

Synthesis of Zinc Oxide Supported on Titanium Dioxide for Photocatalytic Oxidative Desulfurization of Dibenzothiophene

Hitam, C.N.C.¹, Jalil, A.A.^{1,2*}, Triwahyono, S.³

¹Department of Chemical Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

²Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

³Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

*Corresponding author: aishahaj@utm.my

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Abstract

Photocatalytic oxidative desulfurization (PODS) has received much attention due to low energy consumption and high efficiency, as well as simple and pollution-free operation. In this study, zinc oxide supported on titanium dioxide (ZnO/TiO₂) catalysts were prepared via a simple electrochemical method. The presence of anatase phase TiO₂ and wurtzite ZnO was confirmed by X-ray diffraction (XRD) analysis while band gap energies were determined by UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS). The photocatalytic activity was tested for desulfurization of 100 mg/L dibenzothiophene (DBT). The highest desulfurization rate (2.20×10^{-3} mM/min) was achieved using 1 g/L of 10 wt% ZnO/TiO₂ after 2 hr under UV irradiation.

Keywords: ZnO/TiO₂, photocatalytic oxidative desulfurization, dibenzothiophene, electrochemical.

1.0 INTRODUCTION

Acid rain, global warming, atmospheric pollution, and several health effects are among crucial environmental problems that are majorly caused by the emission of sulfur oxides (SO_x) produced from combustion of fuels. In order to reduce negative effects on environment and health, the acceptable sulfur level in fuel has been restricted to 10 mg/L in most developed countries and in the near future, zero-emission is accepted worldwide [1, 2]. In recent years, considerable attention has been paid to efficient desulfurization of fuel due to stringent environmental regulations [3]. A common removal process of organosulfurs in industry is called hydrodesulfurization (HDS), which is performed under high hydrogen pressure and temperature, as well as high purity of hydrogen, and this makes the process inappropriate for further reduction of sulfur content [4]. Hence, it is necessary to introduce other approaches to overcome those drawbacks, such as extractive desulfurization (EDS), adsorptive desulfurization (ADS), and biodesulfurization (BDS). Oxidative desulfurization (ODS) has become one of the most capable alternative methods than other techniques to replace HDS [5].

As one of the processes in ODS, photocatalytic oxidative desulfurization (PODS) is less harmful, has high catalytic activity, low energy consumption, and is also recyclable [6]. Heterogeneous photocatalytic removal of organic pollutant is a promising method because it can transform toxic pollutants into harmless products using mild conditions [7]. Photocatalytic reaction consists of the irradiation of a photon with the energy equal or higher than the band gap energy (E_g) of the catalyst [8], followed by the excitation of electrons from the valence band (VB) to the largely vacant conduction band (CB). Simultaneously, a hole (h^+) with strong oxidizing ability is formed. Excited electrons (e^-) are able to carry out

reduction reactions and h^+ can perform oxidation reactions.

Among various types of catalysts, titanium oxide (TiO_2) has been extensively used in the photocatalytic degradation of organic pollutants due to its inexpensiveness, chemical stability, non-toxicity, and excellent photocatalytic activity [5, 9]. However, TiO_2 has some drawbacks such as lower interface and easy recombination of the electron-hole pair [10]. To overcome this shortcoming, researchers have sought to improve the photoactivity of TiO_2 by coupling the catalyst with other inorganic materials such as transition metals. Coupled semiconductor photocatalysts are a crucial step to enhance interfacial charge transfer to adsorbed substrates, improve the separation of electron-hole pairs, and extend the lifetime of electron-hole pairs [11].

The most capable candidate is probably zinc oxide (ZnO) because of its low cost, wide band gap metal oxide (~ 3.30 eV), and comparable photocatalytic performance to TiO_2 [12]. Nowadays, coupled photocatalyst ZnO/TiO_2 has been studied comprehensively and the results revealed that ZnO/TiO_2 has superior photocatalytic performance than that of the single one. Currently, there are several studies reported on the electrochemical technique for the preparation of nanometal oxide including CuO , $\alpha-Fe_2O_3$, ZnO , and $\alpha-FeOOH$ [7, 13-15]. Further loading of these oxides onto supports enhanced their properties toward consequent reactions, thus improved catalytic activity. Considering all the factors, the objectives of this study are to synthesize ZnO/TiO_2 and evaluate its performance in PODS.

2.0 METHODOLOGY

2.1 Materials

Dibenzothiophene (DBT), potassium peroxydisulfate, triethanolamine, sodium hydrogen carbonate, and isopropanol were provided by Merck Sdn. Bhd., Malaysia. Ammonium hydroxide (NH_4OH) and acetonitrile were purchased from QRec, Malaysia. Commercial TiO_2 (JRC- TiO_2 -2) was obtained from the Catalysis Society of Japan. All of the chemicals were utilized without further purification whereas tetraethyl ammonium perchlorate (TEAP) was prepared according to a previously reported method [16].

