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Optimizing the synthesis of cobalt aluminate pigment using fractional factorial design

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Abstract

The increasing use of experimental design techniques comes from the growing need to optimize products and processes while minimizing costs and maximizing efficiency, productivity and quality of products. Ceramic pigments have wide application in ceramic industries in which the quality and advanced properties of materials are widely investigated. However, studies are required to improve the procedure for obtaining cobalt aluminate ($CoAl_2O_4$) using the Complex Polymerization Method (CPM). With the objective of optimizing this method, a $2^{(5-2)}$ fractional factorial design was performed using data from UV–vis spectroscopy analysis as a response surface. To determine the best conditions for obtaining ($CoAl_2O_4$) in this study, five factors were chosen as input variables at levels determined for this study: citric acid concentration (stoichiometric), pyrolysis time (*h*), temperature (°C), calcination heating time and rate (°C/min). Through statistical application in the process of obtaining $CoAl_2O_4$, it was possible to study which of these factors may have greater influence in optimizing the synthesis. The precursor powders were characterized using TG/DSC thermogravimetric analysis, and the calcined powders were analyzed using X-ray diffraction (XRD) and energy dispersive scanning electron microscopy (SEM/EDS) to confirm the structural and morphological aspects of $CoAl_2O_4$. It was found that with increased calcination temperature 700 °C < 800 °C < 900 °C, the UV–vis bands decreased with increasing absorbance intensity, and with increasing pyrolysis time (*h*), there is a proportional increase in the UV–vis bands. The model was generated with the conditions proposed in this study due to the determination coefficient of 99.9%, variance (R^2), and satisfactory response surfaces, thus obtaining optimization of the process according to the needs and applicability in the ceramic industry of pigments.

Keywords: $CoAl_2O_4$; Pigment; Optimization; Fractional factorial design; Complex Polymerization Method (CPM)

1. Introduction

$CoAl_2O_4$ has a spinel cubic structure and exhibits an intense blue color, characteristic of cobalt aluminate, which is a consequence of this type of structure and the existence of a tetrahedral site for the metal ion that removes the restriction of the Laporte selection rule present in the octahedral symmetries. The thermal and chemical stability is due to the location of the Co^{2+} ion in a compact packaging arrangement of oxide ions as investigated by Meseguer et al. [1] and Akdemir et al. [2]. Currently, cobalt aluminate ($CoAl_2O_4$) has received attention for use in different applications due to its colorimetric properties, being widely used for coloring plastics, inks, fibers, paper, rubber, phosphorus, glass, cement, enamel, ceramic and porcelain bodies, as well as for TV tubes and as contrast reinforcement for luminescent pigments, according to Kakihana [3], Cho et al. [4], Kock and Waal [5]. Various chemical methods have been used to synthesize inorganic pigments, such as the conventional ceramic method as reported by Costa et al. [6] and Gargori et al. [7], combustion synthesis, co-precipitation as demonstrated by Mimani, Ghosh [8] and Gunawidjaja et al. [9], sol-gel method as found that Kakihana et al. [3]

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and Yang et al. [10], polymeric precursor as reported by Gaudon et al. [11] and hydrothermal method as noticed by Lu et al.[12] and Kim et al. [13].

$CoAl_2O_4$ is typically synthesized using inorganic precursors (primarily nitrate), followed by calcination at high temperature to obtain the spinel structure. A synthesis route frequently investigated in the literature for obtaining $CoAl_2O_4$ at low temperatures is the Complex Polymerization Method (CPM) as reported by Gaudon et al. [11], Lu et al.[12], Gong et al. [14], Chu et al. [15] and Onfroy et al. [16].

The Complex Polymerization Method (CPM) is based on the Pechini method and offers the possibility of preparing complexes of good homogeneity at molecular scale and a good stoichiometric control. The temperatures required for the CPM are lower than those in conventional methods, as in the reactions between materials in the solid state or decompositions as presented by Gaudon et al. [10]. Many variables can influence the synthesis of oxides via the CPM as investigated by Ozbay et al. [17], Gunawidjaja et al. [9] and Jacroux et al. [18].

The most important statistical activity is not data analysis but rather the planning of experiments in which these data can be obtained. The essence of good planning is to design an experiment able to provide exactly the type of information important for the improvement of the process for obtaining the desired material as reported by Montgomery [19].

