EFFECT OF SOLVENTS AND TEMPERATURES ON PHOTO-REDUCTION OF CARBON DIOXIDE USING ALUMINA DOPED TIO_2 CATALYSTS

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A thesis submitted to the Faculty of Chemical and Natural Resources Engineering in partial fulfillment of the requirement for the Degree of Bachelor of Engineering in Chemical Engineering (Gas Technology)

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

SUPERVISOR 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 Degree of Bachelor of Chemical Engineering (Gas Technology)”

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STUDENT DECLARATION

I declare that this thesis entitled "*Effect of Solvents and Temperatures on Photo-Reduction of Carbon Dioxide Using Alumina Doped Tio$_2$ Catalysts*" 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 other degree.

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Date : 31st JANUARY 2013

In the name of ALLAH, Most Gracious, Most Merciful

To my beloved father, mother and siblings.

ACKNOWLEDGEMENT

In the name of Allah S.W.T the Most Beneficent and the Most Merciful. The deepest sense of gratitude to the Almighty for the strength and ability to complete this final year project. Infinite thanks I brace upon Him.

I would like to take this opportunity to express my sincere appreciation to my supervisor Madam Nor Khonisah Binti Daud for encouragement, guidance, morale support, and critics in bringing this project fruition. Without her outstanding support and interest, this thesis would not been at the best it would right now.

I would also like to express my deepest appreciation to my father and mother whom always support me and motivate me to complete this final year project.

Last but not least, I am also in debt to Faculty of Chemical and Natural Resources Engineering for the usage of workstation lab for my research. My sincere appreciation also extends to all my colleagues, housemates, and friends whom had provided assistance at various occasions.

Finally to individuals who has involved neither directly nor indirectly in succession of this thesis. Indeed I could never adequately express my indebtedness to all of them. Thank you.

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ABSTRACT

Photo-reduction is the most promising method to reduce carbon dioxide to a valuable product such as methanol. Apart of a simple process, photo-reduction also has a great potential to become a method for renewable energy in the future. In this study, the effects of solvents and temperatures in photo-reduction of CO_2 were examined. The sol-gel method used for Al_2O_3-TiO_2 catalysts preparation was also reported. The result shows for both solvents which are H_2O and NaOH were able to react with CO_2 to concentration methanol. Somehow, solubility of CO_2 in NaOH is rather higher than H_2O to concentration the methanol. The result analysed shown that the concentration of methanol in both NaOH and H_2O were increasing with time. Somehow, the application of NaOH as solvent has shown better result compared to H_2O where the concentration of methanol in NaOH was always greater than H_2O for every time elapsed. The highest concentration of methanol in NaOH was 63 ng/µL while 43 ng/µL in H_2O. Meanwhile, the effectiveness of temperatures shown the highest concentration of methanol was found at T= 60 ^{o}C. Since the boiling point of methanol is 65 ^{o}C, the production of methanol was limited. The liquid phase of methanol has changed to vapour phase which leads to the concentration of methanol was maximized within the ranges of temperatures as analyzed.

KESAN PELARUT DAN SUHU PADA FOTO REDUKSI KARBON DIOKSIDA MENGGUNAKAN KATALIS ALUMINA DIDOPKAN TIO_2

ABSTRAK

Foto-reduksi adalah cara yang paling menjanjikan untuk menukarkan karbon dioksida menjadi produk yang berharga seperti metanol. Selain dari proses yang mudah, foto-reduksi juga memiliki potensi besar untuk menjadi sebuah cara untuk pembaharuan tenaga pada masa hadapan. Dalam kajian ini, pengaruh pelarut dan suhu dalam foto-reduksi CO_2 telah diperiksa. Cara sol-gel digunakan untuk penyediaan Al_2O_3-TiO_2 katalis juga dilaporkan. Hasilnya menunjukkan untuk kedua-dua pelarut iaitu H_2O dan NaOH mampu bertindak balas dengan CO_2 untuk menghasilkan metanol. Walau bagaimanapun, kelarutan CO_2 di NaOH agak lebih tinggi berbanding H_2O untuk menghasilkan metanol. Hasilnya dianalisis menunjukkan bahawa kepekatan metanol dalam kedua-dua NaOH dan H_2O meningkat dengan masa. Namun, apabila NaOH digunakan sebagai pelarut telah menunjukkan hasil yang lebih baik berbanding H_2O dimana kepekatan metanol dalam NaOH adalah sentiasa lebih besar berbanding H_2O untuk setiap masa berlalu. Kepekatan tertinggi metanol dalam NaOH ialah 63 ng / μL manakala 43 ng / μL dalam H_2O. Sementara itu, keberkesanan suhu telah menunjukkan hasil tertinggi metanol didapati di $T = 60\ ^oC$. Takat didih metanol ialah 65 ^oC, maka penghasilan metanol menjadi terhad. Fasa cecair metanol telah berubah menjadi fasa wap yang membawa kepada hasil metanol telah dimaksimumkan dalam julat suhu sebagaimana di analisa.

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CHAPTER ONE

INTRODUCTION

1.0 Research Background

Carbon dioxide (CO_2) is the most significant component for greenhouse gas produced by human activities. The main source of CO_2 production is the combustion of fossil fuels. Since the Industrial Revolution, the concentration of CO_2 has risen by more than 30 percent and grows up till now. One of the effects of excess CO_2 formation is global warming which lead to raise the sea level and melt the ice at the North Pole. The concentration of CO_2 in the atmosphere also becomes a toxic gas to human body. The effects to human are headache, sweating, restlessness, short of breath, increased heart beat and blood pressure and visual distortion (Robert and John, 1960).

It is important to treat the excess of CO_2 to be a useful product. Therefore, photo-catalytic reduction is the best method to achieve that purpose. According to this method,

CO_2 was transform to methanol by the presence of catalyst. In this study, Al_2O_3/TiO_2 catalyst was used in photo-catalytic reduction process assisted by UV light.

Photo-catalytic reduction process is the acceleration of a photoreaction in the presence of a catalyst. Photo-catalytic reduction of CO_2 process is used UV light as energy to break the CO_2 bonds and lead to the production of methanol. Al_2O_3 catalyst is widely used in different industrial chemical processes such as hydrodesulphurization, dehydration and cracking. As transition alumina has higher surface area and chemical activity, it has been used extensively as a catalyst or catalyst support because of the excellent properties such as high surface area, good catalytic activity, good mechanical strength, high hardness, and transparency. Generally, Wang et. al., (2005) stated that the stabilization of alumina can be promoted by doping it with foreign elements such as alkaline-earth metals, rare-earth metals and silicon. In this study, metal alumina was doped with TiO_2 as a heterogeneous catalyst in photo-reduction process to produce methanol as a valuable product.

Methanol is widely used in various fields. It is not only for heating purpose, but also important to form goods. About 40 % of methanol is converted to formaldehydes diverse as plastics, plywood, paints, explosives, and permanent press textiles. Another application of methanol is used as a solvent and antifreeze in pipelines and windshield washer fluid. In some wastewater treatment plants, a small amount of methanol is added to wastewater to provide a carbon food source for the denitrifying bacteria, which convert nitrates to nitrogen to reduce the nitrification of sensitive aquifers (Valerie et. al., 2003).

Methanol has a long history of use in racing vehicles where it is valued both its power producing properties and its safety aspects where methanol is harder to ignite, creates less radiant heat and burns without producing black smoke. Methanol use in non-racing vehicles has been much less successful. There was significant interest in using methanol as a gasoline blending component for its octane value and emissions. Several methanol or co-solvent blends were approved for use but the oxygenate methyl tertiary butyl ether which used methanol in its manufacture was preferred (Richard et. al., 2007).

The concentration of CO_2 in atmosphere seems need to be reduced as maximum as we can so that the global warming phenomena can be reduced to the minimum level. The photo-catalysis reduction of CO_2 to methanol contributes a lot of benefit to the world. This study was focused on two types of solvents which were NaOH and H_2O to find the best solvent in photo-catalytic reduction process. Effect of reaction temperature in photo-catalytic reduction process was also studied in range of 30 ^{o}C to 120 ^{o}C.