2.2 Synthesis of Catalysts

In this study, ZnO/TiO_2 nanoparticles were synthesized by electrolysis technique using commercial TiO_2 support with ZnO contents varied from 5–15 wt% based on a previously reported technique [17].

2.3 Material Characterization

X-ray diffraction (XRD) analysis was performed on a D8 ADVANCE Bruker X-ray diffractometer using $Cu-K\alpha$ radiation at $2\theta = 2$ to 90° . The Joint Committee on Powder Diffraction Standards (JCPDS) files were used to classify the phases. UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded by a PIKE Technologies DiffusIR at room temperature in the range of wavelengths from 300 to 800 nm to determine the band gap energy (E_g) of the catalysts.

2.4 Photocatalytic Oxidative Desulfurization Reaction

The photocatalytic experiment was carried out by oxidative desulfurization of model oil in a batch reactor fixed with UV lamps and a cooling system. DBT was dissolved in acetonitrile to prepare model oil with sulfur content of 100 mg/L. Photocatalytic oxidative desulfurization was conducted by adding 1.0 g/L catalysts into 50 mL of model oil. Under constant stirring, a solution was formed and placed in the dark for 60 min to achieve adsorption-desorption equilibrium. Then, the suspension was irradiated with UV lamps after an appropriate amount of hydrogen peroxide (H_2O_2) was added into the reaction system. The next steps were similar with those reported in our previous studies [17, 18].

3.0 RESULTS AND DISCUSSION

Fig. 1 presents the XRD patterns of the catalysts. Pure TiO_2 exhibited the characteristic of anatase phase with a series of diffraction peaks at 25.4° (1 0 1), 38.5° (1 1 2), 48.2° (2 0 0), 53.9° (1 0 5), and 55.3° (2 1 1) (JCPDS file no. 00-004-0477) [19]. For ZnO/TiO_2 , the anatase phase was still preserved with an additional peak of wurtzite ZnO at $2\theta = 31.8$, 34.5 , and 36.3° [14]. However, the different amount of ZnO loading gave a remarkable effect on the intensity of TiO_2 diffraction peak. It could be seen that the peak intensity was reversely proportional to the amount of loaded ZnO , signifying a probable structural degradation of TiO_2 [20].

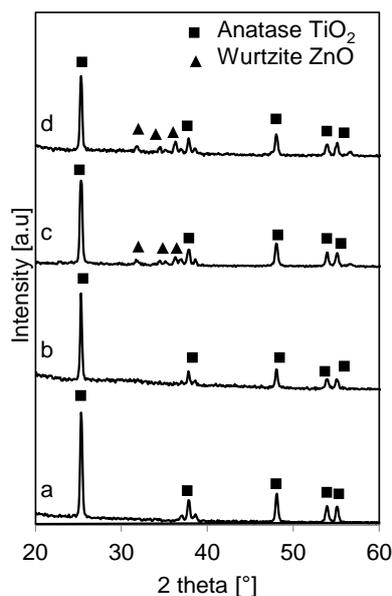


Figure 1. XRD patterns of (a) TiO₂, (b) 5 wt% ZnO/TiO₂, (c) 10 wt% ZnO/TiO₂, and (d) 15 wt% ZnO/TiO₂

The optical property of a semiconductor is known as an important factor in its photocatalytic performance, which is related to its electronic structure. Table 1 represents the direct band gap energy (E_g) of the catalysts. The values of E_g of pure TiO₂ and ZnO were found to be 3.22 and 3.30 eV, respectively. The absorption edge of TiO₂ suffered a blue shift after the incorporation of ZnO, indicating a possible interaction between TiO₂ and ZnO [21]. The altered light absorption of the synthesized catalysts may prevent the electron-hole pair recombination in the same light irradiation, which consequently improved photocatalytic activity [5].

Table 1. Band gap energy of catalysts

Catalyst	Band gap, E_g (eV)
TiO ₂	3.22
5 wt% ZnO/TiO ₂	3.24
10 wt% ZnO/TiO ₂	3.26
15 wt% ZnO/TiO ₂	3.29
ZnO	3.30

