Synthesis and characterization of spinel pigment CaFe$_2$O$_4$ obtained by the polymeric precursor method

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Abstract

The CaFe$_2$O$_4$ composition was studied, in order to analyze its physical and chemical behavior, verifying its stability under industrial conditions, when applied as pigments. The characterization was accomplished using thermal analysis, X-ray diffraction (XRD), nitrogen adsorption, scanning electronic microscopy (SEM) and diffuse reflectance. It observed successions exothermic reactions, adequate in events of thermal decomposition of the organic material, reach your stability in 700°C. The material became completely crystalline at 800°C. Between 700 and 1100°C, the color was stabilized, showing an absorption band in the region of 650 to 750 nm, characteristic of the red color.

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1. Introduction

Ceramic materials with spinel structure have been studied for decades, due to its wide applicability as ceramic pigments, magnetic devices, semiconductors, refractories and others. In order to obtain powder-ceramics with high quality, there are important factors—synthesis method determines not only stoichiometric and morphologic control but also physical and chemical properties.

Color is an optical property that takes to countless applications. For ceramic tiles, pigments give a stable coloration to a glaze, through a simple mechanical dispersion in the middle to be colored. The final color of each pigment is due to the addition of a chromophore ion (usually transition metals) into an inert matrix, or this ion may be part of the own matrix, as in the case of ferrites [1]. In this work, a ferrite pigment was synthesized with applicability as pigments, besides magnetic devices, semiconductors, among others.

After synthesis, the Fe$_2$O$_3$/CaO material (consists of calcium ferrite) exhibits a red brick coloration having the spinel structure [2], which usually leads to a high thermal stability. The spinel structure RO.R$_2$O$_3$, is formed by association of a trivalent oxide (acid character) with a bivalent oxide (alkaline character). Such a ceramic pigment is able to develop stable color in relation to temperature and chemical agents, resisting to the aggressive attacks, specially by glaze material during its melting, in other words, the pigment should be insoluble in glazes (substrate) [3].

The chemical synthesis was based on polymeric precursors method, which was developed by Pechini. This method consists of formation of a polymeric net starting from a polyhydroxy alcohol and an alpha-hydroxycarboxylic acid, with metallic cations homogeneously distributed throughout the matrix [4,5]. After synthesis, CaFe$_2$O$_4$ physical and chemical behavior was studied, verifying its stability as pigment under industrial conditions.

2. Experimental procedure

2.1. Resin preparation using the polymeric precursors method (PECHINI)

The polymeric precursor solution was prepared using the Pechini method, which has been used to synthesize poly-
cationic powders. The process is based on metallic citrate polymerization using ethylene glycol. A hydrocarboxylic acid, such as citric acid, is used in an aqueous solution in order to chelate cations. The addition of a polyalcohol, such as ethylene glycol, leads to the formation of an organic ester. Polymerization, promoted by heating, results in a homogeneous resin in which metal ions are uniformly distributed throughout the organic matrix.

The citric acid (Vetec) was added into water with constant agitation, at 60–70 °C. Then, the polymeric net former was added—iron III nitrate (Vetec). After its dissolution, the polymeric net modifier was placed—calcium acetate (Reagen). After the mixture of the salts and their total dissolution, ethylene glycol (Synth) was added into the solution, with a proportion (in mass) of citric acid/ethylene glycol of 60:40 [4,5]. The temperature was increased up to 90–110 °C, in order to promote the esterification. At the end of the reaction, a polymeric gel (resin) was obtained.

2.2. Powder preparation

The resin was heat treated at 300 °C for 1 h (primary calcination), leading to the partial decomposition of the polymeric gel forming an expanded resin, constituted of a semi-carbonized material, of black color, with aspect similar to a foam.

The resultant material of the primary calcination was removed from the becker, deagglomerated in porcelain mortar, going by 100-mesh sieve. The thermal decomposition of the organic precursor, as well as the crystalline phase formation, was evaluated by differential thermal analysis (Shimadzu, DTA-50) and thermogravimetry (Shimadzu TGA-50), in order to analyze the mass loss and possible energy transitions.

After primary calcination, the powders, rich in organic residues, were calcined on aluminum plates at temperatures varying from 500 to 1100 °C for 1 h, with a heating rate of 10 °C min⁻¹ in ambient atmosphere. The pigment powder was gone by 200-mesh sieve.

