Applied Catalysis B: Environmental 87 (2009) 181–189

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Structure and photocatalytic performance of magnetically separable titania photocatalysts for the degradation of propachlor

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ARTICLE INFO

Article history:
Received 10 April 2008
Received in revised form 4 September 2008
Accepted 10 September 2008
Available online 26 September 2008

Keywords:
TiO_2
γ-Fe_2O_3
Magnetically separated photocatalysts
Organic pollutants

ABSTRACT

A magnetic photocatalyst was prepared by modification of TiO_2 nanoparticles (Degussa P25) with nanocrystalline γ-Fe_2O_3 nanoparticles through a protective lining made up of two oppositely charged polyelectrolytes. As-prepared magnetically separable photocatalysts differing in γ-Fe_2O_3 loading (3, 8, 13, 20 and 30 wt.%) were characterized by XRD, TEM, thermal analysis, Mössbauer and magnetic measurements. The photocatalytic efficiency of the nanocomposite catalysts was evaluated using a chloroacetanilide herbicide (propachlor) in water as model compound. The primary degradation of propachlor followed pseudo-first-order kinetics according to the Langmuir–Hinshelwood model. Generally, all magnetic photocatalysts exhibit good catalytic activity towards organic pollutants, do not suffer from photodissolution and can be reused several times without any decrease in their photocatalytic activity.

1. Introduction

Semiconductor photocatalysts have attracted much attention because of their potential application in the removal of organic and inorganic species from aquatic environments [1,2]. Nowadays, TiO_2 is widely recognized as the most promising photocatalyst for environmental applications. A major disadvantage of semiconductor oxides is the need of an additional and expensive separation step involving the removal of the photocatalyst from the treated water. In order to overcome this problem magnetically separable photocatalysts have been developed enabling the easy recovery of the photocatalyst by an external magnetic field [3–13].

The magnetic photocatalytic systems that have been developed so far contain magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) [3–10] or spinel-like ferrites ($NiFe_2O_4$, $Zn_{0.35}Ni_{0.65}Fe_2O_4$) [11–13] serving as magnetic cores.

It has been established that direct contact between titanium oxide and iron oxide, i.e. TiO_2/Fe_3O_4 or TiO_2/γ-Fe_2O_3, is responsible for low photoactivities because Fe_3O_4 or γ-Fe_2O_3 act as recombination centres for electrons and positive holes, especially in the case of magnetite [3]. For example, it has been shown that the absorption of strong light by γ-Fe_2O_3 nanoparticles causes low photocatalytic activity when the amount of γ-Fe_2O_3 exceeds that of TiO_2 in the composite [5]. On the other hand, the use of a SiO_2 layer between the Fe_3O_4 or γ-Fe_2O_3 core and the TiO_2 shell, i.e. TiO_2/SiO_2/magnetic oxide, has been found to promote the photocatalytic activity of the catalyst by preventing the injection of charges from TiO_2 particles to magnetic particles [7,8]. In other words, the SiO_2 layer inhibits the photodissolution of the catalyst. In order to be then potentially applicable, the insulator has to be chemically inert and electronically passive toward titanium oxide.

Regarding the TiO_2/spinel-ferrite systems, the $TiO_2/SiO_2/Zn_{0.35}Ni_{0.65}Fe_2O_4$ photocatalyst shows high activity in the photoxidation of oxalate [12]. Similarly, the $TiO_2/SiO_2/NiFe_2O_4$ photocatalyst displays enhanced photoactivity for decomposition of methylene blue [11]. Furthermore, the magnetically separable nitrogen-doped photocatalyst $TiO_{2-x}N_x/SiO_2/NiFe_2O_4$ is a good photocatalyst for the degradation of methyl orange, under UV and visible light irradiation [13]. However, the activity of the composite system was considerably lower than that of the prestine $TiO_{2-x}N_x$ because of the non-perfect coating of SiO_2 around the surface of $NiFe_2O_4$.

