ELECTROSYNTHESIS OF COPPER OXIDE SUPPORTED ON AMORPHOUS TITANIUM DIOXIDE NANOPARTICLES BASED CATALYSTS FOR PHOTOCATALYTIC OXIDATIVE DESULFURIZATION

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Specially dedicated to my husband and sons,
(Ahmad bin Abas, Luqman Alhakim bin Ahmad and Alif Firdaus bin Ahmad)
'Thank you for always standing next to me and wait for me patiently'

To Aboh and Mokteh
(Che Ku Hitam bin Chik and Fatimah bt Musa)
'Thank you for always being there; your endless love, faith and encouragement never fail to strengthen me'

To my late mom,
(Meriam bt Musa)
'You may be gone from my sight but you are never far from my heart'

&

To my beloved siblings and family,
'Thank you for your endless love and encouragement during my hard time'

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ABSTRACT

The high level of sulfur in fuel has contributed to the emission of sulfur oxide (SO_x) which is a major cause of air pollution, acid rain and global warming. Among desulfurization techniques, photocatalytic oxidative desulfurization (PODS) has received much attention due to low energy consumption, high efficiency and ability to convert toxic organic pollutants into non-toxic products. Coupling of the widely used titanium dioxide (TiO_2) photocatalyst with other semiconductor oxides can produce superior catalyst with a good interaction, appropriate amount of defects and narrower band gap for efficient photoactivity. Amorphous TiO_2 has experienced intensive advances due to larger surface area, high amount of surface defects, as well as easy preparation method. In this study, copper oxide supported on amorphous titanium dioxide (CuO/TiO_2) catalysts were prepared via the electrochemical method. The catalysts were characterized using x-ray diffraction, Fourier transform infrared, nitrogen adsorption-desorption, transmission electron microscopy, x-ray photoelectron spectroscopy, electron spin resonance and ultraviolet-visible diffuse reflectance spectroscopy. The effects of using titanium (IV) isopropoxide (TTIP) or titanium (IV) butoxide (TBOT) for synthesizing the amorphous TiO_2 (AT) and different copper (Cu) loading (5-20 wt%) were investigated on PODS of dibenzothiophene (DBT). AT_{TBOT} showed a higher photoactivity than AT_{TTIP} due to the presence of larger pore diameter and pore volume for adsorption of more DBT molecules, thus enhancing the activity. The loading of 5-20 wt% CuO onto AT_{TBOT} (CAT_{TBOT}) further increased the activity due to the narrow band gap and the presence of Ti-O-C, O-Ti-C, O-Ti-N and Ti-O-Cu bonds that play a role as electron acceptor and transporter. Among all the catalysts, 15 wt% CuO/AT_{TTIP} (15 CAT_{TTIP}) showed the best photooxidation percentage of 51.2%, due to the lower band gap, suitable amount of defects, the existence of high amount of Ti-O-Cu and Ti-O-N/O-Ti-N bonds, as well as synergistic effect between Cu and N. Optimization using the Response Surface Methodology gave the best PODS of DBT at the optimum conditions of 100 mg L^{-1} using 0.8 g L^{-1} of 15 CAT_{TTIP} that was reasonably close to the predicted value. The high PODS using 15 CAT_{TTIP} during reusability study and application on simulated oil indicate the potential of the catalyst for sulfur removal in industry.

