SYNTHESIS AND CHARACTERIZATION OF PIGMENT $Co_xNi_{1-x}Al_2O_4$

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Abstract

Pigment $Co_xNi_{1-x}Al_2O_4$ have advanced properties for application in industrial scale such as the reduction in production cost and environmental damage, the stability in physicochemical characteristics. In this study, pigment $Co_xNi_{1-x}Al_2O_4$ (where x= 0.2, 0.5 and 0.8) was synthesized using the organic precursor method at low calcination temperature. The pigment was analyzed using XRD to determine its spinel structure as well its thermo-stability. The physicochemical properties of the pigment were determined including pH (7.11-7.63), density (3.43 – 4.19), coverage rate (47.67 – 48.9 g/m^2), and oil adsorption (42-45 g of oil / 100 g pigment). SEM result shows that the crystalline structure of the synthesized pigment is almost homogeneous and lies within the nanosize range. The characterization shows that the pigment was successfully synthesized at nanosize and has potential for applications in the industry.

Keywords: Low Calcination Temperature, Inorganic Pigment, Pigment $Co_xNi_{1-x}Al_2O_4$

Introduction

Inorganic pigments have been used in many fields in industry such as plastic, polymer, paints, ink, glasses and ceramics. Most of these pigments are transition metal-based compounds [1]. Pigments with particle size in the nano scale are more important in the market since they have higher surface area, which translates to a better surface coverage, a higher number of reflectance points and therefore improved color scattering.

Most inorganic pigments, which are mixtures of metal oxides or aluminates, are synthesized using various methods. Quite often, the synthesis would start from the blending of oxides, followed by calcination at high temperatures, usually higher than 1200^0C, then grinding to ensure proper particle size distribution of powders [2,3]. The following methods are also used to synthesize inorganic pigment including sol–gel [4], emulsion precipitation [5], hydrothermal [6], Penchini method [7,8], low combustion method [9, 10, 11]. Organic precursor and polyol methods, which are based on metal-organic precursors, quite often produce high purity, homogeneous, and nanosized aluminate particles with narrow size distribution, which eventually result to improvement in the optical and coating properties of the pigment [6,12-18]. Choosing the right synthesis method is very important since it has a significant effect to the physicochemical properties of the inorganic pigment such as color, particle size, and stability in acidic and alkaline environments.

This study tries to synthesize an inorganic $Co_xNi_{1-x}Al_2O_4$ pigment within a nano-sized range using an assisted organic precursor method at low combustion temperature. In this

method, citric acid and ethylene glycol were used to make the precursor with the metal nitrates, then the precursor was calcined to obtain spinel structure at temperature lower than 1000^{o}C. In other studies [20-22], only single metal oxides base on Al_2O_3 was synthesized by other methods at high temperature. Moreover, our target is to develop a suitable method to produce $Co_xNi_{1-x}Al_2O_4$ which have advanced properties for application in industrial scale. The $Co_xNi_{1-x}Al_2O_4$ system allows for a reduction in the production costs and also for minimizing the environmental damage, as the amount of cobalt is reduced. In other words, the physicochemical properties of complex spinel structure of $Co_xNi_{1-x}Al_2O_4$ will be more stable compared with that of the mixture of cobalt and nickel oxide.

Materials and Methods

Chemicals and Instruments

Most chemicals used in this research such as aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), and nickel (II) nitrate hexahydrate $Ni(NO_3)_2.6H_2O$ were purchased from Merck, while the other chemicals (like monohydrate citric acid and ethylene glycol) were sourced from locally commercial sources. Some main instruments that used to synthesized pigment were furnace (up to 1300^{0}C, Nabertherm GmbH, model L5/11/B170, Germany), magnetic stirrer with temperature controller (ARE., VELP. Scientificasrl, Italy), and ball grinder (Ceramic Instruments S.R.L SASSOULO, MULINI SERIE "S", Italy). The pigment powder was characterized by X-ray diffraction (XRD) using a Bruker instrument (Model. D8 ADVANCE, German, λ=1.54 Å).

The CIE L*a*b* colorimetric method, recommended by the Commission Internationale de l'Eclairage (CIE) [19] was followed. In this method, L* is lightness axis: black (0) – white (100), b* is the blue (−) – yellow (+), a* is the green (−) – red (+) axis and CIELAB differenceΔE, $\Delta E = \sqrt{(L^*)^2 + (a^*)^2 + (b^*)^2}$.

Pigment Synthesis

The $Al(NO_3)_3.9H_2O$ and monohydrate citric acid were mixed in distilled water and stirred at 80^{o}C for 1 hour. The cobalt nitrate $Co(NO_3)_2.6H_2O$ and nickel nitrate $Ni(NO_3)_2.6H_2O$ were dissolved in ethylene glycol with the mole ratio of 0.2: 0.8, 0.5:0.5, and 0.8:0.2, respectively. The solution was stirred using a magnetic stirrer at 80^{o}C for 1 hour until the solution becomes transparent.

