

SYNTHESIS OF DOPED NANOPARTICLES IN SUPERCRITICAL CO₂

Héctor Fernández-Rodríguez , Esther Alonso*, and Maria José Cocero
Dpto. Ingeniería Química, Universidad de Valladolid,
Prado de la Magdalena s/n, Valladolid, Spain
calonso@iq.uva.es Phone: +34 983 42 31 75 Fax: +34 983 42 30 13

Supercritical CO₂ is used as reaction medium for the synthesis of doped oxides with transition metals. These materials are subsequently tested for their catalytic activity. With that purpose, anatase TiO₂ nanoparticles have been doped with Fe by chemical decomposition of organometallic precursors in a supercritical CO₂ reaction medium. TiO₂ nanoparticles are interesting for many applications due to their photocatalytic properties. However, TiO₂ activity is reduced to the region of UV light (wavelength around 360 nm). In order to harness the abundant and safe potential of solar energy, the development of processes to enhance and shift the absorption of TiO₂ to the visible region is of the great importance. One of the ways to extend the absorbance of TiO₂ is transition metal doping in the lattice of TiO₂.

INTRODUCTION

Titanium dioxide is a semiconductor which exhibit catalytic properties. It is widely used in environmental application as a photocatalyst for oxidation reactions of organic compounds, in alcohol thermal decomposition reactions, in photocatalytic decomposition of water for hydrogen production, in photovoltaic cells and etc [1].

Generally, the photocatalysis process over a semiconductor involves the absorption, band gap excitation, separation of the photoexcited electron/hole pairs, and redox reactions on the semiconductor surface [2].

As a photocatalyst TiO₂ can act as sensitizers for light – reduced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band. When the photon with an energy of $h\nu$ exceeds the bandgap, E_g , of the semiconductor, an electron e^- , is promoted from the valence band, VB, into the conduction band, CB, leaving a hole h_{vb} behind. Graphically it can be expressed in Fig.1 [3].

TiO₂ (anatase) has wide band gap, $E_g \approx 3,2\text{eV}$, thus only light below 400 nm is absorbed and capable of forming the e^-/h^+ pair [4]. The dyes, impurities and dopants can sensitize TiO₂ to react to a much larger visible light region [1]. The different dopants may not have the same effect on trapping electrons or holes on the surface during the interface charge transfer because of the different positions of the dopant in the host lattice. In general photocatalytic activity of TiO₂ depends of many factors, such as, specific surface area, the absorption affinity and capacity for organic contaminants, electron-hole recombination processes in the bulk and on the surface of the catalyst, intensity and spectral distribution of the illuminating light, crystal morphology, intrinsic solid stated defects, stoichiometry of the catalyst oxide, pH, the presence of electron acceptors, the concentration of the pollutant [4].

The main aim of the research was focused on the efforts to synthesise doped TiO₂ nanoparticles with Fe atoms in order to change catalytic properties of TiO₂ nanoparticles which were tested in the methyl orange oxidation reactions.

EXPERIMENTAL

In the experimental procedure, diisopropoxititanium bis(acetylacetonate), (DIPBAT), is used as titania precursor and Iron (III) acetylacetonate for the doping metal ion. Under the supercritical conditions metal oxide particles are formed as a result of the metal salt hydrolysis and followed dehydration reaction under the supercritical conditions. The great advantage of this technology is that the nanoparticle doping takes place during the synthesis process. The synthesis of doped TiO₂ nanoparticles in batch and continuous flow reactors are presented. It has been performed in a versatile plant developed in the Chemical Engineering Department at the University of Valladolid. Its flow diagram is presented in figure 1. The plant has a stainless steel reactor (R-110) with 100 mL of internal volume and it is equipped with pressure and temperature sensors. The reactor is heated by means of two electrical resistances and it is located into a furnace in order to avoid heat losses. Different percentages (in weight) of iron salt with titanium salt in an alcoholic solution are prepared before pumping it into the reactor. The residual liquids (unreacted precursors, alcohol, byproducts of the reaction...) were collected at the phase separator (S-140) after decompression.

Reaction temperature has been changed in the range 200 – 400 °C and pressure from 200 to 250 bar.

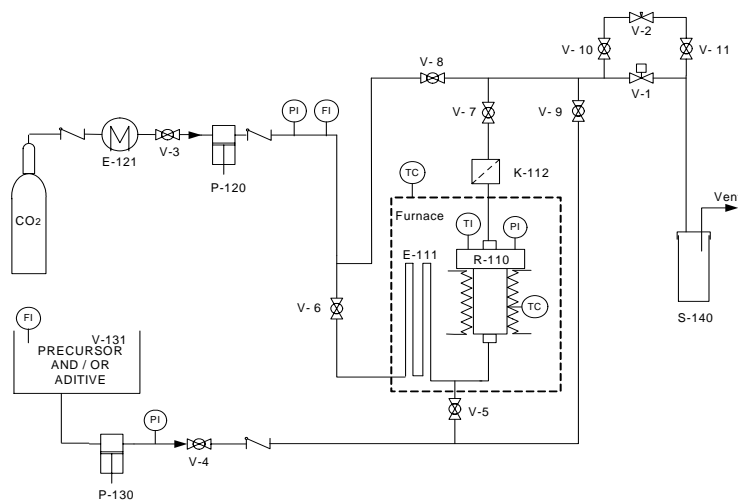


Figure 1. Flow diagram of the laboratory plant used for the synthesis of doped TiO₂ particles in SC-CO₂

Photocatalytic activities for the degradation of methyl orange under visible light irradiation are tested for the doped TiO₂ and they are compared to the non-doped samples. A schema of the photocatalytic set-up is presented in figure 2.

