Journal of Environmental Management 227 (2018) 34–43

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Altering fiber density of cockscomb-like fibrous silica–titania catalysts for enhanced photodegradation of ibuprofen

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ARTICLE INFO

Keywords:
Fibrous-silica-titania
Oil-water ratio
Fiber density
Photodegradation
Endocrine
Disrupting chemicals

ABSTRACT

Fibrous silica–titania (FST) catalysts were synthesized by microemulsion followed by silica seed-crystal crystallization methods under various molar ratios of toluene to water (T/W). The catalysts were characterized by XRD, UV-DRS, FESEM, TEM, AFM, N_2 adsorption–desorption, FTIR, and ESR. The results revealed that altering the T/W ratio affected the growth of the silica and titania and led to different size, fiber density, silica–titania structure, and number of hydroxyl groups, as well as oxygen vacancies in the FSTs, which altered their behavior toward subsequent application. Photodegradation of ibuprofen (IBP) are in the following order: FST(6:1) (90%) > FST(5:1) (84%) > FST(7:1) (79%) > commercial TiO_2 (67%). A kinetics study using Langmuir–Hinshelwood model illustrated that the photodegradation followed the pseudo-first-order and adsorption was the rate-limiting step. Optimization by response surface methodology (RSM) showed that the pH, initial concentration, and catalyst dosage were the remarkable parameters in photodegradation of IBP. The FST (6:1) maintained its photocatalytic activities for up to five cycles reaction without serious catalyst deactivation, and was also able to degrade other endocrine-disrupting chemicals, indicating its potential use for the treatment of those chemicals in wastewater.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are emerging contaminants due to their extensive growth in development, availability and consumption (Wang et al., 2018; Soto-Vazquez et al., 2016). Ibuprofen (IBP), commonly used in treating muscular pain and inflammatory disorders, is one of the PPCPs frequently detected in the aquatic environment that results in harmful effects on the human endocrine system and aquatic wildlife reproduction (Méndez-Arriaga et al., 2009; Rao et al., 2016). Thus, many technologies have been used to remove this destructive compound, including ozonation, conventional activated sludge and biodegradation (Nakada et al., 2007; Santos et al., 2009; Song and Jhung, 2017; Joss et al., 2006). However, complete mineralization of this compound is difficult to achieve; thus, an improved alternative method is urgently required.

Recently, advanced oxidation processes (AOPs), in particular with heterogenous photocatalysis, have shown tremendous promise as alternatives for wastewater treatment of emerging contaminants (Chung et al., 2018; Khusnun et al., 2016). Among them, titania has attracted a great attention because of its strong oxidizing power, excellent chemical stability, cheaper and non-toxicity (Yadav et al., 2017; Nasirian et al., 2017). Nevertheless, the limited usage of TiO_2, due to drawbacks such as low surface area, poor active sites and weak light-harvesting properties, required a new approach to overcome those shortcomings (Singh et al., 2016). Previously, TiO_2 supported on conventional silica such as MCM-41, SBA-15 as well as KCC-1 have a great attention owing to their high surface area (Zhou et al., 2017; Yang et al., 2006). Among these, conventional silica-based, KCC-1/TiO_2 showed excellent performance in dye removal due to greater accessibility of active sites, which enhanced light-harvesting for higher adsorption capacity of dye

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https://doi.org/10.1016/j.jenvman.2018.08.073
Received 17 May 2018; Received in revised form 5 August 2018; Accepted 16 August 2018

molecules (Singh et al., 2016). The properties and applications of KCC-1/TiO_2 are profoundly dependent on its morphology and micro structure; thus, the synthesis procedure is worth investigating for its better performance.

Many preparation methods have been studied for synthesizing catalysts with desired morphology and support. Among them, microemulsion coupled with a seed-crystal crystallization method, followed by a microwave (MW)-assisted technique was essential to fabricate a fibrous nanostructure and to control the morphologies of the fibrous particles (Firmansyah et al., 2016). It has been reported that the formulation, as well as the reaction conditions, play important roles in the synthesis process (Polshittiwar et al., 2010; Bayal et al., 2016). In fact, there is still a lack of reports on the influence of fiber density of metal-loaded fibrous catalysts on the photocatalytic degradation of organic pollutants, particularly endocrine-disrupting chemicals (EDCs). Therefore, in this work, a fibrous silica–titania (FST) was synthesized by varying molar ratios of toluene and water for various fiber densities, and its physicochemical properties, as well as photocatalytic activity towards the degradation of IBP, were investigated in detail. The characterization of the FST was studied by XRD, UV–Vis DRS, FESEM, TEM, AFM, N_2 adsorption-desorption, FTIR and ESR analyses. The mechanism for the formation of FST and photodegradation of IBP are proposed. The kinetics and optimization of the degradation, as well as the reusability, biodegradability and mineralization of the catalysts are also discussed. We believe this important modification in preparation of FST will trigger a new design of catalysts for various applications.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), butanol, urea and toluene were obtained from Merck Sdn. Bhd., Malaysia. Commercial titania (JRC TiO_2) and ibuprofen (IBP) were bought from Sigma Aldrich.

