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Structural, optical and photocatalytic activity of cerium titanium ferrite

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ABSTRACT

Perovskite phase Cerium Titanium Ferrites ($CeTi_{1-x}Fe_xO_{3-\delta}$) are prepared via sol-gel route, by varying mole ratios (X = 0, 0.5 & 1.0) and the synthesized nanocatalysts used for the degradation of Methylene Blue organic pollutant. The as synthesized photo catalysts (CTFO-1, CTFO-2 and CTFO-3) were characterized using UV–vis, FT-IR, TG-DTA, PXRD, SEM and VSM techniques to study their optical, structural, thermal and magnetic properties. The photocatalytic activity on methylene blue dye using the synthesized nanocatalysts was analyzed and the experimental result was recorded using UV–vis spectrophotometer. The percentage reduction of methylene blue dye was estimated and found to be 99% on irradiation under UV lamp and 2.70% in the absence of UV lamp irradiation. The recyclability of the synthesized catalyst for four successive cycles indicates that the catalyst can be estranged and efficiently reused. The performance of $CeTi_{0.5}Fe_{0.5}O_{3-\delta}$ nano photocatalyst was observed to be better than $CeTiO_{3-\delta}$ and $CeFeO_{3-\delta}$. The photo-catalytic property of the prepared nanomaterial makes it suitable in amputation of dye effluents from the fabric industries.

1. Introduction

The unseem discharging of organic dyes onto the land and water bodies has led to stern pollution in worldwide. The major pollutants such as NO_2, CO_2, SO_2, organic hydrocarbons, organic dyes, and gasoline generated from various industries such as paper, textile, leather, cosmetics, plastics, etc turn out to be hazardous and toxic to many organisms. The discharge of the resulting contaminants into water bodies causes severe environmental problems to human and aquatic life besides being aesthetically unpleasant [1].Therefore, effective elimination of organic dyes from waste water of industries remains a massive challenge now days.

Perovskite materials are gaining significant attention due to their unique properties like ion exchange, absorption, catalytic potential, high surface – volume ratio and porosity, good thermal stability and redox properties [2–4]. Solar light driven photocatalysis has found use as an efficient, cost effective and eco-friendly method for degradation of dye effluents from textile industries. Gajendra Kumar et al. [5] studied the photodegradation of phenol, methylene blue and Congo red by using nanoporous iron-cerium mixed metal oxide as photocatalyst. Photo-degradation activity on Gentian violet dye by cerium-iron oxide was reported by Ameta et al. [6].Most investigations on heterogeneous photocatalysis focus on anatase-type TiO_2

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[7,8], than the rutile-phase. A few results [9–11] demonstrate that the photocatalytic activity of TiO_2 can be improved by incorporation of rare earth metals. The varied oxidation state and crystalline structures of cerium oxide has enhanced the electrical, electronic, catalytic, adsorption, optical and sensing properties. From literature it is understood that the photocatalytic activity of cerium oxide is better explored when the particle size is decreased. A combination of CeO_2 with Fe_2O_3 can be a potent material as a photocatalyst [12]. The exceptional stability, cost-effectiveness, oxidative power, high resistance to corrosion, and eco-friendly properties of iron oxide accomplish the need of an excellent photocatalyst. The development of environmentally benign catalyst is of momentous importance due to its potential to be recovered efficiently after the completion of the reaction. Magnetically separable nanocatalysts gains importance as a substitute to conventional catalyst as it helps reduce the work-up procedures [13].

Hence, the present study is aimed at developing perovskite systems with general formula ABO_3 which has gained interest among researchers as sensors [14,15], solid oxide fuel cells [16] and photocatalysis [17] due to their magnetic, piezoelectric, dielectric, superconductivity and catalytic properties. Several methods such as sol–gel, thermal decomposition of precipitated precursors, combustion of precursors, hydrothermal method, solid state reaction, sonochemical method and microwave irradiation have been used for the synthesis of perovskite nanomaterials [18–24]. In our study, perovskite phase $CeTi_{1-x}Fe_xO_{3-\delta}$ was synthesized by the sol-gel method. The synthesized materials were characterized by UV–vis, FT-IR, PXRD, SEM and VSM techniques to study their optical, structural and magnetic properties. The efficiency of the as prepared nano mixed metal oxide catalysts for degradation of Methylene Blue dye was studied.

