Effect of Al^{3+} substituted zinc ferrite on photocatalytic degradation of Orange I azo dye

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ABSTRACT

Aluminum substituted zinc ferrite catalysts were prepared by the sol–gel auto-combustion method and characterized by using Mössbauer spectroscopy and nitrogen adsorption–desorption isotherm measurements. The photocatalytic activity of $ZnFe_{2-x}Al_xO_4$ ($0 \leq x \leq 2$) spinel ferrites was evaluated for the first time on Orange I azo dye degradation under UV light illumination. The results showed that the photocatalytic process was promoted when aluminum cations substituted iron cations located in octahedral sites of zinc ferrite lattice. Therefore, the Orange I azo dye best removal efficiency was observed when the Al^{3+} and Fe^{3+} are presents in equimolar amounts. The dye degradation performance of the $ZnFe_{2-x}Al_xO_4$ ($0 \leq x \leq 2$) catalysts was related to the crystallite size than to the BET surface area values and to the presence of secondary phases, such as α-Fe$_2$O$_3$ and ZnO.

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1. Introduction

Photocatalysis has generated a great interest in the last decade for researchers due to its applications in environmental protection. This technology is very important to remove toxic organic compounds from the environment by photocatalytic degradation, ideally to CO_2 and water [1]. For the purpose, numerous photocatalysts have been investigated [2–5]. Photocatalysts are important materials that are applied in many areas including the elimination of contaminants from water and air, water splitting to produce hydrogen, the inactivation of cancer cells [1]. Photocatalysts utilize light energy (hυ) to carry out oxidation and reduction reactions. When irradiated with light energy, an electron (e$^-$) is excited from the valence band to the conduction band of the photocatalyst, leaving a photogenerated hole (h$^+$). When photocatalytic processes take place in aqueous solutions, water and hydroxide ions react with photogenerated h$^+$ to form hydroxyl radicals ($^\bullet$OH), which is the primary oxidant in the photocatalytic oxidation of organic compounds [2]. Most of the photocatalytic studies use nanosize semiconductive materials (TiO_2, ZnO, Fe_2O_3, CdS, GaP and ZnS) as the photocatalyst due to the efficiency in degradation of organic compounds [3–6]. Several studies have confirmed that ZnO shows

an efficiency at least equal to that of TiO_2, because it generates H_2O_2 efficiently [7] in effective photocatalytic degradation of dyes in aqueous solution [8–11]. However ZnO photocatalyst has the disadvantage to corrode in water, especially below pH = 7 [12].

However, in recent years several spinel oxides have been explored, which has led to attractive developments in UV photocatalysis. These studies have been conducted to evaluate the priority of other metal oxides because common semiconductive catalysts have some disadvantages. For example, the final separation of catalyst TiO_2 from the treated flow is very difficult, which limits the application of this decontamination process on a global scale. Also, during the reaction occurs the catalyst agglomeration because of the small size of TiO_2 particles and high specific surface area, which leads to reduction of specific surface area and limits the multiple application of TiO_2 [13]. Spinel ferrites can act as efficient photocatalysts in many industrial processes [14] such as the decomposition of alcohols and hydrogen peroxide [15], alkylation reactions [16], methylation reactions [17], the catalytic combustion of methane [18], CO_2 reduction [19]. The oxidation–reduction properties can be modified by the introduction of different metals in the lattice structure of spinels. The properties of the ferrites are strongly dependent on the site, nature, and amount of metal incorporated in the structure [1]. Ferrites have been used for the removal of organic contaminants from the environment. The use of ferrites as visible light photocatalysts for the degradation of contaminants in water has gained much interest in recent years and it is a promising process for water purification. Ferrites offer the advantage of having

the spinel crystal structure which enhanced efficiency due to the available extra catalytic sites and magnetic properties. Therefore, magnetic ferrites can be easily separated from the reaction mixture when they are used as catalysts [1]. Particularly, zinc ferrite ($ZnFe_2O_4$) nanoparticles have been widely explored by worldwide researchers due to their potential applications in semiconductor photocatalysis because $ZnFe_2O_4$ exhibits different properties with the change in particle size [20]. Furthermore, catalytic properties of zinc ferrite can be improved by substituting iron in octahedral positions with different trivalent cations [21]. But to date, there are few studies on the photocatalytic degradation of dyes in aqueous solution under UV light using these nano materials.

Dye effluents from textile industries are becoming a serious environmental problem because of their toxicity and biological degradation [14]. Thereby, ferrites are also effective in the degradation of many potential organic contaminants such as reactive blue 5 (RB5) [14], methanol [15], phenol [22], styrene [23], toluene [24], methyl orange [25], rhodamine B (RhB) [26] methylene blue [27].

The current paper presents for the first time the direct application of zinc ferrite substituted with aluminum in combination with UV light to the oxidation of the recalcitrant organic pollutant, Tropaeolin 000 No. 1 (called Orange I), with chemical formula $C_{16}H_{11}N_2NaO_4S$, which is an orange red color dye widely used in the textile industry [28]. It is now known that Orange I is a very dangerous azo dye to humans and can cause tumors, allergies and other disorders. Traditional methods for removal of this dye such as ultrafiltration, hydrogen peroxide, carbon adsorption are not very effective, because Orange I possesses very good solubility in water. Considered as a model molecule of many azo dyes, its degradation under various conditions [29] and using different catalysts such as, iron under oxidizing and inert atmospheres [28], TiO_2 [30–32], was already studied.

