Chemical Engineering Journal 157 (2010) 475–482

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Enhanced photocatalytic activity of Ce^{3+}-TiO_2 hydrosols in aqueous and gaseous phases

Tong-xu Liu [a,b], Xiang-zhong Li [a,*], Fang-bai Li [b]

[a] Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong, China
[b] Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control, Guangdong Institute of Eco-Environment and Soil Science, Guangzhou 510650, PR China

ARTICLE INFO

Article history:
Received 29 April 2009
Received in revised form 7 December 2009
Accepted 10 December 2009

Keywords:
Ce^{3+}-TiO_2
Environmental application
Hydrosols
Preparation
Photocatalytic activity

ABSTRACT

A series of cerium ion-doped titanium dioxide (Ce^{3+}-TiO_2) hydrosols were prepared by a coprecipitation–peptization method and characterized by UV–vis transmittance spectroscopy (T%), particle size distribution (PSD), X-ray diffraction (XRD), and Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halender methods (BJH), respectively. The results demonstrated that as the doped Ce^{3+} content increased, the crystalline size, BET surface area and transmittance decreased significantly, but the particle size increased gradually. The photocatalytic activity of Ce^{3+}-TiO_2 hydrosols was evaluated in aqueous solution for methylene blue (MB) and 2,3-dichloriphenol (2,3-DCP) degradations, and also in gaseous phase for benzene degradation. The results showed that the overall photocatalytic activity of Ce^{3+}-TiO_2 hydrosols in aqueous and gaseous phases under UVA and visible illumination was significantly higher than pure TiO_2 hydrosol due to its better separation of electron-hole pairs and visible light response. Additionally, the formation of the surface complex of TiO_2 and 2,3-DCP with visible light response is also contributed to the 2,3-DCP degradation, and the relevant possible reaction mechanisms were discussed with details. The kinetic data demonstrated that the Ce^{3+}-TiO_2 hydrosols with the content of Ce^{3+} doping between 0.5 and 1% achieved the best performance in both the aqueous and gaseous phases. This study provided the comprehensive understanding of the Ce^{3+}-TiO_2 hydrosol characteristics and reaction mechanisms, and the results indicate that these Ce^{3+}-TiO_2 hydrosols may have good potential for pollutant degradation either in aqueous phase or gaseous phase.

1. Introduction

TiO_2 photocatalysis has become a promising technique for degrading aqueous or gaseous toxic organic pollutants in water and wastewater treatment, and air purification owing to its environmental benign [1,2]. So far, a variety of physical and chemical approaches have succeeded in synthesizing crystalline TiO_2 catalysts by calcinations methods [3–5], while Xie and Yuan [6] synthesized the crystallized TiO_2 hydrosol at low temperature of <100 °C by a hydrothermal method to avoid the serious aggregation by the calcinations methods. In comparison with the conventional TiO_2 powder catalysts, TiO_2 hydrosol is a colloidal solution with much finer TiO_2 particles and much better colloidal stability and homogeneity, and it can utilize the light more efficiently compared to those aqueous TiO_2 powder suspensions. Additionally, a key technique of using TiO_2 for indoor air purification is how to coat the catalysts such as P-25 powder onto walls, windows, or furniture easily and durably, without any blights such as color change and transparency decay of the substrates after coating, while using TiO_2 hydrosol can solve these problems because it is transparent and easy for coating on these substrates. Recently, only a few reports [7,8] have directly used TiO_2 hydrosol to eliminate the air pollution under UV illumination, but there is still lack of the studies on the TiO_2 hydrosol for air purification under visible light illumination.

