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Electrochemical strategy for grown ZnO nanoparticles deposited onto HY zeolite with enhanced photodecolorization of methylene blue: Effect of the formation of Si—O—Zn bonds

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ABSTRACT

Nanoparticles of electrogenerated zinc-supported HY zeolite (EGZnO/HY) catalyst were prepared by a simple electrochemical method. The interaction between zinc species and HY support during the electrolysis was found to affect the EGZnO/HY structure. In addition to the formation of EGZnO nanoparticles (<30 nm in size) that distributed on the surface of HY support, an isomorphous substitution of Al with Zn also occurred in the aluminosilicate framework to result in a Si—O—Zn bonds. The photoactivity of EGZnO/HY was tested on the decolorization of methylene blue (MB). An amount of 0.375 g L^{-1} of 1 wt% EGZnO/HY was found to be the optimum dosage for 10 mg L^{-1} MB, which resulted in 80% of maximum decolorization after 6 h of contact time at pH 3 under fluorescent light (420 nm). Increasing the EGZnO loading led to additional formation of Si—O—Zn bonds and lessened the number of EGZnO nanoparticles, which then reduced the photodecolorization percentage of MB.The photocatalytic reaction was follows the first-order Langmuir–Hinshelwood model, and gives partially mineralization. The photocatalyst was still stable after five cycling runs with no Zn leaching.

1. Introduction

Recently, an environmental problem of water pollution due to rapid industrialization has drawn considerable attention among scientific communities. Approximately 22% of the total volume of industrial wastewater was generated, which comes from the textile industry whereas over 100,000 dyes were available with more than 7×10^5 tons of dyestuff produced annually [1,2]. However, most of the unused dye produces undesirable effluents, which are discharged into the environment with or without further treatment. These effluents enter natural water bodies and can cause severe problems if not treated properly because the dyes are toxic, mutagenic, and carcinogenic to human life [3] as well as inhibit photosynthesis of aquatic life even in small quantities such as 1 ppm [4]. To overcome this problem, several methods for the removal of dyes have been reported, including chemical and biological oxidation [5], adsorption [6], coagulation and flocculation [7], electrochemical oxidation [8], ion exchange [9] and membrane separation [10]. However, these methods have their own limitations of being time consuming, expensive, and commercially unattractive as well as resulting in the generation of secondary wastes.

Advanced oxidation processes (AOPs) using semiconductor metal oxides, such as TiO_2, WO_3, Fe_2O_3, ZnO, CuO, ZrO_2, CdS, In_2O_3, and SnO_2, as photocatalysts have become important because the AOPs can convert a wide range of harmful dyes into non-toxic products, CO_2, and water at ambient temperature [11–13]. In addition, the use of mesoporous materials, such as zeolite, as a support for the metal oxides has recently become the focus of intensive research because the catalyst support influences the catalytic performance through structural features and the interaction between the materials leads to enhancement of the contact between the surface and the irradiation [14] as well as reduction in the amount of metal oxides required [13]. A review of recent studies has revealed that some of the important metal oxide-supported zeolites include TiO_2-HZSM-5, Co-ZSM-5, CuO-X zeolite, and Fe-exchange zeolite [15–18]. The most popular metal oxides used were TiO_2 and ZnO, but in particular, ZnO has attracted much attention with respect to its ability to degrade various pollutants due to its high photosensitivity and

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stability as well as suitable alternative to TiO_2 since it has similar band gap energy, which is equal to 3.20 eV [19,20]. To the best of our knowledge, reports on ZnO-supported zeolite as photocatalysts are still scarce.

The nanosized ZnO has evoked a great deal of interest in recent years, especially in the area of photocatalytic studies for enhancing its performance such as an increase in surface area and changes in surface properties as well as in quantum effect of photocatalyst materials [20–22]. Upon light irradiation, this nanosized ZnO generated a highly active radical species, thus it can easily oxidize an organic waste such as dyes into less harmful residues [22,23]. Various routes to synthesize nanosized zinc particles such as sol–gel, hydrothermal, alkali precipitation, thermal decomposition, organo-zinc hydrolysis, spray pyrolysis, microwave irradiation, and sonochemical synthesis [20,24–26] have been reported, but there are still limitations to study the preparation of nanosized zinc particle using electrochemical technique.

We have reported a new method for preparing very fine particles of electrogenerated zinc metal (EGZn) with high reactivity using a simple electrochemical method and its successful use in the synthesis of anti-inflammatory agents [27]. It was also found that the zinc oxide nanoparticles (EGZnO) led to the generation of protonic acid sites when supported on HZSM-5, which enhanced the *n*-alkane isomerization [28]. By the corresponding method, an α-Fe_2O_3 and $EGZrO_2$ supported HY catalyst was also successfully achieved, which possesses high photoactivity in the decolorization of methyl orange and methylene blue, respectively [29,30].

