

PREPARATION OF VISIBLE-LIGHT-DRIVEN TiO₂ PHOTOCATALYST DOPED WITH IRON IN SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

Iron-doped titanium dioxide nanoparticles have been prepared from organometallic precursors in supercritical carbon dioxide (sc-CO₂). Three different synthesis routes were selected in order to carry out the experiments: (a) co-precipitation (b) mixing and (c) deposition-precipitation. The supercritical synthesis presents numerous advantages in comparison to classical methods. To cite a few examples, any post-calcination treatment or further separation step is required as well as reaction times and synthesis temperatures are comparatively lower. These characteristics lead to superior qualities in the final products. The samples were characterized by various techniques including X-ray diffraction (XRD), scanning electron micrographs (SEM), X-ray micro analysis (EDS), UV-vis diffuse reflectance spectroscopy (DRS-UV) and X-ray photoelectron spectroscopy (XPS). The photocatalytic activity of the iron-doped titania samples was evaluated by the degradation of methyl orange (MeO) from aqueous solution. These synthesized powders present remarkably higher activity than that of pure titanium oxide (TiO₂) anatase under visible light. This is due to the enhancement of the electron-hole separation by the electron trapping of iron particles. The optimized doping concentration is 1 wt. %. When the concentration is higher, iron ions act as recombination centers, leading to a decrease in the photocatalytic activity.

INTRODUCTION

Titanium dioxide is frequently used as a photocatalyst, due to its semiconductor properties, availability, low price and chemical stability. It is extensively applied for the degradation of organic pollutants, photoreduction of dinitrogen to ammonia, splitting of water or hydrogen production, photovoltaic cells and a long list of new pioneering applications [1]. However, the wide band gap energy (3.0 – 3.2 eV) requires near-UV light ($\lambda < 411$ nm for rutile and 384 nm for anatase) to photoactivate this catalyst. For example, in solar energy applications only 3 % of the solar light is absorbed and the solar spectrum includes less than 5 % UV light. Furthermore, the high rate of electron-hole recombination often results in a low quantum yield and poor efficiency of photocatalytic reactions. These basic problems, among others, impede the use of TiO₂ for practical applications. Iron trioxide (Fe₂O₃) has been considered to be promising for applications in solar energy conversion because it has a lower band gap ($E_g = 2.2$ eV). Several methods have been proposed in order to decrease the electron-hole recombination and sensitization towards visible light. The strategies include doping with metals, rare earths, noble metals, and non-metals. The doping using the correct amount of metals can trap the photogenerated charge carriers and inhibit the

recombination of photo-induced electron-hole pairs. Rare earth metals, having incompletely occupied 4f and empty 5d orbitals, often serve as catalyst, restrain the increase of grain size, lead to crystal expansion and matrix distortion and retard the recombination of the photoexcited charge carriers. The nonmetals can be incorporated into the crystal of titanium dioxide, modifying the electronic structure around the conduction band edge resulting in the band gap narrowing and the response to the visible light.

Up to now, nearly all doped TiO₂ samples are prepared by classical methods such as sol-gel, hydrothermal synthesis, wet impregnation, or metal organic chemical vapor deposition (MOCVD). Among these synthesis techniques, the sol-gel method is the most widely used. However, the morphology of the Fe-TiO₂ powders prepared by this method is not very regular. Furthermore, the sol-gel-derived precipitates are usually amorphous and require further heat treatment to induce crystallization. The calcination process frequently gives rise to particle agglomeration and grain growth, which is unfavorable for the acquisition of high activity. The synthesis of nanoparticles in supercritical carbon dioxide provides higher values of specific areas and reaction rates as well as requires lower process temperatures [2]. In addition, there is no need to additional steps such as separations or post-calcination treatments.

