



Influence of titania content on the mesostructure of titania–silica composites and their photocatalytic activity

Godlisten N. Shao^{a,b}, Askwar Hilonga^{a,c}, Sun Jeong Jeon^a, Jae Eun Lee^a, Gideon Elineema^a, Dang Viet Quang^a, Jong-Kil Kim^d, Hee Taik Kim^{a,*}

^a Department of Chemical Engineering, Hanyang University, 1271 Sa 3-dong, Sangnok-gu, Ansan-si, Gyeonggi-do 426-791, Republic of Korea

^b Department of Chemistry, Mkwawa College, University of Dar es Salaam, Iringa, United Republic of Tanzania

^c Nelson Mandela African Institute of Science and Technology in Arusha, Arusha, United Republic of Tanzania

^d E&B Nanotech. Co., Ltd, Gyeonggi-do, Ansan-si, Republic of Korea

ARTICLE INFO

Article history:

Received 15 June 2012

Received in revised form 20 August 2012

Accepted 22 August 2012

Available online 28 August 2012

Keywords:

Peptization

TiO₂ sol

Sodium silicate

TiOCl₂

Photodegradation

ABSTRACT

Titania–silica composites (TSC) with various Ti/Si ratios were synthesized via sol–gel process using less expensive precursors; sodium silicate solution as a silica source and titanium oxychloride as a titania source. The influence of varying Ti content in the composites was examined by FTIR, SEM, TEM, DTA/TGA, N₂ physisorption studies, XRF and XRD. The BET surface area of the raw materials increased with increasing Ti/Si ratio up to 2.9 (461 m²/g) but further increase of Ti content beyond that ratio yielded composites with decreased surface area. The effect of aging evaluated in the sample with Ti/Si = 2.9 revealed that aging the composite for 2 h yields titania–silica powder with the highest surface area (461 m²/g). The FTIR analysis displayed the presence of a vibration band at 945 cm^{−1}, assignable to hetero linkage of the Si–O–Ti depicting the incorporation of TiO₂ into SiO₂ to form a composite. Moreover, photodegradation of methyl orange (MO) by the samples calcined at 800 °C showed that the TSC-5-800 (Ti/Si = 5.6) exhibited the highest maximum photocatalytic activity of all the composites.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Heterogeneous catalysis is a promising technology for the reduction of non-biodegradable and toxic pollutants especially in water purification. This demand was fulfilled mainly by the advent of metal oxides which incur a large variety of structural geometries with an electronic structure and therefore may demonstrate semiconductor or insulator properties. The ability to produce TiO₂ photocatalysts at relatively low costs is the gateway to production of commercial and large scale catalysts suitable for this particular application [1,2].

Typically, titania–silica (TiO₂–SiO₂) composite combines the prime advantages of the n-type TiO₂ semiconductor and thermally stable SiO₂ as they interact to generate a binary oxide with a favorably high surface area and high catalytic activity. Generally, the catalytic superiority of TiO₂–SiO₂ falls on either of the following three categories based on their unique physio-chemical properties: (i) photo-catalysis that is associated with the support effect and the quantum-size effect; (ii) acid catalysis that is related to the generation of new acid sites; and (iii) excellent catalytic support materials that possess enhanced thermal and mechanical stability due to SiO₂ while preserving the catalytic performance of TiO₂ [3]. Therefore, shape of the particles, particle size, TiO₂/SiO₂ ratio and crystallinity must be put

into consideration during synthesis of the TiO₂–SiO₂ photocatalyst with improved photocatalytic efficiency [4,5].

The sol–gel process is a selective method for fabrication of stable metal oxide with better purity and homogeneity [6]. Sol–gel synthesis of TiO₂–SiO₂ composite from inexpensive precursors enhances large scale production for application in various fields especially in the degradation of organic pollutants and supports for versatile reactions [3,7]. Recent studies have extensively focused on the synthesis of TiO₂–SiO₂ composites with high surface area and desirable porosities to improve their catalytic performance or to enhance surface modification in the fabrication of solid superacid [8,9]. The effect of silica or titania content on the microstructure of the TiO₂–SiO₂ systems has been previously reported. Xu et al. [10] reported the effect of silica on the microstructure of TiO₂–SiO₂ composites in TiO₂ ranges from 45% to 40.1%. The evaluation of the photocatalytic properties on the degradation of methyl orange revealed that the composite was more efficient than TiO₂. Consequently, Wang et al. [11] investigated the synthesis and characterization of TiO₂-incorporated silica forms while Tobaldi et al. [12] reported the effects of SiO₂ addition on TiO₂ crystal structure and its photocatalytic activity. These studies simultaneously show clear justification that varying Ti or Si content in TiO₂–SiO₂ systems deliberately influences composition, morphology, surface area and the phase transformation of both raw and calcined samples. However, production of TiO₂–SiO₂ composites with appealing properties are mostly achieved hydrothermally using highly