After that, the mixture solution of two salts was stirred into solution of aluminum nitrate and citric acid. When the solution started to form a sticky gel, the temperature was gradually increased to 300^{0}C in a span of 2 hours. Acidic gas stream composed of team and NO_2 liberated from this reaction were removed by passing through a vessel containing sodium hydroxide solution. The remaining condensed gel in the vessel, containing the intermediate product, was dried at 350^{o}C for 3 hrs with heating rate of 10^{o}C per minute. This was followed by grinding using a ball grinder to obtain the fine powder of the precursor. The precursor was calcinated at a pre-set temperature for 2 hours, then further powderized using the ball grinder. *Figure 1* below shows the flow chart of the synthesis process.

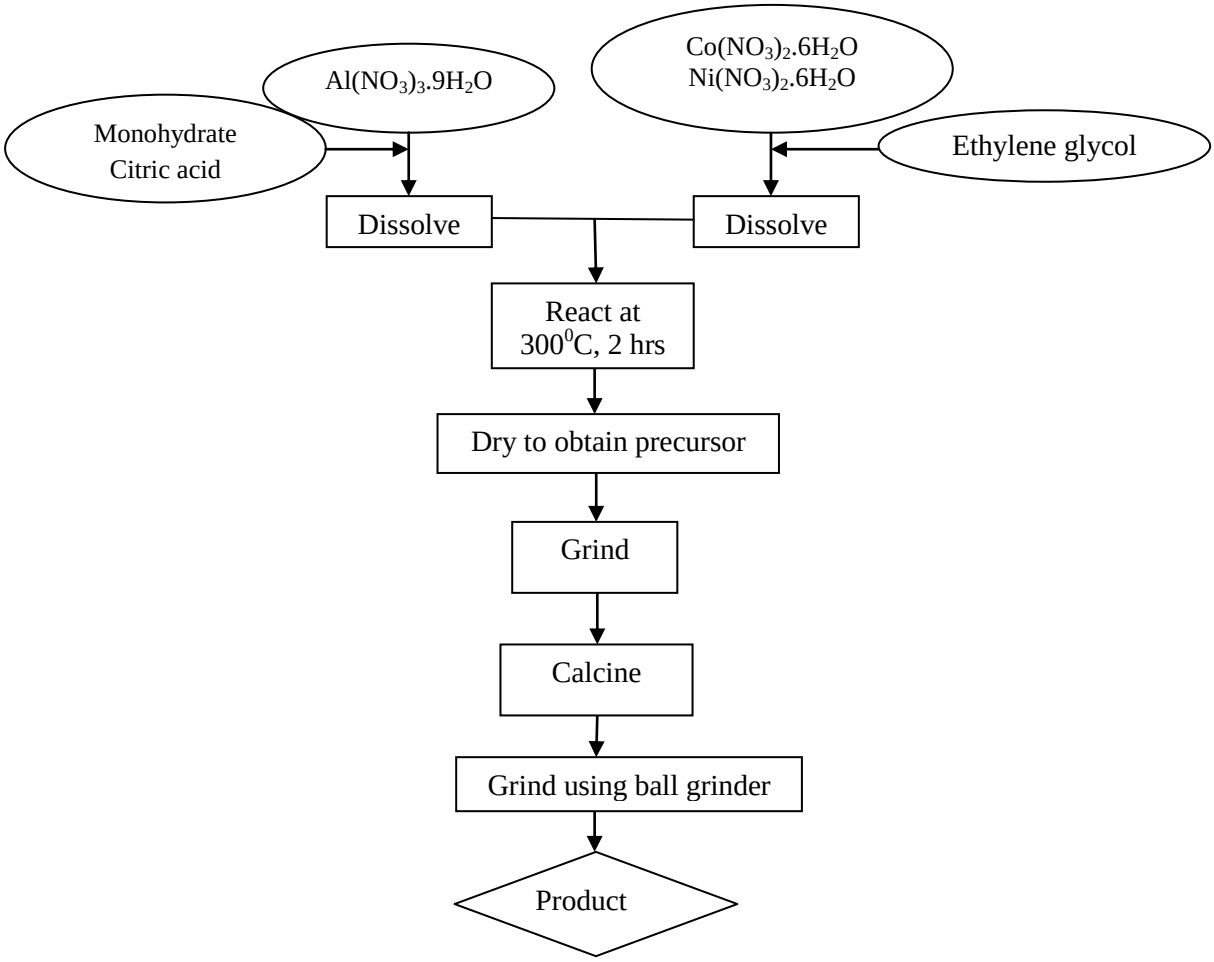

Figure 1. Process of synthesis of pigment $Co_xNi_{1-x}Al_2O_4$

Results and Discussions

XRD Results and Thermo Stability of Pigment

To evaluate to formation of $Co_xNi_{1-x}Al_2O_4$ XRD was employed to analyze the phase of sample. The XRD pattern of $CoAl_2O_4$ (JCPDS) was used as standard. Each of three samples of pigment $Co_xNi_{1-x}Al_2O_4$ with x=0.2, 0.5 and 0.8, was synthesized with calcination temperature of 900^0C. The results are showed in Figure 2.