This study aims to: (i) establish the effect of the three different synthesis methods on the Fe-doped TiO₂ microstructure and morphology and (ii) investigate their photocatalytic activities for degrading MeO under UV and visible light. This organic compound was selected since it is a model industrial contaminant and cannot be photodegraded in the absence of photocatalyst under light irradiation.

MATERIALS AND METHODS

A. Materials

Diisopropoxititanium bis(acetylacetonate) (DIPBAT, 75 wt. % in isopropanol solution) and Titanium (IV) oxide nanopowder (TiO₂, purity 99.7 %) were purchased from Sigma Aldrich. Iron (III) acetylacetonate (Fe(acac)₃, 99.9 %, Sigma Aldrich) and Magnetite nanopowder (Fe₃O₄, 98 %, Sigma Aldrich) were used as iron source. Two different alcohols were tested: absolute ethanol (EtOH, analytical reagent) and isopropyl alcohol (IPA, analytical reagent) both provided by Panreac. The carbon dioxide (CO₂, 99.9 %) was used as received from the commercial supplier Carburros Metálicos S.A.

B. Preparation of the iron-doped TiO₂ photocatalysts

A versatile pilot plant has been developed in the Chemical Engineering Department at the University of Valladolid, to operate up to 35.0 MPa and 400°C. The flowsheet of the experimental facility is shown in **Fig 1**. Experiments were performed in batch conditions and the iron-doped TiO₂ was prepared via three different routes:

- *Procedure 1 (Co-precipitation)*: both metal organic precursors, DIPBAT and Fe(acac)₃, are used as precursors in the synthesis.
- *Procedure 2 (Impregnation)*: Fe₃O₄ nanopowder is used as Fe source
- *Procedure 3 (Deposition-precipitation)*: commercial TiO₂ nanoparticles (size < 20 nm) are used for impregnation with Fe(acac)₃.

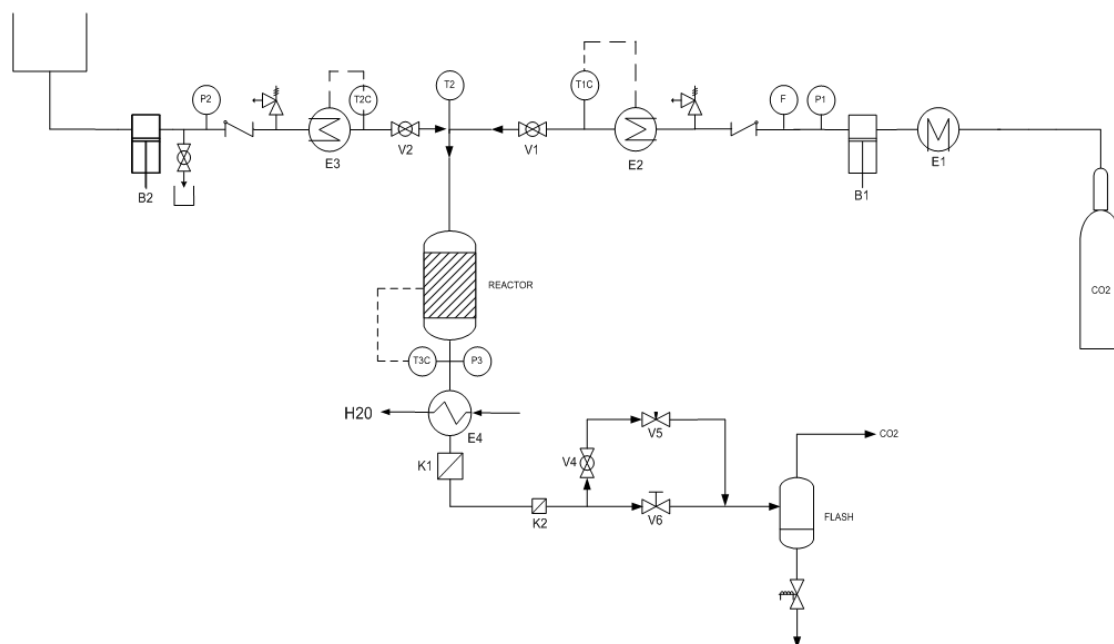


Fig. 1. Flow diagram of the laboratory plant used for the synthesis of Fe-TiO₂ particles in SC-CO₂

