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Synthesis of nano CoAl_2O_4 pigment for ink-jet printing to decorate porcelain

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The CoAl_2O_4 pigment commonly used for coloring ceramic products was synthesized by microwave hydrothermal processing (M-H), and ink-jet printing with this aqueous pigment ink was performed to decorate porcelain. First, a precursor was prepared by adjusting the solution to pH 12. Then, M-H reaction was applied to this precursor at 240°C for 2 h, yielding particles of CoAl_2O_4 . In addition, the precursor concentration of the suspension was shown to greatly affect the color tone of the resulting particles. As the precursor concentration increased, the synthesized particles that were bluish-green at lower concentrations took on a darker blue color. The synthesized CoAl_2O_4 particles were regular octahedrons measuring approximately 70 nm. The particles synthesized by M-H reaction were used to prepare an aqueous suspension, which was then used for printing on tiles by an ink-jet printing system. The synthesized particles were well dispersed in the prepared aqueous suspension, as little sediment was formed in this suspension left for 1 week. The printing system experienced no clogging and the printed image was of good quality.

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Key-words : CoAl_2O_4 , Nano pigment, Microwave, Hydrothermal synthesis, Ink-jet printing, Suspension

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1. Introduction

Cobalt aluminate (CoAl_2O_4) is a highly stable pigment with excellent resistance to light, weather, etc., which has resulted in its widespread use as a ceramic pigment. CoAl_2O_4 is commonly used as a bright blue pigment to decorate porcelain. The oxide is a blue pigment commonly known as Thénard blue or cobalt blue. CoAl_2O_4 is a composite oxide made up of two metallic compounds in a spinel structure. Spinel-structured CoAl_2O_4 and $(\text{Co}, \text{Zn})\text{Al}_2\text{O}_4$, obtained by inserting zinc oxide into the spinel structure, are examples of oxides used extensively as pigments in ceramic products.¹⁾ Due to its unique optical characteristics, the pigment is widely used as a coloring agent for use in glass, paints, plastics, and color TVs.²⁾

CoAl_2O_4 and other pigments for coloring ceramic products are typically synthesized in solid-phase reactions. As this synthesis involves blending two or more types of powder and heating them to temperatures greater than 1000°C, the chemical composition and particle size of the resulting pigment are not uniform and the level of impurities is high.³⁾ Particle size is an extremely important characteristic of these powders, affecting both the sintering and coloring performance. There have been many studies regarding various methods of synthesis, including the sol-gel method,⁴⁾ the hydrothermal method,⁵⁻⁷⁾ and synthesis from an organic or inorganic precursor, as well as on the coloring characteristics of CoAl_2O_4 .^{5,8,9)}

Ink-jet printing technology is very popular because it allows direct printing onto objects and is suitable for printing fine details. Studies are underway to expand the application of the technology from its current uses—in printers for general

consumer use, the printing industry, and design companies—to a greater number of fields, ranging from prototype production of precision parts to parts manufacturing with short lead times. The use of ink-jet printing technology in decorated tableware, tiles, and other ceramic products also has many advantages. There is no direct contact between the printer and the surface to be printed, and the printing process is fast and low cost.¹⁰⁾ For the application of ink-jet printing technology to ceramic product decoration, highly dispersed and fluidized inorganic pigment inks are required. To prepare such inks, the inorganic pigment must be composed of very finely distributed particles.

Hydrothermal synthesis is a process to produce a powder from a solution without calcination. Highly pure and fine particles with uniform chemical composition can be produced at a low temperatures.¹¹⁾ In addition, research has been conducted on a method of hydrothermal synthesis that employs heat generated by interactions between microwaves and the materials undergoing synthesis. A report on this research described rapid synthesis of fine particles with an even more uniform particle size than conventional hydrothermal reaction.¹²⁾

The present study was performed to synthesize thermally stable nano CoAl_2O_4 pigment using a microwave hydrothermal (M-H) method rapidly at low temperature, and to prepare a well-dispersed suspension with the synthesized pigment for ink-jet printing of ceramic products. Furthermore, the suspension with the synthesized pigment was used to decorate porcelain by ink-jet printing, and the process was evaluated.

