

Synthesis and visible light photocatalytic activity of porous CeO₂-TiO₂ composite powders

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Porous CeO₂-20 wt.%TiO₂ composite powders having a homogeneous distribution and nanocrystalline were successfully synthesized by a sol-gel process using titanium iso-propoxide and Ce(NO₃)₃·6H₂O as precursors. The particle sizes of the as-received porous CeO₂-20 wt.%TiO₂ 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 CeO₂-20 wt.%TiO₂ 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 CeO₂-20 wt.%TiO₂ 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 (TiO₂) 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 TiO₂ 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 ($\lambda \geq 410$ nm) [2]. Therefore, in order to improve the thermal stability and the visible light photocatalytic activity of TiO₂, additives such as V₂O₅, WO₃, CdS and SnO₂ 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 TiO₂ 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 CeO₂-20 wt.%TiO₂ composite powders were synthesized using a sol-gel method with titanium iso-propoxide and Ce(NO₃)₃·6H₂O. The crystal structure and microstructure of porous CeO₂-20 wt.% TiO₂ composite powders were investigated using XRD and TEM techniques depending on the calcination temperature. To evaluate the

photocatalytic activity of porous CeO₂-TiO₂ 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%), acetylacetonate (junsei, 99%), isopropanol (dongwoo fine chemical, 98%) and ethylene glycol monoethyl ether (junsei, 99%). The Ti-sol solution was prepared by adding Ti-isopropoxide (0.2 mole, 56.8 g) into acetylacetonate (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(NO₃)₃·6H₂O 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.% TiO₂ composite gels were left in a dry oven at 80 °C for 24 h. The Ce-20 wt.% TiO₂ 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.% TiO₂ 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 ($\lambda \geq 420$ nm) were used. To determine the change of phenol concentrations during UV and visible irradiation, a few

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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 photocatalytic 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

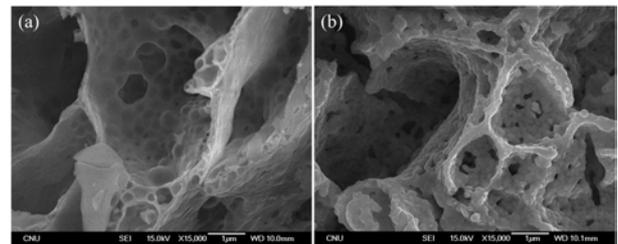


Fig. 2. SEM micrographs of porous CeO_2 -20 wt.% TiO_2 composite powders depending on the calcination temperature; (a) as-received and (b) calcined at 1050 °C.

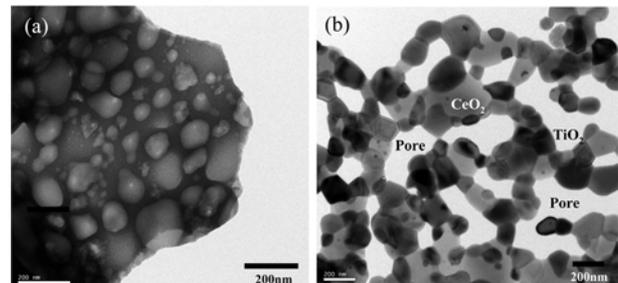


Fig. 3. TEM images of porous CeO_2 -20 wt.% TiO_2 composite powders depending on the calcination temperature; (a) as-received and (b) calcined at 1050 °C.

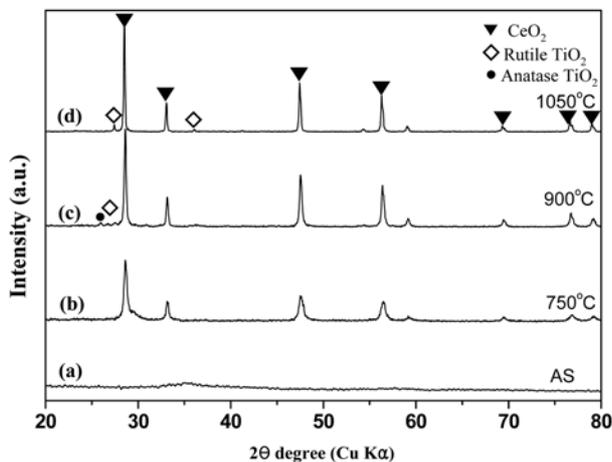


Fig. 1. XRD patterns of porous CeO_2 -20 wt.% TiO_2 composite powders depending on the calcination temperature; (a) as-received, (b) 750 °C, (c) 900 °C and (d) 1050 °C.

