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Controlled synthesis of blue spherical $CoAl_2O_4$ pigment powder in Pickering emulsion assisted with a hydrothermal process

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ABSTRACT

A spherical blue $CoAl_2O_4$ pigment powder commonly used for coloring ceramic products has successfully been synthesized by co-precipitation of Co^{2+} and Al^{3+} ions in Pickering emulsion assisted with a hydrothermal process, and the formation mechanism of the as-prepared powder has briefly been discussed. The effects of pH condition on the crystalline phase and color tone of the pigment powder were investigated at 280 °C by varying the pH value of the reaction system. Then, under an optimized pH condition to produce blue, the pigment powder was synthesized still hydrothermally at different temperatures (210, 240, 270 and 300 °C) to assess the effect of hydrothermal reaction temperature on the pigment particle morphology. The resulting pigment powders were characterized by field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), CIELAB colorimetric analysis (CIE-L*a*b*), laser particle size analysis (LPS), and N_2-adsorption measurement (BET). FE-SEM and TEM observations indicated that the pigment powders of spherical shape obviously were constructed by a core–shell double-layer structure, the radii of which all were ~150 nm or so with a shell of ~25 nm in thickness. XRD results demonstrated that the pigment powders that were obtained from the aforementioned method under a wide range of pH values invariably contained basically crystalline $CoAl_2O_4$ of high purity. CIE-L*a*b* data suggested that the pigment powders at 280 °C and pH ≤ 11.2 appeared different chromas of bluish colors compared with that displaying black which was obtained at pH = 12.3. LPS and BET results showed that the $CoAl_2O_4$ pigment powder prepared under the urea concentration of 3.6040 g for 24 h at the hydrothermal temperatures of 240 °C exhibited a narrow particle size distribution, the specific surface area of which was evaluated to be ~56.4 m^2/g.

1. Introduction

Spinel-structure pigments have widely been used in ceramic and plastic industries to cover a wide range of colors in high-temperature ceramic applications due to their high thermal stability of up to 1400 °C and high resistance to molten glass [1–4]. The primary characteristic of normal spinels is their presence of two types of metallic cations of A^{2+} and B^{3+} in tetrahedral and octahedral positions, respectively, which is distinguished from inverse spinels [5,6]. The composite oxides of spinel structures (AB_2O_4) are important ceramic materials that have widely been used in different fields such as heat-resistant pigments, magnetic materials and wave absorption materials [1–6].

$CoAl_2O_4$ belongs to a class of chemically and thermally stable solids, whose crystal structure falls into the category of normal spinels. Its crystal lattice comprises O atoms of cubic close packing surrounded by tetrahedrally (Td) coordinated Co^{2+} cations (A) and by octahedrally (Oh) coordinated Al^{3+} cations (B) [7]. The coloring performance of Co-containing pigments strongly depends on the molar fraction of the Co^{2+} to Al^{3+} cations, their oxidation states, and the symmetry of occupied sites. It is well known that the Td coordinated Co^{2+} cations are responsible for the blue color of $CoAl_2O_4$ pigments [8,9]. Therefore, the $CoAl_2O_4$ pigments have widely been utilized in ceramics industry as a coloring agent for glaze and bulk tile compositions using conventional screen printing [10] or silicon-roller printing methods [11,12].

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In recent years, new printing methods like drop on demand ink-jet printing (DOD-IJP) can be used to overcome the limitations of conventional printing methods such as cracks on green bodies and wear of screens, and provide high-quality images onto ceramic tile surfaces, which involve the satisfaction of the physical and chemical (viscosity, surface tension, density, color strength, etc.) requirements during ink utilization of ink-jet printers, to ensure adequate image quality and avoid issues such as nozzle clogging [13–15]. The ink preparation usually requires a pigment powder of diameters smaller than 1/100 that of the nozzle of a few to dozens of micrometers; this means that the powder should be ~0.2–1 μm in diameter, otherwise the nozzle clogging would normally occur. Therefore, nanoparticles of all the sizes for ink purposes can meet the demands of ink-jet printing; however, a significant decrease in the size increases the difficulty of producing highly concentrated, stable dispersions due to their aggravated agglomeration, which makes it necessary to modify the nanoparticle surfaces. For instance, the spherical surfaces of nanoparticles can inhibit their agglomeration or clustering, which leads to low-viscosity and sedimentation-resistant inks that are essential to ensure the high performance of printable fluids.

It is facile to fabricate nanostructural $CoAl_2O_4$ using different synthetic strategies [7,16–18], of which template-assisted processes have been demonstrated to be the most efficient strategy. In this strategy, nanostructures are constructed on the inner or outer surfaces of a template through various methods, such as the emulsion route where the water droplets in a water-in-oil (w/o) emulsion can be used as reactors to obtain spherical particles [19,20], which is one of the effective soft-template techniques for the preparation of spherical μm- or nm-sized structures. The stability of water droplets used as reactors is crucially dependent on the hydrophile–lipophile balance (HLB) of the surfactant, the oil/water volume ratio, temperature, etc. [21,22]; e.g., with an increase in the temperature, the stability of emulsion coordinated by the surfactant quickly is reduced, which then leads to a coalescence of the particles. Nevertheless, it has generally been known that finely dispersed solid particles can act as the stabilizer in Pickering emulsions since the beginning of the last century, in which even mm-sized drops coated by particles are shown to be extremely stable against coalescence [23], an accomplishment which has never been reached in the case of surfactant-stabilized emulsions.

