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$CoAl_2O_4$ blue nanopigments prepared by liquid-feed flame spray pyrolysis method

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ABSTRACT

$CoAl_2O_4$ pigments were synthesized through Liquid-Feed Flame Spray Pyrolysis (LF-FSP) method using metallorganic precursors of cobalt propionate and alumatrane. The precursors were dissolved in ethanol and aerosolized into a methane/oxygen flame where it was combusted to result in nanopowders at a single step. The resulting nanopowders were collected in electrostatic precipitators and analyzed by x-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), colorimetry, Field Emission Scanning Electron Microscopy (FE-SEM) and BET (Brunauer–Emmett–Teller) nitrogen adsorption. Results show formation of single phase blue nanopigments, suggesting that LF-FSP is an excellent method to produce nanoparticles with high quality in a continuous process for new industrial applications. The nanoparticles presented spherical morphology with specific surface area of 50 m^2/g, corresponding to average particle size of 27 nm. The pigments were calcined at 500, 600, 800, 1000, 1200 and 1300 °C, aiming to find the color stability whereby the colors were measured using the color space CIE L*a*b* under standardized D65 light. The brightest and bluest was obtained at calcination temperature of 1200°C and its application into a glaze was carried out at 1200 °C to evaluate the color performance and stability after a decoration process. Finally, LF-FSP produced pigments were compared with those produced by solid state reaction. Differences in the color due to the average particle size and process conditions were observed. It is possible to obtain new hues for ceramic applications by LF-FSP method.

Keywords: Liquid-feed flame spray pyrolysis, nanopigments, metallorganic precursors, colorimetry, spinel.

1. INTRODUCTION

Until now, spinel structured Thenard's blue ($CoAl_2O_4$) has been synthesized by solid state reaction and several non-conventional methods such as Pechini, sol gel, and hydrothermal methods, due to its interesting optical properties, and high thermal, chemical and photochemical stability [1,2].

In ceramic decoration, $CoAl_2O_4$ exhibits a widely used blue color, which presents several hues dependent on particle size. Commonly, the particle sizes of pigments obtained by the conventional route are between 1-10 μm. However, nanopigments are becoming important due to their high surface area, which provides higher surface coverage, brighter colors and a larger number of reflectance points, which are desirable to applications as cosmetic, ceramic, coatings, screens and also in new techniques as Ink Jet procedure [3]. Hence, the non-conventional methods to produce nanoparticles are gaining importance.

The LF-FSP process was invented and is currently used at the University of Michigan, as a facile method to produce mixed metal oxide nanoparticles [4-6]. Experimental procedure of LF-FSP consists of aerosolization of precursor solution into the chamber where it is ignited by methane/oxygen torches. After that, the resulting oxide powders are collected in electrostatic precipitators. The temperatures of the flame are about 1500-2000 °C, generating nanopowder soots in a single step, with typical average particle sizes between 15-100 nm and specific surface areas of 30-100 m^2/g which are usually unaggregated, although slightly agglomerated. The method's advantages are process efficiency, product quality, and easy control of mixed metal oxide compositions which is done by simply modifying the precursor solution [7-9]. Figure 1 represents the experimental equipment.

In this work, $CoAl_2O_4$ blue pigment nanopowders are synthesized by liquid-feed flame spray pyrolysis

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method starting from metallorganic precursors, as an alternative to the traditional ceramic method. The pigments were subject to calcination at different temperatures in order to analyze the color stability. The pigments were characterized by XRD, FT-IR, colorimetry, BET and SEM.

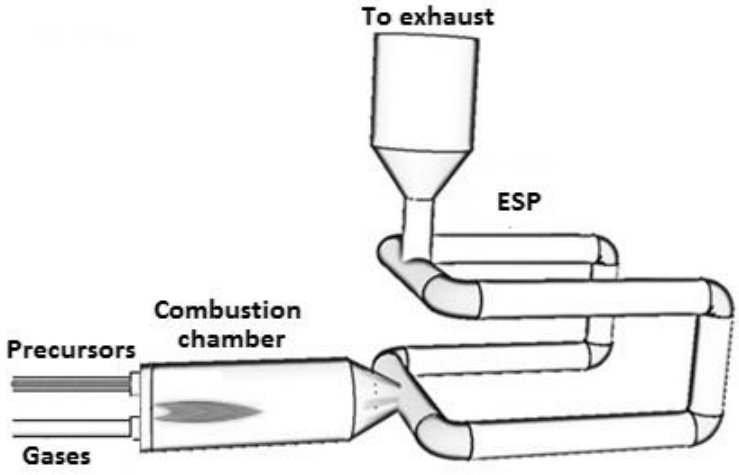

Figure 1: Schematic representation of liquid-feed flame spray pyrolysis (LF-FSP) equipment.

