Integrated Mg/TiO_2 – phosphate based ionic liquid system for deep desulfurization of diesel oil

by

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Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

Chemical Engineering

January 2013

Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the Chemical Engineering Programme Universiti Teknologi PETRONAS in partial fulfillment of the requirement for the BACHELOR OF ENGINEERING (Hons) (CHEMICAL ENGINEERING)

Approved by,

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May 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

YEE CIA YIN

ABSTRACT

Photooxidative-extractive sulfur removal process is the application of photocatalytic oxidation of the sulfur compounds in model oil followed by ionic liquid extraction. The reaction was carried out under ambient temperature and pressure. A series of Mg/TiO₂ photocatalyst were prepared with magnesium loading and calcination temperature as research parameters. Imidazolium based ionic liquids were used as the extractant. These Mg/TiO₂ were sent for characterization to determine their morphologies and physico-chemical properties. The average particle size of Mg/TiO₂ ranges between 25nm to 36nm and Mg/TiO₂ has lower band gap energy as compared to TiO₂ enabling it to oxidize refractory sulfur compound under visible light irradiation. Ionic liquids were used for extractive desulfurization after the photooxidation process which could also be carried out in ambient temperature and pressure. The best performing photocatalyst is 0.25Mg400, 0.25 wt% magnesium doped on TiO₂ calcined at 400°C. It was able to photooxidize 98.5% of sulfur compounds. The best ionic liquid was 1-ethyl-3-ethyl imidazolium diethylphosphate (EEIM[DEP]) with extraction efficiency of 97.84%. Thus, the overall sulfur removal efficiency was 96.37%.

ACKNOWLEDGEMENT

I would like to express my gratitude to all who gave me the opportunity to complete my Final Year Project. First, I would like to thank University Technology of Petronas for giving me the golden opportunity be a student here and have the opportunity to accomplish this project work, providing me with access to all necessary information through Information Resource Centre and aid from laboratory technologist, laboratory executive for allowing me to utilize ionic liquid centre.

I also would like to extend my utmost appreciation to my supervisor, Associate Professor Dr. Chong Fai Kait, who guided me, helped me to adapt and work well throughout this project persistently and patiently. She has never failed to lead me to the right direction, give advice and explain all the problems associated with my project providing me with the necessary materials and also permission for using analysis laboratory.

Special thanks to my project guide, Kak Hayyiratul, a PhD student, whom has guided me throughout the project. Working with her has helped me gained useful experience and knowledge needed for the project. And also to my family back home for their sacrifices and continuous encouragement heading me towards my dream.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

One of the exhaust emissions, sulfur oxides compound which is hazardous to human and environment is the most notorious and undesirable petroleum contaminants. Sulfur by-products will be generated during the combustion of diesel oil unless the sulfur compounds are removed before the fuel is burnt. Strict standards have been imposed for sulfur content of diesel fuel in order to meet the increasingly strict environmental standards. A vast variety of sulfur compounds are present in diesel oil. These sulfur compounds are classified into four main groups namely mercaptans (thiols), sulfides, disulfides and thiophenes (Fromm, 2012)

They will eventually generate SO₂ and airborne particulate emissions during combustion. Therefore, desulfurization of diesel is extremely important in the petroleum-processing industry. Hydrodesulfurization (HDS) is the current industrial method to remove aliphatic and acyclic sulfur containing compound from diesel oil. This method usually applies CoMo and NiMo type catalyst and allows removing sulfur compounds by converting to H_2S . However, it is important to note that this process requires high temperature up to 400°C and high pressure up to 100 atm, the use of large reactors and long reaction time, thus higher operational cost. This conventional method is not effective for deep desulfurization to further remove sulfur compounds with high stearic hindrance, which makes it impossible to reduce sulfur compound to be less than 10 ppm, a Euro 5 standard, the Europian Union emission regulations for new light duty vehicles ("Emissions Standards-Cars and Light Trucks," 2012). Malaysia is required to meet the Euro 5 standard in 2015 (Agency, 2013). Currently, diesel in Malaysia contains 300 ppm of sulfur content. Sulfur dioxide is the major precursors of acid rain, which has

acidified soils, lakes and streams, accelerated corrosion of buildings and monuments, damaged trees, and reduced visibility. Sulfur dioxide is also a major precursor of fine particulate soot, which possesses a significant health threat.

Table 1.1 shows the health effects due to respiratory exposure to sulfur dioxide (from occupational health guideline for sulfur dioxide from NIOSH).

 Table 1.1 Extracted from Occupational Health Guideline for Sulfur ("Occupational Health Guidelines for Sulphur Dioxide,")

Exposure Limits (ppm)	Health Effects
1.5	Threshold for respiratory response in healthy individuals
1-5	upon exercise or deep breathing.
3 5	Gas is easily noticeable. Fall in lung function at rest and
5-5	increased airway resistance.
5	Increased airway resistance in healthy individuals.
6	Immediate irritation of eyes, nose and throat.
10	Worsening irritation of eyes, nose and throat.
10-15	Threshold of toxicity for prolonged exposure.
20+	Paralysis or death occurs after extended exposure.
150	Maximum concentration that can be withstood for a few
150	minutes by healthy individuals.

There are few other alternatives that have been researched and investigated for desulfurization of fuel for instance extraction, adsorption, absorption, oxidation, biodesulfurization and so on and so forth. One of the most promising processes is photooxidative desulfurization combined with extraction.

Thus, photooxidative-extractive deep desulfurization in the presence of ionic liquid is a novel approach, which is easy to control and saves energy. This method will be employed in this project.

1.1.1 Photocatalyst

Photocatalysis is an acceleration of photo-reaction in the presence of catalyst. A catalyst does not change its properties or being consume in a chemical reaction.

When titanium dioxide (TiO₂), a photocatalyst, absorbs ultraviolet radiation from sunlight and produces pairs of electrons and holes. The valence electron of titanium dioxide will be excited in the presence of light. This creates electron-hole pairs. Titanium dioxide is close to being an ideal photocatalyst in few aspects, for instance, it is highly stable chemically, and the photogenerated holes are highly oxidative (Fujishima, Rao, & Tryk, 2000). The high oxidizing property enables it to effectively desulfurize diesel oil. TiO₂ is also one type of photochemicals responsible for photocatalysis and hydrophilicity is completely different, even though both can occur simultaneously on the same surface. In titania, the species are relatively long lived, thus allowing the electron or hole to travel to the crystallite surface to perform possible redox reactions. TiO₂ is extensively studied due to its excellent photocatalytic performance, non-toxicity, low cost and high resistance to photo-corrosion.

The surface of TiO_2 electrode was irradiated with light consisting of wavelengths shorter than ~390nm. Absorption of light energy equal to or greater than the band gap energy of TiO_2 which is 3.2eV (anatase) can result in rejection of electron from the valence band to the conductance band generating electron and a positive hole. Figure 1.1 below shows the band gap energy for titanium dioxide to reject its valence electron from valence band.



Figure 1.1 Band gap energy for TiO₂

Calculation for band gap energy is as shown follow:

$$E = hv \tag{1.1}$$

$$v = \frac{c}{\lambda} \tag{1.2}$$

Thus,

$$E = \frac{hc}{\lambda} \tag{1.3}$$

Whereby,

E: Energy (Joule), $1eV=1.6 \times 10^{-19} \text{ J}$

h: Planck's constant, 6.626 x 10^{-34} m² kg/s

v: frequency (s^{-1})

- c: speed of light, 3.0×10^8 m/s
- λ : wavelength, m

From the equation, we know that the band gap energy is inversely proportional to the wavelength. Therefore, provided the band gap energy of TiO_2 is 3.2eV, thus through calculations the wavelength of TiO_2 is 388nm, at the ultraviolet region. This actually creates difficulty of its potential applications because less than 5% of solar beams are within such range. Therefore, we need to reduce the energy band gap by extending the TiO_2 response to visible light region (Chen, Yao, & Wang, 2008). This will be possible by metal doping TiO_2 which will be further discussed in the next section. Visible light has longer wavelengths ranging from 400nm to 700nm. However, this result will be achievable if titanium dioxide is metal doped.