To further enhance the photocatalytic performance of TiO_2 hydrosols, some literatures have proved that the incorporation of lanthanide ion doping could improve the photochemical properties by increasing the photocurrent response and the separation of electron-hole pairs under UV illumination [9–13]. Some reports [14] showed the overall photocatalytic activity for 2-mercaptobenzothiazole degradation under UV or visible light irradiation was significantly enhanced by doping with the cerium ions with a special 4*f* electron configuration because the higher adsorption equilibrium constant and the higher separation efficiency of electron-hole pairs were obtained simultaneously for Ce^{3+}-TiO_2 powder catalysts and the introduction of Ce 4*f* level led to the optical absorption band between 400 and 500 nm, resulting its visible-induced photocatalytic activity. Xie and Yuan [15] reported Ce^{4+}-TiO_2 sol catalysts had photocatalytic activity for X-3B degradation under visible light irradiation, and they speculated

---

* Corresponding author. Tel.: +852 27666016; fax: +852 23346389.
E-mail address: cexzli@polyu.edu.hk (X.-z. Li).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.12.010

the possible mechanisms. However, the photocatalytic activity of Ce^{3+}-TiO_2 hydrosol catalyst has only been studied with very limited data about dye degradation in aqueous solution. Especially, there is a lack of studies about its photocatalytic activity for degrading pollutants in gaseous phase. Recently, the development of non-TiO_2 photocatalysts (such as β-Ga_2O_3, InOOH, and Zn_2GeO_4) [16] is one of the alternative approaches for treating gaseous benzene at ambient conditions, but these semiconductors usually have wide bandgap which should be excited by the light with the wavelength less than 300 nm. Comparatively, the Ce^{3+}-TiO_2 hydrosols with the ability of benzene degradation under UVA or visible light, is more suitable for the practical application, especially for the indoor air purification.

In this study, Ce^{3+}-TiO_2 hydrosol was prepared by using a chemical coprecipitation-peptization method and its colloidal properties and nanoparticle properties were characterized with details. The degradations of methyl blue (MB) and 2,3-dichlorophenol (2,3-DCP) with the Ce^{3+}-TiO_2 hydrosols in aqueous solution were first investigated and the degradations of benzene (C_6H_6) with the Ce^{3+}-TiO_2 hydrosols in gaseous phase were then conducted to evaluate its photocatalytic activity under UV or visible illumination. This study was aimed at investigating the enhanced photoactivity of Ce^{3+}-TiO_2 hydrosol photocatalyst for its environmental applications in aqueous and gaseous phases.

2. Experimental

2.1. Materials

Metatitanic acid ($TiO_2{\cdot}2.5H_2O{\cdot}0.3SO_4$), a precursor of titania powder, was supplied from Panzhihua Iron & Steel Research Institute, China. While the MB and 2,3-DCP chemicals were obtained from BDH and Aldrich Chemical Company, respectively, NH_4OH, HNO_3, $Ce(NO_3)_3$ and other chemicals with analytical grade were obtained from Shanghai Reagent Ltd. The benzene gas with a certified concentration of 1000 ppm/v in air was purchased from Foshan Kedi Gas Ltd. in China. Deionzied distilled water (DDW) was used for preparation of all solutions.

2.2. Preparation of Ce^{3+}-TiO_2 hydrosols

The Ce^{3+}-doped TiO_2 hydrosols were prepared by a chemical coprecipitation–peptization method, in which 90 g of metatitanic acid was added into DDW and stirred continuously until a uniform metatitanate suspension was obtained. 2.3 g of $Ce(NO_3)_3$ was dissolved into DDW to obtain cerium nitrate solution, which was then added into the metatitanate suspension and uniformly mixed. Excessive amount of ammonia was dropped therein to adjust the pH value to be above 9. The resulting suspension was stirred continuously for 3 h and heated at the temperature of below 40 °C, and then filtered to get filter cake. The filter cake was washed repeatedly for several times until no sulfate ion was detected by titration using a 0.5 mol L^{-1} barium chloride solution. Finally, the filter cake was uniformly mixed with water to form uniform suspension. 190 mL of nitric acid (10%) was dropped therein to adjust the pH value to be 1.5. The resulting suspension was stirred continuously for 2 h at room temperature, followed by stirring and heating at the higher temperature of 65 °C. The suspension was peptized for 24 h to eventually obtain a Ce^{3+}-TiO_2 hydrosol solution in slight yellowish color with a doped amount of cerium at 1.0% (mol/mol). This hydrosol sample was named "1.0%Ce^{3+}-TiO_2". With the same procedure, 0.5%Ce^{3+}, 1.5%Ce^{3+}, 2.0%Ce^{3+}, and 2.5%Ce^{3+} doping TiO_2 hydrosol samples were also prepared and named "0.5%Ce^{3+}-TiO_2", "1.0%Ce^{3+}-TiO_2", "1.5%Ce^{3+}-TiO_2", "2.0%Ce^{3+}-TiO_2", and "2.5%Ce^{3+}-TiO_2", respectively.

