# PHOTO-CATALYTIC REDUCTION OF CARBON DIOXIDE OVER ALUMINA DOPED TITANIUM DIOXIDE CATALYST

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## SUPERVISOR DECLARATION

“I hereby acknowledge that the scope and quality of this thesis is qualified for the award of the Bachelor Degree of Chemical Engineering (Gas Technology).”

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Date : 25 JANUARY 2013

## STUDENTS’S DECLARATION

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Date : 25 JANUARY 2013

*In the name of ALLAH, Most Gracious, Most Merciful*

To my beloved my father, mother, sisters and brothers.

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# PHOTO-CATALYTIC REDUCTION OF CARBON DIOXIDE OVER ALUMINA DOPED TITANIUM DIOXIDE CATALYST

## ABSTRACT

Carbon dioxide ($CO_2$) is a major source of greenhouse gas effect which causes the increasing in the Earth's temperature. The continuously increasing $CO_2$ level into the atmosphere is one of the most serious problems with regard to the greenhouse effect. One of the remediation to overcome this problem by using Photo-reduction process with prepared catalysts assisted by UV light. In this process, $CO_2$ was converted to methanol ($CH_3OH$) as a main product. In this study, the influence of the parameters on the catalytic activity with and without visible light irradiation and also effect of percentage of $Al_2O_3$ loading on $TiO_2$ were focused. The catalyst was prepared using sol-gel method. The percentage of $Al_2O_3$ loading on $TiO_2$ were set in range of 1.50 wt.% - 5.0 wt. %. In photo-reduction process, highly industrial $CO_2$ was first flowed through NaOH solution with presence of $Al_2O_3$-$TiO_2$ catalyst in the reactor. The main product was analyzed using High Performance Liquid Chromatography (HPLC). The results show that for maximum loading of $Al_2O_3$ into $TiO_2$ catayst, the performance of photocatalytic activity was enhanced due to the metals will act as electron traps, facilitating electron–hole separation and promote the interfacial electron transfer process. In photo-reduction process, the conversion of $CO_2$ into methanol was more effective with UV light compared to the process without UV light. As a conclusion, with presence of higher percentage of $Al_2O_3$ on $TiO_2$ and UV light, the reduction of $CO_2$ can be done successfully.

**PENUKARAN KARBON DIOKSIDA DENGAN MENGGUNAKAN CAHAYA DAN PEMANKIN ALUMINA DIMUATKN PADA TITANIUM DIOKSIDA**

## ABSTRAK


Karbon dioksida ($CO_2$) adalah sumber utama kesan gas rumah hijau yang menyebabkan peningkatan dalam suhu bumi. Peningkatan $CO_2$ ke atmosfera adalah salah satu masalah yang paling serius dengan mengambil kira kesan terhadap rumah hijau. Salah satu daripada pemulihan untuk mengatasi masalah ini dengan menggunakan proses penukaran dengan menggunakan cahaya beserta pemangkin dan juga cahaya UV. Dalam proses ini, $CO_2$ telah ditukar kepada metanol ($CH_3OH$) sebagai produk utama. Dalam kajian ini, pengaruh factor-faktor aktiviti pemangkin dan penyinaran cahaya dan juga kesan peratusan $Al_2O_3$ pada $TiO_2$ ditumpukan. Pemangkin disediakan menggunakan kaedah sol-gel. Peratusan $Al_2O_3$ pada $TiO_2$ telah ditetapkan dalam julat berat 1.50% -5,0. %. Dalam proses penukaran ini, $CO_2$ dialirkan melalui NaOH dengan kehadiran $Al_2O_3$-$TiO_2$ sebagai pemankin dalam reaktor. Produk hasil dari proses ini dianalisis dengan menggunakan Prestasi Tinggi Cecair Kromatografi (HPLC). Keputusan menunjukkan bahawa untuk memuatkan maksimum $Al_2O_3$ ke $TiO_2$, prestasi aktiviti penukaran telah dipertingkatkan kerana logam akan bertindak sebagai perangkap elektron, memudahkan pemisahan elektron dan menggalakkan proses pemindahan elektron ke permukaan. Dalam proses ini, penukaran $CO_2$ ke metanol adalah lebih berkesan dengan cahaya UV berbanding proses tanpa cahaya UV. Sebagai kesimpulan, dengan kehadiran peratusan yang lebih tinggi $Al_2O_3$ pada $TiO_2$ dan cahaya UV, pengurangan $CO_2$ dapat dilakukan dengan jayanya.

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# CHAPTER ONE

# INTRODUCTION

## 1.0 Research Background

The continuously increasing carbon dioxide ($CO_2$) level into the atmosphere is one of the most serious problems with regard to the greenhouse effect (Slamet, 2009*)*. The increasing of $CO_2$ is due to our present dependence on fossil fuel.  It is due to increasing of demand for energy inevitably. $CO_2$ is emitted in a number of ways. It is emitted naturally through the carbon cycle and through human activities like the burning of fossil fuels (Jiang, 2010).

The continued increase in $CO_2$ concentration will cause changes to our global climate. Because it is a greenhouse gas, elevated $CO_2$ contribute to an additional absorption and emission of thermal infrared in the atmosphere, which produce net warming. This is because $CO_2$ is a prominent greenhouse gas. It absorbs and emits infrared radiation at wavelength of 4.26 μm that is asymmetric stretching vibrational mode and 14.99 μm bending vibrational mode (Petty, 2004).

It has been shown in many researches it takes longer time for natural removal of $CO_2$. If we delay about reductions in $CO_2$ it will cause major problem and the effect of $CO_2$ emission could be extremely far reaching. There are several methods proposed that can be uses to reduce the concentration of $CO_2$ due to the increasing of $CO_2$ such as electrochemical, photochemical, photo reduction and photo electrochemical (Petty, 2004).

In this study, photo-catalytic reduction of $CO_2$ using catalyst was studied to convert it to valuable product that is methanol. Methanol is a hydrocarbon, comprised of carbon, hydrogen and oxygen. Its chemical formula is $CH_3OH$. Methanol is an alcohol and is a colourless, neutral, polar and flammable liquid. It is miscible with water, alcohols, esters and most other organic solvents. It is only slightly soluble in fats and oils (Fiedler, 1990).

Methanol has many uses. In the fuel cell application, methanol is widely considered to be one of the most promising fuels for fuel cell applications currently being developed for cell phones, portable computers and small scale transportation such as commuter scooters. Several distinct attributes of methanol make it an ideal hydrogen source for future fuel cell vehicles and may one day provide an alternate source of energy in homes(Wiley, 1985). For the waste water treatment, when wastewater is collected in a treatment facility, it generally contains high levels of ammonia. Through a bacterial degradation process, this ammonia is converted into nitrate. In a subsequent process called denitrification, the nitrate is removed through a combination of chemical treatment and bacterial degradation. Methanol is a simple molecule that serves as an ideal carbon source for the bacteria used in denitrification. Accelerated by the addition of methanol, anaerobic bacteria will rapidly convert the nitrate ($NO_3$) to harmless nitrogen gas

($N_2$), which is vented into the atmosphere(Wiley, 1985). In the primary uses of methanol it used as chemical intermediate and fuel. Methanol is used in the production of formaldehyde, acetic acid and a variety of other chemical intermediates which form the foundation of a large number of secondary derivatives. These secondary derivatives are used in the manufacture of a wide range of products including plywood, particleboard, foams, resins and plastics (Wiley, 1985).

