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Effect of calcination temperature on colorant behavior of cobalt-aluminate nano-particles synthesized by combustion technique

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In this investigation, the normal nano-crystalline cobalt-aluminate spinel has been successfully synthesized by the combustion technique. In order to study the colorant behavior of powders after heat treatment, quantitative and qualitative experiments such as color spectroscopy, X-ray and Raman spectroscopy were applied. Transmission electron microscopy technique was used to estimate the particle size and observe the morphology of pigments. The green powder was identified as an inverse spinel structure whereas a normal spinel corresponding to blue color was produced at higher temperatures. For obtaining powder with the high colorant efficiency, it is better to carry out calcination at 1000 °C.

1. Introduction

Recently, the spinels containing transition metals have been of great importance due to their potential in electrochemical, catalytic and pigment applications [1–4]. Spinels are generally formulated as $A^{2+}B_2{}^{3+}O_4$ in which the crystalline structure is classified as a cubic, isometric, having the anions arranged in a cubic close-packed lattice. Also, the A and B cations occupy some or all of the octahedral and tetrahedral sites in the lattice [5]. There are two ideal structures: normal spinel structure and inverse spinel structure. Normal spinel structure is usually identified by cubic close-packed oxides with one octahedral and two tetrahedral sites for each anion. The tetrahedral interstices are smaller than the octahedrals therefore, the B^{3+} ions occupy half of the octahedral holes whereas A^{2+} ions occupy 1/8th of the tetrahedral holes because of a charge factor. The lattice energy is maximized when the diameter of ions are similar [6,7]. On the other hand, an inverse spinel structure is slightly different due to the presence of transition metals in the crystal field. If the A^{2+} ions have a strong preference in the octahedral site, they displace half of the B^{3+} ions from the octahedral sites to the tetrahedral ones. If the B^{3+} ions have a low or zero octahedral site stabilization energy, OSSE, then they have no preference and adopt the tetrahedral site [8].

One of the most frequently used spinels is the cobalt-aluminate system, $Co^{II}Co^{III}{}_xAl_{2-x}O_4$, in which x value is between zero and 2. The chemical analysis of cobalt-aluminate spinels are more like Co_3O_4, Co_2AlO_4 and $CoAl_2O_4$ [3,9]. The coordination of Co^{2+} is one of the most important factors, affecting the colorant performance of cobalt pigment [10,11].

$CoAl_2O_4$ is the best known member of cobalt spinels and is widely used in ceramic, glass, paint industry and color television tubes as a contrast-enhancing luminescent pigment to produce Thenard's blue color [12]. $CoAl_2O_4$ is opaque and presents good hiding power in the form of micron-sized pigment whilst the most attractive feature of the nano-sized $CoAl_2O_4$ is transparent [8,13]. $CoAl_2O_4$ is classified into the category of normal spinels in which aluminum and cobalt are located in octahedral and tetrahedral sites, respectively [14,15].

The most common method for manufacturing cobalt spinels is through a solid-state reaction in which the oxides are mechanically ground at high calcination temperatures about 1300 °C for a long time. Though the mentioned process is relatively inexpensive, undesired products can be produced due to a lack of homogeneity, larger and uneven grains due to poor control of stoichiometry [11,16]. Recently, spinels have been synthesized using several wet-chemical techniques such as sol–gel [17–19], emulsion precipitation [20], hydrothermal crystallization [16,21] and coprecipitation [22,23]. Among the available solution chemistry routes, the combustion technique is an inexpensive method that allows the preparation of highly purified, nano-sized crystalline powders at lower calcination temperatures in a significantly shorter time [24–26].

Extensive literature is available about production and evaluation of nano-sized $CoAl_2O_4$. Salem et al. concluded that the

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microwave-hydrothermal synthesis technique is not suitable technique for production of $CoAl_2O_4$ spinel via a reaction in a microwave digestion system with a limited residence time, controlled temperature and pH, while a very pure nano-crystalline spinel $CoAl_2O_4$ is produced by combustion synthesis via a reaction of metal nitrates and glycine [27]. The authors also showed that the pH of the synthesis environment strongly affects the colorant behavior [28]. The synthesis of a pigment at acidic condition shows a flaming combustion type that is not preferred from the industrial point of view. The effect of nano-sized cobalt-aluminate powder on thermal behavior of a typical frit has been investigated by hot stage microscopy [29]. The results indicate that the thermal behavior is strongly influenced by calcination temperature of the cobalt-aluminate powder. However, the inverse variation, expansion, is observed on shrinkage between 900 and 1030 °C if the powder calcined at 800 °C is added into the frit. The experimental data showed that the addition of powders synthesized at a low fuel ratio and calcined at 800 °C leads to an expansion between 940 and 1040 °C and beyond this range, the shrinkage decreases, normally [30]. The fuel ratio is efficient in the thermal behavior of modified glaze. When a fuel ratio of 0.75 is used the expansion region disappears with the exception of the glaze containing the powder synthesized in an acidic environment.

