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Crystalline structure, surface chemistry and catalytic properties of Fe^{3+} doped TiO_2 sol–gel catalysts for photooxidation of 2,4–dichlorophenoxyacetic acid

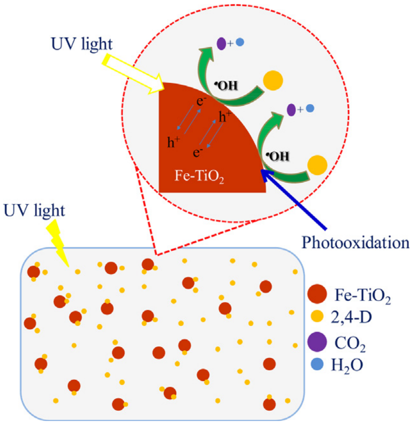
U. Arellano [a, b], J.A. Wang [a, *], M. Asomoza [b], L.F. Chen [a], J. González [a], A. Manzo [a], S. Solís [b], V.H. Lara [b]

[a] ESIQIE, Instituto Politécnico Nacional, Col. Zacatenco, Av. Instituto Politécnico Nacional s/n, 07738, Ciudad de México, Mexico
[b] Departamento de Química, Universidad Autónoma Metropolitana–Iztapalapa, Av. San Rafael Atlixco No. 186, Iztapalapa, Ciudad de México, Mexico

HIGHLIGHTS

- Several roles of the calcination in the synthesis of Fe-TiO_2 were determined.
- Surface chemistry and crystalline structure Fe-TiO_2 catalysts were investigated.
- Fe^{3+} bridged the oxidation half cycle and reduction half cycle in the photoreaction.
- 2,4–DA photodegradation was favored under acid condition with Fe-TiO_2 anatase.

GRAPHICAL ABSTRACT



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ABSTRACT

Highly active Fe^{3+} doped TiO_2 (xFe–TiO_2 where $x = 3$ or 5 wt%) photocatalysts were synthesized by the sol–gel method and their structures were refined with the Rietveld method. Several important effects of calcination temperature on the crystalline structure, textural features, phase concentration, Fe^{3+} distribution, optical properties, and photocatalytic activity were determined. When Fe–TiO_2 materials were calcined at 400 °C, most of Fe^{3+} were formed α-Fe_2O_3 and some of them were incorporated in the network of TiO_2 anatase; as calcination temperature increased to 800 °C, α-Fe_2O_3 and $FeTiO_3$ coexisted on the TiO_2 rutile phase. High calcination temperature also led to surface area sharply diminishing and the surface oxygen reducibility significantly decreasing. The interatomic distances of Fe–TiO_2 catalysts obtained from the method of radial distribution function (RDF) were: $Ti\cdots O = 1.93$ Å (anatase), $Fe\cdots O = 2.59$ Å, $Ti\cdots Ti = 3.08$ Å, $Ti\cdots Fe = 3.69$ Å, $Ti\cdots Ti = 3.79$ Å, $Ti\cdots O = 4.83$ Å (rutile). In the photooxidation of 2,4-dichlorophenoxyacetic acid (2,4-DA), the photocatalytic activity of Fe–TiO_2 catalyst increased with increase of Fe^{3+} content in anatase phase. The 2,4-DA photooxidation followed the first-order kinetic reaction model and favored under acidic condition. Approximately 95% 2,4–DA were photooxidized with the best catalyst 5Fe–TiO_2–400 after 120 min of reaction under UV irradiation. TiO_2 phase transformation from anatase to rutile and $FeTiO_3$ formation at 800 °C negatively impacted on the

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* Corresponding author.
E-mail address: jwang@ipn.mx (J.A. Wang).

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photocatalytic performance. The catalytic activity of the catalysts correlated well with variations of textural properties, phase concentration, and surface oxygen reducibility that were all controlled by the calcination temperature.

1. Introduction

For minimizing organic contaminants in wastewater, a variety of technologies have been developed; among those the photocatalytic oxidation has been highlighted as it is particularly interesting for the treatment of water contaminated by non-biodegradable substances [1,2]. This technique is based on the formation of highly oxidizing species, principally hydroxyl radicals ($^{\bullet}OH$) which possess high oxidation power and can be generated under ultraviolet (UV) irradiation in the surface of semiconductors or photocatalysts [3,4]. TiO_2 is one of the most investigated semiconductors and has a wide spectrum of applications in the heterogeneous photocatalysis field [5,6]. TiO_2 powders would be synthesized using various routes, and among those, the sol-gel method is widely applied. In general, the sol-gel process implies transition of a system so-called “sol” containing colloidal solid particles with nanometric size to a suspended mixture with fine particle size denominated as “gel” [7]. The sol-gel TiO_2 materials usually show large surface area and uniformed particle size distribution.

