

Evaluation of two different methods to synthesize cobalt-aluminate spinel

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The aim of this research is to study the efficiency of both microwave-hydrothermal and combustion methods to synthesize CoAl_2O_4 spinel. To attain the objectives, precursor solutions of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were applied to prepare cobalt aluminate spinel by a microwave-hydrothermal method and the effects of pH (4, 8 and 12), residence time (1 and 2 h), and temperature of the digestion system (190 and 220 °C) on the properties of final powders were studied. Moreover, mixed solutions of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and glycine were used as a precursor in the combustion synthesis method and the effect of different molar ratios of fuel to nitrate (0.36, 0.56) and calcination temperatures (800, 1000 °C) were evaluated. The powders obtained were characterized by XRD, XPS, SEM, TEM, FT-IR and UV-Vis. The results show that CoAl_2O_4 spinel is not formed by the microwave-hydrothermal method under the variable conditions studied, while the combustion synthesis method is capable of producing nano-particles of CoAl_2O_4 spinel and according to the results of TEM and Scherrer's equation most of the particles have sizes less than 100 nm.

Key words: Microwave- hydrothermal, Combustion, Spinel, CoAl_2O_4 .

Introduction

CoAl_2O_4 is a double oxide with a spinel structure and is well known as Thenard's Blue. It has been widely used in ceramics, glass, the paint industry, and color TV tubes as a contrast-enhancing luminescent pigment [1-4]. In order to obtain the required physical and chemical properties of CoAl_2O_4 , various processes are available. The oldest of these relies on mechanical size reduction and calcination of raw materials. This approach is no longer satisfactory due to the increasing demand of improved optical properties and physical structure of the pigments, such as crystal structure and particle size, shape and distribution and reduction of processing time [5, 6]. Recently CoAl_2O_4 has been synthesized by several wet-chemical techniques including sol-gel [7, 8], emulsion precipitation [9], hydrothermal crystallization [10, 11], co precipitation [12], etc.

In recent years, the potential applications of microwave-assisted hydrothermal synthesis (MH) have been deeply investigated. In particular in the MH process the hydrothermal conditions have been obtained by using a microwave field. It has been shown to be superior to the conventional hydrothermal method (CH) because it leads to a reduction of heating time during the synthesis process due to an extremely rapid kinetics of crystallization (one-to-two orders of magnitude) and the formation of novel or metastable phases. The attractive features of this technique include efficient energy transfer and rapid pro-

cessing of materials with cost reduction [1]. Although this technique has been applied to produce different types of nano powders [13, 14], no literature has been reported to synthesize the spinel CoAl_2O_4 by the MH process.

Also among the available solution chemistry procedures, the combustion technique is an inexpensive method capable of producing nano structured powders of oxide ceramics at lower calcination temperatures in a surprisingly reduced time. Moreover, solution-based combustion synthesis offers advantages in terms of better compositional homogeneity and purity of the final product [15, 16]. It is based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuel (e.g. citric acid, urea, glycine or glycol, etc.), producing a voluminous and fluffy product with a large surface area [16]. Li *et al.* [6] applied citric acid (CA) as a fuel to produce nano CoAl_2O_4 . They produced homogeneous crystalline CoAl_2O_4 powders with different particle sizes ranging from 9 to 110 nm. No literature has been reported applying glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), the lowest cost amino acid, as a fuel to synthesize the spinel CoAl_2O_4 by the combustion method. Glycine is known to act as a complexant agent for a great number of metal ions because it contains a carboxylic acid group at one end and an amino group at the other [17].

In this research both microwave-hydrothermal and combustion methods were applied to synthesize cobalt-aluminate powders. In the microwave- hydrothermal method, a precursor solution of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and in solution-based combustion method, precursor solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and glycine, were used to prepare spinel cobalt aluminate. The properties of the final powder were characterized by X-ray diffraction

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measurements, X-ray photoelectron spectroscopy, scanning and transmission electron microscopies, Fourier transform Infrared spectroscopy and UV-Vis spectroscopy.