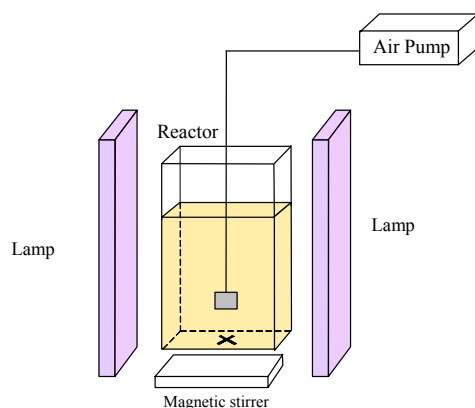


Figure 2. Schema of the photocatalytic reactor set-up

RESULTS

The experimental results show that TiO₂ particles with high (5%) or low Fe content (1%) can be synthesised by chemical decomposition of DIPBAT and Iron (III) acetylacetonate using supercritical CO₂ as solvent reaction. UV-Vis diffuse reflectance spectra presented in figure 3 show a slight shift to longer wavelengths and an enhancement of the absorption in the visible region (>400 nm) for the Fe doped TiO₂ nanoparticles, compared to the non-doped powder. The implanted Fe ions could decrease the band gap of the TiO₂ to enable the absorption in the visible light.

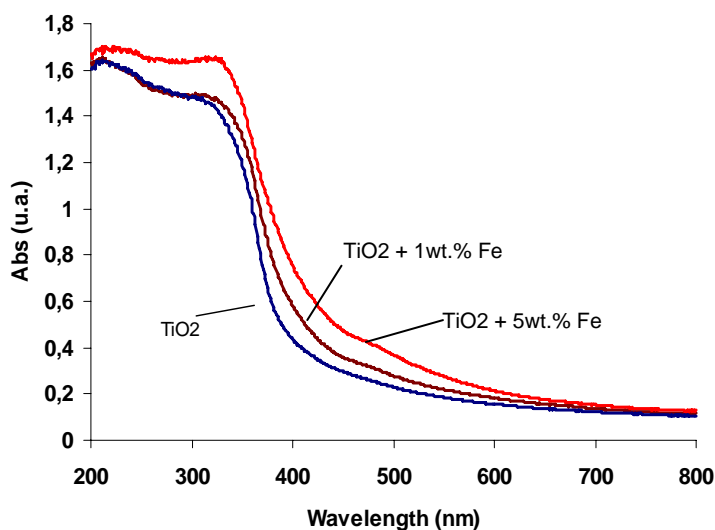


Figure 3. UV-Vis spectra of doped TiO₂. Effect of iron content.

The addition of Fe into the titanium precursor allows TiO₂-Fe particles to be synthesized with the improved photocatalytic activity using visible light compared to TiO₂. The particles with lower content of Fe (1 %) exhibit more efficient photocatalytic effect than those obtained with higher content of Fe (5 %), as it is shown in figure 4.

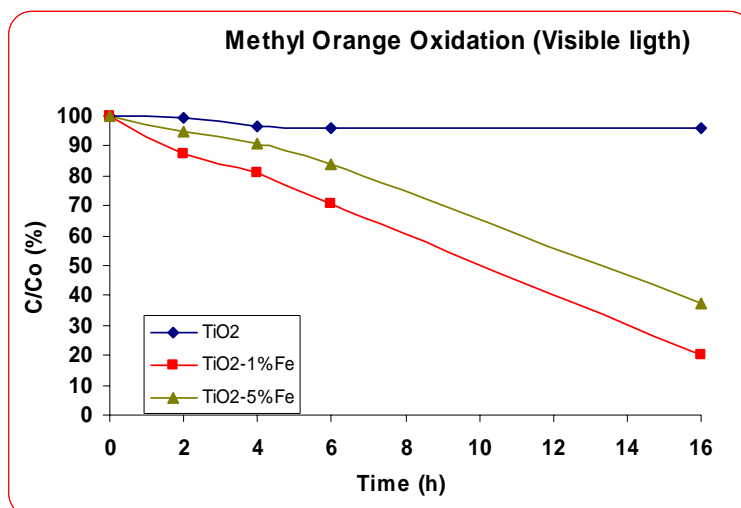


Figure 4. Photocatalytic test of doped TiO_2

ACKNOWLEDGEMENTS

Authors thank Spanish Education and Science Ministry, Project Reference: CTQ 2006-02099/PPQ and Regional Project of Junta de Castilla y León: Programa General de Apoyo a Proyectos de Investigación (JCYL) Reference GR11, for financial support.

REFERENCES:

- [1] M. Kitano, M. Matsuoka, M. Ueshima and M. Anpo, Applied Catalysis, A. General, 1, **2007**, 325.
- [2] D. Wang, J. Ye, T. Kako, T. Kimura, J. Phys. Chem. B, 32, **2006**, 110.
- [3] M.R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, Chem. Rev. 95, **1995**, 69.
- [4] S. Al-Qaradawi, S. R. Salman, Journal of Photochemistry and Photobiology A: Chemistry, 148, **2001**, 161.