C. Characterization of the prepared photocatalysts

The synthesized iron-doped TiO₂ samples were characterized for structural, morphological and chemical properties. The crystalline phases were identified by X-ray diffraction (XRD) using Cu K α radiation (Philips PW 1710 diffractometer). The particle size and external morphology were observed by scanning electron microscopy (SEM) and X-ray micro analysis (EDS) using a JEOL JSM-T300. Diffuse reflectance UV–vis spectroscopy (DRS-UV) was applied to study the threshold wavelengths and absorption intensities of the prepared samples using a UV-vis spectrophotometer. The element composition and the chemical state of particle surface were determined by X-ray photoelectron spectroscopy (XPS). All the binding energies were referenced to the C 1s peak at 284.6 eV. The purity of the samples was determined by elemental analysis of the carbon (analyzer Leco Cs-225 determinator), since it is assumed that all the contamination of the samples comes from the organic part of the precursor molecule.

D. Photocatalytic activity measurement

The photocatalytic evaluation of the Fe-doped TiO₂ was tested using aqueous solutions of methyl orange (MeO). The initial concentrations were 1g/l of the photocatalyst and 35 ppm of the model contaminant. The pH of the solution was adjusted to 2.7 using hydrochloric acid. Two different sources of light (UV and visible) were individually used to compare the activity of the catalyst. The experiments were carried out with the equipment described elsewhere [3].

RESULTS

A. Crystallographic analysis

Anatase phase is essentially present for all samples. In addition, no characteristic peaks of iron oxides phases are identified, which meant that the iron oxide exists as amorphous phase or the concentration is so low that it cannot be detected by XRD. The average grain size calculated from the broadening of the (101) XRD peak using Scherrer's equation was about 7 - 16 nm. Furthermore, an elementary carbon analysis was carried out to confirm the total decomposition of the precursor. The results were percentages lower of 1 wt. % in C.

B. Morphology

The size and morphology of Fe-doped TiO₂ nanoparticles was investigated by scanning electron microscope (SEM). This technique was coupled with Energy dispersive X-ray Spectroscopy (EDS) to determinate the elementary composition. The spherical particles are in the range 50-100 nm of diameter within agglomerates of 500 nm in size. The Fe/Ti ratio is determined by EDS in 5 different points of the sample and reveals a uniform distribution of the iron in the powder. The use of Fe(acac)₃ (Procedures 1 and 3) provides a homogeneous distribution of the dopant on the particle surfaces.

C. UV-vis diffuse reflectance spectra (DRS)

The spectra of Fe-doped TiO₂ nanoparticles displayed a red shift in the band gap transition with the increasing doping content, accompanied with colour appearance changes in the samples from white to reddish yellow. The origin of this visible light absorption is due to the formation of a dopant energy level within the band gap of TiO₂.

D. X-ray photoelectron spectroscopy analysis

The O 1s and Fe 2p XPS spectra of a typical doped sample have been analyzed. The peak of O 1s can be decomposed into two contributions. The main peak at 529.6 eV derived from the crystalline TiO₂ and a smaller one at higher binding energy. According to the literature sources [4], the XPS O 1s peak component at 532 eV could be associated with the presence of surface oxygen containing carbonaceous species. This is corroborated by the Fe 2p spectrum.

E. Photodecomposition of methyl orange (MeO)

The photocatalytic activity of non-doped and doped TiO₂ samples was determined by the photocatalytic degradation of methyl orange (MeO). It was selected as a model pollutant because it is a common contaminant in industrial wastewater and cannot be photodegraded in the absence of photocatalyst under light irradiation. The iron doping did not improve the photocatalytic properties of TiO₂ (anatase) under UV light, in fact the addition of Fe slowed down the catalysis.