ABSTRAK

Tahap sulfur yang tinggi dalam bahan api telah menyumbang kepada pelepasan sulfur oksida (SO_x) yang merupakan punca utama pencemaran udara, hujan asid dan pemanasan global. Antara teknik penyahsulfur, fotopemangkinan penyahsulfur oksidatif telah mendapat banyak perhatian kerana penggunaan tenaga yang rendah, kecekapan tinggi dan dapat menukar pencemar organik toksik kepada produk bukan toksik. Gandingan fotomangkin yang digunakan secara meluas iaitu titanium dioksida (TiO_2) dengan semikonduktor oksida lain boleh menghasilkan mangkin unggul dengan interaksi yang baik, jumlah kecacatan yang sesuai dan jurang jalur sempit untuk aktiviti foto yang cekap. TiO_2 amorfus telah mengalami kemajuan yang intensif kerana luas permukaan besar, jumlah kecacatan permukaan yang tinggi serta kaedah penyediaan mudah. Dalam kajian ini, kuprum oksida disokong pada mangkin titanium dioksida amorfus (CuO/TiO_2) telah disediakan melalui kaedah elektrokimia. Mangkin telah dicirikan menggunakan pembelauan sinar-x, spektroskopi inframerah transformasi Fourier, penjerapan-penyahjerapan nitrogen, mikroskopi penghantaran elektron, spektroskopi fotoelektron sinar-x, resonans putaran elektron dan spektroskopi cahaya-nampak ultraungu-pantulan serapan. Kesan penggunaan titanium (IV) isopropoksida (TTIP) atau titanium (IV) butoksida (TBOT) untuk mensintesis TiO_2 amorfus (AT) dan jumlah kuprum (Cu) yang berbeza (5-20 wt%) telah dikaji dalam PODS terhadap dibenzotiofena (DBT). AT_{TBOT} menunjukkan aktiviti foto yang lebih tinggi daripada AT_{TTIP} kerana kehadiran garis pusat liang dan isipadu liang yang lebih besar untuk penjerapan lebih molekul DBT, dengan itu meningkatkan aktiviti. Penambahan 5-20 wt% CuO ke dalam AT_{TBOT} (CAT_{TBOT}) terus meningkatkan aktiviti kerana jurang jalur yang rendah dan kehadiran ikatan Ti-O-C, O-Ti-C, O-Ti-N and Ti-O-Cu yang memainkan peranan sebagai penerima dan pembawa elektron. Di antara semua mangkin, 15 wt% CuO/AT_{TTIP} (15 CAT_{TTIP}) menunjukkan kadar fotopengoksidaan terbaik iaitu 51.2%, disebabkan oleh tenaga jurang jalur yang lebih rendah, jumlah kecacatan yang sesuai dan kewujudan lebih banyak ikatan Ti-O-Cu dan Ti-O-N, serta kesan sinergi antara Cu dan N. Pengoptimuman menggunakan Kaedah Gerak Balas Permukaan memberikan PODS DBT terbaik pada keadaan optima 100 mg L^{-1} menggunakan 0.8 g L^{-1} 15 CAT_{TTIP} yang hampir menyamai dengan nilai anggaran. PODS yang tinggi menggunakan 15 CAT_{TTIP} semasa kajian kebolehgunaan semula dan aplikasi terhadap simulasi minyak menunjukkan potensi mangkin untuk penyingkiran sulfur di industri.

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LIST OF ABBREVIATIONS

ADS	-	Adsorptive desulfurization
AT_{TBOT}	-	Amorphous TiO_2 nanoparticles synthesized using TBOT source
AT_{TTIP}	-	Amorphous TiO_2 nanoparticles synthesized using TTIP source
BDS	-	Biodesulfurization
DBT	-	Dibenzothiophene
EDS	-	Extractive desulfurization
ESR	-	Electron spin resonance
FTIR	-	Fourier transform infrared
HDS	-	Hydrodesulfurization
ODS	-	Oxidative desulfurization
RSM	-	Response surface methodology
TBOT	-	Titanium (IV) butoxide
TEAP	-	Tetraethylammonium perchlorate
TEM	-	Transmission electron microscopy
TTIP	-	Titanium (IV) isopropoxide
UV-Vis DRS	-	Ultraviolet-visible diffuse reflectance spectroscopy
x CAT_{TBOT}	-	*x* wt% Cu loaded on amorphous TiO_2 nanoparticles synthesized using TBOT source by electrochemical method (*x*= 5, 10, 15, 20)
x CAT_{TTIP}	-	*x* wt% Cu loaded on amorphous TiO_2 nanoparticles synthesized using TTIP source by electrochemical method (*x*= 5, 10, 15, 20)
x IMP	-	*x* wt% Cu loaded on amorphous TiO_2 nanoparticles synthesized using TTIP source by impregnation method (*x*= 10 and 15)

x PM	-	*x* wt% Cu loaded on amorphous TiO_2 nanoparticles synthesized using TTIP source by physical mixing method (*x*= 10 and 15)
XPS	-	X-ray photoelectron spectroscopy
XRD	-	X-ray diffraction

