J. Chem. Chem. Eng. 8 (2014) 794-799

Effect of Microwave Power on the Zn_2SnO_4 Synthesis and Its Use for Photodegradation of Phenol

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Abstract: Spinel structure Zn_2SnO_4 was successfully synthesized by microwave-assisted hydrothermal process. The effects of the microwave power on the formation and physical properties of the Zn_2SnO_4 particles are discussed. The products were characterized by X-ray diffraction, atomic force microscopy, infrared spectroscopy, and N_2 adsorption. The results indicated that the microwave power had important influence on the formation of the spinel phase. The results also revealed that the physical properties of Zn_2SnO_4 particles did not change with the increase of the microwave power above 600 W, with 20 min of reaction time. Furthermore, the photocatalytic activity of the Zn_2SnO_4 particles for the phenol degradation under sunlight was also investigated.

Key words: Zn_2SnO_4, zinc stannate, synthesis, microwave, porous material, photocatalysis.

1. Introduction

Zn_2SnO_4 ternary oxide is an important semiconductor material with a typical inverse spinel structure and has attracted much more attention in recent years. Zn_2SnO_4 has potential applications in advanced technologies, such as gas sensors [1], electrode material for Li-ion batteries [2], synergistic flame retardants [3], dye-sensitized solar cells [4], photoluminescence material [5], and photovoltaic material [6]. In addition, a few available works of the application of Zn_2SnO_4 as photocatalyst are mostly on degrading of water-soluble organic pollutants such as dyes [7-10]. However, works concerning use of Zn_2SnO_4 for the degradation of phenol molecules are scarce. Recently, Zn_2SnO_4 particles synthesized by hydrothermal route have been tested as photocatalyst in the degradation of phenol under sunlight [11]. In recent years, various routes have been developed to prepare Zn_2SnO_4 spinel, such as chemical vapor deposition [5], thermal evaporation [12], ball-milling [13], solid-state [14], coprecipitation followed by calcination in air [15], thermal plasma [16], hydrothermal reaction [17-19] and microwave [20, 21]. Among these methods, the microwave method has proved to be a simple and rapid way to prepare highly crystalline Zn_2SnO_4 particles. Nevertheless, works approaching the Zn_2SnO_4 synthesis by microwave route are scarce yet in Refs. [20, 21]. Phase-selective microwave synthesis and inkjet printing applications of Zn_2SnO_4 quantum dots have been realized [21]. Recently, the influence of reaction time on the synthesis of particles at a constant irradiation power (1,000 W) has been investigated [20]. In this work, Zn_2SnO_4 sample has been obtained in a short time (20 min). Thus, the microwave route demonstrates to be a rapid and efficient synthesis method.

In this context, the aim of this work was to verify the effect of microwave power on the Zn_2SnO_4

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synthesis by microwave-assisted hydrothermal method. Its physical properties were investigated by the characterization techniques XRD (X-ray diffraction), FTIR (infrared spectroscopy), N_2 adsorption-desorption isotherms and AFM (atomic force microscopy). In addition, the synthesized samples were evaluated as catalysts in the phenol photodegradation.

2. Materials and Methods

2.1 Synthesis and Characterization of the Catalyst

Tin tetrachloride ($SnCl_4 \cdot 5H_2O$) and zinc acetate ($ZnAc_2 \cdot 2H_2O$) were used for the synthesis of Zn_2SnO_4 powders. The aqueous solution of zinc acetate (25.7 g in 115 mL) was added into aqueous solution of tin tetrachloride (17.6 g in 100 mL) slowly. Aqueous solution of NaOH (5 M) was added dropwise into the mixture under magnetic stirring, resulting in a final pH of 7.5. The final mixture was charged into a microwave oven (multiwave 3,000 microwave system, Anton Paar, Graz, Austria). The microwave-heating program was started by applying (1) 400 W with a ramp of 5 min, (2) 400 W for 20 min and (3) 0 W for 20 min (cooling step). The procedure was similar for the microwave powers of 600, 800 and 1000 W. The formed solids were filtered, washed with distilled water and dried at 110 ^oC for 24 h.