Bessekhouad, Robert, & Weber (2003) reported that there are few methods of preparing TiO_2 nanoparticles and one of it is mixing tetraisopropylorthotitanate $Ti(OC_3H_7)_4$ (TTIP) and 1,4-cyclohexane diol $C_6H_{14}O_2$ (CHD) were dissolved in 300 ml of absolute EtOH with the molar ratio (1:1). The reaction mixture was stirred at 80°C for 3 h. After cooling, a controlled amount of water was added drop-wise to the solution. The initial pH of solutions obtained were adjusted to 6 by NH₄OH or HNO₃, and then dispersed in 100 ml of hexane in the presence of 2-10g/ml surfactant (Agar-Agar) emulsifying agents. After gelation, stirring was continued for 1 h. The gel was filtered and washed subsequently by water (500 ml) and EtOH (200 ml), dried at room temperature for 12 h. (Bessekhouad, Robert, & Weber, 2003)

Figure 1.2 below shows the photocatalytic process using titanium dioxide for decomposition of organic compounds.



Figure 1.2 Photocatalysis oxidation of TiO₂ (Fujishima et al., 2000)

The photocatalysis of TiO_2 doped with platinum to increase its photocatalytic activity in separating the electrons and holes in visible light. The separated electrons cause reduction and the holes aids oxidation. The process above shows the removal of OH⁻ ions by reacting it with the holes to become hydroxyl group. The same principle applies to sulfur oxides components whereby it will be oxidized into less harmful product. The hydroxide and oxide anion produced will oxidize and remove refractory sulfur compounds such as dibenzothiophene (DBT).

Through literature research and studies, titanium dioxide as the photocatalyst for oxidation of polynuclear heterocyclic sulphides for instance DBT into the corresponding sulphoxides and sulphones is attainable in good yield. (Abdel-Wahab & Gaber, 1998)

1.1.2 Ionic Liquid

Ionic liquid is a salt in liquid state, there are even room temperature ionic liquids (RTIL). Ionic liquids have many applications such as organic synthesis, electrochemistry, liquid phase extraction, catalysis for clean technology and polymerization processes. Ionic liquids are generally composed of large asymmetric organic cations and inorganic and organic anions. The dissolving properties of ionic liquids offers a broad range of separation processes, for instance, as an entrainer in

extractive distillation such as separation of ethanol and water, extraction processes such as aromatic and aliphatic, and biorefinery. In chemical processing and fine chemicals, ionic liquids can be a tool to help achieve higher yield and lower manufacturing cost for example in nucleophilic substitution reactions and catalytic reactions like biocatalytic and enzymatic reactions. Ionic liquids are also used in aluminium processing. The high electrochemical stability of ionic liquids allows deposition of less noble metal. Some of the examples are electroplating of aluminium onto steel, chromium electroplating and steel or other metals electropolishing. ("Ionic Liquid Applications: Offering Outstanding Advantages,"). Due to the properties and behavior of ionic liquids which can be used to suit an individual, they can be considered as designer solvents. By choosing the correct ionic liquid, products with high yield can be obtained and there will be a reduced amount of waste in a chemical reaction. Ionic liquids can also be recycled, thus, this will reduce the cost of processing. The reactions are faster and easier as compared to conventional organic solvent. (Earle & Seddon, 2000).

According to Han & Row (2010), the most prominent cations are pyridinium and an imidazolium ring species with alkyl group attached to te oxygen or nitrogen atoms. The presence of alkyl chain on the cation will determine its solubility in less polar fluids and te ionic interactions which involves mutual electrostatic attraction or repulsion of charged particles, making them miscible with polar substance. The flexibility of application helps in extraction of organic compounds and this is the property that gained attraction for the usage for this project. (Han & Row, 2010)

1.2 Objectives

- To prepare and characterize Mg/TiO₂ photocatalysts for oxidation of sulfur species in diesel oil under visible light radiation.
- To investigate the performance of the photooxidative-extractive system for sulfur removal from diesel oil using phosphate based ionic liquid as extractant.

1.3 Scope of Study

In this project, suitable photocatalysts was prepared for oxidation of sulfur species from diesel oil. The photocatalyst prepared was magnesium doped titanium dioxide (Mg/TiO₂). The prepared photocatalyst will also be characterized to determine the properties using Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffusion (XRD), Field Emission Scanning Electron Microscopy (FE-SEM) and Temperature Programmed Reduction (TPR) and Thermogravimetric Analysis (TGA).

Three phosphate-based ionic liquid will be investigated and used for extraction of sulfur in order to improve the desulfurization efficiency. The three types of ionic liquids used were 1-butyl-3-butyl imidazolium dibutylphosphate (BBIM[DBP]), 1 butyl-3-ethyl imidasolium diethylphosphate (BEIM[DEP]), and 1-ethyl-3-ethyl imidazolium dibutylphosphate (EEIM[DEP]). The photo-oxidative desulfurization of fuels using metal doped TiO₂ as photooxidative catalyst and the imidazolium-based ionic liquid as the extractant will be studied.

1.4 Problem Statement

Current industrial technology for sulfur removal requires high temperature and high pressure via hydrodesulfurization (HDS) method. This process is costly as the reactor used to achieve optimal condition for removal of sulfur is complicated and it has to be in big scale to minimize the processing cost. In addition, hydrodesulfurization is limited to the removal of aliphatic and acyclic sulfur species but not refractory sulfur species. Malaysia will need to meet Euro 5 standard, with sulfur species which is less than 10 ppm by the year 2015; HDS is not able to achieve the requirement.

Titania is an oxidant but is only active under UV-light with wavelength of 388 nm. To oxidize sulfur, it requires the presence of ultraviolet rays which is costly.

Thus, this project will focus on reducing the sulfur component in diesel oil using photo-oxidative catalyst which is active under visible light region and extraction using phosphate based ionic liquid. This process only requires room temperature and ambient pressure.

CHAPTER 2

LITERATURE REVIEW

2.1 Metal doping on TiO₂ photocatalyst

TiO₂ is commonly known as titania. It is a semiconductor which is photoactive however it has its limitations as it is only photoactive under ultraviolet rays only. It has large band-gap width (3.2eV) of TiO₂ which confines its photocatalytic activity within the range of UV light, which means only a small fraction of solar light spectrum can be utilized by TiO₂ (Feng, Yu, & Zhang, 2013). Thus, metal doping will help minimize the limitations by (Chen et al., 2008):

- Preventing the recombination of the photo-induced electrons which can occur in a split second of less than 1ns. The time is too short for any other reaction to occur.
- Shift or extend TiO₂ photoreactive spectrum range to the visible light region.

In previous studies, one of the most active metals for photocatalytic enhancement is platinum (Pt), which can produce the highest Schottky barrier among the metals that facilitate electron capture. The capture of electrons by Pt is postulated to produce a longer electron-hole pair separation lifetime, and hinders the recombination of electron/hole pairs. This enhances the transfer of holes and possibly electrons to O_2 adsorbed on the TiO₂ surface. Afterwards, excited electrons migrate to the metal, where they become trapped and the electron/hole pair recombination is suppressed. (Li & Li, 2002)

The less recombination of electrons/holes in the $Pt-TiO_2$ catalyst can be explained in the following manner. Firstly, the excited electrons from the valence band to the conduction band migrated to Pt clusters, then migrated to O_2 molecules adsorbed on the surface of

the Pt. The Pt deposited on the TiO_2 surface produced the highest Schottky barrier among the metals that facilitated the electron capture. Secondly, Pt^{4+} species trapped the excited electrons, which migrated to O_2 . The overall process of charge carrier trapping, migration, and transfer was promoted due to the presence of Pt. Thirdly; the defect energy level might act as a separation center. Ti^{3+} could enhance the oxygen chemisorption and promote the excited electrons trapped by O_2 (Li & Li, 2002).