1.1 Problem Statement

Nowadays, the concentration of CO_2 in atmosphere is getting higher. Due to the difficulties to reduce or treat CO_2 in environment, photo-catalytic reduction of CO_2 is the most promising method compared to conventional method to convert CO_2 to valuable products such as methanol.

Treating CO_2 is very important due to the long term effects to the environment. In conjunction to that purpose, photo-reduction process assisted with catalyst is the best method to be considered to treat CO_2 due to the process will converting CO_2 to methanol or methane without produces more poisonous gaseous.

1.2 Research Objectives

The objectives of this study are:

- To study the best solvents in photo-catalytic reduction of CO_2.
- To study the effect of temperature on photo-catalytic reduction process.

1.3 Scopes of Study

Titanium dioxide, (TiO_2) was selected as a catalyst in photo-reduction process due to its photo-stability, non-toxicity, redox efficiency and availability. Recently, it was shown that this self-organized TiO_2 exhibit very high photo-catalytic efficiency that can be used for the decomposition of organic compounds in the contact mode either in the Ti substrate or in flow-through UV irradiated membranes. The decomposition efficiency can be further enhanced by using a bias voltage or by coating TiO_2 with noble metal nanoparticles as stated by Kalbacova et. al., (2008).

According to Miyazaki and Iaon, (n.d) said that various chemical species especially ions, are known to be absorbed onto alumina. Thus, alumina is a typical support for the catalyst. In photo-reduction process, they are a lot of metal supported catalysts are prepared using alumina as their support. Therefore, in this study Al_2O_3/TiO_2 as heterogeneous catalyst was used in photo - reduction process to convert waste to useful product.

1.4 Organization of the Thesis

This thesis consists of five chapters. In chapter one which is introduction was generally to identify all related elements for this study. The topic discussed in this chapter was introduction to CO_2, Al_2O_3-TiO_2 as a catalyst and methanol as a main product. The objectives and the scope of the experiment were also stated in this chapter.

Chapter two is the Literature Review where all elements stated in Chapter one were elaborated in more details. At the beginning of this chapter, the introduction to CO_2 was spoken in large aspects where the causes, processes, advantages and disadvantages of CO_2 were revealed. Next part is photo-reduction process of CO_2. In photo-reduction process, there were several elements were discussed. They were catalysts, solvents and temperatures. Then, the last part was discussed about methanol as a main product. In this part, the introduction to methanol was exposed in more specific where the concentrations of methanol and usage and alternatives route for methanol production were discussed.

The processes to obtain methanol was described on chapter three which labelled as methodology. In this part, all the steps from the very early to the end were clearly described. First step was the preparation of catalysts via sol-gel method. Then, the photo-reduction process was done regarding to the both parameters which were effects of solvents and reaction temperatures. The last part was analysis by using high performance liquid chromatography (HPLC). In this part, the procedures to obtain methanol were extended to the chapter four.

Chapter four is the part for results and discussion. In this part, the graphs were plotted to identify the highest concentration of methanol for every parameters. Then, the variation of the results were also discussed where the problem and weakness of the method used was defined.

Finally, chapter five is the part to conclude the experiment according to the result obtained. In this part also, several suggestions were inspired to deliver better result for the future.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction to Carbon Dioxide (CO_2)

Asian Global Atmosphere Watch (GAW) Greenhouse Gases Newsletter, (2010) was reported that greenhouse gases such as carbon dioxide (CO_2), methane (CH_4) and chlorofluorocarbons (CFCs) are the primary causes of global warming. Among them, CO_2 is released mainly by the burning of fossil fuels. Over the past decades, the atmospheric concentration of CO_2 has been increasing owing to the expanded human activity, which consequently has accelerated the greenhouse effect. On the other hand, the consumption of fossil fuels worldwide gradually increases year after year because of the strong demand for human activities. Therefore, converting CO_2 to valuable hydrocarbons is one of the best solutions to both the global warming and the energy shortage problems (Hussain et. al., 2003).

In nature, CO_2 is removed from the environment by photosynthesis. The energy obtained from sunlight is ultimately used to convert CO_2 into glucose or a sugar molecule that stores sun energy in the form of chemical energy. Except geothermal or nuclear energy, most energy forms, such as fossil fuel, bio-material, hydropower and wind are simply transformations of sun energy either in the past or present. Thus, solar energy is the Earth’s ultimate energy supply. One of the promising routes is that artificial photosynthesis may be implemented via the photo-reduction of CO_2 to produce hydrocarbons. Therefore, solar energy is directly transformed and stored as chemical energy.

Jeffrey (2009) was stated that photo-catalytic reduction of CO_2 whose transform to chemicals such as methane or methanol is particularly interesting and achieving a high efficiency for this reaction and extremely desired. Methanol can be easily transported, stored and used as gasoline-additives for automobiles. Moreover, methanol can be transformed into other useful chemicals using conventional chemical technologies.

2.1 Photo-Reduction of CO_2

The energy grade of CO_2 is low from a thermodynamic perspective, which is why any transformation to hydrocarbon requires energy infusion. **Eq. (2.1)** gives an example of the overall photo-reduction of CO_2 to methanol as stated by Jeffrey (2009).

$$CO_2 + 2H_2O \xrightarrow{hv} CH_3OH + 3/2O_2 \text{.............................. (2.1)}$$

Based on thermodynamics as stated by Jeffrey (2009), converting one mole of CO_2 into methanol requires 228 kJ of energy at 298 K. Furthermore, the Gibbs free energy of **Eq. (2.1)** is 698.7 kJ at 298 K indicating that the equilibrium is highly unfavorable to the product, methanol and oxygen. The energy source should be provided without producing more CO_2.

Photo-catalytic reduction is defined as "acceleration by the presence of a catalyst". A catalyst does not change in itself or being consumed in the chemical reaction. This definition includes photosensitization, a process by which a photochemical alteration occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity called the photosensitized (Marta et. al., 2011).

2.2 Efficiency of CO_2

Nature captures and recycles atmospheric CO_2 efficiently in its photosynthetic cycle. To chemically recycle CO_2 to methanol, it is necessary to be able to capture it from industrial or natural sources conveniently and economically in a pure form. This is currently best achieved by capturing and recycling CO_2 from sources where it is present in a sufficiently high concentration, through physical-chemical absorption and desorption cycles coupled when needed with chemical purification particularly from H_2S, SO_2 and other accompanying pollutants (George et. al., 2008).

2.3 Significance of CO_2 recycling for methanol production

The recycling of CO_2 from industrial or natural emissions and capture of CO_2 from the atmosphere provides a renewable, inexhaustible carbon source and could also allow the continued use of derived carbon fuels in an environmentally carbon neutral way. As discussed presently, the captured CO_2 would be stored/sequestered in depleted gas and gas and oil- fields, deep aquifers, underground cavities, at the bottom of the seas, etc. This, however, does not provide a permanent safe solution, nor does it help our future needs for fuels, hydrocarbons, and their products (George et.al., 2008).

Recycling of the CO_2 via its chemical reduction with hydrogen to produce methanol offers in contrast a viable new permanent alternative. As fossil fuels are becoming scarcer, capture and recycling of CO_2 and eventually atmospheric CO_2 would continue to support production and use of carbon-containing fuels such as methanol, DME, and all the synthetic hydrocarbons and their needed products. We do not believe that humankind is facing an energy crisis. We are, after all in the final analysis, obtaining most of our energy in one form or another from the sun. Using this approach, there will be no need to change drastically the nature of our energy use, storage, and transportation infrastructure or the continued use of synthetic hydrocarbons and products. As CO_2 is available to everybody on Earth, it would liberate us from the reliance on diminishing and nonrenewable fossil fuels frequently present only in geopolitically unstable areas (George et. al., 2008).

2.4 Introduction to Catalyst

Catalyst can be defined as a substance that causes or accelerates a chemical reaction without itself being affected. Catalyst usually used in small amounts relative to the reactants that modifies and increases the rate of a reaction without being consumed in the process (Ricardo et. al., 2006).

2.4.1 Alumina (Al_2O_3)

Al_2O_3 catalysts are widely used in different industrial chemical processes such as hydrodesulphurization, dehydration, cracking and others. Most of the Al_2O_3 produced commercially is obtained by the calcinations of aluminum hydroxide which also frequently termed alumina tri-hydrate or ATH. The aluminum hydroxide is virtually all made by the Bayer Process. This involves the digestion of bauxite in caustic soda and the subsequent precipitation of aluminum hydroxide by the addition of fine seed crystals of aluminum hydroxide (Gaurav et. al., 2010).

