PHOTOCATALYTIC REDUCTION OF CO_2 USING ZnS PILLARING ON KAOLIN CATALYST

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ON KAOLIN CATALYST

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A thesis submitted in fulfilment
of the requirement for the award of Degree of
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SUPERVISOR'S DECLARATION

"I hereby declare that I have read this thesis and in my opinion this thesis has fulfilled the qualities and requirements for the award of Bachelor Degree of Chemical Engineering (Gas Technology)".

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Date   :

STUDENT'S DECLARATION

"I declare that this thesis entitled " Photocatalytic Reduction of CO_2 Using ZnS Pillaring on Kaolin Catalyst" 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 in candidature of any another degree."

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ABSTRACT

Increasing of carbon dioxide (CO_2) concentration in atmosphere has gain major attention by the researchers. This is due to CO_2 ability to absorb heat from the UV light and emits the heat to atmosphere resulted in earth warming. In order to overcome this problem, the researchers come out with many solutions. Conventional method and also Advanced Oxidation Process (AOP) have been invented as a way to reduce the concentration of the predominant greenhouse gases especially CO_2. However, AOP has come out as the emerging technologies due to its practicality in reduction process in industry. This study will be focusing on one of the AOP which is photocatalytic reduction process of CO_2. In this process, a photocatalyst was needed. In this research, photocatalyst used was ZnS-Kaolin, a combination of semiconductor ZnS and phyllosilicate mineral, Kaolin. ZnS-Kaolin was prepared by using two methods which are hydrothermal method and simpler impregnation method. In this photocatalytic reduction process, the catalyst was dispersed in medium solution, NaOH aqueous and hence help to catalyze the process. The characteristics of the developed ZnS-Kaolin were observed by using Scanning Electron Microscope (SEM) and Thermal Gravimetric Analyzer (TGA). The effect of parameters such as irradiation time and dosage of ZnS-Kaolin used were observed and studied. This process was produced usable products such as methanol and was analyzed by using High Performance Liquid Chromatography (HPLC). Based on the results, from SEM analysis, it was found that raw Kaolin was constructed from hexagonal flakes structure. Meanwhile, both ZnS-Kaolin prepared from Hydrothermal and Impregnation methods are consists of leaf-like layers structure with ZnS nanoparticles deposited on Kaolin structure. From TGA analysis, it was found that ZnS-Kaolin prepared from Hydrothermal method has higher thermal resistance compared to ZnS-Kaolin prepared from Impregnation method. Meanwhile, for photoreduction process of CO_2, methanol production was observed to be

maximum by using ZnS-Kaolin prepared from Hydrothermal method at dosage of 0.75 g and at 2 hours irradiation time. In conclusion, ZnS-Kaolin prepared by using Hydrothermal method shows better performance in photoreduction process of CO_2 compared to ZnS-Kaolin prepared from Impregnation method.

ABSTRAK

Peningkatan kepekatan karbon dioksida (CO_2) di dalam atmosfera telah mendapat perhatian ramai penyelidik. Hal ini kerana CO_2 boleh menyerap haba daripada cahay UV dan memancar kembali haba tersebut ke dalam atmosfera dan menyebabkan pemanasan global. Bagi mengatasi masalah ini, para penyalidik telah mencipta pelbagai penyelesaian. Kaedah konvensional dan juga Advanced Oxidation Process (AOP) telah dicipta sebagai satu cara untuk mengurangkan kepekatan gas-gas rumah hijau terutamanya CO_2. Walaubagaimanapun, AOP muncul sebagai teknologi pilihan kerana bersifat praktikal dalam proses penurunan di industri. Kajian ini memfokuskan salah satu daripada AOP iaitu Proses Penurunan CO_2 yang menggunakn foto-pemangkin. Di dalam proses ini, foto-pemangkin diperlukan. Dalam kajian ini, foto-pemangkin yang digunakan ialah ZnS-Kaolin, iaitu kombinasi antara semikonduktor, ZnS dan mineral filo-silika, Kaolin. ZnS-Kaolin dihasilkan melalui 2 kaedah iaitu kaedah 'Hydrothermal' dan kaedah 'Impregnation'. Di dalam proses penurunan yang menggunakn foto-pemangkin, pemangkin digunakan di dalam medium cecair, NaOH dan seterusnya memangkinkan proses. Ciri-ciri pemangkin ZnS-Kaolin yang telah dihasilkan diperhati dan dianalisis dengan menggunakan 'Scanning Electron Microscope' (SEM) dan 'Thermal Gravimetric Analyzer' (TGA). Kesan-kesan seperti masa pancaran cahaya UV dan dos ZnS-Kaolin yang digunakan dianalisis dan dikaji. Proses ini menghasilkan produk yang berguna seperti metanol yang kemudiannya dianalisis dengan menggunakan 'High Liquid Performance Chromatography' (HPLC). Berdasarkan keputusan eksperimen, daripada analisis SEM, didapati bahawa Kaolin terdiri daripada struktur kepingan-kepingan yang berbentuk heksagon. Sementara, kedua-dua ZnS-Kaolin yang dihasilkan melalui kaedah 'Hydrothermal' dan 'Impregnation' terdiri daripada struktur lapisan-lapisan yang berbentuk seperti daun dengan zarah-zarah nano ZnS terlekat pada

struktur Kaolin. Seterusnya, berdasarkan analisis TGA, didapati bahawa ZnS-Kaolin yang dihasilkan melalui kaedah 'Hydrothermal' menunjukkan sifat rintangan haba yang tinggi jika dibandingkan dengan ZnS-Kaolin yang dihasilkan melalui kaedah 'Impregnation'. Sementara itu, berdasarkan proses penurunan CO_2 dengan menggunakan foto-pemangkin, penghasilan metanol secara maksima diperhatikan berlaku apabila menggunakan ZnS-Kaolin yang dihasilkan melalui kaedah 'Hydrothermal' pada dos 0.75 g dan selepas 2 jam pancaran cahaya UV. Kesimpulannya, ZnS-Kaolin yang di hasilkan melalui kaedah 'Hydrothermal' menunjukkan kesan yang lebih baik dalam proses penurunan CO_2 jika dibandingkan dengan ZnS-Kaolin yang dihasilkan melalui kaedah 'Impregnation' .

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LIST OF ABBREVIATION

AOP	-Advanced Oxidation Process
CO	- Carbon Monoxide
NOx	- Nitrogen Oxides
CO_2	- Carbon Dioxide
FTIR	- Fourier Transform Infrared Spectroscopy
SEM	- Scanning Electron Microscope
ZnS	- Zinc Sulfide
TiO_2	- Titanium Oxide
ZnO	- Zinc Oxide
VB	- Valence Band
CB	- Conduction Band
Fe_2O_3	- Iron Oxide
ZB	- Zinc Blende
WZ	- Wurtzite
UV	- Ultraviolet
Na_2S	- Sodium Sulfide
MMT	- Montmorillonite

LIST OF SYMBOLS

□ C	- Degree Celcius
Å	- Angstrong
atm	- Atmospheric
cm^{-1}	- per centi meter
e^-	- Negative electron
eV	- Electron volt
g	- gram
g/cm^3	- gram per centimetre cube
h	- hour
h^+	- Positive electron
kV	- kilo Volt
mA	- mili ampere
min	- minute
mL	- mililitre
m^2/g	- meter square per gram
nm	- nanometer
rpm	- Revolutions per minute
s	- second
V	- Voltage
W	- Watt
□mol/g	- micro mol per gram
λ	- lambda

CHAPTER 1

INTRODUCTION

1.1   Research Background

The global warming effect is believed to be associated with the increasing concentrations of greenhouse gases in the atmosphere, where the major contribution comes from carbon dioxide (CO_2) emissions from fossil fuel consumption (Zhang et. al., 2011). Currently, there is around 1 tera ton excess CO_2 in the atmosphere which is man-made and stemming mainly from the combustion of fossil fuels (Jensen et. al., 2011). Recent research has shown that once CO_2 has been emitted to the atmosphere, it will take centuries for natural removal. Clearly, the longer we delay deep reductions in CO_2, the greater the risk that total greenhouse gas emissions will exceed prudent limits for avoiding dangerous anthropogenic change (Moriarty and Honnery, 2009).

The concentration of CO_2 can be reduced by using several conventional methods such as activated carbon and air stripping by packed column (Zhao et. al., 2011). However, these conventional methods are only removes the CO_2 from air content without any conversion to useful products. Hence, advanced oxidation process (AOP) was proposed. AOPs are technologies based on the intermediary of

hydroxyl or other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds to various by-products and eventually to inert end-products. AOP includes heterogeneous and homogeneous photocatalysis based on near ultraviolet (UV) or solar visible irradiation, electrolysis, ozonation, the Fenton's reagent, ultra-sound and wet air oxidation (Klavarioti et. al., 2008).

Reduction process of CO_2 is difficult since it is inert and stable compound. Conventional process requires high pressure and high temperature (Kozak et. al., 2010). Hence, photocatalytic reduction process by using photocatalyst is the most promising method since CO_2 can be reduced to useful compounds by irradiating it with UV light at room temperature and constant pressure (Lo et. al., 2007). Photocatalysis or photocatalytic reduction of CO_2 by UV light involves photocatalyst and UV irradiation. Photocatalytic reduction of CO_2 is not only reducing but also recycling the CO_2 into useful products such as CH_4, CH_3OH, $CHOOH$ and C_2H_5OH. In the process, semiconductors like TiO_2 and ZnS were widely used (Li et. al., 2010).

Heterogeneous semiconductor photocatalysis using TiO_2 as the photocatalyst is an emerging technology with key advantages including operation at ambient condition as well as the fact that the catalyst itself is inexpensive, commercially available at various crystalline forms and particles characteristics, non-toxic and photochemically stable (Doll and Frimmel, 2004). When exposed to a UV light source with wavelength < 380 nm, an electron along with an electron vacancy, or hole (h^+) is produced within a TiO_2 particle (Turchi and Ollis, 1990).

