Effects of Titanium Oxide on the Optical Properties of Cerium Oxide

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Cerium oxide and CeO_2-TiO_2 mixed oxide particles were prepared using sol-gel method. Addition of TiO_2 changed the apparent bandgap energy to shift the UV-absorption edge to higher wavelengths, and the maximum UV-A absorption was attained in the $50CeO_2$-$50TiO_2$ (in mol%) sample. The results on XRD and TEM showed that crystallinity of the particles became lower with increasing in the TiO_2 content, and both thermal- and photo-catalyses were deactivated by the formation of CeO_2-TiO_2 mixed oxides.

Recently, the harmful effects of ultraviolet rays to human skin have become well known.[1] Sunburn is caused mainly by UV-B (290–320 nm). UV-A (320–400 nm) does not contribute appreciably to sunburn, but causes suntanning as well as other detrimental changes in the skin. While the primary health hazard of UV radiation is skin cancer, other deleterious effects include aging acceleration, as evidenced by formation of wrinkles and blotches. Previously, these problems were dealt with by clothing styles that limited exposure to the sun. Currently, there is a considerable demand for UV filter more effectively, especially in cosmetics.

Cerium oxide (CeO_2) has been regarded as a candidate of UV blocking materials for sunscreen in cosmetics.[2–4] Band gap energy of CeO_2 is 3.1 eV[5] and refractive index in the visible region is about 2.1.[6] This means that CeO_2 absorbs UV light but shows transparent character in visible light. However, UV-A is not completely filtered and high catalytic activity is undesirable when CeO_2 is employed as a sunscreen agent. In this study, therefore, titanium dioxide was added to cerium oxide nanoparticles to enhance the UV-A filtering ability and to decrease in catalysis.

The samples were synthesized by a sol-gel method. Cerium chloride hexahydrate and titanium isopropoxide were dissolved in 300 dm^3 of isopropyl alcohol. The mole ratio of titanium to cerium was adjusted from 10 to 90 mol%, and total cation amount in the solution was fixed to 20 mmol. The mixed solution was added to 200 dm^3 of 3.0 $mol{\cdot}dm^{-3}$ ammonia water. The precipitate was aged with stirring overnight and then was centrifuged and washed with methanol several times. The obtained powder was dried at 353 K overnight and subsequently was calcined at 773 K for 3 h.

The obtained oxide particles were characterized by means of X-ray powder diffraction (XRD, 40 kV and 50 mA, Cu$K\alpha$, MacScience M18XHF-SHA). Size and morphology of the obtained particles were characterized using transmission electron microscopy (Hitachi H-800). Optical reflectance of the powder was measured with a UV-VIS spectrometer (Shimadzu UV-2200) using barium sulfate as a reference. Catalysis was measured by the conductometric determination method (CDM), which utilized oxidation of castor oil.[7] A sample of 0.3 g was mixed with 5 g of castor oil and maintained at 403 K for 3 h with bubbling of air. Volatile molecules produced by the oxidation of the castor oil were trapped into the deionized water placed in an electric conductivity measurement cell. Photocatalysis of the samples was also estimated by light irradiation for 9 h using a solar simulator instead of heating. The degree of catalysis was estimated by the measured conductivity σ after heating or irradiation, which was normalized by the following equation using castor oil only as a blank.

$$I_{ca} = (\sigma_{\text{sample}} - \sigma_{\text{blank}})/\sigma_{\text{blank}}$$

The smaller I_{ca} value means lower catalysis.

XRD patterns of the CeO_2 and $(1\text{-}x)CeO_2$-$xTiO_2$ mixed oxides revealed that doping of TiO_2 decreased crystallinity, and only a halo pattern was observed in the samples that contained titanium more than 50 mol%. The TEM images of the particles and size distribution histograms of them are shown in Figures 1 and 2, respectively. With the increase in TiO_2 content, particle size became smaller and size distribution widths changed narrower. The average particle size of CeO_2, $70CeO_2$-$30TiO_2$, and $50CeO_2$-$50TiO_2$ (in mol%) were 16, 7.5, and 7.2 nm, respectively, which were determined by measuring maximum diameter of more than 150 particles on the TEM photographs. Since cerium oxide and titanium oxide do not form solid solutions in the whole range of the composition,[8] it is considered that the mixed oxide particles became amorphous nanocomposites and that the particle growth was inhibited.

