Synthesis and visible light photocatalytic activity of porous CeO$_2$-TiO$_2$ composite powders

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Porous CeO$_2$-20 wt.%TiO$_2$ composite powders having a homogeneous distribution and nanocrystalline were successfully synthesized by a sol-gel process using titanium iso-propoxide and Ce(NO$_3$)$_3$·6H$_2$O as precursors. The particle sizes of the as-received porous CeO$_2$-20 wt.%TiO$_2$ composite powders were measured in the range from 0.3 to 10 µm by SEM. As the calcination temperature was increased up to 1050 °C, the porous composite powders having pores ranging from 0.1 nm to 3 µm in pore size were obtained. The pore frames of CeO$_2$-20 wt.%TiO$_2$ composite powders were less than 500 nm thick and they were nanocrystalline with a dense structure. From a comparison of the photocatalytic activity, the porous CeO$_2$-20 wt.%TiO$_2$ composite powders calcined at 900 °C showed an excellent efficiency for the removal of phenol under UV light. However, in the powders calcined at 600 °C, there was a relatively higher photocatalytic activity than that of other powders under visible light. Hence this sample had a strong edge band at a blue-green wavelength range.

Key words: Nanoparticle, microstructure, photoactivity, visible light.

Introduction

Titanium dioxide (TiO$_2$) having intrinsic properties such as a strong oxidizing power, non toxicity, and long-term photo stability, is the most important material in the area of environmental purification and preparation of solar energy cells [1]. Although TiO$_2$ has excellent properties, its applications are limited due to its poor thermal stability at high temperature as well as a relatively low photocatalytic activity under visible light (λ ≥ 410 nm) [2]. Therefore, in order to improve the thermal stability and the visible light photocatalytic activity of TiO$_2$, additives such as V$_2$O$_5$, WO$_3$, CdS and SnO$_2$ have been added. These oxides can be act as a Lewis acid because they can easily generate photons and also the oxide particles can play a significant role as a thermal stabilizer against phase transformations [3, 4]. The dispersion of the secondary phase into the TiO$_2$ phase has been carried by a sol-gel process. This method can be easily controlled to give a stoichiometric solid solution and a homogeneous distribution of nano particles [4-6].

In this study, porous CeO$_2$-20 wt.%TiO$_2$ composite powders were synthesized using a sol-gel method with titanium iso-propoxide and Ce(NO$_3$)$_3$·6H$_2$O. The crystal structure and microstructure of porous CeO$_2$-20 wt.% TiO$_2$ composite powders were investigated using XRD and TEM techniques depending on the calcination temperature. To evaluate the photocatalytic activity of porous CeO$_2$-TiO$_2$ composite powders, the removal of phenol in an aqueous solution was carried out.

Experimental

For the preparation of Ti-sol, the starting materials used for the sol-gel process were titanium iso-propoxide (Ti(O-iPr)$_4$, Aldrich chemical, 99%), acetylacetone (jussei, 99%), isopropanol (Dongwoo fine chemical, 98%) and ethylene glycol monoethyl ether (Jussei, 99%). The Ti-sol solution was prepared by adding Ti-isopropoxide (0.2 mole, 56.8 g) into acetylacetone (0.2 mole) which was refluxed for 2 h at 90 °C and under vigorous stirring. Isopropanol and ethylene glycol monoethyl ether were mixed and maintained in the same condition for 2 h. After 309 g of Ce(NO$_3$)$_3$·6H$_2$O solution was slowly added using a peristaltic pump, an homogeneous Ce-Ti gel was obtained by gelling under heating and stirring at 80 °C for 2 h. The synthesized Ce-20 wt.% TiO$_2$ composite gels were left in a dry oven at 80 °C for 24 h. The Ce-20 wt.% TiO$_2$ composite powders were calcined in air at temperatures of 450, 600, 750, 900 and 1050 °C.

To investigate the performance of phenol decomposition, 0.2 wt.% of porous Ce-20 wt.% TiO$_2$ composite powders were dispersed in an aqueous solution in a pyrex glass beaker. As a UV and visible radiation source, a 40 W medium-pressure mercury lamp having a range of 250~390 nm in wavelength and visible light irradiation (λ ≥ 420 nm) were used. To determine the change of phenol concentrations during UV and visible irradiation, a few
millilitres of solution were taken from the reaction solution. UV-visible spectrometer (HP8453, Hewlett Packard, USA) simultaneously measured the absorbance of phenol within the range from 200 nm to 700 nm and determined the residual concentration of phenol at the secondary absorption band of 270 nm using a 3-point calibration curve. The crystal structure and the morphology of porous CeO$_2$-TiO$_2$ composite powders were studied using X-ray diffraction (D/MAX2500H, Rigaku, Japan) and FE-TEM (Technai G2F3S-Twin, FEI Netherlands).

