



Photocatalytic performance of nano-photocatalyst from TiO₂ and Fe₂O₃ by mechanochemical synthesis

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ABSTRACT

Nano-particles of homogeneous solid solution between TiO₂ and Fe₂O₃ (up to 10 mol%) have been prepared by mechanochemical milling of TiO₂ and yellow Fe₂O₃/red Fe₂O₃/precipitated Fe(OH)₃ using a planetary ball mill. Such novel solid solution cannot be prepared by conventional co-precipitation technique. A preliminary investigation of photocatalytic activity of mixed oxide (TiO₂/Fe₂O₃) on photo-oxidation of different organic dyes like Rhodamine B (RB), Methyl orange (MO), Thymol blue (TB) and Bromocresol green (BG) under visible light (300-W Xe lamp; λ > 420 nm) showed that TiO₂ having 5 mol% of Fe₂O₃ (YFT1) is 3–5 times higher photoactive than that of P25 TiO₂. The XRD result did not show the peaks assigned to the Fe components (for example Fe₂O₃, Fe₃O₄, FeO₃, and Fe metal) on the external surface of the anatase structure in the Fe₂O₃/TiO₂ attained through mechanochemical treatment. This meant that Fe components were well incorporated into the TiO₂ anatase structure. The average crystallite size and particle size of YFT1 were found to be 12 nm and 30 ± 5 nm respectively measured from XRD and TEM conforming to nanodimensions. Together with the Fe component, they absorbed wavelength of above 387 nm. The band slightly shifted to the right without tail broadness, which was the UV absorption of Fe oxide in the Fe₂O₃/TiO₂ particle attained through mechanochemical method. This meant that Fe components were well inserted into the framework of the TiO₂ anatase structure. EPR and magnetic susceptibility show that Fe³⁺ is in low spin state corresponding to μ_B = 1.8 BM. The temperature variation of μ_B shows that Fe³⁺ is well separated from each other and does not have any antiferromagnetic or ferromagnetic interaction. The evidence of Fe³⁺ in TiO₂/Fe₂O₃ alloy is also proved by a new method that is redox titration which is again support by the XPS spectrum.

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1. Introduction

Photocatalytic oxidation of organic compound by wide band gap semiconductor studies is an important area of investigation. In this regard studies with TiO₂ and modified TiO₂ are area of intense investigation [1–10].

The photocatalytic property of a multicomponent system is strongly influenced by the composition and the preparation procedure. In recent years, the application of heterogeneous photocatalysis on the removal of contaminants in air and wastewater has fetched some interest [11–15]. Due to the high photocatalytic activity and stability of titanium dioxide, it is generally used as a photocatalyst for the removal of organic pollutants from water or air [16–20].

However, TiO₂ follows a relatively high electron–hole recombination rate, which is detrimental to its photoactivity. The doping of TiO₂ with transition metal ions like Ni(II) [21], Cu(II) [22], Nb(V) [23], Cr(III) [24,25], Fe(III) [26–29], and metal molybdates [13] were reported to improve the photocatalytic properties with enhanced absorption of visible/ultraviolet light. Binary metal oxides such as TiO₂/WO₃, TiO₂/MoO₃, TiO₂/SiO₂ and TiO₂/ZrO₂ have been widely studied for their unique chemical, physical and photocatalytic properties [30–33]. Studies with a Fe₂O₃/SrTiO₃ mixed oxide photocatalyst have shown improved photocatalytic activity for photo-oxidizing methanol under visible light irradiation [34]. Adel Ali Ismail has prepared the ternary heterogeneous mixed oxides i.e. Y₂O₃/Fe₂O₃/TiO₂ nanoparticles [35], which showed better photooxidation for EDTA than pure TiO₂. Recently, Fe₂O₃/TiO₂ heterogeneous mixed oxides [36–39] have shown better photocatalytic activity than pure TiO₂ for oxidation of different organic compounds such as methylene blue, chloroform and formaldehyde but it is inferior to Degussa P 25. In this study a homogeneous solution between Fe₂O₃ and TiO₂ has been made by high energy mechanical milling using various source of Fe³⁺ which shows high