2. MATERIALS AND METHODS

2.1. Materials

Cobalt (II) carbonate hydrate [$CoCO_3 \cdot xH_2O$ (43-47 wt% Co)], triethanolamine [$N(CH_2CH_2OH)_3$], and isobutyric acid 99 wt% were purchased from Sigma-Aldrich. Isobutyric anhydride (97 wt%) from Acros Organics and $Al(OsBu)_3$ from Chattem chemicals. Aluminum oxide, Al_2O_3 was acquired from Sumicol S.A. and cobalt carbonate [$CoCO_3$, 99 wt%] was acquired from Producciones químicas S.A.

2.2. Powder preparation

$CoAl_2O_4$ pigments were prepared by both LF-FSP and ceramic route. Table 1 summarizes the nomenclature and preparation conditions of the samples.

Table 1: Nomenclature and preparation conditions

SAMPLE	SYNTHESIS METHOD	PRECURSORS	CALCINATION TEMPERATURE (°C)	TIME	NOMENCLATURE
$CoAl_2O_4$	LF-FSP	Metallorganic precursors	As-prepared	-	$CoAl_2O_4$
$CoAl_2O_4$	LF-FSP	Metallorganic precursors	500	6 h	Co500
$CoAl_2O_4$	LF-FSP	Metallorganic precursors	600	6 h	Co600
$CoAl_2O_4$	LF-FSP	Metallorganic precursors	800	6 h	Co800
$CoAl_2O_4$	LF-FSP	Metallorganic precursors	1000	6 h	Co1000
$CoAl_2O_4$	LF-FSP	Metallorganic precursors	1200	6 h	Co1200
$CoAl_2O_4$	LF-FSP	Metallorganic precursors	1300	6 h	Co1300
$CoAl_2O_4$	Ceramic route	Metal oxide/metal carbonate	1200	6 h	CoT

2.3. LF-FSP method

The $CoAl_2O_4$ spinel was prepared through LF-FSP using metallorganic precursors in stoichiometric amounts. The starting solution was prepared using 43,08 g (0,21 mole) of cobalt propionate ($Co(O_2CCH_2CH_3)_2$,), and

169,53 g (0,97 mole) of alumatrane [$Al(OCH_2CH_2)_3N$]. These precursors were dissolved in ethanol at 3 wt% loading and subsequently aerosolized with O_2 into a chamber where it was combusted with methane/oxygen torches. The resulting powders were collect in electrostatic precipitators. The metallorganic precursor preparations are described below.

Cobalt propionate ($Co(O_2CCH_2CH_3)_2$): 132,16 g (1,11 mole) of cobalt carbonate ($CoCO_3.H_2O$) was reacted with 444,525 g (6 mole) of propionic acid and 240 g (1,84 mole) propionic anhydride in excess. The reaction took place in a 500 mL flask equipped with a still head with N_2 sparging and constant magnetic stirring. The solution was heated to 140°C for 12 hours in order to distill off excess propionic acid, propionic anhydride, and water. Cobalt propionate precipitated on cooling and was ground and stored in a nalgene bottle.

Alumatrane [$Al(OCH_2CH_2)_3N$]: Alumatrane was synthesized starting from $Al(OsBu)_3$ and $N(CH_2CH_2OH)_3$ as described in previous work [10].

As-produced powders were subject to calcination at 500, 600, 800, 1200 and 1300 °C at a heating rate of 10 °C/min and a dwell time of 6 hours in order to analyze the pigments' color stability before the ceramic decoration.

2.4. Ceramic route

$CoAl_2O_4$ pigment was prepared through solid state reaction or ceramic route as a reference. To obtain 2,5 g of $CoAl_2O_4$, 1,70 g (0,014 mole) of cobalt carbonate and 1,46 g (0,014 mole) of aluminum oxide were used. The metal oxides were milled in acetone in an Agate mortar without any flux agent. The acetone was evaporated at 100°C. The powder was ground and fired at 1200°C for 6 hours.

