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Synthesis of ternary zinc spinel oxides and their application in the photodegradation of organic pollutant

Chayene G. Anchieta[a], Daniela Sallet[a], Edson L. Foletto[a,*], Syllos S. da Silva[b], Osvaldo Chiavone-Filho[b], Claudio A.O. do Nascimento[c]

[a]Department of Chemical Engineering, Federal University of Santa Maria, 97105-900 Santa Maria, Brazil
[b]Department of Chemical Engineering, Federal University of Rio Grande do Norte, 59066-800 Natal, Brazil
[c]Department of Chemical Engineering, University of São Paulo, 05508-900 São Paulo, Brazil

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Abstract

Ternary zinc spinel oxides such as Zn_2SnO_4, $ZnAl_2O_4$ and $ZnFe_2O_4$ were synthesized and characterized, and their activities in the photodegradation of phenol molecules were investigated. Zn_2SnO_4, $ZnAl_2O_4$ and $ZnFe_2O_4$ powders were synthesized by hydrothermal, metal–chitosan complexation and solvothermal routes, respectively. The face-centered cubic spinel structure of each material was confirmed by powder X-ray diffractometry (XRD) and its porous structure by N_2 adsorption–desorption isotherms. The characterization of spinels was complemented with Fourier transform infrared spectroscopy (FTIR) and X-rays fluorescence (XRF), revealing the formation of spinel structures with high purity. The photocatalytic activity in the degradation of phenol was observed only with Zn_2SnO_4 oxide. Mineralization degree of phenol molecules by Zn_2SnO_4 photocatalyst determined by total organic carbon analysis (TOC) reached 80% at 360 min under sunlight.

Keywords: Synthesis; Zn_2SnO_4; $ZnAl_2O_4$; $ZnFe_2O_4$; Photocatalysis

1. Introduction

Zinc aluminate ($ZnAl_2O_4$) and zinc ferrite ($ZnFe_2O_4$) are ternary oxide semiconductors of the form AB_2O_4, while zinc stannate (Zn_2SnO_4) has the chemical formula A_2BO_4, where A represents a divalent metallic cation that usually occupies a tetrahedral site and B represents trivalent or tetravalent metallic cations that normally occupy the octahedral sites of a cubic structure [1,2]. As important semiconductor materials these three spinels have received much more attention recently. Due to the high electron mobility, high electrical conductivity and attractive optical properties, the Zn_2SnO_4 semiconductor is suitable for a wide range of applications such as solar cells, sensors for the detection of humidity and various combustible gases, and negative electrode material for Li-ion battery [2]. $ZnAl_2O_4$ is of interest due to its combination of desirable properties such as high mechanical resistance, high thermal stability, low temperature sinterability, low surface acidity and better diffusion. Therefore, it is used as high temperature ceramic material, optical coating or host matrix but most importantly as catalyst or catalyst support [3,4]. $ZnFe_2O_4$ has attracted significant research interest based on its magnetic and electromagnetic properties [5–7]. In addition, zinc ferrite shows potentially wide applications in photo induced electron transfer, photo-electrochemical cells and photo-chemical hydrogen production [8]. Ternary semiconductors oxides have also been used as catalysts and catalyst supports in several reactions [9–13], but its application in the field of the photocatalysis yet is limited. They have been applied more on degrading of different organic dyes [1,14–16]. However, the use of these spinel oxides as photocatalysts in the degradation of phenol has still been under explored. To the best of our knowledge, the evaluation of the photocatalytic activity of ternary zinc spinel oxides in the degradation of phenol under sunlight is scarce. Phenol is widely used in many petrochemical industries and petroleum refineries as well as chemical and pharmaceutical industries. Phenol pollution

*Corresponding author. Tel.: +55 55 3220 8448; fax: +55 55 3220 8030.
E-mail address: efoletto@gmail.com (E.L. Foletto).

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inhibits or even eliminates micro-organisms in biological wastewater treatment plant [17].

In this context, the aim of this work was to evaluate the photocatalytic activity of three zinc spinel oxides in the degradation of phenol molecules under solar irradiation. The oxides were synthesized by different methods and its physical properties were investigated by the characterization techniques powder X-ray diffraction (XRD), infrared spectroscopy (FTIR), X-rays flourescence (XRF) and N_2 adsorption–desorption isotherms.

2. Materials and methods

2.1. Synthesis of the spinel photocatalysts

2.1.1. Synthesis of Zn_2SnO_4

The zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) aqueous solution (12.85 g in 59 mL of water) was added into the tin tetrachloride ($SnCl_4 \cdot 5H_2O$) aqueous solution (8.80 g in 50 mL of water) slowly. The NaOH aqueous solution (5 M) was added dropwise into the mixture under magnetic stirring, until the solution reach pH 7.5. The final mixture was charged into a PTFE-lined stainless autoclave and the hydrothermal reaction was carried out at 200 °C for 10 h. Subsequently, the autoclave was allowed to cool naturally. The precipitate was filtered, washed with distilled water, and dried at 100 °C for 12 h.

