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Synthesis optimization and characterization of $CoAl_2O_4$ nanoparticles as blue pigment

Nurul Hidayati Fithriyah[1*], Erdawati[2] and Athiek Sri Redjeki[1]

[1] Chemical Engineering Department, Universitas Muhammadiyah Jakarta, Indonesia
[2] Chemistry Department, State University of Jakarta, Indonesia
**Corresponding Author: nurul.fithriyah@umj.ac.id*

ABSTRACT

Blue ceramic pigment was prepared as $CoAl_2O_4$ nanoparticles. Alumina and Co_2O_3 was used for the synthesis of pigment by sol-gel method where heating and dissolution was conducted in a soundwave bath, followed by calcination at 400 – 800 ºC and cooling in a hydrothermal autoclave at 200 ºC. The process of supersaturation and deposition upon cooling facilitated the growth of nanoparticle. Response surface methodology (RSM) were utilized to reveal the optimum values of pH, calcination time and calcination temperature. The maximum absorbance by $CoAl_2O_4$ occurred at pH of 10, calcination temperature at 800 ºC, and calcination time of 2 hours. Morphological and thermal characterization employing XRD, TEM, TGA and DSC confirmed the optimum calcination temperature as the Cobalt pigment stabilize its crystal structure.

Keywords: blue pigment, cobalt aluminate, optimization, RSM, sol-gel method

1. Introduction

Cobalt aluminate ($CoAl_2O_4$) is a blue pigment which is high-temperature resistant [1] and so is widely used for ceramic glaze [2]. $CoAl_2O_4$ as a composite oxide contains two metallic elements in a spinel structure, in which Co^{2+} cations are positioned in tetrahedral positions, while Al^{3+} cations are positioned in octahedral positions [3]. Various techniques have been employed to synthesize $CoAl_2O_4$. Stangar *et al*. [4] synthesized $CoAl_2O_4$ with sol gel method at a calcination temperature of 700 °C. The study revealed good mechanical properties, thermal stability and suitable colour coordinates (x = 0.412, y = 0.394, z = 0.194). The characteristic blue coloration corresponds to electronic transitions of Co^{2+} in a tetrahedral coordination, which is favoured when the heat treatment of the xerogel film is performed at 700 °C.

Synthesis of oxide-based pigments can be more environmentally friendly by employing non-polluting methods of utilizing non-toxic raw materials and intermediates and also minimum energy consumption. Cobalt (II)-aluminate was obtained by a polymeric precursor method which involved non-toxic citric acid and ethylene-glycol [5]. Visinescu *et al*. [6] produced a novel, less-toxic, flexible as well as reproducible synthesis of cobalt aluminate based on soluble starch as a low-cost, naturally abundant, and renewable polysaccharide, fulfilling environmental friendliness requirements. Kim *et al*. [7] prepared $CoAl_2O_4$ nanoparticles for ceramic blue pigments in an ultrasonic-assisted hydrothermal apparatus with low energy consumption. The morphology of resulting ultrasonic-assisted powder was uniform in square shape and has a narrow size distribution which average particle size was less than 100 nm. In comparison, mechanically stirred $CoAl_2O_4$ pigment indicates an irregular morphology which size distribution was wider at 100–200 nm.

Because synthesis of $CoAl_2O_4$ involves several factors, a factorial experimental design needs to be applied to pigment

preparation. Response surface methodology (RSM) and central composite design were applied for pigment production to establish the optimal concentrations of raw and supporting materials [8]. Swamy *et al*. [9] extracted natural pigment and examined the combined effect of raw material mass, as well as extraction time and temperature using RSM optimization approach so that the experimental yield were close to that of predicted value. Gomes *et al*. [10] optimized the synthesis of cobalt aluminate employing fractional factorial design of stoichiometric concentration, pyrolysis time and temperature, as well as calcination rate and time. The study revealed that increasing calcination temperatures at 700 - 900 ºC increased absorbance intensity with decreasing UV–Vis bands, while increasing pyrolysis time proportionally increased the UV–Vis bands.

