PHOTO-REDUCTION OF CARBON DIOXIDE USING ZnS SUPPORTED KAOLIN IN A PHOTO-CATALYTIC BATCH REACTOR SYSTEM

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SUPERVISOR DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this has fulfilled the quality and requirement for the award of Bachelor's degree in Chemical Engineering (Gas Technology).

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Date : 11th January 2013

STUDENT DECLARATION

I hereby declare that this thesis entitled *"Photo-Reduction of Carbon Dioxide using ZnS Supported Kaolin in a Photo-Catalytic Batch Reactor System"* is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted for award of another degree.

Signature :

Name : TENGKU MOHD NURUL NAIM BIN TENGKU JAAPAR

Date : 11th January 2013

Dedicated especially to my beloved parents, siblings, lecturers and friends who give me inspiration and support that made this work possible.

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PHOTO-REDUCTION OF CARBON DIOXIDE (CO_2) USING ZnS SUPPORTED KAOLIN IN A PHOTO-CATALYTIC BATCH REACTOR SYSTEM

ABSTRACT

Carbon dioxide (CO_2) accounts for the largest share of the world's greenhouse gas emissions. There is a growing need to mitigate CO_2 emissions. Some of the strategies to mitigate CO_2 emissions are energy conservation, carbon capture and storage and using CO_2 as a raw material in chemical processes. One of the best routes to remedy CO_2 is reduce the concentration of CO_2 is transforming-it to biofuels via photo reduction process. In this study, CO_2 is photocatalytically reduced to produce methanol using ZnS supported kaolin in a photo-catalytic batch reactor assisted by UV lamp. The potential application of photocatalysis is to remove or mitigate a wide range of global warming contributors from the atmosphere. By harnessing UV light, photocatalytic process consumes less energy than conventional methods. The synthesis of heterogeneous catalyst from low cost materials was studied in order to produce valuable product which is methanol. The paramaters that affect the reaction such as effect of dosage and reaction time was studied. From this study, the methanol yield will be increased when there is an increasing of the dosage of catalyst used. The yields of product was analysed by using High Performance Liquid Chromatography (HPLC). In this study, it have been prove that the higher amount of dosage catalyst used may give high methanol yield. The 2.0 g ZnS-Kaolin catalyst that used in the photo-reduction process have produced the highest of methanol yield which is 70.5 ng/µL.

PENGURANGAN FOTO KARBON DIOKSIDA (CO_2) MENGGUNAKAN ZnS DISOKONG OLEH KAOLIN DALAM SEBUAH SISTEM REAKTOR FOTOPEMANGKINAN

ABSTRAK

Karbon dioksida (CO_2) merupakan penyumbang terbesar pelepasan gas rumah hijau di dunia. Terdapat beberapa strategi yang boleh dilakukan bagi mengurangkan pelepasan CO_2. Sebahagian daripada strategi untuk mengurangkan pelepasan CO_2 adalah pemuliharaan tenaga, pengumpulan karbon dan penyimpanan dan menggunakan CO_2 sebagai bahan mentah dalam proses kimia. Salah satu strategi terbaik untuk memulihkan CO_2 adalah mengurangkan kepekatan CO_2 dengan mengubah ia kepada biofuel melalui proses pengurangan foto. Dalam kajian ini, CO_2 dikurangkan untuk menghasilkan methanol menggunakan ZnS disokong oleh kaolin dalam reactor foto-pemangkin dan dibantu oleh lampu UV. Penggunaan strategi ini dapat meningkatkan potensi fotopemangkinan untuk menghapuskan atau mengurangkan kepada penyumbang pemanasan global dari atmosfera. Dengan pemanfaatan cahaya UV, proses foto pemangkinan hanya menggunakan tenaga kurang daripada kaedah konvensional. Sintesis mangkin heterogen daripada bahan kos rendah telah dikaji untuk menghasilkan produk yang berharga iaitu metanol. Paramaters yang mempengaruhi tindak balas seperti kesan dos dan masa reaksi telah dikaji. Daripada kajian ini, hasil methanol akan meningkat apabila terdapat peningkatan dos pemangkin yang digunakan. Hasil produk akan dianalisis dengan menggunakan Kromatografi Cecair Prestasi Tinggi (HPLC). Dalam kajian ini, ia telah membuktikan bahawa jumlah yang lebih tinggi dos mangkin yang digunakan boleh memberikan hasil methanol tinggi. 2.0 g ZnS-Kaolin pemangkin yang digunakan dalam proses fotopengurangan telah menghasilkan metanol tertinggi yang merupakan 70,5ng / uL.

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LIST OF SYMBOLS

^{o}C	Degree celcius
Wm^{-2}	Watt per metre square
%	Percent
g	Gram
µm	Micro metre
h	Hour
MPa	Mega pascal
ng/µL	Nano gram per micro liter

LIST OF ABBREVIATIONS

CO_2	Carbon Dioxide
C2ES	Center for Climate and Energy Solutions
HPLC	High Performance Liquid Chromatography
HTAC	Hexadecyltrimethylammonium Chloride
MeOH	Methanol
MI	Methanol Institute
MIT	Massachusetts Institute of Technology
UV	Ultraviolet

CHAPTER ONE

INTRODUCTION

1.1 Overview

At present, carbon dioxide (CO_2) is the largest contributor among greenhouse gases. According to current levels, the concentration of CO_2 in the atmosphere is quite high relative to last 10 years. Due to the fossil fuel used in industry and transportation, manufacture of cement, building air conditioning and deforestation. According to Ritchter and Caillol, (2011), with a global radiative forcing of 1.74 Wm^{-2}, CO_2 is the largest contributor among well-mixed long-lived greenhouse gases, accounting for more than 63 % of the total. Therefore, this will affect to the global warming in our environment and also may give lots of bad impacts to the human being especially children, the elderly, and communities living in poverty are among the most vulnerable. This population group will be easily affected by this climate change and may cause death due to the rising of the temperature in everyday life. Other than that, the human also easily to be affected by the cataract, asthma symptoms, fever and many more (Ritchter and Caillol, 2011).

Based on the data from Center for Climate and Energy Solutions (C2ES), industry is one of the largest contributors of CO_2 emissions in the atmosphere. Therefore, due to this problem, in order to reduce the concentration of CO_2in the environment, this will be one alternative to the industry to utilize the waste (CO_2) or by-product by converting CO_2 to valuable product such as hydroxyl group or alkanes. Currentlymany technologies are available for the capture of CO_2 from flue gas removed by the industry. Such technologies include gas absorption into chemical solvents, permeation through membranes, cryogenic distillation, and gas adsorption onto a solid sorbent etc.

Based on the awareness of these issues, this study was focused to overcome this problem by converting CO_2 as a waste by product to beneficial products. However, photo-catalytic reduction process by using catalyst assisted by UV light is the most promising technologies compared to other conventional methods.In order to investigate the generation of methanol, kaolin, ZnS/kaolin and ZnS-HTAC/kaolin prepared catalysts were used in photo-reduction process assisted by UV light. Effect of catalyst dosage also was studied in range of 0.50 to 2.0 g in photo-catalytic batch reactor system.

1.2 Problem Statement

Due to increasing of concentration of CO_2 in environment nowadays, this study will be proposed to overcome this problem. Photo-catalytic process will be introduced using heterogeneous catalyst assist by UV light to convert CO_2 as a waste product to valuable product and also helpsfor the environment awareness actions.

Photocatalytic reduction of CO_2 by UV light involves photocatalyst and UV radiation. Reduction process of CO_2 is difficult since it is inert and stable compound. Conventional process requires high pressure and high temperature. Hence, photocatalytic process by using photocatalyst is the most promising method because the reduction process can be proceeds at room temperature and atmospheric pressure. Possible reduction products including CO, HCOOH, HCHO, CH_3OH or CH_4 have been obtained by photo-reduction of CO_2 or aqueous carbonate.

1.3 Research Objectives

Based on the overview and problem statement described in the previous section, the following are the objectives of this research:

- To synthesis the heterogeneous catalyst by hydrothermal method.
- To study the ability the performance of catalysts prepared.
- To study the effect of catalyst dosage in photo-reduction process.

