SYNTHESIS OF PLATE-LIKE CERIUM PHOSPHATES AND THEIR PHOTOCHEMICAL PROPERTIES VIA SOFT CHEMICAL REACTIONS

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Keywords: Cerium phosphates, Plate-like particle, Hydrothermal synthesis, Morphology transcription, UV-shielding.

Abstract: Plate-like cerium phosphates have attracted attention because of their unique UV-shielding ability with low photocatalytic activity and excellent comfort when applied on skin. Plate-like hydrated cerium phosphate, Ce$_2$(PO$_4$)$_2$HPO$_4$·H$_2$O, ca 3 µm in diameter, was obtained by the hydrothermal reaction of Ce(SO$_4$)$_2$ in H$_3$PO$_4$ aqueous solution at 200°C for 3 h. Ce$_2$(PO$_4$)$_2$HPO$_4$·H$_2$O transformed to CeP$_2$O$_7$-CePO$_4$, mixture around 700°C with the transcription of plate-like morphology. Plate-like CePO$_4$ and CeP$_2$O$_7$ were also synthesized as single phase by heating plate-like Ce$_2$(PO$_4$)$_2$HPO$_4$·H$_2$O with cerium hydroxide and NH$_4$H$_2$PO$_4$, respectively. Plate-like cerium phosphates showed excellent comfort, absorption ability of UV-light and lower oxidation catalytic activity than undoped ceria. The UV-shielding ability of them was in the order Ce$_2$(PO$_4$)$_2$HPO$_4$·H$_2$O > CeP$_2$O$_7$ > CeP$_2$O$_7$-CePO$_4$ mixture > CePO$_4$ > K$_{0.8}$Li$_{0.266}$Ti$_{1.734}$O$_4$.

(Received March 10, 2009; Accepted March 25, 2009)

INTRODUCTION

The damaging effects of UV rays have attracted attention and various UV-shielding materials have been developed in response. Nanoparticles of titania (TiO$_2$), zinc oxide (ZnO) and calcia-doped ceria (Ce$_{1-x}$Ca$_x$O$_{2-x}$) have been commercially used as inorganic sunscreens in personal care products in order to improve the transparency in the visible light region. However, nanoparticles of inorganic materials are not comfortable and do not provide good coverage over the skin because of the agglomeration of the particles. The plate-like particles such as mica, talc, etc. are often used to improve the comfort and covering ability of inorganic UV shielding nanoparticles. The mixing with mica and talc, however, generally results in a decrease in the UV-shielding performance since mica and talc do not possess UV-absorption ability. In a previous paper$^{[9]}$ we reported that the comfort of wearing calcia-doped ceria nanoparticles was successfully improved without loss of UV-shielding performance by using plate-like lepidocrocite type potassium lithium titanate, K$_{0.8}$Li$_{0.266}$Ti$_{1.734}$O$_4$, possessing the band gap energy of ca. 3.5 eV, i.e., the absorption ability of UV ray less than 350 nm of wavelength in stead of mica and talc. From the point of view of UV-shielding, the plate-like particles are required to show absorption ability of UV-ray less than 400 nm. Therefore, we searched the plate-like semiconductor particles possessing the band gap energy ca. 3 eV and found that plate-like hydrated cerium phosphate, Ce$_2$(PO$_4$)$_2$HPO$_4$·H$_2$O, possessing the band gap energy ca. 2.7 eV$^{[9]}$ could be prepared by the hydrothermal reaction of Ce(SO$_4$)$_2$ and H$_3$PO$_4$. However, it showed the catalytic activity for the oxidation of castor oil. It is well known that the morphology of solid material can sometimes be retained even after chemical reaction if the reaction topotactically proceeds. Actually, such topotactic reactions are used to prepare needle-like γ-Fe$_2$O$_3$ and plate-like BaTiO$_3$ by using needle-like α-FeOOH and plate-like K$_{1.07}$Ti$_{1.73}$Li$_{0.27}$O$_2$ precursors, respectively$^{[10,11]}$. Therefore, in the present study we investigated the preparation of plate-like cerium phosphates with low oxidation catalytic activity by the morphology transcription of plate-like Ce$_2$(PO$_4$)$_2$HPO$_4$·H$_2$O precursor and the photochemical properties of the products were evaluated.