2. Experimental procedure

2.1 Sample preparation

Cobalt nitrate [$\text{Co}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Kanto Chemical Co., Inc.] and aluminum nitrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Kanto Chemical Co., Inc.] were used as sources of cobalt and aluminum, respectively.

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Cobalt nitrate and aluminum nitrate were dissolved in ion-exchanged water to prepare Co and Al solutions at a concentration of 1 M. Appropriate amounts of the two solutions, with a Co to Al molar concentration ratio of 1:2, were mixed in a polypropylene beaker, and then titrated with 3 M sodium hydroxide (NaOH; Kanto Chemical Co., Inc.) with magnetic stirring at room temperature in air until the pH became alkaline. The precursors, where the concentrations of Co^{2+} and Al^{3+} were 0.1 and 0.2 M, respectively, were generated in the mixed solution with NaOH. In addition, the ion-exchanged water was added to obtain a suspension with Co concentrations of 0.025 and 0.05 M (hereafter denoted as Co concentration). The suspensions were then stirred for 24 h at room temperature, and the pH of the suspensions was measured. The final pH of the suspensions was adjusted to 9, 10, 11, or 12. The determination of these pH values were based on pH values at which aluminum hydroxide and cobalt hydroxide were precipitated from Al and Co ions in the solution, respectively.¹³⁾

The prepared suspensions were then subjected to the microwave-hydrothermal (M-H) synthesis process. They were placed in a PTFE-lined vessel and kept at 240°C for 2 h in a microwave sample preparation system (Multiwave 3000; PerkinElmer Japan Co., Ltd.) with continuous stirring. The system was a 2.45-GHz microwave and the power was controlled from 0 to 1400 W for precise temperature and/or pressure control. The temperature within the PTFE-lined vessel was measured with an infrared sensor at the lower section of the vessel. To minimize the difference between the actual temperature in the vessel and that measured by the IR sensor, the temperature was raised gradually, with the desired temperature reached in about 20 min. For comparison, the prepared suspensions were subjected to the conventional hydrothermal (C-H) synthesis process at 245°C for 20 h. The reaction products were collected using a centrifugal separator, washed more than five times with ion-exchanged water to remove Na^+ and NO_3^- ions and other impurities, and then dried at 120°C for 24 h.

2.2 Powder characterization

The powders obtained in the process described above were examined with an X-ray diffractometer (XRD) (MXP3; Bruker AXS K.K.) using $\text{Cu K}\alpha$ radiation and a transmission electron microscope (TEM) (H-8100; Hitachi, Ltd.) to evaluate mineral compositions and the particle shapes, respectively. Adding Si powder as an internal standard in the synthesized powder, the spinel-structured compounds were identified by the relative intensity and position of the peaks. Thermal gravity and differential thermal analysis (TG-DTA) (TG-8120; Rigaku Co.) was performed using alumina as a standard in air. A spectrum photometer (TC-1800; Tokyo Denshoku Co., Ltd.) was used to measure the spectral reflection factors of the powders within the range of 400–780 nm, using standard D65 illumination. The absorption spectrum was obtained based on values calculated using the Kubelka–Munk equation,¹⁴⁾ and the color tonalities of the powders were evaluated against this spectrum. In addition, the CIE- $L^*a^*b^*$ colorimetric method, recommended by Commission Internationale de l'Éclairage (CIE, International Commission on Illumination), was followed. In this method, L^* is the lightness axis [black (0)–white (100)], a^* is the green (–) to red (+) axis, and b^* is the blue (–) to yellow (+) axis. The average particle size and particle size distributions were determined by counting 200 particles with a loupe from TEM photographs. The zeta potentials were measured by acoustophoretic spectrometry (DT-1200; Dispersion Technology, Inc.) to determine the particle

surface charge. Measurement of the zeta potential was carried out with 2 vol % suspensions at 25°C.

