Synthesis of Nanoscale CoAl$_2$O$_4$ Pigments

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Abstract

Inorganic pigments, which are used in plastics, polymers, paints, glasses, and ceramics, are traditionally based on transition metal compounds, many of which have spinel structures. This article focuses on CoAl$_2$O$_4$, one of the more intensely colored blue pigments. Some recent studies on the synthesis and coloration of CoAl$_2$O$_4$ are reviewed, starting with a brief overview of its structure, then two synthesis methods for nanosized CoAl$_2$O$_4$, and finally the effectiveness and application of nano- CoAl$_2$O$_4$ in ceramic glazes are discussed.

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1. Introduction

Inorganic pigments, which are used in plastics, polymers, paints, glasses, and ceramics, are traditionally based on transition metal compounds.¹ Some important inorganic pigments in industry are illustrated in Figure 1: CoAl₂O₄ (blue), Cr₂O₃ (dark green), ZnCo₂O₄ (green), Ti₀.₈₅Ni₀.₀₅Nb₀.₁₀O₂ (yellow), α-Fe₂O₃ (red) and Cu(Cr,Fe)O₄ (black).² The majority of ceramic pigments have spinel structures.³

Pigments used in the ceramics industry need to be thermally stable at glaze firing temperatures, have minimal reaction with the molten glaze, and also have good color performance.¹,⁴ These pigments have been traditionally microsized, but recently, synthesis of pigments on the nanosize scale have become a field of interest because the high surface area of nanoparticles ensure better coverage of the pigment and more homogeneous mixing of the pigment into paints and glazes.⁵ Outside of the ceramics industry, nanosized pigments also have use for special applications such as the coloring of plastics and transparent thin films.²

In particular, all but one (vanadium-zircon blue) of the known blue ceramic pigments contain cobalt ion as their source of blue color, some examples of which are: Co₂SiO₄ olivine, (Co,Zn)₂SiO₄ willemite, and the spinels CoAl₂O₄, Co₂SnO₄, (Co,Zn)Al₂O₄, and Co(Al,Cr)₂O₄.⁴

This article will focus on CoAl₂O₄ (also known as Thenard's blue³ or cobalt blue). It is one of the more intensely colored blue pigments,⁴ most notably used in oil painting, glassblowing, as well as ceramic decoration. Some recent studies on the synthesis and coloration of CoAl₂O₄ will be reviewed, starting with a brief overview of its structure, then proceeds to discuss two synthesis methods for nanosized CoAl₂O₄. Finally, the effectiveness and application of nano- CoAl₂O₄ in ceramic glazes will be discussed.

2. Structure

The spinels are a class of mixed metal oxides of general formula M'M₂O₄, of which CoAl₂O₄ is one. They consist of a cubic close-packed array of oxide ions with M²⁺ ions in 1/8 of the tetrahedral sites
and M$^{3+}$ ions in 1/2 of the octahedral sites. This is called the spinel structure, and in the case of cobalt blue, Co$^{2+}$ ions occupy the tetrahedral sites. As noted above, many inorganic pigments used in industry are spinels.

The brilliant color of CoAl$_2$O$_4$ originates from a d–d transition or host-lattice absorption, which can be explained by crystal field theory. As a result, the positions of the ground and excited state of the cobalt ion are influenced relative to each other, and the color of the compound is affected. The color of the pigment is thus related to its crystallinity. Tetrahedral coordination of the cobalt ions is preferred to octahedral coordination for most effective color performance.

3. Synthesis and Characterization

3.1 Traditional methods

The first and traditional method for the synthesis of CoAl$_2$O$_4$ is the ceramic method. An oxygen-containing cobalt precursor, such as cobalt oxalate, is mixed with alumina, and ground in a ball mill. The mixture is then calcinated to form the compound, which becomes thermally stable above 650°C. The high temperatures required of the ceramic method in order to produce high crystallinity of the material comes at the expense of particle size, a significant barrier to the formation of nanoscale particles.

Industrially, CoAl$_2$O$_4$ is prepared by precipitation from aqueous solution, which yields hydroxides. The hydroxides are then heat-treated at temperatures up to 1000°C to obtain the water-free oxide. During heating, condensation and growth of particles occur, and sometimes hard agglomerates can be formed.

Techniques that have been recently attempted to synthesize ceramic materials at low temperatures and small size include sol-gel (from which powders tend to agglomerate or form suspensions with low solids content), emulsion precipitation, hydrothermal method, coprecipitation, alkoxide hydrolysis, and polymerized complex methods. Two methods which have been successfully used to synthesize nanoscale CoAl$_2$O$_4$ are described below.
3.2 Pechini method

The Pechini (or polymeric precursor) method consists of preparing inorganic material via a polymeric resin intermediate. This resin is made by mixing one of the metal precursors with citric acid and a polyhydroxy alcohol, then adding a basic metal precursor. The mixture is then heated to form a solid resin. Calcining the resin removes the organic components, leaving a mixture of fine, uniform particles.\textsuperscript{10}

Kakihana has adapted this method for the preparation of nanosized CoAl$_2$O$_4$, because it is simple and the metal ions are immobilized in the resin network to prevent segregation during the processing, so that purity is facilitated. Co(NO$_3$)$_2$·6H$_2$O was dissolved in ethylene glycol, citric acid was added, and after complete dissolution at 50°C, Al(NO$_3$)$_3$·9H$_2$O was added. The solution was stirred at 80°C until it was transparent, and then was further heated at 130°C and then at 250°C. The solution polymerized until it solidified into an amorphous black solid, which was ground lightly into a powder. This powdered ‘precursor’, when calcinated, crystallizes into cubic CoAl$_2$O$_4$, with no traces of impurities seen in X-ray powder diffraction (XRD) patterns (Figure 2). Crystallinity was found to increase with calcinating temperature between 350°C and 1000°C.\textsuperscript{9}