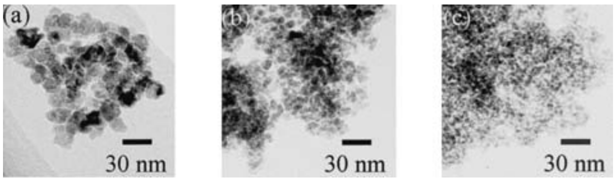

Figure 1. TEM images of (a) CeO_2, (b) $70CeO_2$-$30TiO_2$ (in mol%), and (c) $50CeO_2$-$50TiO_2$ (in mol%) particles.

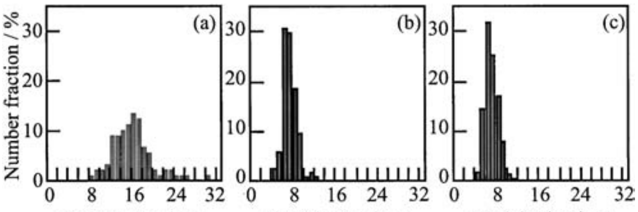

Figure 2. Particle size distribution histgrams of (a) CeO_2, (b) $70CeO_2$-$30TiO_2$ (in mol%), and (c) $50CeO_2$-$50TiO_2$ (in mol%).

From the above results, it is obvious that preparing amorphous particles is necessary to obtain smaller particles.

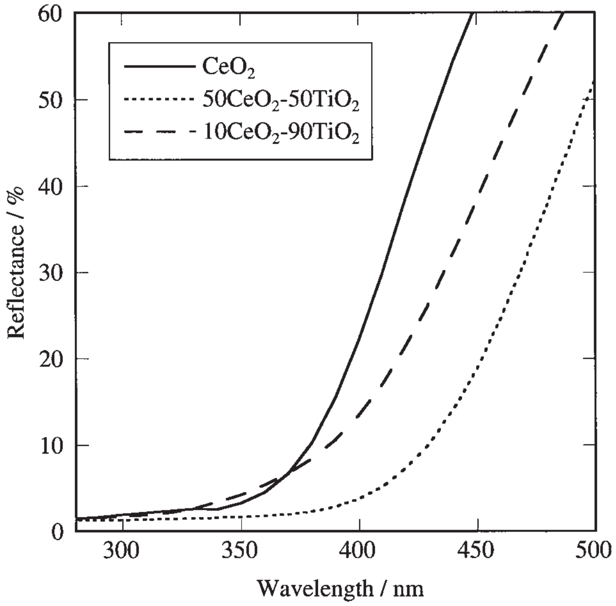

Figure 3. UV-A reflectance spectra of CeO_2, $50CeO_2$-$50TiO_2$ (in mol%), and $10CeO_2$-$90TiO_2$ (in mol%).

The optimization of the composition for UV-A absorption in the amorphous particles was carried out. Figure 3 shows the representative reflection spectra of the pressed powder of the (1-x)CeO_2-$x$$TiO_2$ mixed oxides. In these spectra, low reflectance means high absorption in the corresponding wavelength region. The reflectance of the (1-x)CeO_2-$x$$TiO_2$ samples showed red shift by TiO_2 doping and the maximum absorption of UV-A, 96%, was attained at the composition of $50CeO_2$-$50TiO_2$ (in mol%). It has been reported that decreasing the particle size of oxides induced lattice expansion, decrease in crystallinity, and formation of surface defects, because electrostatic force was decreased by valence reduction or increase in ionicity of metal ions when they became nanoparticles.[9,10] The surface defects also change the color of cerium oxide from pale yellow to dark brown.[11,12] As a result, the apparent bandgap energies of the CeO_2 samples calculated according to the Davis and Mott equation[13] decreased by TiO_2 addition from 3.1 to 2.7 eV at 50 mol% TiO_2 content.

The catalysis indexes I_{ca} are summarized in Table 1. Both thermal and photocatalysis decreased in the (1-x)CeO_2-$x$$TiO_2$ samples. By complexing these oxides, it is considered that the surface defects of the nanoparticles trap oxygen radicals produced from CeO_2 by heating or from TiO_2 by radiation. As a result, both the thermal- and photo-catalyses of cerium oxide and titanium oxide were restrained mutually.

Table 1. Comparison of catalytic activities of the samples

Sample	I_{ca} (thermal)	I_{ca} (photo)
$50CeO_2$-$50TiO_2$ (in mol%)	1.6	0.1
CeO_2	24.5	0.2
TiO_2 (rutile)	4.2	1.7
TiO_2 (anatase)	0.6	75.6
ZnO	11.4	0.3

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