1.4 Scope of Research

In this study, the catalysts were prepared using hydrothermal method. Two types of catalyst that are ZnS and ZnS-Kaolin were used to investigate their performance in photo reduction process. The photo-reduction process was run using prepared heterogeneous catalyst assisted by UV lamps in a batch reactor system. A part from that, one of the parameters that affect the photo-reduction process is dosage of catalyst was studied in range of 0.5-2.0 g to get the highest yield of product (methanol).While running the experiment of effect of dosage, other parameters such as temperature and volume of the solvent was maintained at room temperature and 500 mL of NaOH solution. Methanol as a main product was analysed using high performance liquid chromatography (HPLC).

1.5 Organization of Thesis

This report contains five main chapters to distribute the whole report accordingly. In the first chapter, explained the introduction which gave the briefing about the project. The second chapter contains literature review based on properties of CO2, methanol and its applications, photo-reduction process and the properties of catalysts. The third chapter explained the methodologies of the experiment and fourth chapter contained results and discussions. Finally, fifth chapter contains with conclusions and recommendations.

CHAPTER TWO

LITERATURE REVIEW

2.1 Carbon dioxide (CO_2)

It has become common knowledge that CO_2 is the chief greenhouse gas and the leading cause of global warming. Excessive CO_2in the atmosphere traps heat inside the planet, directly influencing climate change. CO_2 is released into our atmosphere when carbon-containing fossil fuels such as oil, natural gas and coal are burned in air.As a result of the tremendous world-wide consumption of such fossil fuels, the amount of CO_2 in the atmosphere has increased over the past century, now rising at a rate of about 1 ppm per year (Shakhashiri, 2008).

CO_2 gas is formed from the combination of two elements of carbon and oxygen. The CO_2 molecule (O=C=O) contains two double bonds and gas a linear shape. It has no electrical dipole, and as it is fully oxidized, it is moderately reactive and is non-flammable. Moreover CO_2 is very stable, linear molecule in which the oxygen atoms are weak Lewis bases and the carbon is electrophilic. Reactions of

CO_2 are dominated by nucleophlic attacks at the carbon, which are result in bending of the O-C-O bond (Maria Jitaru, 2007).

Increasing emissions levels from combustion fossil fuels in stationary and mobile energy systems, as well as emissions from various industrial processes, have raised many environmental and health concerns in recent years. These emissions into the atmosphere include pollutants such as NO_2, SO_2, particulate matter and greenhouse gases such as methane (CH_4) and CO_2. Besides that, based on the data from Center for Climate and Energy Solutions (C2ES), the largest contributor of CO_2 emitted in the World is electricity followed by transportation and industry. **Figure 2.1** shows the percentage of CO_2emissionsfrom the various sectors

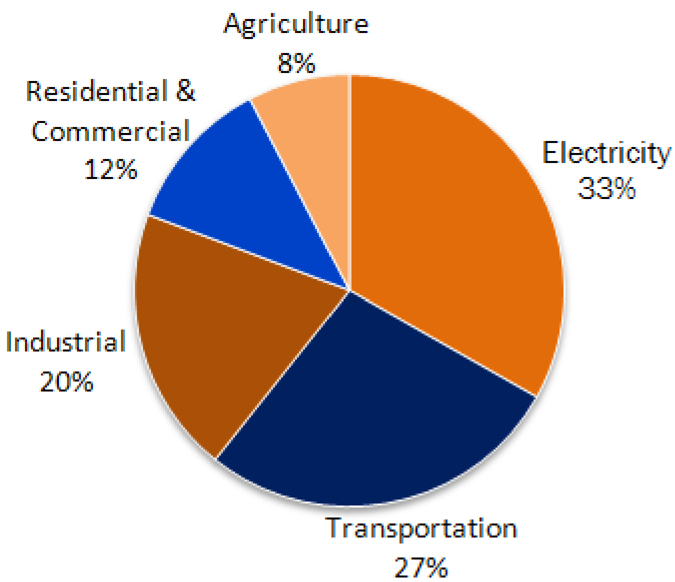


Figure 2.1: Percentage of the CO_2 emission of the various sectors (Climate Text Book, 2011)

Based on **Figure 2.1**, we can see that the industry belongs among the contributors of CO_2 emission in our environment, therefore based on the social responsibility towards the local community life, they need to take drastic measure to ensure that the emission of CO_2 can be reduced as much as possible. So, from this study the industry can demonstrate that they are also taking a serious action to the awareness of the environmental ecosystem stabilization.

2.2 Methanol (CH_3OH)

Methanol is a clean burning fuel that is derived from diverse conventional and renewable energy sources. Also known as methyl alcohol or 'wood alcohol', it is an essential building block for thousands of chemical components used every day in industrial applications and in our homes. Methanol is a versatile, clear, biodegradable liquid produced from a variety of sources which abound in the U.S. including conventional energy sources like coal and natural gas as well as innovative renewable sources like municipal waste, landfill gas, agricultural and timber waste, and even from CO_2 from industrial or power plant emissions and the atmosphere (Methanol Institute (MI), 2007).

An interdisciplinary report by the Massachusetts Institute of Technology (MIT), (2010), entitled "The Future of Natural Gas" states that methanol is the best use of natural gas in transportation technology and is the liquid fuel that is most efficient and inexpensively produced from natural gas. Adding methanol to gasoline drastically reduces the emissions of toxins such as benzene, hexane and xylene.

Vehicles powered by methanol engines can reduce greenhouse gas emissions by 25 to 35 percent compared to traditional gasoline and emissions are also less reactive, reducing urban ozone, a major component of smog.

Methanol, also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits, is a chemical with formula CH_3OH (often abbreviated MeOH). It is the simplest alcohol, and is a light, volatile, colorless, flammable, and liquid with a distinctive odor that is very similar to but slightly sweeter than ethanol (drinking alcohol). At room temperature it is a polar liquid (Nichol, Rand and Williams, 1999)

Methanol is produced naturally in the anaerobic metabolism of many varieties of bacteria, and is ubiquitous in the environment. As a result, there is a small fraction of methanol vapor in the atmosphere. Over the course of several days, atmospheric methanol is oxidized with the help of sunlight to carbon dioxide and water.

Methanol burns in air forming carbon dioxide and water (eq. (2.1)):

$$2\ CH_3OH + 3\ O_2 \rightarrow 2\ CO_2 + 4\ H_2O \qquad (2.1)$$

A methanol flame is almost colorless in bright sunlight.

Methanol is often called wood alcohol because it was once produced chiefly as a by-product of the destructive distillation of wood. Most methanol today is produced from the methane found in natural gas, but methanol is also produced for all types of biomass, coal, waste, and even CO_2 pollution from power plants.

Methanol is a naturally occurring, biodegradable alcohol that is present in our environment and can even be found out in space. Methanol occurs naturally during the decomposition of different plant and animal life, and we come into contact with it every day in fruits, juices, and even wine. Though larger quantities of methanol can be toxic if ingested, this naturally occurring molecule has a very low impact when released into the environment because of how quickly it biodegrades (McNicol, Rand and Williams, 1999).

2.2.1 Application of methanol

Methanol is one of the most versatile compounds developed and is the basis for hundreds of chemicals, thousands of products that touch our daily lives, and is second in the world in amount shipped and transported around the globe every year. A truly global commodity, methanol is a key component of modern life and new applications are paving the way forward to innovation. According to the source from the Methanol Institute (MI), there are a few applications of methanol which are as transportation fuel, wastewater denitrification, fuel cell hydrogen carrier, biodiesel trans-esterification and also for electricity generation.

Methanol is the most basic alcohol. It is easy to transport, readily available, and has a high octane rating that allows for superior vehicle performance compared to gasoline. Many countries have adopted or are seeking to expand methanol fuelling programs, and it is the fastest growing segment of the methanol marketplace today. This is driven in large part by methanol's low price compared to gasoline or ethanol, and the very small incremental cost to modify current vehicles to run on blends of methanol fuel. Methanol also produces much less toxic emissions than reformulated gasoline, with less particulate matter and smog forming emissions (McNicol, Rand and Williams, 1999).