In contrast, pure TiO₂ powders do not have any photocatalytic activity under visible light and iron-doped particles can catalyze this oxidation under the new conditions. Iron

concentrations of 1 wt. % showed better catalytic properties than that of 5 wt. %. An excess of iron (5 wt. %) slows down the oxidation of MeO, since Fe can represent an impurity. Representative photodegradation curves for different tests under visible light are represented in **Fig. 3**.

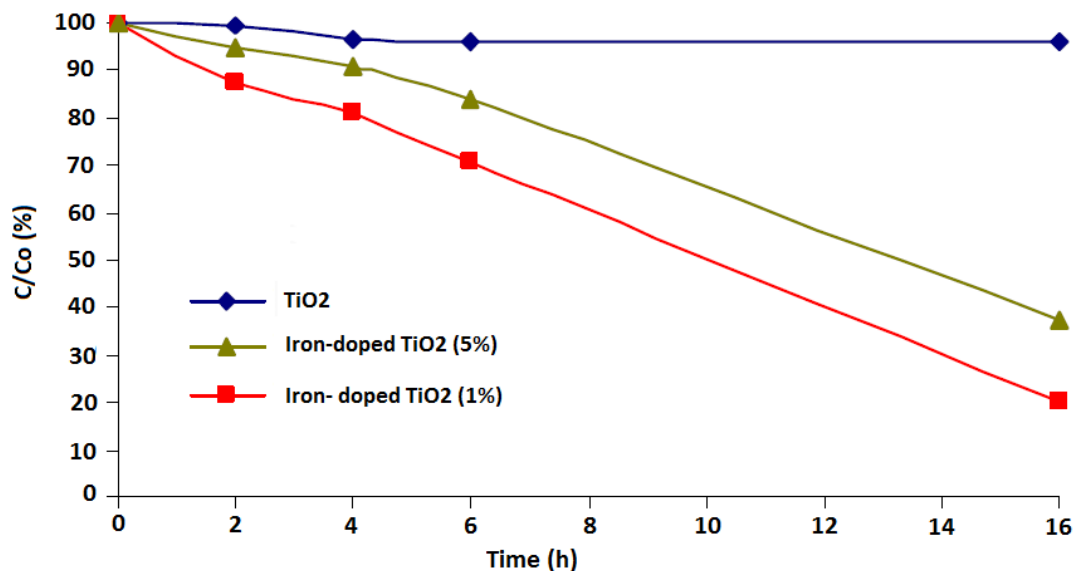


Fig. 3. Results of photocatalytic degradation performed using as a catalyst: commercial TiO₂ (anatase) and Fe-doped TiO₂

CONCLUSIONS

In summary, highly active crystalline anatase TiO₂ doped with iron has been prepared by the decomposition of the corresponding metal organic precursor in sc-CO₂. Spherical-shaped nanoparticles in the range 50-100 nm of diameter within agglomerates around 500 nm in size were directly obtained by three different methods without any further treatment. There is a homogeneous distribution of the iron atoms in the titanium dioxide. The diffuse reflectance spectra displayed a red shift in the band gap transition with the increase of the iron content. A real ion implantation takes place when the synthesis routes are co-precipitation and deposition-precipitation (procedure 1 and 3). When Fe₃O₄ is adsorbed on the TiO₂ powder (impregnation - procedure 2) this shift is not observed. As concerns the photocatalytic degradation, Fe-doped titania photocatalyst could degrade MeO from aqueous solution under visible light irradiation and its photoactivity markedly exceeded than that of TiO₂ (anatase). The optimal concentration in order to reach the highest photocatalytic activity is 1 wt. %. It is concluded that an appreciable improvement in the photocatalytic efficiency of titania nanoparticles was achieved upon the band gap narrowing by iron doping using sc-CO₂ as reaction medium.

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