MATERIALS AND METHODS

Hydrothermal synthesis of plate-like Ce$_2$(PO$_4$)$_2$HPO$_4$·H$_2$O: After placing 5 mmol of Ce(SO$_4$)$_2$:4H$_2$O powder and 2.5 M H$_3$PO$_4$ aqueous solution with the P/Ce atomic ratio of 2.5 in a Teflon-lined autoclave with a capacity of 20 cm$^3$, the autoclave was sealed, placed in an electric furnace or a microwave oven (Berghof, MWS-2) and heated at 200°C for 3 h$^{[12]}$. After cooling the autoclave in air, the precipitate was filtered, washed with distilled water, and vacuum dried at 60°C for 12 h.

Preparation of CePO$_4$-CeP$_2$O$_7$ mixture: The plate-like Ce$_2$(PO$_4$)$_2$HPO$_4$·H$_2$O was calcined in an electric oven at 700°C for 5 h.

Preparation of CePO$_4$: After dispersing plate-like

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Ce₂(PO₄)₂HPO₄ in water with ultrasonic irradiation, equal molar of 1 M CeCl₃ aqueous solution was added and then the solution pH was adjusted at 10 by adding ammonia aqueous solution to precipitate cerium hydroxide. After that the precipitate was filtered, washed with water and calcined in an electric oven at 700°C for 5 h.

Preparation of CeP₂O₇: After mixing equal moles of plate-like Ce₂(PO₄)₂HPO₄·H₂O and NH₄H₂PO₄ powders using an agate mortar, the mixed powder was calcined in an electric oven at 700°C for 5 h.

The morphology of the product was observed using a scanning electron microscope (Hitachi, S-4100L). The phase constitution was characterized by X-ray diffraction (XRD) analysis using graphite monochromatized CuKα radiation (Shimadzu, XD-01). The UV-shielding abilities of samples were evaluated by measuring the transmittance spectra of thin films uniformly dispersing sample powders with an UV-Vis spectrophotometer (SHIMADZU, UV-2450), where 2 g of the sample, 4 g of nitrocellulose of industrial grade, 10 g of ethyl acetate and 9 g of butyl acetate were mixed uniformly by ball-milling using a plastic bottle of 50 cm³ internal volume and 100 g zirconia ball, 2.7 mm in diameter for 40 h. The dispersion mixture was applied onto a quartz glass plate with an applicator. The thickness of the film was 12.5 µm. The catalytic activity for the oxidation of organic material was determined using a conductometric determination method (Rancimat system, Metrohm E679). One gram of the sample powder was mixed with 10 g of castor oil and heated to 120°C while bubbling air at 0.5 dm³ min⁻¹, where the air was introduced into distilled water attached to an electric conductivity measurement cell. The catalytic activity was evaluated by measuring the increase in the conductivity of distilled water resulting from trapping of volatile molecules formed by the oxidation of castor oil on heating. The feeling of wearing the sample powder on skin was evaluated using a friction tester (Katotech, KES-SE) which employs a piano wire as a friction element and artificial leather as a substrate (Idemitsu Technofine Co., Sapurare®), where the sample powder was applied on the artificial leather using a make-up brush.

RESULTS AND DISCUSSION

XRD patterns of (a) Ce₂(PO₄)₂HPO₄·H₂O as-prepared by the hydrothermal reaction of Ce(SO₄)₂ and H₃PO₄ at 150°C for 7 days and after heating at 700°C for 5 h (b) without additive and with equal molar of (c) CeO₂ and (d) NH₄H₂PO₄ are shown in FIGURES 1. The sample as-prepared consisted of single phase Ce₂(PO₄)₂HPO₄·H₂O (FIGURE 1(a)). Ce₂(PO₄)₂HPO₄·H₂O transformed to CePO₄·CeP₂O₇ mixture by calcinations without additive (FIGURE 1(b)) as shown in a previous paper. As-expected, Ce₂(PO₄)₂HPO₄·H₂O was converted to CePO₄ and CeP₂O₇ by heating with cerium hydroxide and NH₄H₂PO₄ respectively (FIGURE 1(c) and (d)). These reactions may be expressed as follows.