Methanol is also used by municipal and private wastewater treatment facilities to aid in the removal of nitrogen from effluent streams. As wastewater is collected in a treatment facility, it contains high levels of ammonia. Through a bacterial degradation process this ammonia is converted into nitrate. If discharged into the environment, the nutrient rich nitrate in sewage effluent can have a devastating effect on water ecosystems - creating miles long algae blooms that sap oxygen and sunlight from aquatic life (Kim et. al., 2007).

Methanol is used as a key component in the development of different types of fuel cells - which are quickly expanding to play a larger role in our energy economy. From large-scale fuel cells to power vehicles or provide back-up power to remote equipment, to portable fuel cells for electronics and personal use, methanol is an ideal hydrogen carrier. With a chemical formula of CH_3OH, have more hydrogen atoms in each gallon than any other liquid that is stable in normal conditions (Wang, 1999).

Different companies are also exploring the use of methanol to drive turbines to create electricity. There are a number of projects currently underway that are using methanol as the fuel source to create steam to drive turbines - which is an excellent option for areas rich in resources other than traditional electricity sources (Kim et. al., 2007).

2.3 Photo-Catalytic Reduction Process

The study of photo catalytic reactions was initiated in 1970's. The concept and the term "heterogeneous photo catalysis" were introduced and developed in Lyon to describe the partial oxidation of alkanes and olefinic hydrocarbons. The reactions took place at ambient temperature in the presence of titanium dioxide (TiO_2, anatase) under UV irradiation (Rajalakshmi, 2011). In addition, photo-catalytic reaction generally includes the following processes, when photons have higher energy than the semiconductor band gap, they are absorbed and electrons in the valence band promoted to the conduction band, leaving positive holes in the valence band. The excited electron is used to reduce substances, while the positive hole is used to oxidize substances on the surface of the photo-catalyst (Rajalakshmi, 2011).

Figure 2.2 shows the mechanisms of CO_2 reduction. In concert, electron and hole pair (e^{-}–h^{+}) is generated. The following chain reactions have been widely accepted and the reaction was shown in Eqs. (2.2) – (2.7):

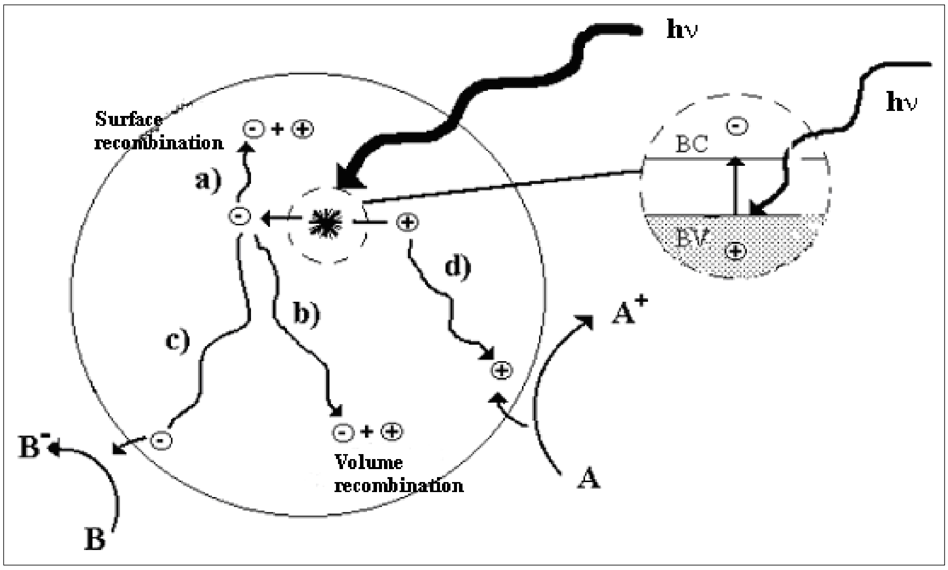


Figure 2.2: Mechanism**s** of CO_2 reduction **(**Shinet. al., 2007)

Photo-excitation:

$TiO_2/SC + h\upsilon \rightarrow e^- + h^+$ (2.2)

Oxygen ionosorption:

$(O_2)\ ads + e^- \rightarrow O_2^{\bullet -}$ (2.3)

Ionization of water:

$H_2O \rightarrow OH^- + H^+$ (2.4)

Protonation of superoxides:

$O_2^{\bullet -} + H^+ \rightarrow HOO^\bullet$ (2.5)

The hydroperoxyl radical formed in Eq. (2.5) has also scavenging properties similar to O_2 thus doubly prolonging the lifetime of photohole:

$$HOO^{\bullet} + e^{-} \rightarrow HO_2^{-} \quad (2.6)$$

$$HOO^{-} + H^{+} \rightarrow H_2O_2 \quad (2.7)$$

Both the oxidation and reduction can take place at the surface of the photoexcited semiconductor photocatalyst. Recombination between electron and hole occurs unless oxygen is available to scavenge the electrons to form superoxides ($O_2^{\bullet}$), its protonated form the hydroperoxyl radical ($HO_2^{\bullet}$) and subsequently H_2O_2.

The photocatalysis reaction is attracting a great deal of attention from the viewpoints of fundamental science and applications. Recently, this type of reaction has been applied to environmental cleaning by utilizing photocatalytic oxidation of organic compounds by semiconductor materials such as TiO_2, ZnO, CdS, and Fe_2O_3.Among the various semiconductor materials, TiO_2 is the most widely used photocatalyst due to its non-toxicity, high activity, large stability, and low cost.The range of organic pollutants that can be completely photo mineralized using TiO_2 is very wide and includes many aromatics, dyes, and pesticides. The photocatalytic activity of titania varies depending on its crystallinity, particle size, crystal phase, surface area, and the method of preparation. It is known that anatase form with small particle size and high crystallinity is required to obtain highly active titania photocatalysts (Funda et. al., 2006).

2.4 Materials Used in Preparation of Catalysts

2.4.1 Zinc Sulphate (ZnS)

In this study, ZnS is used as a heterogeneous catalyst in photo-reduction process of CO_2. This heterogeneous catalyst was prepared by using hydrothermal method. Based on study from Fang et. al., (2011), ZnSwas chosen as a catalyst because it is one of the first semiconductors discovered and it has traditionally shown remarkable fundamental properties versatility. ZnS has a larger bandgap of -3.72 eVand -3.77 eV (for cubic zinc blende (ZB) and hexagonal wurtzite (WZ) ZnS, respectively). In addition, it is also more suitable for visible-blind ultraviolet (UV) light based devices such as sensors or photo-detectors. In fact, ZnS is traditionally the most suitable candidate for electroluminescence devices (Yang et. al., 2003).

Nanostructured materials are a new class of materials, having dimensions in the 1-100 nm range, which provide one of the greatest potentials for improving performance and extended capabilities of products in a number of industrial sectors (Yang et. al., 2003). Nanostructures can be divided into zero-dimensional (0D when they are uniform), one-dimensional (1D when they are elongated), and two-dimensional (2D when they are planar) based on their shapes. The most successful examples are seen in the microelectronics, where ‘‘smaller’’ has always meant a greater performance ever since the invention of transistors such as higher density of integration, faster response, lower cost, and less power consumption (Bando et. al., 2008).

2.4.2 Kaolin

Kaolin is one of the types of clay materials. Clay is a fine-grained material composed largely of a group of crystalline minerals. Clay minerals are hydrous aluminiumphyllosilicates sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths and other cations. Clays have structures similar to the micas and therefore form flat hexagonal sheets. Clay minerals are common weathering products and low temperature hydrothermal alteration products. Clays are ultra-fine grained (normally considered to be less than 2 μm in size on standard particle size classifications) and so require special analytical techniques (Komarneni et. al., 2009).