Undoubtedly, the two important factors that determine the photoactivity, as well as the stability and the magnetic properties

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0926-3373/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.apcatb.2008.09.012

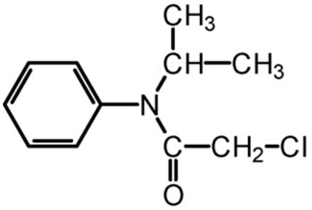

Fig. 1. The molecular structure of the herbicide propachlor.

of all photocatalysts, are the silica layer and the heat treatment during the preparation process. It has been demonstrated that the heat treatment step has important implications on the magnetite properties of the prepared photocatalysts due to chemical or physical changes of the magnetic core [3]. The use of calcined magnetic cores for the preparation for the preparation of Fe_3O_4–SiO_2–TiO_2 [7] or $Zn_{0.35}Ni_{0.65}Fe_2O_4$–$SiO_2$–$TiO_2$ [12] photocatalysts does not solve the problem, because the sol–gel synthesis of TiO_2 requires a heating step for anatase growth.

This study is focused on overcoming the disadvantages from heating by exploiting the use of Degussa pristine TiO_2 nanoparticles for the fabrication of stable magnetic photocatalysts. This novel method based on a protective lining made up of two oppositely charged polyelectrolytes avoids the heat treatment step and results in highly efficient and magnetically separable photocatalysts. The structural and magnetic nature of photocatalysts were investigated by several techniques and their photocatalytic efficiency was evaluated for degradation of propachlor, a chloroacetanilide herbicide (Fig. 1) that is commonly used.

2. Experimental

2.1. Materials

Ammonium peroxydisulfate $(NH_4)_2S_2O_8$, ammonium iron (II) sulphate hexahydrate $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$, potassium hydroxide KOH, poly(diallyldimethylammonium)chloride 20 wt.% with typical Mw ∼100,000–200,000 and poly(sodium 4-styrenesulfonate) average with typical Mw∼70,000 were obtained from Aldrich and used as received. Commercial titania nanoparticles of P25 (ca. 80% anatase, 20% rutile, BET area ca. 50 m^2/g) were supplied by Degussa (Germany). Propachlor analytical standard was purchased from Riedel-deHaen (Seelze, Germany).

2.2. Preparation of materials

2.2.1. Preparation of negatively charged maghemite $[\gamma\text{-}Fe_2O_3/PSS]^-N\alpha^+$

At first γ-Fe_2O_3 was prepared according to the following procedure. To a solution of 2 g of $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ in 50 mL of distilled water a solution of 1.14 g KOH in 30 mL of H_2O was added followed by 0.20 g of $(NH_4)_2S_2O_8$ in 20 mL of H_2O. The black mixture was homogenized with magnetic stirring and kept at 60 °C for 1 h. The precipitated magnetic solid was cooled to room temperature, separated from the solution by centrifugation (1000 rpm/2 min), washed with deionized water (2× 50 mL), peptized in a 0.01 M hydrochloric acid solution under magnetic stirring for 1 h, recentrifuged and finally dispersed in water (pH 4.5, $Z = -10$ mV). Negatively charged γ-Fe_2O_3 nanoparticles were fabricated by wrapping the surface of the magnetic oxide with a 2 wt.% solution of poly(sodium 4-styrene sulfonate) polyanion (PSS^-Na^+). The resulting product was left under stirring for 2 h (pH 5.7, $Z = -45$ mV, $S \approx 2100$ nm). Subsequently, the product was isolated by centrifugation, washed with deionized water (2× 50 mL), redispersed in 50 mL water, stirred overnight (pH 5, $Z = -23$ mV, $S \approx 350$ nm) and isolated by centrifugation. The product is labelled as $[\gamma\text{-}Fe_2O_3/PSS]^-Na^+$.

In a similar manner, a sample was prepared by reacting the $[\gamma\text{-}Fe_2O_3/PSS]^-Na^+$ with the positively charged poly(diallyldimethylammonium)chloride (PDD^+Cl^-) polyelectrolyte, i.e. $[\gamma\text{-}Fe_2O_3/PSS^-/PDD^+]$. This γ-Fe_2O_3 derivative has a positive charge ($Z = +40$ mV).