Experimental

Sample preparation

For microwave-hydrothermal synthesis, a mixed aqueous chloride solution of Co-Al ($\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) with a molar ratio of 1 : 2 was prepared and the final pH of the solution was adjusted to 4, 8 and 12 by adding an appropriate amount of diluted NaOH or HNO_3 under magnetic stirring in an atmospheric environment. Then the feedstock was charged into the microwave digestion system (Model. MDS-200, CEM, Matthews, NC. The system uses 2.45 GHz microwaves and is controlled by both temperature and pressure ($P_{\text{max}} = 14 \text{ atm}$)). The temperature was controlled at 190 and 220 °C (the maximum allowed temperature of the instrument) and residence times of samples were fixed to 1 and 2 h (the maximum allowed residence time). After synthesis reactions, the suspensions obtained were repeatedly washed with distilled water to eliminate chloride ions. The suspensions were then centrifuged and dried in an oven at 110 °C. The general flowchart for the process is shown in Fig. 1.

For the combustion method, analytical-grade $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and glycine (GI) were used as starting materials. A mixed solution of metal nitrates was prepared by dissolving $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in de-ionized water with a Co/Al molar ratio of 1 : 2. Appropriate amounts of glycine were added to this solution to adjust the GI/ NO_3 -molar ratio (R) to 0.36 and 0.56. Subsequently, ammonia was added to set the pH of the solution to 2.5. The mixed solutions were heated on a hot plate maintained at 110 °C. As water evaporated, the solution formed a viscous liquid. The viscous precursor was then heated rapidly in a pre-heated furnace maintained at 500 °C. The combustion of the precursor solutions lasted less than 1 minute. The voluminous and foamy combustion

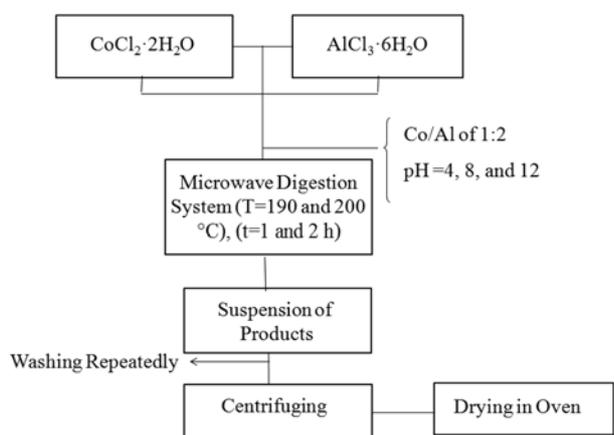


Fig. 1. A general flowchart of the microwave-hydrothermal process for the synthesis of cobalt-aluminates.

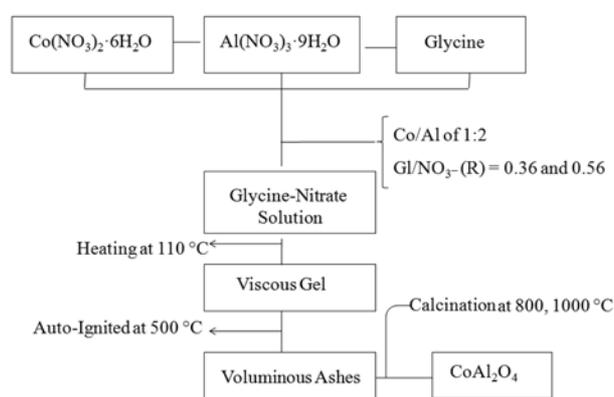


Fig. 2. A general flowchart of the combustion process for the synthesis of cobalt-aluminates.

ashes were easily crushed into powders. The crushed powders were further calcined at 800 and 1000 °C for 60 minutes to observe their thermal behavior. The general flowchart for this process is shown in Fig. 2.

Sample characterization

X-ray diffraction measurements (XRD) were carried out on burnt and calcined powders using a conventional Bragg-Brentano diffractometer (X'PERT PRO, Philips Research Laboratories) with Ni-filtered Cu K α radiation. The patterns were recorded in the 10-80° 2 θ range at room temperature, with a scanning rate of 0.001° s⁻¹ and a step interval of 0.02°. Crystallite size was estimated from X-ray line broadening measurements according to the Scherrer formula (Eq. 1):

$$D_c = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where β is the breadth of the observed diffraction line at its half-intensity maximum, K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the wave length of the X-ray source used in XRD [18].