Kaolin was used as supported catalyst for their long-term stabilization because they tended to agglomeration in the aqueous solution as demonstrate by UV spectra and the advantage is supported catalyst also to always keep their size in the nano-range. These kaolin based catalyst combined the functions of the nanostructures and kaolin together and exhibited synergetic effects (Ogawa et. al., 2001).Kaolin is one of the most common phyllosilicate clay minerals with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral. Successive 1:1 layers are held together by hydrogen bonding of adjacent silica and alumina layers. The tetrahedral sheet carries a small permanent negative charge due to isomorphous substitution of Si^{4+} by Al^{3+}, leaving a single-negative charge for each substitution. Both the octahedral sheet and the crystal edges have a pH-dependent variable charge caused by protonation and deprotonation of surface hydroxyl (SOH) groups. Kaolin has a low shrink–swell capacity and a low cation exchange capacity (1–15 meq/100 g). It is a soft, earthy, usually white mineral (Ogawa et. al., 2001).

Kaolin is used in ceramics, medicine, coated paper, as a food additive, in toothpaste, as a light diffusing material in white incandescent light bulbs, and in cosmetics. It is also used in most paints and inks. Kaolin type clays undergo a series of phase transformations upon thermal treatment in air at atmospheric pressure. **Table 2.1** shows the properties of kaolin:

Table 2.1: Properties of Kaolin (Sposito, 1989).

Properties	Value
Chemical formula	$Al_2Si_2O_5(OH)_4$
Colour	White, sometimes red, blue or brown tints from impurities
Physical state	White to off white powder
Molecular weight (g/mol)	258.16
Transparency	Crystal are translucent
Specific gravity	2.6

2.4.3 Hexadecyltrimethylammonium Chloride (HTAC)

Hexadecyltrimethylammonium chloride (HTAC) is a quaternary ammonium salt that is widely used in consumer products. This synthetic organic chemical is an active ingredient for hair conditioner, anti-static agents, detergent sanitizer, and performs as a disinfection agent. It is present in wastewaters and usually biodegraded and adsorbed in wastewater treatment plants, but small amounts will enter natural ecosystems. Generally, the HTAC can be used as emulsifier, sterilizer, antistatic and antiseptic agent. Therefore, in the photocatalytic reduction process, HTAC is used as a stabilizer to the reaction that will be occurred during the generation of the methanol. So, in this study HTAC was used in order to get a stable reaction and the yield of methanol (Shieder, et. al., 1994).

2.4.4 Zinc Acetate, $Zn(O_2CCH_3)_2$

Zinc acetate is the chemical compound with the formula$Zn(O_2CCH_3)_2$, which commonly occurs as a dihydrate $Zn(O_2CCH_3)_2(H_2O)_2$. **Figure 2.3** show structure of zinc acetate and **Table 2.2** shows the properties of zinc acetate. Both the hydrate and the anhydrous forms are colorless solids that are commonly used in chemical synthesis.

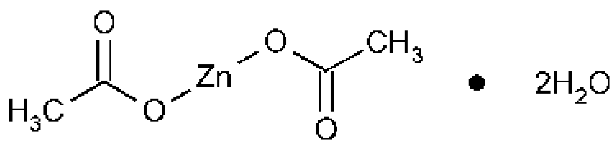


Figure 2.3: Structures of Zinc Acetate(Sposito, 1989).

Table 2.2: Properties of Zinc Acetate (Sposito, 1989).

Properties	Value
Molecular formula	$Zn(O_2CCH_3)_2$
Molecular weight (g/mol)	183.48
Physical state	White solid

2.4.5 Zinc Nitrate Hexahydrate, $Zn(NO_3)_2 6H_2O$

Zinc Nitrate Hexahydrate is a white tetragonal crystal with melting point 36.5^oC, losing all water moles at 105^oC to form anhydrous one. It is soluble in alcohol and water. It is used in the field of electro-galvanizing, agriculture, rubber industry, water treatment industry, explosives and catalysts. **Table 2.3** was shown the properties of zinc nitrate hexahydrate.

Table 2.3: Properties of Zinc Nitrate Hexahydrate (*Sposito1989).*

Properties	Value
Molecular Formula	$Zn(NO_3)_2.6H_2O$
Molecular weight (g/mol)	189.4
Boiling point (^oC)	1050
Melting point (^oC)	360
Physical state	Colourless or white crystal or flakes, slight nitric acid odor

2.4.6 Sodium Sulfide, Na_2S

Sodium sulfide is the name used to refer to the chemical compoundNa_2S, but more commonly it refers to the hydrate $Na_2S{\cdot}9H_2O$. Both are colorless water, soluble salts that give strongly alkaline solutions. The **Table 2.4** was shown the properties of zinc sulfide. Sulfide is too strong base to coexist with water. Thus, the dissolution process can be described in Eqs (2.8) – (2.9) as follows:

$$Na_2S(s) + H_2O(l) \rightarrow 2Na^+(aq) + HS^- + OH^- \qquad (2.8)$$

Sodium sulfide can oxidize when heated to sodium carbonate and sulfur dioxide:

$$Na_2S + 3O_2 + 2\ CO_2 \rightarrow 2Na_2CO_3 + 2SO_2 \qquad (2.9)$$

Table 2.4: Properties of Zinc Sulfide (Sposito,1989)

Properties	Value
Molecular formula	Na_2S
Molecular weight (g/mol)	78.0452
Density (g/cm^3)	1.856
Melting point (^oC)	1176
Physical state	Colourless, solid state

2.5 Hydrothermal Method

In order to obtain a good photo-catalyst, many structural parameters are important such as particle size, crystalline quality, morphology, specific surface area, surface state, etc. In this study,hydrothermalmethod was chosen to synthesize the ZnS-kaolin based on characterization results from the previous study (Hafiza, 2012).

The hydrothermal method with an aqueous solvent as reaction medium is environmentally friendly since the reaction are carried out in a closed system and the contents can be recovered and reused after cooling down to room temperature and pressure. It is important to note that hydrothermally obtained powders are produced with different microstructure, morphology and phase composition by varying parameters such as temperature, pressure, duration of process, the concentration of chemical species, solution concentration and pH (Kolen'ko et. al., 2004).

The hydrothermal process including aqueous solvents as reaction medium is eco-friendly since it is carried out in a closed system and the contents can be recovered and reused after cooling down to room temperature. The equipment and processing required are simpler and reaction is low energy consumption. By controlling hydrothermal temperature and duration of the treatment, various crystalline products with different composition, structure and morphology could be obtained. Fine particle size can be obtained with more uniform distribution and high dispersion either in polar and nonpolar solvents (Shigeyuki and Rustum, 2000).

Possible advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapor pressure near their melting points can also be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good quality crystals while maintaining good control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows (Sayikan et. al., 2007).

Hydrothermal synthesis is a promising method to obtain nanocrystallinetitania particles. The hydrothermal process, in which the chemical reaction could take place under auto-generated pressure uponheating, is efficient to achieve the crystalline phase at relatively low temperatures. The hydrothermal processproceeds with aqueous and/or non-aqueous systems as the reaction medium and is environmentally friendlysince the reactions are carried out in a closed system.

The phase, particle size, and crystallinity can easilybe controlled by hydrothermal conditions (Funda et. al., 2006).

2.6 Study of Dosage of Heterogeneous Catalyst

The catalyst was synthesized by hydrothermal method by using kaolin as a support for the application of photo-reduction of CO_2. The prepared heterogeneous catalyst was used in the photo-reduction process of CO_2 within the range of 0.50 g to 2.0 g. The sample produced was tested using high performance liquid chromatography (HPLC) in order to get the highest percentage yield of CH_3OH produced in this experiment.

Several researchers have investigated the efficiency and selectivity of processes by modifying the photocatalyst surface with metal was show the greatest improvement in the performance of CO_2photoreduction. Because of the metal contacts with the semiconductor surface, the electrons can easily flow from the semiconductor to the metal and distribute on the surface. Additionally, the holes are then free to diffuse to the semiconductor surface where oxidation of organic species can occur (Usubharatana et. al., 2006).

