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Synthesis of Zinc Aluminate ($ZnAl_2O_4$) Spinel and Its Application as Photocatalyst

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$ZnAl_2O_4$ spinel was synthesized by co-precipitation using ammonia as precipitating agent, followed by thermal treatment at 750 °C. The structural properties of particles were investigated by X-ray diffraction (XRD), atomic force microscopy (AFM), differential thermal analysis (DTA), and N_2 adsorption/desorption isotherms (BET) techniques. The photocatalytic activity was evaluated in the degradation of organic pollutant in aqueous solution under sunlight. The results showed that the $ZnAl_2O_4$ particles exhibited a mesoporous structure, and a promising photocatalytic activity for the degradation of pollutant molecules.

Keywords: *$ZnAl_2O_4$, synthesis, characterization, co-precipitation, photocatalysis*

1. Introduction

$ZnAl_2O_4$ is a spinel type oxide[1], which have high chemical and thermal stability, high mechanical resistance and low surface acidity[2-4], being suitable for a wide range of applications, such as optical coating or host matrix, high temperature ceramic material, catalyst and catalyst support[5-7]. In recent years, $ZnAl_2O_4$ spinel has been largely used as catalyst in several reactions such as degradation of gaseous toluene[8], ethanol steam reforming[9], hydroformylation and hydrogenation[3,10], combustion of soot under NO_x/O_2 atmosphere[11], transesterification of vegetable oil[12] and iso-butane combustion[13].

The photocatalytic degradation of organic pollutants in the water such as dye[14-16], phenol[17] and pesticide[18] using different semiconductor materials has attracted much attention recently. $ZnAl_2O_4$ is also a semiconductor material suitable for ultraviolet (UV) photoeletronic application[19] due it wide energy bandgap (about 3.8 eV)[20]. A few studies involving the degradation of organic dyes using $ZnAl_2O_4$ as a photocatalyst are reported in the literature. Recently $ZnO/ZnAl_2O_4$ nanocomposite has been evaluated for the photodegradation of methyl orange dye under artificial UV light irradiation[21]. Foletto et al.[22] observed satisfactory photocatalytic activity of $ZnAl_2O_4$ particles for degradation of Procion Red dye from aqueous solution. The photocatalytic activity of mechanochemically synthesized gahnite ($ZnAl_2O_4$) was tested for the degradation of Chromium Acidic Black dye under UV light irradiation[23]. $ZnAl_2O_4$ nanospheres synthesized by a wet chemical solution-phase method exhibited a good photocatalytic activity in degrading Rhodamine B dye[24]. Photocatalytic evaluation under UV irradiation shows that the $ZnO/ZnAl_2O_4$ microspheres exhibit highly enhanced photodegradation performance to Methylene Blue dye in comparison with the commercial ZnO powder[25].

In this context, the aim of this work was to synthesize $ZnAl_2O_4$ particles by co-precipitation and subsequent thermal treatment and to evaluate their capacity in the degradation of tannery dye molecules under solar irradiation. The particles synthesized were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), differential thermal analysis (DTA) and surface area (BET).

2. Experimental

2.1. *Synthesis and characterization of the catalyst*

Aluminum nitrate [$Al(NO_3)_3.9H_2O$, analytical grade] and zinc nitrate [$Zn(NO_3)_2.6H_2O$, analytical grade] were used as aluminum and zinc sources, respectively. The aqueous solution of zinc nitrate (11.88 g in 20 mL) was added into aqueous solution of aluminum nitrate (30 g in 20 mL). Afterwards, the appropriate amount of aqueous solution of ammonia (28 wt.%) was added to the resulting solution, and the mixture was stirred until complete precipitation at pH = 8.5. The powder was filtered, washed with distilled water, and dried. Afterwards, the solid was treated at 750 °C[26] for 3.5 h to obtain the $ZnAl_2O_4$ particles. The resulting powder was characterized by X-ray diffraction, atomic force microscopy, differential thermal analysis (DTA) and Brunauer-Emmett-Teller (BET) methods. X-ray diffraction (XRD) pattern was obtained using a Bruker D8 Advance diffractometer. The X-ray source was Cu-K radiation, powered at 40 kV and 40 mA. Data were collected from 25-70° (2θ) with a step size of 0.03° and a count time of 35 s. The crystallite size of the sample was estimated using the Scherrer's equation[27] (Equation 1) applied to the peak at 2θ = 36.75° (see XRD in Figure 1):

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$$d = \frac{0.9 \cdot \lambda}{B \cdot \cos \cdot \theta} \tag{1}$$

where d is the average crystallite size, λ is the wavelength of X-ray, B is the peak width at half maximum height and θ the Bragg's angle. The morphology of particles was examined by atomic force microscopy (AFM) (Agilent Technologies 5500 equipment). The Brunauer-Emmett-Teller (BET) surface area measurements were carried out by N_2 adsorption-desorption at 77 K using an ASAP 2020 instrument in the range of relative pressure (P/Po) of 0 to 0.99. Differential thermal analysis (DTA) was carried out on Netzsch STA 409 analyzer at a heating rate of 10 °C min^{-1} at an airflow rate of 50 mL min^{-1}.