LIST OF SYMBOLS

%	-	Percentage
°C	-	Degree Celsius
cm	-	Centimeter
eV	-	Electron volt
g	-	Gram
$g\ L^{-1}$	-	Gram per liter
h	-	Hour
K	-	Kelvin
mA	-	Miliamphere
s	-	Second
T	-	Temperature
W	-	Watt

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Sulfur oxides (SO_x) resulting from combustion of sulfur compounds in fuels have become one of the increasingly serious environmental problems in the world as it is the major reason for acid rain, global warming effect, and atmospheric pollution. In addition, sulfur existing in fuel causes poisoning of the catalysts in catalytic converter of vehicles (Triantafyllidis and Deliyanni, 2014). Thus, in recent years considerable attention has been paid to the deep desulfurization of gasoline due to the increasingly stringent environmental regulations being imposed, in order to reduce the sulfur content to very low levels (Nejad *et al*., 2013). New environmental regulations regarding the sulfur content in oil fuel products have forced researchers and refineries to develop efficient processes for production of cleaner fuels. Consequently, ultra-deep desulfurization of liquid hydrocarbon fuels has become an increasingly important subject worldwide (Huang *et al*., 2011).

Recently, the conventional process for the removal of organosulfurs in industry is known as hydrodesulfurization (HDS), which is carried out under high hydrogen pressure and temperature using a suitable catalyst. The HDS technology is highly efficient in removing aliphatic and acyclic sulfur-containing compounds. However, this technology is not effective for dibenzothiophene (DBT) and its derivatives (Li *et al*., 2012). Hence, it is essential to introduce other approaches for desulfurization to overcome those drawbacks, such as biodesulfurization (BDS), adsorptive desulfurization (ADS) and extraction desulfurization (EDS) (Zhang *et al*., 2013). Among all these methods, oxidative desulfurization (ODS) is one of the most promising ways to complement HDS due to its mild operating conditions, low cost, no consumption of hydrogen and high efficiency (Wang *et al*., 2014).

The photocatalytic oxidation process, with unique advantages of low energy consumption and high efficiency, as well as simple and pollution-free operation, has proved to be a practical advanced oxidization technique for disposal of the pollutants. It is also more attractive than other systems and can efficiently eliminate environmental contaminants under mild conditions (Su *et al*., 2013). Photocatalytic oxidative desulfurization as one of the processes in ODS is promising because of its safety, high catalytic activity, low energy consumption and recycling availability (Zhu *et al*., 2013). Numerous studies on the photochemical desulfurization for light oils such as gasoline have been conducted by combining ultraviolet (UV) irradiation and liquid–liquid extraction. Due to the difficulty of desulfurization under UV light in industry, researchers also investigated the visible light induced DBT desulfurization using photosensitizer to extend its absorption range to visible light region. Other than that, using photocatalysts with narrow band gaps that can absorb visible light is a simple approach to desulfurize under visible light irradiation (Li *et al*., 2012).

Thus far, TiO_2-based catalyst as one of the most suitable semiconductor photocatalysts has been extensively investigated. TiO_2 was also comprehensively used in

other applications such as water treatment and air purification, as well as sterilization, sanitation, and remediation purposes (Lin *et al*., 2016). To improve sulfur removal, researchers also used TiO_2 photocatalysts because of its non-toxicity, chemical and photochemical stability, low cost, and excellent photocatalytic activity (Li *et al*., 2012). However, the use of TiO_2 requires UV radiation due to its wide band gap energy (3.2 eV), making it rather difficult into practical application. Therefore, it is imperative to develop new photocatalysis materials that enable the expenditure of renewable energy resources such as solar light which can provide cleaner and more efficient removal of sulfur species from fuel oils (Li *et al*., 2016). In addition, in the bare TiO_2 nanoparticles, a fast recombination can occur for the photogenerated electron–hole pairs. Such disadvantages has limited worldwide use of the TiO_2 for various applications (Zarrabi *et al*., 2015).