Calcination without additive:

\[
\text{Ce₂(PO₄)₂HPO₄·H₂O} = \text{CePO₄} + \text{CeP₂O₇} + 3\text{H}_2\text{O} \quad (1)
\]

Calcination with cerium hydroxide:

\[
\text{Ce₂(PO₄)₂HPO₄·H₂O} + \text{Ce(OH)₃} = 3\text{CePO₄} + 3\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \quad (3)
\]

Calcination with NH₄H₂PO₄:

\[
\text{Ce₂(PO₄)₂HPO₄·H₂O} + \text{NH₄H}_2\text{PO₄} = 2\text{CeP₂O₇} + \text{NH}_3 + 3\text{H}_2\text{O} \quad (4)
\]

Scanning electron micrographs of the samples prepared are shown in FIGURES 2. It is seen that...
Ce$_2$(PO$_4$)$_2$HPO$_4\cdot$H$_2$O (a) consisted of plate-like particles, ca. 3 µm in diameter. Plate-like morphology did not change so much after heat treatment without and with cerium hydroxide although the samples changed to CePO$_4$-CeP$_2$O$_7$ mixture (b) and CePO$_4$ (c), respectively. On the other hand, CeP$_2$O$_7$ prepared by the calcination of Ce$_2$(PO$_4$)$_2$HPO$_4\cdot$H$_2$O with NH$_4$H$_2$PO$_4$ consisted of plate-like particles and small amounts of irregular shaped particles, indicating that the plate-like morphology was partly collapsed probably due to the collapse of the particles during the powder preparation since the powders were mixed using an agate mortar.

Transmittance spectra of the thin film of Ce$_2$(PO$_4$)$_2$HPO$_4\cdot$H$_2$O (a), CePO$_4$-CeP$_2$O$_7$ mixture (b), CePO$_4$ (c) and CeP$_2$O$_7$ (d) are shown in FIGURE 3 together with those of calcia-doped ceria, Ce$_{1.8}$Ca$_{0.2}$O$_{1.8}$, nanoparticles (e) and plate-like particles of potassium lithium titanate, K$_{0.8}$Li$_{0.26}$Ti$_{1.73}$O$_4$ (f). Transparency of visible light region of plate-like cerium phosphates (a)-(d) and K$_{0.8}$Li$_{0.26}$Ti$_{1.73}$O$_4$ (f) were almost identical and lower than that of Ce$_{1.8}$Ca$_{0.2}$O$_{1.8}$ nanoparticles, probably due to the scattering of light by large particles. As reported in a previous paper, the onset of absorption of K$_{0.8}$Li$_{0.26}$Ti$_{1.73}$O$_4$ was around 350 nm. In contrast those of Ce$_2$(PO$_4$)$_2$HPO$_4\cdot$H$_2$O, CeP$_2$O$_7$ and CePO$_4$ were around 420, 400 and 380 nm, respectively, which is close to that of Ce$_{1.8}$Ca$_{0.2}$O$_{1.8}$, 400 nm, indicating that the absorption abilities of UV-A (320-400 nm) of cerium phosphates were higher than that of K$_{0.8}$Li$_{0.26}$Ti$_{1.73}$O$_4$. It is also seen that the absorption ability of UV-light around 300 nm was in the order of Ce$_{1.8}$Ca$_{0.2}$O$_{1.8}$ > Ce$_2$(PO$_4$)$_2$HPO$_4\cdot$H$_2$O > CeP$_2$O$_7$ > CePO$_4$-CeP$_2$O$_7$ mixture > CePO$_4$ > K$_{0.8}$L$_{0.26}$T$_{1.73}$O$_4$, indicating that UV-absorption ability of tetravalent cerium phosphate, CePO$_4$, was lower than that of tetravalent cerium phosphates, Ce$_2$(PO$_4$)$_2$HPO$_4\cdot$H$_2$O and CeP$_2$O$_7$, but still higher than that of K$_{0.8}$L$_{0.26}$T$_{1.73}$O$_4$.

