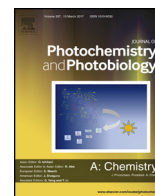




Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Invited feature article

Morphological change and photocatalytic activity of titanium phosphates


 Youngyong Kim^a, Hee-Chan Kim^b, Jaesang Lee^{c,*}, Sang-Hyup Lee^{b,d,**}, Ki-Young Kwon^{a,*}
^a Department of Chemistry, Gyeongsang National University and RINS, Jinju 660-701 South Korea^b Water Environment Center, Korea Institute of Science and Technology, Seoul 136-791, South Korea^c School of Civil, Environmental, and Architectural Engineering, Korea University, Seoul 136-701, South Korea^d Graduate School of Convergence Green Technology and Policy, Korea University, Seoul 136-701, South Korea

ARTICLE INFO

Article history:

Received 29 September 2016

Received in revised form 12 December 2016

Accepted 12 January 2017

Available online 3 February 2017

Keyword:

Photocatalyst

Titanium phosphate

Titanium dioxide

Organic pollutant

Photodegradation

ABSTRACT

Titanium phosphates with wide range of phosphate content (phosphate/Ti = 0 ~ 2) are prepared by one step hydrothermal method, and their photocatalytic property are evaluated based on the rate of oxidative degradation of organic pollutants (4-chlorophenol, trichlorophenol and bisphenol A). The crystal phase, optical property, and morphology of samples are investigated by XRD, diffuse reflectance Uv–vis spectroscopy and SEM/TEM. We find that TiP_0.2 Exhibits 100 ~ 500 nm elliptical spherical structure which is composed of individual anatase phase of TiO₂. As the content of phosphate increases, rice grain-shaped TiO₂ with anatase phase is change into jagged intertwined crystals with layered structure, followed by fibrous structure (TiP_2). The Uv–vis absorbance spectra of TiPs shift to shorter wavelength as the phosphate content increases. Therefore, the photocatalytic activity of TiPs has tendency to decrease, as the phosphate content increases. However, TiP_0.2 exhibits better photocatalytic property than pure TiO₂ for the photo-degradation of organic pollutants. We attribute this enhanced photocatalytic property of TiP_0.2 to the larger surface area and smaller crystallite of TiP_0.2 which originates from the incorporation of phosphate in TiO₂ acting as a crystal growth inhibitor.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Group IV metal oxides and metal phosphates represent outstanding physical and chemical stability such as excellent corrosion resistance against various chemicals including strong mineral acids. Simultaneously, these compounds, titanium oxide (TiO₂) and titanium phosphates (TiP), represent their unique chemical reactivity. For example, various types of photocatalytic reactions were carried out on the surface of titanium oxides. It is well known that Uv–vis irradiation on TiO₂ induces electron/hole pairs in which the photogenerated holes on TiO₂ perform catalytic centers acting as a strong oxidant. In the case of titanium phosphates, they can be existed in stoichiometrically more diverse types of compounds such as α -Ti(HPO₄)₂·2H₂O [1,2], γ -Ti(H₂PO₄)₂·2H₂O [3], TiO(OH)(H₂PO₄)₂·2H₂O [4], and Ti₂O₃(H₂PO₄)₂·2H₂O [5], etc. Due to this compositional flexibility of

titanium phosphate with comparison to titanium oxide, various morphology of titanium phosphate, such as layered, pillared or mesoporous titanium phosphates are reported [6–8]. These derivatives of titanium phosphate have been applied for ion exchangers with specific ions, removal or storage of radioactive compounds, and the substrates for the heterogeneous catalysts [9–13]. Recently, metal titanium phosphates have been intensively investigated due to their potential application to anode materials for lithium ion batteries [14–16].

Previously, the treatments of phosphates on titanium oxides have been mainly investigated in the context of the improvement of photocatalytic properties of titanium oxides [17–21]. It was reported that the phosphate group bound to the titanium oxide surface showed enhanced catalytic property for the photo-degradation of ethanol in gas phase [18] and 4-chlorophenol dissolved in water [19]. In contrast, Colón et al. reported catalytic activity decreased due to the formation of pyrophosphate-like species on the surface of TiO₂ [22]. Recently, Fujishima group showed that phosphate modified TiO₂ nanotubes proved better catalytic property than unmodified one in photocatalytic decomposition reaction of acetaldehyde [23]. The improvement of photocatalytic power of TiO₂ by the incorporation of phosphate

* Corresponding authors.