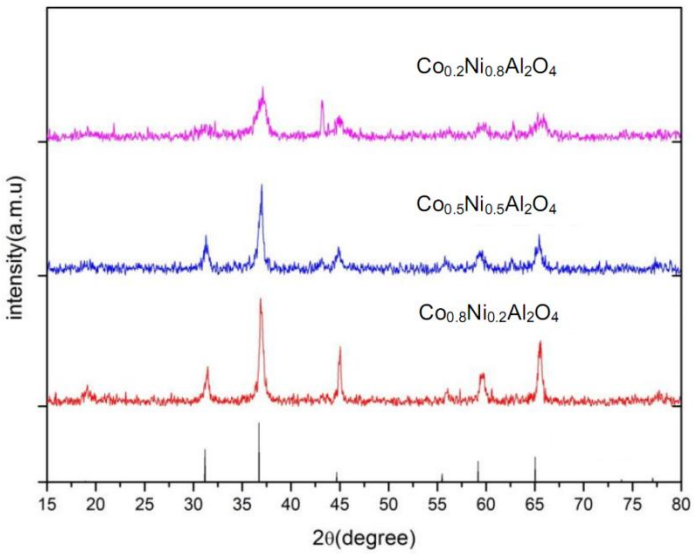

Figure 2. XRD patterns of the three samples at x = 0.2, 0.5, and 0.8

The XRD analysis confirmed the single-phase of $Co_xNi_{1-x}Al_2O_4$ spinel. The results show that when the molar ratio of Co/Ni is increased higher of intensity and clearer peaks of spinel structure were obtained, as compare to standard pattern. It can be concluded that better crystalline will be obtained with increasing of the molar ratio of Co/Ni. In additional, we can observe the left-shift of the main peaks, which can be explained by the insert of Ni^{2+} to the main structure of $CoAl_2O_4$ resulting in the change of unit cell.

In the other hand, we also investigate the effect of calcinating temperature to the stability of the spinel structure by studying XRD pattern. The XRD pattern of $Co_{0.5}Ni_{0.5}Al_2O_4$ calcinated at 900^oC (sample 1), 1200^0C (sample 2), and sample 3, which was calcinated at 900^0C, then grinded and re-calcinated at temperature of 1200^oC. All calcinations were carried out for 2 hrs. The XRD spectrums of these three samples are showed in Figure 3.

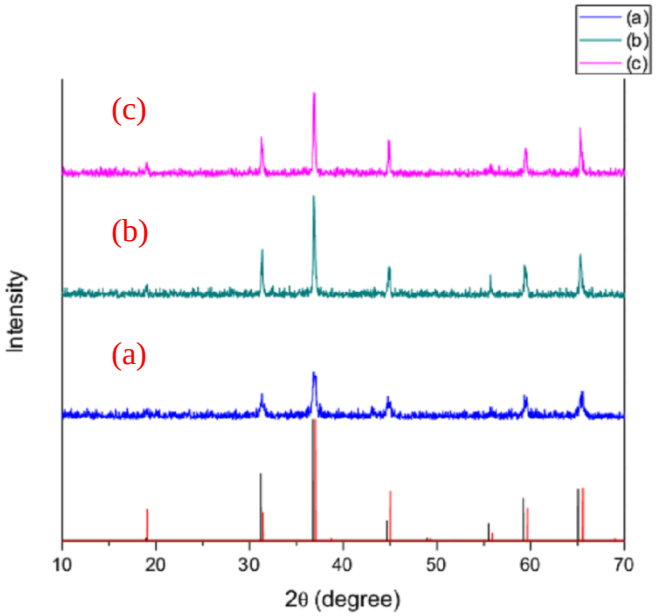

Figure 3. XRD patterns of the three samples: Calcination at 900^oC (a), 1200^oC (b) and 900^oC followed by 1200^oC (c).

As shown in Figure 3, the peak boarding spectrum of sample 1 confirmed the formation of nanoparticle of $Co_{0.5}Ni_{0.5}Al_2O_4$. Moreover, the strong peaks of three samples are identical with the standard data, suggested that high temperature (1200^{o}C) does not change the spinel structure of the crystal. However, the sample at 1200^{o}C has the highest intensity peak (sharpest peak), which can be explained by the agglomeration in calcination. The sample that was calcinated twice, at 900^{o}C and then 1200^{o}C, has fine grain size because of the grinding before second calcination. Therefore, with the above mole fraction of the chemical, calcination at 900^{o}C already form the spinel structure stable with temperature.