As shown in Fig. 2, the desulfurization rates of ZnO/TiO₂ are higher than TiO₂, which might be due to the charge carrier separation by the incorporation of ZnO. With the increasing loading of ZnO from 5 to 10 wt%, the desulfurization rate increased from 1.63×10^{-3} to 2.20×10^{-3} mM/min, respectively. The photocatalytic performance of TiO₂ mainly depends on its effective charge carrier separation [11]. The photogenerated e^- and h^+ can change in various ways on TiO₂ surface. The most important probable steps in photocatalytic reaction are capture and recombination, which are two competitive processes. The reaction is efficient when the photogenerated electrons-holes can be captured. In the absence of proper capturers of e^- or h^+ , the recombination step occurs and heat is emitted inside or on the surface of semiconductor. Improving the separation efficiency of the photogenerated electron-hole pairs and increasing the amount of the photogenerated activity species are the two essential ways that must be considered to enhance the photoactivity of TiO₂. Previous study showed that ZnO is a good co-participant oxide because its energetic CB and VB positions are favorable redox. Additionally, it increases the lifetime of photogenerated electron-hole pairs by preventing recombination process [22]. Coupling TiO₂ and ZnO is a beneficial way to enhance photoactivity due to their comparable band gap (ZnO ~3.3 eV, TiO₂ ~3.2 eV) and the positions of CB and VB [23]. The CB of ZnO is higher than TiO₂, thus facilitates the electron transfer from ZnO to TiO₂. Simultaneously, holes migrate from the VB of TiO₂ to the VB of ZnO upon light irradiation.

However, further increase of ZnO loading (15 wt%) decreased the desulfurization rate to 1.79×10^{-3} mM/min. When excess of ZnO was incorporated, the active site of TiO₂ might be blocked, thus influence the reaction rate.

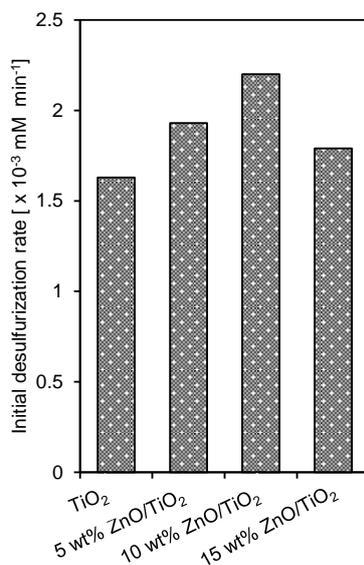


Figure 2. Catalytic performances for desulfurization of dibenzothiophene

Isopropanol (IP) slightly reduced the initial reaction rate as compared to those in the absence of a scavenger (Fig. 3), while the rate was decreased to 1.60×10^{-3} and 1.70×10^{-3} mM/min with the addition of triethanolamine (TEOA) and sodium hydrogen carbonate (SHC), respectively. Nevertheless, the photocatalytic activity was greatly inhibited using potassium peroxodisulfate (PP), signifying the noteworthy role of e^- in the system. Accordingly, it is proposed that an electron-hole pair is generated in both ZnO and TiO₂ sites upon irradiation of ZnO/TiO₂. The high potential and negativity of e^- at the CB are capable to reduce O₂ to enable the formation of superoxide radical $\bullet O_2^-$ [24]. Some of the e^- at CB of ZnO might be transferred to the CB of TiO₂. Simultaneously, h^+ can easily migrate from VB of ZnO to TiO₂ due to the energetic CB and VB positions of ZnO, thus preventing electron-hole recombination. The generated h^+ in VB of ZnO/TiO₂ can thermodynamically oxidize water and hydroxyl ions to produce hydroxyl radicals (OH \bullet). With the presence of $\bullet O_2^-$ and OH \bullet , DBT was successfully oxidized to DBT 5-oxide (DBTO) and DBT 5,5-dioxide (DBTO₂) [25].

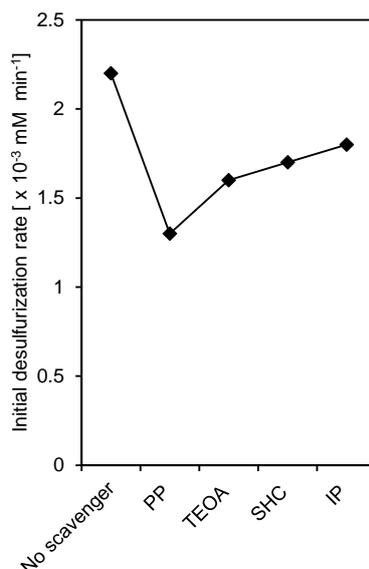


Figure 3. Desulfurization rates of dibenzothiophene in the existence of e^- , h^+ , $\bullet OH_{ads}$, and $\bullet OH$ scavengers

4.0 CONCLUSION

In this study, ZnO/TiO₂ catalysts were synthesized via a simple electrochemical method. The synthesized catalysts were characterized by XRD analysis and UV-Vis DRS. The XRD results showed that pure TiO₂ exhibited the characteristic of anatase phase. Similarly, ZnO/TiO₂ also displayed the anatase phase with an additional peak of wurtzite ZnO. Based on UV-Vis DRS, the absorption edge of TiO₂ suffered a blue shift after the incorporation of ZnO, indicating a possible interaction between TiO₂ and ZnO. The photocatalytic activity was tested on the desulfurization of 100 mg/L of DBT. The highest desulfurization rate was obtained using 10 wt% ZnO/TiO₂, which might be due to the electron-hole pair separation by the inclusion of ZnO.

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