2. Experimental

2.1. Materials and methods

The chemical purchased was analytical graded and used as such without any further purification. Nanocrystalline $CeTi_{1-x}Fe_xO_{3-\delta}$ was synthesized via sol-gel route by varying the mole ratios, using citric acid as the gelling agent. The gel was dissolved in ethylene glycol at 100 °C. Cerous nitrate, iron nitrate and titanium isopropoxide were used as sources of the respective metals. The precursors were prepared by dissolving metal nitrates in deionized water and titanium isopropoxide in ethanol. The mixture was stirred in a magnetic stirrer at 150 °C until a clear transparent solution was obtained. The obtained solution was kept for gellation at 300 °C for three hours in an air oven. The solid mass was sintered in a muffle furnace at 800 °C for eight hours at a rate of 5 °C/min.

2.2. Photocatalytic studies

The photocatalytic studies was done using a multi UV lamp photoreactor [Heber HML —COMPACT- LP-MP88] fitted with six numbers of 8W mercury vapor lamps (Sankyo denki, Japan) emitting wavelengths with maximum spectral intensity at 365 nm. The reaction chamber is made of highly polished anodized aluminum with built-in cooling fans. 25 ppm of methylene blue dye solution in 500 mL standard flask was prepared as the stock solution. The experimental studies were carried out by taking 100 mg of the catalyst and 100 mL of methylene blue dye solution. The solution containing nano-photo catalysts ($CeTi_{1-x}Fe_xO_{3-\delta}$) and the dye solution was aerated continuously, which served as the oxygen source for the thorough mixing of the solution. Preliminary reactions were done to observe the variations in dark and under UV-lamp. The degradation studies were performed for about 3 h. The samples were drawn for every 30 min, centrifuged and the absorbance was measured with UV–vis spectrophotometer.

3. Results and discussion

3.1. Fourier-Transform infrared spectroscopic analysis

The FT-IR technique was used to determine the metal-oxide vibrational frequencies and surface functional groups. Fig. 1 represents the FT-IR spectra of $CeTi_{1-x}Fe_xO_{3-\delta}$ (x = 0, 0.5 and 1) perovskite oxides. The metal-oxygen stretching frequencies range from 400 to 1000 cm^{-1}. The pure $CeTiO_{3-\delta}$ (CTFO-1) and $CeFeO_{3-\delta}$ (CTFO-3) shows absorption frequencies at 767, 535, 553 and 496 cm^{-1} respectively. $CeTi_{0.5}Fe_{0.5}O_{3-\delta}$ (CTFO-2) showed spectral vibrations at 834, 700 and 526 cm^{-1} which confirmed the presence of characteristic metal- oxygen bond. The absorption around 3400 cm^{-1} corresponds to surface adsorption of water and the absorption at 1600 cm^{-1} is due to the compactions of powder specimen with KBr. This feature is more prominent in CTFO-2 than in pure mixed metal oxides.

3.2. Powder XRD analysis

The X-ray diffractograms of the as synthesized samples (CTFO-1, CTFO-2 and CTFO-3) recorded using Bruker AXS D8 Advance instrument with Cu Kα radiation (λ=1.540598 Å) in the 2θ range 10 – 80° are shown in Fig. 2. The 2θ values of pure CTFO-1 at 28.32, 32.80, 47.25, 56.11, 69.20 and 76.50 matched with standard JCPDF NO- 49-1606 49–1606 and the 2θ values of pure CTFO-3 at 28.26, 32.82, 47.22, 56.09 and 76.48 matched with standard JCPDF NO- 22-0166 [25]. Both the above samples were indexed with orthorhombic perovskite structure. The 2θ values of cerium titanium ferrite (CTFO-2) of