To overcome those shortcomings, many researchers have sought for improved photocatalytic activity of TiO_2 by coupling it with other non-metal or metal elements (Vu *et al*., 2012). These non-metal and metal atoms can substitute in the lattice structure of TiO_2 causing substantial enhancements in the visible light activity as compared to that of pure TiO_2 (Zarrabi *et al*., 2015). Currently, the non-metal dopings that usually used to pursue highly active TiO_2 photocatalysts are carbon (C), nitrogen (N), sulfur (S), fluorin (F) and boron (B). The generation of an intermediate energy state by the introduction of these dopants between the conduction and the valence band, allows the promotion of electrons with light energy lower than in the undoped TiO_2 (Trevisan *et al*., 2014).

In addition, transition metals such as copper (Cu), nickel (Ni), gold (Au) and silver (Ag) can be doped onto TiO_2 to promote its photocatalytic efficiency. Among various types of metal doping, copper oxide (CuO) is found to be an effective dopant of TiO_2 due to its high electronic conductivity, low cost and high availability (Carvalho *et al*., 2013). CuO supported on TiO_2 (CuO/TiO_2) composite has served as an efficient photocatalytic material in various applications such as the decomposition of gas-phase alcohols, acid orange 88, methylene blue, etc. (Choudhury *et al*., 2013). CuO/TiO_2 even possesses

higher activity than some noble metals loaded TiO_2, which further affirms the huge potential of cost-effective CuO/TiO_2 in photocatalysis. There are numerous methods for preparing CuO/TiO_2 such as sol–gel, impregnation, modified ammonia evaporation-induced synthetic and deposition–precipitation (DP) method (Liu and Zhou, 2015). Several studies have recently been done on electrochemical methods for preparation of metal oxide nanoparticles including Fe_2O_3, CuO, ZnO, and α-FeOOH. Further loading of these nanometal oxides onto supports improved their properties toward the subsequent reactions. This contributes to enhancement of the catalytic activity (Jaafar *et al*., 2012; Jusoh *et al*., 2013; Jusoh *et al*., 2015a; Jusoh *et al*., 2014).

Meanwhile, the efforts so far have been mostly focused on improving the photocatalytic properties of the crystalline phases of TiO_2, as the amorphous TiO_2 structure has been reported to be a poorer photoactive substance due to its disordered structure and defective states (Huang *et al*., 2012). Nevertheless, amorphous TiO_2 compared to crystalline TiO_2, has a larger surface area which is responsible for the higher absorptivity as well as highly amount of surface defects for enhancing the photoactivity (Kaur and Singh, 2012). Indeed, amorphous TiO_2 is easy to prepare, does not require any thermal treatment, has less demand for substrate materials and can be potentially deployed in practical applications. These useful characteristics have led to recent attention in exploring amorphous TiO_2 as an alternative to crystalline TiO_2 phases for various photocatalytic reactions (Li *et al*., 2008; Pham and Wang, 2015).

Although large efforts have been undertaken to find a suitable catalyst for photocatalytic oxidative desulfurization, there is still lack of report on the possible interaction between metal and support material for enhanced photocatalytic activity. Herein, we report a synthesis of amorphous TiO_2 nanoparticles and CuO supported on amorphous TiO_2 nanoparticles via sol-gel and electrochemical method, respectively, in a relatively low temperature and simple experimental set up. The role of different titanium sources to prepare amorphous TiO_2 and effect of CuO loading to the formation of metal-

support interaction were studied in photocatalytic oxidative desulfurization. Then, the kinetics, mechanism, as well as the reusability study of the best catalyst was also performed before the optimization process was carried out using response surface methodology (RSM). Lastly, the performance of the catalyst was applied for photocatalytic oxidative desulfurization of simulated oil.

