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Sulfated Fe_2O_3–TiO_2 synthesized from ilmenite ore: A visible light active photocatalyst

York R. Smith[a,b], K. Joseph Antony Raj[a], Vaidyanathan (Ravi) Subramanian[b], B. Viswanathan[a,*]

[a] Department of Chemistry, National Centre for Catalysis Research, Indian Institute of Technology-Madras, Chennai 600036, India
[b] Chemical & Materials Engineering Department, University of Nevada, Reno 89557, USA

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ABSTRACT

Sulfated Fe_2O_3–TiO_2 (SFT) was synthesized by treatment of ilmenite ore with sulfuric acid. The presence of sulfated Fe_2O_3–TiO_2 and mixed phases of Fe_2O_3–TiO_2 was confirmed by DRIFT spectra and XRD. The dispersion of sulfate displayed thermal stability up to 500 °C. The adsorption–desorption of pyridine investigated by DRIFT spectra revealed the presence of both Brønsted and Lewis acid sites for the samples calcined up to 500 °C. The DRS/UV–vis spectra showed UV and visible light absorbance for samples calcined up to 900 °C. A band gap value of 2.73 eV is obtained for 500 °C calcined sample. The photocatalytic activity was evaluated by the oxidation of 4-chlorophenol (4-CP) in aqueous medium under UV–vis and visible light irradiation. SFT calcined at 500 °C demonstrated the highest photocatalytic activity. When compared with high surface area sulfated titania ($275\ m^2/g$), the photocatalytic activity was greater due to the presence of iron, despite the low surface area of the SFT samples ($12–17\ m^2/g$).

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1. Introduction

An increasing awareness of the environmental impacts from pollution and stringent standards on emission regulations has prompted the development of catalytic routes for waste management. The development and practical application of systems that are *clean and green* have shown to be a formidable challenge for scientists and engineers. Photocatalytic technologies have shown practical application in antibacterial and deodorant filters for air purification owing to its property of promoting various chemical reactions such as the degradation of aqueous organic pollutants and sources of offensive odors using light. Titania-based materials have received considerable attention for their potential in environmental catalytic applications such as air purification, water disinfection, hazardous wastewater remediation, and deodorization [1–6]. Recently, the application of titania with different architectures such as nanotubes has been examined [7–9]. Owing to its large band gap ($E_g = 3.2$ eV) titania, however, can only utilize photons in the UV region (<380 nm), which limits its practical application for sun light irradiation [7,8,10–13]. One of the promising approaches to overcome this disadvantage is coupling titania with other narrow band gap semiconductors capable of promoting charge separation in the visible light spectrum [14,15]. Many studies have reported sensitizer-loaded titania, such as CdS/TiO_2 [16,17]. $CdSe/TiO_2$ [18,19], $Bi_2O_3/SrTiO_3$ [20], Bi_2S_3/TiO_2 [17,21], $ZnMn_2O_4/TiO_2$ [22], TiO_2/Ti_2O_3 [23] under visible light irradiation and have shown efficient visible light photoactivity. In most of these catalysts, the addition of sensitizers reduces the band gap of the material enabling the coupled material to absorb visible light. The conduction band (CB) of the loaded sensitizer has a more negative reduction potential than that of titania enabling visible light photoinduced electrons to be injected into the lower-energy CB of titania. However, the photogenerated holes of the sensitizer remain in the valence band (VB) resulting in an accumulation of holes on the sensitizer leading to photocorrosion of the catalyst. As a result, the stability of the composite photocatalyst becomes less [24]. Furthermore, most currently produced sensitizers are heavy metal chalcogenides (e.g., CdSe, PbS). These may constitute harm to ecological systems and humans as well due to their nanoscale and toxic metal release. A recent study by King-Heiden and coworkers [25] examined the toxicological effects of CdSe/ZnS nanoparticles on the growth of zebrafish embryos and showed Cd toxicity even at very low levels of CdSe nanoparticles.