X-ray photoelectron spectroscopy (XPS) was carried out to obtain information on the oxidation of the cobalt ion. Measurements were carried out with non-monochromatic Mg K α photons ($h\nu = 1253.6 \text{ eV}$) from a vacuum generator XR3 dual anode source operated at 15 kV, 18 mA. Data were recorded with a double pass Perkin Elmer PHI 15-255 G cylindrical-mirror electron analyser (CMA) operated at constant pass energy. The axis CMA was set to 15° from the sample normal. The energy resolution was set to 1 eV.

Scanning electron microscopy (SEM) images were obtained on the XL-30 (FEI). Sample morphology was also examined by transmission electron microscopy (TEM, JEM 2010, JEOL, Tokyo, Japan) equipped with EDS (EDAX PV9900, Philips). Specimens were prepared for TEM observation by dispersing the powders in distilled water and then placing a drop of the suspension on a copper

grid with a transparent polymer, followed by drying.

Fourier transform infrared spectroscopy (FT-IR analysis) was performed on the powders in the attenuated total reflectance mode with an Avatar 330 spectrometer (Thermo Nicolet, Germany). A minimum of 64 scans with a resolution of 4 cm^{-1} was used.

Color measurements on calcined powders were determined by UV-Vis spectroscopy (model Lambda 19, Perkin Elmer) using the CIE Lab method in order to obtain a^* , b^* and L^* value.

Results and Discussion

Fig. 3 shows the XRD patterns of powders synthesized by the microwave-hydrothermal method at the same pH 8, 1 h residence time and different temperatures of the microwave digestion system at 190 and 220 °C. It is clear that $\text{Co}_6\text{Al}_2\text{CO}_3(\text{OH})\cdot 16\text{H}_2\text{O}$ and $\text{AlO}(\text{OH})$ are the final products of this synthesis method and increasing the temperature from 190 to 220 °C just increases the crystal size of the products. Fig. 4 shows the XRD patterns of powders at the same pH at 8, the same temperature of the microwave digestion system at 220 °C and different residence times of 1 and 2 h. As can be seen both patterns show the same products. Also the XRD patterns of powders with the same temperature of microwave digestion system at 220 °C and the same residence time of 2 h and different pH values of 4, 8 and 12 (Fig. 5) show exactly

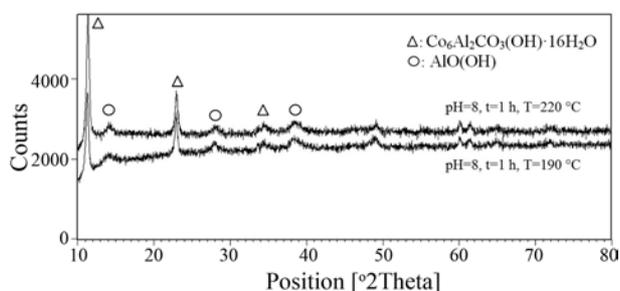


Fig. 3. XRD patterns of powders synthesized by the microwave-hydrothermal method (with the same pH of 8, same residence time of 1 h and different temperatures of microwave digestion system at 190 and 220 °C).

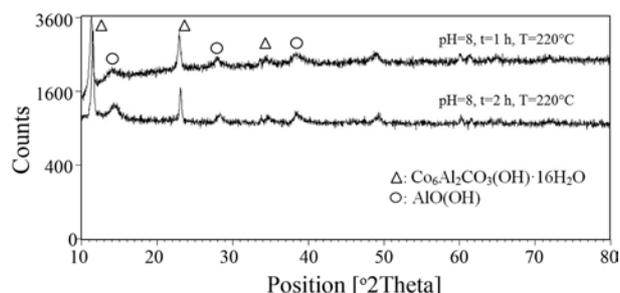


Fig. 4. XRD patterns of powders synthesized by the microwave-hydrothermal method (with the same pH of 8, the same temperature of microwave digestion system at 220 °C and different residence times of 1 and 2 h).

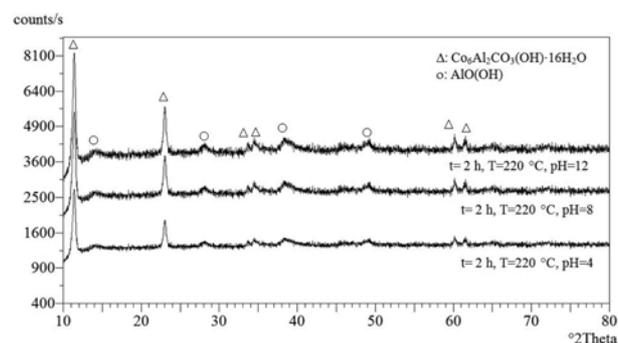


Fig. 5. XRD patterns of powders synthesized by the microwave-hydrothermal method (with the same residence time of 2 h and the same temperature of microwave digestion system at 220 °C and different pH values).