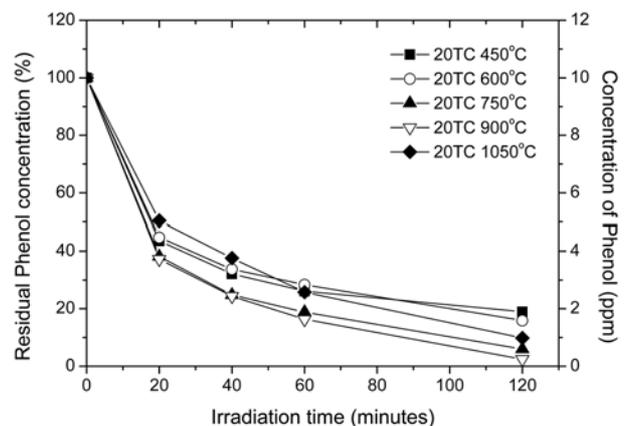


Fig. 4. The degradation of phenol by porous CeO_2 -20 wt.% TiO_2 composite powders under a UV light source.

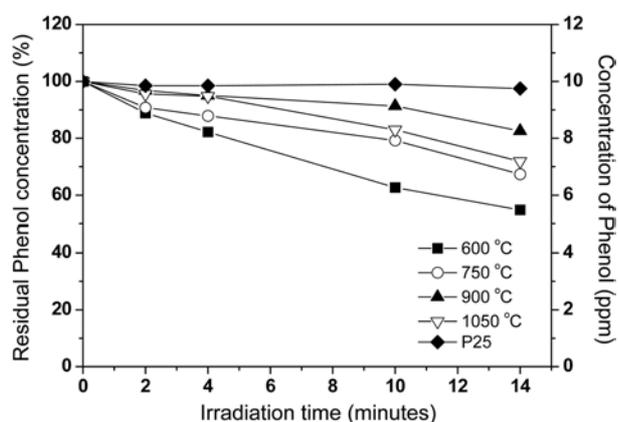


Fig. 5. The degradation of phenol by porous CeO₂-20 wt.%TiO₂ composite powders under a visible light source.

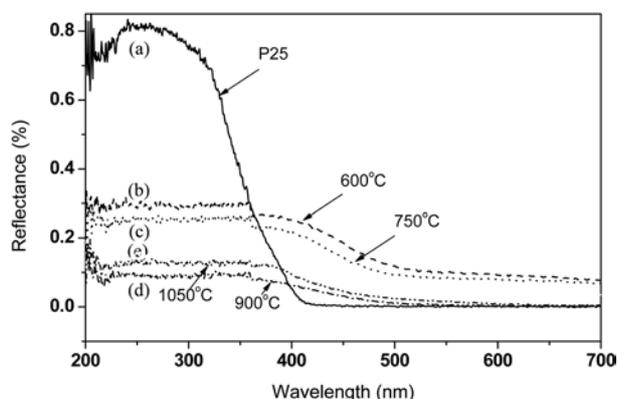


Fig. 6. The UV-visible diffuse reflectance of (a) TiO₂ (Degussa P-25) powder and porous CeO₂-20 wt.%TiO₂ composite powders calcined at (b) 600, (c) 750, (d) 900, and (e) 1050 °C.

the porous CeO₂-20 wt.%TiO₂ composite powders calcined at 600, 750, 900 and 1050 °C were 15.9, 5.9, 2.4 and 9.8 ppm, respectively.

To investigate the visible light catalytic activity, porous CeO₂-20 wt.%TiO₂ composite powders were examined under visible light irradiation ($\lambda \geq 420$ nm). Fig. 5 shows the performance for phenol decomposition with porous CeO₂-20 wt.%TiO₂ composite powders calcined at various temperatures. However, in the case of visible light irradiation, their photocatalytic activity shows a relatively lower behavior than that of ultraviolet light irradiation. After 14 h of visible irradiation, the residual concentration of phenol were measured at 5.5 ppm, 6.7 ppm, 8.3 ppm and 7.2 ppm for samples calcined at 600 °C, 750 °C, 900 °C and 1050 °C,

respectively. Their 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 TiO₂ (Degussa P-25) showed a single sharp edge at 360 nm, while porous CeO₂-20 wt.%TiO₂ 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 CeO₂-20 wt.%TiO₂ 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 CeO₂-20 wt.%TiO₂ composite powders have a strong edge band at the blue-green wavelength range, porous CeO₂-20 wt.%TiO₂ composites were expected to show photocatalytic activity under visible light.

Summary

Porous CeO₂-20wt.%TiO₂ composite powders were successfully synthesized by a sol-gel process. The TiO₂ phases strongly depended on the calcination temperatures. For a sample calcined at 1050 °C, CeO₂ peaks were sharp and also most of the anatase phase was transformed to the rutile phase. The porous TiO₂-80 wt.%CeO₂ composite powders calcined at 900 °C showed excellent photocatalytic behavior under UV light. But porous CeO₂-20 wt.%TiO₂ 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.

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