Zn_2SnO_4 powders were characterized by XRD (equipment Bruker D8 Advance, with Cu Kα radiation). The average size of the Zn_2SnO_4 crystallite was determined through the Scherrer equation [22]:

$$D = K \cdot \lambda \,/\, (h_{1/2} \cdot \cos\theta) \quad (1)$$

where, D is the average crystallite size, K is the Scherrer constant (0.9), λ is the wavelength of incident X-rays (0.15405 nm), $h_{1/2}$ is the width at half height of the most intense diffraction peak and θ corresponds to the peak position (in this work, 2θ = 34.43°). N_2 adsorption-desorption isotherm measurements were carried out at 77 K using an ASAP 2,020 apparatus, at a relative pressure (P/P_0) from 0 to 0.99. FTIR spectra were recorded on a PerkinElmer FTIR spectrum spectrophotometer in the region of 375-4,000 cm^{-1}, using KBr pellets. The image of particles was obtained by AFM (Agilent Technologies 5,500 equipment).

2.2 Photocatalytic Essays

The photocatalytic essays were carried out in the same apparatus presented in a Ref. [23]. The reaction system consists of a transparent vessel ($\varnothing_{int.}$ = 10 cm) of 200 mL capacity and a magnetic agitator. The experiments were carried out under solar irradiation between 9:00 a.m. and 15:00 p.m. during the month of July 2013 (winter season) at Natal city (05°47'42" S and 35°12'34" W), located in a northeastern state of Brazil. For the photocatalytic tests, 100 mL of aqueous solution of phenol at an initial concentration of 20 $mg \cdot L^{-1}$ and 0.15 g of catalyst were prepared. This suspension was then irradiated under sunlight using continuous stirring. Samples were taken at pre-determined times, and filtered before being subjected to a TOC (total organic carbon) analyzer (Shimadzu 5,000A, Japan). Thus, the photodestruction performance of phenol was expressed in terms of TOC removal.

3. Results and Discussion

Fig. 1 shows the XRD patterns of the prepared samples at different microwave powers. As shown in Fig. 1, all main diffraction peaks of the samples prepared at powers above 600 W are consistent with the JCPDS (Joint Committee on Powder Diffraction Standards) (74-2184) data of the pure inverse-spinel Zn_2SnO_4. The main characteristic peaks at 2θ values of 29.25°, 34.43°, 35.96°, 41.79°, 45.67°, 51.74°, 55.14° and 60.49° are corresponding to (220), (311), (222), (400), (331), (422), (511) and (440) diffraction planes of the Zn_2SnO_4 spinel, respectively. No additional peak of the other phase was observed in the XRD patterns for these samples. In addition, at a low power (400 W), a less crystalline Zn_2SnO_4 phase was observed. It indicates that a well crystallized Zn_2SnO_4

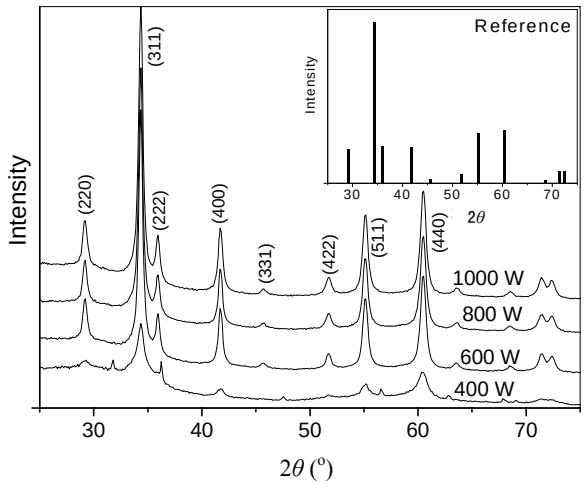

Fig. 1 XRD patterns of synthesized Zn_2SnO_4 samples at different microwave powers (the insert figure shows a reference JCPDS 74-2184 card).