In principle, the metal dopants can narrow the band gap width and thus extend the active range of TiO₂ to visible light for utilizing more solar energy. Eight metal-ions doped TiO₂ (M-TiO₂) were successfully synthesized by an ultrasonic method, including Fe, Co, Ce, Cr, Mn, Mg, Ni and Ag ions. The optimal doping concentrations of the Mg/TiO₂ and Ni/TiO₂ were 1%, whereas the Co/TiO₂, Mn/TiO₂, Fe/TiO₂, Cr/TiO₂ and Ce/TiO₂ were 3%. Among them, the 1% Mg/TiO₂ shows the highest photocatalytic efficiency under solar light. Moreover, it shows no obvious loss of photocatalytic activity after five cycles of usage. (Feng et al., 2013)

Table 2.1 Photocatalytic efficiency under solar light of each M/TiO_2 at various doping concentrations (Feng et al., 2013):

Samples	1% doping	3% doping	5% doping
Ag-TiO ₂	71.1	68.8	63.7
Mg-TiO ₂	87.4	82.6	72.0
Ni-TiO ₂	79.3	76.6	69.1
Co-TiO ₂	71.2	77.4	62.5
Mn-TiO ₂	77.9	79.5	67.3
Fe-TiO ₂	81.7	83.6	76.4
Ce-TiO ₂	81.5	84.8	76.7
Cr-TiO ₂	82.0	84.2	73.1
Undoped TiO ₂		74.8	

According to Avasarala, Tirukkovalluri, & Bojja (2011), upon doping TiO_2 with magnesium ion, the catalyst exhibits absorption in visible light region. Since Mg^{2+} is more electropositive, the electronic cloud in each TiO_2 might be loosely held, favoring formation of less dense anatase phase. XRD data has shown anatase phase, indicating that the magnesium ions in TiO_2 did not influence the crystal patterns of TiO_2 particles. Based on trial photocatalytic degradation pattern of organophosphate (monochrotophos) with Mg/TiO₂, samples have shown that maximum degradation of the organophosphate

was at 1wt% Mg/TiO₂. It has better photocatalytic activity. In a UV-visible absorption study, the titania doped with magnesium absorption shifted to a higher wavelength region of 400-550nm. The absorption shift is due to the reduced band gap. (Avasarala, Tirukkovalluri, & Bojja, 2011)

The activities of the doped photocatalysts depended on the size of dopant ions and doping methods. The optimum content of dopant ions Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} were 1.25, 1.25, 2.25, 2.25 and 2.25 at.%, respectively. The optimum calcination temperature and time were 400 °C and 1 h. (Peng, Li, Jiang, Lu, & Li, 2004)

Since the 1% Mg/TiO₂ showed better photocatalytic efficiency than other M/MINTiO₂ samples, in this project, we will investigate more on doping of TiO₂ with Magnesium. This metal shows photocatalytic activity and the surface are suitable for photoactive species, which improve the photoactivities in anatase phase. Most metal doped TiO₂ samples exhibited some enhancement in photo-catalytic activity as compared to undoped nano-particulate TiO₂ be it in anatase phase or rutile phase. (Choi, Park, & Hoffman, 2009)

There are few methods of doping transition metals to semiconductors including complex precipitation, deposition precipitation, sol-gel method, wet impregnation method, and photodeposition method.

For complex deposition method, appropriate amounts of metal salts were weighed and dissolved in distilled water. Next, glycerol is added to metal with a ratio of 2:1 molar ratio ad stirred continuously stirring for one hour. The precipitates were obtained during titration of mixture with 0.25M NaOH, temperature maintained at around 8-10°C until a pH of 14. The precipitates were filtered and dried in in oven at 75°C for 18 hours. For deposition precipitation method, the procedures are similar to complex deposition method but the temperature is maintained at 25°C and the final pH is pH 8.5. (Riaz, Chong, Ela, & Khan, 2011)

According to Mul and Moulijn, impregnation is a preparation technique whereby the precursor of active phase in our case titania is brought into contact with the metal salt. In the case of wet impregnation method, the solute will transport to the outer surface of

titania. Depending on the process conditions, different profiles of the metal doped titania will be obtained. The drying or calcination step which is right after the impregnation step is essential to remove the hydrates and will result in a more homogenous profile. (Mul & Moulijin)

Wet impregnation method, the desired amount of metal salt is added to TiO_2 . The suspension is stirred for 1 hour. The solvent is evaporated in water bath at 80°C to get a super saturated solution. The paste was then oven dried at 120°C for 18 hours. (Riaz et al., 2011)

In the photodeposition method, metal doped on TiO₂ was prepared by photoreducing metal ions to metal molecule on the TiO₂ surface according to the following steps. First, 3g of TiO₂ is added to 100ml of deionized water. TiO₂ suspension is adjusted to pH 3 by addition of perchloric acid. Then, the required amount of metal salt is added to the TiO₂ suspension. The mixtures are then irradiated with *UV* light (30*W*, *UV-C*, λ_{max} =254nm, manufactured by Philios, Holland) for 3 hours and then dried in an air oven at 100°C for 12 hours. The dried solids were ground in agate mortar and calcined at 400°C for 6 hours in a furnace. (Behnajady, Modirshahla, Shokri, & Rad, 2008)

2.2 Sulfur Removal Process

Photo-oxidative extractive is a photocatalytic oxidation and ionic liquid extraction for desulfurization of diesel. Under normal temperature (room temperature) and pressure, photocatalyst was added to model oil to be oxidized under visible light after which it will be extracted using ionic liquid.

Photooxidative desulfurization is a method using high-pressure mercury lamp of visible light into the sulfur contaminated diesel, so that the sulfur compounds can be photo-oxidized. This process can be carried out under the normal temperature and pressure, and the sulfur can be extracted by solvent extraction agents, thus greatly reduce the sulfur content to achieve the purpose of desulfurization (Zhang, Yu, & Wang, 2009).

Photocatalytic oxidation has few advantages including simple and easy to control reaction, react under normal pressure at normal temperature, saves energy. The sulfur-

containing compounds like sulphides, disulphides and thiols are carried out mostly via hydrodesulfurization (HDS). This method is hard to remove some difficult sulfur compounds with stereo hindrance such as 4-methyldibenzothiophene (4-MDBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), dibenzothiophene (DBT) and so on. Hyrdrodesulfurization also has some drawbacks for example severe operating condition, high temperature and pressure of hydrogen, and high capital cost. Therefore, approaches based on oxidation, extraction, biodesulfurization and absorption have been extensively researched. (Jiang et al., 2011).

According to Zhang, Zhu, Li, Jiang, Huang, & Yan (2009), one of the reliable methods is photooxidation combined with extraction for desulfurization. In this process, the sulfur compounds in the model oil are oxidized into sulphones or sulphoxides, and further removed using the ionic liquids. Thus, to save energy, metal doped photocatalyst will be used for oxidation as it will be activated even with the presence of visible light. It is explained in the previous section 2.1. Room temperature ionic liquids has gained wide attention for application in electrochemistry, catalysis, synthesis of nanomaterials because of their low melting point, high thermal stability and negligible vapor pressure as it has high viscosity. There are few types of ionic liquids namely imidazolium based ionic liquids, pyridinium based ionic liquids and pyrrolidinium based ionic liquid and the extractive performance of it is the best. (J. Zhang et al., 2009) It will be further discussed in the next section.

2.3 Phosphate based ionic liquid

Ionic liquids have been studied for applications related to green chemical processes, such as liquid/liquid extractions. Ionic liquids are typically nonvolatile, non-flammable, and thermally stable. In general Ionic liquids have higher density than organic liquids and water. Therefore, many ionic liquids exist as a separate phase when in contact with organic and aqueous phases. These features make it possible to readily recycle Ionic liquids for multiple extractions without the additional environmental concern.

Extractive desulfurization (EDS) is a well-established process that can be carried out at or around ambient temperature and pressure. EDS process also operates without the need of hydrogen and catalyst as in HDS. More importantly, some BT and DBT sulfur compounds can be extracted quite efficiently. The chemical structure of the fuel oil components is not changed through this process. The organosulfur components can be recovered at high concentration following the extraction process if the solvents chosen for such a process can be regenerated.

Yi Nie et al. 2008, did a research on the N-butylimidazole-derived dialkylphosphate Ionic liquids on the extractive removal of aromatic sulfur compounds from fuel ionic liquids. The sulfur partition coefficient (K_N) between the IL and furl at 298.15 K are determined experimentally over a wide range of sulfur content. The results obtained showed that the sulfur removal selectivity for a specific IL depends on the molecular structure of the sulfur compounds and follows the order of DBT>BT>3-MT.