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photochemical activity and it is more active than Degussa P 25 in visible light for oxidative degradation of various dyes. It is observed that the photocatalytic activity of Fe–Ti oxides alloy largely depends on iron content, preparative condition and sintering temperature having optical adsorption edge around 2.2 eV, which facilitates a strong absorption of visible light. The $\text{Fe}_2\text{O}_3/\text{TiO}_2$ alloys in different mole ratio were prepared by mechanical milling method (using a ball mill) and their photocatalytic activities were evaluated by the photooxidations of different dyes like Rhodamine B (RB), Methyl orange (MO), Thymol blue (TB) and Bromocresol green (BG) under visible light (300-W Xe lamp; $\lambda > 420$ nm) irradiation. The alloy of Fe_2O_3 (5 mol%) with TiO_2 (anatase) is a better photoactive material compared to Degussa P25 TiO_2 and other compositions of $\text{Fe}_2\text{O}_3/\text{TiO}_2$.

2. Experimental

2.1. Synthesis of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ photocatalysts

A stoichiometric mixture of TiO_2 (Aldrich, 99.99%) and yellow/red Fe_2O_3 (5, 7 and 10 mol%) (99.9%, Tata-Pigment, India) was prepared by mechanical grinding in a planetary ball mill using small amount of water. This mechanical milling was allowed for 4 h for complete mixing of the oxides forming a solid solution. The milling was performed in Fritsch Pulverisette No. 6 planetary ball mill, using a rotational speed of 250 rpm at a constant rotation direction and a ball to powder weight ratio of 10:1. Both the container and balls were made of aluminium oxide. The prepared samples were dried at 100 °C for 15 h in an oven and photocatalytic activity was studied. The sources of Fe^{3+} were yellow iron oxide, red iron oxide and precipitated ferric hydroxide. The heat-treatment of the sample at a temperature higher than 200 °C had poor photocatalytic activity. Rhodamine B (RB), Methyl orange (MO), Thymol blue (TB), Bromocresol green (BG) were A.R. reagents procured from MERCK India.

2.2. Photocatalytic experiment

Photocatalytic experiments were conducted using nanophotocatalysts in presence of photocatalytically degradable different dyes in water solution. The photocatalytic reaction was carried out under visible light irradiation with slow stirring (using magnetic stirrer) of the solution mixture and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ photocatalysts. The light source was a 300-W Xe lamp (ILC technology; CERMAX LX-300F). The container was made of Petridis of volume 200 ml. The reactions were performed by adding nano powder of each photocatalyst (0.1 g) into each set of a 100 ml of different solution of dyes.

2.3. Analytical methods

A small volume (1 ml) of reactant liquid was siphoned out at regular interval of time for analysis. It was then centrifuged at 1100 rpm for 15 min, filtered through a 0.2 μm -millipore filter to remove the suspended catalyst particles and concentration of dye was measured by absorption spectrometry using UV-VIS spectrometer (UV-1601, SHIMADZU) at its wavelength of maximum absorption.

2.4. Characterization

The crystal structure of the prepared samples was determined by the X-ray diffractometer (XRD) (Model: Philips PW 1710) equipped with a $\text{Cu K}\alpha$ radiation. The accelerating voltage and current used were 40 kV and 20 mA, respectively. The 2θ ranged from 15 to 70°.

Crystallite sizes (D) of the obtained powders were calculated by the X-ray line broadening technique performed on the direction of lattice using computer software (APD 1800, Philips Research Laboratories) based on Scherer's formula [40].

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (1)$$

where D is the crystallite size, λ is the X-ray wavelength, θ is the Bragg's angle and β is half width. The stoichiometry of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ alloys have been examined by energy dispersive X-ray spectroscopy (EDX) (JEOL JMS-5800) which is consistent with the amount taken of Fe_2O_3 and TiO_2 during synthesis.

The FT-IR analysis was performed using a Perkin-Elmer Paragon 1000 FT-IR spectrometer and BET surface area measurements were carried out using a BECKMAN COULTER SA3100 through nitrogen adsorption-desorption isotherm at 77 K. X-ray photoelectron spectroscopy (XPS) measurements were carried out in an Axis-Ultra X-ray photoelectron spectrophotometer in vacuum (1×10^{-5} Pa).

