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Synthesis and Photocatalytic Activity of TiO_2-ZrO_2 Nano-Sized Powders by Sol-Gel Process

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ABSTRACT

TiO_2-ZrO_2 powders were successfully synthesized by the sol-gel process using titanium iso-propoxide as a precursor. The amorphous TiO_2 particles, 70 nm in size, homogenously adhered to the surface of ZrO_2 the powders. After calcination at 450°C, most of the TiO_2 powders appeared as an anatase type, whereas they changed to a rutile phase at 750°C. For comparison of photocatalytic activity, TiO_2-ZrO_2 nano-sized powders calcined at 450°C, 600°C, and 750°C were used. In the TiO_2-20 wt%ZrO_2 powders calcined at 450°C, there was excellent removal efficiency of Methyl Orange (MO). For the calcination temperature increased, TiO_2-ZrO_2 nano-sized powders increased ZrO_2 contents showed the good photoactivity for the photooxidation of MO.

Key words : Nanocrystalline, TiO_2-ZrO_2 nano-sized powders, Methyl orange, Photocatalytic activity, Sol-gel method

1. Introduction

Titanium dioxide (TiO_2) has used widely in environmental fields because of its intrinsic properties such as strong oxidizing power, nontoxicity, non-energy consuming and long-term photostability.[1-6] In order to improve photocatalytic activity, additives such as V_2O_5, WO_3, CdS, and SnO_2 were added to the TiO_2 phase.[7-10] These oxides can be acted on as a Lewis acid because they can easily generate the photon. Thus, the dispersion of above the oxide ceramics in the TiO_2 increases the efficiency of photocatalytic activity.[9] However, they have some disadvantages for application due to their poor thermal stability and phase transformation at high temperatures. Therefore, many studies have focused on the development of thermal resistance catalysts using secondary phase. ZrO_2 is an especially good candidate material as a secondary phase because of its good mechanical properties, chemical inertia, corrosion resistance and high temperature stability.

Photocatalytic activity depends on the mole ratio of each particle, thermal treatment conditions, the crystalline size and the specific surface area. The effect of crystalline size is especially significant appearing in the purification of pollutants in water, and the optimum particle size was measured to be less than 20 nm the depending on the experimental conditions. Therefore, the properties of catalyst were closely related to the fabrication methods including flame oxidation,[11] co-precipitation,[12] chemical vapor deposition,[13] and the sol-gel process.[14-16] Among them, the sol-gel process is considered as a good approach for the synthesis of ultra fine powders because it can easily control the solid solution with a stoichiometry and a homogeneous distribution of all components.[16,17] In particular, the morphology and crystallization of TiO_2 particles is closely related to the calcination conditions such as temperature and duration of time.

In this study, using the sol-gel process, TiO_2-ZrO_2 nano-sized powders were synthesized to study the retardation effect of anatase-to-rutile phase transformation depending on the ZrO_2 content and calcination temperatures. And also, the performance of Methyl Orange (MO) degradation was investigated using the UV-visible spectroscopy.

2. Experimental Procedure

$TiO_2(1-\chi)-\chi ZrO_2$ (χ = 0.2, 0.4, 0.6, and 0.8) nano-sized powders were synthesized using the sol-gel method with titanium iso-propoxide (Aldrich chemical, 99%) and ZrO_2 nano powders (Tosoh Co., Japan). Detailed synthesis process was followed by paper.[18] Synthesized $TiO_2(1-\chi)-\chi ZrO_2$ nano-sized powders were calcined at 450°C, 600°C, and 750°C for one hour in air.

The crystal structures of TiO_2-ZrO_2 nano-sized powders were identified by X-ray diffraction (D/MAX250, Rigaku) with CuKα radiation (λ = 1.54056 Å). The morphology and microstructures of TiO_2-ZrO_2 composite powders were studied using TEM (JEM-2010, Jeol).

To investigate the efficiency of removal of Methyl Orange (MO), 0.2 wt% of TiO_2-ZrO_2 composite powders were dispersed in an aqueous solution in a pyrex beaker. As an UV

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irradiation source, 40 W medium-pressure mercury lamp was used. To determine the residual concentration change of MO during UV irradiation, small amounts of solution taken from the reaction solution were analyzed by UV-visible spectrometer. An UV-visible spectrometer (HP8453, Hewlett Packard) was used to measure the absorbance of MO within a range from 200 nm to 700 nm and determine simultaneously the concentration of MO at the maximum wavelength of 465 nm using a 3-point calibration curve.

