Journal of the Taiwan Institute of Chemical Engineers 43 (2012) 132–139

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

A simple route for the preparation of P-modified TiO_2: Effect of phosphorus on thermal stability and photocatalytic activity

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ARTICLE INFO

Article history:
Received 28 February 2011
Received in revised form 30 April 2011
Accepted 5 June 2011
Available online 15 August 2011

Keywords:
TiO_2
Phosphorus content
Particle growth
TiP_2O_7
Thermal stability

ABSTRACT

Phosphorus-modified dioxide nanoparticles were prepared by sol–gel method. The effect of phosphorus precursor and calcination temperatures on phase transformation, grain growth and surface area were investigated using various spectroscopic and basic techniques (ICP-AES, XRD, BET, ^{31}P MAS NMR, FT-IR, and UV–vis methods). It was found that the phosphorus existed as amorphous titanium phosphate in TiO_2 framework after calcination at temperature of 500–700 °C. As results, slows down the particle growth of anatase and increases the anatase-to-rutile phase transformation. The average crystallite size of P-modified TiO_2 increased dramatically from 8 to 59 nm when the temperature increased from 500 to 900 °C. This change was associated with the formation of pyrophosphate TiP_2O_7 species through condensation of the concentrated phosphate species. The BET surface area of modified samples was 3.4-fold higher than that of unmodified TiO_2 and was 70% higher than that of commercial Degussa P-25. The photocatalytic activity of P-modified TiO_2 was 1.5-fold higher than that of commercial Degussa P-25 and was 49% higher than that of unmodified TiO_2 under UV irradiation. Phytotoxicity was assessed before and after irradiation against seed germination of tomato (*Lycopersicon esculentum*).

1. Introduction

TiO_2 is considered to be the most promising heterogeneous photocatalyst, because of its high photocatalytic activity, non-toxicity, inexpensiveness, chemical stability and favourable optoelectronic properties. Titania exists in three different forms: anatase, rutile, and brookite, of which anatase generally show the best photocatalytic activity performance [1,2]. Without any modification, transformation of anatase to rutile usually occurs at 500–700 °C, which may result in the decrease in photocatalytic ability of TiO_2 [3–5].

In addition to the crystallite transformation obtained by high-temperature calcination, crystallite growing and serious sintering are observed with increasing the temperature of calcinations leading to the drastic decrease in surface area and photocatalytic activity. Hence, the inhibition of the growth of the anatase crystals could maintain the anatase metastability at high temperature and control crystallite size. To improve the thermal stability and photocatalytic activity, titania has been modified with La_2O_3 [6], ZrO_2, SiO_2 [7], or doped by inorganic nonmetal such as sulphur [8] and fluor [9,10]. Lv *et al.* [10] developed a simple and novel synthetic method for the fabrication of $TiOF_2$ via a microwave-assisted hydrothermal route using tetrabutyl titanate and hydrofluoric acid as raw materials. The prepared anatase TiO_2 from $TiOF_2$ shows very high thermal stability and the phase transformation temperature from anatase to rutile is up to 1000 °C. The high thermal stability and the photocatalytic enhancement of catalysts were attributed to the adsorbed Fluoride ion on the surface of anatase after calcination at 700 °C. Among the various methods, modification and doping of TiO_2 by phosphorus seems to be a another promising approach [11–16]. Kõrösi and Dekany [13] prepared a series of phosphate modified-TiO_2 samples by the sol–gel method. They argued that the surface bound phosphate have delayed the formation of the anatase phase, crystallite growth and inhibited the anatase–rutile phase transformation. Lin *et al.* [14] demonstrated that the doping of phosphorus could efficiently inhibit the grain growth and enhance the surface area of TiO_2 nanoparticles. The above researches in literature seem discrepant and complicated. This is probably due to the variety of synthetic methods adopted to prepare the solid and the different phosphorus contents. The present work aims at complementing such investigations with P-modified TiO_2 nanoparticles which are synthesized through an easy procedure. The thermal stability, the control of crystalline structure and the effect of phosphorous content on the photocatalytic degradation of 4-chlorophenol were extensively investigated. To the best of our knowledge, there is no report on the impact of the 4-CP solution before and after photocatalytic treatment to environment using P-modified TiO_2. In fact, chlorophenols constitute a group of serious environmental pollutants that must be eliminated [17–21]. As a result of their widespread use in mothproofing, miticides, pesticides, herbicides, germicides and

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doi:10.1016/j.jtice.2011.06.011

fungicides, chlorophenols pose a serious threat to the environment. The US Environmental Protection Agency [22] and the European Union directive [23] have labelled chlorophenols as "priority pollutants", which means that they need to be constantly monitored in the aquatic environment. Considering the potential effect of this compound on the ecosystem, a phytotoxicity test using tomato (*Lycopersicon esculentum*) seeds was successfully applied in ecological risk assessment of 4-CP phototreated solutions.

2. Experimental

2.1. Chemical and catalyst preparation

Titanium (IV) isopropoxide ($Ti(OC_2H_5)_4$, 97%, Aldrich) and isopropylic alcohol were obtained from Fluka ($(CH_3)_2CHOH$, 99.8%, Riedel de Haeën), phosphoric acid (H_3PO_4, 85%, Aldrich,), the commercially available TiO_2 (Degussa P25) was obtained from Degussa Chemical and UHQ (Milli-Q 18.2 MΩ) water.

