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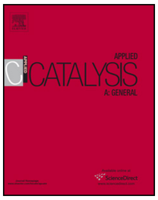

Sequential desilication–isomorphous substitution route to prepare mesostructured silica nanoparticles loaded with ZnO and their photocatalytic activity

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ABSTRACT

A simple electrochemical method followed by impregnation was employed to prepare a coral-like zinc oxide catalyst loaded on mesostructured silica nanoparticles (ZnO/MSN). The introduction of zinc species onto a silica framework was found to form an interaction between the host and support material. XRD analysis suggested the presence of zinc on the internal pore walls of MSN. FE-SEM and TEM analyses displayed nanorods, nanoparticles and coral-like shapes of ZnO, MSN and ZnO/MSN, respectively. ^{29}Si NMR and FTIR results showed that desilication occurred in the silica framework of the MSN accompanied by isomorphous substitution of Zn^{2+} cations to form an active species Zn–O–Si bond. The photocatalytic activity of the ZnO/MSN was tested by decolorizing methyl orange (MO). It was found that increasing the ZnO loading led to a higher recombination rate of photoinduced electron–hole pairs, which resulted in decreased photocatalytic activity. The highest decolorization rate was obtained using 1 g L^{-1} of 5 wt% ZnO/MSN with an optimum dosage of 3.06×10^{-2} mM MO after 8 h contact time at pH 2 under UV irradiation. A kinetic study demonstrated that the photocatalytic reaction followed the pseudo first-order model. The photocatalyst was still stable after five cycling runs with a small amount of Zn was leached (<3.0%).

1. Introduction

Dyes widely used in the textile, paper, cosmetics and plastics industries have led to severe environmental contamination due to their emission of toxic and colored wastewater into water bodies [1]. This phenomenon seriously affects the nature of water, inhibits sunlight penetration and reduces photosynthetic reactions. In addition, some dyes are either toxic or carcinogenic. Many treatment methods including biological, adsorption, coagulation and flocculation, ion exchange and membrane separation have been reported for the removal of dyes to varying degrees [2–7]. However these methods are usually non-destructive, inefficient and costly or just transfer pollutants from water to another phase.

An advanced oxidation process (AOPs) using heterogeneous semiconductor photocatalysts such as TiO_2, Fe_2O_3, ZnO, CuO, ZrO_2, CdS, and SnO_2 can be an alternative to conventional methods for the removal of dye pollutants from water [8,9]. Among them, ZnO has become very well established in photocatalytic approaches as well as in the environmental catalysis area. The photocatalytic activity of ZnO was recently recognized to be comparable with TiO_2 and has received much attention because of its unique properties and numerous advantages, such as high photosensitivity and stability in degrading various toxic substances [10]. However, even though ZnO has sufficient photocatalytic activity, photodegradation of diluted pollutants cannot proceed efficiently because of insufficient contact with the catalyst surface, which is an important factor in hindering photocatalytic activity. The mass transfer to the catalyst surface limits the photodegradation rate of diluted pollutants [11]. Thus, a suitable method to improve the contact between pollutant molecules and a catalyst should be found in order to enhance the adsorption of pollutant molecules. One method is incorporation of ZnO into a mesoporous material support, which has been discussed by several research groups in recent years [12–14]. A review of recent studies revealed some important supports for ZnO, including HZSM-5, SiO_2, MCM-41 and MCM-22 [15–17].

Recently, we reported a new electrochemical method for preparation of metal oxide nanoparticles including ZrO_2, α-Fe_2O_3, CuO and ZnO [18–21]. Further loading of these nanometal oxides onto

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zeolite supports led to enhanced catalytic activity, which was exhibited by efficient photodecolorization of various dyes as well as isomerization of *n*-alkane [18–20,22–24]. It was found that in most cases, dealumination accompanied by isomorphous substitution readily occurred in the aluminosilicate framework of the zeolites during preparation of these catalysts, which then improved their properties toward the subsequent reactions. Thus, we anticipated a similar perturbation occurs in the framework of mesoporous silica when using a similar simple electrolysis system. This would be of interest because silica is recognized as a less active material for many heterogeneous catalytic reactions due to the absence of active sites. Immobilization of a metal onto an inexpensive silica support would improve its acidic properties and thus activate the catalyst [25]. To our knowledge, reports on desilication accompanied by isomorphous substitution of foreign ions such as Zn for Si in a silica framework are still scanty. In addition, most ZnO studied were nanoparticles, but little information has been reported for alternate shapes of supported ZnO.