Kakihana investigated the evolution of the CoAl$_2$O$_4$ microstructure during crystallization using high-resolution transmission electron microscopy (HRTEM). The transformation from resin to crystalline CoAl$_2$O$_4$ was speculated to take place through four steps:

1. Transformation of the resin to amorphous CoAl$_2$O$_4$
2. Nucleation of CoAl$_2$O$_4$ crystals in the amorphous matrix
3. Crystal growth from the nuclei
4. Grain growth by solid-state reaction.\textsuperscript{9}
3.3 Modified polyol method

The polyol method is used to make fine single elemental metal particles. Precursors such as oxides, nitrates, and acetates are dissolved or suspended in a polyol: usually ethylene glycol, diethylene glycol, or 1,2-propanediol. The polyol acts as both a solvent and reducing agent. The mixture is refluxed, and the precursors are reduced, causing the metal particles to precipitate. Increased reaction temperature or addition of foreign nuclei can reduce the size of the synthesized particles.11

This relatively simple method is effective for synthesizing nanoparticles because the alcohol acts as a stabilizer that limits particle growth and agglomeration. High temperatures may then be applied to the system to yield highly crystalline oxides7 in suspensions with up to 20 wt.% solids content.2

Feldmann has used this method to synthesize a variety of nanoscale materials, including color pigments. To prepare CoAl2O4 nanoparticles, AlOH(CH3COO)2 and Co(CH3COO)2·4H2O were combined with diethylene glycol and stirred with the addition of a small amount of water. The mixture was then refluxed at 140°C and then at 180°C, then cooled and diluted with ethanol. This suspension is stable for a few weeks and can be used as-is for spin coating, dip coating, or spraying, or can be separated into a powder by centrifugation. The nanoparticles are 50-200 nm in size, are purple, and require an additional a brief period of heating (15 minutes at 600°C) to complete the crystallization and obtain the characteristic blue color.

SEM micrographs (Figure 3) show that particle aggregates are present, but agglomeration is not. This is because the diethylene glycol covers the surface of the particles immediately after their formation, stabilizing the particles. Also, at the reaction temperatures, most of the metal hydroxyl groups of the particles condense within one oxide particle instead of condensing between particles.8

Figure 4 illustrates the results from laser diffraction tests to determine the particle size distribution of the CoAl2O4 particles in the diethylene glycol suspension. Once water is added to the mixture, diethylene glycol is gradually removed from the surface of the particles, and the particles start to agglomerate.8
4. Application in Ceramic Glazes

Both micro- and nanosized CoAl₂O₄ pigment appear to behave as a dye in ceramic glazes, fully dissolving into the glaze and leaving no trace of crystalline CoAl₂O₄ or cobalt phases. Tetrahedrally coordinated Co²⁺ is found dissolved in the glaze, giving rise to color. The dissolution of Co²⁺ into the glassy coating of glaze begins to occur at a calcinating temperature of 900°C.⁵

Colorimetric evaluation has shown that CoAl₂O₄ exhibits increasing intensity of blueness with increasing calcinating temperature between 1000 and 1200°C.³ This is attributed to a varying ratio between Co²⁺ in tetrahedral and octahedral coordinations and structural rearrangement of the cobalt ions in the glass. Up until 1000°C, color development is incomplete because cobalt has not become fully incorporated into the glaze.⁵

Although CoAl₂O₄ fully dissolves in glaze, it reacts minimally with the glaze even at high temperatures, as compared to olivine and willemite-based blue pigments, retaining color intensity.³,⁴ CoAl₂O₄ also has best color yield compared to olivine and willemite-based pigments, making it suitable for applications in bulk coloration of fast-fired, high-temperature-processed (porcelainized) ceramics.⁴

5. Conclusion

The studies discussed above show that a variety of novel methods for synthesizing CoAl₂O₄ (and other) pigments on the nanoscale have been developed in recent years, but that the actual mechanisms for the observed changes in coloration effects under different heating conditions have yet to be fully understood.

Considering the potential range of uses for nanopigments, the study of color effectiveness of nanoscale materials as pigments is still a developing field of study. As well, although CoAl₂O₄ is the traditional blue pigment, cobalt is toxic and expensive, so that the development of more cost-effective and safe alternatives is also of interest.
6. References


Figure 1. Photo of various color pigments in suspension and as powders.\textsuperscript{7}

Figure 2. XRD patterns of powders obtained by heating the resin ‘precursor’ in air for 2h at (a) 350°C, (b) 400°C, (c) 500°C, (d) 600°C, (e) 700°C, (f) 800°C, (g) 900°C, and (h) 1000°C.\textsuperscript{9}
Figure 3. SEM micrograph of CoAl2O4 powder (after 15 min at 600°C).\textsuperscript{8}

Figure 4. Measurement of particle size of CoAl2O4 in diethylene glycol suspension (4.0 wt.\%, solid) as well as 10 min (dotted) and 60 min (dashed) after mixing with water (DEG : H\textsubscript{2}O = 1 : 10).\textsuperscript{8}