Structural rearrangement of mesostructured silica nanoparticles incorporated with ZnO catalyst and its photoactivity: Effect of alkaline aqueous electrolyte concentration

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ABSTRACT

ZnO-incorporated mesostructured silica nanoparticles (MSN) catalysts (ZM) were prepared by the introduction of Zn ions into the framework of MSN via a simple electrochemical system in the presence of various concentrations of NH_4OH aqueous solution. The physicochemical properties of the catalysts were studied by XRD, ^{29}Si MAS NMR, nitrogen adsorption–desorption, FE-SEM, TEM, FTIR, and photoluminescence spectroscopy. Characterization results demonstrated that the alkaline aqueous electrolyte simply generated abundant silanol groups on the surface of the catalysts as a consequence of desilication to form the hierarchical-like structure of the MSN. Subsequent restructuring of the silica network by the creation of oxygen vacancies and formation of Si–O–Zn during the electrolysis, as well as formation of new Si–O–Si bonds during calcination seemed to be the main factors that enhanced the catalytic performance of photodecolorization of methyl orange. A ZM prepared in the presence of 1.0 M NH_4OH (ZM-1.0) was determined to be the most effective catalyst. The catalyst displays a higher first-order kinetics rate of $3.87 \times 10^{-1}\,h^{-1}$ than unsupported ZnO ($1.13 \times 10^{-1}\,h^{-1}$) that prepared under the same conditions in the absence of MSN. The experiment on effect of scavengers showed that hydroxyl radicals generated from the three main sources; reduced O_2 at the conduction band, decomposed water at the valence band and irradiated H_2O_2 in the solution, are key factors that influenced the reaction. It is also noted that the recycled ZM-1.0 catalyst maintained its activity up to five runs without serious catalyst deactivation.

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1. Introduction

Heterogeneous photocatalysis is a promising technology for the removal of dyes from wastewater [1]. It has great potential as an environmental friendly, low cost, and sustainable technology. Various semiconductors, including TiO_2, Fe_2O_3, ZnO, and CuO, were used as photocatalysts because of their ability to decolorize dye-containing wastewater [2,3]. Of the various semiconductor materials, ZnO stands out due to its properties and wide applications. ZnO features a band gap of 3.37 eV, efficient absorption

in a larger fraction of solar energy, and has a low cost. Therefore, it is considered as a favorable semiconductor with potential uses in photocatalysis [4]. It has been demonstrated that the photocatalytic activity of semiconductors are correlated to the morphology, crystalline phase, porosity, and surface area of the materials [5]. Additionally, the surface defect sites of the catalyst are thought to be a main factor affecting the electron–hole recombination process during photocatalysis [6]. To achieve the target, many researchers have tried to improve the photocatalytic activity of the semiconductors by using mesoporous materials as the support.

Recently, studies on the synthesis of mesoporous silica (MS) materials have received much attention and the field has advanced rapidly. The MS materials, such as MCM-41 and SBA-15, have been extensively investigated due to their unique properties [7]. In response to this, mesostructured silica nanoparticles (MSN) have become increasingly important because of their high surface area,

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highly uniform pore distribution, tunable pore size, and unique hosting properties. Previously, we reported the great potential of MSN as a support material in ibuprofen delivery [8], CO_2 methanation [9], cumene cracking [10], and adsorption of organic pollutant [11].

Although the catalytic ability of the semiconductors could be enhanced by using these mesoporous materials, many problems still arise. At times, the pores in these materials are not large enough to help the fast internal diffusion and mass transfer [12]. It is believed that the modification of mesoporous material to form hierarchical structures is a beneficial approach to improve the properties and effectiveness of the catalysts without changing the chemical composition of the materials [13]. Miao et al. reported an efficient catalytic ability of Fe_2O_3 supported on hierarchically porous silica (Fe_2O_3/HPS) for the degradation of Orange II due to the excellent pore structure of HPS [14]. Based on this information, many researchers have pursued the creation of hierarchically structure materials.

