Synthesis and Powder Properties of Cerium Phosphate White Pigments

Hiroaki ONODA and Haruka MURAKI

Department of Informatics and Environmental Sciences, Kyoto Prefectural University, 1-5, Shimogamo Nakaragi-eyo, Sakyo-ku, Kyoto 606-8522, Japan

E-mail: h-onoda@kpu.ac.jp

Abstract. Catalytically active cerium dioxide is used as light reflection materials for cosmetic applications. Herein, as novel white pigments for use in cosmetics, cerium phosphates were prepared under various conditions. The chemical composition, powder properties, photocatalytic and oxidation catalytic activities, color phase, and smoothness of the cerium phosphates were evaluated. Samples prepared from cerium (+III) nitrate solution indicated XRD pattern of cerium phosphate hydrate. All samples prepared in this work had large particles and no specified shape. The obtained cerium phosphates exhibit little photocatalytic activity and no oxidation catalytic activity. These samples exhibit a little low reflectance within the range of visible light and 71-78 in L* value.

1. Introduction
Titanium dioxide and zinc oxide are used as white pigments for cosmetic applications [1]. These oxides are known to be photocatalytically active; therefore, cosmetics containing these pigments cause decomposition of a certain amount of sebum on the skin under ultraviolet radiation in sunlight [2,3]. In our previous works, titanium and zinc phosphates without photocatalytic activity were prepared as novel white pigments for cosmetics [4,5]. These compounds have a possibility to replace titanium dioxide and zinc oxide with photocatalytic activity. Cerium dioxide is also used as light reflection materials for cosmetic applications [6,7]. This oxide is known to be oxidation catalysts; therefore, cosmetics containing this pigment too much cause oxidation of the skin under. Therefore, the substitute for cerium oxide is required to prepare the cosmetics without oxidation activity.

Phosphates have been used as ceramic materials, catalysts, fluorescent materials, dielectric substances, metal-surface treatments, detergents, food additives, in fuel cells, as pigments, and so on [8-11]. Phosphate materials are recognized to have high biocompatibility and are therefore expected to be useful as white pigments in cosmetics [12,13]. White pigments that are not oxidation active are required for skin protection during cosmetic use. Furthermore, the moisture retention of the materials used in cosmetics is also important for preventing dry skin. Because phosphates were hydrophilic materials, phosphate pigments are suitable to use for cosmetics from this viewpoint.

The particle shape and the size distribution of phosphates are important parameters for cosmetic pigment application [14]. Spherical, homogenous particles are expected to spread well on the skin. However, overly small particles are unsuitable because the pigments may enter the pores of the skin. Generally, pigments with sub-micrometer dimensions are used in cosmetic applications.

In this study, to obtain a novel white pigment without the catalytic activity, cerium phosphate is prepared under various conditions. The respective chemical compositions, powder properties,
photocatalytic and oxidation catalytic activities, color phases, and smoothness of the obtained materials were studied for application of the developed pigments in cosmetics.

2. Experimental

Cerium nitrate solution (0.5 mol L\(^{-1}\)) was mixed with phosphoric acid (0.5 mol L\(^{-1}\)) in a molar ratio of P/Ce(+III) = 1/1 and 2/1 at room temperature for more than 1 hour. The mixed solutions were treated with ultrasound for 1 hour. The precipitates were then filtered off, washed with water, and dried at room temperature over 3 days [5]. For comparison, samples were also prepared without ultrasonic treatment. Di-ammonium cerium nitrate solution (0.5 mol L\(^{-1}\)) was also mixed with phosphoric acid in a molar ratio of P/Ce(+IV) = 4/3, and then treated with the above process. All chemicals were of commercial purity and were acquired from Wako Chemical Industries Ltd. (Osaka Japan) and used without further purification.

The crystalline phase compositions of these materials were analyzed using X-ray diffraction (XRD; MiniFlex; Rigaku Corp., Akishima, Japan) with monochromated Cu-K\(\alpha\) radiation. The IR spectra of materials were recorded on a HORIBA FT-IR 720 (Horiba Ltd., Kyoto, Japan) using the KBr disk method.

The shapes and sizes of the particles comprising the precipitates were estimated from the scanning electron microscopy (SEM; instrument: JSM-5510LV; JEOL Ltd., Akishima, Japan) images and particle size distributions. The particle size distributions of these materials were measured using a centrifugal precipitation particle-size distribution analysis system (SA-CP3L, Shimadzu Corp., Kyoto, Japan).

The cosmetic properties of the developed precipitates were estimated by analysis of the color phase, photocatalytic and oxidation catalytic activities, and smoothness. The color of the phosphate pigments was estimated using ultraviolet-visible (UV-Vis) reflectance spectra acquired with a UV2100, Shimadzu Corporation instrument (Kyoto, Japan) (reference compound: BaSO\(_4\)). The color of materials was also estimated with a TES135 plus color analyzer (TES Electrical Electronic Corp, Taipei, Taiwan). In this estimation, the L\(^*\) value means the whiteness of powder, in which 100 is white, on the opposite site, 0 is black. The a\(^*\) value means the redness of materials, with positive (maximum; +60) and negative (-60) values are corresponding with red and green, respectively. The b\(^*\) value indicates the yellowish, in which positive (maximum; +60) and negative (-60) values are correspond with yellow and blue, respectively.