To counter the potential negative environmental problems of using heavy metal sensitizers, iron as a dopant in titania-based systems has been investigated to enhance the photocatalytic efficiency under visible light irradiation [26–30]. Iron is one of the most abundant elements found in the Earth's crust. Similar to titania, iron and its oxides show promise as an eco-friendly catalyst in many applications. For example, $FeTiO_3$ has a band gap of 2.58–2.9 eV, [31–34] and has been used as a chemical and as a photocatalyst. [32,33] Ye et al. observed that under UV irradiation of TiO_2–Fe_3O_4 mixed

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* Corresponding author. Tel.: +91 44 22574241; fax: +91 44 22574202.
E-mail address: bvnathan@iitm.ac.in (B. Viswanathan).

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oxide coatings exhibited higher photocatalytic efficiency than titania alone due to the formation of $FeTiO_3$ [33,34], which may form a p–n junction with titania to induce spatial separation of the photogenerated electron/hole pairs. Iron-doped titania has shown to exhibit higher photocatalytic activity in visible light. A report by Choi and coworkers [35] shows that creating a shallow trap in the titania lattice due to its half-filled electronic configuration induces a red shift in the band gap and alters electron/hole pair recombination rates. Although the mechanism of narrowing the band gap and reducing the recombination rates of titania with the aid of iron remains in the realm of debate, [36–39] in general, it is assumed that the photocatalytic behavior and efficiency are greatly influenced by the doping of iron oxides [40]. Hence, further investigations are essential to explore iron as a doping catalyst through appropriate synthesis processes. The objective of this study is to address some of the questions raised in previous related work and provide a photocatalyst which possesses high catalytic activity, non-toxic, inexpensive, and allows for the use of visible light directly to carry out photocatalytic reactions. Herein, we report the synthesis of sulfated Fe_2O_3–TiO_2 (SFT) using ilmenite ore and sulfuric acid as the starting material and its effect of photocatalytic activity is evaluated by the oxidation of 4-chlorophenol (4-CP) in water.

2. Experimental

2.1. Synthesis of sulfated Fe_2O_3–TiO_2

10 g of ball milled ilmenite ore was homogeneously mixed with 20 g of concentrated H_2SO_4 and aged for 2 h at 30 °C. To this mixture, 10 g of water was added while stirring to initiate the reaction and maintaining constant stirring of the reaction mass for about 1 h. Thereafter the reaction mass was treated with 100 g of water to remove any remaining soluble residues. The remaining mass obtained was then dried in air at 100 °C for 12 h. The samples were calcined in air at various temperatures to prepare Fe_2O_3–TiO_2 containing different quantities of sulfate. The ilmenite ore was analyzed and found to have the composition of 55 wt.% of TiO_2, 42 wt.% of Fe_3O_4, 2.9 wt.% of SiO_2 and traces of alumina, zirconia, vanadia and chromia was used for preparation of the catalyst.

2.2. Characterization

Wide-angle XRD patterns for the calcined and as-synthesized materials were obtained using a Rigaku Miniflex II, with CuKα irradiation with a scan range of $2\theta = 0$–$60°$ with a scan rate of 5°/min. The composition of the catalysts was analyzed using an XRF spectrometer. The pyridine adsorption–desorption measurement for the identification of Brønsted and Lewis acidity was determined by diffuse reflectance infrared Fourier transform (DRIFT) spectra and recorded using a Bruker Tensor-27. The thermal analyses of the samples were performed on PerkinElmer TG/DTA with alumina as the reference. The BET-surface area of the samples was determined by the nitrogen adsorption and desorption isotherms at −195.6 °C and measured by a Micromeritics ASAP-2020 analyzer after the samples were degassed in vacuum at 300 °C for 3 h. The UV–vis/DRS studies of the samples were performed on a Thermo Scientific instrument.

