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Tailoring the metal introduction sequence onto mesostructured silica nanoparticles framework: Effect on physicochemical properties and photoactivity

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ABSTRACT

Cu with variable weight loading (1–5 wt%) was introduced to 5 wt% Zn mixed mesostructured silica nanoparticles (MSN) via an electrochemical method to synthesize CuO–ZnO/MSN (C-ZM) catalysts. The physicochemical properties of the catalysts were characterized by XRD, FTIR, XPS, N_2 adsorption–desorption, ESR, and cyclic voltammetry. 3 wt% Cu and 5 wt% Zn were also introduced alternately to MSN (3C-ZM and Z-3CM) to study the metal introduction sequence effect on the properties and catalytic activity. The characterization data showed that an altered arrangement of the silica network was observed with a different structure, particularly in the numbers of Si—O—Si, Si—O—Zn, and Si—O—Cu bonds as well as oxygen vacancies. The catalytic activity regarding the photodecolorization of methyl orange (MO) was in the following order: 3C-ZM > 5C-ZM > Z-3CM > 1C-ZM. The higher numbers of Si—O—Zn, oxygen vacancies, and the higher pore volume of the 3C-ZM catalyst seemeed to be the main factors behind its higher photoactivity compared to the other catalysts. Further optimization by response surface methodology (RSM) with a central composite design (CCD) model was performed for the decolorization of MO. RSM demonstrated that the experimental value (99.89%) was reasonably close to the predicted value (99.99%) with only 0.1% error for MO decolorization at pH 3.5 using 1.6 g L^{-1} catalyst with 4 wt% Cu loading.

1. Introduction

Metal oxides are widely present in nature and some of them are of great practical use. ZnO which is a typical kind of II–VI compound semiconductor with a wide direct band gap (3.37 eV) [1], has received considerable attention due to its wide potential applications in luminescence, photocatalysts, piezoelectric materials, gas sensors, solar cells, surface acoustic wave filters, etc. [2]. Recently, photocatalytic oxidation using ZnO as a photocatalyst has been extensively investigated as an advanced oxidation process for the degradation of various pollutants in industrial wastewaters [3]. However, ZnO can only absorb a small portion of solar spectrum in the UV region, which results in low photocatalytic efficiency [4]. In order to improve the efficiency further, many studies have been performed to modify this metal oxide. Generally, four major techniques have been highlighted in improving the photocatalytic efficiency of this semiconductor: (i) increasing the surface area of the metal oxide by synthesizing nanosized materials, (ii) adding a support such as silica, alumina, zeolite, etc., (iii) modification of the semiconductor with metal or other semiconductor, (iv) generation of a defect structure to induce space-charge separation [5,6].

In parallel with the first two methods, we have successfully synthesized several nanosized particles of α-Fe_2O_3, ZrO_2, ZnO, CuO, and α-FeOOH supported on zeolites or silica by a simple electrochemical method [7–10]. Their outstanding uses as photocatalysts in the photodegradation of organic pollutants as well as in isomerization encourage additional modification. Next, the combination of ZrO_2–ZnO supported on HY zeolite was found to further enhance the photodecolorization of methylene blue dyes [8]. The new active species of Si coordinated with Zr and Zn in the HY framework as a consequence of dealumination were elucidated to play important role in lowering the band gap of the catalyst, which accelerated the reaction. Recently, we also improved the electrolysis system by using an economical alkaline aqueous electrolyte [11] to prepare

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ZnO supported on mesostructured silica nanoparticles (MSN) catalyst. The catalyst, rich with surface oxygen vacancies and defect sites, enhanced the photoinduced electron-holes separation for efficient decolorization of methyl orange (MO).

In fact, studies on the synthesis of mesoporous silica (MS) materials have received much attention recently and the field has advanced rapidly. MS materials, such as MCM-41 and SBA-15, have been extensively investigated due to their unique properties [12–14]. In response to this, MSN have 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 MSN as a support material in ibuprofen delivery [15], CO_2 methanation [16], cumene cracking [17], and the adsorption of an organic pollutant [18].

Based on these data, we believe that this simple electrosynthesis method has excellent prospects for designing various types of catalysts for various applications. Besides shortening the conventional synthesis time, this method can also be carried out under mild conditions without using strong acidic conditions, hydrothermal treatment, higher temperature, and/or reactive compounds [19,20]. Due to these advantages, an extension of this study is worth continuing. Herein we report a new finding on the effect of the metals introduction sequence onto a MSN support that affected the physicochemical properties and photoactivity of the catalysts. To the best of our knowledge, reports on tailoring the metal introduction sequence onto support materials are still rare. Cu and Zn were introduced alternately to a weak alkaline solution containing MSN, and the physicochemical properties of these catalysts were characterized by XRD, FTIR, XPS, N_2 adsorption–desorption, ESR, and cyclic voltammetry. Based on these results, the structures of the catalysts were proposed. Optimization by response surface methodology (RSM) using a central composite design (CCD) model was also performed to achieve the best conditions for photodecolorization of MO.

