

Ilmenite (FeTiO₃) as low cost catalyst for advanced oxidation processes



P. García-Muñoz^{a,*}, G. Pliego^a, J.A. Zazo^a, A. Bahamonde^b, J.A. Casas^a

^a Sección departamental de Ingeniería Química, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain

^b Instituto de Catálisis y Petroleoquímica (CSIC), C/Marie Curie, 2, 28049 Madrid, Spain

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ABSTRACT

The role of ilmenite mineral (FeTiO₃) in different AOPs processes (photocatalysis, catalytic wet peroxide oxidation (CWPO) and CWPO-Photoassisted processes) was evaluated using phenol as target compound. Our results endorse its role as solar photoassisted catalyst for H₂O₂ decomposing into HO[•] radicals. In photocatalytic process, despite both the higher TiO₂ content and a band-gap lower than titanium dioxide P25, ilmenite showed a scarce activity. On the other hand, ilmenite results a feasible catalyst in CWPO process, although it requires high induction periods, around 200 min. This drawback can be overcome by combining CWPO with solar light irradiation, since the latest provokes a faster Fe(III) reduction into Fe(II) that decomposes H₂O₂ into HO[•] radicals. Working at pH₀=3, T₀=25 °C, an almost complete phenol (100 mg L⁻¹) mineralization (X_{TOC}>95%) was obtained after 480 min reaction time using the stoichiometric H₂O₂ dose (500 mg L⁻¹), ilmenite (450 mg L⁻¹) and 550 W m⁻². Besides, Ilmenite showed a high stability after five consecutive CWPO-Photoassisted runs, where TOC reduction, above 90%, was maintained working at the previous experimental conditions. The total Fe leaching from ilmenite was around 2% of the initial load.

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1. Introduction

Ilmenite mineral (FeTiO₃) have been traditionally used as a raw material for production of TiO₂. Other applications include solar cells, gas sensors and catalysts [1,2].

Since ilmenite contains high percentages of iron and titanium in its structure, it is starting to be employed as heterogeneous catalyst in Advanced Oxidation Processes (AOPs) for the removal of pollutants in wastewater [3].

AOPs represents an interesting alternative to treat wastewater containing pollutants which cannot be eliminated by conventional treatments. These processes generate oxidizing species (especially hydroxyl radical, HO[•]) which oxidize organic chemical compounds [4].

Research on the degradation of hazardous chemical compounds in water by ilmenite as catalyst have been studied upon two different AOPs: as photocatalyst and as catalyst for Catalytic Wet Peroxide Oxidation (CWPO).

Photocatalysis is based on producing hydroxyl radical through irradiating an aqueous TiO₂ suspension with light of λ < 385 nm for

generate valence band holes (h_{VB}⁺) and conduction band electrons (e⁻_{CB}) which can migrate to the interface reacting with suitable adsorbed redox species to generate oxidizing species [4].

The results obtained by Moctezuma et al. [5] showed a scarce activity of a synthesized FeTiO₃ for phenol photodegradation. On the other hand, ilmenite has demonstrated ability in CWPO process to decompose H₂O₂ due to its iron percentage at acid pH through the redox catalytic cycle of iron combined with H₂O₂ (reaction 1–2) [6].

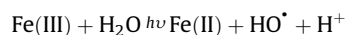


Teel et al. compared the rates of H₂O₂ decomposition mediated by several minerals at pH 3 to promote the generation of HO[•] radicals [6]. Despite the high percentage of iron in ilmenite (around 40% in weight), the H₂O₂ decomposition rate was very slow compared to that obtained with the catalysts commonly used in this process, where iron (around 5% in weight) is supported on different materials like carbon, alumina, silica or zeolites. This would indicate that H₂O₂ decomposition occurs mainly on the surface of the catalyst. Nonetheless, the presence of iron in the mineral matrix that acts as active phase in CWPO could lead to a more stable catalyst [7]. Therefore, the feasibility of ilmenite as a

* Corresponding author at: Ingeniería Química, Facultad de Ciencias, C/Francisco Tomás y Valiente 7, Universidad Autónoma de Madrid, 28049 Madrid, Spain.

E-mail addresses: patricia.garciam@uam.es, pgmunoz89@gmail.com (P. García-Muñoz).

catalyst in these processes require new research to increase the efficiency. In this sense, the activity of iron-containing catalyst can be greatly enhanced by irradiation with light. The reasons of this positive effect on the degradation rate include the photoreduction of Fe(III) to Fe(II) (reaction 3) which produce new HO• radicals with H₂O [8].



Therefore, this work aims to study the feasibility of using ilmenite mineral as a catalyst for CWPO process and the synergies of irradiating with solar light. Phenol will be used as target compound since it is a representative industrial wastewater pollutant widely used in AOPs studies and will allow comparing the results obtained with previous iron-supported catalysts.

2. Materials and methods

2.1. Sample characterization

The porous structure of the fresh catalysts was characterized by means of nitrogen adsorption–desorption isotherms at -196°C using a Micromeritics Tristar 3020 apparatus. The samples were previously outgassed overnight at 150°C to a residual pressure of 10^{-3} Torr. The iron and titanium content of ilmenite was determined by total reflection X-ray fluorescence (TXRF), using a TXRF spectrometer 8030c. The crystalline phases in the catalyst were analyzed by X-ray diffraction (XRD) using a Siemens model D-5000 diffractometer with Cu K α radiation. SEM micrographs were obtained in a Hitachi S-3000N apparatus. This equipment was coupled with an energy dispersion X-ray analyser (EDX). Band-gap determination (to estimate the electronic properties) was carried out plotting $(\alpha h\nu)^{1/n}$ versus $h\nu - E_g \pm E(\Omega)$ (where $n=2$ for indirect semiconductors) giving a linear absorption edge and its cut with base line corresponds to band-gap energy. The diffuse reflectance spectra were recorded with a UV–vis AgilentVarian, Cary 5000. Ilmenite was also characterized by X-ray Photoelectron Spectroscopy (XPS) using a K-Alpha–Thermo Scientific equipped with a AlK α X-ray excitation source, (1486.68 eV).