In this study, photo-catalytic reduction of $CO_2$ assisted by UV light in the presence of a catalyst was used as a treatment to produced methanol. In catalyzed photolysis, light is absorbed by an adsorbed substrate to enhance photo reduction activity. The photo-catalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals for able to undergo secondary reactions (Jeannie, 2012). Prepared Al/$TiO_2$ catalyst was used in photo-reduction process by using Sol Gel method. Parameters that affect the photo-reduction process were studied. The effect of aluminium oxide loading into titanium dioxide and UV light were investigated in photo reduction reaction. This process is to produce methanol as a valuable produce.

## 1.1 Problem Statement

Carbon dioxide ($CO_2$) is a major source of greenhouse gas effect which causes the increasing in the earth's temperature. The concentration of atmospheric $CO_2$ has increased by about 35 % since the beginning of the age of industrialization. This is due to the globalization and human activities such as the combustion of fossil fuels and deforestation. In order to overcome this problem, the researchers work hard to find the best remediation for this matter. Due to this problem, one of the best methods was introduced by using photo-reduction process with prepared catalysts by using Sol Gel method assisted by UV light. The sol-gel process is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. $CO_2$ as a waste product were converted to valuable product that is methanol. Methanol became important product because it has many uses especially as fuel cell application.

## 1.2 Objectives

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

- To synthesize photo-catalyst, $Al_2O_3$-$TiO_2$ that used in photo-reduction process of $CO_2$.
- To study the performance of the prepared catalysts and the influence of the parameters on the catalytic activity.

## 1.3 Scope of Study

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

- Synthesizing the photo-catalyst by doping $Al_2O_3$ on $TiO_2$ catalyst by using sol gel method. In sol gel method, the catalyst were prepared in powder form.
- The effect of loading of $Al_2O_3$ into $TiO_2$ was studied in the range of 0.50 -5.0 wt. % of $Al_2O_3$ on $TiO_2$. The effects were measured by analyzed methanol produce.
- Photo-reduction process was studied with and without UV light to see the effect of UV light on yield of methanol in photo-reduction process Main product (methanol) was analyzed by using High-performance liquid chromatography (HPLC).

## 1.4 Organization of Thesis

This report contains five main chapters to distribute the whole report accordingly. In the first chapter, explained the introduction which gave the briefing about the project. In the first chapter also contain problem statement, objective and scope of study. The second chapter contains literature review which is based on photocatalytic reaction and preparing aluminum-titanium dioxide catalyst. The review in this chapter were made from the studied of researcher from all over the world. The third chapter explained the methodologies of the experiment. The constant value and standard curve preparation were shown in this chapter. The fourth chapter contained results and discussions. The result obtained from this studied were illustrated in table and chart form. The result obtained were discussed and compared with other research result. Finally, fifth chapter contains with conclusions and recommendations. The conclusion were made to support objective of this studied whether the result obtained is achieve the goal of this studied. The recommendation was made to give addition information for the further studied on this topic to get better result and for expending the studied on this topic.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.0 Introduction

Carbon dioxide ($CO_2$) is one of the gases in our atmosphere, being uniformly distributed over the earth's surface at a concentration of about 0.033% or 330 ppm (Shakhashiri, 2008). $CO_2$ is released into our atmosphere when carbon-containing fossil fuels such as oil, natural gas, and coal are burned in air. As a result of the tremendous world-wide consumption of such fossil fuels, the amount of $CO_2$ in the atmosphere has increased over the past century, now rising at a rate of about 1 ppm per year. Major changes in global climate could result from a continued increase in $CO_2$ concentration (Shakhashiri, 2008).

Beside that, $CO_2$ has increased in the atmosphere from fossil fuel use in industry and transportation, manufacture of cement, building air conditioning and deforestation. With a global radioactive forcing of 1.74 $W.m^{-2}$, $CO_2$ is the largest contributor among well-mixed long-lived greenhouse gases, accounting for more than 63 % of the total (Richter, et al., 2011). $CO_2$ is a greenhouse gas as it transmits visible light but absorbs strongly in the infrared and near-infrared, before slowly re-emitting the infrared at the same wavelength as what was absorbed. The resulting accelerating accumulation of $CO_2$ in the troposphere, with projections of continued warming in the absence of resolute changes in $CO_2$ management and this will cause the greenhouse effect with a significant atmospheric temperature rise and which will produce net warming (Revkin, et al., 2000).

In Malaysia, the emissions of $CO_2$ also occur. There are many factors that affect the emissions of $CO_2$.Electricity generation, transportation, industrial and residential are the main sectors identified to contribute to the emission of $CO_2$ in Malaysia. It was projected that without any mitigation measures being taken up by the country, 285.73 million tonnes of $CO_2$ will be released in 2020, which is a 68.86% increase compared to the amount of $CO_2$ emitted in year 2000. Electricity generation, which gives 43.40% out of total of emissions, was discovered to be the largest emitting sector among all sectors (Nor Sharliza Mohd Safaai, 2010). From **Figure 2.1** and **Figure 2.2,** total $CO_2$ emissions represent the mass of $CO_2$ produced during the combustion of solid, liquid, and gaseous fuels. Carbon dioxide emissions are often calculated and reported to see the emission of $CO_2$ in our atmosphere. The trend of $CO_2$ emission is increasing by year. From year 1970 until 2010, the differences between those years are really large due to development of industry sector in our country. This increasing of $CO_2$ is serious problem because it has many effects to our environment and our health.