This work aims at the synthesis of blue spherical $CoAl_2O_4$ pigment powder in Pickering emulsion assisted with a hydrothermal process. The hydrothermal process as a solution technique is applicable to synthesize pure nano-sized powder from a precursor without high temperature calcination. In addition, spherical shape is the most frequently observed morphology in Pickering emulsion, which has well been supported by a lot of practical and theoretical evidence [24,25]. As a soft template, Pickering emulsion was applied to prepare spherical $CoAl_2O_4$ particles using a hydrothermal method. The effects of pH condition on the crystalline phase and color tone of as-synthesized pigment powder are investigated in detail, based on which the effect of hydrothermal reaction temperature on particle morphology is probed.

2. Experimental

2.1. Materials

liquid paraffin (≥99%), cobalt(II) chloride, hexahydrate ($CoCl_2{\cdot}6H_2O$), aluminum chloride ($AlCl_3$), sodium hydroxide (NaOH), urea, surfactant Span-80 ($C_{24}H_{44}O_6$), and ethanol all were purchased from Sinopharm (Shanghai) Chemical Reagents Co., Ltd, China, and used as starting materials without further purification. For solution preparation and synthesis, deionized water was home made in our laboratory using an *aqua pura* machine (Pinguan, China, PGF-10).

2.2. Methods

2.2.1. Preparation of suspension of aluminum hydroxide (2 M) and cobalt hydroxide (1 M)

In a typical room-temperature synthesis, 5.9500 g of $CoCl_2{\cdot}6H_2O$ and 6.6700 g of $AlCl_3$ according to a 1:2 M ratio of Co^{2+} to Al^{3+} were dissolved together into 25 mL of deionized water. The solution mix was stirred for 10 min into which 50 mL of aqueous NaOH (4 M) was then added dropwise; the resulting mixture was homogenized with a homogenizer (IKA, T25) at 12,000 rpm for 5 min to prepare a suspension without apparent flocculation. The suspension subsequently was centrifuged for 0.5 h with a high-speed centrifuge (Sorvail, Evolution RC) at 13,000 rpm to separate the pink sediment; upon removal of the top liquid, the sediment in the tube finally was sonicated and washed with deionized water. The sonication/washing–centrifugation cycle was performed repeatedly until the final pH of the sonicated suspension measured by a pH meter (Mettler Toledo, FE20) was approximate to 7.

2.2.2. Preparation of spherical $CoAl_2O_4$ pigment powders

0.7140 g of $CoCl_2{\cdot}6H_2O$ and 0.8004 g of $AlCl_3$ in the Co^{2+}/Al^{3+} molar ratio of 1:2 were dissolved together into 15 mL of the suspension obtained from 2.2.1 to form a new suspension. Then, urea was added to the new suspension at different concentrations (3.6040, 5.4060, 7.2080, 9.0100 and 10.8120 g) to obtain the feed solutions, which subsequently were added into a 50-mL Erlenmeyer flask filled with 20 mL of liquid paraffin and 0.1 mL of Span-80 ($C_{24}H_{44}O_6$) to obtain a series of mixtures. The mixtures were homogenized for 3 min with a sonicator (Qsonica, Q700) to result in stabilized w/o emulsions. Upon transferal into a 100-mL autoclave, the w/o emulsions each were heated at 280 °C for 24 h to yield a pigment powder, during which the primary reactions to produce the powders were given as follows [26]:

$$CO(NH_2)_2 + 3H_2O \rightarrow CO_2 + 2NH_3 \cdot H_2O \quad (1)$$

$$NH_3 \cdot H_2O \rightarrow NH_4^+ + OH^- \quad (2)$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \quad (3)$$

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2 \quad (4)$$

$$xAl(OH)_3 + (1-x)Co^{2+} + (2-3x)OH^- + xCl^- + nH_2O \rightarrow [Co_{1-x}Al_x(OH)_2](Cl^-)_x \cdot nH_2O \quad (5)$$

$$Al(OH)_3 \rightarrow \gamma - AlO(OH) + H_2O \quad (6)$$

$$[Co_{1-x}Al_x(OH)_2](Cl^-)_x \cdot nH_2O + (3x-1)\gamma - AlO(OH) + (1-x)OH^- \rightarrow CoAl_2O_4 + xCl^- + (1+n+x)H_2O \quad (7)$$

Upon completion of the reactions, the pH values of the w/o emulsions, which depended on the hydrolytic behavior of urea, were measured with the pH meter at room temperature (RT) to be 8.24, 9.33, 10.17, 11.18, and 12.30, respectively. The as-synthesized mixtures were centrifuged at 5000 rpm for 5 min, followed by sonication/washing of the resultant sediments; such a cycle was conducted 7 times, with deionized water for the first 4 times and then with ethanol for the remaining 3 times as the washing solvent, to remove residual liquid paraffin, inorganic ions, and other impurities. The obtained suspensions were filtrated to

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