Theme: Nanotecnology

PHOTOCATALYTIC ACTIVITY OF ZINC OXIDE NANOSTRUCTURED SYNTHESIZED BY COMBUSTION IN SOLUTION*

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Abstract

With the growth of nanoscience and nanotechnology, the synthesis of nanostructured oxides has received a special attention. Metal oxides are widely used in the manufacture of microelectronic circuits, piezoelectric devices, fuel cells, catalysts, filters and bactericides systems. These metal oxides represent a large class of semiconductor materials suitable for photocatalytic processes. In recent years, new materials of this class such as TiO2 and ZnO have been developed due to their photo-catalytic abilities to degrade various environmental pollutants. This work aimed to evaluate the photocatalytic activity of zinc oxide previously synthesized by combustion synthesis in solution using citric acid as fuel and different reasons fuel/oxidant. After synthesis, the powders were subjected to heat treatments at different temperatures and photo-catalysis. The photocatalytic activity was evaluated by the degradation of a solution of methyl orange in a photochemical reactor of UV illumination, after which the transmittance of the samples measured with the assistance of a spectrophotometer. To analyze the results, a commercial zinc oxide was used as standard. The products of combustion synthesis in solution showed that photocatalytic activity varied according to the ratio fuel/oxidant and as a function of heat treatment. The results showed a higher photocatalytic activity for the products obtained with disabilities fuel in the reaction and heat treated.

Keywords: Photocatalysis; Zinc oxide; Nanostructured; Combustion in solution.

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1 INTRODUCTION

Zinc oxide (ZnO) is a semiconductor non-stoichiometric n-type due to the presence of native defects that may be generated by vacancy formation of oxygen atoms [1]. It has high binding energy (60meV), "bandgap" of about 3.37 eV, high optical and luminescent activity. In addition to being an excellent material for the field of semiconductors, zinc oxide degrades organic dyes through photo-catalysis. ZnO can be obtained by various procedural routes. The technique employed in this work is the combustion synthesis in solution (CSS) [2]. This method has the advantages of inexpensive raw materials, a relatively simple preparation process, and a fine resulting powder with high homogeneity.

Photo-catalysis is an advanced oxidation process widely used in water treatment and industrial effluents. In this process, the metal oxide semiconductor absorbs radiant energy (visible or ultraviolet) and makes a pair of electron/hole (e-, h+) in the conduction and valence bands [3-6]. The combination of water molecules with gaps can generate hydroxyl radicals (OH •) highly reactive that will act on the surface of the contaminant and promote degradation.

The aim of this work is to evaluate the photocatalytic activity of nanostructured ZnO, which was obtained by CSS, in methyl orange compound degradation, a dye widely used in textile industries.

2 MATERIAL AND METHODS

Figure 1 shows the flowchart of the experimental procedure.