2.2.2. Preparation of positively charged TiO_2 particles

Because of the amphoteric nature of TiO_2, the surface charge of TiO_2 nanoparticles can be controlled by adjusting the pH of the colloidal suspension below or above the isoelectric point of TiO_2 (pH 6.3). Positively charged TiO_2 was prepared using poly(diallyldimethylammonium) chloride solution as a positively charged binder to negatively charged TiO_2 particles (pH 10). Specifically, a 0.5 wt.% suspension of TiO_2-P25 was prepared by stirring (pH 3.8, $Z = +18$ mV, $S \approx 500$ nm). The pH of the suspension was adjusted to 10 by a NaOH solution 20% w/v (pH 10, $Z = -19$ mV, $S \approx 600$ nm). Then a 5 wt.% solution of poly(diallyldimethylammonium) chloride was added and the resulting mixture was stirred for 2 h (pH 10, $Z = +54$ mV, $S \approx 1100$ nm). The resulting solid was isolated by centrifugation, washed with deionized water (2× 50 mL), dispersed in water and stirred overnight (pH 7.7, $Z = +48$ mV, $S \approx 620$ nm). The solid was isolated by centrifugation and air dried by spreading on a glass plate. It is labelled as $[TiO_2/PDD]^+Cl^-$.

2.2.3. Preparation of $[\gamma\text{-}Fe_2O_3/PSS^-/PDD^+/TiO_2]$ photocatalyst particles

A colloidal dispersion containing appropriate amount of negatively charged maghemite particles in the form of $[\gamma\text{-}Fe_2O_3/PSS]^-Na^+$ was added dropwise to a positively charged titanium oxide dispersion in the form of $[TiO_2/PDD]^+Cl^-$ under continuous stirring and the mixture was left under stirring for 1 h (pH 6.3–6.4, $Z = (+35)$–$(+45)$ mV, $S \approx 620$–700 nm). The product was isolated by centrifugation, washed with deionized water (2× 50 mL), redispersed in water and stirred overnight (pH 5.4, $Z = (+26)$–$(+35)$ mV, $S \approx 350$–1000 nm). Five samples containing nominally 3, 8, 13, 20 and 30 wt.% γ-Fe_2O_3 were prepared. The samples are denoted as Fe(3)Ti, Fe(8)Ti, Fe(13)Ti, Fe(20)Ti and Fe(30)Ti, meaning, for example that Fe(3)Ti is nominally $[\gamma\text{-}Fe_2O_3(3\%)/PSS^-/PDD^+/TiO_2\ (97\%)]$.

2.3. Characterisation of photocatalysts

X-ray powder diffraction (XRD) patterns were recorded by a D-500 Siemens diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). Zeta-potential measurements were carried out on a Zeta Sizer instrument (Malvern Instruments) using the electrophoresis method. The measurements based on electrophoretic mobility of the nanoparticles in diluted aqueous suspensions were performed at least in triplicate with independent particle batches. Thermal analysis measurements were conducted under air flow with a temperature ramp of 10 °C/min on a PerkinElmer Thermogravimetric/Differential Analyser. Zero-field Mössbauer spectra were collected at 5 K in a constant acceleration mode with a 50-mCi ^{57}Co(Rh) source moving at room temperature, while the sample was placed in a variable temperature cryostat. Isomer shift values are reported with respect to α-Fe. In-field Mössbauer measurements were performed at a temperature of 5 K in an external magnetic field of 5 T applied parallel to the gamma-ray direction (Oxford Instruments). A superconducting quantum interference device (SQUID, MPMS XL-7, Quantum Design) was used for magnetic measurements. The hysteresis loops were recorded at 2 and 300 K in external magnetic fields ranging from −7 to +7 T. The percentage of TiO_2 and γ-Fe_2O_3 in the samples was