The goal of this report is to explore for the first time UV light induced photocatalytic degradation performance of Al^{3+} substituted Zn ferrite nanoparticles, prepared by sol–gel auto-combustion method, on Orange I in the aquatic environment. Surprisingly, the aluminum substituted $ZnFe_2O_4$ is much more active in UV light to the degradation of pollutant Orange I. The synthesis, characterization by using Mössbauer spectroscopy and nitrogen adsorption–desorption isotherm measurements, and ability to degrade this contaminant are discussed.

2. Experimental

2.1. Preparation and characterization of $ZnFe_{2-x}Al_xO_4$

Nanopowders of $ZnFe_{2-x}Al_xO_4$ ($x = 0$, 0.25, 0.5, 0.75, 1.0, 1.50, 2.0) have been synthesized in air by sol–gel auto-combustion technique using tartaric acid as combustion-complexing agent. Analytical grade $[Fe(NO_3)_3 \cdot 9H_2O]$ (99.9%, Aldrich), $[Al(NO_3)_3 \cdot 9H_2O]$ (99.9%, Aldrich) and $[Zn(NO_3)_2]$ solutions were mixed in stoichiometric proportions. Zinc nitrate solution was obtained in situ from ZnO (99%, Sigma–Aldrich) and nitric acid (Merck) 20% solution. A solution of tartaric acid $[C_4H_6O_6]$ (Merck) was mixed with each sample of metal nitrates mixture in 3:1 molar ratio of tartaric acid to metallic cations. The mixed solutions were heated for 3 h at 80 °C through gel phase transformation. The gel was gradually heated at 300 °C, when the auto-ignition was clearly observed. The obtained powders were sintered in two step: up to 500 °C/7 h and up to 700 °C/14 h. The protocol of synthesis was extensively described in a previous study [33].

IR spectroscopy, XRD and SEM are methods most often employed in order to verify the success of synthesis and spinel structure formation [34–36].

Mössbauer spectra for three representative samples, i.e. $x = 0.25$, 1.0, 1.50 were recorded at room temperature in transmission mode for ^{57}Fe, at a speed of 12 mm s^{-1} (at the source). A standard least-squares minimization routine was used to fit the spectra as a superposition of Lorentzian lines.

Textural properties including surface area and pore size were measured by nitrogen adsorption–desorption isotherms method at 78 K on a ASAP 2020 analyzer. Samples were degassed at 250 °C for 4 h prior to each measurement. The specific surface area S_{BET} was determined using the BET method. The mean pore size (D_{pore}) corresponds to maximum of pore size distribution curve.

2.2. Photocatalytic degradation of Orange I

A Pyrex cylindrical photo-reactor was used to conduct photocatalytic degradation experiments, in which a low pressure Hg lamp emitting a wavelength of 185 nm was positioned at the center of the reactor and was used for photoreaction under UV light. This cylindrical photo-reactor was surrounded by a Pyrex circulating water jacket to control the temperature during the reaction. The photocatalytic activities of the obtained photocatalyst were measured by the decomposition of Orange I (Sigma–Aldrich) in an aqueous solution at constant temperature. In each experiment, 0.40 g of photocatalyst was added into 75 mL Orange I solution with a concentration of 80 mg L^{-1} and pH = 3. The suspension was magnetically stirred in the dark for 30 min to reach adsorption–desorption equilibrium at constant temperature, then the solution was irradiated. During irradiation, stirring was maintained to keep the mixture in suspension. At regular intervals, the analytical samples were taken from the suspension. The change in the concentration (absorbance) of each degraded solution was monitored on UV–Vis spectrophotometer (Perkin Elmer Lambda 35) by measuring the absorbance in 200–700 nm range for Orange I. At $t = 0$ min and equilibrium in the dark (blank tests), the Orange I concentrations of the solutions were measured by UV–vis spectrometer and decomposition rate of Orange I on pure $ZnFe_2O_4$ or Al substituted $ZnFe_2O_4$ catalysts were calculated based on a concentration of the dye before and after degradation, respectively.

Distilled water was used as the reference sample. The absorbance set at 475.97 nm is due to the color of the dye solution and it is used to monitor the degradation of dye.

3. Results and discussion

3.1. Catalyst characterization

XRD patterns, IR spectra and SEM micrographs of studied materials were reported in a previous work investigating the effect of Fe^{3+} substitution with Al^{3+} in $ZnFe_2O_4$ on structural features, magnetic and electrical properties [33]. However, we can remind that the IR spectra of $ZnFe_{2-x}Al_xO_4$ ($0 \leq x \leq 2$) oxides recorded in the region 1000–300 cm^{-1} show the presence of two significant broad absorption bands at $\bar{\upsilon}_1$ and $\bar{\upsilon}_2$, characteristic of spinel structure for all samples. XRD patterns have revealed spinel monophase completion, observed in all samples, and no impurities such as Fe_2O_3 and ZnO were found, which are usually observed when the catalyst has been prepared by the coprecipitation or hydrothermal methods [21]. It is observed that lattice constant and crystallite size are slightly decreased with increasing aluminum content, which is attributed to the smaller ionic radii of the Al^{3+} ion than the Fe^{3+} ion. SEM micrographs showed that the grains are similarly spherical and show the decreasing trend with increasing aluminum content in system. Particles size was determined of SEM micrographs using ImageJ free program. The average particle size decreases by 66.8–45.5 nm with aluminum content increase.