order to obtain a good signal to noise ratio. The binding energies (BE) were referenced to the spurious C1s peak (284.6 eV) used as internal standard to take into account charging effects. The areas of the peaks were computed by fitting the experimental spectra to Gaussian/Lorentzian curves after removal of the background (Shirley function). Surface atom ratios were calculated from peak area ratios normalized by the appropriate atomic sensitivity factors [32].

A solar photoreactor based on Compound Parabolic Collectors (CPCs) installed at the Plataforma Solar de Almería (PSA) was employed to study the photodegradation of phenol under natural solar light; the characteristics of this reactor and the experimental set-up employed can be found elsewhere [3,33]. The total volume in the experiments was 35 L and the volume irradiated in the solar collector was 22 L. The starting conditions were the following: 50 mg/L of phenol, 500 mg/L of H_2O_2 and 200 mg/L of catalyst, added to the 10 L stirred tank; an initial pH value of ca. 6.5 was typically obtained under these conditions in the reactant dispersion. Evaluation of weather conditions required normalizing the intensity of the solar irradiance for experiments done in different days; irradiation was measured by means of a Kipp&Zonen CUV3 broadband UV radiometer with UV range (285–400 nm). It was inclined 37° (local latitude in PSA) and oriented to the south as the CPC photoreactor. A normalized illumination time defined elsewhere [34] was selected to normalize the solar irradiation. In this approach, the average solar UV flux on a perfect sunny day is considered to be $30 \text{ W}_{\text{UV}} \text{ m}^{-2}$; accordingly, the irradiation time will be represented as $t_{30 \text{ W}}$ (Eq. (1)).

$$t_{30 \text{ W},n} = t_{30 \text{ W},n-1} + \Delta t_n \frac{\text{UV } V_i}{30 V_f} \quad (1)$$

The total organic content (TOC) of aqueous samples was determined with a Shimadzu TOC-5050A analyzer equipped with a Shimadzu ASI-5000A autosampler. Phenol or aromatic intermediates concentrations were monitored by High Performance Liquid Chromatography with UV detection (HPLC-UV), employing a nucleosil C-18 column at 50°C and water/methanol at 65/35 ratio as mobile phase. The H_2O_2 content was measured by iodometric titration using KI 0.2 M, $\text{Na}_2\text{S}_2\text{O}_3$ 0.05 M and a starch indicator. Measurements of iron (II) and total iron lixiviates to the reaction medium were made by the 1,10-phenanthroline method (an adaptation of ISO 6332) by means of a UV–Vis Unicam-III spectrophotometer at 510 nm (maximum wave length of the iron–phenanthroline complex) and using a path length cuvette fixed in 5 cm, which multiplies the sensitivity of the technique.

3. Results and discussion

3.1. Catalysts characterization

Characterization results for some of the catalysts here examined were in part reported in previous contributions [3,27].

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