2.5. Characterization

The ceramic yield of starting materials was determinate by Thermal Gravimetric Analysis (TGA) using a Q600 simultaneous TGA/DSC (Differential Scanning Calorimetry) (TA Instruments, Inc., New Castle, DE)

Diffuse Reflectance Infrared Fourier Transform Spectroscopy characterization was used to observe the chemical species present, which were recorded on a Mattson Galaxy Series FTIR 3000 infrared spectrometer (Mattson Instruments, Inc., Madison, WI).

Colorimetry was carried out using a Glacier TM X spectrometer between 400-700 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) where 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.

The phases present were determinated by XRD using a Rigaku Rotating Anode Goniometer (Rigaku Americas, the Woodlands, TX). CuKα (λ=1.54 Å) radiation with Ni filter, was used with a voltage of 40 kV and a current of 100 mA. Continuous scans were made from 10 ° to 70 °2θ with a step-size of 0.01.

Specific surface areas (SSA) were obtained by Micromeritics ASAP 2020 sorption analyzer. Samples (400 mg) were degassed at 400 °C/5 h. Each analysis was run at - 196 °C (77 K) with N_2. The SSAs were determined by the BET multipoint method using ten data points at relative pressures of 0.05 - 0.30.

Particle size and morphology were evaluated by Field Emission Scanning Electron Microscopy using a microscopy model JSM JEOL 6701.

3. RESULTS AND DISCUSSION

The objective of the work is to present an alternative method as to the traditional ceramic route to synthetize $CoAl_2O_4$ ceramic pigment with nanometric size and to analyze the color changes in the spinel structure at different calcination temperatures in order to find a stable color. Also, comparison between LF-FSP and solid state reaction method produced $CoAl_2O_4$ pigments are made in order to evaluate the influence of the production method on the pigments features.

The metallorganic precursors are easily vaporized on combustion, allowing the formation of nanometric sized particles. The precursors were characterized by TGA to determine the ceramic yield which is used in determining the amount and ratio of precursors to be dissolved in EtOH. The thermal decomposition results gave an ceramic yield of 29,46% (theoretical ceramic yield: 36,54%) for cobalt propionate and 10,2% for alumatrane (theoretical ceramic yield: 58,88%).

X ray powder diffraction of as-prepared $CoAl_2O_4$ is given in Figure 2. The figure indicates that the spinel phase was obtained with high crystallinity. However, small peaks at 36, 43 and 61° 2Ɵ belonging to

CoO impurities were also detected, indicating the precursor solution was slightly off-stoichiometry. Nevertheless the peaks are very weak, and the Rietveld refinement suggests 99.5 wt% $CoAl_2O_4$ and 0.5 wt% CoO. The reference patterns used in the analysis were PDF 01-082-2251 for $CoAl_2O_4$ and PDF 00-009-0402 for CoO. Overall, the XRD pattern showed high crystallinity and the formation of the spinel structure. Therefore the calcined powders were not analyzed by XRD.

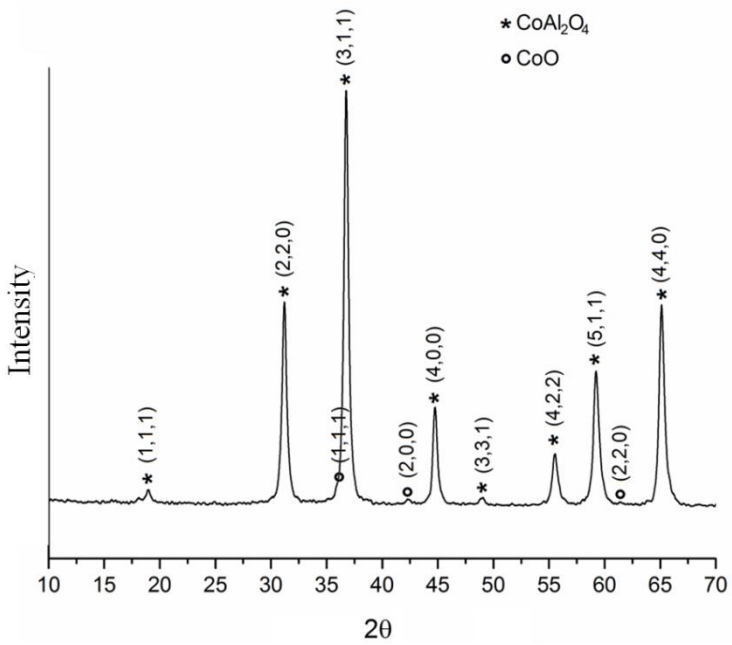

Figure 2: XRD patterns of the as-prepared $CoAl_2O_4$ spinel.