Few publications exist about evaluation of colorant behavior of powder from green to blue as a function of calcination temperature to achieve an optimum condition in the heat treatment of cobalt spinel. The aim of present investigation is to synthesize nano-sized $CoAl_2O_4$ using a solution-based combustion method to evaluate the effect of the successive calcination step on powder properties. Laboratory investigation was carried out to determine the color changes by evaluating some properties of green and blue powders. This article reports the results of the study on colorant behavior of cobalt-aluminate spinel by analyzing the carbon content, crystallite size, amount of crystalline phase, structure and morphology of particles.

2. Materials and methods

2.1. Sample preparation

Analytical grade $Co(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, both from Sigma–Adrich Company with minimum purity of 99 wt.% as received, and glycine, NH_2CH_2COOH from Sigma Adrich Company, 99.5 wt.%, were used as starting materials. A mixed solution of metal nitrates was prepared by dissolving above salts in de-ionized water with a Co/Al molar ratio of 0.50. The appropriate amount of glycine was added to adjust the glycine/NO_3 molar ratio at 0.56. Subsequently, ammonia was added to control the level of pH around 7 [28].

In order to obtain a viscous gel, the mixed solution was heated on a hot plate kept at a steady temperature of 110 °C. The viscous precursor was then heated rapidly in a preheated furnace kept at 500 °C. During the smoldering type combustion, which lasted for more than 7 min, the material underwent foaming followed by decomposition, generating a large volume of gases. The obtained voluminous and foamy combustion ashes were easily crushed to produce the powders. The crushed powders were further calcined at 600, 800 and 1000 °C for 1 h to study their thermal behaviors. The powders calcined at 600, 800 and 1000 °C had green, dark and bright blue colors, respectively.

2.2. Sample characterization

In order to obtain a^* and b^* values by the CIE Lab method, the color measurements were conducted using UV–vis spectroscopy (Model Lambda 19, Perkin Elmer, USA) [31]. The diffuse reflectance spectra were used to calculate Kubelka–Munk absorption function, $F(R)$, as a follows:

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R} \tag{1}$$

where R is the fractional reflectance, K is the absorption coefficient and S is the scattering coefficient at each wavelength of light in the visible region, 400–700 nm, [32].

In order to better understand the colorant behavior of synthesized pigments, the residual carbon content of the powders, was determined by elemental analyses (Carlo Erba, Model EA 1110, Italy).

The specific surface area of the powders was measured by the Brunauer, Emmett and Teller, BET, technique (Gemini 2360 Apparatus, Micromeritics, Norcross, GA, USA) after degassing under vacuum at 150 °C.

X-ray diffraction measurements, XRD, were carried out on the calcined powders using a conventional Bragg-Brentano diffractometer (X'PERT PRO, Philips Research Laboratories) with Ni-filtered CuKα radiation. The patterns were recorded in the 10–80°2θ range at room temperature, with a scanning rate of 0.001 $^\circ s^{-1}$ and a step size of 0.02°. The X-ray diffraction technique was used not only to identify the phases in the powders but also to evaluate the average crystal size by using Sherrer equation [33].

The quantitative X-ray analyses of the synthesized powders were determined by the Rietveld-RIR (Reference Intensity Ratio) method that allows both the crystalline and the amorphous fractions to be determined in a polyphase mixture. In fact, the scattering contribution of any amorphous component eventually existing in the sample is a part of the background and allows its quantification using an internal standard, suitably chosen, which is added in a known amount to the investigated mixture and treated as a mixture component itself. At the end of the Rietveld process, the refined phase fractions are converted into weight fractions and rescaled to the values of the original mixture by the ratio between the refined and the known amount of added standard. Whenever, an amorphous phase exists in the system, the values of the weight fractions are overestimated to satisfy the normalization condition. The percentage of the amorphous phase in the original mixture can be calculated directly from the weight of the internal standard. For all the samples, the powder diluted with 10 wt.% corundum (NIST SRM 674a) as internal standard, was side loaded into an aluminum flat holder to minimize preferred orientation. Data were recorded in the 5–140°2θ range (step size 0.02° and 6 s counting time for each step). The phase fractions extracted by the Rietveld-RIR refinements, using GSAS and EXPGUI [34,35], were rescaled on the basis of the absolute weight of corundum originally added to the mixtures as an internal standard, and therefore internally renormalized. All the agreement indices ($R_{wp} < 2\%$ and $R_p < 1.5\%$) and the additional statistical indicators supplied by GSAS ($\chi^2 < 1.2$) are indicative of the very good quality of the refinements and testify the accuracy of the estimated weights.

The morphology of the resulted powder was examined with a scanning electron microscope (SEM, Model XL-30, FEI). Finally, transmission electron microscopy (TEM, JEM 2010, JEOL, Tokyo, Japan) equipped with EDS (EDAX PV9900, Philips) was used in characterizing the particles. For this purpose, the samples were prepared by dispersing the powders in distilled water and then placing a drop of suspension on a copper grid with a transparent polymer followed by drying in laboratory oven.

Differential thermal analyses (DTA, Model 409, Netzsch, Germany) were performed on the powders calcined at 600, 800 and 1000 °C in order to further investigate the effect of subsequent calcination temperature using ceramic pans as sample holders. Approximately, 10 mg of each powder was subjected to a thermal treatment from 20 to 1200 °C at a heating rate of 10 °C min^{-1}.