2.3 Preparation of pigment suspension and printing

Ammonium polycarboxylate salt (CELUNA D-305; Chukyo Yushi Co., Ltd.) was used as a dispersant. A wetting agent (SN-Wet 366; Sun Nopco Ltd.) was used to reduce surface tension of the pigment suspension. The pH of the suspensions were adjusted with tetramethyl ammonium hydroxide [TMAOH, $(\text{CH}_3)_4\text{N}(\text{OH})$] and HNO_3 . Water, glycerin, a dispersant, and a wetting agent were added to the pigment obtained above, and the mixture was subjected to 24 h of ball milling to prepare a 5 mass % pigment suspension. Water and glycerin were mixed at a ratio of 8:2 and used as the solvent. The wetting agent was added at 0.2 vol % with respect to the solvent, and the dispersant, with respect to the pigment, was used. Zirconia balls 0.5 mm in diameter were used as the milling balls. An ink-jet printing system with a piezoelectric actuator (Kegon; Afrit Co.) was used as decoration system for porcelain with a resolution of 360 dpi. Printing was carried out on a calcined tile of dimensions 10 mm × 10 mm × 8 mm. The printed tile was glazed with Zn–Ca glaze and then fired at 1250°C.

3. Results and discussion

3.1 Effects of precursor pH

Before M-H processing, NaOH was added to the solutions to alter the pH to between 9 and 12. The resulting precursors were subjected to XRD to determine the main components. The results showed that they consisted mainly of layered double hydroxides of Co and Al. In addition, a distribution peak indicating aluminum hydroxide [$\text{Al}(\text{OH})_3$] was observed, but there was no peak attributable to cobalt hydroxide. **Figure 1** shows the XRD patterns of powders obtained after 2 h of M-H reaction at 240°C as a function of precursor pH adjusted to 9, 10, 11, and 12. The precursor concentration was 0.05 M (Co). For all pH values, the XRD results showed a peak indicating a spinel structure. In addition, for pH values from 9 through 11, there was another peak indicating boehmite [$\gamma\text{-AlO}(\text{OH})$] (JCPDS File No. 21-

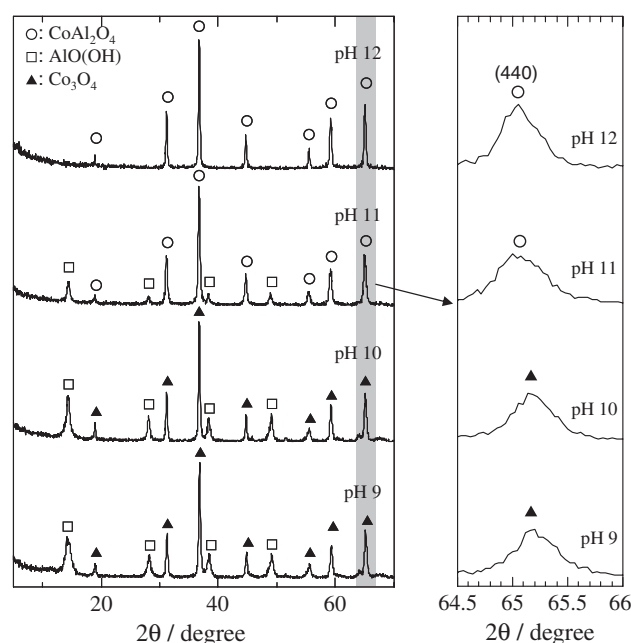


Fig. 1. XRD patterns of powders obtained after 2 h of M-H reaction at 240°C as a function of precursor pH adjusted to 9, 10, 11, and 12.