As transition alumina has higher surface area and chemical activity, it has been used extensively as a catalyst or catalyst support because of the excellent properties such as high surface area, good catalytic activity, good mechanical strength, high hardness and transparency. But, when it is used at higher temperature such as the catalytic combustion of hydrocarbons and catalytic purification for the exhaust of vehicle, the superiority of alumina will lose in both structural grounds (transformation of active alumina to corundum) and textural grounds (loss of surface area and porosity). It is the reason that increasing physical properties and thermal stability of transition alumina is of primary industrial interest (Xiaohong et. al., 2005).

Generally, the stabilization of alumina can be promoted by doping it with foreign elements such as alkaline-earth metals, rare-earth metals and silicon, and by improving the synthesis method or by a combination of two means above (Xiaohong et. al., 2005).

2.4.2 Titanium Dioxide (TiO_2)

TiO_2 is a fine white powder. It is more effectively than any other white pigment. Therefore, TiO_2 are highly used to whitening product. TiO_2 is one of the most applied and important material used by the paints and plastics industry for whiteness and opacity (Chor et. al., 1992).

TiO_2 particularly in the anatase form, is a photo-catalyst under ultraviolet (UV) light. Recently, it has been found that TiO_2, when spiked with nitrogen ions or doped with metal oxide like tungsten trioxide, is also a photo-catalyst under either visible or UV light. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic materials directly. TiO_2 is thus added to paints, cements, windows, tiles, or other products for its sterilizing, deodorizing and anti-fouling properties and is used as a hydrolysis catalyst. It is also used in dye-sensitized solar cells, which are a type of chemical solar cell (Ana-Lilia and Juan-Carlos, 2008).

The photo-catalytic properties of TiO_2 were discovered by Akira Fujishima in 1967 and published in 1972. The process on the surface of TiO_2 was called the Honda-Fujishima effect. TiO_2 has potential for use in energy production. As a photo-catalyst, it can carry out hydrolysis where it can break water into hydrogen and oxygen. As the hydrogen collected, it could be used as a fuel. The efficiency of this process can be greatly improved by doping the oxide with carbon. Further efficiency and durability has been obtained by introducing disorder to the lattice structure of the surface layer of TiO_2 nano-crystals, permitting infrared absorption (Afendi and Mutalib, 2009).

2.4.3 Mechanism of titanium dioxide (TiO_2)

When photo-catalyst TiO_2 absorbs ultraviolet (UV) radiation from sunlight or illuminated light source (fluorescent lamps), it will produce pairs of electrons and holes. The electron of the valence band of TiO_2 becomes excited when illuminated by light and the mechanism of photo-catalysis is shown in **Fig. 2.1**. The excess energy of this excited electron promoted the electron to the conduction band of TiO_2, therefore creating the negative electron (e^-) and positive hole (h^+) pair. This stage is referred as the semiconductor's 'photo-excitation' state. The energy difference between the valence band and the conduction band is known as the 'Band Gap '. Wavelength of the light necessary for photo-excitation is 388 nm (Nano Protection, n.d).

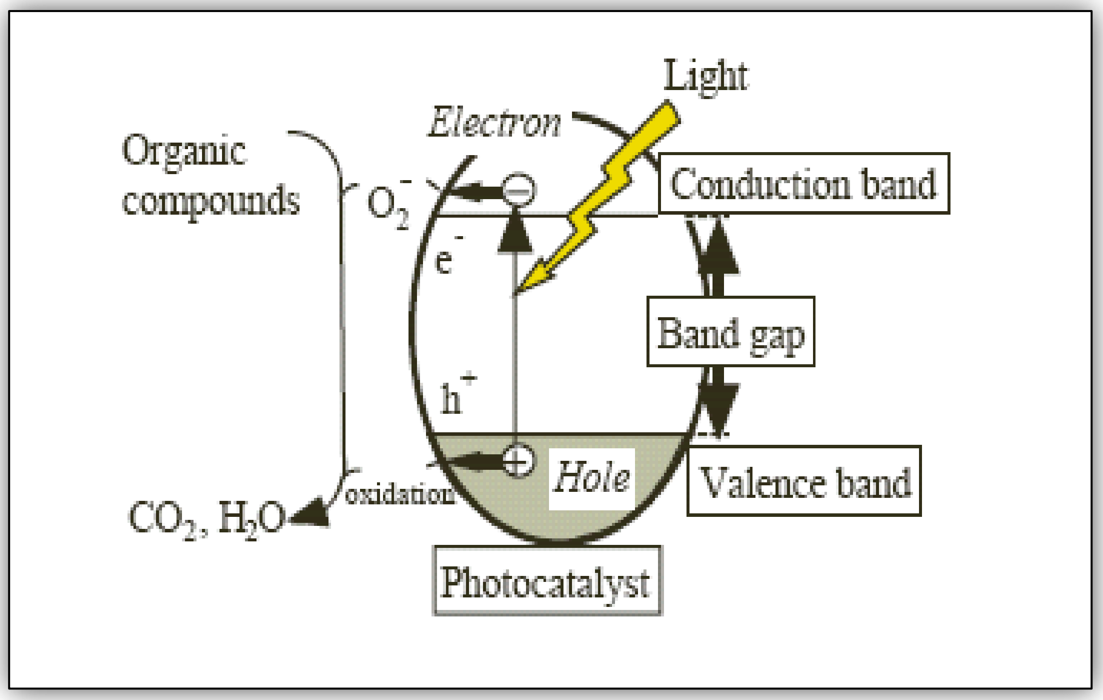


Fig. 2.1: Mechanism of Photo-reduction (MCH Nano Solution, n.d.)

The positive-hole of TiO_2 breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available (kathirvelu et. al., 2008).

2.5 Effect of Solvents

In this experiment, solvent was used in order to complete one reaction cycle. As the appearance of solvent is justified, it will change the production quality. The ratio of products was greatly influenced by the kind of solvent and increased dielectric constant of the solvent. Solvent is very important for the production purpose. It can determine what the product formed. For example, if propylene carbonate was used as the solvent, methanol is produced with the bulk TiO_2 photocatalyst. Meanwhile, photo-catalytic reduction of CO_2 on the alumina doped TiO_2 film in acetonitrile in the presence of 2-propanol was resulted in the formation of formate and carbon monoxide as the reduction products (Liu et. al., 1997).

Another effect of solvent is polarity. As for photochemical reduction process, the selectivity of the formation of CO and/or HCOOH is determined by the adsorption strength of CO. If a metal electrode, such as a transition metal, that allows strong adsorption of CO is used, the negative charge of the oxygen atom of CO will increased as a result of back-donation from an occupied metal orbital to an unoccupied CO_2

orbital. Then, protonation is promoted to break the oxygen atom from the anion radical to yield carbon monoxide as the reduction product. When low polar solvents such as CCl_4 and CH_2Cl_2 are used, the CO^- with anion radicals formed may be adsorbed strongly on Ti sites of the TiO_2 because the anion radicals are not highly solvated in solvents of low polarity (Liu et. al., 1997).

The negative charge of one oxygen atom of CO^- is increased as mentioned above. Carbon monoxide formation occurs readily with removal of the oxygen atom of the CO^- anion radical by a proton. If solvents of high dielectric constant such as water and propylene carbonate are used, the CO^- anion radicals formed may be greatly stabilized by the solvents resulting in weak interaction with the photo-catalyst surface. Then the carbon atom of the CO^- anion radical tends to react with a proton to give formate. It is concluded that the polarity of solvents used in the photo-reduction of CO_2 plays the most crucial role in determining the kind of reduction products either CO or formate (Liu et. al., 1997).

2.5.1 Water as Solvent

Water is a good solvent due to its polarity. The solvent properties of water are vital in biology, because many biochemical reactions take place only within aqueous solutions. When an ionic or polar compound enters water, it is surrounded by water molecules. The relatively small size of water molecules typically allows many water molecules to surround one molecule of solute. The partially negative dipoles of the water are attracted to positively charged components of the solute, and vice versa for the positive dipoles (Giakos, 2006).

