Preparation and Photoactivity of $\alpha$-K$_2$Ti$_6$O$_{13}$ from Anatase TiO$_2$ Powder by Hydrothermal Treatment

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Abstract

The $\alpha$-K$_2$Ti$_6$O$_{13}$ was prepared by hydrothermal treatment of 100-300 nm anatase TiO$_2$ in 10 M KOH aqueous solution at temperatures of 200°C or higher for 24 h. The products had fibrous morphology, and were of 10 nm in thickness and several hundreds nm in length. Photodegradation activity of prepared samples was measured by degradation of Reactive blue 171 dye following the first order reaction. Reaction rate constants ($k_{605}$) of the TiO$_2$ starting particle and the prepared $\alpha$-K$_2$Ti$_6$O$_{13}$ (KT-24-220) were 0.0337 min$^{-1}$ and 0.0039 min$^{-1}$, respectively.

Key words: Anatase, Titanium, Dioxide, Photoactivity, Hydrothermal

Introduction

Titanate compounds in the form of A$_2$Ti$_N$O$_{2N+1}$ (where N = 2–8 and A = alkaline) have been recently investigated for a variety of applications.$^{6, 1}$ A K$_2$Ti$_6$O$_{13}$ is one of the major titanate compounds, and is utilized as a reinforced filler in plastics and metals, photocatalyst, gas sensor, high energy cell, etc.$^{(6)}$ The K$_2$Ti$_6$O$_{13}$ has two forms, $\alpha$- and $\beta$- K$_2$Ti$_6$O$_{13}$ which can be prepared from different starting materials. For instance, the $\alpha$-K$_2$Ti$_6$O$_{13}$ can be prepared from a 10-nm anatase, while the $\beta$-K$_2$Ti$_6$O$_{13}$ can be prepared from a 150-nm brookite in aqueous solution of KOH.$^{(6)}$

Conventional treatment methods of textile wastewater are absorption process, ozone treatment process, activated sludge process etc. For the absorption and activated sludge processes, it has been reported that the majority of dyes were only adsorbed on the sludge and were not degraded.$^{(5)}$ The ozone treatment process is expensive and may generate highly toxic compounds. Many research groups have been attempting to apply a photocatalytic reaction for textile wastewater treatment. Titanium dioxide (TiO$_2$) mostly in the form of anatase is widely used as a photocatalyst. Recently, the have been reported that titanate layer compounds in an alkaline form exhibited high absorption property (Lee, et al. 2007), while those of a protonate form gave high activity for dye photodecomposition.$^{(5)}$

In this study, we prepared the $\alpha$-K$_2$Ti$_6$O$_{13}$ by hydrothermal treatment of a low-cost, rather coarse-particle anatase TiO$_2$ (100–200 nm) at 140–220°C for 24 h. Phase and morphology of prepared samples were characterized. Their photoactivities are determined by decomposition of Reactive blue 171 (RB 171) dye.

Materials and Experimental Procedures

Materials and Reagents

A commercial TiO$_2$ powder (Cotiox KA-100) was used as a starting material and purchased from a Cosmochemical Limited (Korea). A KOH was used as a potassium source for the preparation of potassium titanate and purchased from a Nippon Soda (Japan).

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A typical experimental procedure can be described as follow. A 250 mL of 10 M KOH aqueous solution and 25 g of TiO₂ powder were loaded into a Teflon-lined 316 type stainless steel autoclave having an internal volume of 430 mL. After sealing the autoclave, it was placed in an oven at the temperature in a range of 140-220°C. After hydrothermal treatment for 6-72 h at the desired temperature, the autoclave was taken out from the oven and allowed to cool down to room temperature. The product was separated from the solution by filtration with a polyamide membrane (pore size = 0.2 μm), washed three times with de-ionized water, and dried at 105°C overnight.

Photoactivity of Photocatalysts

Photoactivity of the prepared samples was measured by decomposition of the Reactive blue 171 dye in a Pyrex reactor. The Reactive blue 171 dye; C₄₀H₂₃Cl₁₅N₁₅Na₆O₁₉S₆, was a reactive dye. Its maximum absorptions are at 283 and 605 nm for the absorption of an aromatic group and of the π conjugate of an -N=N- group in the dye molecule (as shown in Figure 1). The photodecomposition was carried out in the 1.2 L of Pyrex reactor. The reactor had 1 L of working volume and had two lamps of 18-W Toshiba black light. A 1.0-g sample was suspended in 10 ppm of dye solution. The suspension was air-bubbled for 30 minutes to get saturated with oxygen, and then the black light was turned on. The solution was sampling every 20 minutes to measure the dye concentration. The sampling solution was filtered using a polyamide membrane (pore size = 0.2 μm, Goettingne Ltd., Germany) to separate the photocatalyst. The clear solution was measured for its absorption at the wavelengths of 605 and 283 nm to determine the dye concentration. The reaction rate was calculated by the first order photodegradation of dye. The reaction rate constants, $k_{605}$ and $k_{283}$, were calculated from the absorption intensity at 605 and 283 nm, respectively.