* Corresponding author. Tel.: +82 31 400 5274; fax: +82 31 419 7203.

E-mail addresses: khtaik@yahoo.com, khtaik@hanyang.ac.kr (H.T. Kim).

pure and expensive alkoxide precursors (tetraethylorthosilicate, TEOS and tetrabutylorthotitanate, TBOT) and perhaps involves the consumption of templates essentially for structure directing agents.

Recently, we exquisitely reported synthesis of TiO₂-SiO₂ composites using titanium oxychloride solution (TiOCl₂) as a titania precursor and sodium silicate as a silica precursor [13–16]. It was established that synthesizing TiO₂-SiO₂ composites using TiO₂ sol yields a composite with high surface area and desirable porosities suitable for degradation of organic pollutants [13]. The TiO₂ sol is usually formed by condensation and peptization of TiOCl₂ in the presence of ammonium hydroxide and aqueous nitric acid respectively. Therefore, synthesis of TiO₂-SiO₂ composites by varying the Ti content through changing the feeding weight of TiO₂ sol will elucidate the suitable circumstances necessary for formation of a composite with desirable properties. Apart from being less expensive precursor, TiOCl₂ is easy to handle because the dimerization behavior observed during consumption of TiCl₄ as a titania source can largely be avoided [13,16,17]. The reaction time can also be reduced when TiOCl₂ is consumed, for example; using Ti (SO₄)₂ needs extended incubation time which is more than 24 h [7].

In this study a series of TiO₂-SiO₂ composites was synthesized via a novel sol-gel process to investigate the effect of varying Ti/Si ratio using titanium oxychloride and sodium silicate as titania and silica sources respectively. The Ti/Si ratio was controlled between 0.7 and 5.6 and the respective hydrogels were aged for 2 h. The effect of aging was investigated in the sample with the Ti: Si = 2.9:1. Moreover, the efficiency of the composites on the degradation of methyl orange was attempted so as to evaluate the practical reliability of the composites synthesized using these less expensive precursors.

2. Experimental methods

2.1. Materials

The present work consumed chemical reagents received from their chemical sources which were used without further modifications. Sodium silicate (28.08% SiO₂, 8.58% Na₂O) and 25 wt.% TiOCl₂ were obtained from Shinwoo Materials Co. Ltd, South Korea. HNO₃ (60%) was purchased from Aldrich. Ammonium hydroxide solution (28%) and methyl orange were obtained from Dae-Jung Chemical and Metal Co. Ltd, South Korea.

2.2. Synthesis

TiO₂-SiO₂ composites with various Ti/Si ratios were prepared by varying the feeding amount of TiOCl₂ and a fixed mass of sodium silicate solution. For synthesis, 2 ml of ammonium hydroxide solution was added drop-wise into a mixture of 3 g of TiOCl₂ and 3 g of de-ionized (DI) water in a beaker under vigorous magnetic stirring to form a gel while cooling the reactor in an ice bath. The gel was peptized in 8 ml, 0.02 M HNO₃ under vigorous stirring at room temperature for 30 min to obtain a transparent stable sol. Simultaneously, 10 g of sodium silicate and 10 g of DI water was added into another beaker and stirred for 30 min. Titania solution and sodium silicate solution were reacted slowly under vigorous stirring. The reaction mixture was aged at 80 °C for 2 h while stirring thoroughly and adjusting pH to 6–7. After 2 h, the reaction mixture was cooled to room temperature and the product was obtained by vacuum filtration, washed with a copious amount of DI water to remove Na⁺ and NO₃⁻ ions and finally dried at 100 °C for 6 h. The obtained powder was named TSC-1 (titania-silica composite, 1 for the first sample collected when amount of TiOCl₂ was 3 g). The powder was further calcined at various temperatures ranging from 600 to 1000 °C. the calcined samples were dubbed TSC-1-calcination temperature; for example, the sample calcined at 800 °C was labeled TSC-1-800. The same synthetic routes were performed through varying the feeding weight of TiOCl₂ to 9, 15, 21 and 27 g in order to yield TSC-2, 3, 4 and 5 composites respectively. The volume

ratio of NH₄OH:HNO₃ was kept at 1:4 throughout the entire experiments. A summary of the chemical reagents used in this experiment are given in Table 1.