The FT-IR spectrum of as-prepared $CoAl_2O_4$ is shown in Figure 3. In agreement with work presented by Meyer *et al.* and Zhizhan Chen *et al.*, the FT-IR plot shows two principal bands overlap representing the molecular vibrations of transition metal-oxygen. In the spinel $CoAl_2O_4$, the absorption band at 480-590 cm^{-1} indicates the presence of Co-O stretching frequencies and the band at 640-760 cm^{-1} range belongs to Al-O vibrations with octahedral AlO_6, while the shoulder band at 800 cm^{-1} is associated to tetrahedral Al-O vibrations (AlO_4); also, the Al-O-Co interactions have frequencies in the range of 450-800 cm^{-1} [11-14].

$CoAl_2O_4$ is a normal spinel with slight inversion between Co^{2+} and Al^{3+}, where the aluminum ions have a preference to occupy octahedral sites while cobalt ions prefer tetrahedral sites [15]. Therefore the presence of a slight band associated to tetrahedral Al-O vibrations is attributed to slight inversion in the spinel.

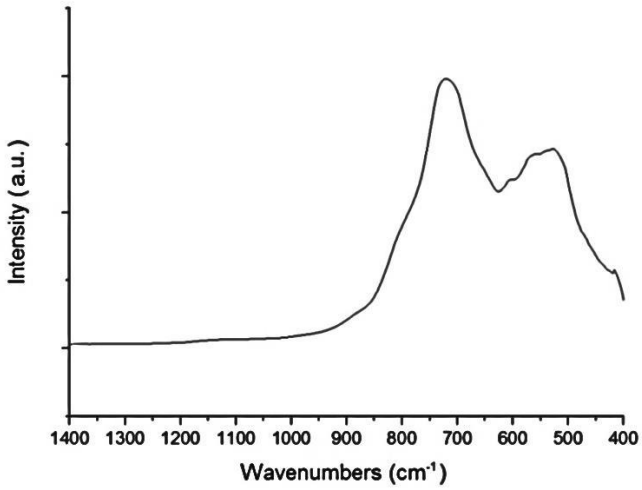

Figure 3: FT-IR spectrum of $CoAl_2O_4$ as-prepared.

The color measurements of as-prepared pigments and after calcination are present in Table 2. The darkest color was prepared by ceramic route (CoT) and the brightness by Co1200.

For LF-FSP produced powders the b* coordinate had the highest negative value of -53,48, which correspond to an intense blue color as a consequence of Co^{+2} cations. The coordinate a* had negative values close to the achromatic point in the as-prepared powders to after calcination at 600 °C. After calcination at 800 to 1300 °C the a* parameter present positive values corresponding to red color, resulting in a reddish blue color which is broadly used in the industry. The color changes presented after calcination could be due to the interchange between Al^{3+} and Co^{2+} in tetrahedral and octahedral places and also due to neck formation between the particles as a consequence of the sintering phenomenon during the calcination, which change the interaction among light and particles in comparison to the original powder. The solid state reaction produced pigment shows negative value for a*, indicating a contribution of yellow, but the predominant coordinate is still b*, where the values correspond to blue hues. The lightness was highest for as-prepared $CoAl_2O_4$ than CoT sample as expected, due to the samples change in the particle size and morphologies, because the morphology of the traditional pigments is irregular and the particles are in micrometric sizes.

The application of different calcination temperatures lead to shift in color parameters with an enhancement of blue color [2, 3, 16].