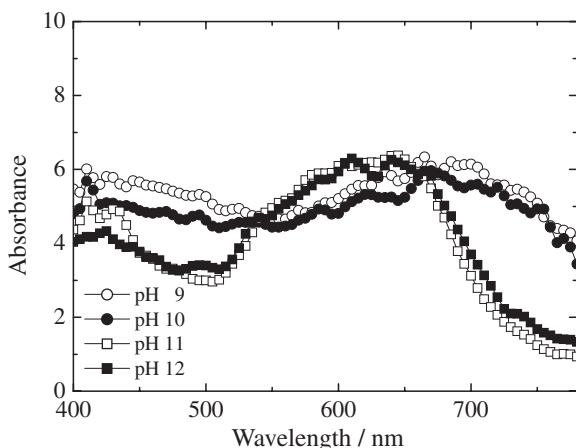


Fig. 2. Absorption spectra of powders obtained after 2 h of M-H reaction at 240°C as a function of precursor pH adjusted to 9, 10, 11, and 12.

1307). CoAl_2O_4 and tricobalt tetroxide (Co_3O_4) were indicated as the spinel-structured compounds in the synthesized materials by M-H reaction. Adding silicon powder as an internal standard, these spinel-structured compounds were identified by correcting the peak positions, because standard lattice parameters of CoAl_2O_4 and Co_3O_4 had almost the same values. The identification of spinel-structured components was confirmed from the relative intensity (I/I_0) of the (111) peak ($2\theta \approx 19^\circ$) and the position of the (440) peak ($2\theta \approx 65^\circ$). The relative intensities of the powders obtained by M-H reaction at precursor pH 9–10 and those of the powders obtained at precursor pH 11–12 were around 17% and 8%, respectively. These were almost equivalent to the standard values of Co_3O_4 (19%)¹⁵ and CoAl_2O_4 (8%),¹⁶ respectively. Moreover, the (440) peak positions of the powders synthesized by precursor at various pH were analyzed; those of the powders prepared from precursors at pH 9 and 10 were different from those of the powders at precursor pH 11 and 12. The (440) standard peak positions of Co_3O_4 and CoAl_2O_4 were 65.24° and 65.04° , respectively. To show this result clearly, an enlarged view is presented in the inset of Fig. 1. Based on these results, it was considered that Co_3O_4 was generated from precursor at pH 9 and 10, and the main material in powders synthesized by precursor at pH 11 and 12 was CoAl_2O_4 . **Figure 2** shows the absorption spectra of powders obtained after 2 h of M-H reaction at 240°C as a function of precursor pH adjusted to 9, 10, 11, and 12. The energy-level diagram for Co^{2+} ($3d^7$ configuration), in both octahedral and tetrahedral coordination, presents three spin-allowed transitions. Co^{2+} in a tetrahedral coordination shows a characteristic triple absorption peak in the visible region at around 540 nm (green region), 590 nm (yellow–orange region), and 640 nm (red region). This absorption peak and multiple reflection valley around 496 and 465 nm (blue region) gives rise to the blue color.¹⁷ At precursor pH values of 9 and 10, the spectra of powders had no notable peaks in the range 400–780 nm, and the powders were strongly blackish-green in color. At precursor pH values of 11 and 12, the powders showed a wide range of absorption peaks between 500 and 700 nm with a reflection valley around 500 nm. The maximum absorption of these powders was around 600 nm. This result indicated that CoAl_2O_4 was generated at pH 11 or above. A high concentration of CoAl_2O_4 was synthesized from the precursor adjusted to pH 12 by M-H reaction at 240°C for 2 h, as the XRD pattern of this powder showed no peak other than that indicating CoAl_2O_4 ,

