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Strategies for introducing titania onto mesostructured silica nanoparticles targeting enhanced photocatalytic activity of visible-light-responsive Ti-MSN catalysts

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ABSTRACT

Titanium-mesostructured silica nanoparticles (Ti-MSN) catalysts which are excellent photocatalytic materials for the environment were prepared by supporting mesostructured silica nanoparticles (MSNs) with titanium species synthesized by three different approaches: microwave and in situ and ex situ electrochemical methods, denoted as Ti-MSN-M, Ti-MSN-I, and Ti-MSN-E, respectively. The physicochemical properties of the catalysts were investigated via XRD, ^{29}Si NMR, N_2 adsorption-desorption, FTIR, ESR, and UV-DRS analyses. Characterization results revealed that the introduction of mesoporous titania nanoparticles (MTNs) prepared by the microwave method onto MSNs (Ti-MSN-M) did not significantly affect the silica framework. However, the silica network in the Ti-MSN-I and Ti-MSN-E was rather disrupted, particularly for the former catalyst, due to the desilication accompanied by isomorphous substitution of Ti in the MSN framework to form Si—O—Ti bonds. Ti was also found to be exchanged with the terminal hydroxyl groups of all catalysts to form the Si—O—Ti bonds. The addition of Ti species onto MSNs also increased the number of oxygen vacancies (V_o) and metal defect sites. Photocatalytic testing on the decolorization of Congo red (CR) resulted in the following order: Ti-MSN-I (94%) > Ti-MSN-M (90%) > Ti-MSN-E (34%). The V_o and metal defect sites were responsible in lowering the band gap of catalysts and decreasing the electron—hole recombination, while the great numbers of Si—O—Ti bonds as well as large surface area and pore volume increased the active sites and offered a good surface contact with light to enhance the activity of catalysts. A kinetic study demonstrated that the photodegradation followed the pseudo-first-order Langmuir-Hinshelwood model. Ti-MSN-I and Ti-MSN-M maintained their activities for up to five runs without serious catalyst deactivation, indicating their potential for the degradation of dye in wastewater. Mineralization measurements of CR by TOC and BOD_5 analyses after 3 h of contact time were 85.7% and 87.6% using Ti-MSN-M, while 83.7% and 80.3% using Ti-MSN-I, respectively. Optimization by response surface methodology showed that the catalyst dosage, pH, and TiO_2 loading were the significant factors in the decolorization of CR. This study demonstrated that these two green technologies; electrochemical and MW have a great potential to be used in synthesis of various advanced materials for greener and more sustainable processes.

1. Introduction

Recently, advanced oxidation process (AOPs) particularly heterogeneous photocatalysis has appeared as a promising approach for the treatment of several types of environmental pollutants due to its simple and low cost processes (Fujishima et al., 2000; Khusnun et al., 2016). In the presence of suitable light irradiation and a specific catalyst, the hydroxyl radicals (•OH) formed in the oxidation process become the most important species in mineralizing the targeted pollutant into stable inorganic compounds such as carbon dioxide and water (Jaafar et al., 2015a,b).

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Consequently, over the years, many photocatalysts have been synthesized and their photocatalytic properties have been investigated.

Nowadays, titanium dioxide (TiO_2) is an excellent photocatalytic material for the environment due to its peculiarities of chemical inertness and thermal and long-term stability against photo and chemical corrosion (Cheng et al., 2016; Ananpattarachai and Kajitvichyanukul, 2016). However, it has some drawbacks such as a low surface area and high photogenerated electron–hole recombination rate, which cause poor photocatalytic activity (Chong et al., 2015; Liu et al., 2014, 2015). In order to overcome these shortcomings, many approaches have been explored including the use of titanium incorporated in silicalite-1 (TS-1) on zeolite to improve the contact with pollutant molecules and hinder charge carrier recombination. TS-1 is a highly versatile molecular sieve with MFI structure, specially designed for selective oxidation reactions under mild conditions using hydrogen peroxide as oxidant (Serrano et al., 2009). However, like most of the conventional zeolites, TS-1 zeolite suffers from intracrystalline diffusion limitations due to the small size of its micropores. Accordingly, intensive research has been done to overcome this limitation, focusing on the synthesis of Ti-containing materials with enhanced accessibility to the reactive sites by using Ti-zeolites with large pores such as Ti–MCM-41 mesoporous materials, Ti-delaminated zeolites, nanocrystalline TS-1, and mesoporous TS-1 (Corma et al., 1994; Corma et al., 1999; Cundy et al., 2003; Ke et al., 2007). Recently, mesostructured silica nanoparticles (MSNs) have also become increasingly important because of their high surface area, highly uniform pore distribution, tunable pore size, and unique hosting properties. Previously, we reported the great potential of MSNs as a support material in ibuprofen delivery (Kamarudin et al., 2014), CO_2 reforming of methane (Sidik et al., 2015), cumene cracking (Sazegar et al., 2014), and adsorption of organic pollutant (Karim et al., 2014).