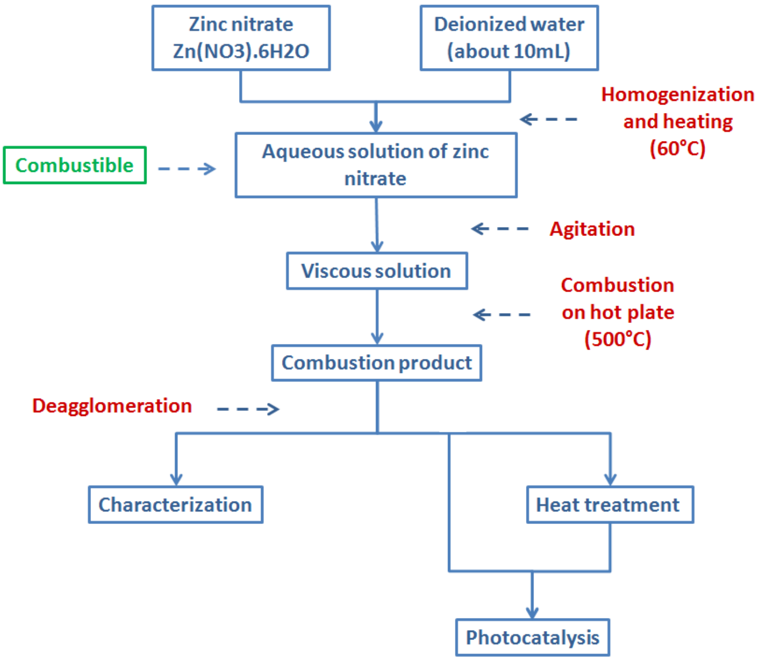

Figure 1. Flowchart of the experimental procedure adopted.

2.1 Combustion Synthesis of ZnO in Solution

The precursor solutions were prepared using zinc nitrate hexahydrate and citric acid monohydrate produced by Vetec Química Ltda. Additional information about the reagents is listed in Table 1.

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Table 1. Characteristics of the reagents involved in CSS of ZnO

Chemical reagent	Formula	Purity (%)	Reaction function
Zinc nitrate hexahydrate	$Zn(NO_3)_2.6H_2O$	98	Oxidant
Citric acid monohydrate	$C_6H_8O_7.\ H_2O$	99,5	Fuel

The fuel/oxidant ratios were defined from the thermodynamic modeling based on the chemistry of propellants and explosives [7]. Precursor solutions were prepared with different quantities of chemical reagents according to the calculated stoichiometric equation. The quantities of reagents used in reactions were 50 and 25% excess in fuel, stoichiometric ratio between fuel and zinc nitrate and 50 and 25% deficient in fuel.

Firstly, the metal nitrate was dissolved with deionized water (approximately 10 mL). Secondly, the solution was heated at 60°C under constant magnetic stirring. After 10 minutes, fuel was added. Then, the solution was agitated for 10 minutes. The electric plate was heated up to 500°C to accomplish combustion reactions. Due to the output of reactive gases, the procedure was performed under forced exhaustion. The reaction products of synthesis were comminuted for 5 minutes and sieved through 325 mesh (opening of 44μm).

2.2 Characterization of the Powders Obtained

Crystalline phases and crystallite sizes were determined using X-ray powder diffraction (Phillips diffractometer, X'Pert MPD model). The diffractometer has a graphite monochromator, Cu-Kα radiation (λ= 1,5406), and a fixed anode operated at 40 kV and 40 mA.

Table 2 shows the selected parameters for the phase analysis and determination of crystallite size.

Table 2. Parameters for XRD analysis.

Parameter	Phase analysis	Crystallite size
Δ2θ	5° - 75°	41.5° - 51.5°
Step	0.05	0.02
Time per step (s)	1	4
Cracks	1/4	1/4

The crystallite size was calculated with WinFit software (version 1.2). The experimental peaks are fit using asymmetric Pearson VII functions. They can be corrected for instrumental broadening and decomposed into two components: Gaussian and Lorentzian. Gaussian contribution characterizes the effect on crystallites size and Lorentzian contribution characterizes the effect of microstrain on the breadth of diffraction peaks. Therefore, determining Pearson VII specific functions for each diffraction maximum allows us to calculate the average size of crystallites [8].

2.3 Heat Treatment

The heat treatment of the reaction products consisted in heating the synthesized powders in electric muffle furnace at temperatures 600°C and 800°C, with a heating rate of 10°C/min and one hour of dwell time.