Fractional factorial design is a reliable method to simplify the process of identifying the most influential preparation variable. This approach reduces the number of experiments required to identify the process of variables in a statistically significant manner as demonstrated by Mason [20] and Nejad et al. [21].

Fractional factorial design was used to optimize the synthesis process of cobalt aluminate ($CoAl_2O_4$) at operating conditions to determine a means to save time, thus reducing the number of experiments analyzing the input variables that would influence the process as noticed by Kavanloui et al. [22].

This study used a factorial planning of variables of the process of obtaining resin at different citric acid concentrations and pyrolysis times along with the process of obtaining pigments at different temperatures, times, and calcination heating rates, totaling five input variables ($k=5$) for the synthesis process for obtaining the ceramic pigment as discussed by Lu et al. [12], Llusar et al. [23] and Beal et al. [24].

2. Experimental procedure

Determining the parameter of greater statistical significance in the preparation of the precursor resins of cobalt aluminate ($CoAl_2O_4$) using the Complex Polymerization Method (CPM) derivative from the Pechini method was performed in two steps. The study explored the five main processing parameters in the method. Subsequently, based on this result, further analysis was designed using the fractional factorial design. This analysis corresponded to peaks of higher absorbance intensity in cobalt aluminate. Thereafter, the fractional factorial design was designed based on the final optimized factors to confirm that the interaction between the pyrolysis time (*h*) and the calcination heating rate (°C/min) has greater statistical significance compared to the other factors studied.

2.1. Materials and reagents

Aluminum nitrate ($Al(NO_3)_39H_2O$), cobalt nitrate (CoN_2O_6 6 H_2O), citric acid ($C_6H_8O_7$) and ethylene glycol ($HOCH_2$-CH_2OH) were used to prepare the precursor resins of cobalt aluminate ($CoAl_2O_4$) as reported in Mimani et al. [8] and Kim et al. [13].

2.2. Experimental design and characterization of the material

The fractional factorial design used increases the amount of information obtained and reduces the number of experiments. The designed experiment determines the influence of these parameters on the syntheses of cobalt aluminate as demonstrated in Meseguer et al. [1], Akdemir et al. [2], Gong et al. [14], Chu et al. [15], Onfroy et al. [16] and Pavia et al. [25]. The five factors studied include citric acid concentrations ($C_{\text{citric acid}}$), puff time (time $_{\text{puff }(h)}$), temperature (T), calcination time (time $_{\text{calcination }(h)}$), calcination rate (°C/min) and their encoded values (Table 1). If low and high values were assigned for each of these variables, there is a 2^5 factorial design; as a result of the combinations, there would be 32 experiments to determine the influence of these five parameters on the synthesis of cobalt aluminate. The syntheses performed according to scheme are listed in Table 1.

According to the $2^{(5-2)}$ fractional factorial design, resin was obtained based on different ratios among the citric acid masses at concentrations of 2:1, 3:1 and 4:1 and standard ethylene glycol 60/40, with a constant value of approximately 1.5 for the ratio by weight of citric acid and ethylene glycol. The pyrolysis of the resin obtained was performed at 350 °C at time intervals of 60 min, 120 min and 180 min with a calcination heating rate of 5 °C/min. The precursor powders obtained from synthesis were de-agglomerated using a mill for 90 min, 150 min and 210 min to obtain homogeneous powder. The calcinations were performed at temperatures of 700 °C, 800 °C and 900 °C in times of 120 min, 240 min and 360 min with heating rates of 5 °C/min, 8 °C/min and 11 °C/min with cooling to a temperature of 25 °C.

The $2^{(5-2)}=2^3$ fractional factorial approach used reduced the number of experiments to 11, including eight factorial and three central points **as reported by Montgomery** [19] **and Mason** [20].

Table 1
Values and Levels of the Operating Parameters.

	Levels		
Operating factors	−1	0	1
$C_{\text{citric acid}}$	2:1	3:1	4:1
time $_{\text{puff }(h)}$	1	2	3
T (°C)	700	800	900
time $_{\text{calcination }(h)}$	2	4	6
Calcination rate (°C/min)	5	8	11