In order to investigate the effect of aging, a total of five samples were collected from TSC-3 reactor. The first sample was taken before aging (TSC-30) while others were collected after every 1 h for 4 h. Technically, a small portion of the sample was taken from the reaction mixture, filtered and then dried at 100 °C for 6 h and labeled TSC-30, TSC-31, TSC-32, TSC-33 and TSC-34 respectively.

2.3. Photocatalytic experiments

The efficiency of TSC catalysts was attempted to evaluate the effectiveness of the composites in the degradation of methyl orange (MO) using glass reactors in the presence of natural solar radiation. All utilized glassware was made from borosilicate glass (Pyrex) to minimize the absorption of UV light by the glass container [2]. Briefly, 80 ml of a 10 mg/l solution of MO was placed in the 100 ml Pyrex beaker followed by the addition of 2 g/l of the composite. Prior to irradiation, the suspensions were magnetically stirred in darkness for 30 min to establish an adsorption/desorption equilibrium. The glass reactors were then exposed to sunlight for a total of 7 h (11.00 am–3.00 pm) on 21st and 22nd May 2012 (Ansan, Korea; 37°17'49"N, 126°50'12"E). In every hour, 10 ml of the suspension was withdrawn using a pipette, centrifuged and the supernatant was analyzed using a UV-vis spectrometer. The efficiency of degradation was calculated from the equation $D\% = (A_0 - A) / A_0 \times 100\%$, where A₀ is the characteristic absorption of MO at 460 nm and A is absorbance at time, t at wavelength 460 nm too [10,18].

2.4. Characterization of the composites

Fourier Transform infrared (FTIR) spectroscopy was used to determine the bonding pattern of the synthesized materials using FTIR Spectrometer (Avatar 360 E.S.P, Nicolet). The IR spectrometer was equipped with a DTGS KB detector and the transmittance measurement was carried out by making KBr pellets containing 2 wt.% of the sample to be analyzed. An average of 64 scans with a wavenumber resolution of 4 cm⁻¹ and optical velocity of 0.6334 cm⁻¹ were collected from 400 to 4000 cm⁻¹. The Brunauer-Emmett-Teller (BET) surface area and the porosity of the samples were studied by a nitrogen adsorption instrument (Micrometrics ASAP 2020). All the samples measured were degassed at 250 °C for 3 h prior to actual analysis. Pore size distribution (PSD) and specific desorption pore volumes were obtained using the Barrett-Joyner-Halenda (BJH) method and desorption branches were used to determine the PSD. The XRD patterns of the raw and calcined powders were collected by X-ray Diffractometer (XRD-6000, Shimadzu) at 2θ from 15° to 60°. The accelerating voltage and applied current were 40 kV and 100 mA respectively. The Field emission scanning electron microscopy (FE-SEM, MIRA-3 Tescan) with an accelerating voltage of 15.0 kV was used to study the morphology of the composite. Thermogravimetric analysis (TGA) and differential TGA were done using a DTA/Thermogravimetric

Table 1

A summary of the chemical reagents and their respective quantities used in the synthesis of titania-silica composite with different Ti/Si ratios.

Sample name	Amount of TiOCl ₂ (g)	Volume of NH ₄ OH (ml)	Volume of 0.02 M HNO ₃ (ml)	Amount of sodium silicate (g)	Total amount of H ₂ O (g)	Ti/Si
TSC-1	3	2	8	10	13	0.7
TSC-2	9	6	24	10	19	1.7
TSC-3	15	9	36	10	25	2.9
TSC-4	21	13	42	10	31	4.6
TSC-5	27	17	68	10	37	5.6

Download English Version:

<https://daneshyari.com/en/article/236921>

Download Persian Version:

<https://daneshyari.com/article/236921>

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