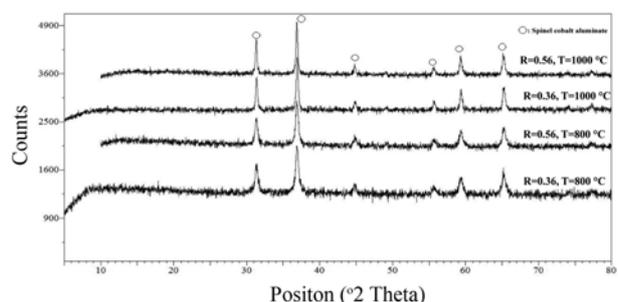


Fig. 6. XRD patterns of CoAl_2O_4 powders synthesized by the combustion method.

the same XRD patterns. From these results, it is concluded that the microwave-hydrothermal method performed by a microwave digestion system with a limited residence time (maximum 2 h) and a controlled temperature (maximum 220 °C) is not capable of producing spinel CoAl_2O_4 and control of the pH has no effect on the final products.

Fig. 6 shows the typical XRD patterns of the powders synthesized by the combustion method with different R values and calcination temperatures. These patterns indicate that crystalline spinel CoAl_2O_4 is formed at all the R values and temperatures studied and there is no clear difference among the XRD patterns of powders with different R values. Only different calcination temperatures give some diversity, i.e. an increase of the crystallite size with higher calcination temperatures. This result is confirmed by the average crystallite size calculated with Scherrer's equation (Table 1). According to this table, when the

Table 1. Average crystallite size of synthesized powders by the combustion method after calcination at 800 and 1000 °C (calculated with Scherrer's equation) and CIElab colorimetric coordinates

Temperature (°C)	R	Average particle size (nm) by XRD	b^*	a^*	L^*
800	0.36	30	-8.5	-6.4	45
	0.56	31	-14.4	-8.1	44
1000	0.36	52	-22.6	-9.6	49
	0.56	49	-20.0	-9.1	46

temperature of the calcination step is 800 °C, the crystallite size is approximately 30 nm and, as expected, the crystallite size increases with an increase of calcination temperature. There is a rise to 52 nm by increasing the calcination temperature to 1000 °C.

Fig. 7 shows X-ray photoelectron spectroscopy data of powder calcined at 800 and 1000 °C. The Co 2p_{1/2} and the Co 2p_{3/2} binding energy is 797.8 and 781.3 eV, respectively. The lineshape, relatively narrow peak width, the 2p_{3/2} to 2p_{1/2} peak separation of 15.5 eV and the positions of the satellite structures indicate that Co is in +2 oxidation state, mainly in a tetrahedral configuration [16]. As seen, the spectra of powders calcined at 800 and 1000 °C appear to be very similar suggesting that they have the same oxidation state and configuration.

Fig. 8 shows FT-IR spectra of synthesized powders by combustion method with the same R value of 0.36, calcined at 800 and 1000 °C. It can be seen that spinel CoAl₂O₄ has been formed in both powders due to the two characteristic bands (assigned to Al-O stretching vibrations) at around 550, and 640 cm⁻¹, with a shoulder at around 590 cm⁻¹, which are attributed to the vibrational bands of spinel Co²⁺Al₂O₄ [5, 7]. Powders with an R value of 0.56, not reported here, have FT-IR spectra similar to powders with an R value of 0.36.

SEM and TEM images of powders calcined at 1000 °C with an R value of 0.36 are shown in Fig. 9(a) and (b), respectively. It is clear that the spinel samples are agglomerated with most of the particles having sizes less than 100 nm. This result is in agreement with the

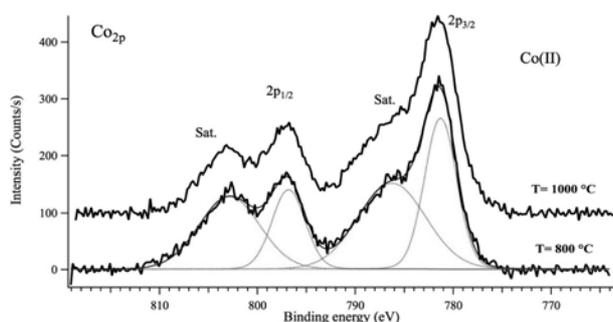


Fig. 7. X-ray photoelectron spectroscopy data of powder calcined at 800 and 1000 °C.