![Fig. 1 XRD patterns of samples prepared in various conditions, (a) P/Ce(III) = 1/1, ultrasonic; 0 h, (b) P/Ce(III) = 1/1, 1 h, (c) P/Ce(III) = 2/1, 0 h, (d) P/Ce(III) = 2/1, 1 h, and (e) P/Ce(IV) = 4/3, 0 h, CePO\(_4\)\(\cdot\)nH\(_2\)O.](image1)

![Fig. 2 IR spectra of samples prepared in various conditions, (a) P/Ce(III) = 1/1, ultrasonic; 0 h, (b) P/Ce(III) = 1/1, 1 h, (c) P/Ce(III) = 2/1, 0 h, (d) P/Ce(III) = 2/1, 1 h, and (e) P/Ce(IV) = 4/3, 0 h.](image2)
The photocatalytic activity of the samples was assessed from the decomposition of methylene blue using 365 nm irradiation \([\text{11–13}]\). A 0.01 g portion of the sample was placed in 4 mL of methylene blue solution \((1.0 \times 10^{-5} \text{ mol-L}^{-1})\) and this solution was then irradiated. The decrease in the absorption at about 660 nm was monitored over the course of 120 min. Furthermore, the oxidation catalytic activity of samples was estimated with ascorbic acid solution. A 0.05 g of sample was put into 2 mL of 0.01 mol/L of ascorbic acid solution. The color of solution changes to brown by oxidation catalyst.

As the smoothness of sample powders, the static friction resistances were estimated on artificial leather with Portable Friction Meter 94i-II (SHINTO Scientific Co., Ltd., Tokyo, Japan). The sample powders were spread on the leather, and then a sensor was run over the powders.

3. Results and Discussion

3.1. Chemical composition and powder properties of cerium phosphates

Figure 1 shows the XRD patterns of the samples prepared under various conditions. Samples prepared from cerium (+III) nitrate solution indicated the peak pattern of cerium phosphate hydrate (Fig.1(a)-(d)). On the other hand, sample prepared from di-ammonium cerium (+IV) nitrate solution had unknown peaks (Fig. 1(e)). Figure 2 shows IR spectra of the samples prepared under various conditions. In the same manner with XRD patterns, sample prepared from di-ammonium cerium (+IV) nitrate solution indicated the different IR spectrum with other samples. The absorption peak at 1630 cm\(^{-1}\) was attributed to the water of crystallization. The peaks at 1380 cm\(^{-1}\) were attributed to nitrate anion. The peaks at 1050, 620, and 540 cm\(^{-1}\) were attributed to phosphate anions \([\text{14}]\).

Spherical morphology of the particles is desirable for cosmetic applications. Figure 3 shows representative SEM images of the samples prepared in various conditions.

![SEM images](image)

**Fig. 3** SEM images of samples prepared in various conditions, (a) P/Ce(III) = 1/1, ultrasonic; 0 h, (b) P/Ce(III) = 1/1, 1 h, (c) P/Ce(III) = 2/1, 0 h, (d) P/Ce(III) = 2/1, 1 h, and (e) P/Ce(IV) = 4/3, 0 h.

All samples prepared in this work had large particles and no specified shape. Small and homogeneous particles are suitable for cosmetic applications. However, overly small particles have a major shortcoming in that they enter the pores of the skin \([\text{3}]\). Generally, pigments with sub-micrometer dimensions are used in cosmetics. The standard size of white pigment particles used in cosmetics is difficult to determine because the size of the pores in skin is affected by factors such as age, gender, and climate. Furthermore, overly large particles are inappropriate for cosmetic purposes owing to cracking of their coating on the skin. It is therefore important to control the particle sizes of the pigment. Figure
4 shows the particle size distribution of the samples prepared in various conditions. All samples prepared in this study had a large amount of particles with dimensions of over 1 µm. Sample prepared with ultrasonic treatment indicated higher ratio at 15 µm than those prepared without. Ultrasonic treatment produced the aggregation of phosphate particles.

3.2. Cosmetic properties of cerium phosphates

Figure 5 shows the UV-Vis reflectance spectra of the cerium phosphates prepared in various conditions. Sample prepared from di-ammonium cerium (+IV) nitrate solution indicated higher reflectance at 480-800 nm than those from cerium (+III) nitrate solution. The reference became lower dramatically at 500 nm in sample prepared from di-ammonium cerium (+IV) nitrate solution. Therefore, this sample is yellow powder. On the other hand, others are a little dark white powder.

The color of sample powder was also estimated by L*a*b* color space. Table 1 shows the L*a*b* values of samples prepared in various conditions. Samples prepared from cerium (+III) solution indicated from 71 to 78 in L* values, on the other hand, those from Ce(+IV) solution indicated over 80. Sample prepared from Ce(+IV) solution had higher values in a* and b* ones than others. These results were corresponding with the powder color and UV-Vis reflectance spectra of samples.