1.2 Problem Statement and Hypothesis

High level of sulfur in fuel is a major source of SO_x emission, which contributes to air pollution, acid rain and several health problems such as respiratory illnesses, heart disease, asthma and formation of atmospheric particulates. In refining process and automotive, sulfur is undesirable as they tend to deactivate the catalysts and cause corrosion problem. To address this problem, the sulfur level in fuel must be minimized to meet the environmental regulation and to reduce the environmental pollution. In the near future, the requirements for sulfur content will become more stringent to reduce sulfur emissions of the transport fuel to the zero level. The development of advanced technologies for ultra clean fuel is needed, thus, great efforts have been made to decrease the content of sulfur in fuel (Wang *et al*., 2013a). However, the conventional method for desulfurization (HDS) and other alternative approaches have their main drawbacks such as harsh operating condition and difficulties to achieve deep desulfurization. As a result, oxidative desulfurization (ODS) has been increasing interest nowadays.

In numerous oxidative desulfurization methods, photocatalytic oxidation is considered as a new approach with moderate operating condition compared to traditional chemical oxidation. For these reasons, it has aroused worldwide research, thus become a promising desulfurization technology for gasoline nowadays. Although photocatalytic

degradation of sulfur in gasoline is much harder, some breakthroughs have been achieved. TiO_2, as a great photocatalyst has been widely used in the field of photocatalytic degradation of organic pollutants. However, it also shows some disadvantages such as wide band gap and fast electron–hole recombination which have limited its application range and activity to some extent (Wang *et al*., 2014).

It is hypothesized that the preparation of amorphous titanium dioxide nanoparticles (TiO_2) via sol-gel method followed by incorporation of CuO by electrochemical technique give a great advantage towards photocatalytic oxidative desulfurization. The CuO dopant is expected to form interaction with amorphous TiO_2 support during electrochemical method, producing surface defects and impurity levels between the valence band and conduction band of amorphous TiO_2, thus lowering the band gap energy. Other than the role in enabling the reaction to be carried out in the visible light region, the surface defects and impurity levels also improve the charge carrier separation by preventing the electron-hole recombination for enhanced photooxidation.

1.3 Objectives of Study

The aims of this study are:

I. To synthesize amorphous titanium dioxide (AT) nanoparticles and CuO supported on AT nanoparticles.
II. To investigate the physico-chemical properties of the catalyst.
III. To study the photocatalytic activity of the catalyst on oxidative desulfurization of dibenzothiophene.

IV. To determine the kinetic, mechanism and reusability of photocatalytic oxidative desulfurization.

V. To optimize the photocatalytic oxidative desulfurization by response surface methodology (RSM) and apply for sulfur removal of simulated oil.

1.4 Scope of Study

The amorphous TiO_2 (AT) nanoparticles were synthesized using two titanium sources with different carbon chain which are titanium (IV) isopropoxide (TTIP) and titanium (IV) butoxide (TBOT) via sol-gel method (Ouzzine *et al*., 2014; Xie *et al*., 2015). Then, the CuO was loaded onto both AT using electrochemical method with different CuO loading (5-20 wt%) (Zaid *et al*., 2015).

The physico-chemical properties of the catalysts were investigated using X-ray diffraction (XRD), Fourier transform infrared (FTIR), N_2 adsorption-desorption, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR) and ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS).

The photocatalytic testing on oxidative desulfurization was studied using dibenzothiophene (DBT) as sulfur-containing compound. The screening process was conducted based on literature parameters to determine the optimum conditions including effect of Cu loading (5-20 wt%) (Zaid *et al*., 2015), catalyst dosage (0.6-1.2 g L^{-1}) (Abdelaal and Mohamed, 2014) and initial DBT concentration (100-300 mg L^{-1}) (Zhu *et al*, 2015). The photocatalytic reaction were performed in a batch reactor fixed with cooling system

containing 1 L Pyrex glass placed on the reactor. A 72 W of UV lamp (254 nm) and 160 W metal halide lamp (400 nm) were used for UV and visible light source, respectively.