2.2. Preparation of catalyst

Fibrous-silica-titania was synthesized based on previous reported technique using microemulsion system coupled with crystal-seed crystallization method (Firmansyah et al., 2016). Herein, a TiO_2 (JRC TiO_2-2) was used instead of ZSM5 as a seed and the toluene to water molar ratios were varied as follows; 7:1, 6:1, and 5:1. Firstly, the mixture of CTAB, distilled water and urea was mixed homogeneously for 20 min at room temperature under vigorous stirring, followed by the addition of toluene and butanol and the mixture was continuously stirred. After 20 min, titania seed was added and stirred for another 20 min. Then, TEOS was added to the mixture and kept vigorously stirred for another 2 h at room temperature. The mixture were then treated in hydrothermal condition for 4 h using microwave radiation (400 W). The resulting solution was centrifuged to obtain the white precipitate, washed with acetone and distilled water and then dried at 383 K in air for overnight. Lastly, the solid product was calcined for 3 h at 823 K and ready for characterization and reaction. The catalysts were denoted as FST(T:W = 7:1, 6:1, and 5:1).

2.3. Characterization of catalyst and photodegradation of ibuprofen

X-ray diffraction (XRD) patterns that recorded on powder diffractometer (Bruker Advance D8, USA) were used to confirm the crystallinity of the catalysts. The determination of structural properties and band gap energy were obtained using UV–Vis/DRS spectrophotometer (Perkin Elmer, USA) in the range of 200–800 nm. The morphological properties of the catalysts were investigated using FESEM (JEOL JSM-6701F, Japan), TEM (Philips EM420, USA) and AFM (Bruker Innova, USA). The nitrogen physisorption characterization of the catalysts was measured using a Beckman Coulter SA3100 surface area analyzer (USA) at 77 K. The FT-IR spectroscopy (Perkin Elmer Spectrum GX FTIR Spectrometer, USA) were used to analyse the catalyst functional groups. The surface defect and oxygen vacancy were identified by ESR spectrometer (JEOL JES-FA100, Japan). All details characterization procedures and photocatalytic reaction are provided in the supplementary information.

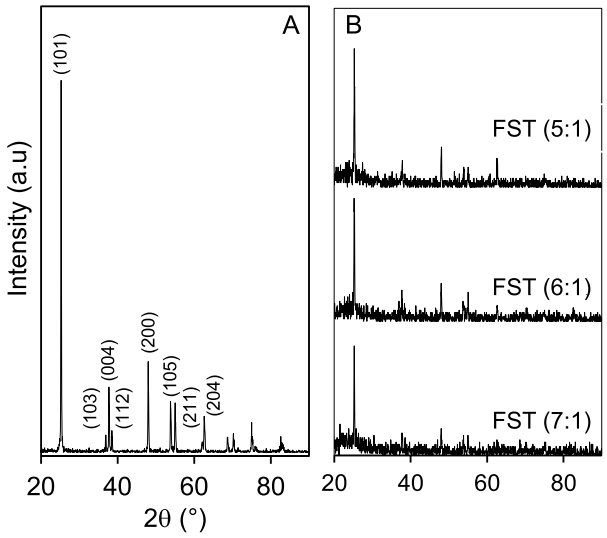

Fig. 1. XRD patterns of (A) commercial TiO_2 (B) FSTs catalysts.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Crystallinity, phase and structural studies

Fig. 1A and B displays a wide-angle XRD diffractogram for the commercial TiO_2 and fibrous silica–titania (FST) catalysts synthesized under different toluene-to-water ratios (T:W), respectively. A series of characteristic peaks were noticed in Fig. 1A at 25.4°, (1 0 1); 36.9°, (1 0 3); 37.8°, (0 0 4); 38.5°, (1 1 2); 48.2°, (2 0 0); 53.9°, (1 0 5); 55.3°, (2 1 1); and 63.2°, (2 0 4), which were assigned to anatase phase of TiO_2 (JCPDS file no. 00-004-0477). Similar peaks belong to anatase phase were obtained when TiO_2 was synthesized by other hydrothermal methods using different precursors (Jaafar et al., 2015; Xu et al., 2017). In fact, the FSTs exhibit a low-intensity and noisy XRD pattern, while retaining the main peaks of TiO_2, implying that the samples are somewhat losing their structural integrity (Fig. 1B). This is most probably due to the formation of dendrimeric silica fibers surrounded the TiO_2 seed. A similar phenomenon was observed when cobalt oxide was coated with silica; the XRD patterns became noisy due to more silica growth on the outer side of the core-shell (Gamonchuang et al., 2016). It is clearly observed that the crystallinity of the FST catalysts increased with decreasing T/W, suggesting the increased amount of toluene may inhibit the growth of the TiO_2 seed due to an enriched growth of SiO_2 fibers. A similar result was reported for the synthesis of a silica–titania photocatalyst, in which their crystallinity decreased with the increasing silicon content, due to the embedding of some SiO_2 portion into the TiO_2 particles, thus inhibiting the growth of the anatase phase titania (Jung and Park, 2000).

The catalysts were then tested using UV–Vis DRS and the spectra are presented in Fig. 2A. Two main peaks were observed at 226 nm and 300 nm, which the former is attributed to the presence of Ti^{4+} and/or Si^{4+} in tetrahedral coordination owing to the ligand-to-metal charge transfer (LMCT) from O^{2-} to Ti^{4+} and/or Si^{4+}, and the latter belongs to Ti^{4+} or/and Si^{4+} ions in octahedral coordination, respectively. The tetrahedrally and octahedrally coordinated Ti^{4+} ions in TiO_2–SiO_2