3. Results and Discussion

3.1. Characterization of TiO_2-ZrO_2 Composite Powders

Fig. 1 shows the typical TEM images of the as-received TiO_2-20 wt%ZrO_2 and TiO_2-80 wt%ZrO_2 nano-sized powders. On the agglomerated particles, the TiO_2 particles adhered to the ZrO_2 surface having a spherical shape. The ZrO_2 particles show a dark contrast and are about 70 nm in diameter while the TiO_2 is about 20 nm in diameter. In the TEM images, we can see that the dark contrast increases as the

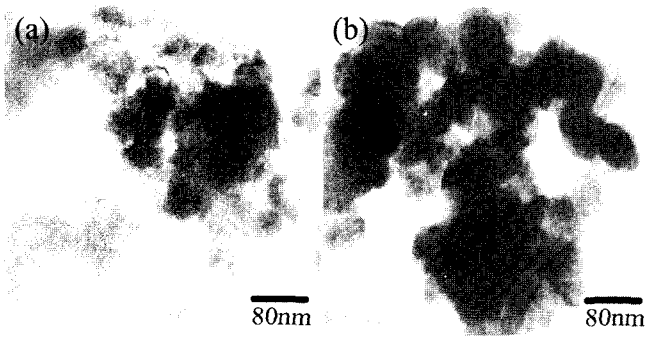

Fig. 1. TEM micrographs of as-received TiO_2-ZrO_2 composite powders depending on the TiO_2 contents; (a) TiO_2-20 wt%ZrO_2 and (b) TiO_2-80 wt%ZrO_2.

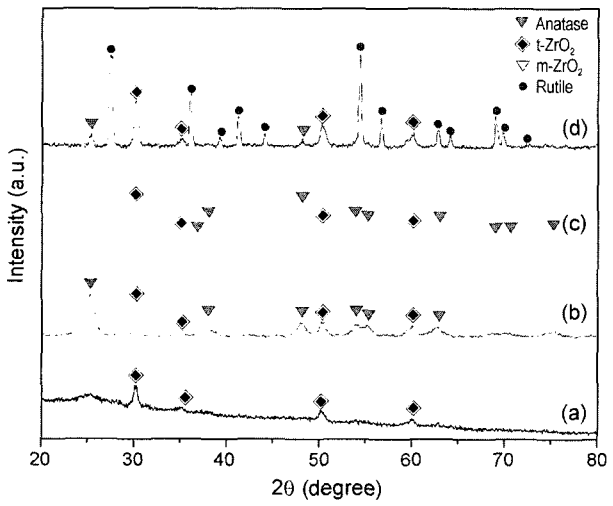

Fig. 2. XRD patterns of TiO_2-20 wt%ZrO_2 composite powders calcined at (a) as-received, (b) 450°C, (c) 600°C, and (d) 750°C.

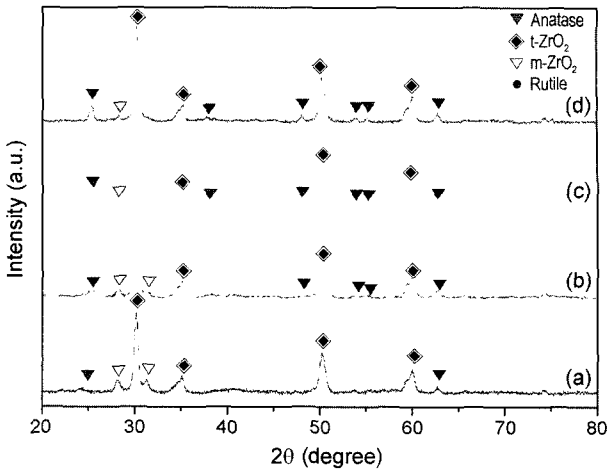

Fig. 3. XRD patterns of TiO_2-80 wt%ZrO_2 composite powders calcined at (a) as-received, (b) 450°C, (c) 600°C, and (d) 750°C.

ZrO_2 content increases. Also, the aggregation of TiO_2 particles remarkably increases as the TiO_2 content increases.