The crystalline phases and cell volume measurements were carried out by X-ray diffraction (XRD), using SiO₂ as an external standard. The measurements were obtained with a Siemens D-5000 Diffractometer with CuKα radiation (λ = 1.5406 Å and θ = 20° to 70°), at room temperature.

The surface area measurements of the pigments were accomplished in a Micromeritics, ASAP 2000 equipment, using N₂ as the adsorption/desorption gas. Scanning electronic microscopy (SEM) was used to characterize the fired pigments by employing a ZEISS DSM, 940 A.

L*a*b* color parameters and diffuse reflectance of fired pigments were measured by the Gretac Macbeth Color-eye spectrophotometer 2180/2180 UV, from 300–800 nm range, using the D65 illumination. The CIE-L*a*b* colorimetric method was used, as recommended by the Commission Internationale de l’Eclairage (CIE), [6]. In this method, L* is the lightness axis [black
3. Results and discussion

Fig. 1 shows the thermal analysis of the expanded resin. Several exothermic peaks were observed during thermal decomposition of the organic material, due to different chain sizes. The DTA results indicate two steps: the first one between 108 and 200 °C, due to water and adsorbed gases elimination; and the second one between 200 and 650 °C, due to polymeric chain decomposition, leading to CO₂ elimination, besides the decomposition of carboxylics linked to metals, with oxide formation from 650 °C.

Fig. 2 presents the X-ray diffraction results, after calcination from 500 to 1100 °C. The samples calcined at 500 and 600 °C are amorphous. Above this temperature, the first nuclei of the desired phase are formed, becoming totally crystalline at 800 °C. This displays the effectiveness of the synthesis method, leading to the desired phase at low temperatures. The obtained phase has orthorhombic structure, whose space group is Pnam (62), being identified by the index card JCPDS 32-0168. The experimental lattice parameters are: \( a = 9.23 \) (7), \( b = 10.68 \) (2) and \( c = 3.01 \) (4).

Crystallite size (Fig. 3) increased about 30% between 700 and 800 °C, probably due to amorphous material crystallization. It almost does not increase ( \( \sim 40 \) nm) up to 1000 °C, reaching the value of 57 nm at 1100 °C. This change in crystallite size evolution indicates a change in growth mechanism.
The surface area results, calculated by BET method [7], are presented in Fig. 4. The average diameter, \( d_{\text{BET}} \), was calculated by Eq. (1).

\[
d_{\text{BET}} = \frac{6}{A_s \rho}, \tag{1}
\]

where \( A_s \) is the specific surface area (m\(^2\)/g) and \( \rho \) is the theoretical density of the phase (\( \rho_{\text{CaFe}_2\text{O}_4} = 4.805 \) g/cm\(^3\)) [8].

The specific surface area of the \( \text{CaFe}_2\text{O}_4 \), calcined at 1000 °C, is 2.24 m\(^2\)/g, while the equivalent spherical diameter is 556 nm. An increase of the particle diameter was verified as a function of temperature, according to Fig. 4. This increase is probably due to the presence of nanometric particles and therefore more reactives, favoring coalescence at smaller temperatures, as presented in Fig. 5.

Fig. 6 shows the curves of diffuse reflectance, which are in agreement to XRD results. After calcination at 500 and 700 °C, samples present low crystallinity, without the desired color. Above 800 °C, the material is crystalline and presents a characteristic band around 650 nm, with a dark red color. Table 1 presents the colorimetric coordinates (\( L^* \), \( a^* \), \( b^* \)), the tonality variation (\( \Delta E \)) and the color number in the Pantone system.

The decrease in the \( L^* \) parameter with the temperature increase can be associated with the abrupt increase of the particle diameter from 200 to 1100 nm, which leads to the decrease of the overall reflecting surface of the power.

Therefore, the samples obtained after calcination at 900 and 1000 °C can be considered as the ones of highest technological potential. However, application tests must be done in order to evaluate pigment stability during glazing.

4. Conclusion

The Pechini method leads to a material with high degree of homogeneity at molecular level, as well as finer powders presenting thus higher surface areas. The color of the pigment depends on the oxidation state of the chromophore ion. Monophasic powders are obtained at temperatures as low as 800 °C and a completely defined color is observed at 900 °C. Between 800 and 1100 °C, the color is stabilized, showing an absorption band in the region of 650 to 750 nm, characteristic of the red color. Therefore, the samples obtained from heat treatments at 900 and 1000 °C can, at first, be considered as the ones of highest technological potential.

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