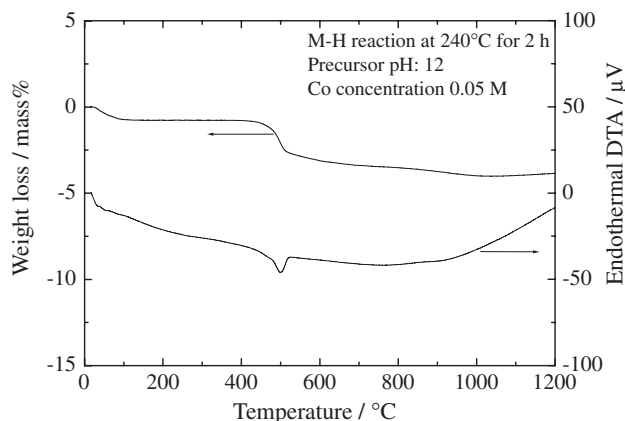


Fig. 3. TG-DTA curves of the powder synthesized by M-H reaction at 240°C for 2 h.

as shown in Fig. 1. The results suggested that this method could be used to synthesize CoAl_2O_4 powder more rapidly than hydrothermal processing at 245°C for 20 h.^{5),6)} However, the absorption peaks of our products were low and had a broad range, and the synthesized powder was bluish-green in color. The TG-DTA curves of the powder synthesized by M-H reaction at 240°C for 2 h are shown in **Fig. 3**. The endothermic peak and weight loss were around 500°C and 2.7 mass %, respectively, and were in agreement with the dehydration of $\gamma\text{-AlO}(\text{OH})$ to $\gamma\text{-Al}_2\text{O}_3$. It was suggested that moderate amounts of $\gamma\text{-AlO}(\text{OH})$ were present although this component was not detected by XRD.¹⁸⁾ The amount of $\gamma\text{-AlO}(\text{OH})$ calculated from the weight loss was around 18 mass %. It was considered that the $\gamma\text{-AlO}(\text{OH})$ in the synthesized powder had an effect on color tone of the powder.

3.2 Effects of precursor concentration

To produce the bluer CoAl_2O_4 pigment from the same precursor (Co concentration 0.05 M, pH 12), the M-H reaction time was changed from 1 to 5 h at 240°C. However, absorption spectra of the resulting powders showed no changes, and the synthesized powders were bluish-green in color. These observations indicated that the M-H reaction time did not affect the color tonality of the end product. In addition, Al concentration of the supernatant in the suspensions after reaction was increased with M-H reaction time, and a peak indicating $\text{Al}(\text{OH})_3$ was observed in the XRD pattern of powders prepared by M-H reactions at 240°C for 5 h. It was suggested that an extended reaction time in M-H processing was not appropriate.

The bluer CoAl_2O_4 powder was synthesized from precursors prepared from suspensions, in which the concentration was adjusted to a Co:Al molar ratio of 1:2. The pH of the precursors was adjusted to 12 and subjected to M-H processing at 240°C for 2 h. **Figure 4** shows the absorption spectra of powders synthesized by M-H reaction as a function of precursor concentration in suspensions of pH 12. The absorption spectra of synthesized powders had a wide ranging peak from 500 to 700 nm including the triple absorption peak attributed to tetrahedral Co^{2+} , and the peak height increased with increasing Co concentration of the corresponding precursor from 0.025 to 0.05 to 0.1 M. The precursor concentration in the suspension had little effect on the absorption spectra around 500 nm (blue region). **Table 1** shows CIE- $L^*a^*b^*$ of the powders synthesized by M-H and C-H reaction from different precursor concentrations in the suspension of pH 12. The blue color is mainly governed by the

parameter b^* , with more negative values corresponding to bluer color. The b^* value decreased with increasing precursor concentration in the suspension. In addition, the b^* value of powders synthesized by the M-H method was lower than that of powders synthesized by the C-H method using the same suspension. These results indicated that increasing precursor concentration in the suspension had a significant effect on the color tone of the resulting product, and it was suggested that bluer powder could be obtained through the M-H reaction at 240°C for 2 h using a suspension with higher precursor concentrations. In addition, the color of the powders synthesized by the M-H reaction using 0.1 M precursor suspension was thermally stable, because the L^* , a^* , and b^* values were