2.4 Photocatalytic Activity

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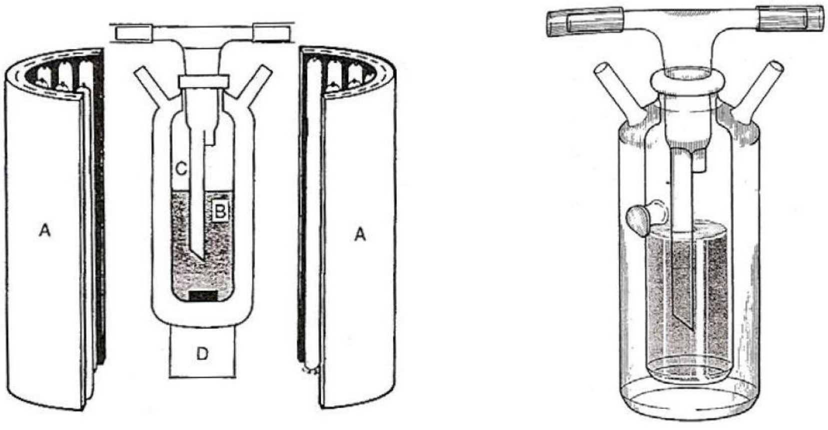
The equipment used in the process was a light irradiation device UV-A, consisting of twelve UV-A lamps (Xelux F8T5/BLB - black light) of 8W, two half-cylinders with reflective internal surface, stir plate, a system for supply of compressed air and a thermostatic bath (Figure 2a). The reactor (Figure 2b) pyrex glass has an orifice sealed by a silicone septum to remove the samples, an external jacket for water circulation, and an exit orifice with a porous membrane at the end.



(a) (b)

Figure 2. (a) UVA radiation system: A-lamp support assembly, B-bottle reactor, C-air bubbler, D magnetic stirrer; (b) details of the bottle reactor [9].

It was added 50 mg of ZnO nanostructure in 125 ml of a 20 ppm solution of methyl orange dye (Sigma-Aldrich). This mixture was homogenized with ultrasound in a dark chamber for 15 minutes for better dispersion of the material and initial adsorption of the dye on the surface of the catalyst. A sample of approximately 4 mL was removed immediately after the homogenization stage. The content was then transferred to a pyrex reactor and its color disappearance was monitored by spectrophotometric measurements at a wavelength of 450 nm. Samples without heat treatment and those calcined at 600ºC were obtained at 5 minutes intervals. The calcined samples at 800°C were obtained at 30 minutes intervals. For transmittance measurements, the samples collected were placed in buckets of polymethylmethacrylate (PMMA). The methyl orange degradation by commercial zinc oxide (Synth) was also investigated.

3 RESULTS AND DISCUSSION

3.1 Characterization of the Powders Obtained by CSS

The X-ray diffraction patterns of powders obtained are shown in Figure 3. For all samples, it was observed the characteristic peaks of zinc oxide (zincite) for values of 2θ 31.85°, 34.55° and 36.36 °, recognized by Miller indices (100), (002) and (101) respectively [10]. All samples showed a sufficient degree of crystallinity. However, the ZnO powders obtained with lower amount of citric acid (poor compositions) showed the most intense peaks on the X-ray diffraction, suggesting that samples are more crystalline.

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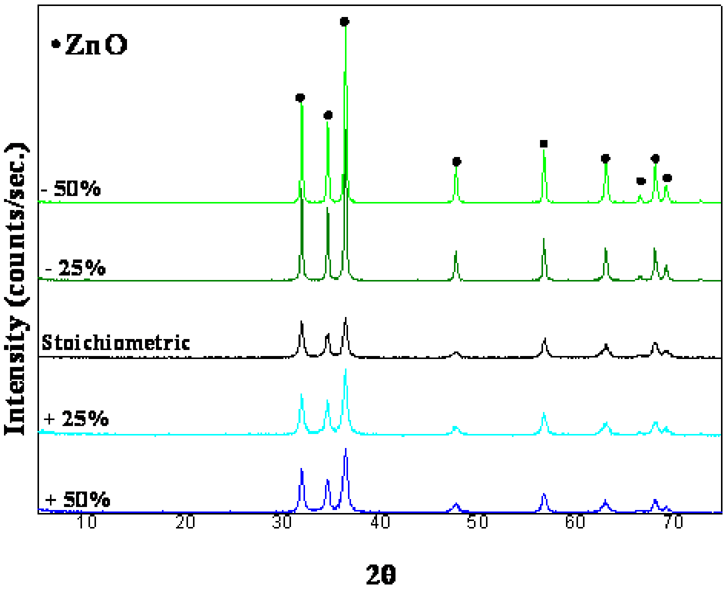

Figure 3. X-ray diffraction patterns of the powders obteined.