A series of preliminary studies were conducted by Erdawati *et al*. [11] to prepare spinel compound of $MgFe_2O_4$ nanoparticles employing sol-gel method as characterised by cyclic voltametry method. The results showed that at 500 ºC calcination produced nanoparticles with good conductivity which was even improved as they were dopped with Cobalt. The spinel structure contributes to acid resistance property of pigment [12]. Gama *et al*. [13] observed that pigment nanoparticles have extensive surface area, higher scattering effect and better image resolution compared to micrometer size particles, resulting in brighter colour intensity and improved stability of dispersion preventing nozzle blocking in inkjet printing. Similar observation was reported by Chen *et al*. [14]. In this study, the effects of calcination temperature and time as well as pH of cobalt aluminate pigment were evaluated. Calcination temperature and time affect the physical properties of pigment [10]. The pH of pigment affects shrinkage of glaze and combustion type during firing, as well as viscosity and surface tension [15].

2. Materials and Methods

2.1. Materials

Cobalt nitrate powder [$Co(NO_3)_3 \cdot 9H_2O$] and aluminium oxide powder [Al_2O_3] were supplied by Sigma–Aldrich. Polyvinyl alcohol, citric acid [$C_6H_8O_7.H_2O$], sodium hydroxide and Tween 80 were supplied by Merck.

2.2. Synthesis of $CoAl_2O_4$ Blue Pigment

$CoAl_2O_4$ pigment was prepared by co-precipitation method. Cobalt nitrate, aluminium oxide, and citric acid were dissolved into de-ionized water and stirred for 30 minutes. PVA and Tween 80 were then slowly added to the solution and stirred for 30 min. Sodium hydroxide 3M was added dropwise until alkaline pH achieved at 6 – 10. These normal-to-basic pH values are favoured in industry due to superior properties [15]. The suspension was stirred at room temperature for 2 hours. The precipitate was separated and washed with de-ionized water to remove impurities prior to drying at 100 ºC. The resulted pigments were then calcinated at 400 – 800 ºC for 2 – 4 hours. The temperatures chosen were lower than previous studies, in order to evaluate the possibility of energy efficiency. The calcination time applied was assumed to be sufficient for the formation of spinel structure.

2.3. Factorial Design

Table 1 shows the high, middle and low values of pH of the solution (X_1), calcination temperature (X_2) and calcination time (X_3) on the production of $CoAl_2O_4$. This 2^3 factorial design was selected based

on some preliminary experiments. The factorial design matrix in each factorial experiment is shown in Table 1. The order of experiments was randomized to avoid errors. The main effects and interactions among factors were determined based on analysis with Design Expert 7.0 software.

Table 1: Levels and factors in factorial design

Factors	Symbol	Low	Middle	High
pH	X_1	6.00	8.00	10.00
Temperature (°C)	X_2	400	600	800
Time (hour)	X_3	2	3	4

Each response (Y) to be analyzed can be calculated by Eq. (1) of second-order polynomial (quadratic model) which represents the three independent variables:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_1b_2X_1X_2 + b_1b_3X_1X_3 + b_2b_3X_2X_3 + b_1X_1^2 + b_2X_2^2 + b_3X_3^2 \quad (1)$$

where Y is the predicted response (maximum wavelength, nm), b_0 is the offset term, while b_1, b_2, and b_3 are the coefficients. As much as 20 experimental runs according to central composite designs (CCD) with six centre points were performed. The absorbance of the $CoAl_2O_4$ has been measured using spectrophotometer Shimadzu 600-A Lakeshore-7304.

2.4. Characterization of $CoAl_2O_4$

Morphology and thermal properties of $CoAl_2O_4$ have been investigated using XRD, TEM, TGA and DSC characterizations.