Figure 6 summarizes the respective photocatalytic activities of the samples prepared in various conditions. Zinc oxide, which is widely used as a white pigment in cosmetics, was evaluated for comparison with cerium phosphates [1]. Methylene blue decomposed under UV irradiation in the presence of zinc oxide (Fig. 6(b)). Samples prepared in this work had little photocatalytic activity in spite of the valence of cerium and the phosphorus / cerium ratios (Fig. 6(d)-(h)).

Figure 7 shows photograph of the oxidation catalytic estimation. Cerium oxide changed the color of ascorbic acid solution to brown (Fig. 7(a)). Samples prepared from cerium (+III) solution produced white dispersed solutions, on the other hand, sample prepared from cerium (+IV) solution was precipitated in colorless transparent solution. Samples prepared in this work had no oxidation catalytic activity.
As described above, pigments with a high level of smoothness spread well across the skin, and powder smoothness is another important factor for cosmetic applications [4]. As the powder smoothness, the static friction resistance of the samples prepared in various conditions was shown in Table 1. This value of cerium dioxide was 0.398. Samples prepared from cerium (+III) nitrate solution indicated from 0.32 to 0.38. The P/Ce ratio and ultrasonic treatment had less influence on the static friction resistance.

Table 1 L*a*b* values and static friction resistances of samples prepared in various conditions

| P/Ce | Ultrasonic | Ce   | L*   | a*   | b*   | Resistance |
|------|------------|------|------|------|------|------------|
| 1/1  | 0          | +III | 77.53| 1.48 | -4.59| 0.375      |
| 1/1  | 1          | +III | 71.53| 1.75 | 0.17 | 0.321      |
| 2/1  | 0          | +III | 76.64| 2.37 | -1.89| 0.354      |
| 2/1  | 1          | +III | 75.91| 2.19 | -1.10| 0.375      |
| 4/3  | 0          | +IV  | 80.82| 6.38 | 5.60 | 0.272      |
4. Conclusion
Various cerium phosphates were prepared with and without ultrasonic treatment. Samples prepared from cerium (+III) nitrate solution indicated XRD pattern of cerium phosphate hydrate. All samples prepared in this work had large particles and no specified shape. The obtained cerium phosphates prepared in this work exhibit little photocatalytic activity and no oxidation catalytic activity. These samples prepared from cerium (+III) solution exhibit a little low reflectance within the range of visible light and 71-78 in L* value. The obtained samples indicated enough low static friction resistance.

References
[1] Monteiro-Riviere N A, Wiench K, Landsiedel R, et al 2011 Toxicol. Sci. 123 (1) 264 http://doi.org/10.1093/toxsci/kfr148
[2] Kockler J, Oelgemöller M, Robertson S, Glass BD 2014 Cosmetics 1 128 http://doi.org/10.3390/cosmetics1020128
[3] Girigoswami K, Viswanathan M, Murugesan R, Girigoswami A 2015 Mater. Sci. Eng. C 56 (1) 501. http://doi.org/10.1016/j.msec.2015.07017
[4] Onoda H, Yamaguchi T 2012 J. Mater. Chem. 22 (37) 19826 http://doi.org/10.1039/e2jm33952h
[5] Onoda H, Haruki M, Toyama T 2014 Ceram. Intern. 40 (2) 3433 http://dx.doi.org/10.1016/j.ceramint.2013.9.088
[6] Davo-Quinonero A, Navlani-Garcia M, Lozano-Castello D, Bueno-Lopez A, Anderson J A 2016 ACS catalysis 6 1723 http://dx.doi.org/10.1021/acscatal.5b02741
[7] Lafaye G, Barbier Jr. J, Duprez D 2015 Catalysis Today 253 89 http://dx.doi.org/10.1016/j.cattod.2015.01.037
[8] Jain A, Shore A M, Jonnalagadda S C, Ramanujachary K V, Mugweru A 2015 Appl. Catal. 489 72 http://dx.doi.org/10.1016/j.apcata.2014.10.020
[9] Cai Y, Feng S, Ming C, Ren X, Qin Y, An L 2016 Resul. Phys. 6 826 http://dx.doi.org/10.1016/j.rinp.2016.09.009
[10] Rao G V, Shashikala H D 2014 J. Non-cryst. Solids 402 (15) 204 http://dx.doi.org/10.1016/j.jnoncrysol.2014.06007
[11] Lee J S, Murphy W L 2013 Adv. Mater. 25 (8) 1173 http://doi.org/10.1002/adma.201203370
[12] Hiromoto S, Inoue M, Taguchi T, Yamane M, Ohtsu N 2015 Acta Biomater. 11 (1) 520 http://doi.org/10.1016/j.actbio.2014.09.026
[13] Radovanovic Z, Jokic B, Veijovic D, Dimitrijevic S, Kojic V, Petrovic R, Janackovic D 2014 App. Surf. Sci. 307 (15) 513 http://doi.org/10.1016/j.apsusc.2014.04.066
[14] Lopes-Heras I, Madrid Y, Camara C 2014 Talanta 124 (15) 71 http://doi.org/10.1016/j.talanta.2014.02.029