The UV-vis diffuse reflectance spectra of the prepared powders were obtained by a UV-VIS spectrophotometer (UV-1601 Shimadzu) at room temperature. The average sizes of nanoparticles were measured in the transmission electron microscopy (TEM) (Model Philips TM-30, Philips Research Laboratories).

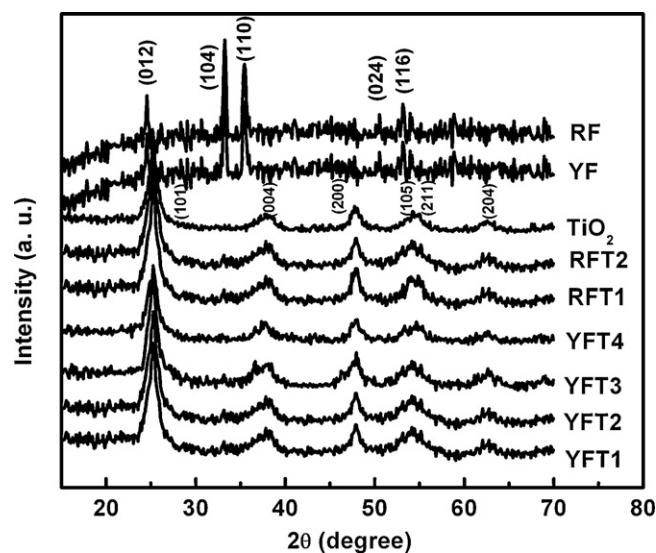


Fig. 1. A comparison of X-ray diffraction patterns of TiO_2 , YFT1, YFT2, YFT3, YFT4, RFT1, RFT2, YF and RF nanopowders prepared by mechanochemical method after heat treatment at 100 °C for 15 h.

The magnetic susceptibility was measured by Guoy balance. The ESR spectrum was obtained by BRUCKER ER083CS model at room temperature (ca. 298 K).

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of TiO_2 , YFT1, YFT2, YFT3, YFT4, RFT1, RFT2, YF and RF (abbreviation presented in Table 1) mixed oxides nanopowders after heat treatment at 100 °C for 15 h in air atmosphere. It has been observed that the phases prepared at different molar ratios of mixed oxides TiO_2 and Fe_2O_3 (YFT1, YFT2, YFT4, RFT1 and RFT2) have anatase phase up to 5 mol% of Fe_2O_3 (as per JCPDS no. 84-1285), and YF, RF are hexagonal phases (as per JCPDS no. 86-0550). The XRD pattern of TiO_2 sample shows distinct peaks of the anatase phases, without any indication of rutile phases. XRD of YFT1, YFT2, YFT3, YFT4, RFT1 and RFT2 indicate no change of crystallographic characteristics before and after the photocatalytic reactions, which is shown in Fig. 1. XRD also indicate that the final products after ball milling have anatase phase of TiO_2 and Fe ions are well inserted into the framework of the TiO_2 anatase structure. The small incorporation of Fe^{3+} in TiO_2 will not change much of the XRD peaks. The change will be in first or second decimal of theta value, because ionic radius of Ti^{4+} and Fe^{3+} are very close (0.68 Å and 0.64 Å). Moreover magnetic data and EPR data does not infer any aggregation of Fe^{3+} as Fe_2O_3 crystal. Due to broad peaks of XRD we are unable to evaluate the accurate d - values of lattices. After photochemical reaction no metal ion leaching was observed. The sample prepared with red Fe_2O_3 and yellow Fe_2O_3 or precipitated $\text{Fe}(\text{OH})_3$ gave same chemical and physical characteristics. Average crystallite sizes of the prepared photocatalysts were calculated according to Scherer's formula and indicated that the crystallite sizes of the samples were approximately (12–15 nm). The atomic level dispersion Fe_2O_3 in TiO_2 have been presented in Fig. 2 through energy dispersive X-ray spectroscopy,

3.2. Specific surface area (BET) analysis

The BET surface area of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composite powders (YFT1) calcined at 100 °C was 58.5 m^2/g , while the surface area of P25 is 49.1 m^2/g and the surface area of other prepared photocatalysts are presented in Table 1. Though surface area of YFT1, RFT1 and Degussa

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