** Corresponding author at: Water Environment Center, Korea Institute of Science and Technology, Seoul, 136-791, South Korea.

E-mail addresses: lee39@korea.ac.kr (J. Lee), yisanghyup@kist.re.kr (S.-H. Lee), kykwon@gnu.ac.kr (K.-Y. Kwon).

group was interpreted by the inhibition of phase transition of anatase to rutile in annealing process and the increase of surface area [24,25]. Therefore, TiO₂ having proper amount of phosphate results in the enhancement of photocatalytic activity. Compared to intensive studies of the incorporation of phosphate into titanium oxide with relevance to photocatalytic properties, the impacts of phosphate on structural and morphological changes have been relatively less studied. Particularly, the earlier massive studies are focused on samples of TiO₂ containing lower level of phosphate content with respect to Ti, in which the amount of phosphate is regarded as a small amount of impurities or additives [18,26]. In this study, we prepared a titanium oxide and titanium phosphates with relatively high phosphate contents (the molar ratio phosphate/Ti=0.0, 0.2, 0.4, 1.0, 1.4, 2.0) and characterized their crystal phase, morphology, and photocatalytic activity. We found that pure anatase phase TiO₂ and titanium phosphate close to Ti₂O(PO₄)₂(H₂O)₂ are obtained under no (P/Ti=0) and high (P/Ti=2.0) phosphate concentration, respectively. In medium molar ratio (0.2 < P/Ti < 1.4), both anatase and TiPs exist as mixture where the morphology of the each sample is strongly dependent on the content of phosphate. Particularly, we first observed the presence of a few hundred nanometer sized elliptical spherical geometry which is composed of individual anatase phase of TiO₂. In the photo-induced decomposition tests of organic pollutants, overall the kinetics of photocatalytic oxidation of organic pollutants have a tendency to decrease as the contents of phosphate increase. However, TiP_0.2 exhibits enhanced photocatalytic activity compared to TiO₂, which can be attributed to the larger surface area and smaller crystallite of TiP_0.2 due to the incorporation of phosphate on TiO₂ resulting in crystal growth inhibition.

2. Experimentals

2.1. Preparation and characterization of titanium phosphate and titanium oxide

All TiO₂ and TiP samples were prepared by hydrothermal method. Ti(SO₄)₂ and H₃PO₄ are used for the source of titanium and phosphate, respectively. A typical procedure is as followed. Phosphoric acid (10 mL) having different concentrations (0.0, 0.40, 0.80, 2.0, 2.80, 4.0 M) were added dropwise into aqueous solution of Ti(SO₄)₂ (0.308 M, 65 mL). Total number of samples is six where the molar ratio of P/Ti is 0.0, 0.2, 0.4, 1.0, 1.4, 2.0, respectively (TiP samples are labeled hereafter TiP_yy, in which yy represents above molar ratio of P/Ti). After vigorous stirring the solution mixtures for 30 min at room temperature and ambient pressure, the solution was transferred into Teflon lined autoclave (volume ≈ 150 mL) and was aged 200 °C for 24 h (While heating, the pressure reached at approximately 10 ~ 12 bar). After cooling the reaction mixture at room temperature, white precipitates were obtained. The resulting precipitates were purified by repetitive centrifugation and washing with DI water for five times. Finally, white powders were dried in an air oven at 70 °C for overnight.

The crystal phase of particles were determined by powder X-ray diffraction (3 kW Cu X-ray Diffractometer, D8 Advance, Bruker AXS Germany). The size, shape and morphologies of the particles were evaluated using a field emission scanning electron microscope (Jeol JSM-6380LV, Japan) and transmission electron microscope (Jeol 200 kV, JEM-2010). Diffuse reflectance UV–vis spectra were obtained using UV-Visble spectrometer (UV-3600, SHIMADZU) equipped with an integrating sphere. Surface area of samples was measured by Brunauer–Emmett–Teller (BET) method (Belsorp Mini II, BEL Japan).