According to Ikeue et. al., (n.d), in photo-catalytic reduction of CO_2 using Ti-β zeolite catalyst, the final products were CH_4 and CH_3OH. They conclude that water molecules can more easily gain access to the tetrahedral coordinated titanium oxide species, Ti-β(OH), but high selectivity for the formation of CH_3OH was observed on Ti- β(F). Meanwhile, higher copper dispersion and smaller copper particles on the titania surface correspond to a greater improvement in CO_2 photo-reduction performance by using sol-gel prepared Cu/TiO_2 as the catalyst and water as the solvent (Tseng et. al., n.d).

2.5.2 Sodium Hydroxide (NaOH) as Solvent

As stated by Tseng et. al., (n.d), photo-catalytic reduction of CO_2 by using NaOH as solvent can lead to the production of methanol by the presence of Cu/TiO_2 as catalyst and emitted by 254 nm of UV light. They stated that higher copper dispersion and smaller copper particles on the titania surface correspond to a greater improvement in CO_2 photo-reduction performance as well as selectivity of methanol as major product when NaOH is applied as solvent for photo-reduction of CO_2 process.

NaOH solution was crucial in the photo-reduction of CO_2. The concentration of methanol substantially increased with the addition of NaOH in our experiments, perhaps due to the following two reasons. First, the high concentration of OH^- where ions in aqueous solution could act as strong hole-scavengers and form OH radicals thereby reduces the recombination of hole–electron pairs. The longer decay time of surface electrons would certainly facilitate the reduction of CO_2. Second, caustic NaOH solution dissolves more CO_2 than does pure water. The initial pH value of 0.20 N NaOH solutions was approximately 13.3 and decreased to nearly 7.3 after bubbling CO_2 in the reactor. Notably, photo-reduction may have been accelerated by the high concentration of HCO_3^- (Tseng et. al., 2002).

2.6 Effects of Temperature

Generally, photon irradiation is the primary source of energy for electron-hole pair formation at ambient temperature for photo-catalysts because the band gap energy is too high for thermal excitation to overcome. However, at high temperatures, the reaction rate can be increased by raising the collision frequency and diffusion rate. Fox et. al., (n.d) stated that, like most photoreactions, photo-catalytic reactions are not significantly sensitive to small variations of temperature.

Gokon et. al., (n.d) studied the effect of ZnO on carbon gasification with CO_2 at high temperature and observed that the presence of ZnO enhanced the CO evolution rate at the lower temperature of 873 K. However, the photo-catalytic effect cannot be induced at higher temperatures (>1037 K), where the carbon thermal reduction of ZnO dominates. This phenomenon occurs because the band-gap energy, chemical potential, and excited electron hole pair lifetime of ZnO decrease with increased temperature. In addition, the luminescence quantum yield of ZnO where the ratio of the number of photons emitted to the number of photons absorbed by the substance is reduced. This translates into lost potential for providing energy to stimulate molecules to the excited state.

Photo-reduction at high temperatures also was attempted using TiO_2 to photo-degrade CO_2 with water. The products CO, H_2, CH_4, and some longer-chain hydrocarbons were detected in small quantities at temperatures up to 700 K. This investigation concluded that high temperatures are beneficial to the rate of thermally activated steps such as desorption, which occur after photochemical reactions. Kohno et. al., (n.d) noted that the photo-excitation step of CO_2 with hydrogen over ZrO_2 can be deactivated with increased temperature. However, the photo-excitation step does not limit the reaction rate. Many researchers have concluded that the improved reaction rate must be due to the thermal step involved in entire reaction process.

2.7 Chronology of Methanol Production

Methanol was first produced as a minor byproduct of producing charcoal by destructive distillation of wood and was therefore called wood alcohol. Methanol produced this way was used in the 19th century for lighting, cooking, and heating purposes but was later replaced by cheaper fuels, especially kerosene. Up to the 1920s, wood was the only source for methanol, which was also needed in increasing quantities in the developing chemical industry. Beginning in the 1920s, the production of methanol from syngas, a mixture of CO and H_2, on an industrial scale was introduced by BASF in Germany. Whereas coal was initially used as a feedstock for the syngas, natural gas became the preferred feedstock after World War II. It offered higher hydrogen content and lower energy consumption and contained fewer harmful impurities such as sulfur, nitrogen, halogenated compounds, and heavy metals (George et. al., 2008).

Today, methanol is a primary raw material for the chemical industry. It is manufactured in large quantities for about 40 million tonnes in 2007 as an intermediate for the production of a variety of chemicals including formaldehyde, methyl *tert*-butyl ether, and acetic acid. Most of these chemicals are subsequently used to manufacture many products of our daily life including paints, resins, adhesives, antifreezes, and plastics. Besides being produced industrially and occurring naturally on earth to a small extent in fruits, and grapes, methanol has also been found recently in outer space. Astronomers have observed an enormous cloud of methanol around a nascent star in deep space that measures approximately 460 billion km across (George et. al., 2008).

Methanol has excellent combustion characteristics making it a suitable and proven fuel for internal combustion engine (ICE) driven vehicles. It contains only about half the energy density of gasoline but has a higher octane rating of 100 which was an average of the research octane number (RON) of 107 and motor octane number (MON) of 92. Due to its high octane rating and inherently safer than gasoline in case of fire safety, methanol has been used in race cars since the 1960s. Gasoline powered cars can be modified to run on methanol at a very modest cost. Flexible fuel vehicles (FFV) running on mixtures of methanol with gasoline, such as M15 or M85, containing 15 %

and 85 % of methanol, respectively, were used extensively commercially in the 1980s. In Brazil, close to 80 % of the cars produced are now FFVs able to run on any mixture of ethanol and gasoline whereas sugar cane based ethanol being available in Brazil at a low cost. The wide commercial use of methanol in ICE vehicles would therefore not represent any difficulty (George et. al., 2008).

2.8 Alternative Method to Produce Methanol as Fuel

The most direct and studied route to methanol from CO_2 is the catalytic regenerative conversion of CO_2 with hydrogen according to **Eq. (2.2):**

$$CO_2 + 3\,H_2 \longleftrightarrow CH_3OH + H_2O \text{ ……………………}(2.2)$$

This reaction has been known to chemists for more than 80 years. In fact, some of the earliest methanol plants operating in the U.S. on 1920 to1930s commonly used CO_2 for methanol production. This route was generally obtained as byproduct of other processes such as fermentation. More recently, efficient catalysts based on metals and their oxides in particular the combination of copper and zinc oxide have been developed for this conversion. As for example, Lurgi AG, a leader in the methanol synthesis process has developed and thoroughly tested a high activity catalyst for methanol production from CO_2 and H_2. In operating at a temperature around 260 °C, the activity was slightly higher than conventional methanol synthesis catalyst (George et. al., 2008).

2.9 Concentration of Methanol

Jeffrey et. al., (2005) was stated that concentration of methanol is proportional with UV irradiative intensity. In photo-reduction of CO_2 to methanol using optical-fiber photo-reactor with the presence of Cu/TiO_2 catalyst, the maximum methanol rate was 0.45 mmole/g_{cat}.h using 1.20 wt.% of Cu/TiO_2 catalyst at 1.29 bar of CO_2, 0.026 bar of H_2O, and 5000 s mean residence time under 16 W/cm^2 UV irradiation. If higher than 1.20 wt % of Cu loading will gave a lower rate of the concentration of methanol because of the masking effect of Cu_2O clusters on the TiO_2 surface.

According to Hsin et.al., (2003), the total concentration of methanol can be decreased if additional H_2 reduction of calcined catalysts before the photo-reduction CO_2 due to the change of copper dispersion and oxidation state. In photo-catalysis of Cu/TiO_2 in CO_2 photo-reduction using sol-gel procedure, the results indicated that the primary Cu served as an active site. The zeta potentials of catalysts were measured and compared showing that a higher positive zeta potential at pH 7 would lead to higher activity. Under 30-h UV (254 nm) irradiation, the best catalyst gave a concentration of methanol above 600 μmol/g_{cat}. Switching to UV (365 nm) resulted in a significant decrease of concentration of methanol in the range of 10 μmol/g_{cat}.