2.2. *Photocatalytic activity*

The photocatalytic experiments under sunlight were carried out in a transparent vessel ($Ø_{int.}$ = 10 cm) between 10.00 am and 4.00 pm during the month of April/2013 (autumn season) at Santa Maria City (29° 43' 23" S and 53° 43' 15" W), Brazil. The scheme of the reaction system used in this work can be found a previous work[28]. The photocatalytic degradation of Direct Black 38 dye (molecular weight = 781.7 g mol^{-1}; see chemical structure in a previous work[29]) was studied in dye concentrations of 80 to 200 mg L^{-1}. Prior to photoirradiation, the suspension containing the dye and zinc aluminate powder (catalyst/solution ratio = 1.0 g L^{-1}) was subjected to ultrasonic dispersion for 15 min. Firstly, the homogenised suspension was magnetically stirred in the dark to establish the adsorption equilibrium. Afterwards, the dye solution (200 mL) was stirred with a magnetic stirrer under sunlight being withdraw aliquots at certain periods of time. These aliquots were centrifuged before the analysis of colour. The concentration of dye in aqueous solution was determined by spectrometry (Spectro vision T6-UV model), at $\lambda_{máx}$ = 590 nm[30].

3. Results and Discussion

The XRD pattern for $ZnAl_2O_4$ is shown in Figure 1. All the diffraction peaks can be perfectly indexed to face-centered cubic spinel-structured $ZnAl_2O_4$[31]. The characteristic peaks at 2θ of 31.2°, 36.75°, 44.7°, 49.1°, 55.6°, 59.3° and 65.3° are corresponding to (220), (311), (400), (331), (422), (511), and (440) diffraction planes[31,32]. The peaks and intensities of the synthesized powder and that of standard present similar behavior. This indicates the complete formation of $ZnAl_2O_4$ spinel phase in the experimental condition employed in this work. In addition, no impurities were detected in the synthesized sample. The average crystallite size estimated by applying the Scherrer equation was about 25 nm. The average crystallite size was also determined by atomic force microscopy, as showed in Figure 2. AFM image revealed an agglomerate of crystallites, com size smaller than 50 nm, corroborating with the result of XRD.

Nitrogen adsorption-desorption isotherms and pore size distribution for the $ZnAl_2O_4$ sample are presented in Figure 3. According to IUPAC classification[33], the isotherms are of type IV, representing predominantly characteristics of mesoporous structure. The mesoporous structure was confirmed by analysis of pore size distribution (see insert in Figure 3), which shows spectra of pore diameter with defined maxima in mesoporous region. Therefore, $ZnAl_2O_4$ had mesopores, most likely due to the interparticles and out-of-order porosity. The pore size distribution curve displays a wide distribution with an average pore size of about 8.3 nm. Additionally, the total pore volume and surface area were 0.20 $cm^3 g^{-1}$ and 93 $m^2 g^{-1}$, respectively. It is well known that the properties of catalyst materials are related to their porous structure. The presence of a large pore size is considered as fundamental for ceramic materials used in field of catalysis.

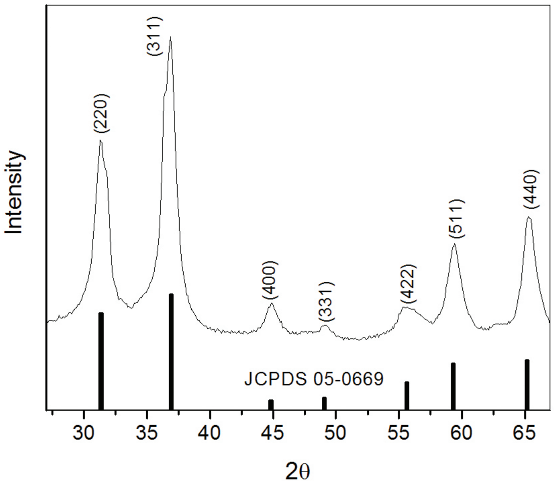

Figure 1. XRD pattern of $ZnAl_2O_4$ and (insert) reference $ZnAl_2O_4$ (JCPDS Card No. 05-0669)[31].

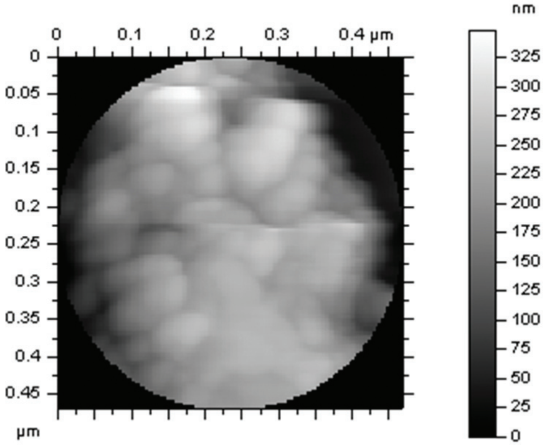

Figure 2. AFM of $ZnAl_2O_4$ powder.

