Structural characterization of Th-doped TiO₂ photocatalyst and its extension of response to solar light for photocatalytic oxidation of oryzalin pesticide: a comparative study

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Received 25 June 2008; Accepted 15 October 2008

Abstract: The degradation efficiency of Th-doped TiO₂ / TiO₂ photocatalysts were investigated under UV and solar light illumination. The model compound chosen for the study was Oryzalin (OZ). Doping of inner transition metal ion Th was intended to modify the electronic properties of TiO₂. The Th-doped TiO₂ were synthesized by incorporating 0.02, 0.04, 0.06, and 0.1 atom percentage of Th into the TiO₂ lattice by solid-state reaction. The stoichiometry of the prepared samples is TiₓTh₁₋ₓO₂, where ‘x’ is the percentage of Th. The samples were characterized by UV-Visible absorption, UV-Visible -Diffused reflectance spectra, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDX) and X-ray Diffraction (XRD). The pore size and surface area of these samples were studied by Brunauer, Emmett and Teller (BET) adsorption method. It was found that metal ion doping at various percentage compositions enables a large shift in the absorption band of the TiO₂ towards visible light region. This is due to the formation of various mid band gaps at 2.84 eV, 2.904 eV, 2.66 eV, and 2.55 eV. The extent of degradation of the pesticide was followed by UV-Visible spectroscopy and GC-MS methods. Based on the spectral analysis, the probable degradation reaction mechanism for OZ is proposed. These results indicate that Th-doped TiO₂ with the modified electronic properties is a good catalyst under solar light irradiation. But these particles show marginal variation in rates under UV-illumination. All the photodegradation reactions follow the first order kinetics.

Keywords: Th-doped TiO₂ • Oryzalin • Photocatalysis • Mid band gaps of TiO₂ • Spectroscopic analysis.

1. Introduction

OZ is a selective pre-emergence surface applied herbicide used for the control of annual grasses and broad leaf weeds in fruit and nut trees. It inhibits the growth of germinating weed seeds by blocking cell divisions in the meristems. OZ shows low to moderate persistence in the field. The contamination of surface water with pesticides is due to the surface runoff from agricultural activities. The concentration of these pesticides has been reported to exceed the maximum contaminant level permitted for the surface waters [1-10]. OZ is resistant to natural decomposition process; its life time in aqueous media in nature is about 20-128 days [11]. No breakdown of OZ by hydrolysis was observed at pH 5, 7, and 9 [12]. Furthermore, the natural decomposition leads to several toxic organic intermediates which affect the immunity of the human population consuming water from polluted sources. The pesticide and its degradation reaction intermediates still persist even after passing conventional water treatment procedure [6,7]. The present wastewater treatment is ineffective in removing these contaminants. These compounds are well known carcinogenic and mutagenic in nature [8,11].

TiO₂ is a very suitable photocatalyst because of its low cost, chemical stability, non-toxic nature, optical and electronic properties [13-15]. However due to its high band-gap energy, TiO₂ utilizes only a very small fraction of the solar spectrum and thus doping with transition metals have been so far employed to extend the light absorption to the visible region [13-18]. The presence of foreign metal species in TiO₂ nanoparticles showed many controversial

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results which are reported in literature. Hoffmann et al. [19], found that doping quantum-sized TiO$_2$ with Fe$^{3+}$, Mo$^{6+}$, Ru$^{3+}$, Os$^{3+}$, Rh$^{3+}$, and V$^{4+}$ at 0.1-0.5% significantly enhanced the photocatalytic activity for the oxidation of CHCl$_3$ and the reduction of CCl$_4$, whereas doping of Co$^{2+}$ and Al$^{3+}$ decreased the photoreactivity. W. Lee et al. found that the photocatalytic activity of TiO$_2$ towards the oxidation of 1,4-dichlorobenzene was improved significantly by introduction of WO$_3$ and MoO$_3$ [20,21] and a beneficial influence of tungsten was found for the photodegradation of 4-nitrophenol [22,23]. Cr$^{3+}$ is reported to significantly reduce the photocatalytic performances of TiO$_2$ [16,24]. But Apno et al. report that Cr and V ion doped TiO$_2$ has shown photocatalytic reactivity three to four times higher than TiO$_2$ for the decomposition of NO under solar beam irradiation [25]. The method of doping and the nature of the reaction obviously determine the properties of the catalyst. To our knowledge, doping of a metal ion with 5f electronic configuration (Th) into the TiO$_2$ matrix has not been reported.