Fig. 2 shows the XRD patterns of as-received TiO_2-20 wt% ZrO_2 nano-sized powders depending on the calcination temperatures. ZrO_2 powders existed with a tetragonal structure while TiO_2 was an amorphous phase as indicated in Fig. 2(a). The amorphous TiO_2 powders were crystallized with an anatase type at 450°C (Fig. 2(b)), and they still existed without any phase transformation although there was some change of sharp peaks, while the anatase structure of TiO_2 was transformed to the rutile type at 750°C (Fig. 2(d)). In the case of the TiO_2-40 wt%ZrO_2, TiO_2-60 wt%ZrO_2 and TiO_2-80 wt%ZrO_2 nano-sized powders, as the ZrO_2 content increases, the peak intensity of the rutile remarkably decreases at the calcination temperature of 750°C while anatase peaks were strong. However, in Fig. 3(d), the anatase peaks were only detected without rutile peaks. This result indicates that when the anatase TiO_2 is transformed to the rutile type, there is a critical particle size of TiO_2; i.e., in the TiO_2-20 wt%ZrO_2 nano-sized powders, the abundant content of TiO_2 attached on the ZrO_2 can be easily grown to a very large size to decrease the surface energy as the of calcination temperature increases, while with the TiO_2-80 wt% ZrO_2 composite powders, the TiO_2 particles exist separately without agglomeration due to the small amount of TiO_2. As a result, it can be understood that ZrO_2 nano-sized particles act as a stablizer of the anatase-to-rutile phase transformation of TiO_2.

3.2. Photodegradation of Methyl Orange

Fig. 4 shows the absorption spectra of Methyl Orange (MO, 25 ppm) depending on the irradiation time in an aqueous solution, in which TiO_2-20 wt%ZrO_2 nano-sized powders calcined at 450°C were dispersed. The wavelength peak of MO showed the primary absorbance at 465 nm. The secondary absorption peak was detected at 271 nm which indicates the phenyl group. The maximum peak indicates that sub-

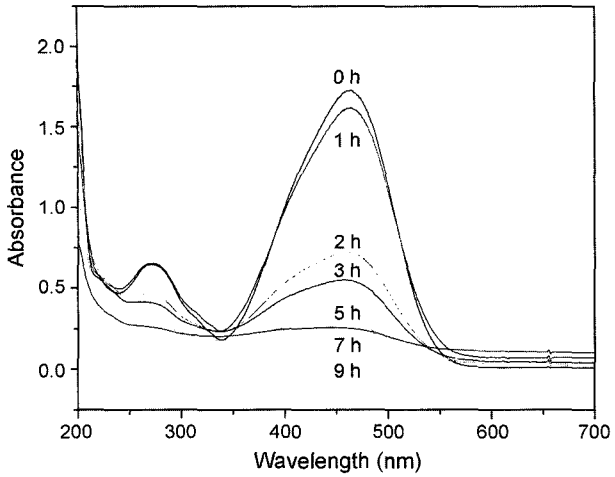

Fig. 4. The UV-visible absorption spectra of methyl orange depending on the irradiation times.

stituents such as the azo, amine and sulfonyl groups can produce a new electron transfer band.[19] An Hg lamp ranging from 250 to 390 nm in wavelength was used as an UV light source. The absorbance of MO decreased as increase the UV irradiation time increased. After 9 h of UV irradiation, the baseline of MO was a flat. From the result, it can be understood that the substituents of benzene and MO were decomposed efficiently by the photocatalytic activity of TiO_2-ZrO_2 nano-sized powders.

Fig. 5 shows the performances of MO decomposition in the TiO_2-ZrO_2 nano-sized powders calcined at 450°C. In the case of TiO_2-20 wt% ZrO_2 and TiO_2-40 wt%ZrO_2 composite powders, the removal efficiency of MO showed a similar pattern; i.e, the arrival time for the half value of initial concentration took about 2 h and then the MO concentration reached about 0% after 10 h. On the other hand, the removal efficiency of TiO_2-60 wt%ZrO_2 and TiO_2-80 wt%ZrO_2 powders was lower than that of TiO_2-40 wt%ZrO_2 nano-sized powders. After UV irradiation for 10 h, the residual concentration of MO in the TiO_2-60 wt%ZrO_2 and TiO_2-80 wt%ZrO_2

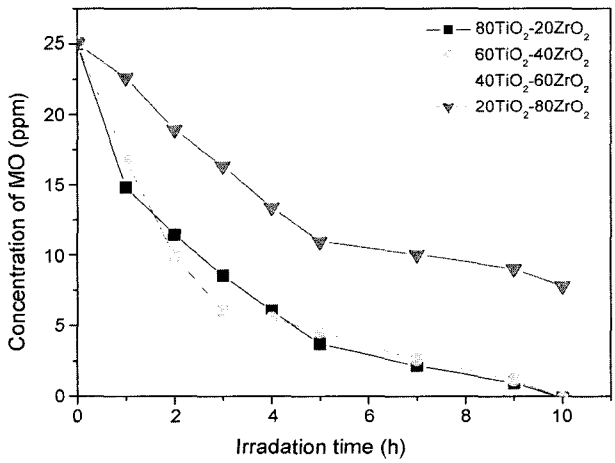

Fig. 5. The performances for MO decomposition compared with TiO_2-ZrO_2 composite powders calcined at 450°C.

