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超臨界水熱法による複合酸化物顔料の調製

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1. Introduction

Complex oxides with spinel structure (AB_2O_4) are important inorganic metalloid materials and are widely used as magnetic materials, catalysts, cathode materials, gas sensitive materials and heat-resistant pigment [(1)]. Recently, there is a growing interest in nanoparticle spinel pigments. Especially, using nano-inks into ink-jet printing technology, it is expected to improve the image quality and to ensure high reliability [(2)]. However, the greatest problem of using nanopigments is agglomeration could occur easily as particle size decreasing. In our research, we verified that crystal growth can be limited and agglomeration can be restrained in favor of small, well-dispersed particles, by means of the properties of supercritical water assisted with organic-ligand molecules[(3)]. In this study, we investigated the synthesis and in-situ surface modification of nanopigments cobalt blue $CoAl_2O_4$ in supercritical and subcritical water assisted with organic molecules.

2. Experiments

Hydrothermal synthesis of in-situ modified nanopigments $CoAl_2O_4$ was carried out using the flow type and the batch type reactors. For the batch type synthesis, a pressure-resistant SUS316 vessel with $5cm^3$ volume was used. The hydrothermal reaction and in-situ modification were performed using homogeneously mixed precursor 2.5ml in the reactor at supercritical and subcritical conditions for 10min. In case of continuous flow type reactor synthesis, high temperature water was fed through a stainless steel tube. The mixture of salt solution precursor and KOH solution was mixed with the preheated water and after that they mixed with the modifier fed by the other line. The product was quenched to room temperature and collected.

3. Results and discussion

The X-ray diffraction of the nanopigments $CoAl_2O_4$ synthesized by batch type and flow type reactor at supercritical and subcritical water hydrothermal conditions were characterized. From the XRD patterns of unmodified and modified samples, Spinel structure $CoAl_2O_4$ was detected. When the organic ligands were introduced into the reaction system, they capped the nanocrystal surface, thereby inhibiting the growth of the particles. As a result, the peaks of XRD patterns became broaden. From the TEM images, it could be confirmed that nearly monodisperse nanoparticles were obtained.

In order to examine the surface nature of these modified particles, FT-IR spectra was analyzed. Bands observed in the 2800-2960 cm^{-1} corresponded to the stretching mode of methyl and methylene groups. The bands at about 1500 cm^{-1} correspond to the stretching frequency of the carboxylate group, which suggested that the organic ligands were chemically bonded to the surface of the nanoparticles. Therefore, it could be concluded that the organic modification of nanoparticles surface was confirmed.

Optical properties of the $CoAl_2O_4$ nanopigments were studied by measuring UV-vis spectra. Fig.1 illustrated that modified sample showed absorption band around 538nm, 578nm and 625nm with a slight shift to lower wavelength as shown in unmodified sample.

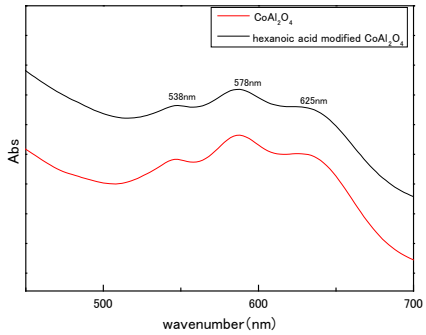

Figure 1 UV-vis spectra of $CoAl_2O_4$ nanopigments

4. References

1) Fortunato, G.; et al., *J. Mater. Chem.* 11, **2001**, 905.

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