Various preparation methods have been studied to synthesize the TS-1 such as aerosol, hydrothermal, and inert-gas condensation. However, all these methods have limitations such as a tendency toward aggregation, leading to a requirement for several post-synthesis processing steps and also high vacuum, which makes the technique difficult and increases the cost (Eswar et al., 2015). Recently, we reported a simple-microwave (MW)-assisted method for preparation of MSNs and its efficient use in drug delivery (Kamarudin et al., 2014). Besides shortening the reaction time, this method provides a uniform and fast reaction environment for producing materials with homogenous and dispersed morphology (Shi et al., 2014). MWs could enhance the crystal growth to improve the hexagonal order and range of the catalyst, leading to a large surface area, pore volume, and pore width (Kamarudin et al., 2015). A further attempt at MW-assisted synthesis of mesoporous titania nanoparticles (MTNs) was also made; these MTNs are rich in surface defect sites, which are thought to be a key factor in constraining the electron–hole recombination during photocatalysis (Jaafar et al., 2015a,b).

Previously, we also reported a simple in situ electrochemical method for preparing various metal nanoparticles such as NiO, ZnO, and FeOOH as well as AgO supported on MSN and TiO_2 (Sidik et al., 2015; Jusoh et al., 2015b, 2015c; Jaafar et al., 2015a,b). Those catalysts showed high potential for efficient photodegradation of various organic pollutants and also CO_2-reforming of methane. Apart from offering mild process conditions, electrolysis is also an inexpensive technique that mainly uses electrons as the cheapest, purest, and most versatile redox agents, leading to clean and fast reaction performance. Considering the advantages of both electrochemical and MW technologies for greener and more sustainable processes, herein we extend the studies on the preparation of MSN-supported TiO_2 catalysts (Ti-MSN), where the titanium species were synthesized by three different approaches: microwave and in situ and ex situ electrochemical methods, denoted as Ti-MSN-M, Ti-MSN-I, and Ti-MSN-E, respectively. The physicochemical properties of the catalysts were investigated via XRD, ^{29}Si NMR, N_2 adsorption-desorption, FTIR, ESR, and UV-DRS analyses. The photocatalytic performance in the decolorization of Congo red (CR), kinetic studies, proposed mechanism, and reusability of the catalysts are also discussed. The results showed that the catalysts are rich with Ti^{3+} surface defects (TSD), oxygen vacancies (V_o), and Ti–O–Si bonds, which enable the photodecolorization to be carried out under visible light irradiation with high efficiency. Optimization by response surface methodology (RSM) using a central composite design (CCD) model was also performed to achieve the best conditions for the decolorization. We believe these new findings on simple preparation methods for TiO_2 supported on MSNs could contribute to photodegradation strategies for various organic pollutants as well as other reactions.

2. Experimental

2.1. Reagents and materials

Cetyltrimethylammonium bromide (CTAB), ethylene glycol (EG), tetraethyl orthosilicate (TEOS), 3-aminopropyl triethoxysilane (APTES), and propanol were purchased from MERCK Sdn. Bhd., Malaysia. Ammonium hydroxide solution (NH_4OH) was obtained from QRec, Malaysia. Titanium (IV) isopropoxide (TTIP) and congo red (CR) were bought from Sigma Aldrich. The platinum and titanium plates of more than 99.99% purity were obtained from Nilaco Metal, Japan. Tetraethylammonium perchlorate (TEAP), which was used as a supporting electrolyte in electrolysis was prepared in accordance with the procedure reported in the literature (Jalil et al., 2007; Jalil et al., 2010).

2.2. Preparation of the catalyst

The mesostructured silica nanoparticles (MSN) were synthesized by a co-condensation and sol–gel method as reported in previous literature (Karim et al., 2012). The CTAB surfactant, EG, and NH_4OH solution were dissolved in 700 mL of water with the mole composition of CTAB: EG: NH_4OH: H_2O were 0.0032:0.2:0.2:0.1, respectively. After vigorous stirring for about 30 min with heating, 1.2 mmol TEOS and 1 mmol APTES were added to the clear mixture to give a white suspension solution. This solution was then stirred for another 2 h, and the samples were collected by centrifugation. The synthesized MSN were dried at 333 K and calcined at 823 K for 3 h to remove the surfactant.

The mesoporous TiO_2 (MTN) was synthesized by the microwave-assisted process were similar to those reported in the previous study (Jaafar et al., 2015a,b). 4.68 g of CTAB surfactant was dissolved in 720 mL distilled water, 120 mL propanol and 29 mL of NH_4OH. The mixture was stirred continuously for 30 min at 323 K in water bath. After 30 min, the temperature of water bath was increased to 353 K followed by addition of 5.7 mL TTIP and this process was continued for 2 h in water bath in order to dissolve the mixture. The white solution was transfer into a beaker after 2 h of stirring and placed in the microwave. The microwave heating was conducted in a domestic microwave oven (Samsung ME711K) with power 450 W. The heating was intermittently continued for 2 h in order to form a sol–gel of the TiO_2. The obtained product was collected and dried overnight in oven before calcined at 873 K for 3 h.

For Ti-MSN-M sample, the MSN was immersed in propanol (10 mL) and the mixture was stirred for 15 min. Next, 5 wt% of MTN

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