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Feature article

Flame spray pyrolysis synthesis of ceramic nanopigments $CoCr_2O_4$: The effect of key variables

Natalia Betancur-Granados*, Oscar Jaime Restrepo-Baena

Materials and Minerals Department, Universidad Nacional de Colombia, Calle 59A No 63–20, Medellín 050036, Colombia

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ABSTRACT

Spinel structure $CoCr_2O_4$ was synthesized by the non-conventional method flame spray pyrolysis (FSP) and the traditional route solid state reaction, where the optical properties were evaluated. The influences of FSP conditions as pressure of dispersion air and ceramic load of the solution over optical properties were evaluated using a 2^2 full factorial design with one replica. The final products were applied in ceramic glazes to evaluate pigmenting power. Powders were characterized by X ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis-NIR spectroscopy and Colorimetry. Results show that ceramic pigments obtained by FSP have highest percent reflectance and brightness than solid state reaction powders; nevertheless, both pigments are adequate to ceramic application. Besides, experiments showed that ceramic load of the starting solution have a strong influence over particle properties.

1. Introduction

Ceramic pigments are inorganic materials used to color glazes, inks and ceramic bodies, which are traditional produced by solid state reaction from metal oxides. These materials involve a large group of compounds with different chemical composition and crystalline structure. The pigment classification according to the American Dry Color Manufacture's Association (DCMA) has 14 classes of pigments in accordance with the crystal structure. The class XIII corresponds to spinel, which is a big group due to the large variety of cations that can occupy the bivalent and trivalent positions in the structure $A^{2+}B^{3+}{}_2X_4$ [1,2].

Structure $CoCr_2O_4$ is a green bluish color compound which crystallizes in a cubic spinel structure with space group Fd3m and face-centered lattice, where Co^{2+} cations occupy the tetrahedral position and Cr^{3+} cations are in octahedral positions [3,4]. This chromium-based pigment has high thermal stability, good resistance to atmospheric effects and chemical corrosion; hence, it is an interesting ceramic materials to several applications [5–7].

Technological and environmental concerns lead to the use of alternative methods to get pigments with broad tonalities at low price and process environmentally friendly; therefore, research on the topic are being carried out. The advantages of aerosol methods are the process efficiency and product quality, since the less production time required and purity of the phases. Also, the method allows getting multicomponent nanoparticles from a stoichiometry controlled solution [8–11].

Flame Spray Pyrolysis (FSP) is an aerosol method used to generate nanopowders with precise compositional control, where the processing conditions have an important influence over the final properties of the material. Factors as aspersion velocity, temperature and starting solution concentration are fundamental in powders features [12–14].

In this work, it is analyzed the differences in optical properties and morphologies of the ceramic pigment $CoCr_2O_4$ synthetized by the non-conventional method Flame Spray Pyrolysis (FSP) and the traditional method solid state reaction. Also, the statistical technique of factorial design was used to analyze the influence of the synthesis conditions over the particle sizes and evaluated the pigmenting properties in ceramic glazes, minimizing the testing efforts and maximizing the experimental information.

2. Material and methods

2.1. Materials

In this work, it was used cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$, 98%] from J.T Baker® Avantor Performance Materials, Inc., chromium nitrate [$Cr(NO_3)_3{\cdot}9H_2O$, 98%] from Panreac, chromium oxide [Cr_2O_3, 97%] from Nubiola company, cobalt carbonate [$CoCO_3$, 99%] from Producciones Químicas S.A and ethanol [CH_3CH_2OH] purchased from ProtoKimica.

* Corresponding author.
E-mail address: nbetancurg@unal.edu.co (N. Betancur-Granados).

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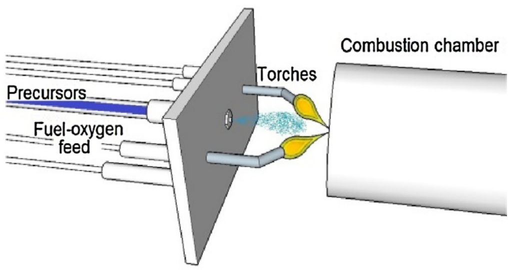

Fig. 1. Flame spray pyrolysis equipment.

Table 1
Factors of the design of experiments.

Factor	Low level	Up lever
Ceramic load	2%	5%
Pressure of dispersion air	137.89 kPa	275.79 kPa

2.2. FSP process

FSP experimental procedure consist of heading an aerosol alcoholic solution to a chamber where is ignited in two cross torches of premixed acetylene and oxygen (C_2H_2 = 4.49 L/min, O_2 = 4.96 L/min). The solutions are pumped to the aerosol generator at a velocity of ∼50 mL/min using air as dispersion gas. After that, the resulting powders are manually collected. Temperatures in the flame are up to 2000 °C, generating nanopowders in a single step. In Fig. 1, it is shown a representation of the experimental equipment.