3. Results and Discussion

3.1. Models for Synthesis of $CoAl_2O_4$

By using multiple regression analysis, the responses (absorption intensity) were correlated using Eq. (1) resulting in quadratic regression model given by Eq. (2):

$$Y = 908.61 - 29.76X_1 - 0.059X_2 + 110.48X_3 - 0.0109X_1X_2 + 11.3975X_1X_3 - 0.20293X_2X_3 \quad (2)$$

One factor coefficients represent the effect of one particular factor, whereas two factors coefficients and those of second order represent the interaction between two factors and quadratic effect, respectively. The positive sign indicates synergistic effect, whereas negative sign indicates antagonistic effect. The goodness of fit was examined by fitting the independent variables into the quadratic equation. Several indicators were used in the evaluation of fitted model adequacy with results shown in Table 2.

Table 2: Results of Fitting Tests

Source	Degrees of freedom (DOF)	Sum of squares (SOS)	Mean square	F-value	P-value
Linear	32	11,427	1,039	0.60	0.778
2FI	8	6,438	808	0.46	0.840
Quadratic	5	5,513	1,103	0.64	0.685
Cubic	1	314	314	0.18	0.688
Error	5	8,677	1,735		

In Table 3, the model significance (F-value) was one of parameters used to evaluate the adequacy of the model [16]. F-value of 1.00 implies the significance of model, as well as the probability value (P-value) less than 0.0500 [17]. P-values also indicate the interaction strength between variable, which become lower as the strength become more significant [18].

Table 3: Sequential models parameters

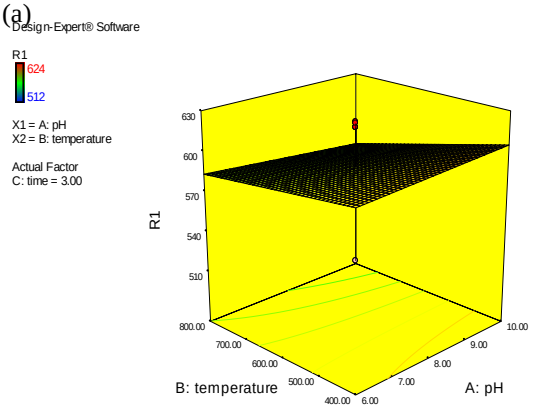
Source	Coeff.	DOF	SOS	Mean square	F-value	P-value
Model	6,985	9	176.75	1,164	1.00	0.46
X_1	14	1	23.84	14	0.01	0.91
X_2	1,886	1	11.19	1,886	1.62	0.23
X_3	95	1	3.59	95	0.08	0.78
X_1X_2	153	1	0.12	153	0.13	0.72
X_1X_3	4,560	1	15.12	24	3.92	0.07
X_2X_3	276	1	1.12	4,560	0.24	0.63
Residual	15,115	13	62.45	1,163		
L/O Fit	6,438	8	61.11	805	0.46	0.84
Error	8,677	5	1.33	1,735		
Corr.	22,100	19	239.20			

3.2. Interactions among the Factors

3.2.1. Effect of initial pH and calcination temperature

The interaction between pH and calcination temperature (T) is shown in Figure 1(a) and 1(b). The lowest absorption intensity was observed at pH 10 and T of 800 ºC. No significant interaction was apparent between the two parameters.

(a)



(b)

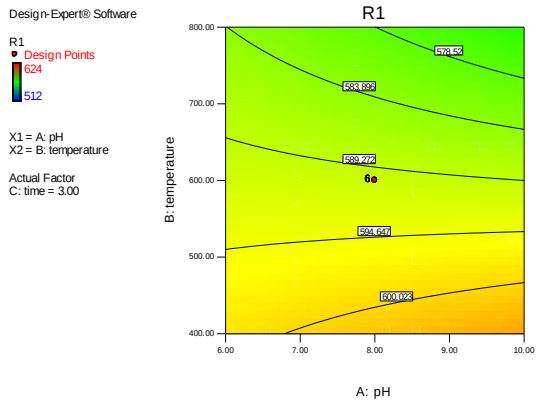
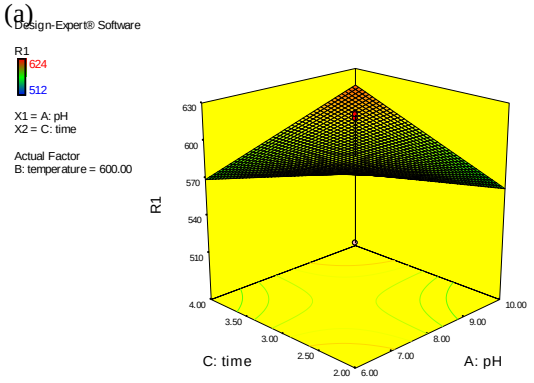


