Visible-light sensitive photocatalytic activity of iron- and phosphorus-modified TiO_2 with rutile structure

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Abstract:

Nanocrystalline rutile TiO_2 particles were prepared via hydrothermal treatment of Ti-containing precursors obtained by low-temperature aging for a transparent diluted HCl solution of amorphous TiO_2. The products were modified with Fe and P and their photocatalytic activities under visible-light irradiation were examined. It was found that the photocatalytic activity of rutile TiO_2 was significantly increased by FeO_x loading and subsequent addition of phosphoric acid. UV-vis results suggested a high dispersion of Fe species on the catalyst surface by the addition of phosphoric acid.

Keywords: TiO_2 photocatalysts, rutile structure, Fe- and P-modification.

1. Introduction

Photocatalytic activities of TiO_2 crystals with the anatase structure have been extensively studied so far among the polymorphs of titanium oxides. On the other hand, TiO_2 crystals with the rutile structure have gained considerable attention in recent years as they have a narrower band gap of 3.0 eV compared to anatase TiO_2 (3.2 eV). It is well known that rutile TiO_2 can be obtained by a high-temperature calcination of anatase particles. However, such calcination treatment leads to agglomeration and growth of the nanoparticles, which are not favorable for catalytic applications. In this study, rutile-type TiO_2 nanocrystals having large surface areas were prepared via a low-temperature aging and subsequent hydrothermal treatment. Using the thus-obtained products, rutile TiO_2 catalysts modified with small amounts of iron oxides and phosphoric acid were prepared and their photocatalytic activities under visible-light irradiation were examined.

2. Experimental

Nanocrystalline titanium oxides having the rutile structure were prepared by a modified procedure based on the recipe reported by Yin et al [1]. First, titanium tetraisopropoxide (TTIP) was added to water, and white precipitates formed were collected by filtration. The precipitates were added to an aqueous solution of HCl (0.5 mol/L), and the mixture was stirred at room temperature to obtain a transparent solution. The resultant solution was aged at 40 °C for 48 h, and the white powders formed were collected by centrifugation. After drying at 100 °C, a portion of the obtained precursor powders (3.0 g) was added to water (10 mL) and the mixture was hydrothermally heated at 220 °C for 4 h in a Teflon-lined autoclave. The product was collected by centrifugation, washed with water repeatedly, and dried in air, followed by calcination at 500 °C in air for 1 h. The sample thus-obtained is designated as TiO_2(R). Loading of iron oxides (1.5 wt% as Fe) was carried out by an impregnation method. To an aqueous solution of $Fe(NO_3)_3$, a portion of TiO_2(R) powders was added and dried, followed by calcination at 300 °C for 30 min. The obtained sample is designated as Fe(1.5wt%)-TiO_2(R). TiO_2(R) or Fe(1.5wt%)-TiO_2(R) was mixed with appropriate amounts of H_3PO_4 aqueous solution (0.37–3.7 wt% as P) and dried at 80 °C.

The photocatalytic activity was evaluated by photocatalytic decomposition of acetaldehyde under visible-light irradiation. The catalyst (0.2 g) was set in a closed glass vessel (1.0 L) and 0.2 mmol of acetaldehyde was injected in the vessel. It was then irradiated with visible light by using a 300-W xenon lamp and a UV cut-off filter (L-42, Asahi Technoglass). After certain periods of the irradiation, the amounts of CO_2 evolved were measured by gas chromatography.