In this study, ZnS-Kaolin (ZnS-K) has been proposed. Heterogenous ZnS-K photocatalyst is a combination of Kaolin, a kind of phyllosilicate mineral and ZnS semiconductor. Kaolin belongs to the kandites mineral group with the chemical composition of $Al_2Si_2O_5 (OH)_4$ (Chong et. al., 2008). The combination combined the functions of the semiconductor and Kaolin together and exhibited

synergetic effects (Miao et. al., 2008). The presence of catalyst supporter, Kaolin improved the activity of photocatalyst. The natural structure and adsorption ability of the clay materials can maintain large specific surface area, stability and consequently enhance the photocatalytic efficiency of the photocatalysts (Chong et. al., 2008). Kozak et. al., (2010) has proved that the yields of photocatalytic reduction of CO_2 by using heterogenous photocatalyst are higher than the yields by using raw semiconductor. ZnS which has wide band gap energy which is about 3.7 eV is very potential material since it can rapidly generates electron-hole pairs during illumination by UV light and has highly negative reduction potentials of excited electrons (Kozak et. al., 2010). Various sites on these particles act as reducing or oxidising centres, which will provide electrons to CO_2. When these semiconductor particles were illuminated by band gap irradiation, electron will be excited from valence to the conductance band. The photocatalytic process involves electrons (e^-) and holes (h^+) generated at these various sites with the aid of photonic energy (hv) from UV light (Kozak et. al., 2010).

Thus, in order to increase the efficiency of photocatalytic reduction process of CO_2, heterogeneous ZnS-K photocatalyst is strongly encouraged. In this study, the effect of operating temperature, irradiation time and percentage of ZnS loading on kaolin in photocatalytic reduction of CO_2 has been studied. ZnS-K was prepared with two different methods; hydrothermal and impregnation method. The performances of both catalysts were studied in photoreduction process. Two parameters that affect the reduction process that are effect of dosage of catalysts and irradiation time were studied.

1.2 Problem Statement

Earth is currently facing global warming due to human activities. Fossil fuel consumption is believed to be the major cause that contributes to this problem. The consumption of fossil fuel will emits high amount of greenhouse gases, predominantly carbon dioxide (CO_2). Global warming happened when the

abundant of CO_2 in atmosphere absorbs heat from UV light and emits the heat to the earth. Due to this problem, some technologies like adsorption by using activated carbon and air stripping were used to capture CO_2 and hence reduced its concentration in atmosphere. However, this method is difficult to be applied in industry because of high cost consumption. Therefore, in this study we proposed an alternative method that offers lower cost and profitable yields which is advanced oxidation process (AOP). The AOP process used in this study is photocatalytic reduction of CO_2 by using heterogeneous catalyst (ZnS-Kaolin) assisted by UV light irradiation. Hence, this study focuses on performances of catalysts in photoreduction process that prepared from hydrothermal and impregnation method. The effect of parameters such as effect of irradiation time and dosage of ZnS-K catalyst used were studied in order to find the optimum condition for this process.

1.3   Objectives of Study

Based on research background and problem statement described previously, the objectives of this research are as follows:

- To prepare ZnS-Kaolin (ZnS-K) as a catalyst to be used in photoreduction process of CO_2.

- To characterize the developed ZnS-Kaolin catalyst.

- To study the performance of both catalysts prepared from hydrothermal and impregnation method in photoreduction process.

1.4   Scope of Research

In order to accomplish the objectives of this research, the following scopes were drawn:

- Synthesizing the new photocatalyst by doping ZnS semiconductor on surface of the kaolin by using hydrothermal and impregnation method.

- Characterizing the developed ZnS-Kaolin catalyst by using Scanning Electron Microscope (SEM) and Thermal Gravimetric analyser (TGA).

- The performances of both catalysts that prepared from hydrothermal and impregnation method were studied in photoreduction process using two different parameters that affect the reaction process; effect of catalyst dosage (0, 0.50 and 0.70 g) and irradiation time (1-5 hours).

- Analyzing the main product (methanol) by using High Performance Liquid Chromatography (HPLC) analyzer.

1.5   Rationale and Significance

Reduction of CO_2 by force (conventional method) is highly cost since the process requires high pressure, high temperature and high cost of materials. The application of photocatalytic reduction process by semiconductor catalyst assisted by UV light is purposely to provide an alternative treatment with low cost because the process could be performed at room temperature under atmospheric pressure and also to form useful products. With using different preparation methods, catalyst with best properties will produced highest concentration of methanol.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

The reduction of anthropogenic CO_2 emissions to address of the consequences of climate change is a matter of all developed countries (Pevida et. al., 2008). The conventional method used is to capture the CO_2 by using solid sorbents such as molecular sieves, zeolites and activated carbon. The method involved adsorption-desorption on the solid sorbents. This method is applied at large stationary source of CO_2 such as power station, cement plants and refineries. The adsorption properties of solid sorbent are determined by its porous structure and surface chemistry. Activated carbon is widely used in industrial process due to its well developed microporosities and mesoporosities, high surface area and high surface reactivity. The capacity of CO_2 adsorbed by the activated carbon was determined by the mass uptake recorded from the expose towards pure CO_2. The adsorbed amount was calculated using ideal gas law at low pressure prevailing, by measuring the pressure drop caused by CO_2 adsorption (Somy et. al., 2009).

Instead of using conventional method, CO_2 concentration can also be reduced by using Advanced Oxidation Processes (AOPs). AOPs are technologies based on the intermediary of hydroxyl or other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds to various by-products and eventually to

inert end-products. AOP includes heterogeneous and homogeneous photocatalysis based on near ultraviolet (UV) or solar visible irradiation, electrolysis, ozonation, the Fenton's reagent, ultra-sound and wet air oxidation (Klavarioti et. al, 2008). In reduction process of CO_2, the AOP used is heterogeneous photocatalysis or photocatalytic reduction process under UV light irradiation. Heterogeneous photocatalysis involves light absorption of sufficient energy by a photocatalytic semiconductor such as TiO_2, ZnS, ZrO_2, V_2O_5, ZnO, CeO_2 and NbO_5 that causing excitation of its valence band electrons into conduction band (Li et. al., 2004). The reaction for photocatalysis is shown in Figure 2.1.
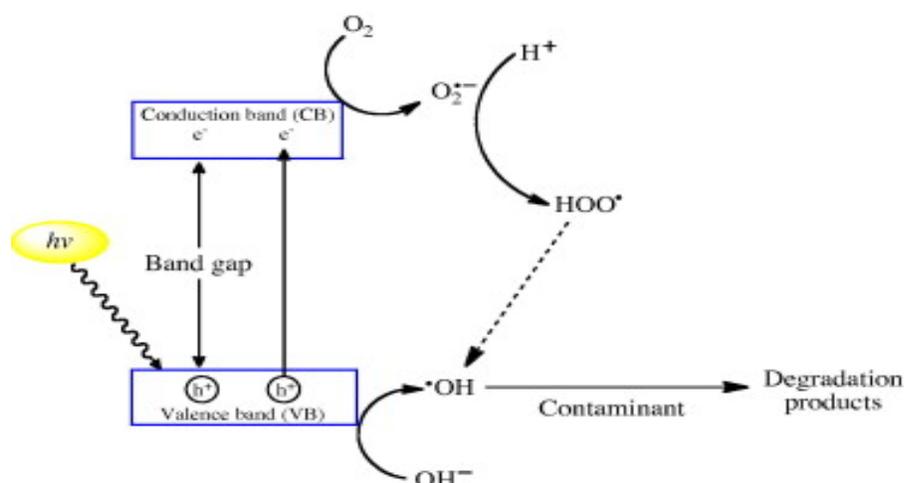
Figure 2.1: Schematic diagram of reaction occurring via photocatalysis

2.2   Photocatalyst Semiconductor

A semiconductor (SC) such as ZnS can be prepared from chemical solution. The methods of preparation include slow addition of Na_2S and bubbling H_2S through an aqueous precursor solutions, coprecipitation, microwave irradiation method and hydrothermal method (Wu et. al., 2008). A semiconductor is characterized by an electronic band structure in which the highest occupied energy band, called valence band (vb) and the lowest empty band called conduction band (cb), are separated by a band gap (Marta, 1999). Photocatalytic activity of the semiconductors is mainly determined by crystal

structure, surface area, size of particles, bang-gap energy and morphology (Taghvae et. al., 2009). The process is considered as the direct absorption of a photon by band gap of the materials and generation of electron–hole pairs in the semiconductor particles. The excitation of an electron from the valence band to the conduction band is initiated by light absorption with energy equal to or greater than the band gap of the semiconductor (Pan et. al., 2007).

Energy will be absorbed by the semiconductor when the photon energy is higher or equal to the band gap energy. An electron from the valence band will be promoted to the conduction band and generates a hole (h^+) in the valence band. Subsequent anodic and cathodic redox reaction in Figure 2.2 will be initiated when the electron (ec^{b-}) and hole (hv^{b+}) react with donor (D) and acceptor (A).
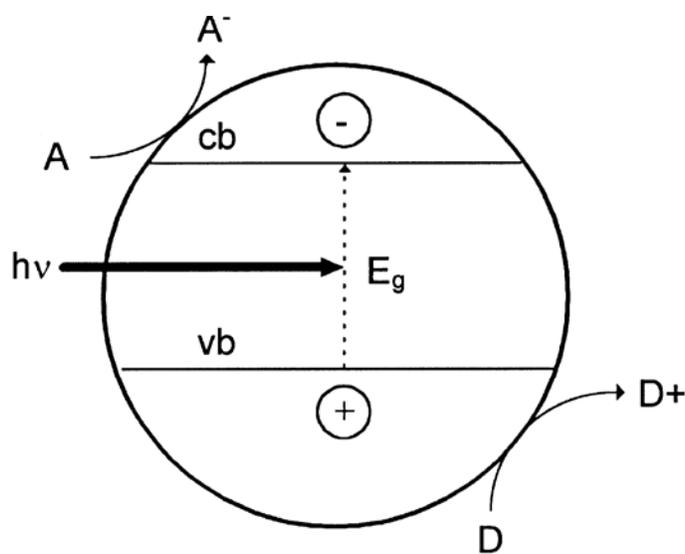
Figure 2.2: Simplified diagram of the heterogeneous photocatalytic process occurring on an illuminated semiconductor particle.