Figure 1: Effects of calcination temperature and pH on absorbance (nm) in: (a) 3 dimension; (b) 2 dimension

3.2.2. Effect of calcination time and pH

The interaction between calcination time (*t*) and pH is shown in Figure 2(a) and 2(b). The lowest absorption intensity was observed at pH 10 and *t* of 2 hours or pH 6 and *t* of 4 hours. The shorter time is, of course, more favourable. It seems that higher pH may shorten calcination time needed.

(a)



(b)

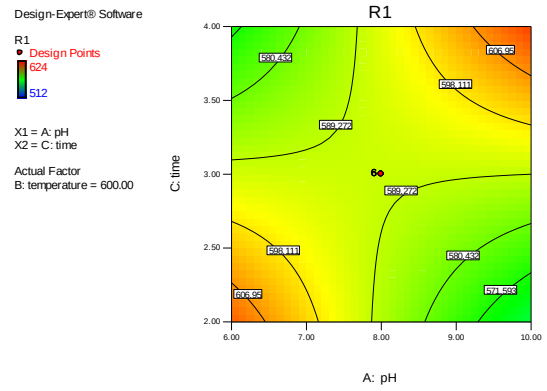


Figure 2: Effects of pH and calcination time on absorbance (nm) in: (a) 3 dimensions; (b) 2 dimensions

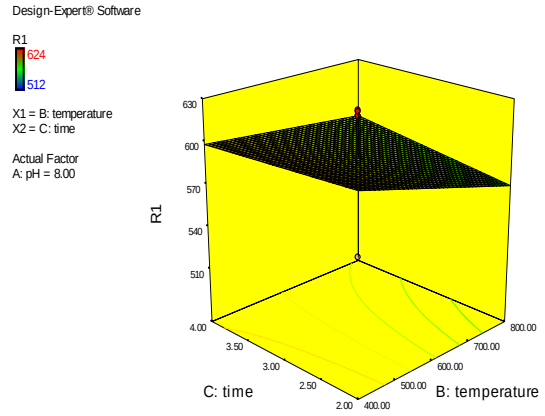
3.2.3. Effect of calcination time and temperature

The interaction between calcination time and temperature is shown in Figure 3(a) and 3(b). The lowest absorption intensity was observed at *t* of 2 hours and *T* of 800 ºC. Apparent interaction between both parameters, if any, is not significant.

3.3. Optimization analysis

The model prediction from Eq. (2) agreed reasonably well with experimental data. The minimum values of absorption intensity (R1) in Figure 1 - 3 were selected as optimum values. The optimum condition was achieved at pH of 10, calcination temperature of 800 ºC, and calcination time of 2 hours.

(a)



(b)

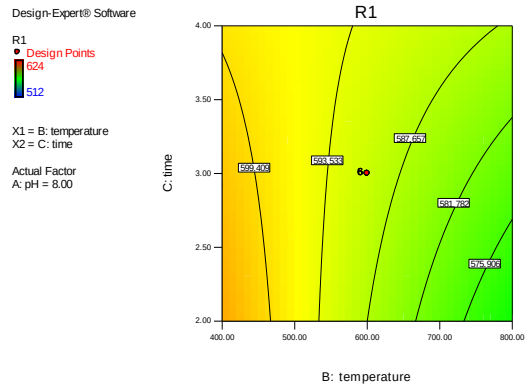


Figure 3: Effects of calcination time and temperature on absorbance (nm) in: (a) 3 dimensions; (b) 2 dimensions

3.4. Characterization of $CoAl_2O_4$

3.4.1. XRD Analysis

According to the Joint Committee on Powder Diffraction Standards (JCPDS) card no. 79-0418, all diffraction peaks of the XRD patterns of $CoAl_2O_4$ correspond to the index of cubic spinel phase. It is suggested that the synthesis method will not affect the peak angles. The pigment sample as calcinated at 800 ºC showed d-spacing of 1.99 Å at 45.53 º2Θ in Figure 4. The d-spacing and peak positions were similar

throughout varying calcination temperatures 500 ºC onwards, indicating the possible onset temperatures of crystal formation at this temperature.