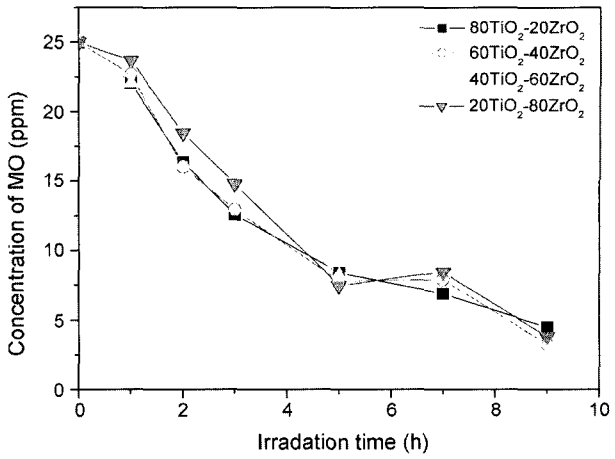

Fig. 6. The performances for MO decomposition compared with TiO_2-ZrO_2 composite powders calcined at 750°C.

nano-sized powders were 5.5 ppm and 7.8 ppm, respectively. This result indicated that removal efficiency increased as the anatase content increased. Also, from the results of similar removal efficiency in the TiO_2-40 wt% ZrO_2 and TiO_2-20 wt%ZrO_2 nano-sized powders, TiO_2-40 wt%ZrO_2 nano-sized powders showing high intensity of anatase peaks is recommended to decompose organic materials.

Fig. 6 shows the performance of MO degradation in the TiO_2-ZrO_2 nano-sized powders calcined at 750°C. Without dependence on TiO_2 concentration, they showed the same tendency. However, the efficiency of the TiO_2-20 wt%ZrO_2 and TiO_2-40 wt%ZrO_2 nano-sized powders was remarkably lower than when calcined at 450°C as shown in Fig. 5. Thus, after 9 h of UV irradiation, the residual concentrations of MO in the TiO_2-20 wt%ZrO_2 and TiO_2-40 wt%ZrO_2 were 4.46 ppm and 3.25 ppm, respectively.

After 9 h of UV irradiation, the residue concentrations of MO determine 4.46 ppm for 80 wt%TiO_2-ZrO_2, 3.25 ppm for 60 wt%TiO_2-ZrO_2, 2.26 ppm for 40 wt%TiO_2-ZrO_2, and 3.78 ppm for 20 wt%TiO_2-ZrO_2, respectively. They have increased the degradation rates in the following order: 40 wt%TiO_2-ZrO_2 > 60 wt%TiO_2-ZrO_2 > 20 wt%TiO_2-ZrO_2 > 80 wt%TiO_2-ZrO_2. As a result, we can analogize that the removal efficiency is related with the state of phase transformation (anatase→rutile). The quantitative analysis of anatase was calculated with Spur and Mayers relation equation.[20] Calculated values and the anatase contents decrease in the following order: 40 wt%TiO_2-ZrO_2 (73.1%) > 60 wt%TiO_2-ZrO_2 (26.4%) > 20 wt%TiO_2-ZrO_2 (20%) > 80 wt% TiO_2-ZrO_2 (13.4%). The order of anatase content is exactly corresponded with the removal efficiency of MO.

4. Conclusions

From the study on the phase transformation and photocatalytic activity of TiO_2-ZrO_2 nano-sized powders synthesized by the sol-gel process, the following results were obtained.

1. In the as-received TiO_2-ZrO_2 nano-sized powders, nano-sized TiO_2 particles having an amorphous structure adhered to the ZrO_2 surface, and the phenomenon of aggregation was increased as the increase of TiO_2 content increased.

2. In TiO_2-ZrO_2 nano-sized powders calcined at 450°C, TiO_2 was an anatase type independent of contents. On the other hand, in the TiO_2-20 wt%ZrO_2 nano-sized powders calcined at 750°C, the anatase to rutile phase transformation increased remarkably while in the TiO_2-80 wt%ZrO_2 nano-sized powders, it was retarded.

3. The TiO_2-40 wt%ZrO_2 and TiO_2-20 wt%ZrO_2 nano-sized powders calcined at 450°C showed an excellent efficiency of photocatalytic activity, but in the sample calcined at 750°C, the efficiency of MO decomposition was reduced due to the appearance of the rutile type, having a low efficiency of photocatalytic activity.

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