2. Experimental

2.1. Synthesis of ZnO/MSN and CuO–ZnO/MSN composite

All of the chemical reagents were purchased and used as received without further purification. Distilled water was used in all experiments. The ZnO/MSN catalyst were prepared using electrochemical method as report in our previous study [21,22]. Prior to electrolysis, 1 M of ammonium hydroxide (NH_4OH), 0.1 M tetraethylammonium perchlorate (TEAP) and 1 g of MSN were added into 10 mL of distilled water. The solution mixture was used an electrolyte 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 ($2 \times 2\,cm^2$). Then, the electrolysis was started using a constant current of $120\,mA\,cm^{-2}$ and 0 °C under air atmosphere. While for CuO loaded ZnO/MSN, the zinc plate anode then was switched to a copper plate anode. A certain electrolysis time was calculated to load 5 wt% of the Zn and/or 1, 3, and 5 wt% of Cu onto the MSN as expressed by the Faraday's law of electrolysis 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 and Cu plates were weighed before and after the electrolysis to confirm the exact amount of metal loading.

After electrolysis, the mixture was impregnated, oven dried overnight at 378 K, and the subjected to calcination at 823 K for 3 h to yield a powder catalyst. The catalysts are donated as ZM (ZnO loaded on MSN) and xC-ZM (where x = 1, 3 and 5 wt% of CuO loaded on ZM catalyst). For comparison of electrolysis sequence, the order of electrolysis was changed, where copper plate was used first before changing into zinc plate, and the catalyst was donated as Z-xCM.

2.2. Characterization of the catalyst

X-ray diffraction (XRD) analysis was carried out in 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 surface area measurements were performed in a Quantachrome Autosorb-1 analyzer using N_2 at 77 K. Before analysis, the catalysts were outgassed overnight at 573 K. Surface areas were calculated from the N_2 adsorption isotherms using the Brunauer–Emmett–Teller (BET) method (S_{BET}) and the pore size distribution was obtained using a Non-Local Density Functional Theory (NLDFT) method from the isotherm. FT-IR (Perkin Elmer Spectrum GX FTIR Spectrometer) was performed using the KBr method with a scan range of $400–4000\,cm^{-1}$. The chemical oxidation of the catalysts were determined using X-ray photoelectron spectroscopy (XPS) conducted on a Kratos Ultra spectrometer equipped with an Mg Kα radiation source (10 mA, 15 kV) over a range of binding energies from 0 to 800 eV. The bandgap energy of the catalysts were plotted using Tauc plot based on the spectra recorded at room temperature over a range of wavelengths from 300 to 800 nm using a PIKE Technologies DiffusIR. The Electron Spinning Resonance (ESR) spectra were recorded at room temperature by JEOL JES-FA100 ESR spectrometer. The electrochemical behaviour of zinc and copper in MSN were studied using cyclic voltammetry (CV) using Digi-Ivy DY2113 Potentiostat driven by the DY2100 series software. The electrochemical cell used in this work contains three electrodes; glassy carbon was used as a working electrode, Ag/AgCl as a reference electrode, and a Pt wire was used as a counter electrode.

2.3. Photocatalytic reaction

The photocatalytic activity of the catalysts were evaluated by measuring photodecolorization of MO under the UV light irradiation (4 × 9 Watt; 365 nm emission). Prior to experiment 0.15 g catalyst was dispersed in 150 mL MO aqueous solution (3.06×10^{-2} mM). Then the suspension was magnetically stirred in dark for 60 min to establish adsorption/desorption equilibrium between MO molecules and the surface of the photocatalyst. Later, the suspension was subjected to UV irradiation. An amount of solution was withdrawn at 1 h time interval, centrifuge and subjected to UV–vis spectrometer to measure absorbance at 506 nm. To ensure the accuracy, each set of experiment was performed three times.

2.4. Experimental design and optimization (DOE)

Response surface methodology (RSM) is an experimental technique invented to find the optimal response within the specified ranges of the factors [23]. In this study, RSM experiment using central composite design (CCD) using Statistica 6.0 StatSoft was employed to optimize photodecolorization reaction parameter. The parameter includes are initial pH: 2–8, adsorbent dosage: $0.4–1.6\,g\,L^{-1}$, and Cu loading: 1–5 wt%, and these parameters were chosen based on the results of preliminary studies that have been conducted. The performance of the catalyst was evaluated by analyzing the response of decolorization percentage of MO.