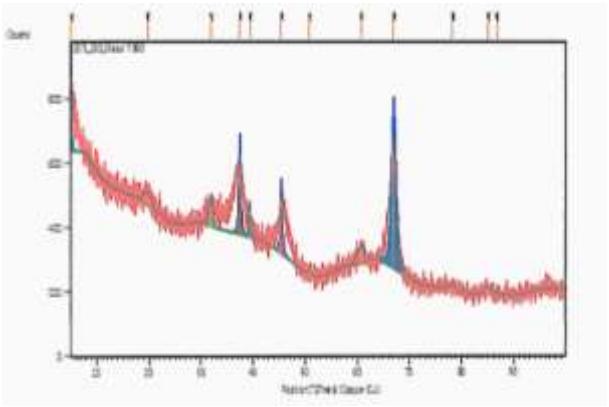


Figure 4: XRD pattern of $CoAl_2O_4$ prepared at the optimum condition

3.4.2. TEM Analysis

TEM image of the $CoAl_2O_4$ material of experiments at temperature of calcination 800 ºC is shown in Figure 5. The width of Cobalt crystals was observed to be around 2 nm. The divalent cobalt crystals were partly formed into hexagonal crystal lattice as identified in diffraction pattern (not shown here). Extended calcination time may be required to improve the crystal structure into cubic spinnel lattice.

Figure 5: TEM image of $CoAl_2O_4$ prepared at the optimum condition

3.4.3. Thermal Analysis

TGA/DSC curves of $CoAl_2O_4$ pigment as calcinated at 800 ºC is shown in Figure 6. It was observed that the pigment was stable during heating and lost only 3.4 % of mass. The analysis also confirmed that the hydrothermal operating temperature at 200 ºC was within the range of pigment exothermic activities between 52 – 241 ºC. Below 700 ºC the cobalt aluminate particles absorbed heat at a constant rate, but beyond that its endothermic activities consumed heat at a steadily increasing rate until the end of measurement. This observation confirmed that 800 ºC is the optimum calcination temperature.

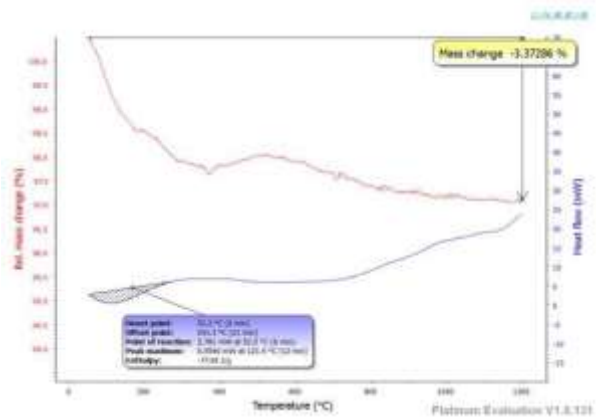


Figure 6: TGA and DSC curves of $CoAl_2O_4$ up to 1200 ºC

4. Conclusion

Response surface methodology involving a full 2^3 factorial experimental design was employed to evaluate the effects of calcination temperature and time as well as pH on maximum wavelength. Validation of experimental data effectively verified the model adequacy. Optimum parameters of the minimum wavelength were obtained at pH 10, calcination time of 2 hours and calcination temperature of 800 ºC. Morphological and thermal analyses of

$CoAl_2O_4$ blue pigment nanoparticles further confirmed the optimum calcination temperature, cubic and partly hexagonal crystal lattice, as well as stability of the pigment in high temperature heating until 1200 ºC.

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