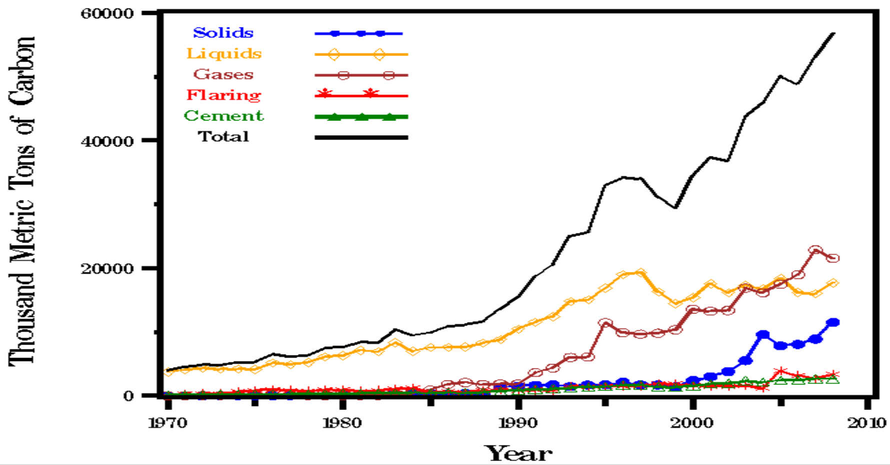


**Figure 2.1**: $CO_2$ emission from Malaysia(http:wwwcdiac.ornl.gov)

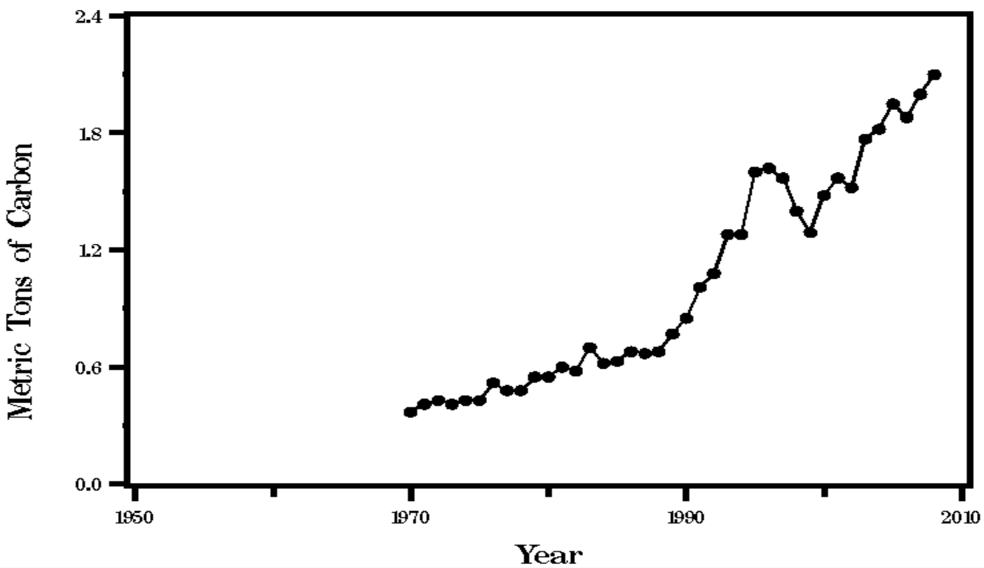


**Figure 2.2**: $CO_2$ emission estimates for Malaysia (http:www.cdiac.ornl.gov)

## 2.1 Photo Reduction Process of Carbon Dioxide ($CO_2$)

Photo reduction may be termed as a photo induced reaction which is accelerated by the presence of a catalyst. These types of reactions are activated by absorption of a photon with sufficient energy that is equals or higher than the band-gap energy of the catalyst. The absorption leads to a charge separation due to promotion of an electron from valence band of the semiconductor catalyst to the conduction band, thus generating a hole in the valence band. The recombination of the electron and the hole must be prevented as much as possible if a photo-catalysed reaction must be favoured. The ultimate goal of the process is to have a reaction between the activated electrons with an oxidant to produce a reduced product, and also a reaction between the generated holes with a reductant to produce an oxidized product (Hameed, et al., 2009).

Photo-catalytic reduction process is a method that can be used to reduce the concentration of $CO_2$ by using photosensitive semiconductor materials such as $TiO_2$, ZnS, $ZrO_2$, $V_2O_5$, ZnO, $CeO_2$ and $NbO_5$ as photo-catalysts. Hoffman (1995) was reported about $TiO_2$ in photo-reduction process that $TiO_2$ has been widely studied for its application as photo-catalyst because of its excellent stability and strong oxidizing property. However, $TiO_2$ is a wide band gap semiconductor with 3.03 eV for rutile and 3.18 eV for anatase and can only absorb about 5 % of sunlight in the ultraviolet region, which limits its photo-catalytic activity (Hameed, et al., 2009).

Mishra et al.,(2007), reported in his study that the photo-catalytic activity is strongly dependent on the electro-optical properties of the photo-catalyst, defects removal, particle size and specific surface area. Therefore different modified $TiO_2$ were also used to improved catalytic reduction.

Photo-catalysis has recently become a common word and various products using photo-catalytic functions have been commercialized. Among many candidates for photo-catalysts, $TiO_2$ is almost the only material suitable for industrial use at present and also probably in the future. This is because $TiO_2$ has the most efficient photo-activity, the highest stability and the lowest cost. More significantly, it has been used as a white pigment from ancient times, and thus, its safety to humans and the environment is guaranteed by history. There are two types of photochemical reaction proceeding on a $TiO_2$ surface when irradiated with ultraviolet light. One includes the photo-induced redox reactions of adsorbed substances, and the other is the photo-induced hydrophilic conversion of $TiO_2$ itself (Kazuhito, et al., 2005).

In this process, UV light is used because it can enhance the process. It can increase the efficiency of the process by reduce the reaction time (Azmi, 2005). However, $TiO_2$ exhibits a relatively high energy band gap that is 3.2 eV and can only be excited by high energy UV irradiation with a wavelength shorter than 387.5 nm. Efforts have been made to extend the light absorption range of $TiO_2$ from UV to visible light and to improve the photo-catalytic activity of $TiO_2$ further by adding metals such as silver, cooper, alumina and other (Wu, et al., 2005). In this experiment, alumina was used to dope on $TiO_2$ as a catalyst for this reduction process.

The main purpose of this study to reduce the emission of $CO_2$ to atmosphere hence to produce valuable product such as methanol and the main reaction was shown in Eq. (2.1),

$$CO_2 + 2H_2O \xrightarrow{UV} CH_3OH + 3/2\ O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.1)$$

The efficiency of photo reduction of $CO_2$ with $H_2O$ is one of the most challenging tasks of environmental catalysts because titania is a photo-excited catalyst. The band gap of anatase form $TiO_2$ is 3.2 eV, making it a perfect candidate for UV illumination (Wu, 2005).

## 2.2 Materials Used as a Catalyst in Photo-Reduction Process

### 2.2.1 Alumina ($Al_2O_3$)

Aluminium is the most abundant metal and the third most abundant element in the earth's crust, after oxygen and silicon. It makes up about 8 % by weight of the earth’s solid surface. Aluminium is too reactive chemically to occur naturally as the free metal. Instead, it is found combined in over 270 different minerals. The chief ore of aluminium is bauxite, a mixture of hydrated aluminium oxide ($Al_2O_3 \cdot H_2O$) and hydrated iron oxide ($Fe_2O_3 \cdot 2H_3O_6$). Another mineral important in the production of aluminium metal is cryolite ($Na_3AlF_6$). However, cryolite is not used as an ore; the aluminium is not extracted from it (Shakhashiri, 2008).