According to the research from Tseng et. al., (2002), the different amount of dosage catalystwas affected to the methanol production in photo-reduction process. This was occurred due to the action of the catalyst which is speeding up the reaction by lowering the activation energy of that reaction. Other than that, obviously, more catalyst loading can increase methanol yield because of the amount of active sites.

CHAPTER THREE

METHODOLOGY

3.1 Materials

For this study, materials thatwere used are zinc acetate ($Zn(O_2CCH_3)_2$), sodium sulfide (Na_2S), zinc nitrate hexahydrate($Zn(NO_3)_2 6H_2O$), kaolin ($Al_2Si_2O_5(OH)_4$), hexadecyltrimethylammoniumchloride (HTAC), carbon dioxide (CO_2) and sodium hydroxide (NaOH).

3.2 Preparation of ZnS-kaolin

3.2.1 Pre-treatment of Kaolin (K)

Kaolin was treated with Na_2S aqueous solution. The mixture then was undergoing successive centrifugation-washing treatment with distilled water.

3.2.2 Preparation of HTAC-K

2 g of kaolin was treated with 100 mLof HTAC aqueous solution and was stirred for 4 hours. Then, the mixture was filtered and washed with distilled water for several times to obtain HTAC-K. The product was dried in vacuum oven at 60^{o}C for 10 hours.

3.2.3 Hydrothermal Method

1.0 g of HTAC-K was dispersed in 10 mL of $Zn(NO_3)_2 \cdot 6H_2O$ aqueous solution and were stirred continuously for 30 minutes. The mixture then was transferred into a 15 mL of high-pressure stainless steel autoclave. The autoclave was sealed and maintained at 120 ^{0}C for 4 hours. Then, the autoclave was cooled to 0 ^{0}C in ice-water. The resulting product was separated via centrifugation and washed for five times with distilled water. The product was dried in vacuum oven (ca. 0.1 MPa) at 60 ^{o}C for 6 hours and calcined at 500 ^{o}C for 1 hour in furnace.

3.3 Photo-reduction Process

During the photo - reduction process of CO_2, the process will be run by using a rig which is consisted of a pressure bottle of CO_2, UV light source and also reactor with magnetic stirrer. The schematic diagram for this process is shown in **Figure 3.1**:

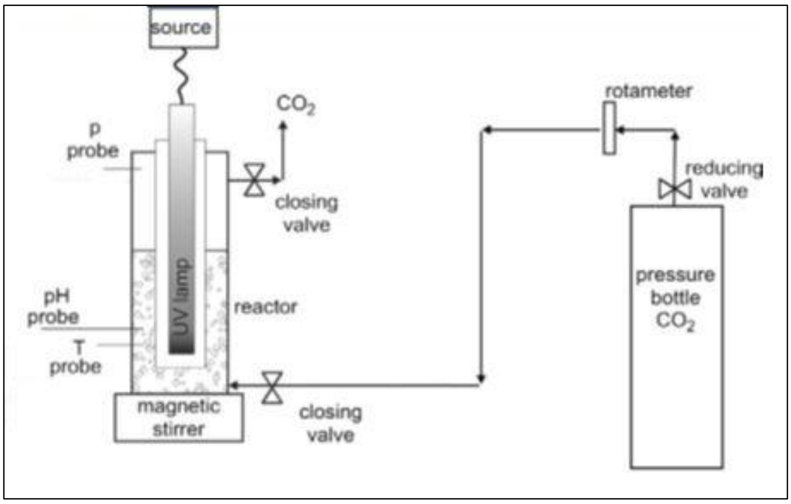


Figure 3.1: Schematic Diagram of an apparatus for the CO_2photocatalytic reduction

Highly purified $CO_2$was flowed through NaOH solution in the reactor. The rig was isolated with a pressure of approximately 1 - 2bars above ambient pressure. After the whole rig is properly set -up, the rig and its contents were allowed to settle for 2 hours before the first sample was withdrawn. The UV light then has been turned ON. The light was allowed to remain ON continuously for 6 hours. The sample products accumulated inside the reactor werewithdrawn for every hour of interval time within six hours of reaction time. The samples were analysed usinghigh performance liquid chromatography (HPLC). These procedures were repeated by using another dosage of heterogeneous catalyst which is1.0, 1.5 and 2.0 g.

3.4 Analysing Samples

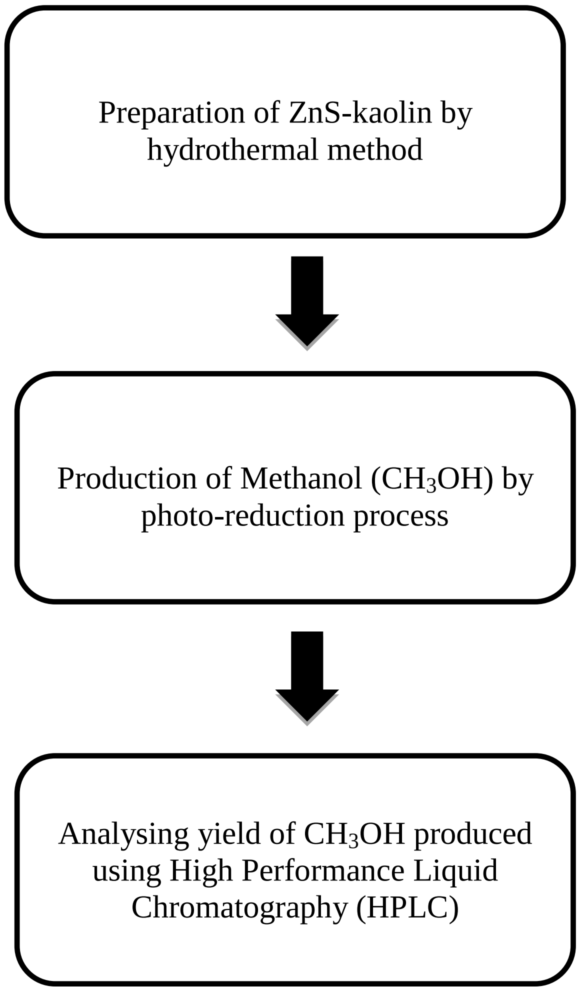
3.4.1 Mobile phase preparation

Mobile phase that used in this analysis is acetonitrile and water. It was prepared by the ratio 400 mL of acetonitrile and 600 mL of water.

3.4.2 Sample measurement

The samples were analyzed by using HPLC analysis. The samples were filtered by using syringe filter into the 2 ml vials. Three data were collected for each vial. Finally, after all the data were collected, the graph was plotted for methanol yield versus time that gets from standard curve.

3.5 Flow diagram of research design



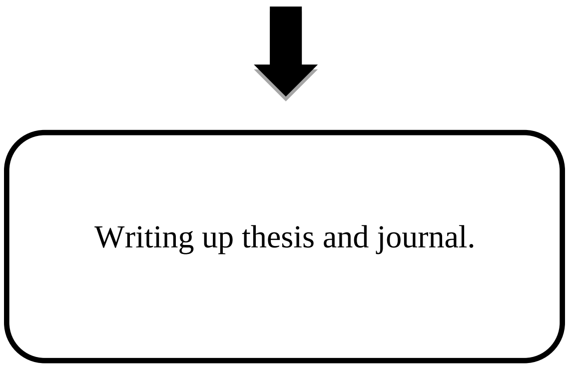


Figure 3.2 Flow diagram of research design

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

In this study,ZnS and ZnS-Kaolin catalyst have been prepared by using the hydrothermal method respectively. The prepared catalysts have been used in photo-reduction process to gain the yield of methanol produced for six hours irridiation. These methanol yields have been analyzed by using HPLC and the results were discussed to investigate the effect of catalysts used for the production of methanol.

4.2 Photo-reduction process using ZnS catalyst

In this study, photo-reduction process has been done by using ZnS catalyst with the different amount of dosage catalyst which is 0.50 g, 1.0 g, 1.5 g and also 2.0 g. This catalyst does not supported by kaolin during the preparation. Therefore, based on the **Figure 4.1**, it shows the result of the methanol yield produced by different amount of dosage catalyst.

