Applied Catalysis B: Environmental 125 (2012) 311–323

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

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

Isomorphous substitution of Zr in the framework of aluminosilicate HY by an electrochemical method: Evaluation by methylene blue decolorization

N. Sapawe[a], A.A. Jalil[a,*], S. Triwahyono[b], S.H. Adam[a], N.F. Jaafar[b], M.A.H. Satar[a]

[a] Institute of Hydrogen Economy, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b] Ibnu Sina Institute for Fundamental Science Studies, Faculty of Science,Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

ARTICLE INFO

Article history:
Received 5 March 2012
Received in revised form 20 May 2012
Accepted 27 May 2012
Available online 15 June 2012

Keywords:
Isomorphous substitution
$EGZrO_2/HY$
Electrochemical
Photodecolorization
Methylene blue

ABSTRACT

Isomorphous substitution of Zr in the framework of aluminosilicate HY occurred during the preparation of electrogenerated zirconia supported HY ($EGZrO_2/HY$) catalyst via a simple electrochemical method. Dealumination accompanied by an ion exchange with Zr^{4+} formed Si—O—Zr bond, which controlled the formation of active species $EGZrO_2$ that influenced the efficiency of the photodecolorization of methylene blue (MB). An amount of 0.375 g L^{-1} 1 wt% $EGZrO_2/HY$ was found to be the optimum dosage for 10 mg L^{-1} MB, which resulted in 97% decolorization after 6 h of contact time at pH 11. The kinetics study indicates that the reaction follows the Langmuir–Hinshelwood model, where the reaction may occur both on the surface of the catalyst and in the bulk solution. The mineralization of MB was measured by removal of chemical oxygen demand (COD), five days biochemical oxygen demand/chemical oxygen demand (BOD_5/COD), and total organic carbon (TOC/TOC_0), and the results obtained were 95%, 7.14, and 0.08, respectively. After five cycling runs, the catalyst was still stable and showed no leaching effect. This study is believed to be extendable to the synthesis of other catalysts with different characteristics and be used in various applications.

1. Introduction

Over the past few decades, environmental issues involving water pollution have become an important issue. The major pollutants in wastewater, such as organic dyes, are produced from the dyeing processes in which approximately 15% of the total world production of dyes is released in textile effluents [1,2]. Approximately 97% of local dye effluents are produced by the food, chemical, and textile industries [3]. Among these industries, approximately 22% of the total volume of wastewater is produced by the textile industry, which commonly uses basic dyes such as crystal violet, rhodamine B, methyl violet, and methylene blue, to dye wool, silk, cotton, linen, and modified acrylic fibers [4]. Most of the unused dye results in undesirable effluents and is discharged into the environment with or without further treatment. These effluents run into natural water bodies and can cause severe problems if not treated properly because the dyes are toxic, mutagenic and carcinogenic to human life [5] as well as prohibit the photosynthesis of aquatic life when present even in small quantities like 1 ppm [6]. To overcome this problem, several methods for the removal of dyes have been reported, including chemical and biological oxidation [7], adsorption [8], coagulation and flocculation [9], electrochemical oxidation [10], ion exchange [11], and membrane separation [12]. However, these methods have their own limitations including being time-consuming, expensive, and commercially unattractive as well as resulting in the generation of secondary wastes.

Advanced oxidation processes (AOPs) using semiconductors such as TiO_2, ZnO, WO_3, Fe_2O_3, 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 [13–15]. Mixed metal oxides such as TiO_2–ZrO_2, Ag–ZnO, Fe_2O_3–TiO_2, TiO_2–ZnS, Sn–ZnO, and Ag–TiO_2 exhibit better performance and enhance photocatalytic activity [16–21]. 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 the enhancement of the contact between the surface and irradiation [22] as well as reduction in the amount of metal oxides required [15]. Zeolitic supports are important because of their high surface area, thermal stability, eco-friendly nature, specific photophysical properties, and their potential ability to control charge and electron transfer processes [23,24]. A review of recent studies has revealed that some of the

---

* Corresponding author. Tel.: +60 7 5535581; fax: +60 7 5536165.
E-mail address: aishah@cheme.utm.my (A.A. Jalil).