TiO$_2$ semiconductor has been widely used as catalyst for UV irradiation and was considered the best choice among several other oxides because it has low band-gap values of approximately 3.0 and 3.2 eV for rutile and anatase, respectively. Besides fulfilling the thermodynamic requirements

needed for the occurrence of most of the photocatalytic reactions usually investigated, TiO_2 is reasonably cheap, photo-stable and non-toxic that making it a perfect candidate for photocatalytic process (Tan et. al., 2006).

Meanwhile, ZnS semiconductor behaves as an effective catalyst with wide band gap (E_g~3.6 eV) together with its distinguished energy band properties. It becomes good host material and possesses photoluminescence and electroluminescence characteristics (Taghvae et. al., 2009). However, Kočí et. al., (2010) has proved that the performance of heterogeneous semiconductor catalyst is better than raw semiconductor catalyst.

2.3   ZnS-Kaolin as photocatalyst

Photocatalysts are important materials that provide a relatively simple means for the conversion of solar energy for use in oxidation and reduction process (Casbeer et. al., 2011). These photocatalysts use their interlayer space as reactions sites, where the electron–hole recombination process could be retarded by physical separation of the electron–hole pairs generated by photo-absorption. One characteristic of these layered materials is that the interlayer guests are ion-exchangeable with various foreign species. The pillaring of layered compounds by inorganic compound is a promising method for fabricating function materials. Cationic species such as Pt, Fe_2O_3, TiO_2, CdS and SiO_2 have been introduced into interlayer galleries as precursors of photocatalytically active sites (Huang et. al., 2009).

Incorporation of a semiconductor catalyst in the interlayer region of a lamelar compound via chemical reactions is a promising method for fabricating a nanocomposite consisting of host layers with ultrafine particles in the interlayer and enhancing photocatalytic activity of the semiconductor. Another interesting feature is that the catalytic activity can be highly improved by partial substitution on A-and /or B-site, with only small changes in the average structure. It is well-known that the photocatalytic activity of a semiconductor is largely determined by

the energetic of position of the band gap. Initially, a variety of transition metals (such as Cr, Fe and others) was employed to dope photocatalyst in order to reduce the band gap and allow it to absorb visible light (Huang et. al., 2009).

ZnS-Kaolin photocatayst is a kind of heterogeneous photocatalyst formed from the combination of semiconductor, ZnS and inert supporter of kaolin. It can be prepared through some methods such as sol-gel method, ion-exchange method, impregnation method and hydrothermal method. The semiconductor, ZnS has wide direct band gap energy which is 3.7 eV which performed rapid generation of electron-hole pairs by photoexcitation with lower wavelength of UV light. It also has highly negative reduction potentials of excited electrons (Miao et. al., 2006).

Meanwhile, Kaolin or China clay contains as the mineral kaolinite, which is a hydrated aluminiumsilicate ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) (Chandrasekhar et. al., 2001). It has fine particle size, brightness and whiteness, chemical inertness and platy structure. Kaolin acts as supporter for ZnS nanoparticles. It also can act as an immobilizer that will prevent the semiconductor to aggregate in the NaOH solution. These properties will increase the effective surface area and photocatalytic efficiency. Kaolin also can changes the asidobasic properties of the catalyst surface and prevents the crystallite growing. Koči et. al., (2010) has proved that heterogeneous semiconductor catalyst will performed better in photocatalytic reduction process. It provides effective surface area due to lower agglomeration in suspension, lower recombination rate of electron–hole pairs, changes of the acidobasic properties of the catalyst surface and lower crystallite size where the yields of the CO_2 photocatalytic reduction products increase with the decrease of crystallite size (Koči et. al., 2010).

2.4   Zinc Sulphide (ZnS)

ZnS is one of the first nanostructured materials discovered and has shown remarkable fundamental properties versatility and a promise for novel diverse applications, including light-emitting diodes (LEDs), electroluminescence, flat

panel displays, infrared windows, sensors, lasers and biodevices. Its atomic structure and chemical properties are comparable to more popular and widely known ZnO. However, certain properties pertaining to ZnS are unique and advantageous compared to ZnO. ZnS has a larger bandgap of 3.72 eV and 3.77 eV (for cubic zinc blende (ZB) and hexagonal wurtzite (WZ) ZnS, respectively) than ZnO which is 3.4 eV (Fang et. al., 2010).

ZnS has two commonly available allotropes, one with a ZB structure and another one with a WZ structure. The cubic form, ZB is the stable low-temperature phase, while the latter, WZ is the high-temperature polymorph which forms at around 1296 K. Figure 2.3 shows three different views of these structures. Alternatively, ZB consists of tetrahedrally coordinated zinc and sulphur atoms stacked in the ABCABC pattern, while in WZ, the same building blocks are stacked in the ABABAB pattern. The WZ phase has a higher band gap of 3.77 eV while the ZB structure of 3.72 eV that describes ranges of energy that an electron is forbidden or allowed to have (Fang et. al., 2010).
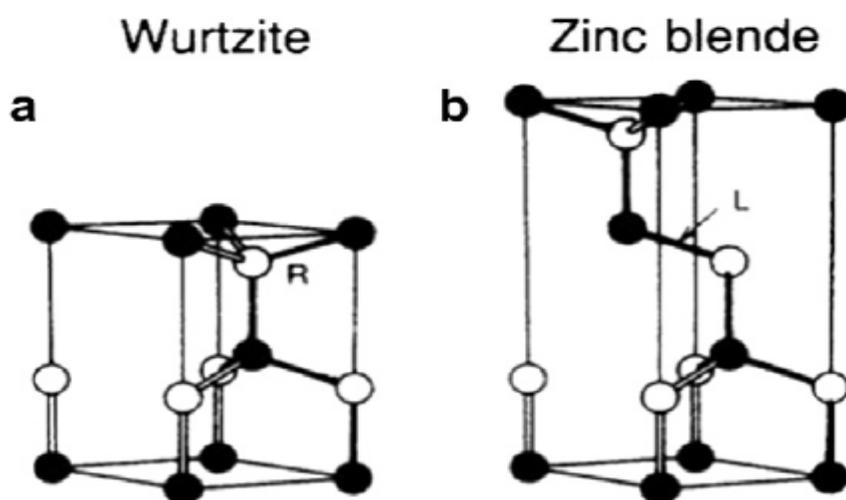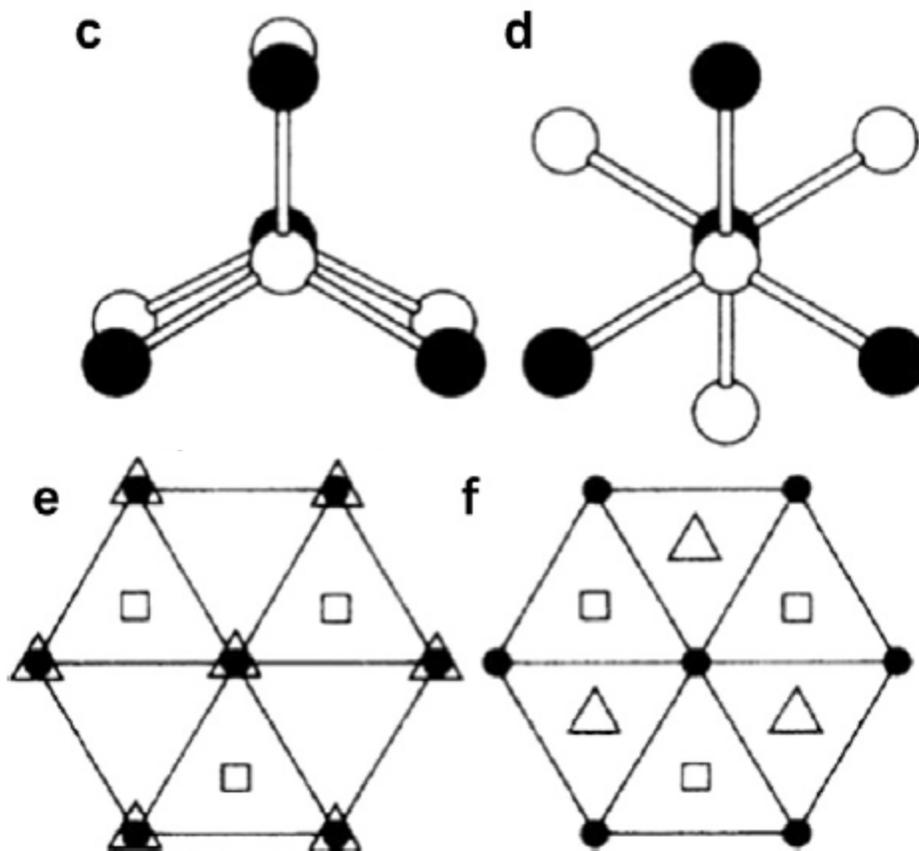
Figure 2.3: Model of wurtzite, WZ and zinc blende, ZB crystal structures where a and b show handedness of the fourth interatomic bond along the right (R) for wurtzite and along the left (L) for zinc blende, c and d show the respective eclipsed and staggered dihedral conformations, meanwhile e and f show atomic arrangement along the close packing axis.

2.5   Kaolin

Clays are nanoparticles with layered structures that possess net negative charge that is neutralized by cations such as Na^+, K^+ and Ca^{2+} which occupy the interlamellar space. The amazing amenability of clays formodification is the fact that these interlamellar cations can be very easily replaced by other cations or other molecules. Molecules can be covalently anchored to layer atoms. This provides tremendous scope for altering the properties of clays like acidity, pore size, surface area, polarity and other characteristics that govern their performance as catalysts (Nagendrappa, 2010).