Meor Yusoff and Masliana, (2007) were defined alumina ($Al_2O_3$) as a white powder that normally produced from bauxite ores. It is one of the most widely used advanced ceramic materials with applications ranges from spark plugs to catalyst materials. $Al_2O_3$ attractive for engineering applications due to its chemical and thermal stability, relatively good strength and electrical insulation characteristic combined with availability in abundance have made. Other than that, it is also a relatively low cost material, and by using a number of fabrication methods, it can easily be formed and finished. $Al_2O_3$ has several allotropic forms, but only the usual type or α-alumina is considered. It has an internal crystal structure where the oxygen ions are packed in a closed packed hexagonal (cph) arrangement with aluminium ions in two-thirds of the octahedral sites. Tshang et. al., (1979) stated that $Al_2O_3$ have a high quality optical and di-electric properties and therefore suitable for antireflection coatings on a semiconductors.

### 2.2.2 Titanium Oxide ($TiO_2$)

Titanium dioxide ($TiO_2$) or titania is a very well-known and well researched material due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties. It exists in four mineral forms that are anatase, rutile, brookite and titanium dioxide (B) or $TiO_2$(B). Anatase type $TiO_2$ has a crystalline structure that corresponds to the tetragonal system (with dipyramidal habit) and is used mainly as a photo-catalyst under UV irradiation. Rutile type $TiO_2$ also has a tetragonal crystal structure (Rajalakshmi, 2011). This type of titania is mainly used as white pigment in paint. Brookite type $TiO_2$ has an orthorhombic crystalline structure. $TiO_2$(B) is a monoclinic mineral and is a relatively newcomer to the titania family. $TiO_2$, therefore is a versatile material that has applications in various products such as paint pigments, sunscreen lotions, electrochemical electrodes, capacitors, solar cells and even as a food coloring agent and in toothpastes. The possible application for this material as a photo-catalyst in a commercial scale water treatment facility is due to several factors. Firstly, the photo-catalytic reaction takes place at room temperature. Secondly, photo-catalytic reactions do not suffer the drawbacks of photolysis reactions in terms of the production of intermediate products because organic pollutants are usually completely mineralized to non-toxic substances such as $CO_2$, HCl and water. Thirdly, the photo-catalyst is inexpensive and can be supported on various substrates such as, glass, fibers, stainless steel, inorganic materials, sand, activated carbons (ACs), and allowing continuous re-use. Lastly, photo-generated holes are extremely oxidizing and photo-generated electrons reduce sufficiently to produce superoxides from dioxygens (Rajalakshmi, 2011).

Besides that, $TiO_2$ is widely used in many photo induced processes because of its comparatively low cost, low toxicity and its ability to resist photo-corrosion. The effect of transition metal ion on $TiO_2$ was studied for $CO_2$ photo-reduction. Addition of metal to $TiO_2$ can change the distribution of electrons and they prevent the electron hole recombination, thereby enhancing the photo-catalytic efficiency of $TiO_2$ (Rajalakshmi, 2011).

Titanium Oxide ($TiO_2$), as a wide-band gap energy semiconductor, has been intensive and in-depth studied on coprecipitation, impregnation, and method improvement to obtain the useful materials for photo-electrolysis of water, photo-catalytic degradation of toxic organic and inorganic contaminants , and some of catalytic reaction. By using solid-state reaction aluminum oxide had been doped into the framework of anatase $TiO_2$ to form alumina-doped titania ($Al_2O_3$-$TiO_2$). The mesoporous $Al_2O_3$-doped $TiO_2$ material, not only possessed high thermal stability hexahedral mesostructure, large surface area and narrow distribution of pore size, but also showed excellent photo-degradation behavior (Liu et al., 2009).

## 2.3 Method in Preparation of Heterogeneous Catalyst

### 2.3.1 Sol Gel Method.

Nowadays, sol gel method have become very popular recently due to their high chemical homogeneity, low processing temperatures, and the possibility of controlling the size and morphology of particles. Sol gel provides excellent matrices for a variety of organic and inorganic compounds when the material is derived. One of the most important features of this method is its ability to preserve the chemical and physical properties of the dopants. Thus, make it as unique hosts for a biologically important molecule which can be apply in biomedical aspects (Subramanian, et al., 2008).

Sol–gel is one of the most exploited methods. It is used mainly to produce thin film and powder catalysts. Many studies revealed that different variants and modifications of the process have been used to produce pure thin films or powders in large homogeneous concentration and under stoichiometry control( Akpan and Hameed, 2010).

Based on Akpan and Hameed(2010), the doping $TiO_2$ with transition metal ions usually resulted in a hampered efficiency of the $TiO_2$ catalyst, though in some few cases, enhancements of the photo reduction activity of $TiO_2$ were recorded by doping it with some transition metal ions. In most cases, co-doping of $TiO_2$ increases the efficiency of its photo reduction activity. Based on their review reveals that there are some elemental ions that cannot be used to dope TiO2 because of their negative effects on the photo reduction activity of the catalyst, while others must be used with caution as their doping will create minimal or no impacts on the $TiO_2$ photo reduction efficiency(Akpan and Hameed, 2010). **Figure 2.3** shows the flow preparation of catalyst with doping $Al_2O_3$ into $TiO_2$ by using Sol-Gel method. The process are aimed to added

$Al_2O_3$ into $TiO_2$ based catalyst. The process beginning with $Al_2O_3$-$TiO_2$ mixture were alcoholate and then added with acidifying reagent to perform gel. The process of gel performing is called sol gel process. Finally the sample is drying and calcination.

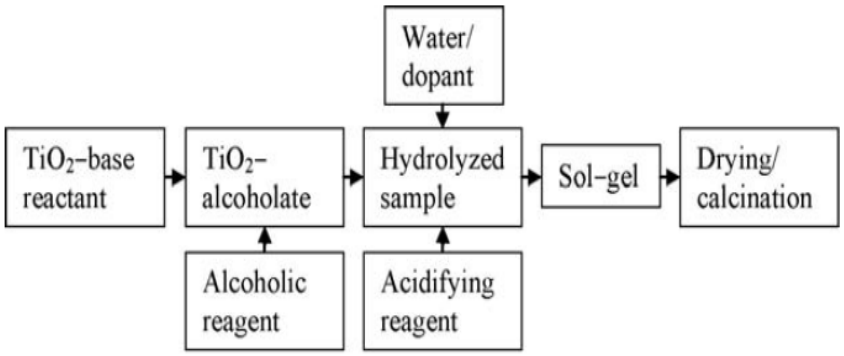


**Figure 2.3** : Process flow chart for the preparation of $TiO_2$-based catalysts by sol–gel method( Akpan and Hameed, 2010).