The catalyst P-modified TiO_2, were prepared by the sol–gel method. In a typical preparation procedure, titanium (IV) isopropoxide was diluted in isopropylic alcohol (molar ratio 1:4). Deionized water was added dropwise to $Ti(OPri)_4$ solution during stirring (molar ratio between water and alcohol 1:5). White precipitate starts appearing indicating the hydrolysis process. After being aged for an hour, 100 ml of a phosphoric acid aqueous solution with concentration 34.5 mM was added to the resulting titania suspension to prepare TiO_2 sample of phosphorus content. For comparison, unmodified TiO_2 was also prepared by the same procedure without the addition of H_3PO_4. The dried materials were calcined at 500, 700, 900 and 1000 °C in air for 3 h and with heating rate 10°/min and the calcined powders are labelled according to its phosphorus content and calcination temperature. TP_t, and T_t, where t means the calcination temperature.

2.2. Structural characterization

The powder X-ray diffraction patterns were recorded at room temperature on a (advanced D8, Bruker, Germany). The experimental conditions for refinement of XRD data of TP_{1000} are the following: X-ray tube operating at 40 kV and 40 mA, 0.6 mm fixed divergence slits, diffracted beam curved graphite monochromator (Cu $K_{\alpha+1}$ radiation, λ_1 = 1.540600 Å, λ_2 = 1.544390 Å) and 0.1 mm fixed slit in front of the scintillation detector. The data were collected in the 2θ range 2–70° with a step size of 0.02° and a counting time of 5 s/step. Infrared absorption spectra were measured on a (Nicolet 380 ATR/FT-IR, International Equipment Trading Ltd., USA) spectrometer by the transmission method using the KBr pellet technique with 4 cm^{-1} resolution. The Brunauer–Emmett–Teller (BET) surface area was measured by a fully automated surface area analyzer (ASAP 2020 Accelerated Surface Area and Porosimetry, Micromeritics, USA). The samples were degassed in vacuum overnight at 180 °C prior to adsorption measurements. The UV–Vis diffuse reflectance (DR UV–Vis) spectra were recorded by a Varian Cary 5/UV–Vis-N.I.R.spectrometer. The ^{31}P and (coupling polarization) $^{1}H–^{31}P$ CP NMR/MAS spectra of the prepared TiO_2 solids were recorded on a (300 ultra shield, Bruker, USA) spectrometer at 300 MHz, resonance frequency operating at 121.5 MHz and the external magnetic field was 9.4 T. The pulse repetition is 10 s, pulse width of 7 μs and a spinning speed of 8.0 kHz. Chemical shifts were indicated using an external H_3PO_4 (85%) reference (0 ppm).

2.3. Determination of phosphorus content

2.3.1. First method

The Ti and P content of the samples was determined by all argon sequential (Thermo Jarrell ASH, USA) inductively coupled plasma atomic emission (ICP-AES) spectrometry. The intensity of the spectral lines of 213.6 and 336.1 nm were measured.

2.3.2. Second method

The concentration of phosphate in the above samples was measured using UV-Vis Double Beam PC, Scanning spectrophotometer (UVD-2950) following the ascorbic acid reduction method [24].

2.4. Surface acidity measurement

Surface acidity was determined volumetrically by the adsorption of sodium hydroxide NaOH from solutions of different concentrations. 0.2 g of the solid oxide was mixed with 30 ml of the base solutions for 10 h, with continuous stirring then left 24 h. For each sample, a blank run was carried out first on the base alone and the difference between the blank run and that with the sample gave the amount adsorbed.

2.5. Photocatalytic reaction experiment

Photodegradation of 4-chlorophenol (4-CP) (98%) was conducted in a laboratory-scale photoreactor. It is a 120 cm^3 cylindrical photoreactor, operating in a closed recirculating circuit driven by a centrifugal pump and with a stirred reservoir tank equipped with a device for withdrawal of samples. Illumination was carried out using a lamp (11 W low-pressure mercury lamp, Philips, Holland) with a wavelength (λ_{max} 254 nm). At given time intervals, about 4 ml aliquots were sampled, centrifuged and filtered with a cellulose acetate membrane filter membrane (0.45 μm pore size, 25 mm diameter) to remove all solid particles. The 4-CP concentration was estimated by measuring their absorbance at 225 and 280 nm using a UV-Vis Double Beam PC, Scanning spectrophotometer UVD-2950.

Free chloride ions are quantified directly after each irradiation period with an ion chromatograph (HIC-6A Shimadzu, Japan) equipped with a conductivity detector and a Shim-pack column. The separation was achieved using an isocratic elution at a flow rate of 1.5 ml/min. A mobile phase of 1 mM of tris(hydroxymethyl)aminomethane and 1 g/l of sodium chloride was used as standards solution. Chemical oxygen demand (COD) was measured according to standard methods described in the Japanese International Standard handbook [25].

2.6. Phytotoxicity (germination tests)

4-Chlorphenol phytotoxicity was assessed before and after irradiation against seed germination of tomato (*L. esculentum*). Phytotoxicity was determined using a modified Zucconi test [26] by measuring seed germination. Twenty seeds were placed on filter papers in 9 cm Petri dishes and 6 ml of treated solution was then uniformly added to each dish. Dishes were incubated in the dark at 26 ± 2 °C for 5 days. Distilled water was used as control. All samples, including controls, were triplicated. A germination index (GI) was calculated by counting the number of germinated seeds and the average root length observed in each sample compared to control treatments [27]. Results finally expressed according to the following formula:

$$\mathrm{GI} = \frac{\text{number of germinated seeds in sample}}{\text{number of germinated seeds in control}} \times \frac{\text{average of root lengths in sample}}{\text{average of root lengths in control}} \times 100$$

A seed was considered germinated when the root length exceeded 5 mm. For root lengths below 5 mm, it was considered