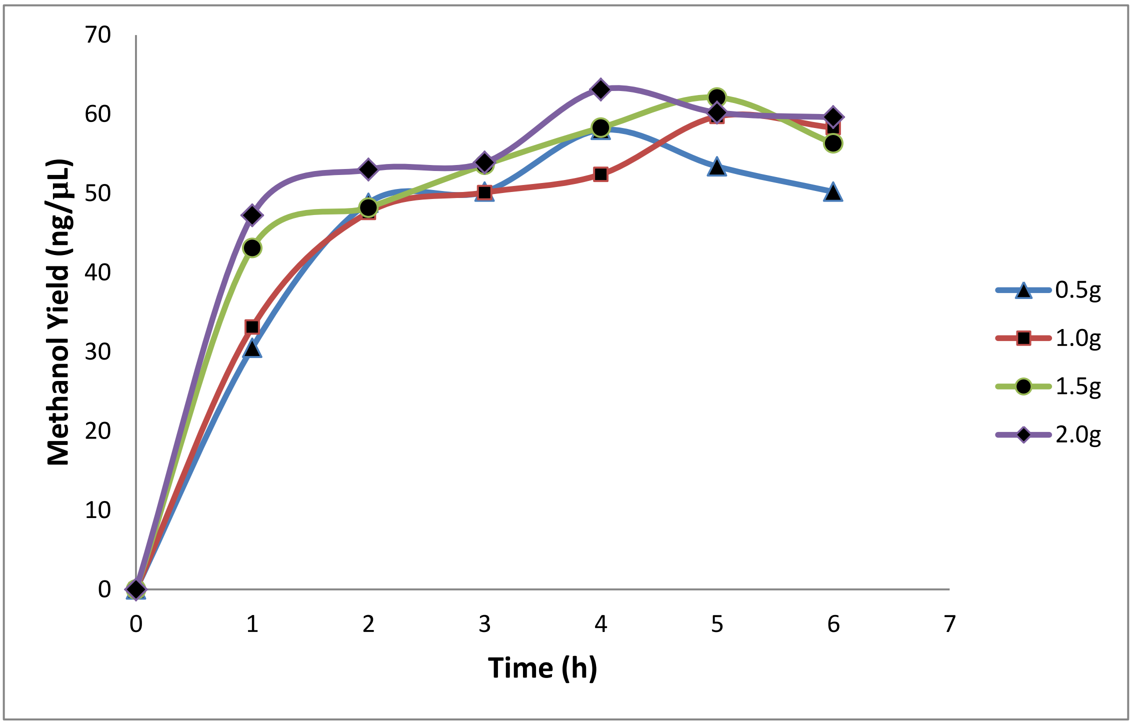


Figure 4.1 Methanol yield from different amounts of ZnS catalyst

From **Figure 4.1**, at initial time of reaction the graph showswhen the higher amount of catalyst is employed then the reaction has higher initial rate. On the other hand when the smallest amount of catalyst is employed the experiments follow the same tendency for both amounts of catalyst, showing that there is not a great improvement in the reaction. So the methanol yield produced is speeding up due to the reaction have been initiated by the catalyst used. This wasoccurred due to the action of the catalyst which is speeding up the reaction by lowering the activation energy of that reaction. Other than that, obviously, more catalyst loading can increase methanol yield because of the amount of active sites (Tseng et. al., 2002).

Besides that, for a higher amount of dosage catalyst used the yield of methanol produced is much higher compared to the low amount of the dosage used. For 2.0 g dosage catalyst used, the maximum methanol yield produced was 63.1 ng/µL followed by 1.5 g dosage catalyst with 62.1 ng/µL yield methanol produced. The lowest amount of dosage catalyst used has been proof that the lowest of yield methanol have been produced. For 0.50 and 1.0 g of catalyst dosage, the yields of methanol produced were 58.0 ng/µL and 59.7 ng/µL respectively.

4.3 Photo-reduction process using ZnS-Kaolin catalyst

In this study, photo-reduction process has been done by using ZnS-Kaolin catalyst with the different amount of catalyst dosage which is 0.50 g, 1.0 g, 1.5 g and also 2.0 g. Kaolin was used as supported catalyst for their long-term stabilization because they tended to agglomeration in the aqueous solution as demonstrate by UV spectra and the advantage is supported catalyst also to always keep their size in the nano-range (Ogawa et. al., 2001). These kaolin based catalyst combined the functions of the nanostructures and kaolin together and exhibited synergistic effects (Ogawa et. al., 2001). Therefore, based on the Figure 4.2, it shows the result of the methanol yield produced by different amount of dosage of catalyst.

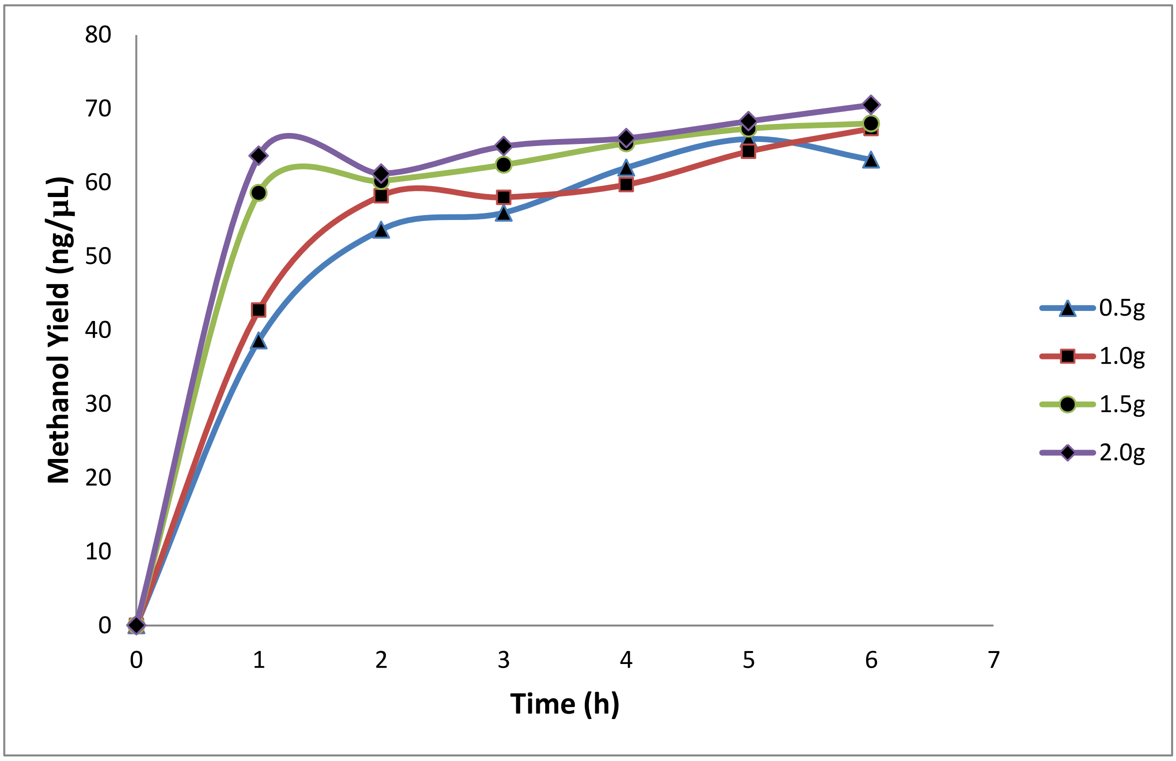


Figure 4.2 Methanol yield from different amounts of ZnS-Kaolin catalyst

From **Figure 4.2**, same as ZnS catalyst, we can see that at initial time of reaction the methanol yield produced are rapidly increasing for each amount of dosage catalyst. This analysis has shown when the highest amount of catalystdosagewas used in the reaction therefore the highest methanol yield has been produced. Since the kaolin was used as supporter to this catalyst, it indicates that ceramic materials may be used for catalytic application provided the particle size is lowered to nano range. Itis noted from the isotherms that higher surface area and optimum amateurs content are essential for adsorption(Raj and Viswanathan, 2009).