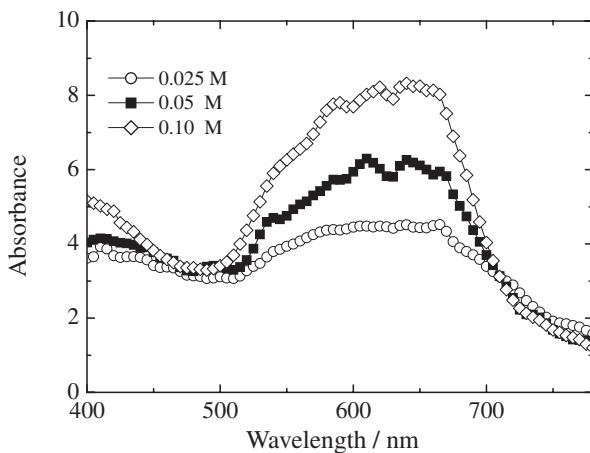


Fig. 4. Absorption spectra of powders synthesized by M-H reaction at 240°C for 2 h as a function of precursor concentration in suspension at pH 12.

Table 1. CIE- $L^*a^*b^*$ of the powders synthesized with different precursor concentrations in suspension at pH 12

Precursor concentration (Co)/M	L^*	a^*	b^*
0.025 (M-H method)	36.05	-6.37	-3.60
0.05 (M-H method)	38.68	-6.52	-5.19
0.1 (M-H method)	43.63	-6.21	-10.91
0.1 (Fired at 1300°C, M-H method)	44.50	-6.51	-11.72
0.1 (C-H method)	44.30	-8.05	-4.95

M-H method: 240°C-2 h, C-H method: 245°C-20 h.

equivalent to those of powders fired at 1300°C, as shown in Table 1. Compared with coloring of the pigment synthesized using the 0.1 M precursor suspension, the bluer CoAl_2O_4 powder was not synthesized from precursors prepared from suspensions with Co concentrations of more than 0.1 M, because the inhomogeneous precursor was prepared from the high viscous suspension by the addition of NaOH.

Figure 5 shows TEM images of powders synthesized by the M-H reaction as a function of different precursor concentrations. The particle size of the synthesized powder did not depend on the precursor concentration in the suspension, and the particle sizes of the powder synthesized from the various precursor concentrations were 60–80 nm. However, the particle morphology changed from spherical to polygonal with increasing precursor concentration in the suspension, and the particles synthesized from the 0.1 M precursor were octahedral. We considered that the octahedral shape of the particles affects the tonality of the product, as the half bandwidth of XRD peak of the synthesized powder became narrower and the crystallinity of the powders was improved with increasing precursor concentration in the suspension. The mean particle diameter of the powder obtained through the M-H reaction at 240°C for 2 h using 0.1 M precursor suspension was 68 nm, and that of the powder obtained through the C-H reaction at 245°C for 20 h using 0.1 M precursor suspension was 76 nm.

Table 2 shows the characteristics of the powders synthesized by M-H and C-H reaction from suspensions with different precursor concentrations at pH 12. The level of impurities in the

Table 2. Characteristics of the powders synthesized from different precursor concentrations in suspension at pH 12

Precursor concentration (Co)/M	Impurity	Particle morphology	Mean particle size/nm
0.025 (M-H method)	γ -AlO(OH) 21 mass %	spherical	67
0.05 (M-H method)	γ -AlO(OH) 18 mass %	polygonal	61
0.1 (M-H method)	γ -AlO(OH) 7 mass %	octahedral	68
0.1 (C-H method)	γ -Al(OH) ₃ , 17.7 mass % γ -AlO(OH)	octahedral, polygonal	76

M-H method: 240°C-2 h, C-H method: 245°C-20 h.