Additionally, exploring a new application dealing with the use of the nanoparticles EGZnO would be of interest, particularly in the area of photocatalytic reaction. Therefore, in the present study, we report for the first time, the preparation of EGZnO supported on HY zeolite (EGZnO/HY) and its photoactivity toward a decolorization of methylene blue (MB). The prepared catalyst was characterized by X-ray diffraction (XRD), thermogravimetric simultaneous differential thermal analysis (TG-SDTA), field emission scanning electron microscopy coupled with energy dispersive X-ray (FE-SEM/EDX), transmission electron microscopy (TEM), Fourier transform infrared (FTIR), ultraviolet–vis diffuse reflectance spectroscopy (UV–vis DRS), photoluminescence (PL), Brunnauer–Emmett–Teller (BET) surface area analysis, ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma mass spectrometry (ICP-MS). A new structural model for EGZnO/HY was proposed on the basis of characterization and photodecolorization results. The decolorization of MB was optimized under various parameters such as the effect of pH, EGZn loading, catalyst dosage, and initial MB concentration. The kinetics behavior of the catalyst was also studied to determine the surface interaction of the catalyst with MB.

2. Experimental

2.1. Materials

The HY zeolite had a Si/Al ratio of 80 and was purchased from Zeolyst International. *N*,*N*-dimethylformamide (DMF) was purchased from Merck and naphthalene was obtained from Fluka. Sodium hydroxide (NaOH), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), and methylene blue (C.I. 52015 for microscopy) were obtained from QReC™. Ammonium oxalate was purchased from Riedel–De Haen AG Seelze–Hannover while isopropanol was purchased from Systerm®. The platinum (Pt) and zinc (Zn) plate cells were obtained from Nilaco Metal, Japan. All reagents were of analytical grade and were used as received. 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

EGZnO was prepared following a previously reported protocol [27,31]. A DMF solution (10 mL) containing 0.1 M tetraethylammonium perchlorate was electrolyzed in the presence of a naphthalene mediator (6 mmol) in a normal one-compartment cell fitted with a Pt plate cathode (2 cm × 2 cm) and Zn plate anode (2 cm × 2 cm) at a constant current density of 120 mA/cm^2 under a nitrogen atmosphere at 273 K. After electrolysis, the mixture was impregnated, oven dried overnight at 378 K, and calcined at 823 K for 3 h to yield a white powder (EGZnO) for characterization and photocatalytic testing.

The EGZnO/HY catalyst was prepared using the same procedure except for the addition of the HY zeolite (1.5 g) prior to electrolysis, and a white powder was obtained as the final product. The required weight percent of the EGZnO supported on HY and the time required for complete electrolysis was calculated based on Faraday's law of electrolysis,

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

where t = total time for the constant current applied (s); F = 96,486 C mol^{-1}, which is the Faraday constant; I = the electric current applied; z = the valency number of ions of substances (electrons transferred per ion); and n = the number of moles of Zn (no 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_α radiation at a 2θ angle ranging from 3° to 90°. The particle sizes of the catalysts were calculated using the Debye–Scherrer equation,

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

where k = 0.94 is a coefficient, λ = 1.5406 Å is the X-ray wavelength, β is the full width half maximum (FWHM) of the sample and θ is the diffracting angle. The phases were identified with the aid of the Joint Committee on Powder Diffraction Standards (JCPDS) files.

The thermal stability behavior of establish catalysts was examined by thermogravimetric simultaneous differential thermal analysis (TG-SDTA) (TGA/SDTA851 Instrument). The measurement was carried out from 278 to 1173 K with heating rate of 278 K min^{-1} under nitrogen flow at rate of 40 mL min^{-1}. The topological properties as well as semi-quantitative determination of percentage metal loaded were observed by field emission scanning electron microscopy coupled with energy dispersive X-ray spectrometer (FE-SEM/EDX) (JSM-6701F). The morphological properties of nanosized EGZnO and the EGZnO/HY catalyst as well as the distribution of EGZnO deposited on the HY surface were examined by TEM (JEOL JEM-2100F). FTIR (Perkin Elmer Spectrum GX FTIR Spectrometer) was performed using the KBr method with a scan range of 400–4000 cm^{-1}. The optical absorption properties of the catalyst were obtained using a UV–vis DRS (Perkin Elmer Spectrophotometer) in the range of 200–800 nm at room temperature. The photoluminescence (PL) (JASCO Spectrofluorometer) (FP-8500) with 150 W Xe lamp as excitation source were employed to study the electronic structure, optical and photochemical properties of semiconductor materials, by which information such as surface oxygen vacancies and defects, as well as the efficiency of charge carrier trapping, immigration and transfer can be obtained. The band gap of EGZnO was determined from plots of the Kubelka–Munk (K–M) function [$f_{K\text{-}M} = (h\nu/\lambda)^{1/2}$] as a function of the energy of the excitation light [$h\nu$].