Therefore, in this study we report for the first time the preparation of ZnO supported on mesostructured silica nanoparticles (MSN) and its photocatalytic performance toward decolorization of methyl orange (MO). In fact, the MSN used has a large surface area with a uniform and tunable pore size, which offers considerable potential as an excellent solid support for immobilization of heterogeneous catalysts [26]. The tortuous and winding shape of the coral-like ZnO/MSN is expected to afford a larger surface area for favorable results. The prepared catalyst was characterized by X-ray diffraction (XRD), field emission scanning electron microscopy coupled with energy dispersive X-ray (FE-SEM/EDX), transmission electron microscopy (TEM), ^{29}Si magic angle spinning nuclear magnetic resonance (MAS-NMR), Fourier transform infrared (FTIR), adsorbed pyridine and carbon monoxide FTIR, photoluminescence (PL), and Brunnauer–Emmett–Teller (BET) surface area analysis. A new structural model for ZnO/MSN was proposed on the basis of the literature, characterization and photodecolorization results. The decolorization of MO was optimized under various parameters such as the effect of pH, catalyst dosage, and ZnO loading. The kinetic behavior of the catalyst was also studied to determine the rate constant.

2. Experimental

2.1. Materials

Cetyltrimethylammonium bromide (CTAB), ethylene glycol (EG), tetraethyl orthosilicate (TEOS), methyl orange (MO), 3-aminopropyl triethoxysilane (APTES), sodium hydroxide (NaOH), and hydrochloric acid (HCl), were purchased from MERCK Sdn. Bhd., Malaysia. Ammonium hydroxide solution (NH_4OH) was obtained from QRec, Malaysia. The platinum and zinc 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 [27]. Deionized water was used for the preparation of the pH solution and adjustments to the pH were performed using a 0.1 M HCl and NaOH solution.

2.2. Catalyst preparation

The mesostructured silica nanoparticles (MSN) were prepared by a co-condensation and sol–gel method as reported in previous literature [26]. 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 ZnO nanorods were prepared according to previous reported protocol with some modification [28,29]. An open system electrolysis cell was fitted with a magnetic stirrer and a platinum plate cathode ($2 \times 2\,cm^2$) facing a zinc plate anode ($2 \times 2\,cm^2$). A 10 mL distilled water and 4 mL NH_4OH were added into a 0.1 M CTAB and 0.1 M TEAP, which act as a capping agent and supporting electrolyte, respectively. The electrolysis was conducted at a constant current of $120\,mA\,cm^{-2}$ and 0 °C under air atmosphere. After electrolysis, the obtained mixture was impregnated and dried at 383 K for 12 h before being calcined at 823 K for 3 h to yield grayish ZnO nanorods.

The ZnO/MSN catalyst was prepared via the same procedure as ZnO nanorods, except the MSN was added to the mixture after electrolysis. The mixture was then impregnated, dried and calcined as above to give a white powder catalyst which is ready for a characterization. The required weight of the ZnO supported on the MSN was calculated based on duration time of the electrolysis according to the Faraday's law of electrolysis as follows:

$$t = \left(\frac{F}{I}\right)(z \times n) \qquad (1)$$

where t is a total time for the constant current applied (s); F is a Faraday constant, 96,486 C mol^{-1}; I is an electric current applied; z is a valency number of ions of substances (electrons transferred per ion); and n is an amount of substance (number of moles, liberated $n = m/M$).

2.3. Characterization

The crystalline structures of the catalysts were studied by XRD recorded on a D8 ADVANCE Bruker X-ray diffractometer using Cu $K\alpha$ radiation at a 2θ angle ranging from 2° to 90°. The phases were identified with the aid of the Joint Committee on Powder Diffraction Standards (JCPDS) files.

The morphological properties of ZnO, MSN and ZnO/MSN catalysts as well as the dispersion of ZnO onto MSN surface were examined by field emission scanning electron microscopy (FESEM) (JSM-6300F FESEM) with energy dispersion X-ray (EDX) and transmission electron microscopy (TEM).

The textural properties (i.e., specific surface area, pore volume, and pore diameter) were determined from nitrogen physisorption at 77 K using a Quantachrome Autosorb-1 analyzer. Prior to measurements, the samples were evacuated for 24 h at 573 K. Specific surface area (S_{BET}) values were calculated from the BET isotherm plots, while the total pore volume and pore size distributions were calculated using the Barrett, Joyner, and Halenda (BJH) method from the desorption isotherm.

Nuclear magnetic resonance measurements were carried out using ^{29}Si magic angle spinning nuclear magnetic resonance (MAS-NMR) Spectroscopy, which was performed at room temperature on a Bruker Solid NMR (JEOL 400 MHz) spectrometer using tetramethylsilane (TMS) as an external reference. The spectra were recorded using 4 μs radio frequency pulses, a recycle delay of 60 s and spinning rate of 7 kHz using a 4 mm zirconia sample rotor.

FT-IR (Perkin Elmer Spectrum GX FTIR Spectrometer) was performed using the KBr method with a scan range of 400–4000 cm^{-1}. IR spectroscopy of adsorbed pyridine was used as a tool to evaluate the Brönsted and Lewis acid sites. In addition, carbon monoxide was used to evaluate the active sites on the ZnO/MSN catalyst. Before the analysis, catalyst was activated according to the method described in the literature [24]. In brief, a self supported wafer placed in an