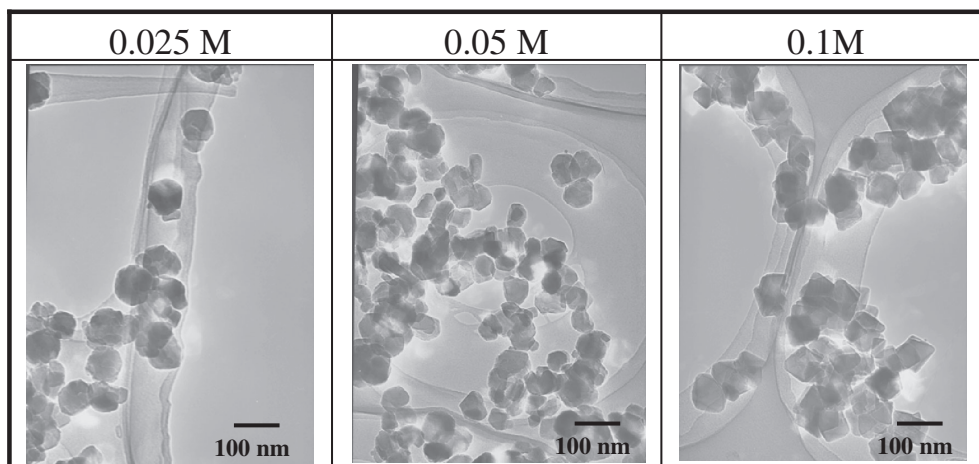


Fig. 5. TEM images of CoAl_2O_4 particles synthesized by M-H reaction at 240°C for 2 h as a function of precursor concentration in suspension at pH 12.

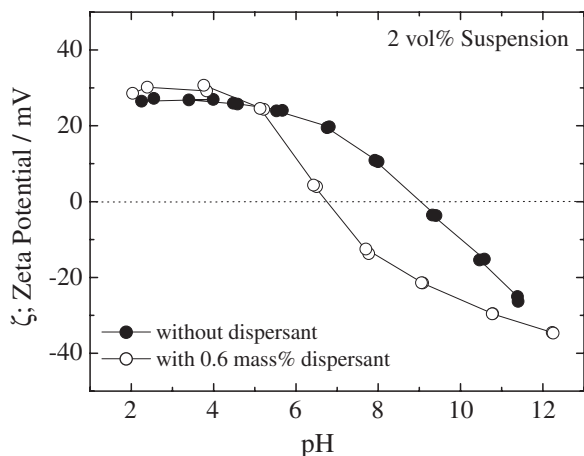


Fig. 6. Zeta potentials of synthesized CoAl_2O_4 particles in suspension with or without 0.6 mass % dispersant as a function of pH.

synthesized powder was determined by XRD and TG-DTA measurements, and the total amounts were calculated from the TG-DTA measurement. The amounts of impurities in the powders decreased with increasing precursor concentration in the suspension. The amount of $\gamma\text{-AlO}(\text{OH})$ in the powder synthesized from the 0.1 M precursor in the suspension was estimated as around 7 mass %. On the other hand, the impurities in the powder synthesized by the C-H method were $\text{Al}(\text{OH})_3$ and $\gamma\text{-AlO}(\text{OH})$, and their total amount was larger than that in the powder synthesized by the M-H method using the same suspension. The polygonal and octahedral particles coexisted in the powder synthesized by the C-H method. These results indicated that the color tone of the powder was affected by the amounts of impurities in the synthesized powder and the crystallinity of the powders. Using suspensions with higher precursor concentrations, it was suggested that this M-H method could be used to synthesize thermally stable CoAl_2O_4 blue nano powder more rapidly than with the C-H method at 245°C for 20 h.