2.3. Characterization of Ce^{3+}-TiO_2 hydrosols

The as-prepared hydrosol samples were first scanned using a TU-1801 UV–visible spectrophotometer (UV–vis TU-1800, Purkinje General, Beijing) in the wavelength range of 200–600 nm to determine their UV–visible transmittance spectra. The particle size distributions (PSD) of the hydrosols were directly determined by a light-scattering size analyzer (Beckman N5, USA). To characterize the crystalline and adsorption properties of the hydrosols, the titania xerogel powder was obtained through gelation treatment at 65 °C for 24 h. The X-ray powder diffraction (XRD) patterns were recorded using a Rigaku D/Max-III A diffractometer at room temperature with 30 kV and 30 mA under a Cu Kα radiation (λ = 0.15418 nm). The crystal sizes were calculated using the Scherrer's formula [17]. The specific surface area and total pore volume of hydrosol samples were measured by the Brunauer–Emmett–Teller (BET) method, in which the N_2 adsorption at 77 K using an ASAP 2020 Sorptometer was applied. The xerogel sample was degassed at 90 °C prior to nitrogen adsorption measurements. The pore size distribution was determined by the Barret–Joyner–Halender (BJH) method according to their desorption isotherm [18]. The nitrogen adsorption volume at the relative pressure (P/P_0) of 0.9733 was used to determine the pore volume and average pore sizes.

2.4. Photoreaction experiments

MB and 2,3-DCP chemicals were used as two model pollutants to evaluate the photocatalytic activity of the hydrosols in aqueous solution, while benzene was also tested to determine the photocatalytic activity of the hydrosols in gaseous phase.

2.4.1. Aqueous phase experiments

The photocatalytic reactions of MB/2,3-DCP degradation in aqueous solution were conducted in a Pyrex cylindrical photoreactor surrounded by a circulation water jacket to control the temperature during reaction. A medium-pressure mercury lamp (Philips, 8 W, 365 nm) was used as a UVA light source (I = 1.28 mW cm^{-2}), and a 300 W Xeon lamp (PLS-SXE300UV, Beijing Trusttech Ltd., China) with a UV cutoff filter at 420 nm was applied as a visible light source. The reaction mixture was prepared by adding hydrosol or P-25 powder into 250 mL of aqueous MB/2,3-DCP solution as colloid solution or powder suspension. In all experiments, the initial concentration of MB/2,3-DCP was 10 mg L^{-1} and the solid content of TiO_2 was 1.0 g L^{-1}. Prior to the photoreaction, the colloid solution/powder suspension was magnetically stirred in the dark for 30 min to establish adsorption/desorption equilibrium. During the photoreaction, the colloid solution or suspension was irradiated by UVA or visible light with air blowing and magnetically stirring. At the given time intervals, the samples were taken from the colloid solution or suspension and stored in the dark before analysis. The MB concentration was determined by a UV–vis spectrophotometer at the wavelength of 665 nm. The 2,3-DCP concentration was determined by HPLC (Finnigan SpectraSYSTEM P4000) with a Pinnacle II C18 reverse-phase column (5 mm, 4.6 mm × 250 mm) and a UV detector (UV 6000LP) using all wavelength, in which a mobile phase was composed of acetonitrile and water (v:v = 3:2) and flowed at 1.0 mL min^{-1}.

2.4.2. Gaseous phase experiments

Gaseous benzene degradation was conducted in a stainless steel column reactor with an effective volume of 100 L (46 cm (D) × 60 cm (H)), which inner surface was coated with a Teflon film for eliminating adsorption. The reactor was placed in a small air chamber where temperature and humidity were well controlled. Inside of the reactor, three medium-pressure mercury