In order to evaluate the comfort of applying sample powder to skin, the kinetic friction coefficients (µ) of the artificial leather before and after applying various sample powders on were determined using a friction tester, where the relationship among the friction force (f), kinetic friction coefficient (µ) and applied force (N) to the material after moving can be written as follow.

$$f = \mu N$$

The results are shown in TABLE 1. As expected, plate-like particles of Ce$_2$(PO$_4$)$_2$HPO$_4\cdot$H$_2$O, CeP$_2$O$_7$-CePO$_4$ mixture and CePO$_4$ showed much lower kinetic friction coefficient than titania nanoparticles which was used as a reference material. CeP$_2$O$_7$ particles showed a little higher kinetic friction coefficient (µ) and applied force (N) to the material after moving can be written as follow.

![FIGURE 3 Transmittance spectra of thin films of](image)

FIGURE 4 shows the results of the oxidation catalytic activity evaluation by the Rancimat method for Ce$_2$(PO$_4$)$_2$HPO$_4\cdot$H$_2$O and CeO$_2$ nanoparticles. It can be seen that the onset of conductivity increase of Ce$_2$(PO$_4$)$_2$HPO$_4\cdot$H$_2$O was around 20 h and those of CePO$_4$-CeP$_2$O$_7$ mixture, CePO$_4$ and CeP$_2$O$_7$ were more than 40 h. These values were much longer than that of CeO$_2$ nanoparticles, i.e., 3 h, indicating that the oxidation catalytic activities of these cerium phosphates were much lower than that of Ce$_{1.8}$Ca$_{0.2}$O$_{1.8}$. It is a great advantage when they are used for cosmetics material.

![FIGURE 4 Results of by a Ranshimat test for the valuation of oxidation catalytic activity of](image)
TABLE 1 Kinetic friction coefficient ($\mu$) of the various samples.

<table>
<thead>
<tr>
<th>Sample powder</th>
<th>$\mu/\mu_0$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_2$(PO$_4$)$_3$HPO$_4$H$_2$O</td>
<td>35.2</td>
</tr>
<tr>
<td>CeP$_2$O$_7$-CePO$_4$ mixture</td>
<td>29.0</td>
</tr>
<tr>
<td>CePO$_4$</td>
<td>33.2</td>
</tr>
<tr>
<td>CeP$_2$O$_7$</td>
<td>46.4</td>
</tr>
<tr>
<td>TiO$_2$ (Degussa P25)</td>
<td>84.0</td>
</tr>
</tbody>
</table>

$\mu_0$: Artificial leather without sample, $\mu$: Artificial leather applied the sample powder on.

CONCLUSIONS

From the present results, following conclusions may be drawn.

1) Plate-like particles of Ce$_2$(PO$_4$)$_3$HPO$_4$H$_2$O were prepared by the hydrothermal reaction of Ce(SO$_4$)$_2$ and H$_3$PO$_4$ at 200°C for 3 h.

2) Plate-like particles of CeP$_2$O$_7$-CePO$_4$ mixture, CePO$_4$ and CeP$_2$O$_7$ were prepared by the heat treatment of the plate-like particles of Ce$_2$(PO$_4$)$_3$HPO$_4$H$_2$O without additive and with cerium hydroxide and NH$_4$H$_2$PO$_4$, respectively.

3) Plate-like cerium phosphates showed low oxidation catalytic activity, excellent comfort and superior UV-shielding ability than plate-like titanate, K$_{0.8}$Li$_{0.27}$Ti$_{1.73}$O$_4$.

4) All of plate-like particles of Ce$_2$(PO$_4$)$_3$HPO$_4$H$_2$O, CeP$_2$O$_7$-CePO$_4$ mixture, CeP$_2$O$_7$ and CePO$_4$ may be useful to improve the comfort of Ce$_{1.8}$Ca$_{0.2}$O$_{1.8}$ nanoparticles without loss of UV-shielding ability instead of K$_{0.8}$Li$_{0.27}$Ti$_{1.73}$O$_4$ particles.

ACKNOWLEDGMENTS

This research was partially supported by the Ministry of Education, Culture, Sports, Science and Technology, Scientific Research of Priority Areas "Panooscopic Assembling and High Ordered Functions for Rare Earth Materials" and “Special Education and Research Expenses, Post-Silicon Materials and Devices Research Alliance”.

REFERENCES