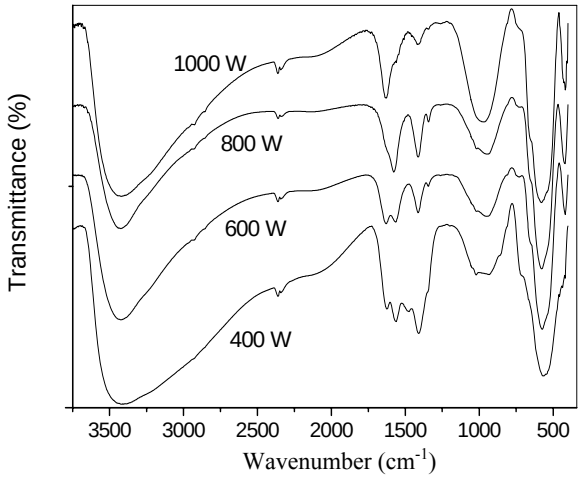

Fig. 2 FTIR spectra of synthesized samples at different microwave powers.

single phase could be obtained when a power above 600 W is applied, at 20 min of reaction time. Compared to the conventional hydrothermal method, the synthesis time by microwave route is very short. Zn_2SnO_4 has been prepared by conventional hydrothermal method at different reaction times such as 10 h [11], 20 h [24], 24 h [25] and 48 h [26].

Fig. 2 shows the FTIR spectra of spinel prepared at different microwave powers. Two main bands can be observed in the range 420-580 cm^{-1} for all spectra of the samples prepared above 600 W. The band at 420 cm^{-1} corresponds to interaction between metal and oxygen in the octahedral site in the crystal lattice, and the band around 580 cm^{-1} corresponds to interaction between metal and oxygen in the tetrahedral site [11]. Thus, the band observed at 420 cm^{-1} involves the Sn-O bonds in octahedral site, and the band observed at 580 cm^{-1} can be assigned to Zn-O bonds at the tetrahedral site. Yet for sample prepared at 400 W, there is not the presence of the band at 420 cm^{-1}, indicating that this power is inefficient for the formation of a single-phase Zn_2SnO_4 spinel. The results obtained in the analysis of FTIR confirm the formation of spinel structures for the samples prepared at powers above 600 W, and corroborate the results obtained in the XRD analysis.

Fig. 3 illustrates the nitrogen adsorption/desorption isotherms and pore size distribution curves of the Zn_2SnO_4 samples prepared at 600, 800 and 1,000 W. The nitrogen adsorption-desorption isotherms (Fig. 3a) and pore size distribution curves (Fig. 3b) presented similar behavior for all samples, indicating that the microwave power did not influenced the physical characteristics of Zn_2SnO_4 particles produced. The isotherms can be classified as type IV in the IUPAC (International Union of Pure and Applied Chemistry) classification [27], which are characteristic of porous materials. Pore parameters of Zn_2SnO_4 particles as well as surface area are shown in Table 1.

The specific surface area of the samples was about 60 $m^2 \cdot g^{-1}$. The pore size distribution plots showed that the Zn_2SnO_4 particles possessed pores with a mean diameter around 70 Å. Table 1 also presents the crystallite size estimated from XRD patterns, which was found to be about 18 nm for all Zn_2SnO_4 samples.

AFM images illustrated in Fig. 4 showed a Zn_2SnO_4 particle prepared at 600 W, with average size of 0.8 μm, formed by an agglomeration of crystallites with size smaller than 50 nm. AFM images indicate that the Zn_2SnO_4 crystallites are reasonably uniform in size. The crystallites size obtained by AFM micrograph is reasonably consistent with the crystalline size estimated from XRD analysis (Table 1).

