Original Article

Synthesis of cerium phosphate white pigments from cerium carbonate for cosmetics

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Catalytically active cerium dioxide is used as light reflection materials for cosmetic applications. In fact, cosmetics containing this pigment cause too much oxidation on the skin. Therefore, the substitute for cerium dioxide is required to prepare the cosmetics without catalytic activity. Herein, as novel white pigments for use in cosmetics, cerium phosphates were prepared from cerium carbonate with hydrothermal treatment. The chemical composition (X-ray diffraction pattern and infrared spectrum), powder properties (scanning electron microscopy images and particle size distributions), the photo and oxidation catalytic activity, color phase (ultraviolet-visible reflectance spectra and L′a′b′ values), and smoothness of the cerium phosphates were evaluated. The photocatalytic activity of the samples was assessed from the decomposition of methylene blue. The oxidation catalytic activity of samples was estimated with ascorbic acid solution. All samples prepared in this work indicated X-ray diffraction pattern of cerium phosphate hydrate. Samples prepared in this work had no photo and oxidation catalytic activities. They indicated the absorption at 300–330 nm and high reflectance within the range of visible light. Because samples indicated higher L′ values than 89, these materials are possible to use as white pigments. All materials prepared in this work had higher smoothness than cerium oxide.

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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. On the other hand, cerium dioxide is also used as light reflection materials for cosmetic applications. This oxide is known to be oxidation catalysts. Therefore, cosmetics containing this pigment cause too much oxidation on the skin [6,7]. A substitute for cerium dioxide is required to prepare the cosmetics without catalytic activity.

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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. Further, the particle shape and the size distribution of phosphates are also important parameters for cosmetic pigment application. Spherical, homogenous particles are expected to spread well on the skin.

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

2. Experimental

Cerium carbonate octahydrate (1.51 g) was mixed with phosphoric acid (0.5 mol L⁻¹, 10 mL) in a molar ratio of P/Ce = 1/1 at room temperature, and then let stand for 1 day to volatilize carbon dioxide. The mixture was put into an airtight container with 98 mL of an inner tube and then heated at 120 °C for 1, 3, 6 h, and 140, 160, 180 °C for 1 h (hydrothermal treatment). The obtained samples were filtered and dried at room temperature over 3 days [5]. Sample without the hydrothermal treatment was also prepared at 50 °C for comparison. 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 monochromatic Cu-Kα radiation. The Infrared (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-CF3L, Shimadzu Corp., Kyoto, Japan).

The cosmetic properties of the developed precipitates were estimated by analysis of the photo and oxidation catalytic activities, color phase, and smoothness. The photocatalytic activity of the samples was assessed from the decomposition of methylene blue using 365 nm irradiation [14,15]. A 0.01 g portion of the sample was placed in 4 mL of methylene blue solution (1.0 × 10⁻⁵ mol L⁻¹) and this solution was then irradiated. The decrease in the absorption at about 660 nm was monitored after 20, 40, 60, 80, 100, and 120 min. Furthermore, the oxidation catalytic activity of samples was estimated with ascorbic acid solution. A 0.05 g of sample was put into 4 mL of 0.01 mol/L of ascorbic acid solution. The color of solution changes to brown by oxidation catalyst.

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: BaSO₄). The color of materials was also estimated with a TES135 plus color analyzer (TES Electrical Electronic Corp., Taipei, Taiwan). The L* value means the lightness 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; +128) and negative (−128) values are corresponding with red and green, respectively. The b* value indicates the yellowness, in which positive (maximum; +128) and negative (−128) values correspond to yellow and blue, respectively [16].

As the smoothness of sample powders, the static friction resistances were estimated on artificial leather with Portable Friction Meter 941-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

Fig. 1 shows the XRD patterns of the samples prepared under various conditions. All samples prepared in this work indicated the peaks of cerium phosphate hydrate [17]. Sample prepared without hydrothermal treatment had the weaker peaks than others. Hydrothermal treatment supported the crystallization of cerium phosphate. Samples prepared for longer time and at higher temperature indicated stronger peaks than samples prepared at 120 °C for 1 h. Fig. 2 shows FTIR spectra of the samples prepared under various conditions.
Fig. 2 – IR spectra of samples prepared under various conditions, (a) commercial CeO₂, (b) commercial Ce₂(CO₃)₂·8H₂O, (c) 50 °C (without hydrothermal treatment), (d) 120 °C, 1 h, (e) 120 °C, 6 h, and (f) 180 °C, 1 h.

Cerium dioxide had the strong absorption at 400–550 cm⁻¹, on the other hand, cerium carbonate indicated bands at 650, 750, 850, 1080, 1330, 1370, 1420, and 1480 cm⁻¹. Since these bands were not observed in the spectra of samples prepared in this work, the reaction between cerium carbonate and phosphoric acid took place. All samples prepared in this work had bands at 540, 620, 1050, and 1630 cm⁻¹. The bands at 540, 620, and 1050 cm⁻¹ were attributed to phosphate anions [18,19]. The band at 1630 cm⁻¹ was attributed to the water of crystallization.

Spherical morphology of the particles is desirable for cosmetic applications [20,21]. All samples prepared in this work had large particles and no specified shape in SEM images (Fig. 3). 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 [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. Fig. 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. It is difficult to obtain small particles of cerium phosphate in this hydrothermal process.