## 2.4 Parameters that affect the photo reduction process

There is many parameter that affect the photo reduction process. In this studied, the concern are only the effect of UV light and the effect of Al loading on $TiO_2$

### 2.4.1 Effect of UV light

There is many research of effect UV light in photo reduction process. Mohsen Padervand et al. reported that due to the wide band gap of $TiO_2$ (3.0-3.2 eV), it is active only under near ultraviolet irradiation(Mohsen Padervand et al 2011). Chih Ming Ma et al. reported that in the reaction process of UV/$TiO_2$ , an electron-hole pair is generated after $TiO_2$ has been exposed to ultraviolet light (UV) with a wavelength ($\lambda$ = 365 nm) in the near visible spectrum. The electrons then reduce the heavy metals and this is the reduction path. The hole generates the free radical through a series of reactions, and then organic matters are oxidized into carbon dioxide and this is the oxidation path. However, a shortcoming of this process is that the electron-hole pair may be bound again, thus decreasing the efficiency of the photo reduction. Hence, the addition of an organic hole scavenger enhances the photo reduction effect. Generally, organic holes scavengers comprise organic compounds such as methanol, ethanol, formic acid, and acetic acid (Chih. Ming Ma et al. 2012).

### 2.4.1 Effect of Al loading on $TiO_2$

The effects of metal loading on $TiO_2$ catalyst are interesting topic because it is the way to improve the catalyst activity. These effects have been theoretically described as an increase in local electromagnetic field nearby metal surfaces which is found when the wavelength of the irradiation sources are correlated with the optical absorption of the surface plasma on resonance (C. Photiphitak, et al. 2010). Shaoyou Liu et al. reported from his study show that the photo reduction activity are better with Al doped into $TiO_2$ than undoped $TiO_{2.}$ He claimed that the phenomenon is due to the macrostructure of Al-doped $TiO_2$ which is that was the results from the modification of the electronic energy band structure of $TiO_2$ through the doping of Al element (Shaoyou Liu et al, 2010). It also has been reported that the conductivity of the Al-doped $TiO_2$ is higher than that of pure $TiO_2$ in a temperature range of 600–900 ◦C. Since ionic radii for Al and Ti are close to each other (0.074 nm for $Ti^{4+}$ and 0.0675 nm for $Al^{3+}$), Al can occupy a regular cation position, forming a substitution solid solution. To maintain electrical neutrality, such substitutions will create oxygen vacancies and donate electrons to make it an n-type semiconductor. Dopant addition in $TiO_2$ also enhances sensitivity and selectivity towards certain gasses. It has been reported that sputtered films of $TiO_2$, principally anatase in structure, are highly selective towards hydrogen gas(Young Jin Choi et al., 2007).

Aluminium doping has been used on $TiO_2$ for a potential application in thermal shock due to its stable thermal expansion coefficient and physical property. $Al_2O_3$ and $Al_2TiO_5$ were observed at $AlCl_3$/$TiCl_4$ ratios higher than 1.1 at 1400 $^0$C. They discovered a formation of new structure connected with Al–O–Ti framework. For Al/$TiO_2$, the anatase structure was stable after calcination at 800 $^0$C, while pure $TiO_2$ was easily transferred to the rutile phase after calcination above 700 8C. The optical property of Al/$TiO_2$ prepared by a thermal plasma method responded visible light. It also found that the size of synthesized powder decreased with increase in the amount of Al because Al species inhibited the particle growth (H.K. Shon et al. 2009). Al/$TiO_2$ has been applied to gas sensor, which needs high conductivity of $TiO_2$ It has been reported that the conductivity of the Al-doped $TiO_2$ is higher than pure $TiO_2$ in a temperature ranging from 600 to 900 $^0$C (Choi et al. 2007).

## 2.5 Methanol

Methanol is the simplest alcohol, containing one carbon atom. It is a colourless, tasteless liquid with a very faint odour and is commonly known as wood alcohol. Methanol or methyl alcohol ($CH_3OH$) is a colourless liquid with a boiling point of 65$^{o}$C. Methanol will mix with a wide variety of organic liquids as well as with water and accordingly it is often used as a solvent for domestic and industrial applications. It is most familiar in the home as one of the constituents of methylated spirits. Methanol is the raw material for many chemicals, formaldehyde, dimethyl terephphalate, methylamines and methyl halides, methyl methacrylate, acetic acid, gasoline etc (Barsby, 1985). **Figure 2.4** show the consumption of methanol based on country. From **Figure 2.4**, china is the largest methanol consumption in the world.

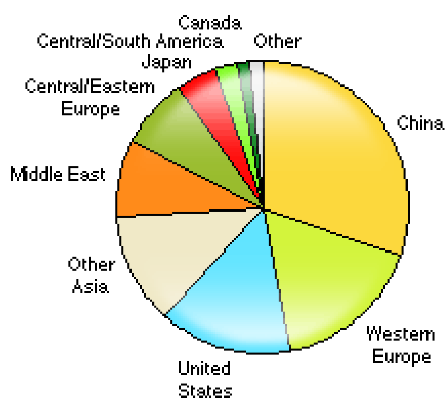


**Figure 2.4**: World Consumption Of methanol ( http:www.chemical.ihs.com)

The primary uses for methanol are the production of chemical products and use as a fuel. It is also being used increasingly for waste water treatment and for producing biodiesel. Methanol is used in the production of formaldehyde, acetic acid and a variety of other chemical intermediates which form the foundation of a large number of secondary derivatives.. Much of the remaining methanol demand is in the fuel sector, principally in the production of MTBE, which is blended with gasoline to reduce the amount of harmful exhaust emissions from motor vehicles. Methanol is also being used on a small scale as a direct fuel and it is fuel for fuel cells (Fiedler et. al., 2009).

## 2.6Analysis method

The sample was analysed by using high performance liquid chromatography (HPLC). HPLC are one of the effective equipment to detect methanol in liquid form.

### 2.6.1 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 physico-chemical properties (Meyer et al., 2002). The nature of the physico-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. Nonionic, ionic and ionisable 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).

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). Of particular importance, is the fact that the mobile phase should be pure and free from impurities, dust, particulate matter and dissolved air (Paul, 1991and 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

# METHODOLOGY

## 3.0 Introduction

The methodology of this studied are divided into two major part which is in the first part is prepared catalyst and the second part is photo reduction process. In the first part, the catalyst were prepared by using sol gel method. In the second part, the photo reduction process of $CO_2$ are analysed by using HPLC based on parameter that have been discussed earlier in chapter one and chapter two.

## 3.1 Chemicals

In this studied, Titatinum tetra isopropoxide ($Ti(OC_3H_7)_4$) were used as a titanium source for the preparation of titania particles. While Aluminium isopropoxide ($Al(OC_3H_7)_3$) were used as aluminium source to prepare aluminium oxide particle. Ethanol was used as a solvent for both precursors. Sulphuric acid ($H_2SO_4$) was act as a peptization agent to form a gel form in sol- gel method. Distilled water was used to act as a cleaner to remove the impurities. In sample analysis, acetonitrile are used as mobile phase.