Table 2: CIEL*a*b* parameter of the $CoAl_2O_4$ pigments

SAMPLE	L*	a*	b*
CoT	40,049	-7,823	-25,836
$CoAl_2O_4$	45,330	-2,196	-33,132
Co500	41,111	-6,673	-26,613
Co600	41,088	-4,205	-34,179
Co800	46,126	1,437	-43,876
Co1000	46,141	6,449	-49,883
Co1200	47,150	11,013	-53,480
Co1300	50,321	5,971	-48,789

The pigments CoT, as-prepared $CoAl_2O_40$ and Co1200 were tested using transparent glazes and ceramic bodies. The applications were carried out using a ratio of 5 wt% pigment and 95 wt% glaze, tested at 1200 °C during 3 hours. The pigments of $CoAl_2O_4$ and Co1200 did not present large deviations from the colorimetric parameters of the pigments, and the dispersion into the glaze was almost homogeneous with the presence of little clear spots. This problem was resolved when the powders were dispersed into the glaze with an ultrasonic bath. On the other hand, the traditional pigment CoT presented a good dispersion into the glaze although the piece showed dark and few clear points in the decor area, and even green spots, which is a consequence of impurities in the pigments due to the limitations of the traditional method for having incomplete reaction between the oxides precursors.

The decoration process showed high performance of the spinel in glaze, where the ceramic piece's color did not present large deviations in the blue hue, comparing the initial color parameters to the final piece. These results are in agreement with work presented by Llusar *et al.* and Cavalcante *et al.* who investigated several blue pigment resources, in which they conclude spinel is the most stable compound into the glazes.

Figure 3 shows micrographs of as-prepared $CoAl_2O_4$ with a magnification of 35000X and 300000X, where it is possible to observe particles with spherical morphologies. The image (a) at low magnifications suggests homogenous particle size distributions, without the presence of large spheres. Therefore, it is possible to conclude that LF-FSP is an adequate method to produce nanoparticles with a narrow particle size distribution. Also, the SEMs show particles in the 10-30 nm range, with the presence of some agglomerates, due to the small particle size.

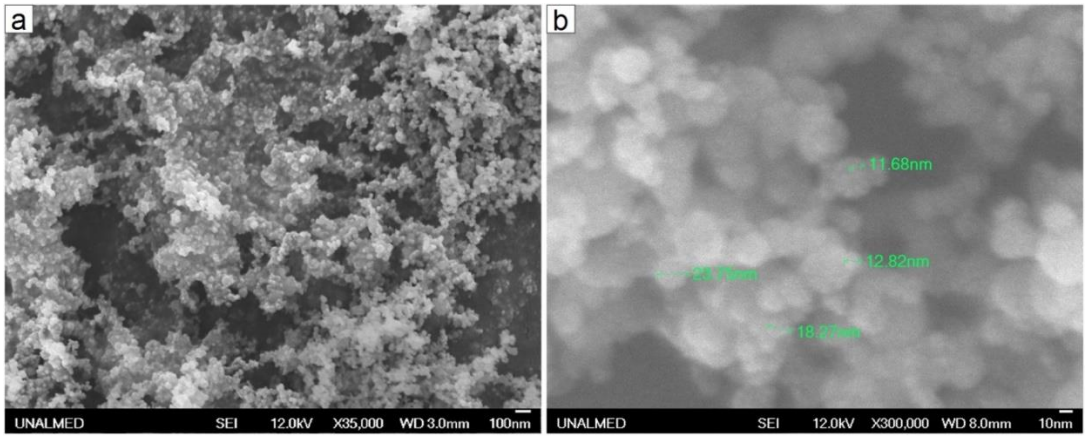

Figure 3: SEM images of as-prepared $CoAl_2O_4$.

Figure 4 shows micrographs of Co1200 and the traditional pigment CoT. Image (a) shows aggregates through neck formation due to the sintering process at high calcination temperatures, which have an effect on the pigment color, as mentioned above. On the other hand, image (b) shows large particles with irregular shape. These irregular shape with the presence of angles affect the interaction between the light and particles, such that the traditional pigments have dark colors due to the loss of reflectance points. This concludes that new hue pigments are obtained by the use of LF-FSP processes, that allow obtain spherical shapes at nano scales.