Physicochemical Properties

To compare the physicochemical properties of synthesized pigment and the commercial pigment $CoAl_2O_4$, three samples of $Co_{0.5}Ni_{0.5}Al_2O_4$ pigment were prepared by calcinating at 800, 900, and 1000^{o}C, respectively. Then, density, coverage rate, oil adsorption and pH of samples were obtained and compared to commercial pigment [20], the experiments were performed under the international standard ISO 105 and ISO 787. Results are showed in Table 1.

Table 1. Physicochemical Properties of Pigment

CalcinatingTemperature (^{o}C)	Density	Oil adsorption ($g_{oil}/100g_{pigment}$)	Coverage rate (g/m^2)	pH
800	3.43	45	48.91	7.63
900	4.19	44	48.66	7.11
1000	3.86	42	47.67	7.25
Commercial pigment	3.8 – 5.4	28- 37	-	7-9

From the results, the physicochemical properties of the samples are comparable to the commercial pigments and the method is applicable for production.

Color Fastness in Acid, Base

The color fastness in acid and base are tested by ISO standard 105 – part E15 - Color fastness to acid, base. In this method, solutions of H_2SO_4 10% and NaOH 10% were used to evaluate the color fastness in acid, base of pigment. Then the specimen is dried and measure the color (L*, a*, b*). The relation between fastness grade and total color difference is given in the following table.

CIELAB total color difference is calculated as $\sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$. Table 2 below presents the colorimetric results of the specimen after immersed in acid, base solution.

Table 2. Colour Fastness in Acid, Base of Pigment

Specimen	L*	a*	b*	ΔL	Δa	Δb	CIELAB difference	Fastness grade
Original pigment	47.15	-1.50	-22.44					
Specimen in acid	47.12	-1.59	-22.65	0.03	-0.09	-0.21	0.214	4-5
Specimen in base	47.16	-1.66	-22.16	0.01	-0.16	0.28	0.324	4-5

According to international standard ISO 105, the synthesized pigments are qualified the standard for the fatness of pigment in acidic and basic environment. It can be seen that after the immersion in acid, base solution, the color of the sample does not change significantly. There is only a small difference compare to the sample before treatment.

SEM Result

Sample of $Co_{0.5}Ni_{0.5}Al_2O_4$ pigment that synthesized at 900^{o}C was used to take SEM to study the morphology. The result is showed in Figure 4.

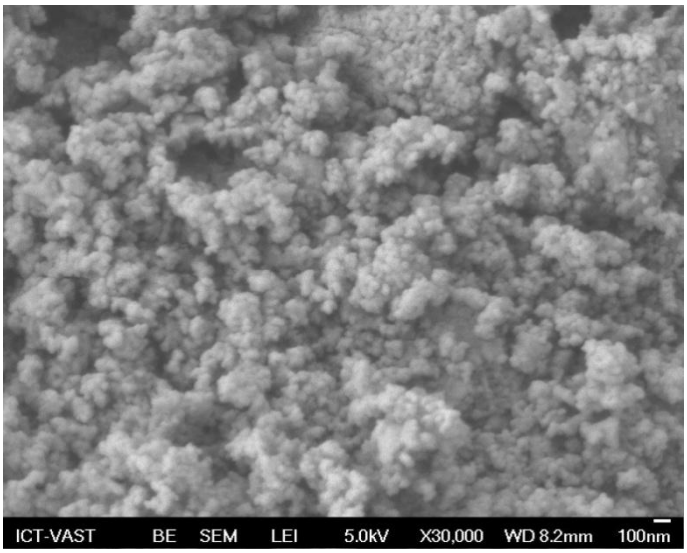

Figure 4. SEM of pigment $Co_xNi_{1-x}Al_2O_4$ with x= 0.5 and 900^{o}C of calcinated temperature

The particle can be seen clearly from the SEM image. The particle size is uniform and less than 50nm.So this method is quite applicable to produce nanoparticle pigment in industry.

Conclusions

Blue pigment$Co_xNi_{1-x}Al_2O_4$ was produced using by the low calcinated temperature synthesis assisted organic precursor method with x is 0.2, 0.5, 0.8. The single phase of spinel structure of synthesized pigment was confirmed by XRD analysis.

Synthesized pigment has physicochemical properties quite in range of commercial standards for nano size pigments.

SEM result showed that its crystalline particles are uniform with nano size, while its physic-properties confirmed that pigment was synthesized by this method has high potential for application in many fields of industry.

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