A phosphate based ionic liquid will be used in parallel with photocatalyst for deep desulfurization of diesel to further reduce the concentration of sulfur species in diesel oil. Liquid-liquid extraction for desulfurization utilizes imidazolium based- phosphate ionic liquids, namely, 1-butyl-3-butyl imidazolium dibutylphosphate (BBIM[DBP]), 1-butyl-3-ethyl imidazolium diethylphosphate (BEIM[DEP]), and 1-ethyl-3-ethyl imidazolium diethylphosphate (EEIM[DEP]). The catalyst oxidation and extraction desulfurization (ECODS) was found to be a promising approach for the reduction of sulfur with a total removal of 85.2% using BBIM[DBP]. This was achieved at low temperature, 70°C and atmospheric pressure. The removal is followed by BEIM[DEP] and EEIM[DEP] which achieved 79.1% and 78.2% respectively. The precatalyst of molybdic compounds was oxidized with H₂O₂ to form peroxomolybdic compounds, which is soluble in ionic liquid and dissolved in oil. The sulfur containing compounds in the model oil were extracted into ionic liquid phase and oxidized to their corresponding sulfones by peroxomolybdic compounds. Imidazolium base phosphate ionic liquids with longer alkyl chain displayed better sulfur removal efficiency. (Mohd Zaid, 2012) ODS process showed a removal of 65.8% with the presence of H_2O_2 and 55.2% removal with the presence of only catalyst.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Preparation of Mg/TiO₂

The photocatalyst was prepared using wet impregnation method as shown in Figure 3.1. The percentages of Magnesium loaded on TiO₂, [P25 (Degussa), 80% anatase, 20% rutile; 20-50nm diameter] are 0.1wt%, 0.2wt%, 0.2swt%, 0.5 wt%, 1 wt%, 2wt% and 4 wt%. A calculated amount of magnesium nitrate hexahydrate, Mg(NO₃)₂.6H₂O, [Brand: R&M Chemicals, Molecular weight: 256.41 g/mol] in distilled water was stirred for 1 hour with suitable amount of TiO₂. The solvent was then evaporated slowly in a water bath at 80°C, followed by oven-drying at 120°C for 18 hours. The dried photocatalyst was then grinded into powder form to maximize its surface area for calcinations. Calcination process was then carried out to activate the photocatalyst at 300°C, 400°C and 500°C for 1 hour.



Figure 3.1 Schematic diagram of wet impregnation method

Mg loading (wt%)	Mass of TiO ₂	Mass of Mg	Mass of
	presursor	required to produce	$Mg(NO_3)_2.6H_2O$
		10g of Mg/TiO ₂	required to
		with different	produce 20g of
		loading	Mg/TiO ₂ with
			different loading
0.10%	9.990g	0.010g	0.1055g
0.20%	9.980g	0.020g	0.2109g
0.25%	9.975g	0.025g	0.2637g
0.50%	9.950g	0.050g	0.5274g
1.00%	9.900g	0.100g	1.0548g
2.00%	9.800g	0.200g	2.1095g
4.00%	9.600g	0.400g	4.2190g

Table 3.1 Amount of Magnesium Nitrate salt needed for Mg loading on TiO₂

Calculation to determine the amount of magnesium nitrate salt needed is calculated in Appendix A.

Notation: 0.25Mg 400 means 0.25 wt% of magnesium doped on TiO₂ calcined at 400°C.



Figure 3.2 Stirring of Magesium doped photocatalyst using magnetic stirrer







Figure 3.4 Photocatalyst slurry after evaporation



Figure 3.5 Oven dry at 120° C for 18 hours



Figure 3.6 Calcination using furnace

3.1.2 Characterization of Mg/TiO₂

We need to characterize Mg doped TiO_2 in order to determine its chemical as well as its physical properties before and after calcinations. These properties will be related to the performance of the photocatalyst.

Field Emission Scanning Electron Microscopy (FE-SEM)

[FE-SEM model: Zeiss Supra55 VP]

FE-SEM is used to observe small structures (as small as 1 nanometer = one billion of a millimeter!) on the surface of cells and material. Additional EDX test will show how well the metal dopant was dispersed onto TiO_2 . It was determined by the morphologies of TiO_2 .

Steps:

- 1. The sample holder was chosen and sample was mounted onto it.
- 2. The sample was then analyzed for its size with 100 kX magnification.

X-Ray Diffusion (XRD)

[XRD model: Bruker AXS D8 Advance X-Ray powder Diffractometer]

XRD is used to determine the crystal structure of TiO_2 photocatalyst which was doped. The phases could also be determined such as the percentages of anatase phase and rutile phase of the TiO_2 . X-ray diffractometer was used to perform this function at ambient temperature.

Steps:

- 1. Powdered samples were scanned from $4-70^{\circ}$ in 2 Θ range with 0.020° step interval and 2s/step counter time.
- 2. Origin lab-6 software was used for deconvolution of the diffractogram.
- 3. A base case spectrum was obtained from here.

Fourier Transform Infrared Spectroscopy (FTIR)

[FTIR Model: Pelkin Elmer, Spectrum One]

FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation was passed through a sample. Some of the infrared radiation was absorbed by the sample and some of it was passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a functional group fingerprint of the sample. Like a fingerprint no two unique functional group structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis such as identification of materials. This test is done to determine the functional group present in TiO_2 . They are identified by the characteristics peaks in the spectrum.

Steps for sample preparation and analyzing:

- 1. Sample of 1 mg-3 mg was ground into a fine powder using agate mortar.
- 2. About 250 mg to 300 mg of KBr was weighed using a small scoop.
- 3. The sample and KBr were grounded together and then the mixture was then transferred into die.
- 4. The die was the placed into the hydraulic press. Vacuum was applied for 1 min and pressure was increased gradually to ten tons for 1 min. Release the pressure and the vacuum.
- 5. KBr disc was then removed and transferred to sample holder. The stainless steel part was cleaned from residue of sample.
- 6. The sample was then placed in the spectrum holder inhrto Spectrum One.
- 7. Key in the sample name and the sample spectrum was scanned.

8. The spectrum was then analyzed for its functional group by interactive interpretation and individual peak functional groups are traced.

Transmission Electron Microscopy (TEM)

[TEM model: Zeiss Libra 200]

TEM specimen stage includes airlocks to allow for insertion of the specimen holder into the vacuum with minimal pressure increase. Once the photocatalyt is inserted into TEM, the sample has to be manipulated to present the region of interest to the beam. The magnification is 200kV giving us the size and shape of the particles.

3.2 Preparation of model oil

Model oil was be prepared to model diesel fuel. Dibenzothiophene (DBT) which is a sulfur species will be added to dodecane which act as the oil. This will aid in helping us to determine the performance of sulfur removal.

The preparation of model oil was by mixing dodecane and dibenzothiophene in a 250 mL volumetric flask. 146.89 mg dibenzothiophene was added to a volumetric flask and it was then added with dodecane until the volume of 250 ml. The solution was then stirred to ensure sulfur species was mixed thoroughly in dodecane. This amount will result in 100 ppm of dibenzothiophene in the solution. Calculation is shown in Appendix B.

Preparation of standard solution of 10 ppm, 20 ppm, 40 ppm, 60 ppm and 80ppm of DBT in dodecane to act as standard for gas chromatograph calibration:

Concentration	Volume of 100 ppm DBT required
10ppm	5ml
20ppm	10ml
40ppm	20ml
60ppm	30ml
80ppm	40ml

Table 3.2 Preparation of 50ml Standard Solutions

3.3 Deep Desulfurization via photooxidative-extractive system

Blank Run

The model oil was irradiated with halogen lamp for 6 hrs. Samples were taken at 15 mins interval for the first half hour, followed by 30 mins interval and 1 hr interval until the 6^{th} hr.

The samples were then sent to gas chromatograph to determine the amount of sulfur oxidized.

Solution containing model oil and H_2O_2 was stirred for 30 mins to ensure well mixing of the mixture. The mixture is then irradiated under halogen lamp for 6 hrs and the samples were sent to gas chromatograph to determine the amount of sulfur oxidized.

[GC Model: Agilent 7890A, 280°C; Oven Program: 40°C for 0 min then 10°C/min to 280°C for 0 min; Injection Volume: 2 μ L; Mode: Split; Heater: 250°C; Split ratio: 20:1; Split flow: 40mL/min; Flow: 2mL/min; Average velocity: 31.745cm/sec. Front detector: temperature = 325°C, H₂ flow = 30mL/min, Air flow = 350mL/min, Makeup flow = 5mL/min. SCD detector: Temperature = 800°C, Pressure = 324 torr, Oxidizer = 4, Hydrogen = 40]

Photooxidative

- 1. The solution containing 10 ml of 100 ppm model oil and 0.01g of 0.5Mg400 photocatalyst was stirred for 30 mins to ensure well mixing of the mixture.
- 2. The mixture was then irradiated with halogen lamp. The reaction was carried out for 6 hrs. The sampling of model oil was taken every 15 min intervals for the first half hour, followed by half hour interval and every hour after that.
- 3. The oil was sent for gas chromatography to determine the amount of sulfur remaining in the oil. The maximum removal of sulfur occurs when the reaction was carried out for 6 hrs. The results are shown in results and discussion section (Section 4.2).
- Step 1 was then repeated using 1Mg400, 2Mg400, 4Mg400, 0.5Mg300, 1Mg300, 2Mg300 and 4Mg300. The mixtures were then irradiated for 6 hrs. The sample

was then sent for centrifugal separation of the oil and Mg/TiO_2 . Later, the oil was sent for gas chromatography to determine the amount of sulfur oxidized in the oil.