## 3.2 Experimental Procedure

### 3.2.1 Preparation of $AL_2O_3$-$TIO_2$ Solution

$Al_2O_3$-$TiO_2$ solution was used in sol gel process. From here aluminum oxide was doped into titanium dioxide as metal doped in the based catalyst with respect the weight percentage of aluminium. Firstly, $TiO_2$ solution were prepared by adding 9 mL of $TiO_2$ with 19 mL of ethanol. Under vigorous stirring the solution were added into ethanol-water solution and stir for 4 hours. The same procedure were applied to produce $Al(OC_3H_7)_3$ solution by replacing 9 mL of $TiO_2$ with 4.5 g of $Al_2O_3$. $Al_2O_3$ solution were mixed with $TiO_2$ solution and stirred for 30 minutes. $Al_2O_3$-$TiO_2$ solution was produced. In order to find the best percentage alumina doped into $TiO_2$, the range from 1.25 wt% - 5 wt % were tested.

### 3.2.2 Sol-Gel Method

In sol gel method, 1.0 M of sulphuric acid was added to $Al_2O_3$-$TiO_2$ solution to let a gel formation. It were stirred for 4 hours and ageing for 12 hours at room temperature. The gel was washed with distilled water, filter and dry at 102 $^0$C for 12 hours. It were grinded into small particles and calcined at 200~800 $^o$C for 2 hours. Every catalyst produced were tested in the photo-reduction process to determine performance of the catalyst

### 3.2.3 Photo-Reduction Process of $CO_2$

In photo-reduction process, highly industrial $CO_2$ was first flowed through $Al_2O_3$-$TiO_2$ in the reactor. The rig was then isolated with a pressure of approximately 2 bar. After the whole rig is properly set-up. The UV light then were turn ON. The light was allowed to remain ON continuously for 6 hours. The products inside the reactor were taken in every hour until 6 hour and the sample were analysed by using HPLC. For without UV light, the same process will be carried out but the UV light will be switch off. The samples will be analysed using HPLC. **Figure 3.4** shows the schematic diagram of photo-catalytic reduction process of $CO_2$.

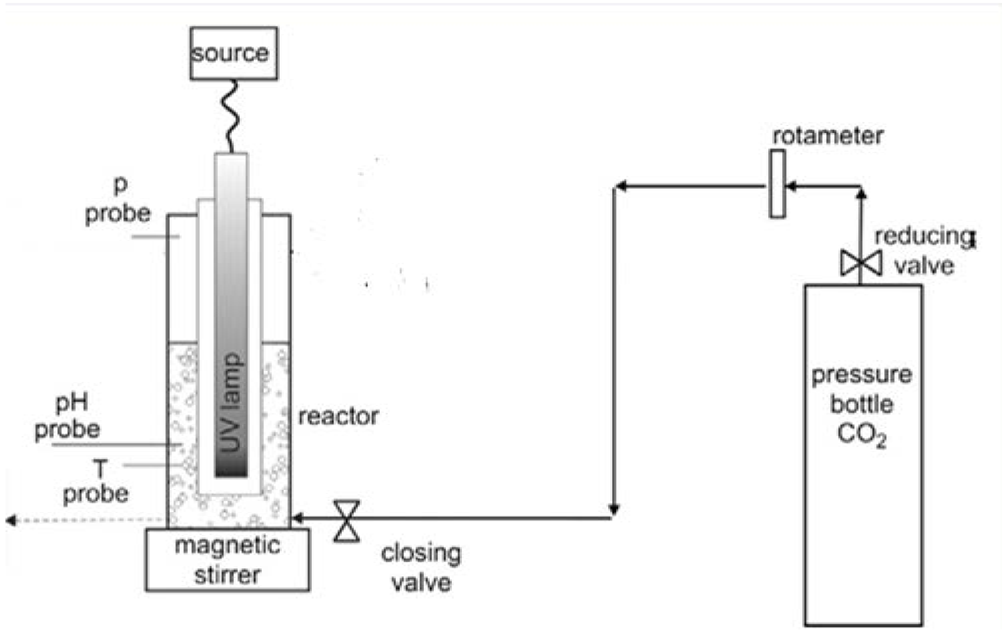


**Figure 3.4**: Schematic Diagram for the $CO_2$ Photo-Catalytic Reduction.

### 3.3 Sample Analysis Method

The sample were analysed by using HPLC to see the performance of catalyst and the effect of UV light based on methanol produce.

### 3.3.1 Mobile phase preparation

Before analysing the samples by using HPLC, firstly mobile phase was prepared. The mobile phase using in this analysis were acetonitrile and water. The ratio for the acetonitrile and water are 400 ml acetonitrile and 600 ml water.

### 3.3.2 Sample Preparation

The sample was taken in every hour for six hour. The sample was labeling as sample A,B,C, and D. Sample A came from reactor 5 wt% catalyst reaction . Sample B came from reactor 3.75 wt% catalyst . Sample C came from reactor 2.5 wt% catalyst reaction and sample D came from reactor 1.25 wt% catalyst reaction. The sample were stored into 10 ml scott bottle. For analysing, the sample are filtered by using membrane filter then transferred into 1.5 ml vial bottle for tested in HPLC

.

### 3.3.3 Standard curve

The sample for standard curve was prepared by dissolved methanol into distilled water. For the standard curve, 5 different concentrations of methanol solution are used. After that, all the samples were filtered into vial for HPLC analysis. The concentration of methanol over water were shown in **Table 3.1**

**Table 3.1**: Standard curve data for analysis

| Vials | % methanol/water |
|---|---|
| 1 | 10 |
| 2 | 30 |
| 3 | 70 |
| 4 | 90 |

# CHAPTER FOUR

# RESULTS & DISCUSSION

## 4.0 Introduction

In this study, two different parameters were studied that are effect of UV light and effect of percentage loading of aluminium oxide on titanium dioxide in production of methanol as a main yield. The results were analysed using high performance liquid chromatography (HPLC).

## 4.1 Effect of percentage loading of Aluminium Oxide Doped on Titanium Dioxide Catalyst

Aluminium oxide-doped on titanium dioxide nanoparticles became of a current interests because of both their effects on the improvement of photo reduction activity of $TiO_2$. In the case of Al are chosen because it has the lowest oxide formation energy. The objective are to find the yield of methanol with 5 wt% maximum aluminium loading on titanium dioxide based catalyst. **Table 4.1** and **Figure 4.1** show the result of aluminium loading on titanium dioxide based catalyst in photo reduction with present of UV light.