The products obtained in this work are nanocrystallites with the sizes ranging between 9.2 and 41.6 nm. According to the results (Table 3), the larger crystalline sizes are correlated with poor compositions in citric acid.

Table 3. Crystallite size of the products of CSS of ZnO

Fuel amount (%)	Crystallite size (nm)
+ 50	9.2
+ 25	28.1
Stoichiometric	10.7
- 50	30.7
- 25	41.6

The results differ partly from those reported in the literature [11-13]. According to Toniolo [11], should be observed crystal growth due to the increase of the fuel/oxidant ratio. The authors believe that the largest crystallite size of the samples deficient in fuel was caused by the less quantity of gas formed during the combustion synthesis. As the particles tend to agglomerate when there is a reduced amount of gas, the crystallite size increases.

3.2 Photocatalytic Activity

Figure 4 shows the variation of the relative concentration (C/Co) of methyl orange dye as a function of reaction time using photo-catalysts ZnO powders obtained by CSS and comercial ZnO. It was observed that the samples deficient in fuel, which have higher crystallinity, showed the best photocatalytic performance. At the same time, the samples with excess in fuel and stoichiometric did not show significant degradation. In these samples, it is suggested that the presence of organic matter in excess interfered in the degradation of methyl orange.

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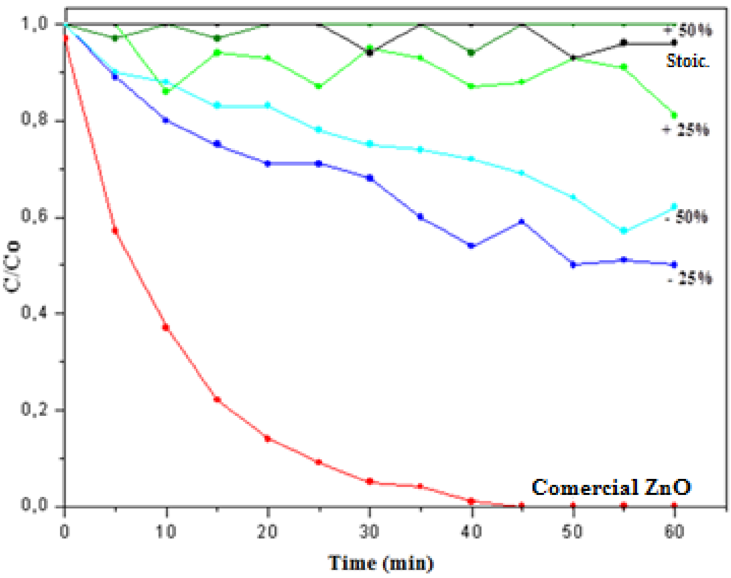

Figure 4. Variation of the relative concentration (C/Co) of the dye as a function of reaction time using ZnO powders obtained via CSS and comercial ZnO.

For the samples heat treated at 600°C, the variation of the relative concentration (C/Co) of methyl orange dye as a function of reaction time can be observed in Figure 5. The degradation efficiency of the samples rich in fuel increases with heat treatment. This enhancement in photocatalytic activity can be explained by the elimination of organic matter and the probable increase in the crystallinity of the material with the thermal treatment.