3. Results and discussion

In Figure 1, XRD patterns of the catalysts are shown. Only the diffraction peaks for the rutile structure were observed for all the samples. The TiO_2(R) sample had a crystallite size of 21 nm and a relatively large BET surface area of 32 m^2/g. As the modifications with Fe and P were carried out at relatively low temperatures, the small crystallite sizes for the Fe- and P-modified samples were same as that of TiO_2(R). On the contrary, the BET surface area decreased slightly because of aggregation of the particles during the modifications. In Figure 2, photocatalytic activities of the obtained catalysts under visible-light irradiation are shown. By the addition of FeO_x to TiO_2(R), a slight increase in the photocatalytic activity was obtained. Yu et al. previously reported a similar increase in the photocatalytic activity for Fe(III)-grafted rutile TiO_2, which was explained by an interfacial charge transfer from the valence band of TiO_2 to the surface Fe(III) species [2]. The addition of sole phosphoric acid also improved the photocatalytic activity, which is due to an effective charge separation of the photo-generated holes and electrons [3]. With an addition of a small amount of phosphoric acid to Fe(1.5wt%)-TiO_2(R), the photocatalytic activity was increased slightly. Here, it should be noted that the addition of increased amounts of phosphoric acid to Fe(1.5wt%)-TiO_2(R) significantly improved the photocatalytic activity. In Figure 3, UV-vis spectra of the samples are shown. The Fe(1.5wt%)-TiO_2(R) sample exhibited a broad absorption between 400 and 700 nm due to FeO_x species. After the addition of phosphoric acid, this absorption became smaller, suggesting a change of the FeO_x species on the surface. It was considered that thus-formed highly dispersed Fe species contributed the enhancement of the photocatalytic activity of the Fe- and P-modified rutile TiO_2 under visible-light irradiation.

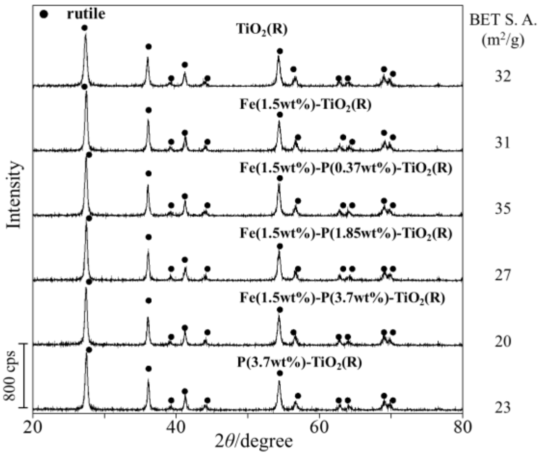

Figure 1. XRD patterns of rutile-type TiO_2 samples modified with Fe and P.

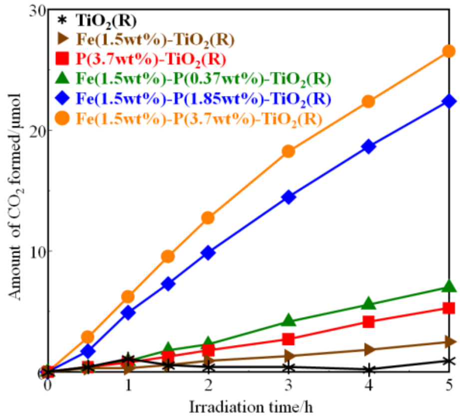

Figure 2. Photocatalytic activities of rutile-type TiO_2 samples modified with Fe and P under visible-light irradiation.

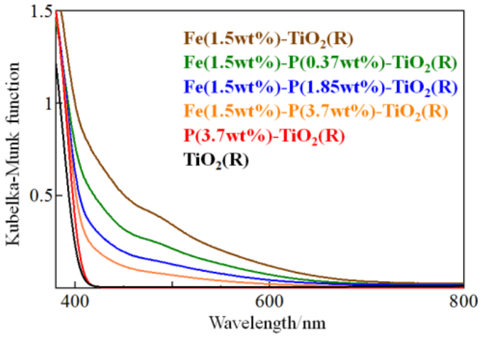

Figure 3. UV-vis spectra of rutile-type TiO_2 samples modified with Fe and P.

4. Conclusions

Nanocrystalline rutile TiO_2 particles modified with FeO_x loading and subsequent addition of phosphoric acid showed significantly enhanced photocatalytic activities under visible-light irradiation. It was suggested that the improved photocatalytic activities were due to the effective charge separation attributed to the phosphate and Fe species on the surface of the catalysts.

References

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