Clays are widespread, easily available and low-cost chemical substances. Clays are versatile materials that catalyze a variety of chemical reactions, both in their native state and in numerous modified forms. (Nagendrappa, 2010). It is estimated that millions of tons of kaolin, a kind of clay are used each year in the world for different applications like paper coating and filling, ceramics, paint, cracking catalyst, cements, waste water treatment and pharmaceutical industries (Lu et. al., 2009).

Kaolin is a commercial available and low cost clay material (Lu et. al., 2009). Kaolin belongs to the kandites mineral group and is a clay mineral with the chemical composition of $Al_2Si_2O_5(OH)_4$ as shown in Figure 2.4.
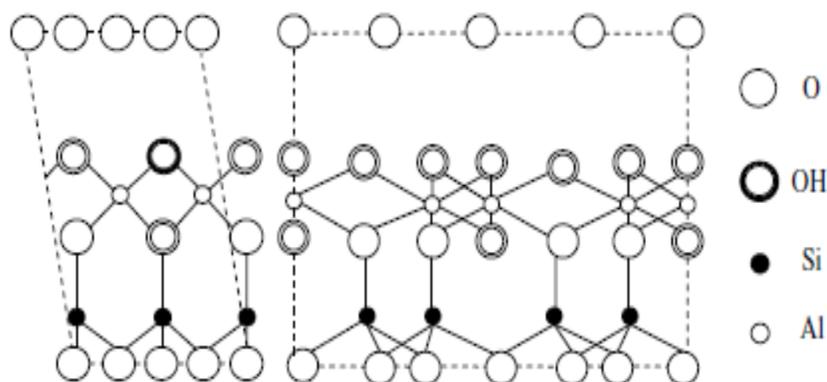
Figure 2.4: The Crystal Structure of Kaolinite

It is a layered silicate mineral with one layer of octahedral, which reacts with one sheet $(Si_2)_3(OH)_2)n$, resulting in a two-layer sheet structure. The siliceous side of Kaolin presents a surface of oxygen, while the aluminous side provides a surface of hydroxyl groups. These double layers are then stacked upon one another with the –OH groups of one such sheet against the oxygen of the next sheets. The interaction between the stacked layered in Kaolin are bonded covalently to each other, rather than Van der Waals or electrostatic forces. This interaction force makes Kaolin suitable as a structurally rigid substrate for supporting and immobilizing the TiO_2. The strong interaction forces make the immobilized particles chemically stable from swelling and can endure high

temperature of up to 950 ℃ (Chong et. al., 2008).

2.6   Characterization of ZnS-Kaolin

2.6.1   Scanning Electron Microscopy (SEM)

In scanning electron microscopy (SEM), a fine probe of electrons with energies typically up to 40 KeV is focused on a specimen and scanned along a pattern of parallel lines. Various signals are generated as a result of the impact of the incident electrons, which are collected to form an image or to analyse the sample surface. These are mainly secondary electrons, with energies of a few tens of eV, high-energy electrons backscattered from the primary beam and characteristic X-rays (Bogner et. al., 2006).

2.6.2   Thermal Gravimetric Analysis (TGA)

Thermo gravimetric analysis or thermal gravimetric analysis is a type of testing performed on samples that determines changes in weight in relation to a temperature program in a controlled atmosphere. Such analysis relies on a high degree of precision in three measurements which are weight, temperature, and temperature change. The TGA instrument is essentially a sensitive microbalance that enables measurement of weight changes at the sub-microgram level during carefully controlled temperature in a dynamic exposure chamber (Rauma et. al., 2006).

2.7   Photoreduction Process of CO_2

The process is using UV light to promote electron (ec^{b-}) from valence band in the semiconductor and hence leaving holes (hv^{b+}) in the valence band. The promoted (ec^{b-}) and (hv^{b+}) may participate in the oxidation and reduction reactions, respectively, with trapped species (Lo et. al., 2007). CO_2 act as (ec^{b-}) acceptor in the conduction band. ($\cdot CO_2^-$) radical will be formed when the adsorbed CO_2 accepts an (ec^{b-}). The efficiency of photocatalysis depends on the

lifetime of the (ec^{b-}) and (hv^{b+}). The photocatalysis reaction rate will be decreased if the (ec^{b-}) and (hv^{b+}) is not accepted by any suitable reactant (Koči et. al., 2010).

This method offers the advantage of destroying the targeted gas and transformed it into useful products such as methane (CH_4) and methanol (CH_3O). This is different from the conventional method which only removes the gas. The reduction of CO_2 using photocatalyst is one of the most promising methods because CO_2 can be reduced by the UV radiation at room temperature and atmospheric pressure (Kozák et. al., 2010). In the photocatalytic reduction of CO_2 by using ZnS-K photocatalyst and saturated NaOH solution, UV light generates electrons and holes from ZnS nanoparticles. The redox reactions during the process are as follows:-

$$\text{ZnS} \xrightleftharpoons[]{h\nu} \text{ZnS} + (e^- + h^+) \tag{1}$$

$$H_2O + 2h^+ \xrightleftharpoons[]{} O_2 + 2H^+ \tag{2}$$

$$2H^+ + 2e^- \xrightleftharpoons[]{} H_2 \, (E^{of} = -0.41 \text{ V}) \tag{3}$$

$$CO_2(aq) + 2H^+ + 2e^- \xrightleftharpoons[]{} CO(g) + H2O \, (E^{of} = -0.51 \text{ V}) \tag{4}$$

$$CO_2 + 6H + 6e^- \xrightleftharpoons[]{} CH_3OH + H_2O \, (E^{of} = -0.38 \text{ V}) \tag{5}$$

$$CO_2 \, (aq) + 8H^+ + 8e^- \xrightleftharpoons[]{} CH_4 \, (g) + 2H_2O \, (E^{of} = -0.24 \text{ V}) \tag{6}$$

$$SO_4^{2-} + 9H^+ + 8e^- \xrightleftharpoons[]{} HS^- + 4H_2O \, (E^{of} = -0.22 \text{ V}) \tag{7}$$
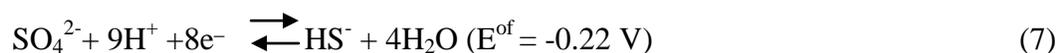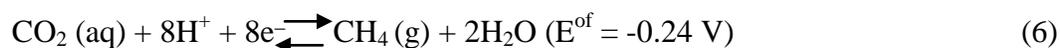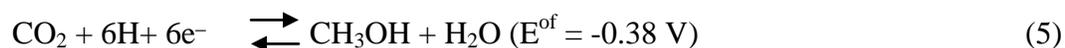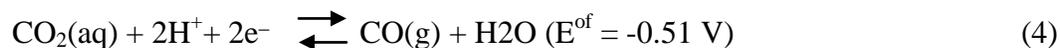
Two main products of this process are methane (CH_4) and methanol (CH_3OH). There are also large amount of hydrogen and low amount of carbon monoxide. Kozák et. al., (2010) has proved that the yields of all products continually increased during the whole experiment. Compared to the photocatalytic reduction process by using TiO_2 which is widely used in industry, the product formed is higher in heterogeneous ZnS. Methane was produced 6-fold higher concentrations in comparison with the application of TiO_2. The production of methanol is in fact 3.5-fold higher amounts than with TiO_2. Meanwhile, the yield of carbon monoxide is 5-fold higher (Kozák et. al., 2010).

2.8 Parameters that affect the photoreduction process

The performance of photocatalytic reduction process can be studied under various parameters such as radiation wavelength, irradiation time, lamp power, percentage of semiconductor loading, operating temperature, pressure and ratio of H_2O/CO_2. However, the parameters focused in this study were the effect of dosage of ZnS-Kaolin catalyst used in this process and irradiation time.

2.8.1   Effect of Dosage of Catalyst

Increasing in catalyst dosage will increase the photoreduction activity. This is due to more active sites present in the system. Adequate dosage of the catalyst increases the generation rate of electron/hole pairs and thus increases the formation of OH radicals for enhancing photodegradation. However, an excess dosage of the catalyst decreases the light penetration via shielding effect of the suspended particles (Chiou et. al., 2007). Slamet et. al., 2005 has proved that the copper loading has affected the methanol yields. The methanol yields increased with Cu loading, but then decreased when the Cu loading exceeded 3 wt%. More Cu loading can increase methanol yield because of the amount of active sites. Copper can serve as an electron trapper and prohibits the recombination of electron and hole, significantly increased the photo-efficiency. However, catalysts with more than 3 wt% Cu loading cannot further increase the methanol yield due to its shading effects.

2.8.2   Effect of irradiation time

The irradiation of semiconductors with neutrons, electrons and ions can have a dramatic effect on their physical properties. Irradiation can change the resistivity of common semiconductors by 5 ± 6 orders of magnitude. The whole photocatalytic reaction can be separated into several steps including light absorption, charge transport to photocatalyst surface, photoreaction with adsorbed reactants at the photocatalyst surface and photoproduct desorption from photocatalyst surface. The product desorption is the rate-limiting step in the photosynthetic methanol formation by CO_2 and H_2O (Yang et. al., 2010).

Kato and Nishimura, (2007) have proved that the reduction yield of CH_4 will be increased with an increasing of UV rays irradiating duration. A longer irradiation time provides more chances of photoexcitation upon the catalyst.

Higher rate of photoexcitation results in more electron-hole pairs. More CO_2 will be trapped in holes (h^+) and more reaction will be occurred. This hence increases the yields of CH_4. It was reported by Yamashita et. al., (2007) that the yields increased steadily with time up to 4 hours after which, a decrease in the reaction rate then occurred.

CHAPTER 3

METHODOLOGY

3.1   Chemicals and Materials

The materials used in this study were Zinc Nitrate Hexahydrate ($H_{12}N_2O_{12}Zn$), Sodium Sulfide (Na_2S), Sodium carbonate (Na_2CO_3), Hexadecyltrimethylammonium Chloride (HTAC), Kaolinite, Sodium Hydroxide (NaOH), CO_2, methanol and acetonitrile.