2.3. Photocatalytic experiments

SFT catalyst samples calcined at various temperatures were studied for the photocatalytic degradation of 4-chlorophenol (4-CP) and compared with the activity of commercial Degussa P-25 (P25), as well as sulfated titania (ST) prepared in this laboratory [41]. In a typical experiment, 40 ml (50 ppm) of aqueous solution 4-CP and 50 mg of catalyst was stirred in the dark at room temperature for 30 min in a jacketed quartz reactor. Subsequently, the solution was irradiated with a high-pressure 500 W mercury lamp (Newport, ORIEL), 35 cm away from the solution while maintaining constant stirring. For visible light experiments, UV irradiation was filtered out using a band pass filter with a cut-off at $\lambda < 420$ nm (HOYA L-42). The decomposition of 4-CP was quantitatively analyzed using a UV–vis spectrophotometer (Jasco V-530) by monitoring the change in absorbance at $\lambda = 250$ nm. The analyzed transparent liquid was segregated from mixture using centrifugation at a speed of ~10,000 rpm. Identification of intermediate products, reaction network, and kinetic modeling in an otherwise similar system is discussed elsewhere [42]. All experiments were conducted and measured consecutively twice. Blank experiments where performed in the absence of photocatalyst and negligible decomposition of 4-CP was observed.

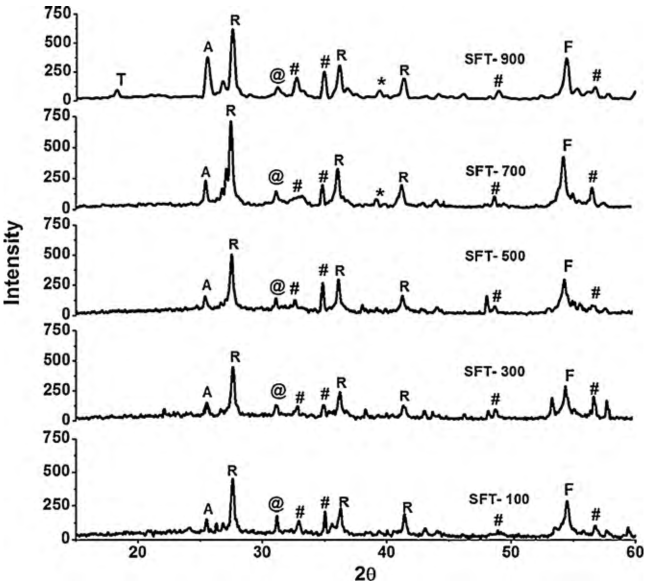

Fig. 1. XRD patterns of sulfated Fe_2O_3–TiO_2 (SFT) samples calcined at various temperatures. The peaks are indexed with standard JCPDS cards for, A – *anatase*, R – *rutile*, F – Fe_2O_3, T – Fe_2TiO_5, # – $FeTiO_3$, @ – sulfated Fe_2O_3–TiO_2, and * – Fe_2TiO_4.

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns of SFT samples calcined at various temperatures are shown in Fig. 1 and have been indexed and compared with standard JCPDS cards. The peaks appeared at 2θ values of 27.5, 36.1, and 41.3 are due to the presence of *rutile* (PDF#: 881172) in the sample. The intensity of peaks at a 2θ value of 27.5 and 36.1 was found to increase with temperature of calcination due to the effect of rutilation. As a result, the *rutile* content [43] was found to increase from 11% to 15% with temperature. The peak obtained at a 2θ value of 25.4, which is due to *anatase* (PDF#: 894203) phase of titania, showed an increase in intensity with temperature. In general, *anatase* forms initially and is subsequently converted to *rutile* on heat treatment. Employing wet chemical-based synthesis protocols for preparing coupled oxides based on titania have shown similar results in related work such as preparation of TiO_2–Al_2O_3. [44] In this study, the *anatase* content was found to increase from 2.9% to 7.2% with temperature. This observation shows the presence of a greater quantity of *rutile* over *anatase* in the acid treated ilmenite samples. The reflections at 32.8, 34.9, 48.8, and 56.7 are due to the formation of $FeTiO_3$ (PDF#: 751212). The peak at a 2θ

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