- 5. After obtaining results from gas chromatography, 0.5Mg400 gave better performance as compared to others.
- 6. Thus, from the result obtained, 0.1Mg400, 0.2Mg400 and 0.25Mg400 were synthesized and steps one to three were repeated to test for the performance of these photocatalyst. The best performance catalyst was calcined at 500°C and tested for its efficiency for photooxidation of sulfur species.
- 7. Steps one to three were then repeated by using the best performance photocatalyst with the addition of hydrogen peroxide. The calculation of hydrogen peroxide used was shown in Appendix C.

Photooxidative-Extractive System

- 1. The photooxidative-extractive system was investigated using the best performing Mg/TiO₂ photocatalyst. The model oil was first photooxidized using the photocatalyst with and without the presence of hydrogen peroxide which was irradiated using halogen lamp.
- 2. The experiment was followed by ionic liquid extraction. Model oil which was photocatalyzed was added 1-butyl-3-butyl imidazolium dibutylphosphate (BBIM[DBP]), at a ratio of 5mL:1mL. The photooxidized model oil with ionic liquid mixture is stirred for 4 hrs without the presence of halogen lamp for extraction to occur. This could determine the ability of sulfur removal using Mg/TiO₂ followed by ionic liquid extraction.
- The sample was then sent for centrifugal separation of the oil and ionic liquid. Later, the oil was sent to gas chromatograph to determine the amount of sulfur remaining in the oil.
- The procedure was then repeated by using different ionic liquids namely 1-butyl-3-ethyl imidazolium diethylphosphate (BEIM[DEP]), and 1-ethyl-3-ethyl imidazolium diethylphosphate (EEIM[DEP]).

Extraction Using Ionic Liquids

The model oil was added to 1-butyl-3-butyl imidazolium dibutylphosphate (BBIM[DBP]), at a ratio of 5mL:1mL. The solution was stirred continuously to ensure equal distribution of the ionic liquid in the model oil. The reaction is carried out for 5 hrs and samples were taken every subsequent hour.

The sample was then sent for centrifugal separation of the ionic liquid with the model oil. The separated model oil was then sent for gas chromatography to determine the amount of sulfur remaining in the model oil.

The procedure was then repeated by using different ionic liquids, 1-butyl-3-ethyl imidazolium diethylphosphate (BEIM[DEP]), and 1-ethyl-3-ethyl imidazolium diethylphosphate (EEIM[DEP]) for extraction after the photooxidation process.

Photolysis of sulfur species (as reference run)

The model oil with and without hydrogen peroxide was irradiated with halogen lamp (500W). The reaction is carried out for 6 hrs and sample was taken at every subsequent hour. The samples were sent to gas chromatograph to determine the amount of sulfur remaining.



Figure 3.7 Desulfurization under visible light



Figure 3.8 Overall procedure of photooxidative desuphurization

Table 3.3 and Table 3.4 shows the Gantt Chart for this study, showing the expected timeline and processes for the entire project.

2013 January to 2013 May			FYP 1													
No.	Detail / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
1	Topic confirmation															
2	Preliminary research work, study on:															
	- Photocatalysis process															
	- Photooxidative catalyst TiO ₂															
	- Metal doped TiO ₂ photocatalyst															
	- Imidazolium phosphate base ionic liquid															
	- Literature Review															
	- Methodology															
3	Preparation of extended proposal															Ч
4	Submission of extended proposal															F
5	Learning about Equipment to be used for															of
5	photocatalyst desulfurization of diesel.															Snd
6	Proposal defense															щ
	Proceed in research/project work, includes:															
	- Experimental preparation of metal doped TiO ₂															
7	- Preparation of metal doped Mg-TiO ₂															
	- Photooxidation of sulfur species in model oil															
	- Characterization of photocatalyst															
8	Submission of Interim Draft Report															
9	Submission of Interim Report															

Table 3.3 Gantt Chart for Final Year Project 1

• Key Milestone



Progress

Table 3.4 Gantt Chart for Final Year Project 2

2013 May to 2013 August				FYP 2													
No.	Detail / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
	Project Works Continue																
	- Photolysis of model oil																
1	- Extraction of model oil using ionic liquid																
	- Photo-oxidative estraction of model oil																
	- Characterization of photocatalyst																
2	Submission of progress report							\bullet									
	Project Work Continues and preparation of report:																5
	- Continue with project work																Υł
3	- Report preparation																fΕ
	- Technical paper preparation																qс
	- Poster preparation																En
4	Pre-SEDEX																
5	Submission of draft report											•					
6	Submission of dissertation (soft bound)																
7	Submission of Technical Paper																
8	Oral Presentation																
9	Submission of Dissertation (Hard Bound)																



Progress

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of Mg/TiO₂ photocatalyst

4.1.1 Field Emission Scanning Electron Microscopy (FE-SEM)

The morphology of the Mg/TiO_2 photocatalysts were determined using FESEM. The samples were coated with a layer of platinum-palladium prior to scanning at 100 kX magnification.

The FESEM micrographs are expected to see how well the dopant material, magnesium is dispersed onto TiO_2 . FESEM of the photocatalyst sample gives irregular spherical shape. The particles size ranged between 20 nm – 60 nm. Figure 4.1 to Figure 4.8 show morphologies of 0.5 wt %, 1 wt%, 2 wt% and 4 wt% of magnesium doped on TiO_2 which were calcined at 400°C and 500°C.

The magnification of FESEM is not enough to determine the morphological structure of the photocatalyst. Magnesium is below the detectable limit and thus it could not be observed. The image indicated that there was no separated of magnesium from the samples. This means that the dispersion of magnesium on titania are even (Hwang et al., 2009). The nanoparticles of titania maintain their shape and size and are well distributed. From the mapping, it is also observed that magnesium is evenly dispersed onto TiO₂.

The more the amount of magnesium is loaded onto titanium dioxide, the bigger the average size of the particle. This may be due to the magnesium crystal affecting the size of particles.


Figure 4.1 FESEM micrographs of 0.1Mg400



Figure 4.2 FESEM micrographs of 0.25Mg400



Figure 4.3 FESEM micrographs of 0.25Mg500



Figure 4.4 FESEM micrographs of 0.5Mg400



Figure 4.5 FESEM micrographs of 1Mg400



Figure 4.6 FESEM micrographs of 2Mg400



Figure 4.7 FESEM micrographs of 4Mg400

Table below shows the average size of the photocatalyst through FESEM analysis:

Weight Percentage	Calcined at 400°C				
of Magnesium	Average particle	Size range (nm)			
loading at 400°C	size (nm)				
0.10	25.69	17.04-56.90			
0.25	31.20	19.50-61.60			
0.50	30.64	23.00-45.00			
1.00	34.99	22.00-62.00			
2.00	35.20	21.68-67.33			
4.00	35.77	22.61-156.40			

Table 4.1 Average Size of photocatalyst

Magnesium mapping on the sample



Figure 4.8 Portion of 0.25Mg400 surface



Figure 4.9 Magnesium dispersed on the TiO₂ surface (EDX mapping)

4.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

In FTIR, the infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared are transmitted while others are absorbed by the sample. The resulting spectrum represents the molecular absorption and transmission, which creates the molecular finger print. No two molecular fingerprints are alike.

This analysis is done to determine the functional group present in the photocatalyst. Also, by using the unique collection of absorption bands, FTIR can be used to confirm the identity of a pure compound or to detect the presence of specific impurities (Christian, 2004). Sample for FTIR analysis was prepared by mixing photocatalyst thoroughly with KBr while being grounded with the pestle. The mixture of sample and KBr is transferred into a die set and is placed just enough to cover the bottom in pellet die. Die is placed into a hydraulic press and a vacuum is applied for 1 min. Pressure is gradually increased to 10 tons and released after 1 min. The KBr pressed disc is then removed and transferred onto a sample holder.

This test is done to determine the functional group present in TiO_2 . They are identified by the characteristics peaks in the spectrum.







Figure 4.11 FTIR spectra for Mg/TiO₂ photocatalyst

According to the wavenumber as shown, the functional group contained in the catalyst photocatalysts which were calcined does not contain nitrate group which means that it has been removed after calcination. From Figure 4.11, photacatalyst before calcination shows presence of nitrate functional group at wavenumber 1384 cm⁻¹. There were no indications of nitrates in the sample after calcination and this means the nitrate groups are completely removed during the calcination process. From Figure 4.10 and Figure 4.11, all sample of photocatalysts showed the presence of O-H bending and stretching around 1600 cm⁻¹ and 3400 cm⁻¹ respectively. However, the percent transmission before calcination is more significant than after calcination. This indicates that most of the hydrates were removed during calcination. Another main peak in is between 400 to 900 cm⁻¹ which is Ti-O stretching vibrations.(Feng et al., 2013).