3.2.1   Properties of materials

3.2.1(a) Zinc Nitrate Hexahydrate

Zinc nitrate hexahydrate was used to prepare ZnS solution. This chemical was purchased from Sigma Aldrich Bhd. Table 3.1 shows the physical properties of Zinc Nitrate Hexahydrate ($H_{12}N_2O_{12}Zn$).

Table 3.1: Physical Properties of Zinc Nitrate Hexahydrate ($H_{12}N_2O_{12}Zn$)

Physical properties	
Molecular formula	$H_{12}N_2O_{12}Zn$
Molecular weight (g/mol)	297.49
Melting point (ºC)	36
Density (g/mL at 25 ºC)	2.065
Water solubility (G/L)	1800
Appearance	White crystal

3.2.1(b) Sodium sulphides

Sodium sulphide was used to prepare ZnS solution. This chemical was purchased from Sigma Aldrich Bhd. Table 3.2 shows the physical properties of Sodium Sulphide (Na_2S).

Table 3.2: Physical Properties of Sodium Sulphide (Na_2S)

Physical properties	
Molecular formula	Na_2S
Molecular weight (g/mol)	78.04
Melting point (ºC)	950
Density (g/mL at 25 ºC)	1.86
Water solubility (G/L)	186
Appearance	Crystal with varied colour and repulsive

3.2.1(c) Sodium Carbonate

Sodium carbonate was used in Kaolin pre-treatment process. This chemical was purchased from Sigma Aldrich Bhd. Table 3.3 shows the physical properties of Sodium Carbonate (Na_2CO_3).

Table 3.3: Physical Properties of Sodium Carbonate (Na_2CO_3)

Physical properties	
Molecular formula	Na_2CO_3
Molecular weight (g/mol)	106
Melting point (ºC)	851
Density (g/mL at 25 ºC)	2.53
Water solubility (G/L)	45.5
Appearance	White crystalline compound

3.2.1(d) Hexadecyltrimethylammonium chloride (HTAC)

HTAC was used as a stabilizer and was purchased from Sigma Aldrich Bhd. Table 3.4 shows the physical properties of HTAC.

Table 3.4: Physical Properties of HTAC

Physical properties	
Molecular formula	$C_{19}H_{42}ClN$
Molecular weight (g/mol)	320
Melting point (ºC)	232-234
Density (g/mL at 25 ºC)	0.968
Water solubility (G/L)	Soluble
Appearance	Colourless to pale yellow liquid with an odor of rubbing alcohol

3.2.1(e) Sodium hydroxide

Sodium hydroxide was used as medium solution in photoreduction process of CO_2. This material was purchased from Sigma Aldrich Bhd. Table 3.5 shows the physical properties of Sodium Hydroxide (NaOH).

Table 3.5: Physical Properties of Sodium Hydroxide (NaOH)

Physical properties	
Molecular formula	NaOH
Molecular weight (g/mol)	40
Melting point (ºC)	318
Density (g/mL at 25 ºC)	2.12
Water solubility (G/L)	Soluble
Appearance	Odorless solid or liquid

3.2.1(f) Kaolin

Kaolin was used as a support to ZnS. This material was purchased from Sigma Aldrich Bhd. Table 3.6 shows the physical properties of Kaolin.

Table 3.6: Physical Properties of Kaolin

Physical properties	
Molecular formula	$Al_2Si_2O_5(OH)_4$
Molecular weight (g/mol)	258.16
Cleavage	001(perfect)
Density (g/mL at 25 ºC)	2.6
Hardness	1.5-2.0
Appearance	Usually white, colorless, greyish or yellowish in color

3.3   Preparation of ZnS-Kaolin catalyst

3.3.1   Hydrothermal Method

3.3.1(a) Pre-treatment of Kaolin (K)

Kaolin was treated with $Na_2(CO_3)$ aqueous solution. The mixture then was undergoing successive centrifugation-washing treatment with distilled water.

3.3.1(b) Preparation of HTAC-K

2.0 g of kaolin was treated with 100 mL of HTAC aqueous solution and was stirred for 4 hours. The mixture then was filtered and washed gently with distilled water for several time to obtained HTAC-K. The product then was dried in vacuum oven at 60 ºC for 10 hours.

3.3.1(c) Preparation of ZnS-K

1.0 g of HTAC-K was dispersed in 10 mL of Zn $(NO_3)_2$•6H2O aqueous solution and was 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 135 ℃ for 4 hours. The resulting product then was separated via centrifugation and washed five times with distilled water. The product was dried in a vacuum oven at 60 ℃ for 6 hours and then calcined at 500 ℃ for 2 hours in furnace before photocatalytic activity measurement.

3.3.2 Impregnation Method

50 mL of aqueous solution of Na_2S and HTAC were added drop-wise into 250 mL of aqueous solution of $Zn(NO_3)_2$•6H_2O under vigorous stirring. The dispersion then was shaken with 0.50 g of Kaolin for 24 hours. The product then was filtered and washed gently with deionized water for several times. The product then was dried at 60 ℃ and was calcined at 500 ℃ for 2 hours in furnace.

3.4 Characterization of ZnS-Kaolin

3.4.1 Scanning Electron Microscopy (SEM)

The morphology, structure and surface characteristics of three samples which are raw Kaolin, ZnS-Kaolin prepared from Hydrothermal method and Impregnation method were analysed by using The Zeiss Supra 5S Ultra SEM instrument equipped with a Robinson backscattered electron (BSE) detector.

3.4.2 Thermal Gravimetric Analysis (TGA)

The weight loss as a function of temperature of three samples which were ZnS-Kaolin prepared from Hydrothermal method and Impregnation method were

analysed by using TA Instruments from temperature 30 ºC until 900 ºC at a heating rate of 10 ºC/min under highly nitrogenised condition.

3.5 Photoreduction Process of CO_2

0.50 g of the ZnS-Kaolin catalyst prepared by using hydrothermal method was dispersed in 600 mL of NaOH aqueous solution in reactor. Industrial CO_2 was first flown through the solution in the reactor at pressure of 1.23 bar and the rig was placed in a room under ambient temperature. After the whole rig was properly set -up, the rig and the contents was allowed to operate for 1 hour before the first liquid sample was withdrawn. Then, UV light was turned ON and irradiation was allowed to remain ON continuously for another 4 hours and sample was withdrawn every one hour. The same procedures were repeated by using dosage of 0.70 g. The same experiment was repeated by using the ZnS-K prepared by Impregnation method. The concentration of methanol present in the product samples were analysed by using High Performance Liquid Chromatography (HPLC). The photoreduction rig set up was shown in Figure 3.1.
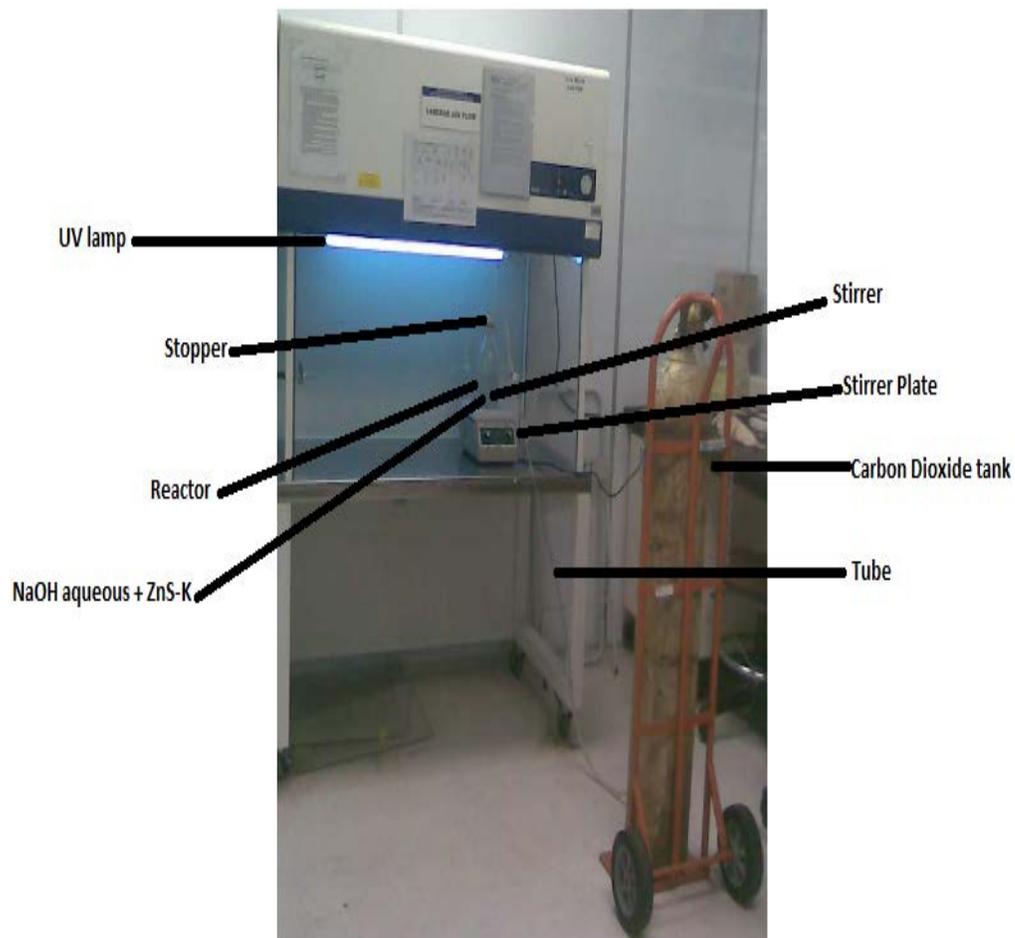
Figure 3.1: Rig set up for photoreduction of CO_2

3.6   Product Analysis

Methanol concentration was analysed by using Agilent Technologies 1200 Series, High Liquid Performance Chromatography (HPLC) with absorbance detector (λ= 280 nm). The pre-column used was Eclipse Plus C18 (250 mm x 4.6 mm x 5 µm). The mobile phase used is acetonitrile-water 40:60 (v/v) and flow rate was 1.0 mL/min. The standard solutions of methanol used are 10 %, 30 %, 50 %, 70 % and 90 % (v/v).

