Fabrication of Ti/TiO₂ Composite Photocatalyst by Spark Plasma Sintering and its Characteristics

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Environmental pollution and energy crisis are two urgent problems for modern society. Since Fujishima and Honda discovered the photocatalytic splitting of water on TiO₂ electrodes in 1972, Photocatalysts, a potential method to solve the above problems has aroused researchers' interests all over the world. Improvement of the photocatalyst by the composite effect is investigated very actively. In the present study, from the practical viewpoint, Ti/TiO₂ composite photocatalyst with comparatively cheap Ti was fabricated using spark plasma sintering (SPS) technique.

TiO₂ powders (ST-01, Ishihara Sangyo Kaisha, Ltd., Japan) with anatase form and an average diameter of 7 nm were used as the matrix material. Ti powders with 99.8 % purity and an average diameter of 35 μm were used as the addition metal. TiO₂ powders adding 0, 1, 3, 5 and 10 wt% Ti powders were mixed by a rotary mixer for 24 h, rotary speed of about 10 rpm. The mixed powders of 3 g were put in a graphite die with 20 mm inner diameter, and sintered at 973 K for 3 min by SPS (SPA-1030, Sumitomo Coal Mining Co. Ltd., Japan) under vacuum and pressure of 30 MPa with the heating rate 100 K/min. The composite photocatalyst fabricated by the above processes was examined by scanning electron microscope (SEM) (JEOL, JSM16100) and electron probe microanalyzer (EPMA) (SHIMADZU, EPMA-1600), and the crystal form was analyzed by X-ray diffractometer (XRD) (JEOL, JDX-3530). Cu-Kα radiations under conditions of 30 kV and 30 mA were used.

Photocatalytic activity was evaluated by measuring the decomposition rate of methylene blue (MB) solution at room temperature. The composite photocatalyst was put on the bottom of a cylinder-shaped cell with φ 20 × 50 mm. Then Photocatalytic activity was evaluated by using 7 ml of MB solution with 26.7 mM (= 10 ppm, where μM = μmol L⁻¹) under an intensity of the ultraviolet radiation of 1 mW/cm² for 7 h at room temperature. These conditions were referenced to Japanese industrial standard (JIS R 1703-2). The absorbance of MB solution was measured by a colorimeter (mini photo 10, Sanshin Kogyo) with a wavelength of 660 nm. The gradient, k [nM·h⁻¹] of time-MB solution concentration line was calculated out by the least-squares method removing the data of the first 1 h, and is used as the degradation constant.

Figure 1 shows element maps of EPMA for the case of 1 wt%Ti. In this figure, the composition image, the maps of Ti and O are shown in (a), (b) and (c), respectively. From Fig. 1 (c), it is found that there is an oxygen distribution with a high intensity on the layer around a Ti particle. It hints that the layer is an oxide of titanium. Figure 2 shows XRD patterns of the composite photocatalysts. In the case of the composite photocatalysts added 0–5 wt% Ti, the crystal form is almost anatase. On the other hand, in case of 10 wt% Ti, the crystal form is a compatible phase with anatase and rutile. Form the results of Fig. 1 and 2, it seems that the layer around Ti powders is rutile form. It is considered that rutile phase increased relatively with increasing the addition amount of Ti.

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The degradation constant, $k$, shows in Fig. 3. It is found that the degradation constant goes up and reaches a peak around 1 wt% Ti, and then decreases with increasing the addition amount of Ti. Also, photocatalytic activity of the case of 1–5 wt% Ti is higher than that of the photocatalyst without addition of Ti powders. However, photocatalytic activity in the case of 10 wt% Ti is lower than that of the photocatalyst without addition of Ti powders. It can be understood that it is related with the separation effect of the electrical charge because of the composite effect between anatase TiO$_2$ and metallic Ti. However, photocatalytic activity was decreased in case of 10 wt% Ti because of decreasing of TiO$_2$ area on the surface of the composite photocatalyst according to a large addition amount of Ti powders.

In the present study, Ti/TiO$_2$ composite photocatalysts with a uniform distribution of Ti powders were fabricated by a process including SPS technique. Anatase crystal form was kept for the composite photocatalyst with 0–5 wt% Ti. The composite photocatalysts with 10 wt% Ti had two crystal forms, anatase and rutile. High photocatalytic activity appeared because of the composite effect. Photocatalytic activity goes up with addition amount of Ti powders and reached a peak around 1 wt% Ti, and then decreased.
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