**Table 4.1**: Concentration of methanol from different of percentage of $Al_2O_3$ loading on $TiO_2$ catalyst

| Sample | Concentration (ng/µL) |
|---|---|
| (5.0 wt%) | 162.576 |
| (3.75 wt%) | 141.152 |
| (2.5 wt%) | 128.224 |
| (1.25 wt%) | 70 |

**Figure 4.1** shows the results of effect of percentage loading of $Al_2O_3$ doped on $TiO_2$ catalyst in photo reduction process with presence of UV light. From Figure 4.1, the results show that the concentration of methanol is decreasing due to the decreasing of percentage of aluminium doped on titanium dioxide. From **Table 4.1** and **Figure 4.1**, the results show that 5.0 wt.% of $Al_2O_3$ doped with $TiO_2$ catalyst produce highest concentration of methanol which is 121.704 ng/μL. The concentration of methanol keep decreasing with respect to decreasing of percentage loading of $Al_2O_3$ on $TiO_2$. Based on the results, the conclusion is the percentage of aluminium loading on titanium dioxide give a big impact on photo reduction reaction.

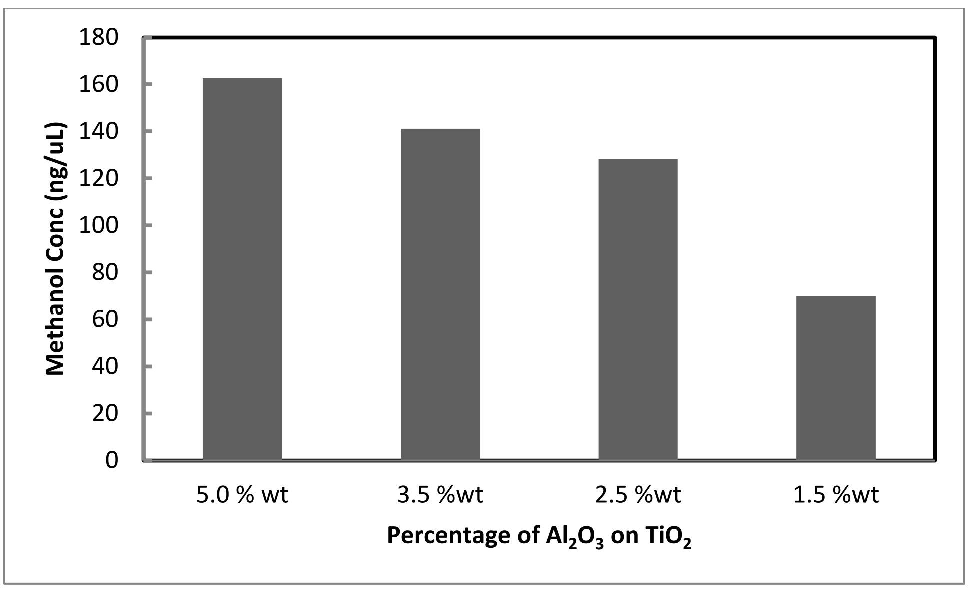


**Figure 4.1**: Effect percentage of $Al_2O_3$ doped On $TiO_2$ catalyst in production of methanol with presence of UV light

The loading of aluminium into titanium dioxide based catalyst is one of the methods to improve the catalytic behaviour. As known, catalyst was found to enhance chemical reaction activity and it sustainability but with a modification of loading metal on based catalyst, the result are showed higher and more sustainable activity than the pure catalyst. Several studies have indicated that an improved $TiO_2$ catalyst can be prepared by substitution doping with metal atoms, such as Fe , and Al. Because the ionic radii for Al and Ti are similar that is 0.053 nm for $Al^{3+}$ and 0.061 nm for $Ti^{4+}$, Al can easily fill into a regular cation position and form a substitution solid solution ( Tsai et. al., 2011). Hsiang Tseng et. al., also reported that from his study of photo reduction of $CO_2$ using sol–gel derived titania and titania-supported copper catalysts, contact between $TiO_2$ and metal generally involves a redistribution of electric charge. In the presence of copper clusters, electrons are enriched owing to the alignment of Fermi levels of the metal and the semiconductor, that is the Schottky barrier. Copper then serves as an electron trapper and prohibits the recombination of hole and electron. In addition, the rapid transfer of excited electrons to the copper cluster enhances the separation of holes and electrons, significantly promoting photo-efficiency. The formation of methanol was more efficient than that of other hydrocarbons in the presence of supported $Cu^+$ on $TiO_2$ from the $CO_2$ and $H_2O$ system (Hsiang Tseng et. al., 2002).

By adding the metal into titanium dioxide, the metals will act as electron traps, facilitating electron–hole separation and promote the interfacial electron transfer process (Anna Zielin´ et. al., 2010). Based in this information it was proved from the result that in **Table 4.1** and **Figure 4.1** showed that the highest aluminium doped into titanium catalyst will give more methanol yield due to the large area for electron transfer process.

### 4.3 The Effect of UV light on Photo Reduction Activity.

In this process, the presence of UV light was studied to investigate the effect of UV light in photo reduction process. The results were shown in **Table 4.2** and illustrated in **Figure 4.2**.Based on the results, its show that with present of UV light, $CO_2$ conversion into methanol in photo reduction process was more effective compared to without UV light.

**Table 4.2** : Methanol Production from Photo Reduction Process With and Without UV Irradiation.

| Sample (wt.% of $Al_2O_3$ on $TiO_2$) | Methanol Concentration Without UV light | Methanol Concentration With UV light |
|---|---|---|
| 5.0 | 59.968 | 162.576 |
| 3.5 | 48.208 | 141.152 |
| 2.5 | 40.896 | 128.224 |
| 1.5 | 34.048 | 70.0 |