2.2. Photocatalytic reaction

Typical aqueous suspensions of TiP and TiO₂ contain 0.5 g/L catalyst and 0.1 mM target substrate (4-chlorophenol (4-CP), trichlorophenol (TCP), and bisphenol A (BA)). The initial pH of the experimental suspensions was adjusted as around 4. The photo-irradiation was performed using six 4-W black light blue (BLB, Philips TL4W) lamps with the emission spectrum ranging from 350 nm to 400 nm (Fig. S1). More than duplicate photolytic experiments were carried out for a given condition. During the kinetics study of photocatalytic reaction, the concentration of substrates was quantified by high performance liquid chromatography (HPLC (PerkinElmer) equipped with a C-18 column (ZORBAX Eclipse XDB-C18)).

3. Results and discussions

Fig. 1 shows the crystal phase of TiPs having different ratio of phosphate/titanium (P/Ti). The sample TiP_0 which does not contain phosphate shows pure anatase phase of TiO₂ (JCPDS file No. 00-21-1272). It is reported that when Ti(SO₄)₂ is applied as the source of titanium, the products of thermal hydrolysis of Ti(SO₄)₂ are commonly anatase phase in either aqueous or water/organic co-solvent [27,28]. The XRD pattern of TiP_0.2 is almost same to that of TiP_0, which indicates that the bulk crystallinity (anatase phase) of the TiP samples is not affected by the phosphate ion up to the P/Ti ratio of 0.2. However, careful analysis indicates that the line broadening of the XRD pattern is observed in TiP_0.2 compared to TiP_0. Average crystal size is calculated from Scherrer equation in which full widths at half maximum (FWHM) of the (101) facet are chosen. The calculated sample sizes of TiP_0 and TiP_0.2 are 25.6 nm and 19.2 nm, respectively. In the sample of TiP_0.4 containing more phosphate ions, new peaks (circles) begin to appear. In the sample of TiP_1, the intensity of main anatase peak corresponding to reflection of (101) facets decreases significantly, and additional new peaks appear (circles). In the sample of TiP_1.4, Bragg reflection peaks of anatase phase only remain as trace. This indicates that anatase phase does not exist when the ratio of P/Ti is greater than 1.4. When XRD pattern of TiP_2 is compared to that of TiP_1.4, there are considerable differences (additional strong new peaks are indicated as squares). Therefore, the amount of phosphate in the synthetic condition is critical to determine the TiP identity because all our experimental setup is same except for the ratio of P/Ti. We found that XRD pattern of TiP_2 is very closely related to Ti₂O(PO₄)₂(H₂O)₂ (JCPDS file No. 01-088-0041) [29].

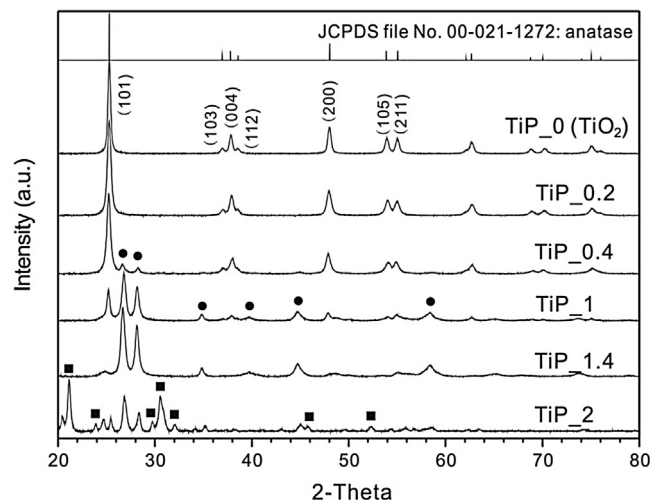


Fig. 1. XRD patterns of TiP_yy.

Download English Version:

<https://daneshyari.com/en/article/4754162>

Download Persian Version:

<https://daneshyari.com/article/4754162>

[Daneshyari.com](https://daneshyari.com)