CHAPTER 4

RESULTS AND DISCUSSION

4.0   Introduction

In this research, two main parts of the process were studied that were characterization of catalysts and photocatalytic reduction of CO_2. For characterization part, TGA and SEM were used to characterize the prepared catalysts. In photocatalytic reduction process, the performance of both catalysts which were prepared from hydrothermal and impregnation methods were analyzed with study two parameters that affect the reaction process. Effect of irradiation time and dosage of ZnS-Kaolin catalyst were studied and methanol as a main product was analyzed using High Performances Liquid Chromatography (HPLC).

4.1   Characterization

4.1.1   Scanning Electron Microscopy (SEM)

The morphology and surface characteristics of raw Kaolin, ZnS-K prepared from hydrothermal method and Impregnation method were characterized by SEM as shown in Figure 4.1(a), (b) and (c), respectively.

| 2μm | EHT = 15.00 kV | Signal A = SE1 | Date :8 Jun 2012 | ZEISS |
| Mag = 2.50 K X | I Probe = 100 pA | WD = 8.0 mm | Time :10:24:12 | |

(a)

| 2μm | EHT = 8.00 kV | Signal A = SE1 | Date :8 Jun 2012 | ZEISS |
| Mag = 4.00 K X | I Probe = 100 pA | WD = 7.5 mm | Time :10:35:16 | |
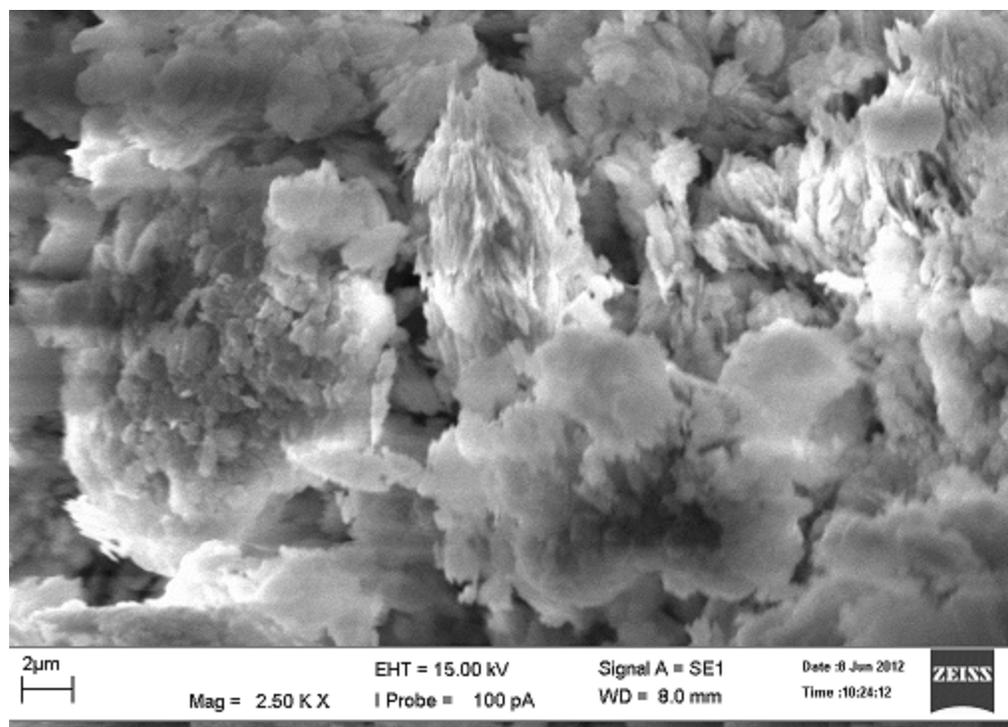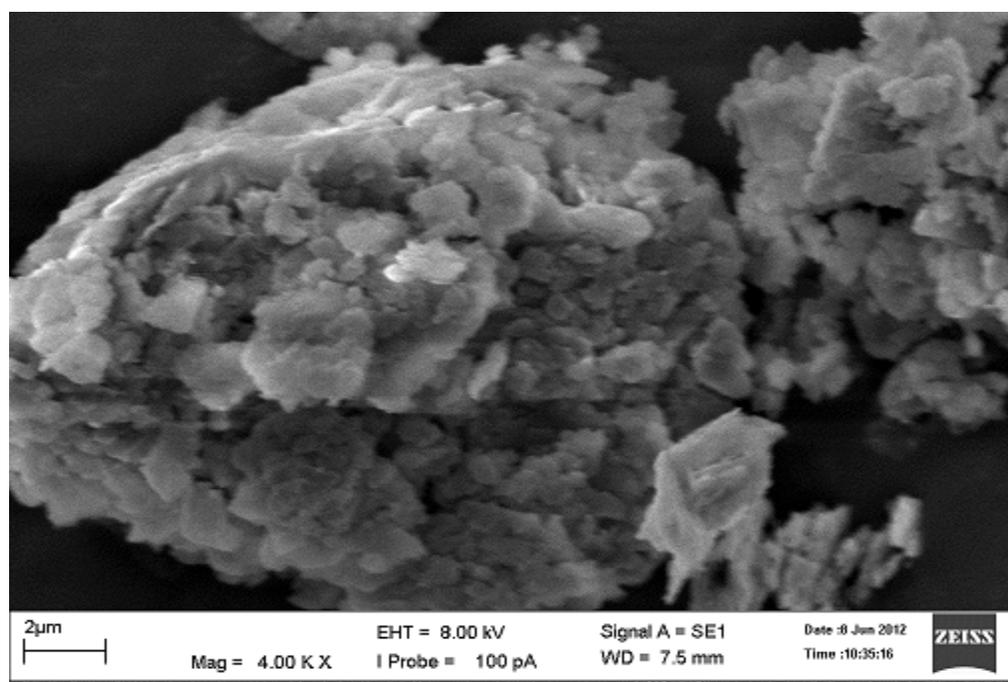
(b)
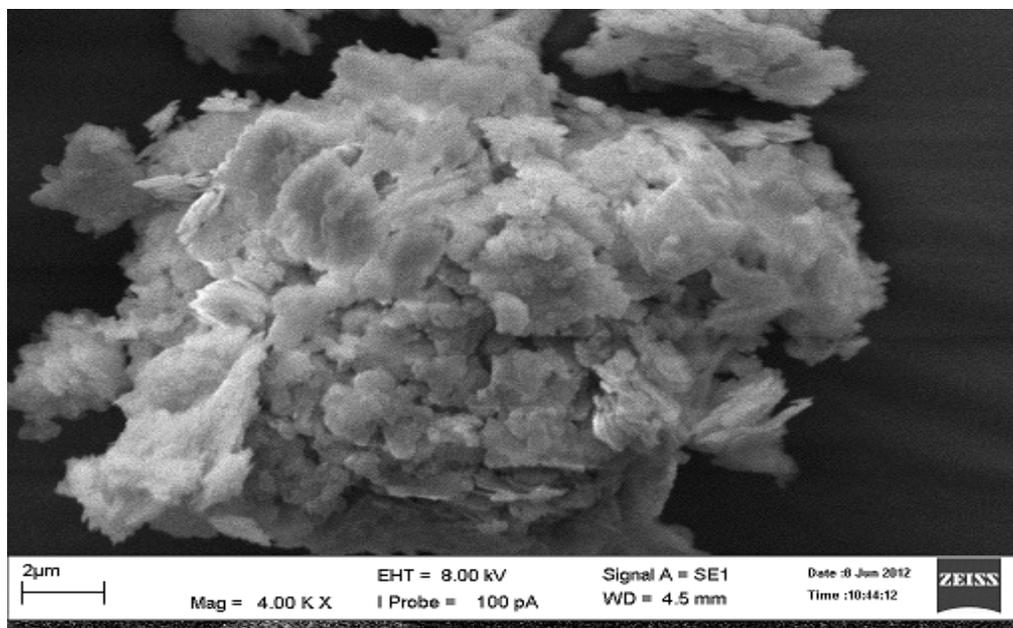
(c)

Figure 4.1: SEM images of (a) raw Kaolin (Mag = 2500 X) (b) ZnS-Kaolin prepared from Hydrothermal method (Mag = 4000 X) and (c) ZnS-Kaolin prepared from Impregnation method (Mag = 4000 X).

Figure 4.1(a) shows the morphological surface of raw kaolin particles, where the scattering of hexagonal flakes were piled up on top of one another and exhibit consistent distribution of pores (Chong et. al., 2008).

Figure 4.1(b) shows the morphological surface of ZnS-Kaolin prepared from hydrothermal method. The figure shows many leaf-like layers with curled edge were produced. This is due to coagulation process in which the surface charges of Kaolin was compensated by $HTAC^+$ cations and the hydrophilic surface of the Kaolin become partly hydrophobic due to presence of surfactant, HTAC molecules. It can also be seen that the nanoparticles of ZnS were homogeneously dispersed on the exfoliated sheets of Kaolin. The nanoparticles of ZnS are deposited on Kaolin layers. This shows that Kaolin can act as a support for ZnS nanoparticles (Miao et. al., 2006). Figure 4.1(c) shows the morphological surface of ZnS-Kaolin prepared from Impregnation method. The figure exhibits

the similar morphology with ZnS-Kaolin prepared from hydrothermal method except for that leaf-like layers produced are more than produced in Hydrothermal method. It can be seen that the nanoparticles of ZnS are deposited on the exfoliated sheets of Kaolin (Miao et. al., 2006).

4.1.3   Thermal Gravimetric Analysis (TGA)

The weight loss as a function of temperature for ZnS-Kaolin prepared from hydrothermal method and Impregnation method were shown in Figure 4.2(a) and (b), respectively.