2.1.2. Synthesis of $ZnAl_2O_4$

the preparation of $ZnAl_2O_4$ powder by metal–chitosan complexation route was similar to that described in previous works, but for the synthesis of magnesium aluminate ($MgAl_2O_4$) [18,19]. For the $ZnAl_2O_4$ synthesis, 9.84 g of chitosan polymer [$(C_6H_{11}O_4N)_n$] (Purifarma, Brazil) were dissolved in 334 mL of acetic acid solution (5% v/v), 11.88 g of $Zn(NO_3)_2 \cdot 6H_2O$ were dissolved in 20 mL distilled water and 31.5 g of $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 30 mL distilled water. The Zn and Al aqueous solutions were then added to the polymer solution under magnetic stirring. The Zn–Al–chitosan solution was added dropwise with a peristaltic pump to a NH_4OH solution (50%, v/v) under vigorous stirring. After adding the solutions, the system was kept under stirring for 3 h to complete the gelification process. The product was separated from the solution and further dried at ambient temperature for 24 h. The material was then treated in an oxidizing atmosphere (air) at the temperature of 750 °C, for 5 h, to form the spinel phase.

2.1.3. Synthesis of $ZnFe_2O_4$

In order to obtain the $ZnFe_2O_4$ powder, stoichiometric amounts of zinc nitrate (3 mmol of $Zn(NO_3)_2 \cdot 6H_2O$) and iron nitrate (6 mmol of $Fe(NO_3)_3 \cdot 9H_2O$) were dissolved in ethylene glycol (90 mL), followed by the addition of 45 mmol of sodium acetate (CH_3COONa) under magnetic stirring. After continuous stirring for 45 min, a homogeneous solution was obtained. The final solution was charged into a PTFE-lined stainless autoclave and the solvothermal reaction was carried out at 200 °C for 15 h. The product was then filtered and washed several times with distilled water and absolute ethanol, and subsequently dried at 110 °C for 24 h.

2.2. Characterization of the spinel photocatalysts

The zinc spinel oxides were characterized by X-ray diffractometry (XRD) (equipment Bruker D8 Advance, with Cu Kα radiation). The average size of the crystallite of each oxide was determined through the Scherrer equation [20]: $D = K\lambda/(h_{1/2}.\cos\Theta)$, where D is the average crystallite size, K the Scherrer constant (0.9), λ the wavelength of incident X-rays (0.15405 nm), $h_{1/2}$ the width at half height of the most intense diffraction peak and Θ corresponds to the peak position. FTIR spectra were recorded on a PerkinElmer FTIR Spectrum spectrophotometer in the region of 375–4000 cm^{-1}, using KBr pellets. The Brunauer–Emmett–Teller (BET) surface area measurement was carried out by N_2 adsorption–desorption at 77 K using ASAP 2000 instrument, in the range relative pressure (P/P_0) of 0 to 0.99. Chemical composition of the oxide powders was determined by X-ray fluorescence (EDX-750, Shimadzu) spectrometry.

2.3. Photocatalytic activity

Three photochemical reactors (Øint. = 10 cm) of 200 mL capacity, irradiated by sunlight, were used simultaneously in the photocatalytic experiments, according to the scheme of the reaction system seen in Fig. 1. The experiments under sunlight were carried out between 8:30 am and 14:30 pm during the month of January/2013 (summer season) at Natal City (05° 47' 42" S and 35° 12' 34" W), located in a northeastern state of Brazil. For all tests, 0.15 g of each spinel oxide was added to 150 mL of the aqueous solution of phenol at an initial concentration of 20 mg L^{-1}. The pH of the suspension was not adjusted (initial pH = 6.3). Prior to irradiation, the resulting suspensions were stirred continuously at constant temperature (25 °C) in the dark to achieve the adsorption equilibrium of phenol on each catalyst. The suspensions were then irradiated using sunlight under continuous stirring. Samples were periodically taken from the reactors, and filtered before being

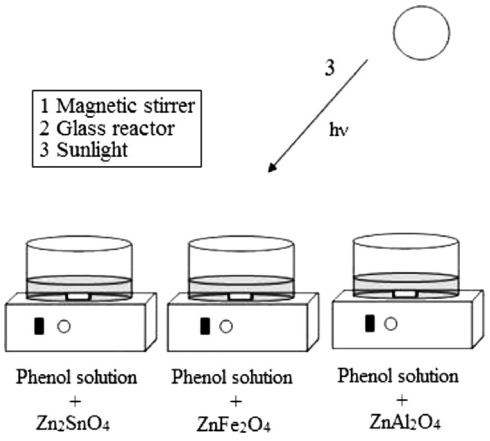

Fig. 1. Apparatus used in the photocatalytic experiments under solar irradiation.