3.3 Suspension preparation and printing

The apparent viscosity of 5 mass % synthesized CoAl_2O_4 pigment suspensions with dispersant decreased abruptly up to the addition of 0.5 mass % dispersant, and had a minimum value with the addition of 0.5–0.6 mass % dispersant, above which it gradually increased with increasing amount of dispersant. These results indicated that the optimum amount of dispersant, which was required for enhancement of fluidity of the CoAl_2O_4 suspension, was around 0.6 mass % with respect to the CoAl_2O_4 powders. The apparent viscosity value of 5 mass % suspension with 0.6 mass % dispersant was about $2\text{ mPa}\cdot\text{s}$ at 100 s^{-1} .

Figure 6 shows the electrokinetic behavior of synthesized CoAl_2O_4 pigment suspensions with or without 0.6 mass % dispersant as a function of pH. The CoAl_2O_4 particles have an isoelectric point (IEP) at around pH 9 without dispersant. At pH >9, the particles exhibit a negative charge. As a result, the mobility values decrease as the pH increases. This was attributed to the adsorption of the OH^- ions onto the particle surface, which enhanced the electrostatic repulsive force. In the acidic or neutral range, a similar phenomenon was observed but with the adsorption of positive H^+ ions in the suspension. As the pH decreased from 9 to 3.5, the value of the zeta potential increased. However, with the addition of more H^+ ions to the suspension, i.e., when the pH decreased from 4.5 to 2.5, the large number of



Fig. 7. (Color online) Photograph of a tile decorated by an ink-jet printing system with aqueous synthesized pigment ink.

positive ions resulted in a reduction of the double layer thickness, and hence a reduction of the repulsive force between the particles. On the other hand, the zeta potential of CoAl_2O_4 particles with dispersant in the suspension showed that the IEP of CoAl_2O_4 shifted to a lower pH. This phenomenon could be attributed to the adsorption of the negatively charged dispersant on the surface of CoAl_2O_4 particles. The electrostatic interaction of the CoAl_2O_4 particles with dispersant was mainly dependent on the carboxyl group, which was hydrophilic in the dispersant. This carboxyl group was not dissociated at acidic pH but existed as $-\text{COO}^-$ at basic pH. For this behavior, the flocculated structure was formed in the acidic to neutral regions due to weak electrostatic repulsive potential of the particles, and these structures collapsed in the basic region. Therefore, at pH >8, the zeta potential of CoAl_2O_4 particles with dispersant gradually increased with increasing pH. Based on this result, the pH of CoAl_2O_4 suspension was adjusted to 9–10 by the addition of TMAOH. In addition, the sedimentation test was carried out to estimate dispersion of synthesized particles in the suspension at pH 10. The sedimentation volume of CoAl_2O_4 left to stand for 1 week decreased with addition of dispersant in aqueous media, and little sedimentation was formed in 5 mass % CoAl_2O_4 suspension with 0.6 mass % dispersant. These observations indicated that dispersion of CoAl_2O_4 particle was enhanced by the addition of dispersant and were well dispersed in the prepared aqueous suspension.

We prepared the aqueous suspension with the particles obtained from 0.1 M precursor by M-H reaction at 240°C for 2 h, and carried out ink-jet printing on calcined tiles. The inks did not cause blockage of the nozzle in printing on the tile and no defects of dots and/or lines were detected on visual check. The picture was decorated using 6 overprinted layers on the tile. The printed tiles were glazed with Ca-Zn glaze and fired at 1250°C . Figure 7 shows a photograph of a decorated tile. The color of the print was dark blue. Thus, the synthesized pigment ink was found to be compatible with an ink-jet printing system.

4. Conclusions

We obtained CoAl_2O_4 particles both rapidly and efficiently from a precursor suspension at pH 12 by microwave hydrothermal synthesis at 240°C for 2 h. The concentration of the suspension during precursor preparation had a significant effect on the color tone of the resulting product, with higher

concentrations resulting in powders of a darker blue color. The synthesized CoAl_2O_4 particles were octahedral, with a diameter of around 70 nm. We prepared aqueous suspension with the powder obtained from the M-H reaction and carried out ink-jet printing on tiles. The resulting print quality was excellent, with no clogging of the printing system.

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