**Results and Discussion**

Fig. 1 shows the X-ray diffraction patterns of porous CeO$_2$-20 wt.%TiO$_2$ composite powders as a function of the calcination temperature. In the sample of the (a) as-received powder, no sharp peaks were observed in the XRD pattern, suggesting that the powder is in an amorphous state. However, in the sample (b) calcined from 450 °C to 750 °C, CeO$_2$ peaks were detected without TiO$_2$ peaks. But in the XRD profile of the sample (c) calcined at 900 °C, a small amount of anatase and rutile phases of TiO$_2$ were detected. On increasing the calcination temperature, CeO$_2$ peaks became sharp and also most of the anatase phase was transformed to the rutile phase.

Fig. 2 shows SEM images of porous CeO$_2$-20 wt.%TiO$_2$ composite powders synthesized by a sol-gel method and calcined at 1050 °C. In Fig. 2(a), the as-received CeO$_2$-20 wt.%TiO$_2$ composite powder shows a large number of pores 0.3~10 µm in diameter randomly dispersed in the sample. After calcination at 1050 °C, Fig. 2(b), the fracture surface was composed of many pores. They were characterized as continuously open pores and also showed a comparatively homogeneous distribution.

Fig. 3 shows typical TEM micrographs of porous CeO$_2$-20 wt.%TiO$_2$ composite powders depending on the calcination temperature. In Fig. 3(a), the as-received sample shows a plate shape with a size range of 0.3~10 µm. The spherical shape of TiO$_2$ particles gives a faint contrast about 20~150 nm in diameter. However, in the sample calcined at 1050 °C, the TiO$_2$ particles existed with a hybrid type; i.e., the nano-sized spherical and large-sized irregular shapes were dispersed in the interior grains of the CeO$_2$ matrix or at its grain-boundaries.

To clearly understand the photocatalytical activity of porous CeO$_2$-20 wt.%TiO$_2$ composite powders, the degradation of phenol was carried out. Phenol as an aromatic compound, is well known as an environmental pollutant in water, has both toxic and corrosive properties. Fig. 4 shows the degradation of phenol by porous CeO$_2$-20 wt.%TiO$_2$ composite powders depending on the light source. In case of irradiating with ultraviolet light, the removal of phenol showed a high efficiency and similar patterns. After UV irradiation for 2 h, the residual concentration of phenol in

![Fig. 1. XRD patterns of porous CeO$_2$-20 wt.%TiO$_2$ composite powders depending on the calcination temperature; (a) as-received, (b) 750 °C, (c) 900 °C and (d) 1050 °C.](image1)

![Fig. 2. SEM micrographs of porous CeO$_2$-20 wt.% TiO$_2$ composite powders depending on the calcination temperature; (a) as-received and (b) calcined at 1050 °C.](image2)

![Fig. 3. TEM images of porous CeO$_2$-20 wt.%TiO$_2$ composite powders depending on the calcination temperature; (a) as-received and (b) calcined at 1050 °C.](image3)

![Fig. 4. The degradation of phenol by porous CeO$_2$-20 wt.%TiO$_2$ composite powders under a UV light source.](image4)
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The porous CeO$_2$-20 wt.% TiO$_2$ composite powders calcined at 600, 750, 900 and 1050 °C were 15.9, 5.9, 2.4 and 9.8 ppm, respectively. The degradation rates were increased in the following order: sample calcined at 600 °C $>$ 750 °C $>$ 1050 °C $>$ 900 °C.

Fig. 6 shows the UV-visible diffuse reflectance of various samples. The TiO$_2$ (Degussa P-25) showed a single sharp edge at 360 nm, while porous CeO$_2$-20 wt.% TiO$_2$ composite powders showed two absorption edges near 450 nm. Although no clear optical absorption peaks in the visible region was observed, the light absorption band significantly shifted in the red direction. At the same time, porous CeO$_2$-20 wt.% TiO$_2$ composite powders calcined at 600 °C showed a higher visible light absorption ability than other samples. As a result, we can understand that all of the porous CeO$_2$-20 wt.% TiO$_2$ composite powders have a strong edge band at the blue-green wavelength range, porous CeO$_2$-20 wt.% TiO$_2$ composites were expected to show photocatalytic activity under visible light.

Summary

Porous CeO$_2$-20 wt.% TiO$_2$ composite powders were successfully synthesized by a sol-gel process. The TiO$_2$ phases strongly depended on the calcination temperatures. For a sample calcined at 1050 °C, CeO$_2$ peaks were sharp and also most of the anatase phase was transformed to the rutile phase. The porous TiO$_2$-80 wt.% CeO$_2$ composite powders calcined at 900 °C showed excellent photocatalytic behavior under UV light. But porous CeO$_2$-20 wt.% TiO$_2$ composite powders calcined at 600 °C, showed a strong edge band at the blue-green wavelength range, with a relatively higher photocatalytic activity than that of other powders under visible light.

References