3.2. Cosmetic properties of cerium phosphates

Fig. 5 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 commercial zinc oxide (Fig. 5(b)). All samples prepared in this work had no photocatalytic activity (Fig. 5(e–h)).

Since cerium dioxide works as an oxidation catalyst, the catalytic activity of samples was estimated with ascorbic acid solution. Fig. 6 shows the oxidation catalytic activity of samples prepared under various conditions. Cerium dioxide
Fig. 4 – Particle size distribution of samples under various conditions, (a) commercial CeO₂, (b) commercial Ce₂(CO₃)₂₈H₂O, (c) 50 °C (without hydrothermal treatment), (d) 120 °C, 1 h, (e) 120 °C, 6 h, and (f) 180 °C, 1 h.

Fig. 5 – Photocatalytic activity of samples prepared under various conditions, (a) blank, (b) commercial ZnO, (c) commercial CeO₂, (d) commercial Ce₂(CO₃)₂₈H₂O, (e) 50 °C (without hydrothermal treatment), (f) 120 °C, 1 h, (g) 120 °C, 6 h, and (h) 180 °C, 1 h.

Fig. 6 – Oxidation catalytic activity of samples prepared under various conditions, (a) CeO₂, (b) Ce₂(CO₃)₂₈H₂O, (c) 50 °C (without hydrothermal synthesis), (d) 120 °C; 1 h (with), (e) 120 °C; 3 h, (f) 120 °C; 6 h, (g) 140 °C; 1 h, (h) 160 °C; 1 h, (i) 180 °C; 1 h.

Fig. 7 – UV-Vis reflectance of samples prepared under various conditions, (a) commercial CeO₂, (b) commercial Ce₂(CO₃)₂₈H₂O, (c) 50 °C (without hydrothermal treatment), (d) 120 °C, 1 h, (e) 120 °C, 6 h, and (f) 180 °C, 1 h.

Table 1 – L’a’b’ values and static friction resistances of samples prepared under various conditions.

<table>
<thead>
<tr>
<th>Temp. /°C</th>
<th>Time/h</th>
<th>L’</th>
<th>a’</th>
<th>b’</th>
<th>Resistance/–</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>1</td>
<td>99.19</td>
<td>0.37</td>
<td>2.42</td>
<td>0.274</td>
</tr>
<tr>
<td>120</td>
<td>3</td>
<td>97.96</td>
<td>0.27</td>
<td>1.36</td>
<td>0.262</td>
</tr>
<tr>
<td>120</td>
<td>6</td>
<td>97.69</td>
<td>0.46</td>
<td>1.14</td>
<td>0.342</td>
</tr>
<tr>
<td>140</td>
<td>1</td>
<td>92.82</td>
<td>0.13</td>
<td>1.66</td>
<td>0.321</td>
</tr>
<tr>
<td>160</td>
<td>1</td>
<td>90.43</td>
<td>0.72</td>
<td>2.27</td>
<td>0.355</td>
</tr>
<tr>
<td>180</td>
<td>1</td>
<td>95.72</td>
<td>−0.09</td>
<td>0.79</td>
<td>0.341</td>
</tr>
<tr>
<td>50</td>
<td>–</td>
<td>92.78</td>
<td>0.34</td>
<td>1.43</td>
<td>0.323</td>
</tr>
<tr>
<td>Ce₂(CO₃)₂</td>
<td>–</td>
<td>93.95</td>
<td>0.12</td>
<td>1.24</td>
<td>0.213</td>
</tr>
<tr>
<td>CeO₂</td>
<td>–</td>
<td>93.07</td>
<td>0.40</td>
<td>4.17</td>
<td>0.377</td>
</tr>
</tbody>
</table>

changed the white color of ascorbic acid solution to brown, on the other hand, samples prepared in this work produced white dispersed solutions without color-change. Cerium phosphate powders had no oxidation catalytic activity.

Fig. 7 shows the UV-Vis reflectance spectra of the cerium phosphates prepared under various conditions. The reflectance of cerium dioxide became lower at the shorter range than 500 nm. Cerium carbonate had the strong absorption at 290 nm. All samples prepared in this work indicated the absorption at 300–330 nm and high reflectance within the range of visible light. Therefore, all samples were 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 at various conditions. Cerium dioxide had high b’ value, which corresponds to yellow color. All samples prepared in this work had small b’ values, therefore the obtained samples were weak yellowish powders. Because samples indicated higher L’ values than 89, these materials are possible to use as white pigments.

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 [22]. The static friction resistance of the samples prepared in various conditions was shown in Table 1. All samples prepared in this work indicated lower resistance than cerium dioxide. These
materials are suitable for a cosmetic pigment from the view of smoothness.

4. Conclusion

Cerium phosphates were prepared under various conditions in hydrothermal process. All samples prepared in this work indicated XRD pattern of cerium phosphate hydrate. These samples had large particles and no specified shape. All samples had no photo and oxidation catalytic activities. Samples prepared in this work indicated the absorption at 300–330 nm and high reflectance within the range of visible light. Because samples indicated higher L* values than 89, these materials are possible to use as white pigments. All materials prepared in this work had higher smoothness than cerium oxide.

References