From **Figure 4.2**, for a higher amount of dosage catalyst used the yield of methanol produced is much higher compared to the low amount of the dosage used.

For 2.0 g dosage catalyst used, the maximum methanol yield produced was 70.5 ng/μL followed by 1.5 g dosage of catalyst with 68.0 ng/μL yield methanol produced. The lowest amount of dosage catalyst used has been proof that the lowest of yield methanol have been produced. For 0.50 g of dosage catalyst, the yield of methanol produced was 65.9 ng/μL and for 1.0 g is 67.3 ng/μL.

In addition, based on this result we can know how the role of a catalyst affected to a reaction. The catalyst does not change the equilibrium constant but the equilibrium approaches earlier. The catalyst physical structure was examined by BET analysis, and the phase state of the catalyst support wasmeasured by X-ray diffraction (XRD) spectral analysis. The analyses found that catalytic activity was related to the catalyst physical structure, such as specific surface area, pore radius, and the phase state of the support (Gen-hui et. al., 1995).

4.4 Comparative study between ZnS catalyst and ZnS-Kaolin catalyst

Based on analysis in section 4.2 and 4.3, we know that the higher amount of dosage catalyst used in the photo-catalytic activity gave higher methanol yield. Therefore, in this section we were discussed about the difference of ZnS catalyst compared to ZnS-Kaolin catalysts that are affected to the production of methanol yield in photo-catalytic activity. So, we take 2.0 g of dosage catalyst as our comparison since it's gave the highest amount of methanol yield produced. **Figure 4.3** shows the result from the experiment and analysis by using HPLC.

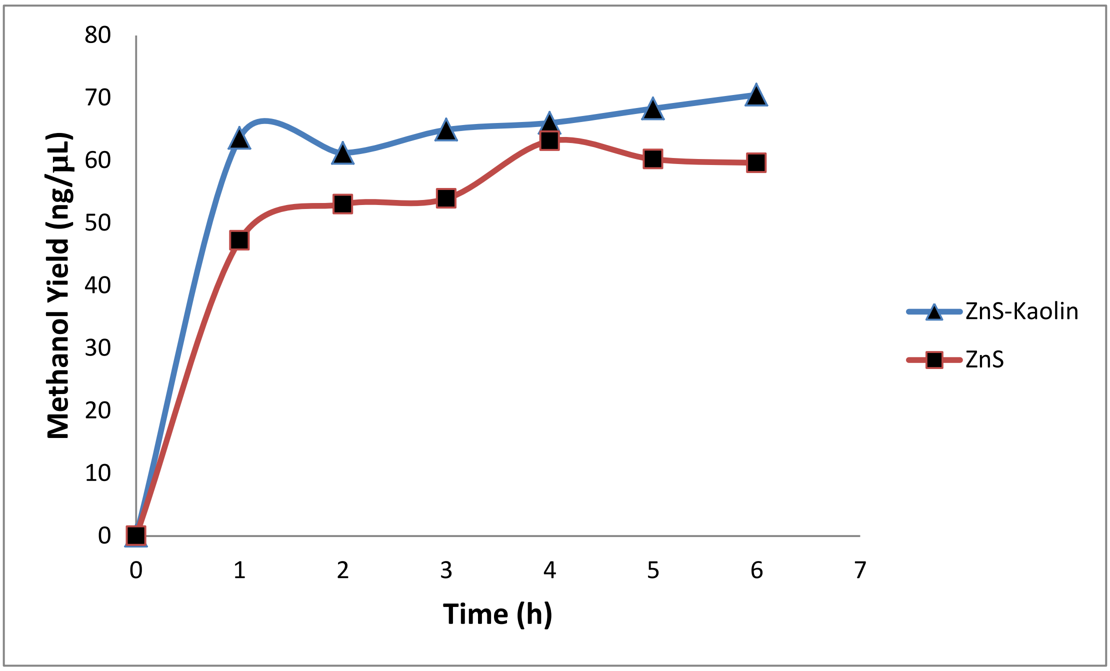


Figure 4.3 Methanol yield for ZnS catalyst and ZnS-Kaolin catalyst

In this study, there is a big difference of methanol yield produced between both catalysts used. The ZnS-Kaolin catalyst shows the highest methanol yield since the initial time of reaction until sixth time of irridation compared to by using ZnS catalyst. After the first hour reaction, methanol yield for ZnS-Kaolin has been produced 63.6 ng/µL whereas for ZnS only 47.2 ng/µL. The methanol yields produced by both catalysts used are increasing respectively to the reaction time. The highest amount of methanol yield by ZnS catalyst is at fourth hour which is 63.1 ng/µL. Furthermore, for ZnS-Kaolin catalyst used, at fourth hour of reaction time it has been produced more methanol yield compared to ZnS catalyst which is 66.0 ng/µL. Although at fourth hour it has been produced methanol more than ZnS catalyst but the maximum yield it has been produced is at sixth hour time reaction which is 70.5 ng/µL.

From this situation, there is important role of kaolin has been shown because the existent of kaolin by supporting ZnS molecule in this photo-reduction process has been produced highest methanol yield. According to Rong and Xiao, (2002), the physical properties of kaolin clays, such as specific surface area, may affect their catalytic cracking activity and have highest thermal stability because the retention rate of its specific surface area is higher. The smaller is the crystallite size, the larger is the specific surface area. The conversion catalysed by kaolin clays increases with an increase in specific surface area.

Kaolin is hydrophilic and can be dispersed in water and in some other systems. Because of the nature of the chemistry of its surface, kaolin can be chemically modified so that it will become hydrophobic or organophilic or both. Generally, an ionic or a polar non-ionic surfactant is used as the surface-treating agent (Murray, 2001).

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The application of ZnS-Kaolin will increase the performance of photo-catalytic reduction process of CO_2. Other than that, the economically preparation of heterogeneous catalysts that used during production n of CH_3OH was helped in order to get a higher percentage of yield. In this study, it has been prove that the higher amount of dosage of catalyst used may give high methanol yield. The 2.0 g ZnS-Kaolin catalyst that used in the photo-reduction process have produced the highest of methanol yield which is 70.5 ng/µL.

Rationally by converting CO_2 from a waste byproduct into valuable products (CH_3OH) will help the growth of the economy and also useful to be used for another process in petrochemical plant utilities. Therefore, the product that was produced by this method may be used as the fuels for the transportation sectors.

This research is also suitable to be handled in order to reduce the concentration of CO_2 in the environment. The known of the prepared catalyst characteristic was beneficial to us about the environmental awareness especially for the global warming issue because it can help in order to reduce the CO_2 concentration in our environment.

5.2 Recommendations

As recommendations for future improvement related to our research as follows:

- ZnS-Kaolin catalyst will be synthesized using another method such as Ion exchange method using alkaline and acid media to compare the performance of available catalysts that prepared using hydrothermal method.

- For the future study, the ZnS-Kaolin catalyst will be characterized first using Brunnauer Emmett Teller (BET), X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscope (TEM) before it is been used for photo-reduction process.

- It is recommended to study the different parameters such as effect of reaction such as temperature and pressure in photo-reduction process.