2.10 High Performance Liquid Chromatography (HPLC)

HPLC is a technique most commonly used for the quantitation of drugs in pharmaceutical formulations. HPLC involves the simultaneous separation and quantitation of compounds in a sample matrix that has been introduced onto a chromatographic column, packed with a stationary phase. Separation is achieved by the use of a stationary phase and a solvent, termed the mobile phase, that is allowed to flow through the stationary phase at a set flow rate, for isocratic chromatography (Dumortier et. al., 2001 and Meyer et. al., 2002).

During analysis, the sample components partition to differing degrees between a stationary and mobile phase, based on their inherent physic co-chemical properties (Meyer et. al., 2002). The nature of the physic co-chemical interaction between the mobile and stationary phase allows solute molecules to emerge from the column in individual component zones or bands, which are then monitored as a function of an appropriate detector response versus time.

HPLC separations, to a large extent, include liquid-liquid chromatography (LLC), liquid-solid chromatography (LSC), size exclusion chromatography, normal, RP-HPLC, ion exchange and affinity chromatography. In reversed-phase chromatography, the stationary phase is usually a hydrophobic bonded phase, such as an octadecylsilane or octylsilane and the mobile phases are usually polar solvents such as water or mixtures of water and water-miscible organic solvents such as methanol, acetonitrile, THF or isopropanol. Non-ionic, ionic and ion is able compounds can be separated using a single column and mobile phase, with or without added buffer salts, using bonded-phase columns that are reproducible and relatively stable (Wysocki, 2001).

Only one solute was being investigated, thus the use of an isocratic system was deemed appropriate for the development of an HPLC analytical method. For samples in which different solutes are present, it may be advantageous to use gradient elution where the composition of the mobile phase is altered during the separation, usually by blending two or more solvents with different eluting powers in continually changing proportions (Paul, 1991) whereas in isocratic systems, a mobile phase of constant composition is used to effect a separation.

In the case of an HPLC system that may not be accurate or precise, the use of an internal standard improves accuracy, by correcting for variable injection volumes of a test solution. A solution containing a fixed amount of internal standard is added to the sample in a precisely measured volume. Any subsequent losses of the analyte sample are accounted for, since losses of the analyte will be mirrored by losses of the internal standard. A chemical substance may be used as an internal standard if it is related to the analyte of interest, is stable and elutes as close as possible to the analyte of interest whilst is still adequately resolved from the analyte and any possible excipients that may be present in the sample matrix being analysed (Wilson, 1990).

2.11 Mobile phase selection

In addition to the stationary phase, the mobile phase composition plays a significant role in the elution or retention of the compounds of interest. HPLC is a multi-faceted process with the appropriate interplay of various parameters being vital during analysis, to produce a desired separation. Parameters such as the physic co-chemical properties of an analyte of interest, the type of stationary phase chosen in addition to the mobile phase selected for analysis play a combined role in effecting a suitable separation, and manipulation of one or all of these factors to optimize a separation and improve the chromatographic behavior of the compound under investigation, may be necessary (Chandrul and Srivastava, 2010).

The important characteristics of solvents for use in HPLC analysis include the need for high purity, immiscibility with the stationary phase, absence of reactivity towards an adsorbent, low boiling point and low viscosity (Skoug et. al., 1996). Mobile phases of extreme pH must also be avoided, *i.e.*, pH<3 and pH>9, as these may damage the bonded phase of the silica backbone or lead to dissolution of the silica. However newer stationary phases are reported to be more resilient to extreme pH conditions. The eluents used in reversed-phase chromatography with bonded non-polar stationary phases are generally polar solvents or mixtures of polar solvents, such as acetonitrile, methanol and/or water (Shah et. al., 1992).

The most importance is the fact that the mobile phase should be pure and free from impurities, dust, particulate matter and dissolved air (Paul, 1991 and Skoug et. al., 1996). Particulate matter can interfere with the pumping action of the solvent delivery module or pump and this can cause damage to the seals and/or check valves, collect on the top of the column causing subsequent column blockages thereby promoting chromatographic anomalies such as changes in retention time and poor peak resolution (Gent, 2002).

CHAPTER THREE

RESEARCH METHODOLOGY

3.0 Introduction

In this study, the sol-gel method was used to prepare the heterogeneous catalyst which is Al_2O_3/TiO_2. The results obtained from the photo-reduction process were analyzed by using High performance Liquid Chromatography (HPLC).

3.1 Chemicals and Materials

The chemicals and materials that were used in this study are Titanium Dioxide (TiO_2) powder, Aluminum Oxide (Al_2O_3) powder, Sodium Hydroxide (NaOH) solution, sulphuric acid (H_2SO_4), ethanol and deionized water.

3.2 Preparation of Catalyst by Sol-Gel Method

In sol-gel method, $Ti(OC_3H_7)_4$ and $Al(OC_3H_7)_3$ solutions were prepared by adding 10 g of TiO_2 powder with 41 mL of ethanol solution and the mixture was continued stirred with magnetic stirrer for 30 minutes. While in the preparation of $Al(OC_3H_7)_3$ solution, the same steps were used with poured 5 g of Al_2O_3 powder in 50 mL of ethanol. The solution was then added with 50 mL of water to achieve ethanol-water solution. After that, both $Al(OC_3H_7)_3$ and $Ti(OC_3H_7)_4$ solutions were mixed and continuously stirred for 4 hours. Finally, $Al(OC_3H_7)_3$-$Ti(OC_3H_7)_4$ solution was formed.

After that, 500 mL of 1.0 M H_2SO_4 was added to $Al(OC_3H_7)_3$-$Ti(OC_3H_7)_4$ solution to form gel formation. The gel formation was stirred for 4 hours followed by ageing process for 12 hours at room temperature. The pH value of the solution was adjusted using 1.0 M of NaOH and 1.0 M of H_2SO_4 until the pH of the solution was achieved at 3.0. Then, the gel solution was heated at 80 ^{o}C to remove ethanol content. The solution was washed gently to remove impurities and then filtered by filter paper. The sample was dried at 12 hours in oven and calcined at 500 °C for 5 hours in the furnace. Lastly, the product formed was grinded into small particles to have Al_2O_3-TiO_2 catalyst. The overall process for preparation of Al2O3-TiO2 catalysts was shown in **Fig. 3.1**.