The original FTIR results are shown in Appendix D.

4.1.3 X-Ray Diffraction (XRD)

X-ray diffraction is carried out to determine the phases and crystal structure of the modified TiO_2 photocatalyst. There are two types of phases which are anatase and rutile. The determination of its phases is by using X-ray diffractometer at room temperature. XRD is a non-destructive technique which could identify crystalline phases and orientation

The XRD technique takes a sample of the photocatalyst and places the powdered sample in a holder, then the sample is illuminated with x-rays of a fixed wavelength and the intensity of reflected radiation is recorded using a goniometer. The data is then analyzed for the reflection angle to calculate the inter-atomic spacing (D value). The intensity (I) is measured to discriminate (using I ratios) the various D spacing and the results are to identify possible matches.

From the results, only titanium dioxide of anatase phase and a small amount of rutile phase is obtained and the magnesium amount is too small to be detected. Anatase TiO_2 exhibit better photacalytic activities as compared to rutile TiO_2 . (Hwang et al., 2009)

The titanium dioxide is known to crystalize to anatase phase and small amount of rutile phase observing a peak at the 2Θ from 2° to 80° :

Anatase		Rutile			
2-Theta (degrees)	Relative intensity(%)	2-Theta (degrees)	Relative intensity(%)		
25.289	100	27.436	100		
36.949	10	36.087	50		
37.791	20	39.183	8		
38.566	10	41.226	25		
48.052	35	44.048	10		
53.902	20	54.313	60		
55.065	20	56.651	20		
62.109	4	62.739	10		
62.688	14	64.030	10		
68.770	6	65.485	2		
70.317	6	69.005	20		
74.024	2	69.791	12		
		72.413	2		
		74.403	1		

Table 4.2 Location and relative intensities of the 2-theta peaks of the X-ray diffraction spectra of rutile and anatase (Wilhelm, 2003):

Figure 4.11 below illustrates the X-Ray Diffraction of 0.25 wt % Mg/TiO₂ which the 2theta degrees shows the presence of anatase and rutile phase TiO₂. XRD results of other photocatalyst are shown in Appendix E.



Figure 4.12 XRD Diffraction of Mg/TiO₂ photocatalysts 0.25Mg400

4.1.4 Transmission Electron Microscopy (TEM)

TEM is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen. An image is formed from the interaction of the electrons transmitted through the specimen, whereby the image is magnified and focused onto an imaging device. TEM are capable of imaging at a significantly higher resolution than light microscope. This enables user to examine the fine detail-even as small as a single column of atoms.

TEM gives clearer morphologies of the photocatalyst.



Figure 4.13 TEM micrographs of 0.1Mg400



Figure 4.14 Fringes of the particles of 0.1Mg400



Figure 4.15 TEM micrographs of 0.25Mg400



Figure 4.16 Fringes of the particles of 0.25Mg400



Figure 4.17 TEM micrographs of 0.25Mg300 (left) and 0.25Mg500 (right)



Figure 4.18 TEM micrographs of 0.5Mg400



Figure 4.19 Fringes of the particles of 0.5Mg400



Figure 4.20 TEM micrographs of 1Mg400



Figure 4.21 Fringes of the particles of 1Mg400







Figure 4.23 Fringes of the particles of 2Mg400



Figure 4.24 TEM micrographs of 4Mg400



Figure 4.25 Fringes of the particles of 4Mg400

From the figures, it could be observed that for every sample, there are fringes with two different spaces between the fringes. One is around 6nm and the other one is around 3nm. This could mean that there are presence of both Magnesium and titanium which are of different particles in it. Most of the figure shows direction of diffraction of anatase phase as illustrated in figure below in direction 2. Direction 1 is the rutile phase.



Figure 4.26 Illustration of diffraction direction showing the presence of rutile and anatase phase (Wu et al., 2011)

Thus, from the diffraction that is obtained, all samples show the presence of anatase

4.1.5 Temperature Gravimetric Analysis (TGA)

It is a thermal analysis. It may change the physical and chemical properties of the compound and may decompose components in it. This will help us to determine the components contained in the compounds. For instance, if there is a sudden decrease of weight at 100° C, it may mean there is presence of moisture. (Fassier, Peyratout, Smith, Ducroquetz, & Voland, 2010). Figure 4.27 shows the TGA analysis of the Mg/TiO₂ photocatalyst.



Figure 4.27 TGA analysis

The TGA analysis shows slight decomposition. This may be due to the doping of Magnesium nitrate hexahydrate onto TiO_2 (Degussa P25). Magnesium nitrate itself decomposes at $425^{\circ}C$ while TiO_2 does not decompose. Thus, the slight decomposition may be due to the presence of magnesium in the photocatalyst. Uncalcined photocatalyst decompose slightly more than the calcined samples.

The equation that could be used to illustrate the thermal degradation of $Mg(NO_3)_2$ (Chemguide, 2013):

 $2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2 \tag{4.1}$

4.2 Desulfurization Reaction

Desulfurization process was conducted in two sequences: photooxidation followed by extraction process. Fifteen Mg/TiO₂ photocatalysts with different Mg loading (0.1 wt%, 0.2 wt, 0.25 wt, 0.5 wt%, 1 wt%, 2 wt%, and 4 wt%), which were calcined at 300°C, 400°C and 500°C were investigated for photooxidation of DBT to DBTO₂. Three ionic liquids BBIM[DBP], BEIM[DEP] and EEIM[DEP] were used as extractant. The reaction was conducted for 6 hrs under visible light illumination. The sampling of model oil was taken at every 15 min intervals, and then followed by every hour after that. The samples were analyzed using gas chromatograph to determine the amount of sulfur converted. From the results as shown in Table 4.3 and Figure 4.28, conversion of DBT to dibenzothiophene-sulfone (DBTO₂) using 0.5 wt% Mg-TiO₂ gives a better performance among 0.5 wt% Mg-TiO₂, 1 wt% Mg-TiO₂, 2 wt% Mg-TiO₂, 4 wt% Mg-TiO₂, which were calcined at 300°C and 400°C.

Weight Percentage	Calcined at 300°C	Calcined at 400°C	Calcined at 500°C	
of Magnesium	Conversion (%)	Conversion (%)	Conversion (%)	
loading				
0.10	-	67.53	-	
0.20	-	92.02	-	
0.25	22.83	98.45	98.56	
0.50	4.12	45.73	-	
1.00	3.73	3.41	-	
2.00	2.31	3.27	-	
4.00	1.81	3.02	-	

Table 4.3 Conversion of DBT to DBTO₂



Figure 4.28 Effect of metal loading and calcination temperature on Conversion of DBT to DBTO₂

From Figure 4.28, 0.5Mg400 gives the best performance by converting 45.7% of DBT to DBTO₂. Therefore, from the results above, 0.1Mg400, 0.2Mg400 and 0.25Mg400 were further prepared to determine if lower percentage of magnesium doped on titanium dioxide will give better performance. Figure 4.29 shows the performance of lower percentage of magnesium doped on titanium dioxide.



Figure 4.29 Effect of Magnesium loading calcined at 400° C on conversion of DBT to DBTO₂

From Figure 4.29, it shows that doping at lower amount of magnesium onto titanium dioxide gave better performance of conversion from DBT to DBTO₂. The best performing catalyst was 0.25Mg 400.

0.25wt% Magnesium doped on titania was then experimented at different calcination temperature (300°C, 500°C).

Table 4.4 Effect of calcination temperature on the performance of DBT to DBTO₂ conversion



Figure 4.30 Effect of calcination temperature of the performance of 0.25 wt% Mg/TiO₂

Although calcination at 500°C will give a better performance, but it only outperform the 0.25Mg 400 by 0.11%, thus, 400°C is preferable as it is more energy saving and green as it is calcined at 400° C instead of 500° C.

It can be observed that higher photocatalytic rate behavior may be displayed by photocatalysis calcined at 400°C. This temperature exhibit well crystallized anatase structure with higher surface area for desulfurization.