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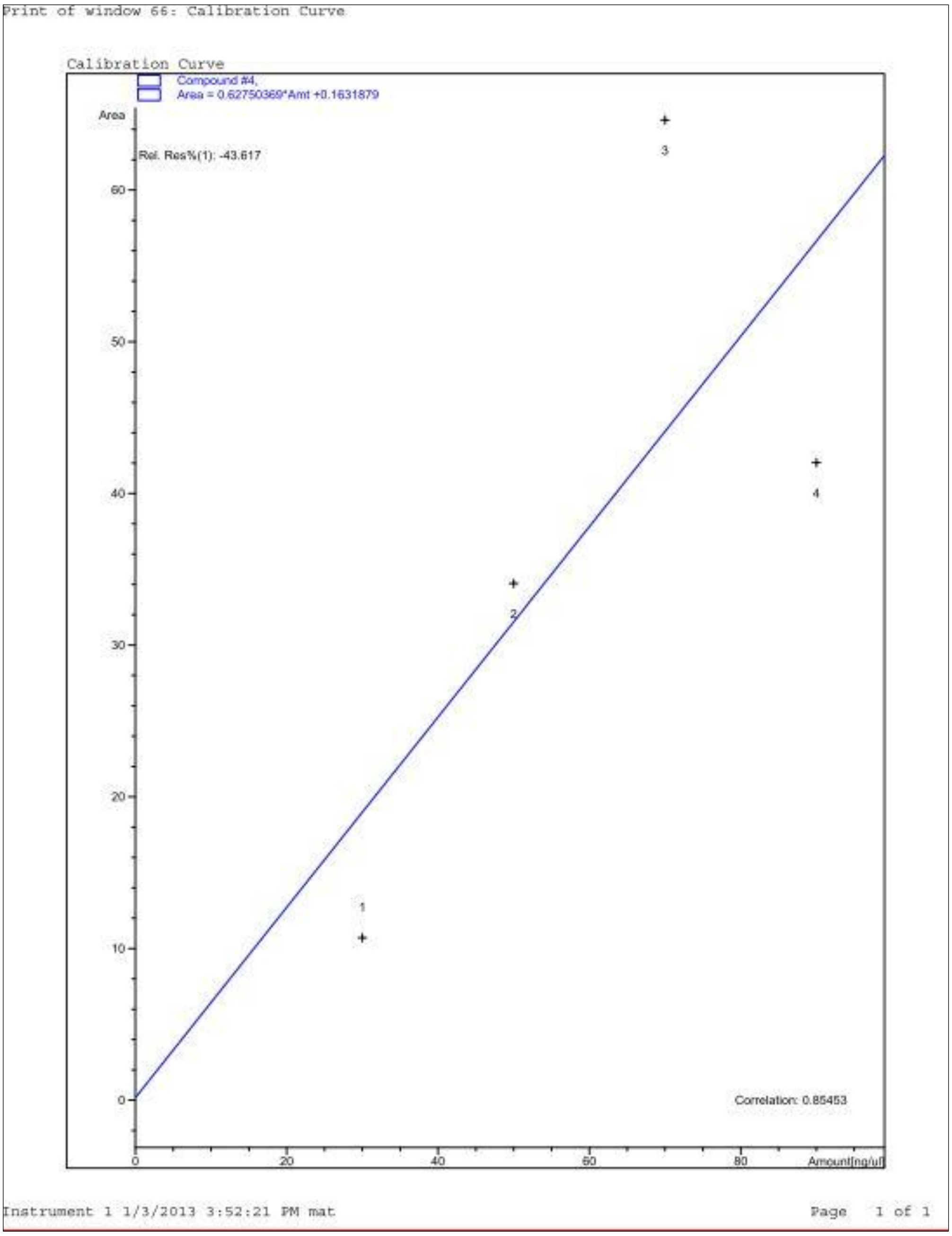
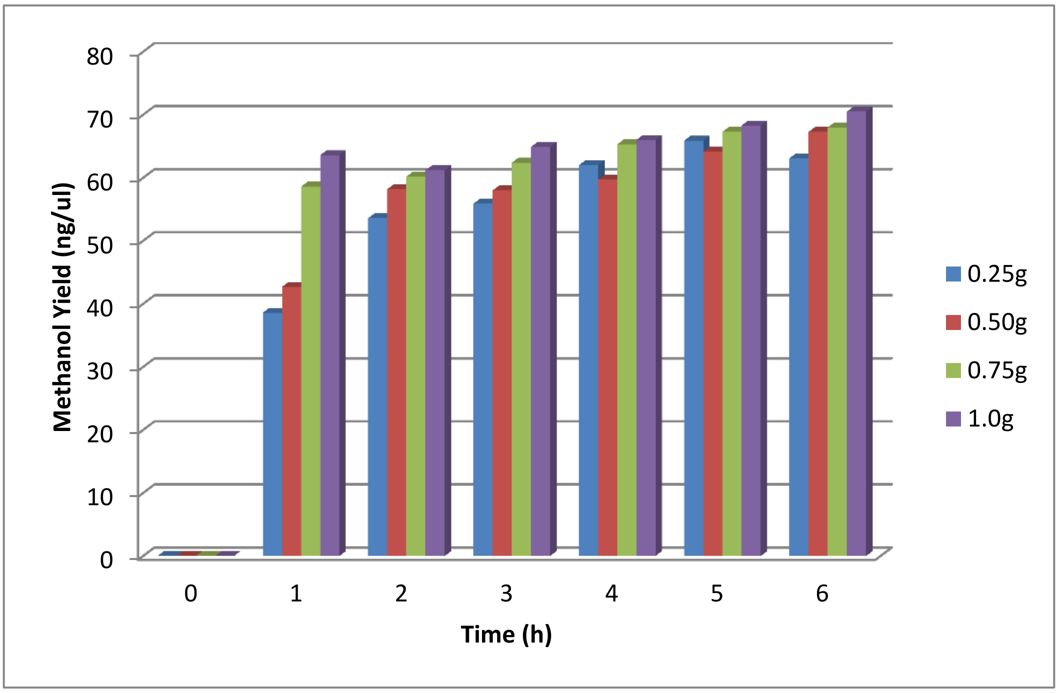
APPENDICES



Appendix A.1 Standard Curve for Methanol Yield



Appendix A.2 Graph of Methanol Yield using ZnS-Kaolin Catalyst

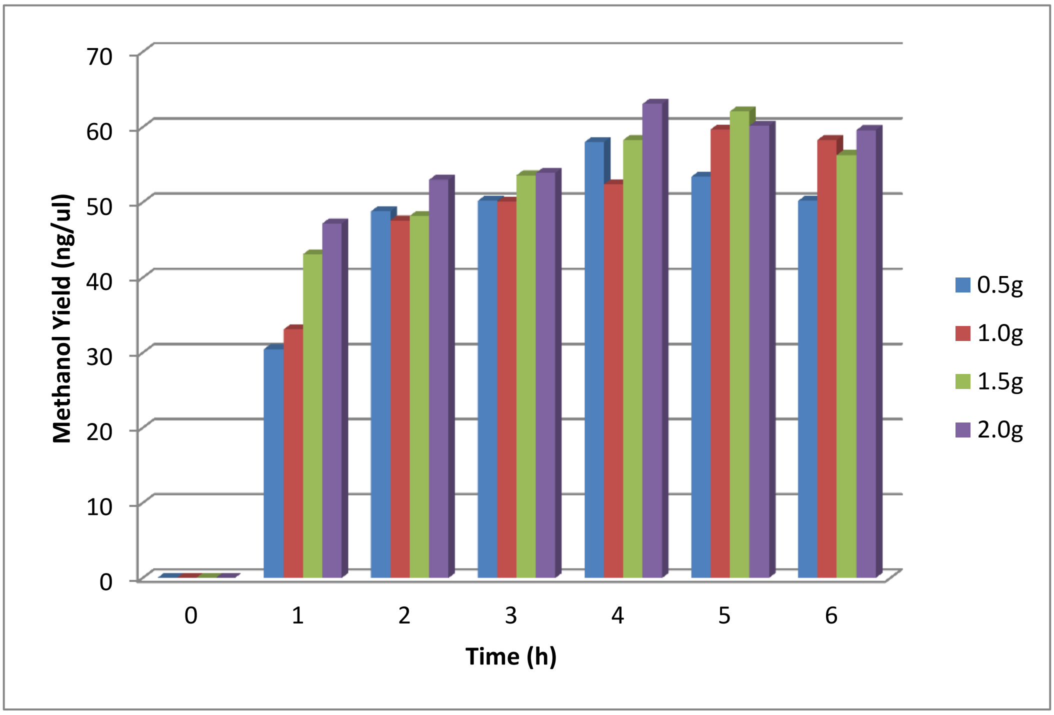


Figure A.3 Graph of Methanol Yield using ZnS Catalyst