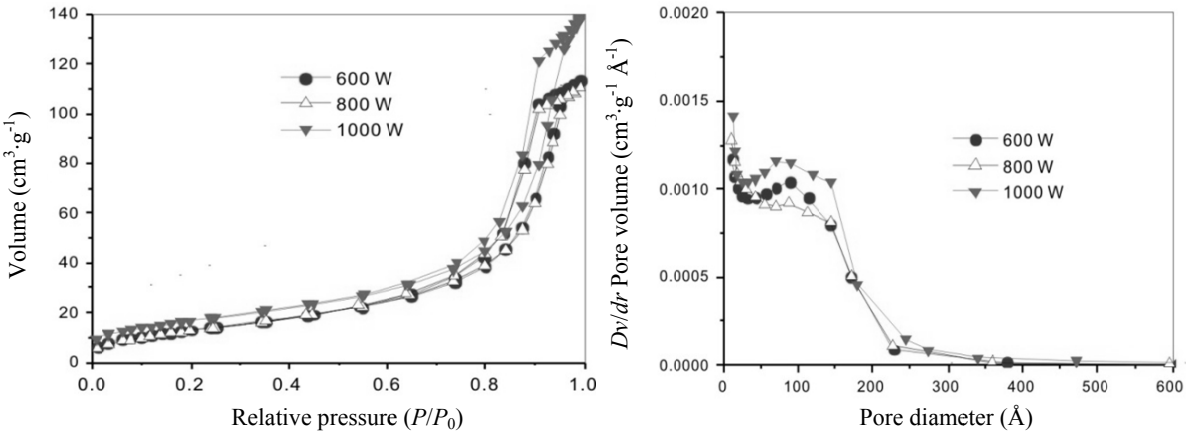

Fig. 3 (a) Nitrogen adsorption-desorption isotherms and (b) the corresponding pore size distribution curves of synthesized Zn_2SnO_4 samples at different microwave powers.

Table 1 Crystallite size, surface area and pore parameters of Zn_2SnO_4 powders synthesized at different powers.

Power (W)	Crystallite size (nm)	Surface area ($m^2 \cdot g^{-1}$)	Total pore volume ($cm^3 \cdot g^{-1}$)	Pore size (Å)
600	18.5	61	0.175	70.56
800	17.8	60	0.170	69.87
1,000	18.2	61	0.186	69.16

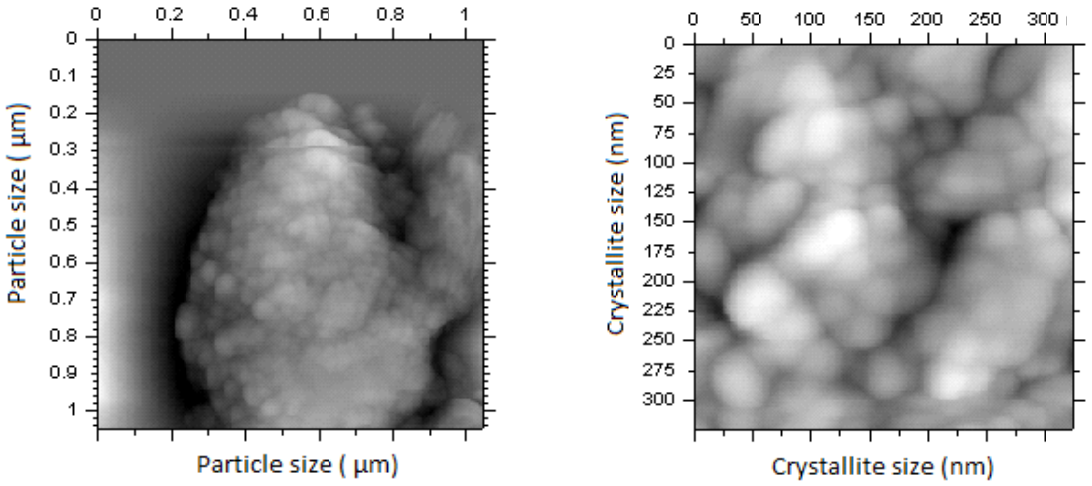

Fig. 4 AFM of (a) Zn_2SnO_4 particle prepared at 600 W and (b) their crystallites.