This paper concentrates on (i) the preparation of Th-doped TiO$_2$ with various percentages ranging from 0.02 to 0.1, (ii) material characterization of photocatalysts, (iii) comparative study of photocatalytic activities under UV and solar light illumination, (iv) spectroscopic analysis of degradation reaction intermediates, and (v) proposal of degradation reaction mechanism.

2. Experimental Procedures

2.1 Reagents

Titanium(IV) Chloride (TiCl$_4$ ≥ 99.9%) is obtained from Merck Chemicals Ltd, Th(NO$_3$)$_4$ (99%) from Sisco-Chem Industries, Bombay. NH$_3$OH (25-28%), HCl (37%), (NH$_4$)$_2$SO$_4$ (98%) and NaOH (97%) were from Sd Fine chemicals and used as supplied. Double distilled water was used for all the experiments. OZ is an organosulphur pesticide which is obtained from M/s. Bayer (India) Ltd. (pure technical grade of 97.8%) and used as received. The molecular weight of the pesticide is 346.36 and its molecular formula is C$_{12}$H$_{18}$N$_4$O$_6$S$_3$. (3, 5-dinitro-N$^4$, N$^4$-dipropylsulfanilamide).

Scheme 1. Structure of OZ

2.2. Preparation of Photocatalysts

The optically pure, fine grained anatase TiO$_2$ is prepared by using sol-gel method. 100 mL of high purity TiCl$_4$ was carefully diluted by adding drop-wise to 250 mL of ice cold, well stirred double distilled water, and the resulting solution was then diluted to 500 mL. 25 mL of above diluted TiCl$_4$ was made acidic by adding around 1 mL of conc. H$_2$SO$_4$ in a beaker and diluted to 1 liter with double distilled water. Liquid ammonia was added until the pH of the diluted solution reached 7-8 in order to obtain the hydroxide of Titanium gel. The gel obtained is allowed to settle down and was washed several times to remove chloride and ammonium ions. The precipitate obtained was oven dried for 12 hours at 100°C. The oven dried TiO$_2$ was then ground in a mortar. The fine powder obtained was subjected to heat treatment at 600°C to obtain the anatase form of TiO$_2$. [26].

The stock solution of Th(NO$_3$)$_4$ was prepared by weighing 0.5050 g in 100 mL of double distilled water. From the stock solution 0.5, 1.0, 1.6, and 2.5 mL was pipetted out and mixed with 2 g of TiO$_2$ in an agate mortar to get 0.02, 0.04, 0.06, and 0.1% of Th-TiO$_2$. These mixtures were manually ground in a mortar. All these samples were oven dried at 100°C for 12 hours. During the process of heating, the samples were repeatedly ground for 6 times in a mortar and finally calcined at 600°C for 4.5 hours in a muffle furnace. The stoichiometry of the prepared samples is Ti$_{1-x}$Th$_x$O$_2$, where ‘x’ is the percentage of Th.

2.3 Instrumentation

X-ray Diffraction: The XRD patterns of the powders were recorded using Phillips powder diffractometer Pw/1050/70/76 with Cu Kα radiation under the scan rate of 2° per min.

Absorption /Diffuse Reflectance Spectroscopy: The absorption and reflectance spectra were recorded by using UV-Visible Shimazu double beam spectrophotometer 3101PC UV-VIS-NIR instrument. The spectra were recorded at room temperature in the range of 190-800 nm. The diffuse reflectance spectra were recorded with BaSO$_4$ as reference.

Scanning Electron Microscopy and Energy Dispersive X-ray Analysis: SEM was performed using a model JSM840 microscope operating at 25 kV on specimens upon which a thin layer of gold or carbon had been evaporated. An electron microprobe is used in EDX mode to obtain quantitative information on the amount and distribution of the metal species in the samples.

FTIR Spectral Analysis: FT-IR spectra were recorded using Nicollet IMPACT 400 D FTIR spectrometer, over the range of frequencies from 4000 - 400 cm$^{-1}$ using KBr as the reference sample.