	Conversion (%)							
	Reaction time							
Sample	0.25hr	0.5 hr	1 hr	2 hr	3 hr	4 hr	5 hr	6 hr
0.25Mg400+MO	9.45	18.95	37.9	62.0	75.4	88.7	98.5	98.5
0.25Mg400+H ₂ O ₂ +MO	2.99	4.1	4.2	4.2	4.2	4.4	5.2	5.2
MO	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
MO+H ₂ O ₂	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2

Table 4.5 Photocatalytic efficiency conversion of DBT to DBTO₂ using 0.25wt% Mg-TiO₂ calcined at 400°C with and without hydrogen peroxide for every subsequent hour



Figure 4.31 Comparison of photocatalytic efficiency of 0.25wt% Mg/TiO₂ with and without hydrogen peroxide during desulfuriztion

By observing the results above, the presence of hydrogen peroxide has decrease the efficiency of sulfur removal. The reason of adding hydrogen peroxide is to provide oxygen fot the conversion of DBT to $DBTO_2$ with the presence of 0.25 wt% Mg/TiO₂. However, the results shown that the addition of hydrogen peroxide inhibits the photocatalytic activity. This may be due to the hydrogen peroxide may have reacted with the photocatalyst preventing the oxidation of sulfur species.

Catalyst that showed the best performance, 0.25% Mg 400, was used to convert DBT to $DBTO_2$ in the model oil with and without the presence of hydrogen peroxide. The reacted model oil is then filtered and combined with BBIM[DBP] ionic liquid,

BEIM[DEP] ionic liquid and EEIM[DEP] ionic liquid respectively. The reaction could investigate the performance of Mg/TiO₂ photocatalysis and ionic extraction.

We can see that doping of 0.25 wt% of magnesium on titania has increased the efficiency for sulfur removal. While, different calcination temperature has shown different performance of desulfurization. Optimum calcination temperature is 400° C, giving good conversion of DBT to DBTO₂. The addition of metals on TiO₂ semiconductor changes the photocatalysis process by changing the surface properties. The metal enhances the yield of a particular rate for the photocatalytic reaction. With the amount of 0.1wt%, 0.2wt%, 0.25wt%, 0.5 wt%, 1 wt%, 2 wt% and 4 wt% of magnesium, where only small area of the titanium dioxide is covered with magnesium dopant by changing the distribution of electrons. It shows that doping of magnesium on the semiconductor shows better photocatalytic performance of desulfurization. The optimum amount of loading magnesium to give the maximum desulfurization rate of the model oil is 0.25wt%. This amount affected the distribution of electron which suits the property to give optimum desulfurization. Metal doped amount of more than or less than the optimum amount of magnesium loading will actually give lesser efficiency.

The converted sulfur is then extracted by using three types of ionic liquids, namely 1butyl-3-ethyl imidazolium diethylphosphate (BEIM[DEP]), and 1-ethyl-3-ethyl imidazolium diethylphosphate (EEIM[DEP]). Below shows the results of extraction using ionic liquid.

Ionic Liquid/Time	0.25hr	0.50hr	0.75 hr	1 hr	2 hr	3 hr	4 hr
BBIM[DBP]	97.09	97.18	97.22	97.22	97.16	97.23	97.22
BEIM[DBP]	97.03	97.64	97.72	97.75	97.74	97.72	97.71
EEIM[DEP]	97.73	97.81	97.82	97.81	97.82	97.82	97.84

Table 4.6 Extraction of DBTO₂ from model oil using different ionic liquids

Figure 4.31 below shows the extraction efficiency of $DBTO_2$ using the three phosphate based ionic liquids as stated above.



Figure 4.32 Extraction efficiency of DBTO₂ from model oil

BBIM[DBP], BEIM[DEP] AND EEIM[DEP] shows extraction of DBTO₂ of 97.22%, 97.71% and 97.84% respectively.

From the results obtained, we can calculate the amount of sulfur removed from our system:

Original sulfur concentration = 100 ppm

Amount of sulfur converted by photocatalyst= 98.5 % of 100 ppm

Amount extracted by ionic liquid = 97.84% of the converted sulfur

Thus the total amount of sulfur removed:

= 100 ppm x 0.985 x 0.9784

= 96.3724 ppm

The amount remaining = 100 ppm - 96.3724 ppm = 3.6726 ppm

It is within the acceptable limit of less than 10ppm of sulfur.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The experimental results for desulfurization of model oil using Mg-TiO₂ photocatalyst with different percentage of magnesium loading of 0.5 wt%, 1 wt%, 2wt% and 4 wt% with calcination temperature of 300° C and 400° C initially. Magnesium loaded titanium dioxide was prepared using wet impregnation method. The percentage of sulfur converted is around 3% to 5% and the better performance was using 0.5wt% Mg/TiO₂ calcined at 400° C which gives performance of 45.73% conversion of DBT to DBTO₂.

Therefore, to further search for better performing photocatalyst, few more catalyst are synthesized namely, 0.1 wt%, 0.2 wt % and 0.25 wt% magnesium loaded on titania. From the result obtained, the best photocatalyst was 0.25Mg400 which was able to convert 98.45% DBT to DBTO₂. The DBTO₂ produced was then extracted using three types of ionic liquids namely BBIM[DBP], BEIM[DEP] and EEIM[DEP] with extraction efficiency of 97.22%, 97.71% and 97.84%. The best extraction efficiency was 96.3724% sulfur removal.

It takes 1 hour for complete conversion of DBT to DBTO₂. Blank runs such as irradiating the model oil for 6 hours and model oil with hydrogen peroxide for 6 hours shows no conversion or removal of DBT.

The best performing photocatalyst was 0.25Mg400 and ionic liquid, EEIM[DEP] gave the best extraction efficiency of 97.84% after 1 hour. The sulfur remaining in the model oil was 3.6726 ppm fulfilling the EURO 5 requirement.

Through characterization, FESEM and TEM give the morphologies of the dopant particles. Their size range varied between 20 nm - 60 nm. The uniformity of dispersion of magnesium was determined though mapping and results shown that magnesium was evenly dispersed and incorporated onto the TiO_2 structure. The more the weight percent of magnesium doped on titania, the bigger its size according to FESEM and TEM.

XRD could not detect the presence of magnesium and the reason was due to magnesium concentration was below the detection limit since it is evenly dispersed onto the surface to TiO_2 .

FTIR results shown significance presence of O-H bending, O-H stretching and Ti-O functional groups before and after calcination. However, nitrates group was only detected before calcination and was not detected after calcination. This indicated that nitrate groups are removed after calcination.

5.2 **Recommendations**

Study more in preparation method of Mg/TiO_2 and preparation of titanium dioxide instead of using P25. Titanium dioxide prepared using sol-gel method and other method may give smaller particle size and thus better performance.

Use magnesium loading of smaller weight percentage gap to be doped onto titanium dioxide to find if it gives better performance of sulfur conversion.

REFERENCES

Abdel-Wahab, Aboel-Magd A., & Gaber, Abd El-Aal M. (1998). TiO₂-photocatalytic oxidation of selected heterocyclic sulfur compounds. *Journal of Photochemistry and Photobiology A: Chemistry*, 114(3), 213-218.

Agency, Environmental Protection. (2013). Efforts to limit sulfur.

- Avasarala, B. K., Tirukkovalluri, S. R., & Bojja, S. (2011). Photocatalytic degradation of monocrotophos pesticide—An endocrine disruptor by magnesium doped titania. *Journal of Hazardous Materials*, 186(2–3), 1234-1240.
- Behnajady, M., Modirshahla, N., Shokri, M., & Rad, B. (2008). Enhancement of Photocatalytic Activity of TiO2 Nanoparticles by Slver Doping: Photodeposition versus Liquid Impregnation Methods. *Global Nest Journal*, 10(1), 1-7.
- Bessekhouad, Y., Robert, D., & Weber, J. V. (2003). Preparation of TiO2 nanoparticles by Sol-Gel route. *International Journal of Photoenergy*, *5*(3), 153-158.

Chemguide. (2013). Thermal Stability of the Group 2 Carbonates and Nitrates.

- Chen, J., Yao, M., & Wang, X. (2008). Investigation of transition metal ion doping behaviors on TiO2 nanoparticles. *Journal of Nanoparticle Research*, 10(1), 163-171.
- Choi, J., Park, H., & Hoffman, M. (2009). Combinatorial Doping of TiO2 with Platinum (Pt), Chromium (Cr), Vanadium (V), and Nickel (Ni) to Achieve Enhanced Photocatalytic Activity with Visible Light Irradiation. *Journal of Materials Research*, 57-88.
- Christian, G. D. (2004). Chemical Analysis (6 ed.): Wiley.
- Earle, M. J., & Seddon, K. R. (2000). Ionic Liquids. Green Solvents for the Future. *IUPAC Pure Applied Chemistry*, 72, 1391-1398.
- Emissions Standards-Cars and Light Trucks. (2012). Retrieved 20 February, 2013, from <u>http://www.dieselnet.com/standards/eu/ld.php</u>
- Fassier, M., Peyratout, C. S., Smith, D. S., Ducroquetz, C., & Voland, T. (2010). Photocatalytic activity of titanium dioxide coatings: Influence of the firing temperature of the chemical gel. *Journal of the European Ceramic Society*, 30(13), 2757-2762.