Before sunlight exposure, the suspension with Zn_2SnO_4 powders and phenol were stirred until establishing the adsorption equilibrium. The phenol degradation was negligible by direct photolysis (with solar irradiation only). Thus, a degradation of the phenol molecules was only observed with the simultaneous presence of sunlight and Zn_2SnO_4 powders. Fig. 5 illustrates the phenol photodegradation expressed in terms of TOC reduction for the prepared samples at 600, 800 and 1,000 W. As observed in Fig. 5, similar photocatalytic activities for TOC removal were obtained for all samples.

The results showed the highest TOC reduction with about 85% of TOC removed at 360 min of sunlight exposure for all samples. The similar results could be

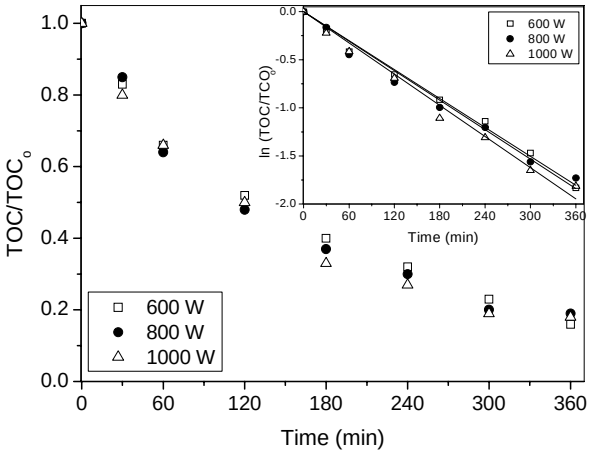

Fig. 5 Decrease of the TOC concentration and kinetics of TOC reduction (figure inside) for the synthesized samples at 600, 800 and 1,000 W.

attributed to the same physical characteristics presented by all samples, as shown in Table 1. The correlation coefficients (R^2) for all samples were superior at 0.99. Various organic pollutants degradation reactions follow first-order kinetics [10, 28, 29]. Here, the reaction kinetic was determined according to Eq. (2):

$$\ln(TOC_t / TOC_0) = -k \cdot t \quad (2)$$

where, TOC_0 is the initial TOC of the phenol solution and TOC_t is its concentration at reaction time t.

The straight line (Fig. 5) indicates first-order kinetics and the slope of the line corresponds to the rate constant of reaction (k), which was found to be similar for all photocatalysts, i.e., $k = 5.0 \times 10^{-3}$ min^{-1} (600 W), $k = 5.1 \times 10^{-3}$ min^{-1} (800 W) and $k = 5.4 \times 10^{-3}$ min^{-1} (1,000 W).

The correlation coefficients (R^2) for all samples were close to 0.99. For comparison purposes, photoelectrocatalytic degradation of phenol with simulated sunlight by TiO_2-film electrodes resulted in a rate constant of 6.0×10^{-3} min^{-1} for the TOC reduction [30].

4. Conclusions

Spinel-type Zn_2SnO_4 was synthesized by the hydrothermal process using microwave irradiation as energy source. The microwave power plays an important role on the formation of well-defined structures at short time. When a microwave power above 600 W is applied, the resulting product is characteristic of single-phase Zn_2SnO_4. The crystals synthesized by microwave-hydrothermal method showed similar physical properties when treated at power above 600 W, with a high surface area and porous structure. In addition, all synthesized Zn_2SnO_4 samples showed to be active for photodegradation of phenol.

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