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Synthesis of spherical $CoAl_2O_4$ pigment particles with high reflectivity by polymeric-aerosol pyrolysis

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Abstract: Spherical cobalt blue particles with good reflectivity characteristics were synthesized by spray pyrolysis. Two different spray solutions were prepared to investigate the differences in the morphology and the reflectivity properties of cobalt blue particles. One was an aqueous solution, and the other was a polycation solution that was obtained by chemically modifying the aqueous solution with NH_4OH. The cobalt blue particles prepared with the aqueous solution had an irregular morphology after heat treatment at 1000°C for 2 h. On the contrary, spherical and dense particles were obtained from the polycation solution. The spherical and dense cobalt blue particles showed remarkable improvement in reflectivity compared with that of irregular morphology particles as well as the commercial.

Key words: inorganic compounds; optical materials; spray pyrolysis; polymeric aerosol

1. Introduction

Most ceramic dyeing materials are transition metal oxides crystallizing in the spinel structure, which provide high thermal stability and chemical resistance. Amongst these, cobalt aluminate $CoAl_2O_4$ is well known as Thenard's blue. It exhibits the normal spinel structure and is widely used in ceramic, glass, and paint industries and is used for color TV tubes as contrast-enhancing luminescent pigment [1-2]. Cobalt aluminate has been paid attention to as an advanced pigment because of its technological significance [3]. The pigment material with fine particle size, nonaggregation, and a narrow size distribution is known to have good reflective characteristics in terms of the contrast-enhancing luminescence. Particularly, the particle morphology can influence the optical property of the pigment. The spherical morphology of pigments is required for high-reflectivity, because pigment particles with spherical morphology decrease the scattering of light from pigment surfaces [4-6].

However, most commercialized pigment particles are prepared by the solid-state route, which requires flux additives, high reaction temperature, long heating time, and post-milling process to obtain high-purity and small-sized particles [7-10]. As a result, the final obtained pigment particles have irregular shape and high aggregated structure. To solve this problem, it is necessary to develop a novel method that can control the shape of the $CoAl_2O_4$ pigment particles with high reflectivity properties. Spray pyrolysis is a promising technique for producing spherical phosphor particles, which have nonaggregated structure, fine size, and narrow size distribution [11-14]. The particles prepared by conventional spray pyrolysis have a hollow structure, which is known as a fatal disadvantage. Hence, it is crucial to develop spray techniques to overcome this weakness of spray pyrolysis [15-17]. Kang *et al.* [18] showed that the colloidal solution was useful for controlling the morphology of the oxide phosphor particles in spray pyrolysis. Flame spray pyrolysis was also developed to form the particles having filled morphology [19]. However, these techniques in spray pyrolysis were only applied to the prepara-

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tion of phosphor particles.

In the present study, the possibility of high reflectivity of the $CoAl_2O_4$ pigment particles by the spray pyrolysis technique was investigated. To control the morphology and reflectivity characteristics of the $CoAl_2O_4$ pigment particles, polycation precursor solutions were introduced in spray pyrolysis. For the first time, the spherical and dense $CoAl_2O_4$ pigment particles were investigated in spray pyrolysis.

2. Experimental

The spray equipment consisted of an ultrasonic aerosol generator with six vibrators (1.7 MHz), a quartz tube (length, 1000 mm and diameter, 50 mm), and a particle collector. The flow rate of air used as a carrier gas was 45 L/min. The residence time of droplets inside the reactor was about 0.6 s.

Two different precursor solutions were prepared with cobalt and aluminum nitrate salts. The first solution, denoted NS, was obtained by only dissolving the nitrate salt precursors of Co and Al in deionized water. The second solution, denoted PS, was prepared as follows. First, aluminum nitrate was dissolved in deionized water and precipitated as a form of bayerite α-aluminum hydroxide by the addition of excess NH_4OH. The precipitate (α-$Al(OH)_3$) was filtrated and dispersed again in deionized water, while HNO_3 was added until the solution turned blue wherein the aluminum hydroxide molecules were hydrolyzed and condensed to form embryos as a type of polycation $[Al_x(OH)_y(H_2O)_z]^{3x-y}$, of which x and y depended on the concentration of aluminum hydroxide and the pH of the solution. Thereafter, cobalt nitrate precursors were added in the aluminum polycation solution. The overall procedure for the preparation of polycation solution is displayed schematically in Fig. 1. In the two different spray solutions, the total salt concentration was maintained at 1 M.

The prepared spray solutions were atomized by the ultrasonic nebulizer to produce droplets, which were carried into the quartz tube maintained at 900°C. The produced $CoAl_2O_4$ particles were collected by a special collector and post-treated at 800-1000°C for 2 h. The formation of a $CoAl_2O_4$ crystal structure was identified from an X-ray diffraction (XRD) pattern obtained by diffractometry (Rigaku D/max 2550 VB^+). The morphology was observed by scanning electron microscopy (SEM, JEOL JSM-6360LV). The reflectivity spectra of the prepared particles were measured using a UV spectrophotometer (Shimadzu UV-365).

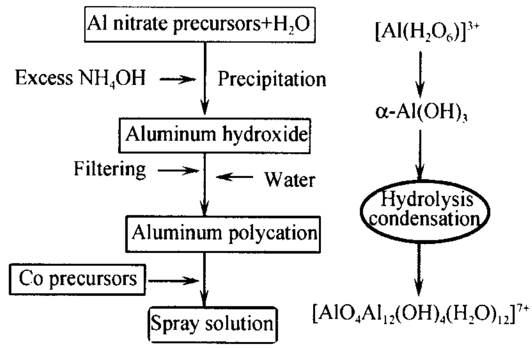

Fig. 1. Schematic diagram displaying the procedure for the preparation of the spray solution containing aluminum polycations.

3. Results and discussion

The as-prepared particles had poor crystallinity in spray pyrolysis. Since high crystallinity of pigment and removal of impurities such as OH^- and NO_3^- ions are generally required for proper energy transfer processing, the as-prepared particles must be annealed at high temperature. To investigate the effects of the annealing process, the annealing temperature was controlled over the range 800-1000°C and the annealing time was set to 2 h. Fig. 2 shows the X-ray diffraction (XRD) patterns of as-prepared and annealed particles. In the $CoAl_2O_4$ pigment particles prepared from aluminum polycation solution, the crystallization begins at 800°C. The intensity of the XRD peaks increase with increasing annealing temperature. The annealed particles at 1000°C have good crystallinity. These XRD patterns coincide with the pattern of $CoAl_2O_4$ registered in the Joint Committee on Powder Diffraction Standards (JCPDS) card. It is seen that the peak intensity of $CoAl_2O_4$ particles prepared from the aluminum polycation spray solution was greater than that of the particles obtained from aqueous nitrate solution as