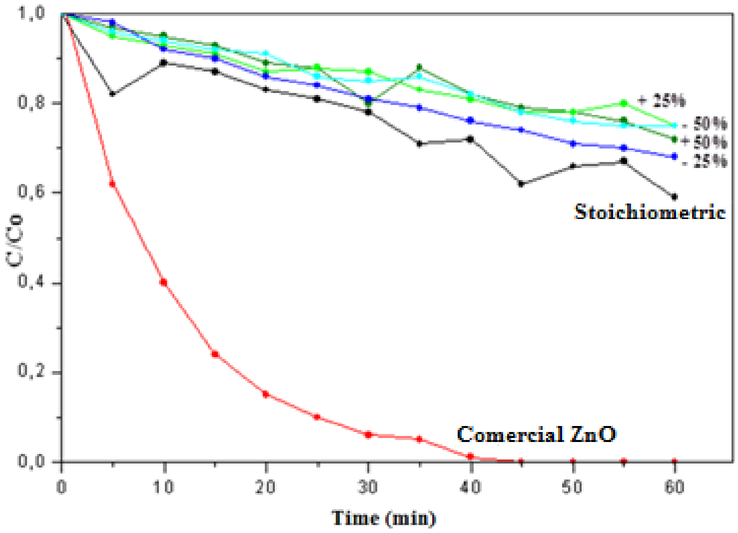

Figura 5. Variation of the relative dye concentration (C/Co) as function of time for the calcined powders at 600°C and the comercial ZnO.

Curves of C/C_0 versus irradiation time for the calcined powders at 800°C are shown in Figure 6. The stoichiometric sample presented higher catalytic activity than other synthesized products investigated.

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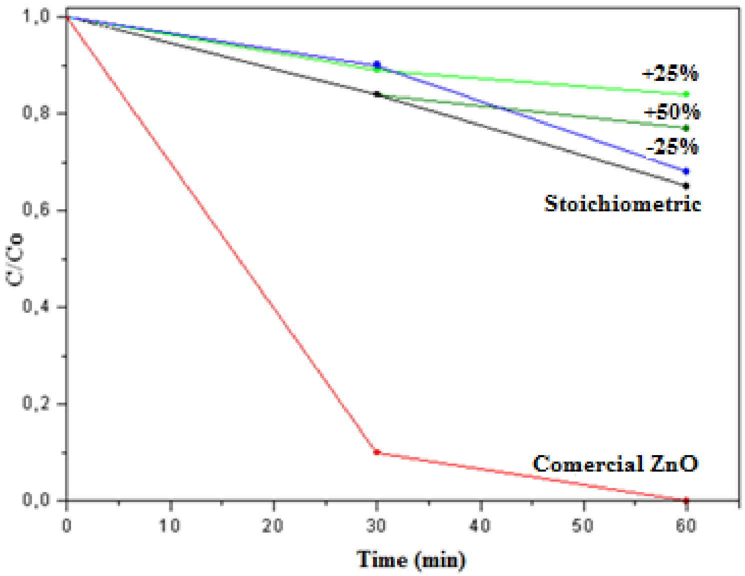

Figure 6. Variation of the relative dye concentration (C/Co) as function of time for the calcined powders at 800°C and the commercial ZnO.

The comercial ZnO, which was not heat treated, presented higher photocatalytic activity compared to powders obtained by CSS. The heat treatment, which had slow heat ratio, reduced the samples' surface area. As a result, this reduction affected the photocalytic activity. Further conclusions can be obtained by testing the sintering with other parameters and assess the effect in the photocalytic activity.

4 CONCLUSION

It was possible to obtain nanostructured zinc oxide by the method of combustion in solution using citric acid as fuel and zinc nitrate as oxidant, for all proportions fuel/oxidant investigated (-50%, -25%, stoichiometric, +25% and +50%).
The synthesized powders with disabilities fuel presented peaks in the X-ray diffraction patterns more intense, suggesting a higher crystallinity.
The photocatalytic activity of the obtained oxide varied according to the ratio of the fuel / oxidant and as a function of heat treatment. The results showed a higher photocatalytic activity for the products obtained from the stoichiometric formulation and heat treated. The commercial ZnO always presented higher photocatalytic activity compared to powders obtained by CSS.

Acknowledgments

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