The photocatalytic process can be initiated via the absorption of photons with energy equal to or greater than the prohibited band energy of TiO_2 (3.2 eV), promoting the generation of many electron (e^-) and hole (h^+) pairs in the surface of the photocatalysts. The electron-hole pairs can be removed by chemisorption giving way to the formation of superoxide radical anions ($O_2^{-\bullet}$) and hydroxyl radicals ($^{\bullet}OH$) surface species; these species are highly reactive, and participate in the process of mineralization of contaminants in a simple and economical way. However, TiO_2 only absorbs light in the UV region due to its relatively large band gap energy. This is its main drawback in the application because only 4–5% of solar spectrum falls in this range [8,9]. Transition metal oxide doping of a TiO_2 solid is an effective way to overcome this problem and to improve its photoactivity [10,11]. It is reported that doping with Fe^{3+} augments the photocatalytic efficiency of TiO_2 because Fe^{3+} acts as a charge trapper, by prolonging the life-time for electron (e^-) and hole (h^+) on the surface [12,13]. Therefore, when TiO_2 doped with Fe^{3+}, the recombination of the e^-–h^+ pairs on the surface can be inhibited to some extent, through the creation of charge trapping sites inside TiO_2 matrix. The most favorable effect occurs when one of the charges is temporarily trapped while the other migrates to the surface where it transfers to the adsorbate for oxidation [11,14].

Iron concentration and calcination temperature are the most important factors in the preparation of an active Fe-TiO_2 sol-gel photocatalyst. Surface chemistry of the Fe–TiO_2 solids varied with the phase composition that was controlled by calcination procedure. Investigation of the influences of phase concentration, textural properties, surface chemistry, and metal doping of TiO_2 on their photocatalytic behaviors is undoubtedly an interesting research task.

The aim of this study is to understand the influences of calcination temperature and Fe^{3+} doping on the textural properties (surface area, pore volume, and pore diameter), the crystalline structure and phase transformation, surface chemistry including surface reducibility, surface interatomic distances, and Fe ions oxidation state, as well as photocatalytic behaviors of Fe^{3+} doped TiO_2 catalysts obtained by the sol-gel method. The crystalline structure was characterized with X-ray diffraction (XRD) technique and refined with the Rietveld method; surface interatomic distances were calculated using the method of radial distribution function (RDF); Fe and Ti oxidation state and concentration were analyzed by X-ray photoelectron spectroscopy (XPS); morphological features were observed by electron transmission microscopy (TEM), textural properties were measured with N_2 adsorption–desorption isotherms method; surface oxygen reducibility was measured by temperature-programed reduction (TPR) method. Finally, the photocatalytic oxidation of 2,4–dichlorophenoxyacetic acid (terms 2,4–DA) was implemented as a model reaction for investigating the photo-kinetics and photocatalytic efficiency of the Fe–TiO_2 catalysts, due to the simplicity of this reaction and easy monitoring of the experimental procedure [15,16]. Roles of calcination temperature on textural properties, phase transformation and Fe^{3+} ions distribution and their effects on the photooxidation of 2,4 – DA were reported. The reaction mechanism and reaction kinetics of 2,4–DA photocatalytic degradation were investigated.

2. Experimental

2.1. Catalysts synthesis

TiO_2 photocatalytic materials were synthesized through the sol-gel method doped with Fe at 3 and 5 wt%. The method consisted of: (1) Mixing 0.67 moles of ethanol and 0.19 moles of titanium ethoxide ($Ti(OC_2H_5)_4$, 97%, Aldrich); (2) Slowly adding a calculated amount of $Fe(NO_3)_3\ 9H_2O$ solution into the above mixture to obtain Fe-TiO_2 mixed materials with 3 and 5 wt% Fe. The pH of the mixture was adjusted to 3 with 0.1 M HCl. The suspended mixture was stirring for 2 h; (3) This suspended mixture was refluxed at 70 °C for 7 h; then the solvents were evaporated at 70 °C and finally a white gel was obtained; (4) The obtained powders were filtered and washed with deionized water and were dried at 100 °C for 4 h in air. One part of the dried sample was calcined at 400 °C and the other part was calcined at 800 °C, each for 8 h. The resulting materials were labelled as xFe–TiO_2–y where x represents the weight percentage of Fe, and y represents the calculation temperature.

2.2. Characterization

2.2.1. X-ray diffraction analysis

The Fe-TiO_2 materials were analyzed with a Siemens D500 diffractometer coupled to a tube of a copper anode with radiation of Cu kα ($\lambda = 1.5406$ Å), 35 kV and 20 mA, and connected with a diffracted-beam monochromator. The XRD patterns of the materials were recorded in the 2θ range between 5° and 70° with a step of 0.02° and a measuring time of 2.67 s at every point.

2.2.2. Rietveld refinement

The crystalline structures of the Fe-TiO_2 catalysts were refined with the Rietveld method. The JAVA based software namely Materials Analysis Using Diffraction (MAUD) was applied to refine each X-ray diffraction spectrum [17]. The atomic fractional