(a)

(b)
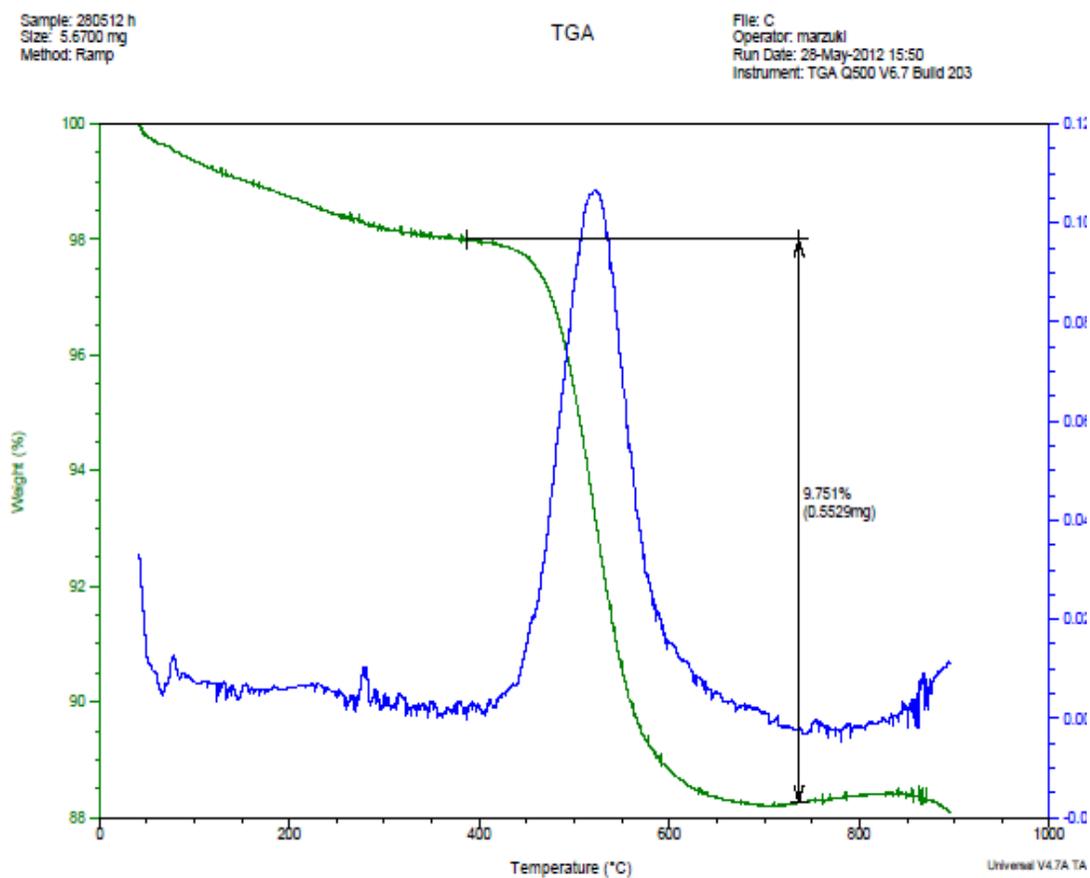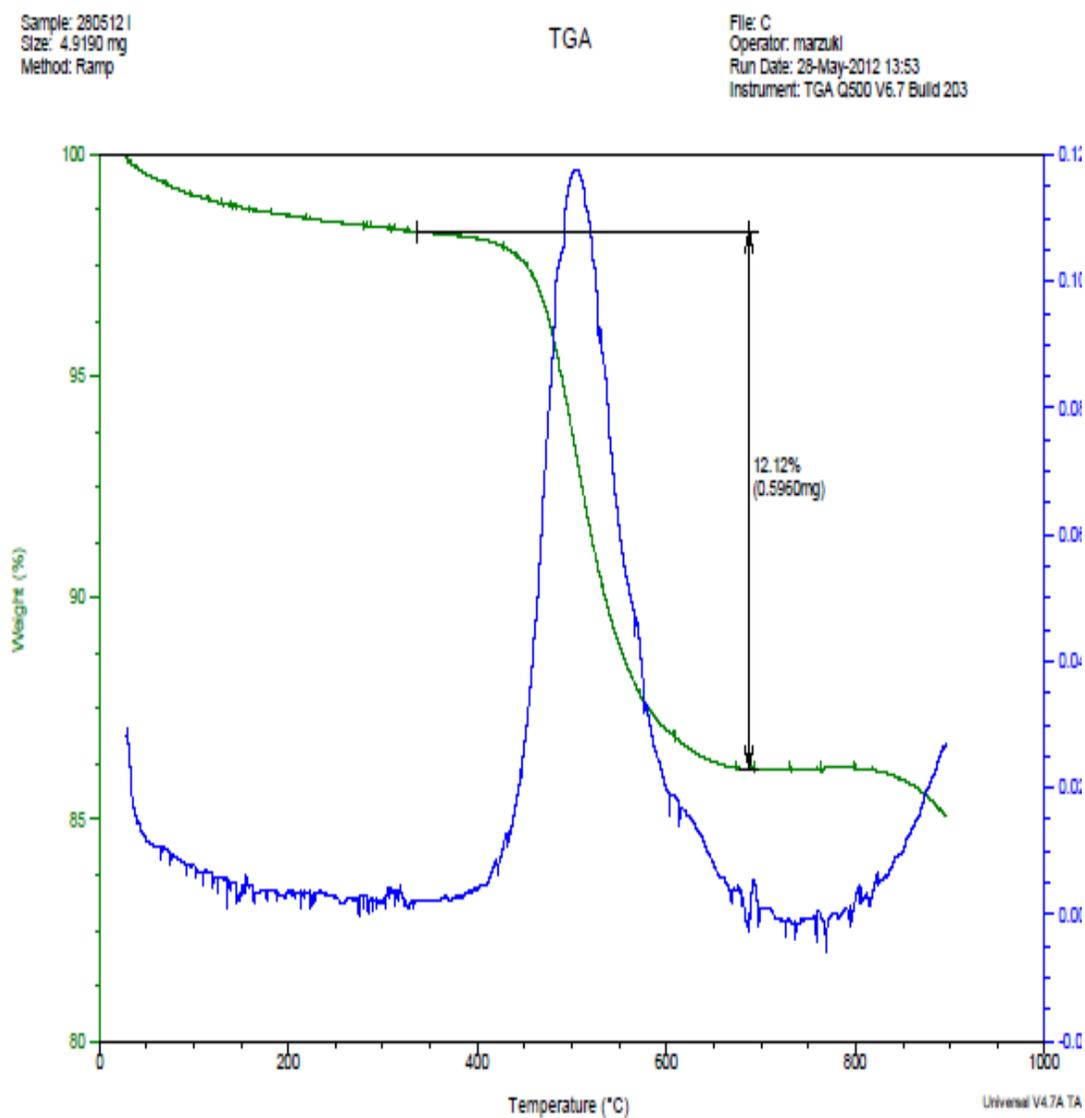
Figure 4.2: Thermo gravimetric images of (a) ZnS-Kaolin prepared from Hydrothermal method and (b) ZnS-Kaolin prepared from Impregnation method

Figure 4.2(a) shows that ZnS-Kaolin prepared from Hydrothermal method loses weight of 9.751 % which corresponds to 0.5529 mg at temperature between 390 °C and 740 °C.

This loses is due to moisture loses. The decomposition takes place at temperature above than 740 ºC.

Figure 4.2(b) shows that the ZnS-Kaolin prepared from Impregnation method loses weight of 12.12 % which is corresponds to 0.5960 mg at temperature between 340 ºC and 690 ºC. This loses is due to moisture loses. The decomposition takes place at temperature above than 690 ºC.

Thermal Gravimetric Analysis (TGA) shows that ZnS-Kaolin prepared from Impregnation method contain 2.449 % water content or moisture more than ZnS-Kaolin prepared from hydrothermal method.

The decomposition of ZnS-Kaolin prepared from Impregnation method occurred at temperature lower than the temperature needed for ZnS-Kaolin prepared from hydrothermal method. This shows that ZnS-Kaolin prepared from hydrothermal method has high thermal resistance compared to ZnS-Kaolin prepared from Impregnation method.

4.2   Photoreduction of CO_2

The performance of ZnS-Kaolin used in photoreduction process of CO_2 was observed by the formation of methanol in photoreduction process. HPLC was used to analyze the concentration of methanol produced. The concentrations of methanol produced were measured from the methanol calibration curve as shown in Appendix A.

4.2.1   Effect of dosage of catalyst

In this study, 0.50 and 0.75 g of ZnS-Kaolin catalysts prepared from Hydrothermal and Impregnation method were studied and the results were shown in Figure 4.4.
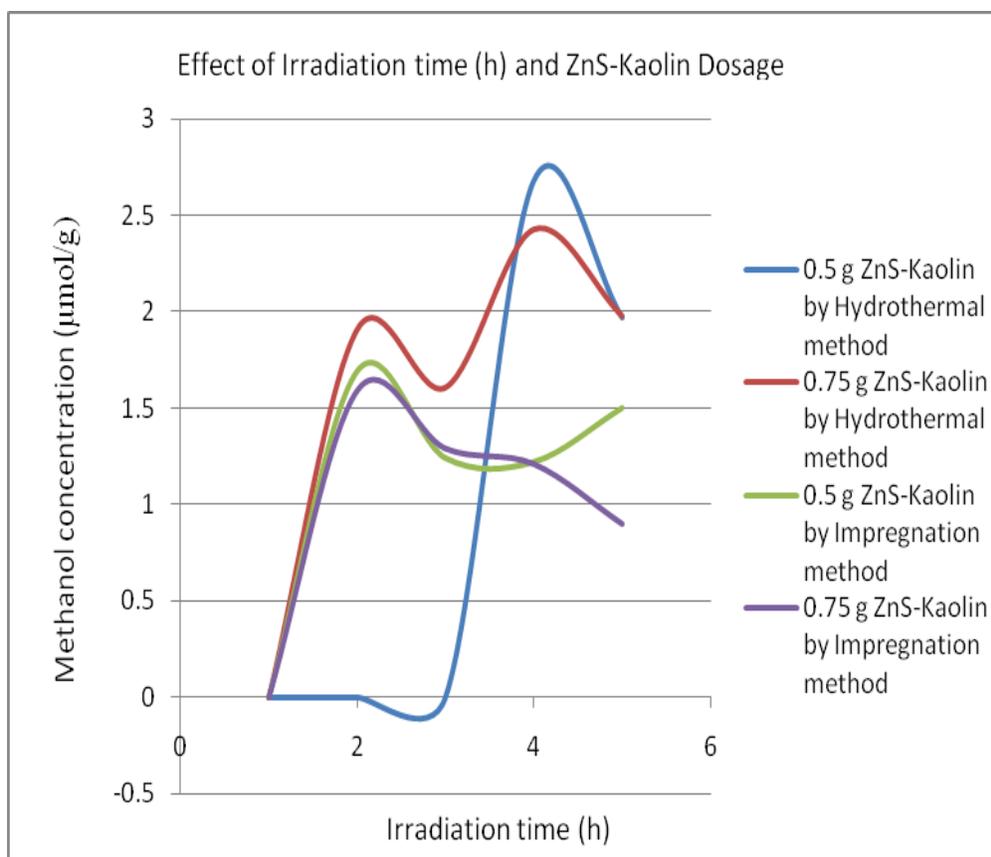
Figure 4.3: Effect of Dosage of ZnS-Kaolin