DTA curve for the synthesized $ZnAl_2O_4$ sample is presented in Figure 4. From this Figure, it is observed that the absence of any exothermic peak on the DTA curve of $ZnAl_2O_4$ spinel indicates that no recrystallization process occurs at temperature up to 900 °C. This result shows a good thermal stability at high temperature of the spinel structure of $ZnAl_2O_4$ phase, a fundamental property for use as catalyst support in reactions at high temperatures.

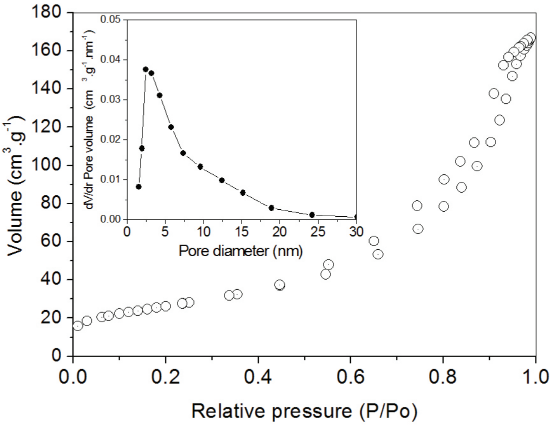

Figure 3. N_2 adsorption/desorption isotherms and (insert) pore diameter distribution of $ZnAl_2O_4$ particles.

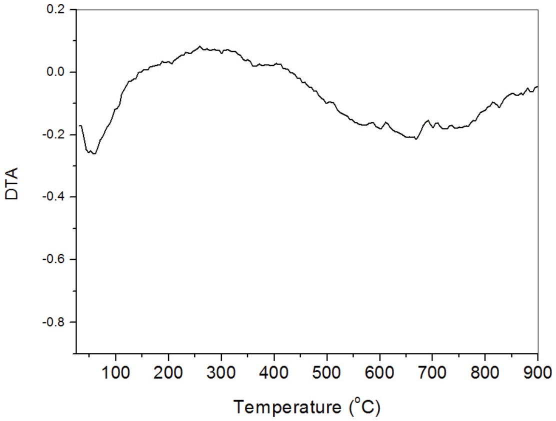

Figure 4. DTA curve of the synthesized $ZnAl_2O_4$ sample.

The effect of the initial dye concentrations on the photocatalytic degradation have been investigated from 80 to 200 mg L^{-1} and the results are shown in Figure 5. The degradation of the dye molecules was negligible by direct photolysis. The degradation of the dye was only observed with the simultaneous presence of catalyst and sunlight. The results showed that the increase of the dye concentration in the aqueous medium decrease the degradation efficiency. Increase in the dye concentration from 80 to 200 mg L^{-1} decrease the degradation from 99 to 30 % in 240 min of solar irradiation. The increase in dye concentration decreases the path length of photon entering into the dye solution. At high dye concentration a significant amount of sunlight may be absorbed by the dye molecules rather than the catalyst and this may reduce the catalytic efficiency[34]. This phenomenon can be also justified by the number of active sites at the $ZnAl_2O_4/H_2O$ interface. Thus, at low concentration of dye, there are too many water molecules that will be adsorbed on the available $ZnAl_2O_4$ particles, producing hydroxyl radicals and leading to fast oxidation process. Otherwise, at high concentration of dye there is a small proportion of adsorbed water molecules on the catalyst surface because the number of available active sites remains the same. Consequently, competitive adsorption among the dye and water molecules increases and leads to a decrease of the photodegradation rate[35].

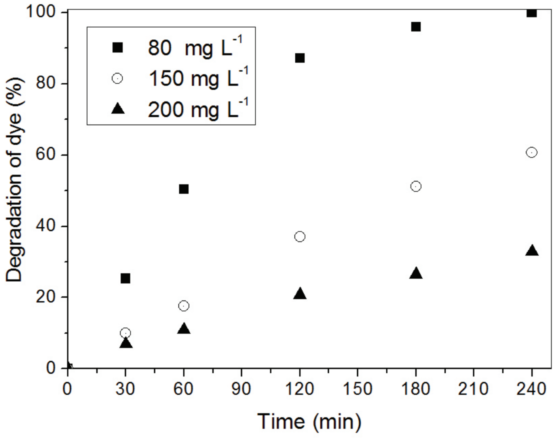

Figure 5. Photocatalytic activity of the $ZnAl_2O_4$ photocatalyst at different initial dye concentrations.

4. Conclusions

The $ZnAl_2O_4$ particles synthesized by co-precipitation followed by calcination at 750 °C presented a mesoporous structure, with a surface area of 93 m^2 g^{-1} and average size crystallite of about 25 nm. Due to its good thermal stability at high temperature, $ZnAl_2O_4$ particles can be used as catalyst supports in several reactions at high temperatures. Herein, it was demonstrated that the efficiency of the photocatalytic process depends on the dye concentration. The highest degradation efficiency was obtained at initial concentration of 80 mg L^{-1}. The results indicated that the $ZnAl_2O_4$ spinel obtained by co-precipitation followed by calcination exhibited promising characteristics to be used for photodegradation of dye pollutants under sunlight and can be used for the treatment of dye wastewater.

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