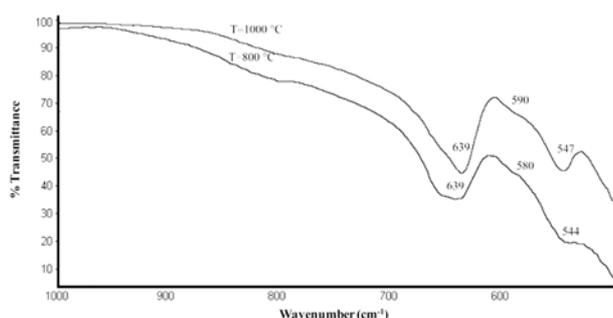
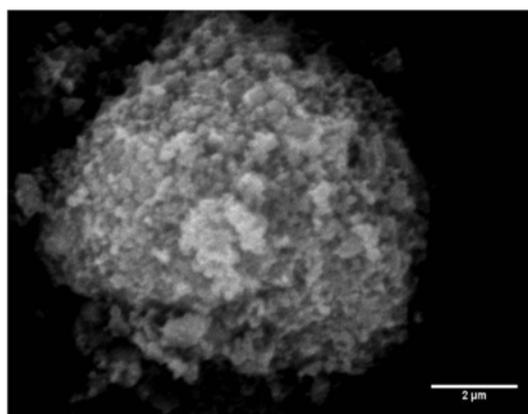
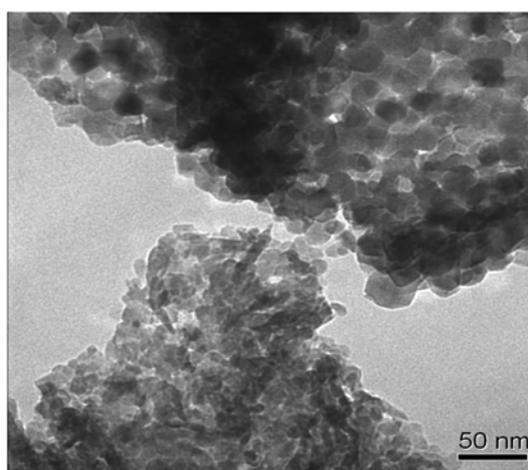


Fig. 8. FT-IR spectra of powders synthesized by the combustion method with the same R value of 0.36 and calcined at 800 and 1000 °C.



(a)



(b)

Fig. 9. SEM (a) and TEM (b) images of powder synthesized by the combustion method after calcination at 1000 °C (with the same R value of 0.36)

data calculated by Scherrer's equation (Table 1).

The CIElab colorimetric coordinates (Table 1) allow characterization of pigment colors. It can be seen that, independently of the R value, an increase in calcination temperature strongly decreases the coordinate b*. According to the TEM data and Scherrer's equation, the average particle size increases by increasing the temperature which results in a better blue color. Also among powders calcined at 800 °C, the R value has a strong effect on the color. Powders with an R value of 0.56, have the best b* value. By increasing of the ratio of fuel to nitrates from 0.36 to 0.56 the temperature of the combustion step increases which results in better crystallization of the pigment and a better blue color.

Conclusions

In line with results of X-ray diffraction measurements, it is concluded that the microwave-hydrothermal synthesis method is not capable of producing spinel CoAl₂O₄ via a reaction in a microwave digestion system with a limited

residence time and controlled temperature and pH, while corresponding to the results of XRD, FT-IR and XPS, a very pure nano crystalline spinel CoAl_2O_4 is produced by combustion synthesis via a reaction of metal nitrates and glycine.

According to the results of TEM and Scherrer's equation most of the particles produced by this method have sizes less than 100 nm.

Acknowledgments

Unfortunately Prof. Seyyed Hamid Jazayeri passed away nearly one year ago. Iran's scientific society has lost a truly erudite scientist. He is dearly missed by his students and colleagues.

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