The kinetic expression was described based on pseudo-first-order Langmuir-Hinshelwood model. Then, the mechanism of the photocatalytic oxidative desulfurization of DBT was proposed and finally, the reusability study was also performed.

Optimization of the photocatalytic oxidative desulfurization of DBT over CuO/TiO_2 was performed using central composite design (CCD) by response surface methodology (RSM) developed by Statistica 6.0 StatSoft. The parameters include Cu loading (10-20 wt%), catalyst dosage (0.6-1.0 g L^{-1}) and initial DBT concentration (100-300 mg L^{-1}). These parameters were chosen based on the results of preliminary studies that have been conducted (Vaez *et al*., 2012; Safari *et al*., 2014; Jusoh *et al*., 2015; Rahman *et al*., 2017). The concentration of DBT before and after the treatment with catalyst was measured using Ultraviolet-Visible (UV-Vis) spectroscopy. Finally, the optimum parameters were applied for removal of sulfur-containing compounds in simulated oil.

1.5 Significant of Study

This study was conducted to synthesize amorphous TiO_2 and CuO supported on amorphous TiO_2 nanoparticles. A detail analysis of physicochemical properties of the catalysts, as well as the photocatalytic activity has been done. The TiO_2 as a great photocatalyst, has been widely used in the field of photocatalytic degradation of organic pollutants. However, it also shows some disadvantages such as narrow spectrum utilization and fast electron–hole recombination which has limited its application range

and activity. Recent studies focused on loading TiO_2 with other materials to improve its activity. Besides, it was shown that coupling of different semiconductor oxides and the doping of non-metal elements can reduce its band gap, extend its absorption range to visible light region, promote electron-hole pair separation under irradiation and, consequently, achieve a higher photocatalytic activity. Among the various types of TiO_2, amorphous TiO_2 nanoparticles experienced intensive advances and a growing number of studies challenged the photoactivity of the amorphous TiO_2. In addition, amorphous TiO_2 has several advantages that require further research such as larger surface area and high amount surface defects, as well as easier preparation method. The study on the modification of amorphous TiO_2 for enhanced photoactivity might be beneficial for the environmental remediation in order to reduce air pollution and other related problems caused by sulfur oxides (SO_x) from combustion of sulfur existing in the fuel.

1.6 Thesis Outline

The current study includes five chapters. Chapter 1 presents the general introduction to the environmental effects of sulfur compounds combustion in commercial fuels. The conventional and alternative methods for desulfurization were mentioned as well. Besides, the potential of amorphous TiO_2 nanoparticles based catalysts as semiconductor photocatalyst for oxidative desulfurization were highlighted. Problem statement was stated to give the main objectives of the present study, while the scopes covered the research work to meet these objectives.

Literature review was presented in Chapter 2 to review the detailed information regarding the sulfur-containing compounds in the commercial fuels, sulfur removal technologies, oxidants, catalysts and extractants used for photocatalytic oxidative

desulfurization, proposed mechanism and products. The synthesis and modification of TiO_2 semiconductor were also reviewed.

The experimental procedure was described in Chapter 3 to introduce the chemicals and materials, method for catalyst preparation, characterization step and photocatalytic reaction which include the experimental setup and calculation for data analysis in the present study.

Chapter 4 focuses on discussion of the experimental results of the study. The first part explains the physicochemical properties of all catalysts by XRD, FTIR, N_2 adsorption-desorption, TEM, XPS, ESR and UV-Vis DRS. Next, their performances towards photocatalytic oxidative desulfurization were observed. Then, in line with the effect of Ti precursors, Cu loading, catalyst dosage and initial DBT concentration, the kinetic, mechanism, reusability study and optimization by RSM, as well as application on simulated oil were studied.

Finally, the conclusion of the study and recommendation for further studies were presented in Chapter 5.

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