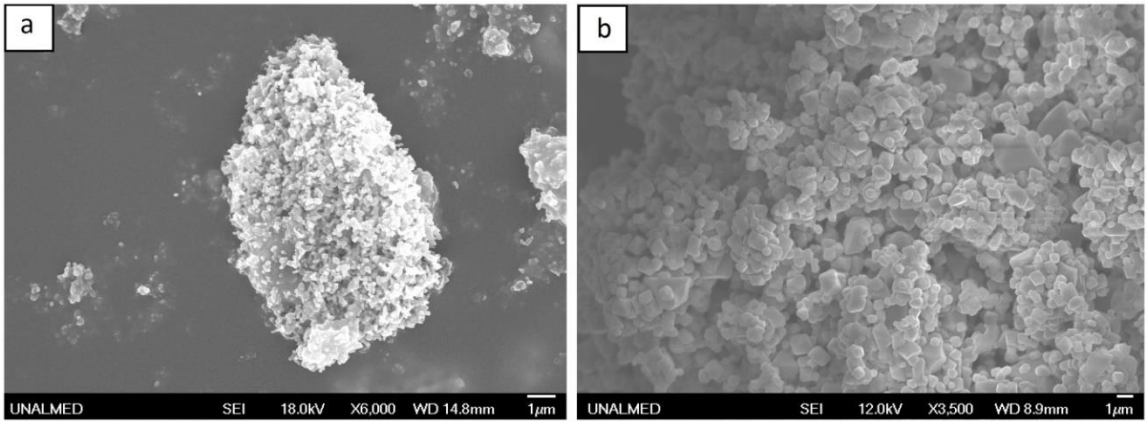

Figure 4: SEM images of Co1200 and CoT samples.

BET analysis was carried out for as-prepared $CoAl_2O_4$ sample, in order to obtain an average particle size. The average particle size was determined by Equation 1, where the ρ is the theoretical density of powder (4,416g/cm^3 [1]) and SSA is specific surface area. The average particle size for as-prepared $CoAl_2O_4$ was 27 nm and the specific surface area was 50 m^2/g, which is quite consistent with the range presented by SEM analysis.

$$d = \frac{6}{\rho \times SSA} \tag{1}$$

The small particle size obtained through LF-FSP, provides a larger number of reflectance points, by which the pigment color presents a remarkable brightness in comparison to the pigment made by the traditional method. Also, after the application of the pigments into the glaze, the nanopigments does not present dispersion problems; instead, the color is uniform in the ceramic piece.

4. CONCLUSIONS

$CoAl_2O_4$ nanopigments were produced by liquid-feed flame spray pyrolysis method, using metallorganic precursors as starting materials. Resulting metal oxide nanopowders were evaluated in terms to phase, color, size and morphology. The results suggest that LF-FPS is an excellent alternative method to produce nano-ceramic pigments, as it is a facile and continuous method which could be used for high quality industrial applications, avoiding the problems and technological limitations of different synthesis methods.

XRD of the as-produced powder show the spinel structure with high crystallinity. However, the stoichiometry of the starting solution could be improved by adjusting the ceramic yield calculation of the metallorganic precursors, to obtain a phase pure products, since the diffraction pattern shows small peaks belonging to CoO.

The pigment produced by LF-FSP method showed spherical morphology and particle sizes between 10-30 nm, which indicates that LF-FSP is an adequate method to produce nano ceramic powders, which has a market potential for new industrial applications. The small particle size provides a larger number of reflectance points and as a consequence the brightness of the pigments is remarkable in comparison to that produced by the traditional method, given the opportunity to develop new interest pigments hues.

All pigments showed blue color, which presented increasing of the blue hue after a calcination process at different temperatures. The color changes presented after calcination could be due to the interchange between Al^{3+} and Co^{2+} in tetrahedral and octahedral places or is attributable to changes in the interaction between the light and particles due to the formation of large particles from partial fusion, aggregates. The bluish color was obtained after calcination at 1200 °C, where the color was preserved after the decoration process. On the other hand, the pigment obtained by the ceramic route gave a dark blue color in comparison to that made by LF-FSP. This can be attributed to the differences of the particle sizes and morphologies.

The surface coverage was satisfactory for the pigments evaluated. CoT, as-prepared $CoAl_2O_4$ and Co1200, showed that the nanoparticles are adequate for use as a pigments and does not present problems when dispersed into the glaze using an ultrasonic bath. The traditional pigment was applied into the glaze without the use of an ultrasonic bath, because the particles have a good dispersion into the glaze; however, the color was not uniform and some bubbles were present on the surface, due to low chemical stability with the glaze.

$CoAl_2O_4$ nanopigments synthesized by LF-FSP showed a nice and intense blue color. After the decoration process, the pigments exhibited high thermal stability and chemical stability into the glaze, without dispersion problems due to the particle sizes.

5. ACKNOWLEDGMENTS

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