Analysis

Crystal structure and microstructure of the titanate photocatalyst were analyzed by using an X-ray diffractometer (XRD, JDX-3530, JEOL, Japan), and a transmission electron microscope (TEM, JEM-2010, JEOL, Japan), respectively. The absorption of dye solution was analyzed by the UV–Vis spectroscopy (Shimadsu UV-1610, Japan).

Results and Discussion

Figure 2 shows XRD patterns of the starting TiO₂ powder and the products hydrothermally treated at 140-220°C for 24 h. The hydrothermal products were assigned as KT-t-T, where t is a time for the hydrothermal treatment and T is a hydrothermal temperature. For instance, a KT-24-220 represents the product hydrothermally prepared at 220°C for 24 h. The starting TiO₂ had pure anatase phase (JCPDF# 21-1272). After hydrothermal treatment at 140 and 160°C for 24 h, the peaks corresponding to the anatase phase is a major phase while the peaks of the K₂Ti₆O₁₃ (JCPDF# 74-0275) is a minor phase (at $2\theta = 29.22$ and 47.7 degrees). After hydrothermal treatment at 180°C, the anatase phase became a minor product while the K₂Ti₆O₁₃ became a dominant phase. By hydrothermal treatment at 200°C and higher, the product was pure K₂Ti₆O₁₃.
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Figure 2. XRD patterns of the products prepared at various hydrothermal temperature for 24 h. where $\bullet$ = Anatase and $\bigcirc$ = K$_2$Ti$_6$O$_{13}$

Figure 3 shows TEM images of the samples whose XRD patterns are shown in Figure 2. The anatase TiO$_2$ was seen as agglomerated particle of 100 – 300 nm in size (Figure 3a). After hydrothermal treatment at 140°C, a fibrous structure of the K$_2$Ti$_6$O$_{13}$ was observed together with some particles of the anatase of the same size as of the starting particle as shown in Figure 3b. After hydrothermal treatment at 160°C, the amount of the anatase particle decreased, while the amount of the fibrous structures increased as well as the increase of the fibrous length (Figure 3c). Well-defined fibrous structure was obtained after hydrothermal treatment at 200°C or higher (Figure 3d-e).

A selected area electron diffraction pattern (Figure. 3d-e) revealed that the fiber was in the form of $\alpha$-K$_2$Ti$_6$O$_{13}$ which was similar to the work of Meng, et al. (2006) who reported that only the anatase phase can be used as a starting powder for preparation of the $\alpha$-K$_2$Ti$_6$O$_{13}$ structure by hydrothermal treatment in 15 M KOH at 180°C for more than 4 days. The fiber prepared in this study was shorter than the product of Meng, et al. (2006) because of the shorter hydrothermal treatment time.

A formation mechanism of the $\alpha$-K$_2$Ti$_6$O$_{13}$ fibers consists of two steps as follow:\(^{(2)}\)

1. TiO$_2$ particles well dissolved in the KOH solution at high temperature to form Ti$^{4+}$ ion,
2. These fibrous structures grew on a surface of the TiO$_2$ particles by recrystallization of the dissolved Ti$^{4+}$ ion (see Figure 3b-c).

Figure 4 shows XRD patterns of the products prepared by hydrothermal treatment at 220°C for 6 - 72 h. No peaks of the anatase TiO$_2$ was observed in all samples, except for the KT-6-220 sample which had a small anatase peak (Figure 4). This XRD result is in good agreement with the TEM result as no TiO$_2$ particle was observed (Figure 5). Increasing the hydrothermal time had no observable effect on the shape and size of the fiber. Based on the XRD and TEM results, we can prepare pure fibrous structure of $\alpha$-K$_2$Ti$_6$O$_{13}$ by hydrothermal treatment at 220°C for 12 h.
Figure 4. XRD patterns of hydrothermal product at prepared at various hydrothermal treatment times at 220°C. where ● = Anatase and ○ = K$_2$Ti$_6$O$_{13}$

Figure 6. Reaction rate constant of the prepared sample under black light irradiation.

Conclusion

The α- K$_2$Ti$_6$O$_{13}$ photocatalyst was prepared by hydrothermal treatment of 100-300 nm anatase TiO$_2$ in 10 M of KOH aqueous solution at temperature 200°C or higher for 24 h. The products had fibrous morphology, and were of 10 nm in diameter and several hundreds nm in length. The photodegradation activity of α- K$_2$Ti$_6$O$_{13}$ was lower than that of the starting TiO$_2$.

References