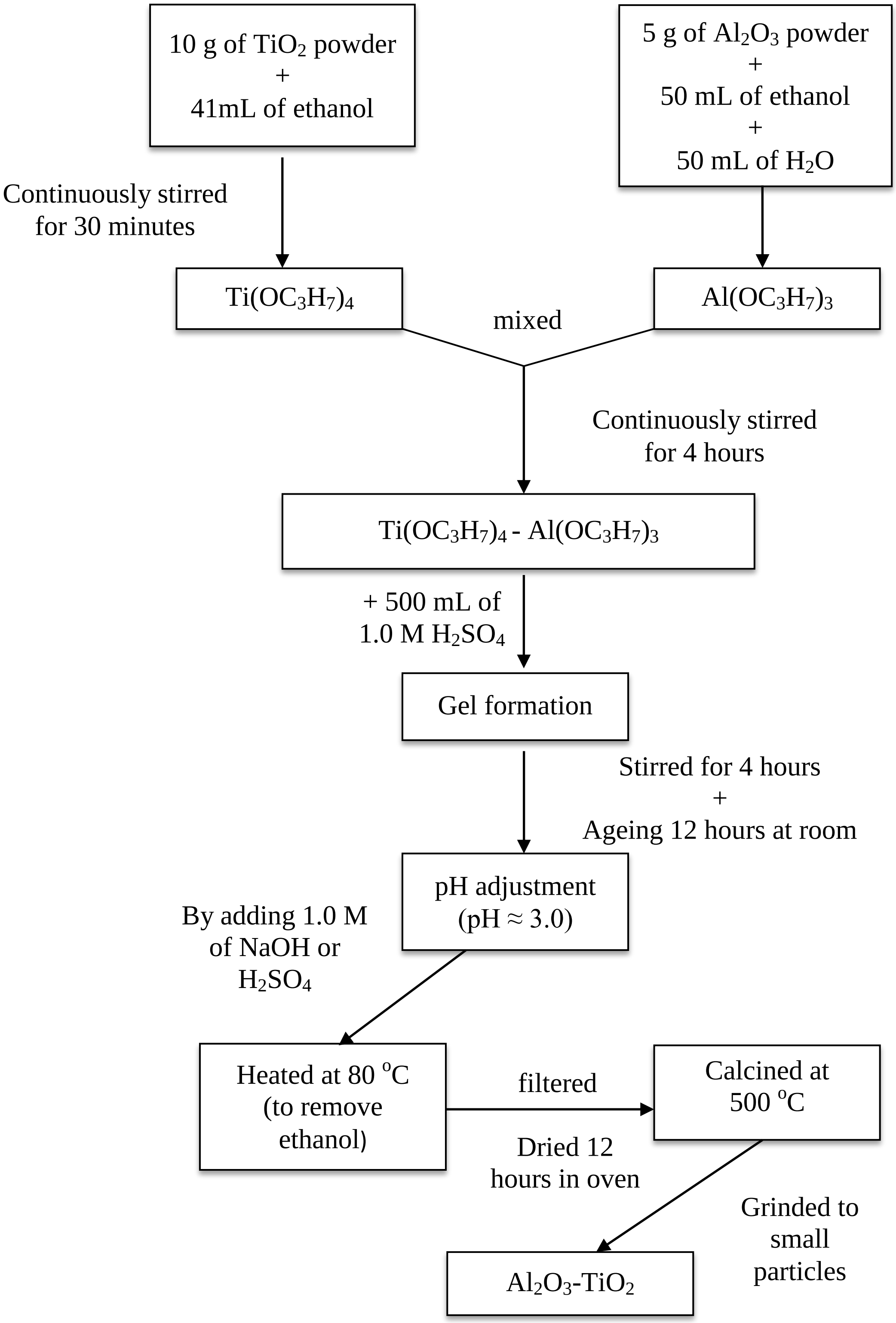


Fig. 3.1. Preparation of Al_2O_3-TiO_2 Catalysts by Sol-Gel Method

3.3 Photo-Reduction of CO_2

The main elements in photo-reduction of CO_2 process were CO_2 gas, solvent, catalyst, and UV light. The photo-reduction of CO_2 was simply done by continuously supplying CO_2 gas for one hour into 1.0 L of conical flask containing a mixture of Al_2O_3-TiO_2 catalyst and solvent. After an hour was elapsed, the blank sample was withdrawn from the flask to evaluate the effectiveness of UV light. Then, the supply of CO_2 stopped and UV light was turned ON. The samples were withdrawn for every one hour within 5 hours of reaction time where UV light was continuously supplied.

3.3.1 Effect of solvents

In this study, 500 mL of NaOH as a solvent was mixed together with 2 g of Al_2O_3-TiO_2 catalyst in a 1.0 L of conical flask. Then, CO_2 gas was supplied into the flask for one hour period. As one hour period elapsed, the supply of CO_2 gas was stopped and the first sample was withdrawn. The UV light then was switched ON for the rest of 5 hours of reaction time. The sample was collected for every one hour of reaction time. The study was repeated using H_2O as a solvent with replacing NaOH to investigate the effect of solvent on photo-reduction process.

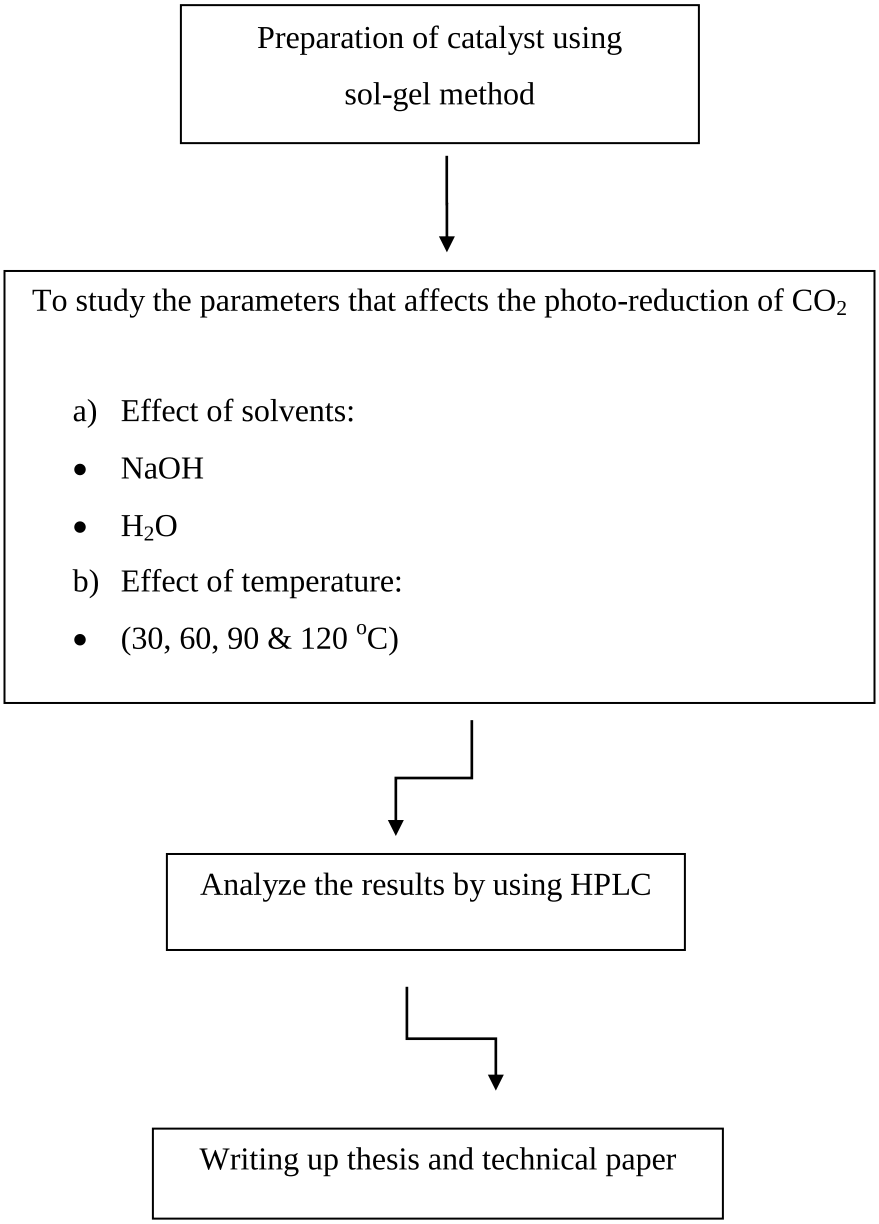
The samples collected were analysed by using HPLC to identify the concentration of methanol produced.

3.3.2 Effect of reaction temperature

The effect of reaction temperature in the photo-reduction process was studied from 30, 60, 90 and 120 ^{o}C of temperature in the 1.0 L conical flask. The parameters of the solution were maintained at 2.0 g dosage of the catalyst in 500 mL of solvent. The reaction was performed within 5 hours of reaction time. The samples obtained were analyzed by using HPLC.

3.4 Analyzing methanol by using HPLC.

The total methanol concentration in aqueous solution was analyzed by HPLC using a C-18 which referred to methanol column. The mobile phase which is the mixture of acetonitrile and ultrapure water in ratio of 3:2 were prepared before running the analysis to help the methanol to flow in the column. The pressure was set to a range of 139 – 147 bar, while the temperature was in 30 ^{o}C. The concentration of methanol was detected by Refractive Index detector (RID) before analyzed by referring to methanol standard solution. The overall flow diagram was shown in **Fig. 3.2.**



Preparation of catalyst using sol-gel method

To study the parameters that affects the photo-reduction of CO_2

a) Effect of solvents:
- NaOH
- H_2O

b) Effect of temperature:
- (30, 60, 90 & 120 ^{o}C)

Analyze the results by using HPLC

Writing up thesis and technical paper

Fig. 3.2: Flow Chart of Overall Experimental Works

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.0 Introduction

In this study, TiO_2-Al_2O_3 was used as a catalyst in photo-reduction of CO_2. The catalysts were prepared by using sol-gel method. The results were analyzed by using High Performance Liquid Chromatography (HPLC) to identify the amount of concentration of methanol in each sample collected.