2.2. CWPO-Photoassisted runs

The experiments were carried out in an artificial weathering in fast-action instrument Suntest XLS+ (Atlas Material Testing Technology BV, Gelnhausen, Germany) coupled with a Xenon arc lamp of 1700 W adjustable power. The equipment has a Solar ID 65 filter to limit the UV radiation at 320 nm, simulating solar exposition according to ICH Q1B guidelines. The runs were performed adjusting the lamp power to 550 W m^{-2} with a simulated solar emission within 300–800 nm, which corresponds to an average solar radiation in a summer day in southern Europe. The irradiance corresponding to UV radiation was 30 W m^{-2} . The reaction volume was 500 mL and the starting concentration of phenol 100 mg L^{-1} . The catalyst load was 450 mg L^{-1} (preliminary studies showed that the photocatalytic system had an optimal charge of ilmenite of 450 mg L^{-1} because higher and lesser amounts not increase the reaction rate) and the H₂O₂ concentration was 100% of the stoichiometric amount needed for complete mineralization, which is 500 mg L^{-1} . The temperature in the reactor was maintained in the vicinity of 25°C along all experiments.

2.3. Analytical methods

Phenol and aromatic oxidation by-products were quantified by means of HPLC (Varian Pro-Star 240) using a diode array detector (330 PDA). A Microsorb C18 $5 \mu\text{m}$ column (MV 100, 15 cm long,

4.6 mm diameter) was used as stationary phase and 1 mL min^{-1} of 4 mM aqueous sulfuric solution was used as mobile phase. Short-chain organic acids and chloride ion were analyzed by an ion chromatograph with chemical suppression (Metrohm 790 IC) using a conductivity detector. A Metrosep A supp 5–250 column (25 cm length, 4 mm diameter) was used as the stationary phase, while an aqueous solution containing 3.2 mM Na₂CO₃ and 1 mM NaHCO₃ was used as the mobile phase at a flowrate of 0.7 mL min^{-1} . Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, model 5000A), while the residual hydrogen peroxide concentration was determined by colorimetric titration using the TiOSO₄ method. Leached iron was obtained by ortho-phenanthroline method [9].

3. Results and discussion

3.1. Characterization

The mineral ilmenite (FeTiO₃), a Fe/Ti mixed oxide, has a hexagonal structure with two-third of octahedral position occupied by cations. Fe and Ti are located in alternative layers. The weight percentage of Fe and Ti in the raw mineral was 36 and 37%, respectively (measured by TXRF). Ilmenite also contains traces of Cr and Mn (0.027% and 1%, respectively). Ilmenite particles were mechanically milled down to $dp < 100 \mu\text{m}$ measured with a $100 \mu\text{m}$ sieve. No further thermal or chemical treatment was applied, in order to address the feasibility of this mineral as received as photocatalyst. The textural analysis from N₂ adsorption–desorption isotherm indicates that ilmenite is a non-porous material with a very low BET Surface, around $6 \text{ m}^2 \text{ g}^{-1}$.

Fig. 1 shows the results of X-ray Diffraction (XRD) analysis. All diffraction lines were compared to JCPDS card no. 21–1276 and 29–277 due to TiO₂ rutile phase and FeTiO₃ phase presence [10]. Intense peaks at $2\theta = 23.9^\circ, 32.65^\circ, 35.3^\circ, 40^\circ, 48^\circ, 53^\circ, 61^\circ, 63^\circ$ indicating FeTiO₃ in the sample with a crystal size of 6.14 nm. Moreover the peaks at $2\theta = 27^\circ, 41^\circ$ and 57° confirming rutile existence. TiO₂ crystals were higher than ilmenite ones which shown a size of 14.9 nm. Phase percentages resulted in 85% FeTiO₃ and 15% rutile.

The existence of isolated TiO₂ particles (rutile) and FeTiO₃ particles was also confirmed by SEM–EDX images (Fig. 2). On the contrary, no isolated iron oxide particles were found in the mineral.

Additionally, XPS analysis were carried out to determine the Fe (II)/Fe(III) ratio in ilmenite surface [11]. Raghavender et al. defines

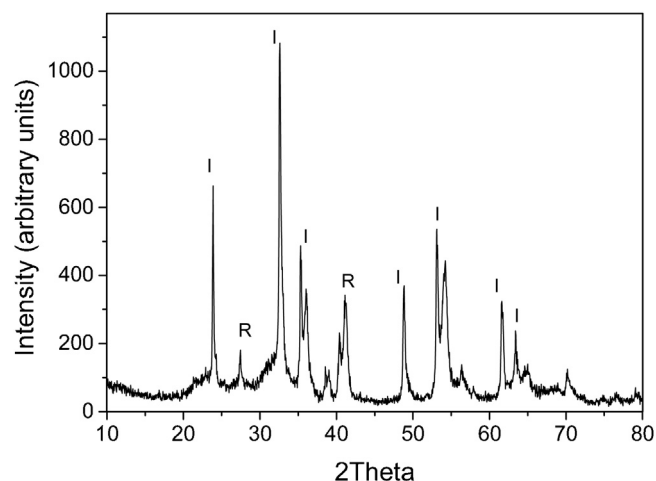


Fig. 1. XRD of ilmenite mineral.

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