In particular, desilication by alkaline treatment was shown to be an effective way to prepare hierarchical porous materials [15]. This selective removal of siliceous species has become a widely used top-down method. The studies on the alkali-treatment of zeolites, which used Na_2CO_3 or NaOH solution, showed that selective removal of the siliceous species from the zeolite framework occurs without changes to the zeolitic structure [16,17]. However, these conventional methods required high temperature, longer reaction times, and included somewhat troublesome steps [18,19]. We have previously reported the dealumination of the aluminosilicate framework of zeolites by a simple electrochemical method under nitrogen atmosphere accompanied by isomorphous substitution of metal ions (Zr^{4+}, Fe^{3+}, and Zn^{2+}). These metal-supported catalysts led to enhanced photodecolorization of various dyes [20,21]. On the other hand, we also reported a sequential desilication–isomorphous substitution method to prepare mesostructured silica nanoparticles loaded with ZnO [22]. The dealumination and desilication were achieved successfully by electrolysis under mild conditions without using strong acidic conditions, hydrothermal treatment, higher temperature, and/or reactive compounds [23]. Therefore, in this study, we further explored the possible preparation of hierarchically ordered structures of MSN using the similar electrochemical system by altering the conditions of electrolyte. We found that by controlling the weak alkaline concentration, a different degree of desilication was achieved and subsequent rearrangement of the silica network during the electrolysis as well as calcination enhanced the catalytic performance for photodecolorization of methyl orange dye. The catalysts were characterized by XRD, ^{29}Si MAS NMR, nitrogen adsorption–desorption, FE-SEM, TEM, FTIR, and photoluminescence. A proposed structure and involvement of both Zn and NH_4OH solution in the silica structural rearrangement were elucidated in detail from the characterization results. A proposed mechanism for photodecolorization, as well as kinetics studies, is also discussed.

2. Experimental

2.1. Materials

All chemicals were reagent grade and used without further purification. For preparation of mesostructured silica nanoparticles (MSN), cetyltrimethylammonium bromide (CTAB), ethylene glycol (EG), tetraethyl orthosilicate (TEOS), 3-aminopropyl triethoxysilane (APTES) as surfactant, co-solvent, silica source and pore expander, respectively were purchase from MERCK Sdn. Bhd., Malaysia. Ammonium hydroxide solution (NH_4OH) was obtained from QRec, Malaysia. The platinum and zinc plates (99.99% purity)

which used in the electrolysis were obtained from Nilaco Metal, Japan. The supported electrolyte, tetraethylammonium perchlorate (TEAP) was synthesized in accordance with the procedure reported in the literature [24]. In the photocatalytic experiment, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust the pH of distilled water for preparation of methyl orange (MO) solution. These materials were also supplied from MERCK Sdn. Bhd., Malaysia. The distilled water was used throughout in the experiment.

2.2. Catalyst preparation

The mesostructured silica nanoparticles (MSN) were prepared by a co-condensation and sol–gel method as reported in previous literature [11], corresponding to the mole composition of 0.0032:0.2:0.2:0.1 for CTAB, EG, NH_4OH and water, respectively. The mixture was stirred vigorously for about 30 min with heating. Then 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/MSN catalysts were prepared according to previous report protocol with some modification [22,25,26]. A 10 mL distilled water with different amount of NH_4OH (0, 0.5, 1.0 and 2.0 M) were added into 1 g of MSN in an open system electrolysis cell fitted with a magnetic stirrer and a platinum plate cathode ($2 \times 2 \, cm^2$) facing a zinc plate anode ($2 \times 2 \, cm^2$). As a supporting electrolyte, 0.1 M TEAP were added into the mixture. The electrolysis undergo in a constant current of $120 \, mA \, cm^{-2}$ and $0 \, ^\circ C$ under air atmosphere. 5 min 26 s was required to load 5 wt% of the ZnO onto the MSN as calculated by the Faraday's law as follows,

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

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 $n = m/M$). The Zn plate was weighed before and after the electrolysis to confirm the exact amount of Zn.

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 a white powder catalyst which is ready for a characterization. The catalysts were denoted as ZM-X, where X is a molarity of the NH_4OH used in the synthesis.

2.3. Characterization

The crystalline structures of the catalysts were confirmed by X-ray powder diffraction (XRD) analysis carried out at room temperature using D8 ADVANCE Bruker X-ray diffractometer using Cu Kα radiation at a 2θ angle ranging from 2° to 10°. The phases were identified with the aid of the Joint Committee on Powder Diffraction Standards (JCPDS) files.

The textural properties (i.e., specific surface area and pore volume) were determined from nitrogen physisorption at 77 K using a Beckman Coulter SA 3100 surface area analyzer. The samples were outgassed at 573 K for 1 h prior to the analysis. 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 Non-Local Density Functional Theory (NLDFT) method from the isotherm. The morphological properties of the catalysts were examined by field emission scanning electron microscopy (FESEM) (JSM-6300F FESEM) and transmission electron microscopy (TEM).