4.1 Effect of Solvents

In this study, NaOH and water were used as a solvent in photo-reduction process and the results was shown in **Fig. 4.1** respectively.

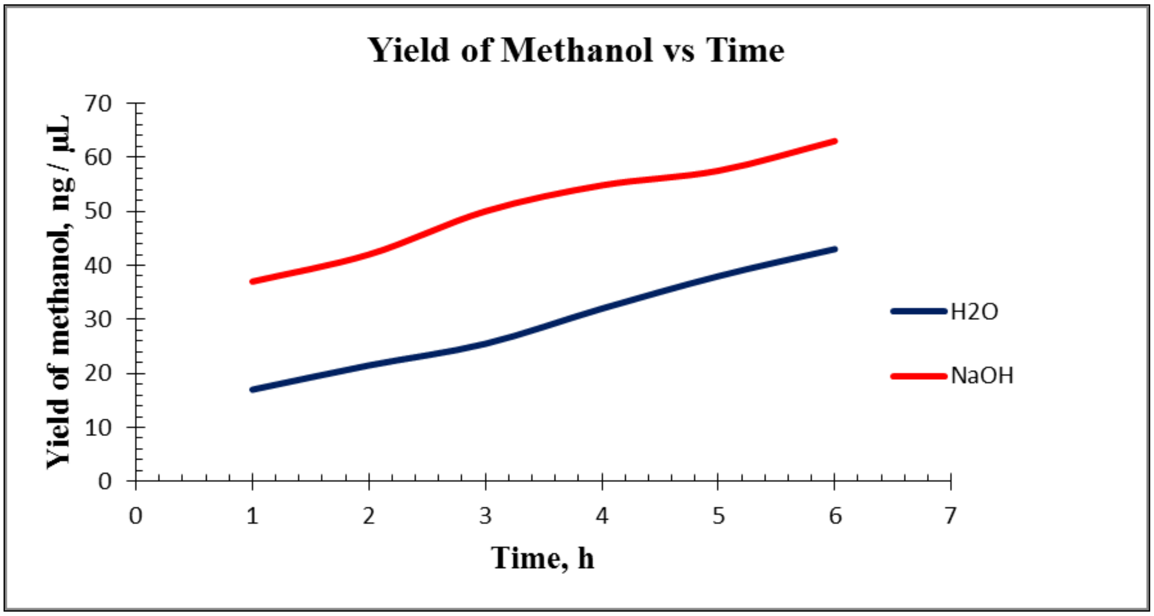


Fig. 4.1: Effect of Solvent in Photo-Reduction of CO_2

According to **Fig. 4.1**, the concentration of methanol was higher when NaOH was applied as solvent compared to H_2O. The concentration of methanol in both NaOH and H_2O goes inclined within 6 hours of residence time. The trend shows that the concentration of methanol in NaOH was always greater than the concentration of methanol in H_2O. The maximum concentration of methanol obtained was 63 ng/µL at the sixth hour. The same trend was shown in application of H_2O as solvent. Somehow, the maximum concentration of methanol found was 43 ng/µL.

According to Takayuki et. al., (1996), the concentration of CO_2 in water is very small because of its low solubility. Furthermore, the photo-reduction process is competitive with H_2 formation via water reduction. Since low concentration of CO_2 in H_2O, the concentration of methanol will be small.

From **Fig. 4.1**, the concentration of methanol was clearly high when NaOH was used as solvent for photo-reduction of CO_2. Martin et. al., (n.d) states that the photo-reduction of CO_2 is not effective in pure water because of the low solubility of CO_2. The solubility of CO_2 is higher in aqueous solutions of hydroxides. In addition, the OH^- ion could act as a strong hole scavenger and forms OH• radicals, thereby reducing the recombination of hole-electron pairs. Among the most used reaction medium for the photo-reduction of CO_2, an aqueous solution of sodium hydroxide belongs.

According to I-Hsiang et. al., (2002), NaOH solution was crucial in the photo-reduction of CO_2. The concentration of methanol substantially increased with the usage of NaOH in the experiments due to the following two reasons. The high concentration of OH^- which is ions in aqueous solution could act as strong hole-scavengers and form OH radicals, thereby reducing the recombination of hole – electron pairs.

The longer decay time of surface electrons would certainly facilitate the reduction of CO_2. Furthermore, caustic NaOH solution dissolves more CO_2 than does pure water. The initial pH value of 0.20 N NaOH solutions was approximately 13.3, and decreased to nearly 7.3 after bubbling CO_2 in the reactor. Notably, photo-reduction may have been accelerated by the high concentration of HCO_3^- which retrieved from **Eq. 4.1:**

$$HCO_3^- \longleftrightarrow OH^- + CO_{2(aq)} \ldots\ldots\ldots\ldots..(4.1)$$

In addition, Jin et. al., (2012) also said that NaOH solution can dissolve more CO_2 than water. The pH value decreased from 14 of 1.0 M NaOH to 7.5 after bubbling CO_2, indicating the solution mainly contains HCO_3^- or with a small amount of CO_3^{2-}, which might accelerate the photo-reduction of CO_2. Then, OH^- can act as hole-scavenger to promote the carrier separation, and resulting in an improved CO_2 reduction efficiency.

Moreover, the concentration of methanol increases slowly once the NaOH concentration is higher than 1.0 M, which can be described to the formation of the saturated HCO_3^- solution after bubbling CO_2. Since the alkaline substance with excessive concentration would damage the chromatographic column, 1.0 M NaOH solution was chosen for the following experiments.

4.2 Effect of Reaction Temperature

In this experiment, the reaction temperature was varied from 30, 60, 90 and 120 ^{o}C to study the effect of temperature on methanol generation and the result was shown in **Fig. 4.2**.

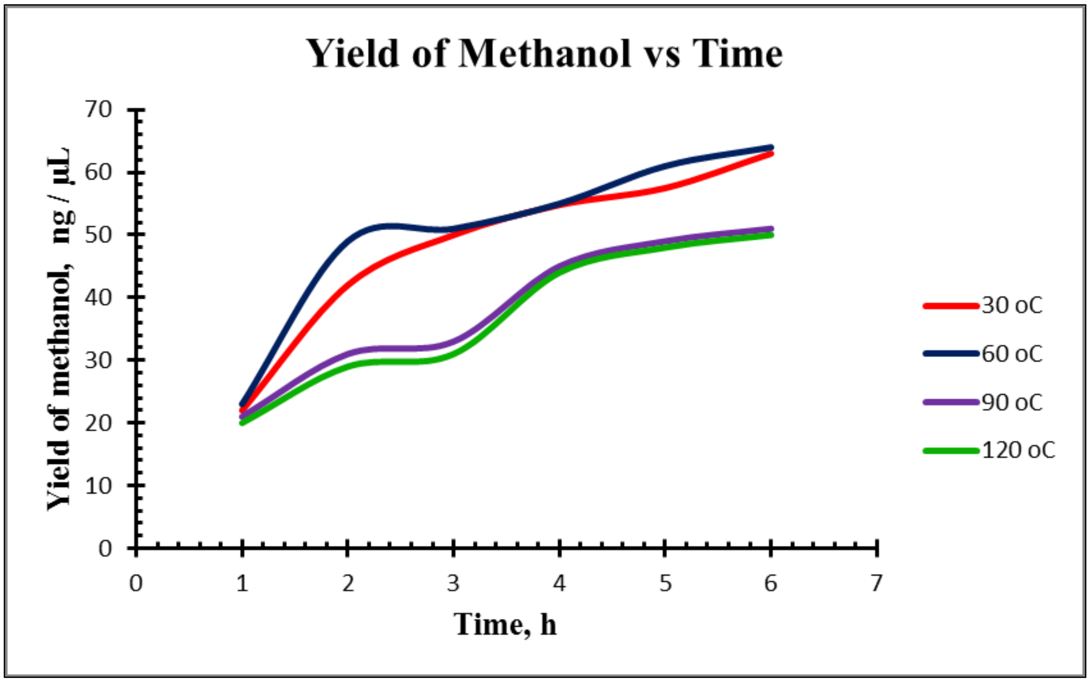


Fig. 4.2: Effect of Temperatures in Photo-reduction of CO_2 with NaOH

Fig. 4.2 shows the effectiveness of temperature variation in photo-reduction of CO_2 with NaOH used as solvent. The ranges of temperature used were 30 ^{o}C to 120 ^{o}C. According to the analysis, the highest concentration of methanol was at temperature, T = 60 ^{o}C which is 64 ng/µL. The second highest order of the concentration of methanol was at T = 30 ^{o}C which is 63 ng/µL. The lowest concentration of methanol were at T = 90 ^{o}C and T = 120 ^{o}C where the concentration s were about 51 ng/µL and 50 ng/µL.