From this Figure 4.3, it can be seen that the formation of methanol for ZnS-Kaolin prepared from Hydrothermal method with dosage of 0.50 g occurred after 3 hours irradiation of UV light. The concentration increases up to 2.68 µmol/g after 3 hours and decreased to 1.97 µmol/g after 4 hours.

When the dosage of ZnS-Kaolin was increased to 0.75 g, the formation of methanol which is 1.91 µmol/g started at earlier hour which is after 1 hour of irradiation. The concentration however decreased to 1.61 µmol/g in the next hour and then increased again to 2.43 µmol/g at third hour and as similar to ZnS-Kaolin with dosage of 0.50 g, the concentration of methanol decreased to 1.98 µmol/g after 4 hours of irradiation. For the 0.50 g of ZnS-Kaolin catalyst prepared by Impregnation method, the formation of methanol occurred after 1 hour of irradiation which is 1.69µmol/g. The concentration of methanol produced decreases to 1.24 µmol/g after 2 hours of irradiation and then decreased again

to 1.22 µmol/g after 3 hours of irradiation. After four hours irradiation time, the concentration of methanol increased to 1.50µmol/g.

Then, when the dosage of the ZnS-Kaolin was increased up to 0.75 g, the production of methanol occurred after 1 hour irradiation but with lower concentration which is 1.59 µmol/g and continued to decrease after 2 hours and 3 hours of irradiation to 1.29 µmol/g and 1.21 µmol/g, respectively. The concentration then decreased again after 4 hours of irradiation which is 0.90 µmol/g. The concentration of methanol produced was decreased compared to methanol production using 0.50 g of catalyst dosage. This is due to some errors that encountered during the experiment, which are inconstant flow of CO_2 and UV light irradiation. Formation of methanol should be increase when the dosage of catalyst increases until up to optimum dosage. This is because, when the catalyst dosage increased, more ZnS-Kaolin particles present in the process. The specific surface area available for photoreduction of CO_2 hence is higher. The increasing of specific surface area will increase the active sites for photoreduction (Slamet et. al, 2005).

4.2.2   Effect of irradiation time

In addition, the photocatalytic activity of ZnS-Kaolin at different irradiation time which were at 0, 1, 2, 3 and 4 were observed. The results were shown in Figure 4.5.
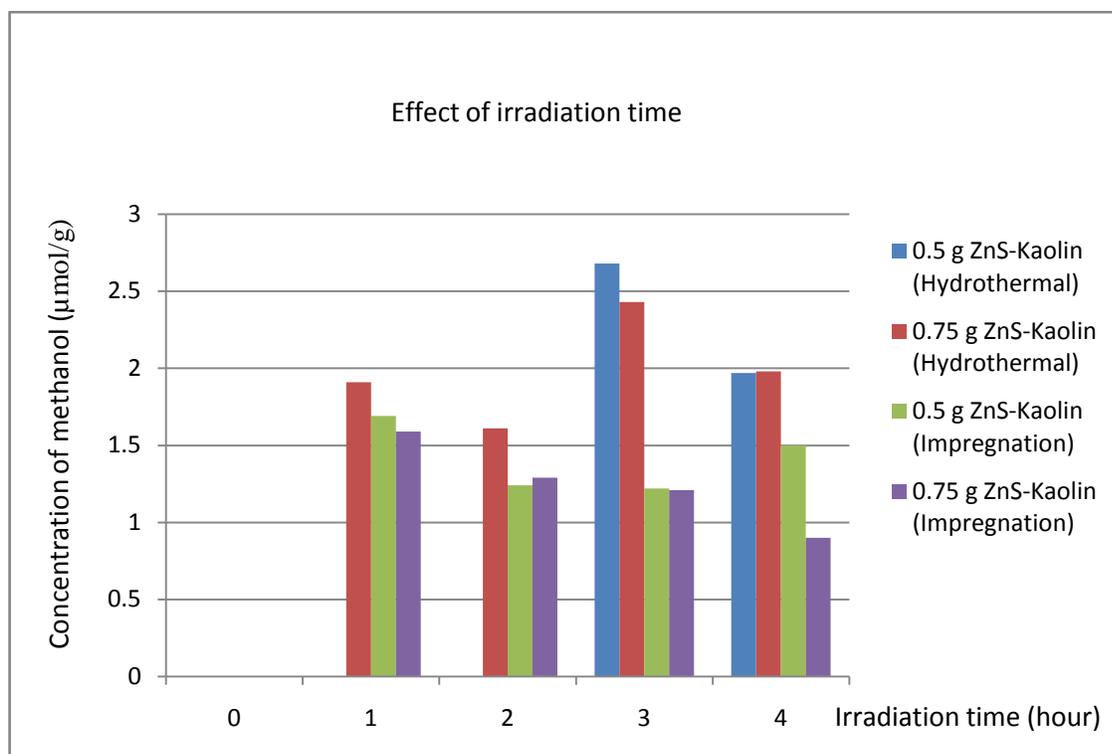
Figure 4.5: Effect of irradiation time

Figure 4.5 shows the effect of irradiation time on photoreduction process of CO_2. It can be seen that at initial time, which is no UV light irradiation, there are no methanol formation.

After 1 hour of irradiation, the maximum yield of methanol which is 1.91 µmol/g was produced when using 0.75 g of ZnS-Kaolin prepared from Hydrothermal method. However, after 2 hours of irradiation, the maximum yield of methanol which is 1.61 µmol/g was produced when using 0.75 g of ZnS-Kaolin prepared from Hydrothermal method that showing decrement of the methanol yield. After 3 hours of irradiation the maximum yield increased to 2.68 µmol/g by using 0.50 g of ZnS-Kaolin prepared from Hydrothermal method. The methanol yield however decreased again to 1.98 µmol/g after 4 hours of irradiation by using 0.75 g of ZnS-Kaolin prepared from Impregnation method. The results have been fluctuated due to some handling and equipment error that occurred during the

experiment. The yield of methanol should be increased as irradiation time increases. This is because when more irradiation time increases, the chances of photoexcitation will be increased (Yamashita et. al., 2007).

4.3   Performances of the prepared catalyst

In comparison, ZnS-Kaolin prepared by Hydrothermal method yielded higher concentration of methanol compared to ZnS-Kaolin prepared by Impregnation method. This was shown in the Table 4.1.

Table 4.1: Concentration of methanol at different parameters

| Type of catalyst | Parameter | | Methanol concentration (µmol/g) |
	Dosage(g)	Irradiation time (hour)	
ZnS-Kaolin by Hydrothermal method	0.50	0	0
		1	0
		2	0
		3	2.68
		4	1.97
	0.75	0	0
		1	1.91
		2	1.61
		3	2.43
		4	1.98
ZnS-Kaolin by Impregnation method	0.50	0	0
		1	1.69
		2	1.24
		3	1.22
		4	1.5
	0.75	0	0
		1	1.59
		2	1.29
		3	1.21
		4	0.9

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.0 Conclusion

ZnS-Kaolin photocatalysts have been developed by using 2 different methods which are Hydrothermal and Impregnation method. The morphology and surface structure of the ZnS-Kaolin and the weight loss as a function of temperature have been characterized by using SEM and TGA respectively. For SEM analysis, it was found that raw Kaolin was constructed from hexagonal flakes structure. Meanwhile, both ZnS-Kaolin prepared from Hydrothermal and Impregnation methods are consists of leaf-like layers structure with ZnS nanoparticles deposited on Kaolin structure. From TGA analysis, it was found that ZnS-Kaolin prepared from Hydrothermal method has high thermal resistance compared to ZnS-Kaolin prepared from Impregnation method. In photoreduction process of CO_2, ZnS-Kaolin prepared from Hydrothermal method shows better performance due to higher methanol production compared to ZnS-Kaolin prepared from Impregnation method. However, the effect of parameters such as effect of UV light irradiation time and dosage of ZnS-Kaolin used were different from the expected results. In the process, the concentrations of methanol were fluctuated as the irradiation time and dosage of ZnS-Kaolin used increased. This is due to the some equipment and procedures handling errors have been identified occurred during the experiment which leads to these fluctuated results.

5.2   Recommendations

There are some recommendations proposed for the future study which are:

- In preparation of ZnS-Kaolin photocatalyst, ion-exchange and sol-gel method will be studied in order to compare the performance of photocatalyst with the available photocatalyst prepared.

- In photoreduction process of CO_2, other solvents such as water and propanol will be studied to investigate the efficiency of solvents in methanol production.

- Other parameters such as effect of pressure and temperature will be studied.

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Appendix A

Calibration curve of Standard methanol

Standard of methanol

y = 8.5442x - 2.0257
R² = 0.8412

Area (mAU*s)

Concentration of methanol (%, v/v)