0926-3373/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2012.05.042

important metal oxide-supported zeolites include TiO_2-HZSM-5, Co-ZSM-5, CuO-X zeolite, and Fe-exchange zeolite [21,25–27]. The popular metal oxides use TiO_2 and ZnO but alternative photocatalysts are still under development and more research is required. ZrO_2 exhibits great potential because of specific optical and electrical properties, thermal stability, and strong mechanical strength as well as the presence of acid–base and redox capabilities [28,29]. To the best of our knowledge, reports on ZrO_2-supported zeolite photocatalysts are still scarce.

Recently, there has been increasing interest in the use of ZrO_2 nanosized photocatalyst in photocatalytic activity because of some principal factors such as increase in surface area and quantum effect, thus enhancing their photoreactivity properties [30,31]. There are various methods of synthesizing nanosized zirconia particles, such as sol–gel, co-precipitation, ball milling, hydrothermal process, gas phase synthesis, microemulsion methods, and emulsion-assisted direct precipitation [28] that have been reported, but there are still very few studies on the preparation of nanosized zirconia particle using an electrochemical method.

We have reported a new method for preparing very fine particles of zinc metal with high reactivity using a simple electrochemical method, and the successful use of a catalyst to synthesize anti-inflammatory agents via cross-coupling reactions [32]. In addition, we found that the zinc oxide nanoparticles prepared by the same method led to the generation of protonic acid sites on HZSM-5 supports resulting in enhancement of *n*-alkane isomerization [33]. Recently, we also found that α-Fe_2O_3 supported HY catalyst exhibits high photoactivity towards the decolorization of methyl orange [34]. The nanosized particles of those metals might play an important role in the reactions. These findings have led to an interest in exploring the synthesis of other nanometal oxides supported on zeolites for photocatalytic reactions. Therefore, the present study reports for the first time, the preparation of a nanoparticle electrogenerated ZrO_2-supported HY zeolite ($EGZrO_2$/HY) catalyst using the corresponding method. The prepared catalyst was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR), ultraviolet–visible diffuse reflectance spectroscopy (UV–vis/DRS), Brunnauer–Emmett–Teller surface area analysis (BET), ^{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). The activity of the catalyst for the photodecolorization of methylene blue (MB) was studied under various conditions to determine the effect of pH, metal loading, catalyst dosage, and initial dye concentration. The kinetics behavior of the catalyst was also studied to determine the surface interaction of the catalyst with MB. Herein, we report the advantage of using the electrochemical preparation method and the effect of the support material on the structure of the $EGZrO_2$/HY catalyst. A new structural model for $EGZrO_2$/HY is proposed that is consistent with the results from characterization of the catalyst and takes into account dealumination and ion exchange.

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 Sdn. Bhd. Malaysia, and naphthalene was obtained from Fluka Sdn. Bhd., Malaysia. Sodium hydroxide (NaOH), hydrochloric acid (HCl), and methylene blue (C.I. 52015 for microscopy) were obtained from QReC™. The platinum (Pt) and zirconia (Zr) plate cells were obtained from Nilaco Metal, Japan. Degussa P25 TiO_2 was obtained from Acros Organics, Belgium. 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.

Table 1
Time required for complete electrolysis and the exact amount of $EGZrO_2$ loading onto HY as detected by ICP-MS.

$EGZrO_2$ (wt %)	Time for complete electrolysis[a] (min)	% Zr detected in catalyst[b]
1	2.23	1.02
8	19.2	7.98
15	38.9	15.3
22	62.0	22.0

[a] Calculated based on Faraday's law (Eq. (1)).
[b] Zr detected determine by ICP-MS.

2.2. Catalyst preparation

$EGZrO_2$ was prepared following a previously reported protocol [30]. 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 Zr 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 ($EGZrO_2$) for characterization and photocatalytic testing.

The $EGZrO_2$/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 $EGZrO_2$ supported on HY and the time required for complete electrolysis was calculated based on Faraday's law of electrolysis (Table 1),

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

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 amount of substance (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 Kα radiation at a 2θ angle ranging from 3° to 90°. The particle sizes of the catalysts were calculated using the Debye–Scherrer equation,

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{2}$$

where $k = 0.94$ is a coefficient, $\lambda = 1.5406$ 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 morphological properties of nanosized $EGZrO_2$ and the $EGZrO_2$/HY catalyst as well as the distribution of $EGZrO_2$ deposited on the HY surface were examined by TEM (JEOL JEM-2100F). FT-IR (PerkinElmer 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