According to Phairat et. al., (2006), CO_2 is a relatively inert and stable compound, its reduction is quite challenging. The majority of conversion and removal methods rely on high-energy input for high-temperature. Therefore, the reaction necessitates high reaction temperature to overcome the activation energy barrier for C-O bond cleavage. Despite of the function of temperature to help break C-O bond cleavage, the boiling point of methanol is 65 ^{o}C. Therefore, the concentration of methanol will be maximized to 60 ^{o}C as according to the experiment result. The excess of the temperature supplied was change the product phase of liquid methanol to vapor as refer to the concentration of methanol at T = 90 ^{o}C and T = 120 ^{o}C.

According to Phairat et. al., (2006), photon irradiation is the primary source of energy for electron-hole pair formation at ambient temperature, because the band-gap energy is too high for thermal excitation to overcome. However, at high temperatures, the reaction rate can be increased by raising the collision frequency and diffusion rate.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.0 Conclusions

Based on the overall experimental results obtained and discussed in chapter four, the summaries are made as listed below:

- Photo-reduction process is the most promising method to reduce CO_2 to a valuable product such as methanol. Other than simple process, photo-reduction also preserves a clean reaction.
- It was justified that the concentration of methanol was depend on the solvent used. Higher concentration of methanol will be retrieved for higher solubility of CO_2 to the solvent. In this study, NaOH has higher solubility characteristics than H_2O which leads to higher production of methanol. The concentration of

methanol in NaOH is 63 ng/µL has much greater than the concentration of methanol in H_2O which is 43 ng/µL.

- While in the study of the effect of temperatures, the boiling point of NaOH at 65 ^{o}C has limited the concentration of methanol. The trend of methanol production goes up for T= 30 ^{o}C and T=60 ^{o}C. Later, the trend shown a decline trend at T= 90 ^{o}C and 120 ^{o}C as the result of phase change to vapor of the methanol. The highest concentration of methanol was at T = 60 ^{o}C where the concentration is 64 ng/µL. the order of the concentration of methanol was then followed by 63 ng/µL at T = 30 ^{o}C. The lowest of the concentration of methanol was found at T = 90 ^{o}C and 120 ^{o}C the concentration s collected were 51 ng/µL and 50 ng/µL.

5.1 Recommendations

Some recommendations for future study are suggested in view of their significance and importance related to the present study:

- It is recommended to study the effect of pressure of CO_2
- Calcined temperature of the catalysts.
- Al_2O_3/TiO_2 catalysts possibly to be characterized by using either FTIR, Transmission Electron Microscope (TEM), X-ray Photoelectron Spectroscopy (XPS) or Brunnauer Emmett Teller (BET) method.

- Manipulation of the catalyst to be used in photo-reduction process since the production has significance effects by the catalysts applied.
- Manipulation of the type of UV band width to the photo-reduction process.

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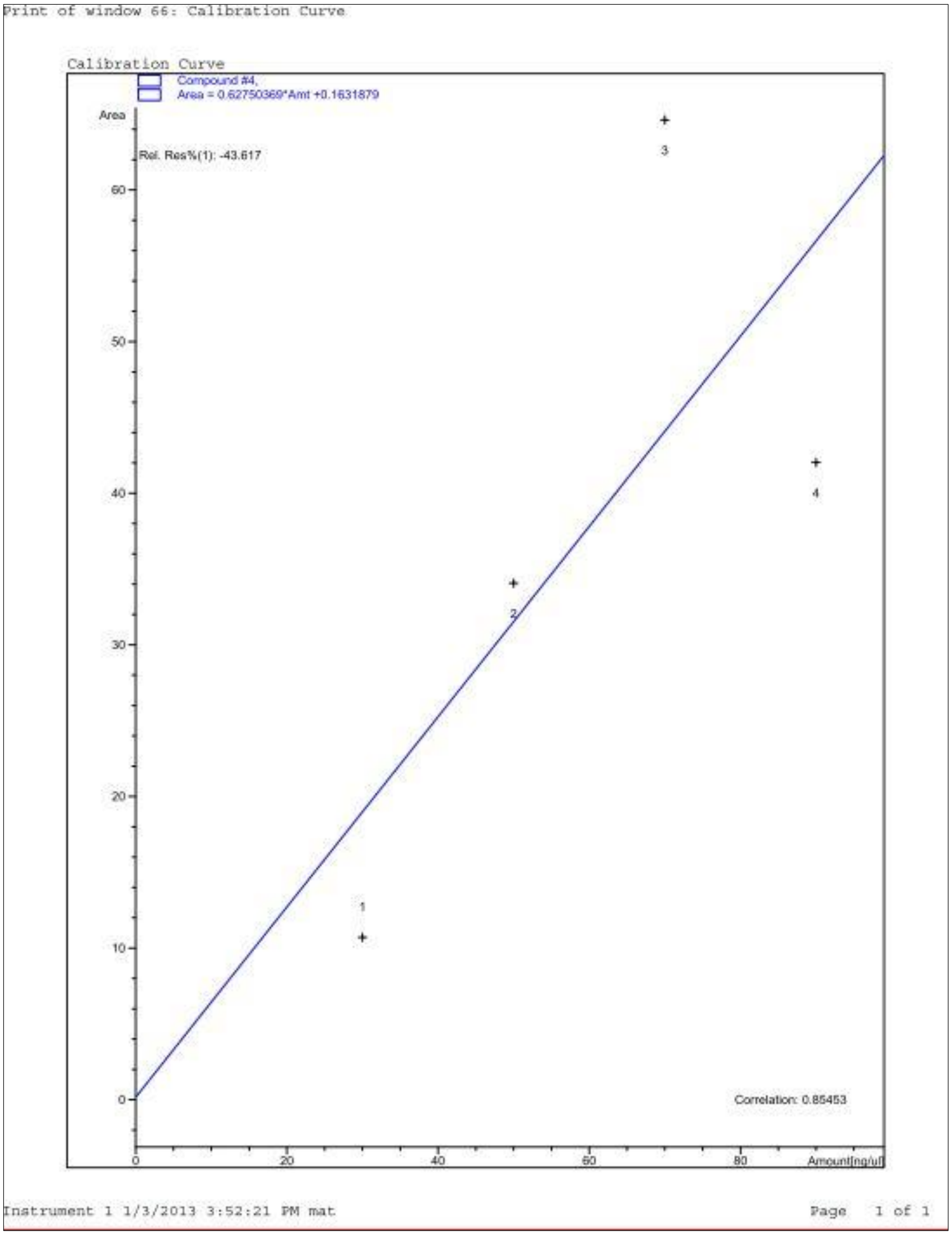
APPENDICES


Print of window 66: Calibration Curve

Calibration Curve

Compound #4,

Area = 0.62750369*Amt +0.1631879

Rel. Res%(1): -43.617

Correlation: 0.85453

Instrument 1 1/3/2013 3:52:21 PM mat

Page 1 of 1

A.1: Standard Curve for Methanol Yield

B.1: Concentration of Methanol in NaOH and H_2O

Time (h)	**concentration of methanol (ng/ µL)**	
	H_2O	**NaOH**
1	17	37.0
2	21.5	42.0
3	25.5	50.0
4	32	54.8
5	38	57.5
6	43	63.0

B.2: Effect of Temperatures in Photo-reduction of CO_2 with NaOH

Time (h)	**Concentration of Methanol (ng/ µL)**			
	30 °C	**60 °C**	**90 °C**	**120 °C**
1	21.0	46.0	45.0	37.0
2	31.0	47.0	49.0	42.0
3	32.0	49.0	49.3	50.0
4	55.0	53.0	53.0	54.8
5	58.5	61.5	61.0	57.5
6	61.0	62.5	63.5	63.0