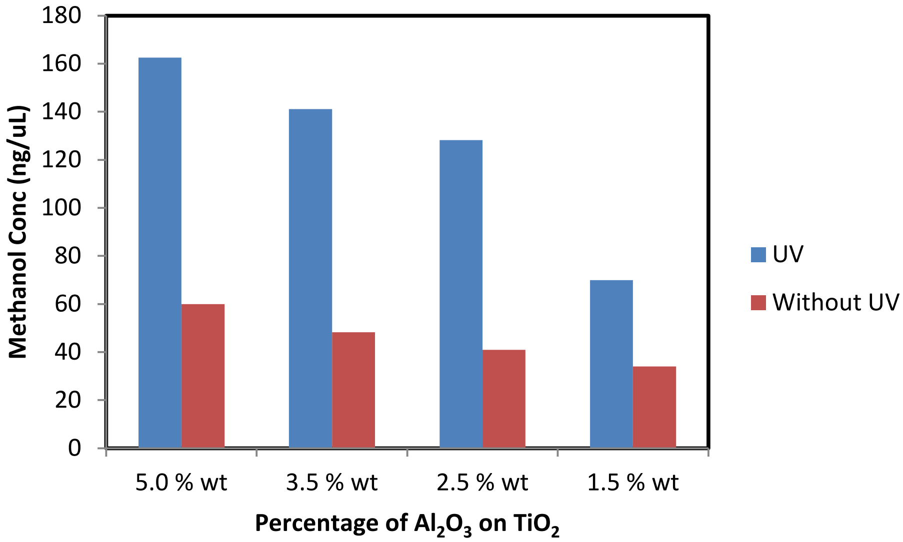


**Figure 4.2**: Methanol Concentration With and Without UV radiation.

Many studied has shown that, photo reduction need UV radiation to enhance the activity. UV light is necessary to excite the electrons on the $TiO_2$ surface. Hazama-cho et. al., (2011) discussed that, among the bands filled with electrons, the one with the highest energy level which is the electron orbit farthest from the nucleus is referred to as the "valence band," and the band outside of this is referred to as the "conduction band." The energy width of the forbidden band between the valence band and the conduction band is referred to as the "band gap." The band gap is like a wall that electrons must jump over in order to become free. The amount of energy required to jump over the wall is referred to as the "band-gap energy." Only electrons that jump over the wall and enter the conduction band which are referred to as "conduction electrons" so it can move around freely. The band gap of titanium oxide is 3.2 eV, which is equivalent to a wavelength of 388 nm. The absorption of ultraviolet rays shorter than this wavelength promotes reactions (Hazama-cho et. al, 2004). Higher amounts of UV radiation increased the degradation of the carbon dioxide in this process. UV absorption produces active oxygen species on the $TiO_2$

surface and when the surface of the rutile $TiO_2$ was irradiated with light consisting of wavelengths shorter than its band gap, about 415 nm (3.0 eV), revealed that the oxidation reaction occurs at the $TiO_2$ surface.

# CHAPTER FIVE

# CONCLUSION & RECOMMENDATION

## 5.1 Conclusion

Methanol was favourably produced on $Al_2O_3/TiO_2$ catalysts in a $CO_2$-NaOH aqueous solution under UV irradiation. 5 wt.% of $Al_2O_3$ doped on $TiO_2$ is the optimum percentage of promoter that loading on catalyst and it is highly efficient photo catalyst for $CO_2$ reduction since aluminium is an effective electron trapper, able to reduce the recombination of electron–hole pairs. The synthesis and doping of Al metals were performed using the sol-gel process.

Besides that, in the presence of UV irradiation can enhance the photo reduction reaction process because UV light is necessary to excite the electrons on the $TiO_2$ surface. With the presence of UV light, the production of methanol yield was increased compared to without UV light.

## 5.2 Recommendation

It is recommended to study another parameter that can be affected to photo reduction process in order to improve the method of $CO_2$ reduction. First recommendation is the metal loading into titanium dioxide can be varying by using another metal such as Zn, Fe and other metal that is suitable to enhance photo reduction activity.

It is also recommended that the light source in photo reduction process can be varying by using another source such as visible light. The effect of another light source can be compared with effect of UV light which is currently used in this study.

In this studied, catalyst used is in powder form. It is recommended to use another form such as in film form of catalyst. Besides, another method of preparing catalyst such as hydrothermal method or other suitable method also recommended to study.

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## APPENDIX A

## STANDARD CALIBRATION CURVE

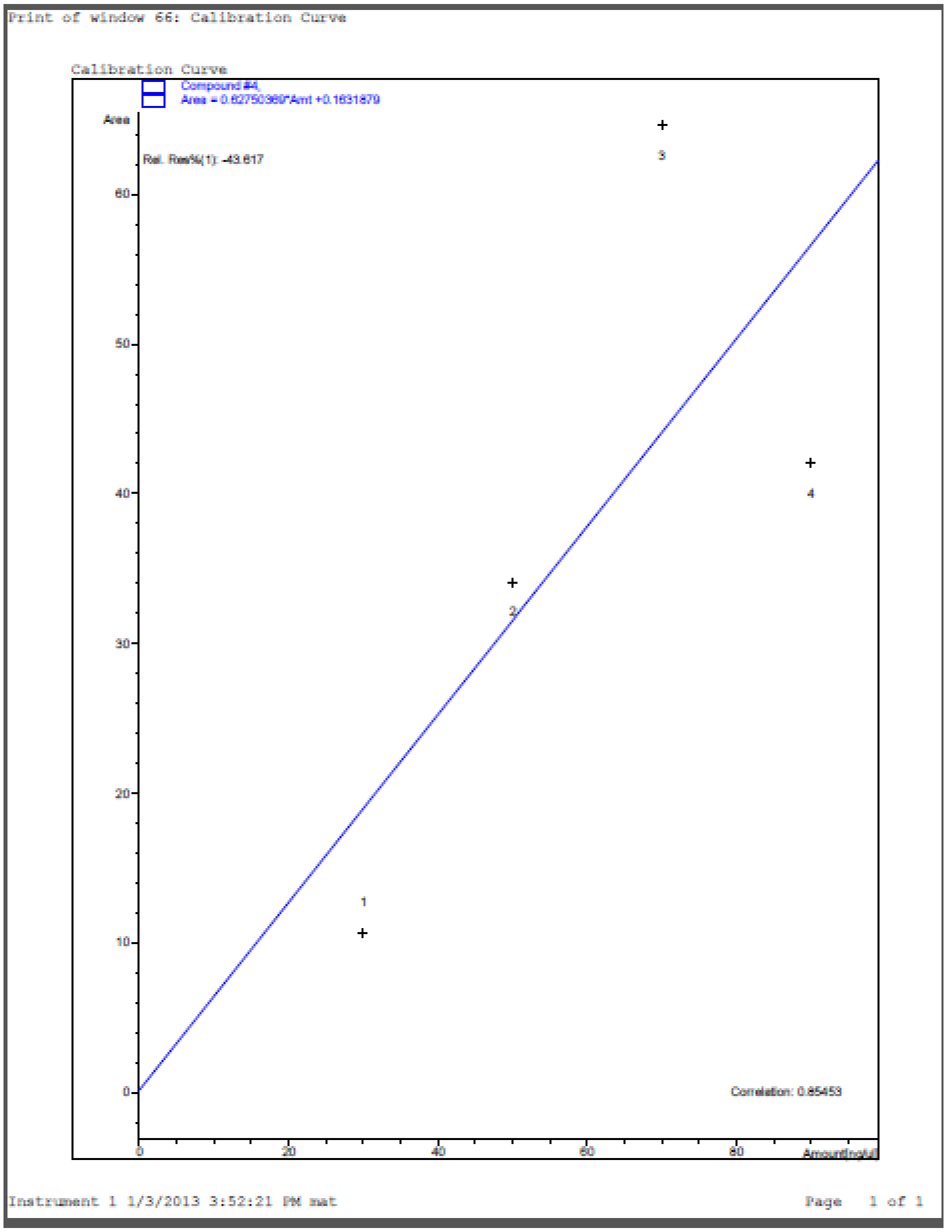


**Figure A.1**: Standard Calibration Curve