- Feng, H., Yu, L. E., & Zhang, M. (2013). Ultrasonic synthesis and photocatalytic performance of metal-ions doped TiO₂ catalysts under solar light irradiation. *Materials Research Bulletin*, 48(2), 672-681.
- Fromm, James Richard. (2012). Introduction to Sulfur Functional Groups. 2013, from http://www.3rd1000.com/chem301/chem301x.htm
- Fujishima, Akira, Rao, Tata N., & Tryk, Donald A. (2000). Titanium dioxide photocatalysis. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 1(1), 1-21.
- Han, Dandan, & Row, Kyung Ho. (2010). Recent Applications of Ionic Liquids in Separation Technology. *Molecules*, 15, 2405-2426.
- Hwang, K.J., Yoo, S.J., Jung, S.H., Park, D.W., Kim, S.I., & Lee, J.W. (2009). Synthesize and Characterization of Nanostructured Titania Films for Dye-Sensitized Solar Cells. *Bulletin Korean Chemistry Society*, 30(1), 172-176.
- Ionic Liquid Applications: Offering Outstanding Advantages.). Retrieved February 20, 2013, from http://www.intermediates.basf.com/chemicals/web/en/content/products-andindustries/ionic-liquids/applications
- Jiang, Y., Zhu, W., Li, H., Yin, S., Liu, H., & Xie, Q. (2011). Oxidative Desulfurization of Fuels Catalyzed by Fenton-Like Ionic Liquids at Room Temperature. *ChemSusChem*, 4(3), 399-403. doi: 10.1002/cssc.201000251
- Li, F. B., & Li, X. Z. (2002). The enhancement of photodegradation efficiency using Pt– TiO2 catalyst. *Chemosphere*, 48(10), 1103-1111.
- Mohd Zaid, Hayyiratul Fatimah. (2012). Desulfurization of Crude Oil Using Imidazolium-based-Phosphate Ionic Liquid. *MSc Thesis, University Teknologi PETRONAS*.
- Mul, G., & Moulijin, J. A. Preparation of Supported Metal Catalyst.
- Occupational Health Guidelines for Sulphur Dioxide. http://www.cdc.gov/niosh/docs/81-123/pdfs/0575.pdf
- Peng, S., Li, Y., Jiang, F., Lu, G., & Li, S. (2004). Effect of Be2+ doping TiO2 on its photocatalytic activity. *Chemical Physics Letters*, 398(1–3), 235-239.

- Riaz, Nadia, Chong, F.K., Ela, N., & Khan, M. Saqib. (2011). Effect of photocatalyst preparation methods and light source on Orange II Photacatalytic Degradation. 2nd International Conference on Environmental Science and Technology IPCBEE, 6, 112-117.
- Wilhelm, J. (2003). Titanium Dioxide: Vincentz Network.
- Wu, J.S., Lo, S.H., Song, K., Vijayan, B.K., Li, W.Y., Gray, K.A., & Dravid, V.P. (2011). Growth of rutile nanorods on anatse TiO₂ thin films on Si-based substrates. *Journal of Material Res.*, 26(13), 1646-1652.
- Zhang, G., Yu, F., & Wang, R. (2009). Research Advances in Oxidative Desulphurization Technologies for the Production of Low Sulfur Fuel Oils. *Petroleum & Coal*, 51(3), 197-207.
- Zhang, J., Zhu, W., Li, H., Jiang, W., Jiang, Y., Huang, W., & Yan, Y. (2009). Deep oxidative desulfurization of fuels by Fenton-like reagent in ionic liquids. *Green Chemistry*, 11(11), 1801-1807.

APPENDICES

Appendix A

Chemicals	Molar Mass
Magnesium Nitrate, Mg(NO ₃) ₂ .6H ₂ O	256.45g/mol
Magnesium, Mg	24.31g/mol
Titanium Dioxide, TiO ₂	79.87g/mol

Sample calculation for 1wt% Mg doping on TiO₂

For 1wt%,

1g of Mg metal is needed for 100g of Mg/TiO₂

Thus,

0.05g of Mg metal is needed for 5g of Mg/TiO₂

Using gravimetry calculation,

 $Mass of Mg(NO_3)_2. H_2O = 0.05g Mg \times \frac{\frac{256.41 \frac{gMg(NO_3)_2.6H_2O}{molMg(NO_3)_2.6H_2O}}{24.31 \frac{g Mg}{mol Mg}} \times \frac{1mol Mg(NO_3)_{2.}6H_2O}{1 mol Mg}$

Mass of $Mg(NO_3)_2$. $H_2O = 0.5275g$

Mass of $TiO_2 = 5 g - 0.05 g = 4.95 g$

Similar calculations for 2 wt%, 4 wt%, 6 wt%, 8 wt% and 10 wt% metal doping of TiO₂.

Chemicals	Molar Mass		
Magnesium (II) Chloride, MgCl ₂ .6H ₂ O	203.31g/mol		
Magnesium, Mg	24.31g/mol		
Titanium Dioxide, TiO ₂	79.87g/mol		

Sample calculation for 1wt% Mg doping on TiO₂

For 1wt%,

1g of Mg metal is needed for 100g of Mg/TiO₂

Thus,

0.05g of Mg metal is needed for 5g of Mg/TiO₂

Using gravimetry calculation,

 $Mass of MgCl_2. H_2O = 0.05g Mg \times \frac{\frac{203.33 \frac{gMgCl_2.6H_2O}{molMgCl_2.6H_2O}}{24.31 \frac{gMg}{molMg}} \times \frac{1mol MgCl_{2.6H_2O}}{1 mol Mg}$

Mass of $MgCl_2$. $H_2O = 0.4182g$

Mass of $TiO_2 = 5 g - 0.05 g = 4.95 g$

Similar calculations for 2 wt%, 4 wt%, 6 wt%, 8 wt% and 10 wt% metal doping of TiO₂.

Appendix B

Preparation of 100ppm dibenzothiophene in dodecane

Molecular formula of dibenzothiophene = $C_{12}H_8S$

Molar mass of dibenzothiophene = 184.26g/mol

184.26mg/mmol Dibenzothiophene (DBT) contains 32 mg/mmol Sulfur

$$32 mg sulfur \equiv 184.26 mg DBT$$

$$25 mg S \equiv \frac{25}{32} \times 184.26 mg DBT$$

Amount of DBT = 143.953 mg

Amount of DBT needed for 98% purity = 143.953mg/0.98

Amount of DBT needed for 98% purity = 146.89mg = 0.14689g

Preparation of standard solution needed for calibration curve 50 ml of 10 ppm DBT M₁V₁=M₂V₂ (100 ppm) V₁ = (10 ppm)(50 ml) V₁=5 ml Similar calculation used for 20 ppm, 40 ppm, 60 ppm and 80 ppm.

Appendix C

Calculation for the amount of hydrogen peroxide needed

$$n_{DBT} = \frac{mass of DBT}{Molar Mass of DBT}$$

$$n_{DBT} = \frac{(\frac{100mg}{L})(0.05L)}{32mg/mmol}$$

$$n_{DBT} = 0.15625mol$$

$$\frac{n_{H_{2}O_2}}{n_{DBT}} = 4$$

$$n_{H_{2}O_2} = 4 \times 0.15625mmol$$

$$n_{H_{2}O_2} = 0.625mmol$$
Mass of $H_2O_2 = 0.625mmol \times 34.01mg/mmol$

Mass of $H_2O_2 = 21.26mg$

Volume of
$$H_2O_2 = \frac{0.02126g}{1.11g/ml} = 0.0191ml$$

By using 30% H₂O₂,

$$30\% H_2 O_2 = 0.064 m l$$

Appendix D

FTIR analysis results



FIGURE D2 FTIR analysis for 0.25Mg400



FIGURE D4 FTIR analysis for 0.5Mg400



FIGURE D5 FTIR analysis 0.25Mg uncalcined

Appendix E









FIGURE E2 X-ray Diffraction of 0.2Mg400





FIGURE E4 X-ray Diffraction of 1Mg400


FIGURE E6 X-ray Diffraction of 2Mg400



FIGURE E8 X-ray Diffraction of 1Mg300



FIGURE E10 X-ray Diffraction of 4Mg300