Four samples with one replica were prepared by FSP changing the starting conditions, resulting in eight nanopowders preparations. Starting solution for 5 g of final product was prepared adding cobalt nitrite (6.41 g, 0.022 mol) and chromium nitrate (17.63 g, 0.044 mol). Ceramic load and pressure of dispersion air were evaluated during the synthesis process. The ceramic loads of the samples were 2% and 5% in ethanol, and pressures of dispersion air were 137.89 kPa and 275.79 kPa. The obtained samples were calcined at 540 °C at a speed of 10 °C/min for 4 h in an electric furnace, in order to eliminate the residual carbon resulting in the combustion flame.

2.3. Design of experiments

A 2^2 full factorial design with one replica was used to study the effect of the variables on the color coordinates and reflectance in order to obtain the maximum information with a minimum amount of experiments. The factorial design consisted of two factors with two levels each, allowing the detection of interactions between the factors. The factors investigated were the ceramic load and the pressure of dispersion air using a level of significance of 0.1 (*p*-value). The low and up values of each factor are show in Table 1. The statistical analyses of the data were performed using the Minitab® software.

2.4. Ceramic route

Solid state reaction method or ceramic route for obtain 2.5 g of $CoCr_2O_4$ was carried out using cobalt carbonate (1.32 g, 0.011 mol) and chromium oxide (1.73, 0.011 mol), which were homogenized in acetone media in an agate mortar without any flux agent. The acetone was evaporated using a muffle at 100 °C, after that, the precursors were fired at 1200 °C at a speed of 10 °C/min for 6 h in an electric furnace.

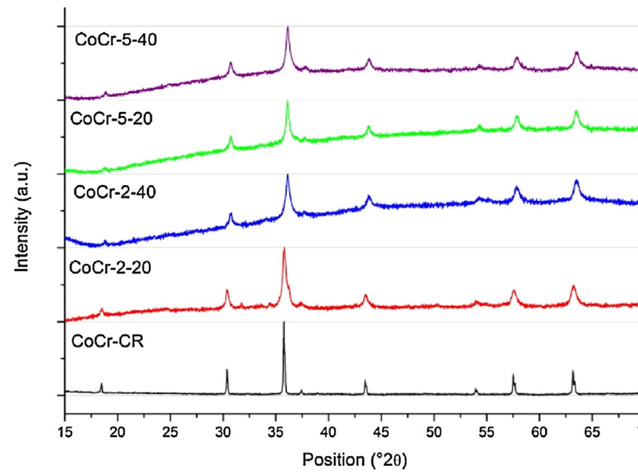

Fig. 2. XRD patterns of the samples.

2.5. Ceramic decoration

The pigments performance was evaluated by a ceramic decoration process. Transparent glazes were applied on ceramic bodies using a ratio of 5 wt.% pigment and 95 wt.% glaze. The glaze composition was frit 40%, silicon dioxide 7%, potassium feldspar 34%, dolomite 4% and kaolin 15%. During the application, an ultrasonic bath was used to improve the dispersion of the pigment into the glaze. The mixes were applied using a brush and then each piece was fired at 1250 °C for 3 h.

2.6. Characterization

X-ray diffraction (XRD) was carried out on a X'PertPro diffractometer of Panalytical using CuKα (λ = 1.54 A) radiation. Scans were continuous from 15° to 70° 2θ with a step scan of 2°2θ/min and increments of 0.05.

Morphologies were evaluated by a field emission scanning electron microscopy FE-SEM (Model JSM JEOL 6701 and Model JSM.7100F). Particle size distribution measurements were carried out in a Mastersizer Malvern Model 2000 with an obscuration between 4.15–4.90%, taking five measurements to get an average result.

UV-vis-NIR spectroscopy was carried out using a Glacier TM X spectrometer between 230 and 1050 nm. L*a*b* color parameters of samples were measured using a standard D65 illuminant at 45° degree, following the CIEL*a*b* method recommended by the CIE (Commission Internationale de I'Eclairage) were the L* means the lightness axis (Black = 0, White = 100), b* is the blue (negative) to yellow (positive) axis and a* is green (negative) to red (positive) axis.

In Table 2, it is summarized the information about the nomenclature and preparation conditions of the pigments prepared by FSP and ceramic route.

3. Results and discussion

The characterization of four samples with their replication was performed by each technique. Since the original and replication samples presented the same tendency, this section show the results obtained for the original samples in order to easily observe the differences for each synthesis conditions. However, the statistical analysis performed used the data of color coordinates and reflectance of all nanopigments preparations.

X ray diffraction patterns to the spinel $CoCr_2O_4$ obtained by FSP and solid state reaction are shown in Fig. 2. The XRD peaks in all

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