Development of Catalyst for Methanol Production

by
Nur Azeanni binti Abd Ghani
15318

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2015

Universiti Teknologi PETRONAS,
32610, Bandar Seri Iskandar,
Perak Darul Ridzuan.

CERTIFICATION OF APPROVAL

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Approved by,

____
(Dr. Bawadi bin Abdullah)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR
September 2015

CERTIFICATION OF ORIGINALITY

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

NUR AZEANNI BINTI ABD GHANI

ABSTRACT

This research will be focusing on preliminary development studies on catalyst that can help to increase the selectivity and yield of methanol production. Over recent years, the research for methanol production via catalytic routes have extensively studied by the researchers. Thus, this project paper covers the development of catalyst for methanol production by using aluminium oxide (Al_2O_3) at different type of promoters which are un-promoted, single promoter (Niobium) and double promoter (Niobium and Zirconium) and to synthesize the Cu/ZnO catalyst at different type of supports which are silicon carbide (SiC), Santa Barbara amorphous silica (SBA-15) and aluminium oxide (Al_2O_3). The characteristics of the catalyst are studied using SEM, EDX, TPR, and TGA. The characteristics of the catalyst depended on the type of support and promoters which influenced the catalytic performances. In order to investigate the effect of the mentioned catalysts, the hydrogenation of CO_2 is performed in the micro-activity fixed bed reactors and stirred high-pressure slurry reactor at 523.15K, 2.25MPa and a H_2/CO_2 ration of 3:1. The results of the reactor performances were find out that the methanol selectivity of using Al_2O_3 as catalyst support incorporated with Niobium and Zirconium as promoters has the highest value which is 71.61% methanol selectivity.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

The increasing demand of methanol is due to the awareness of fossil fuels usage in a last decades. Furthermore, the global warming that will caused greenhouse effect also became a crucial issue nowadays. These two realities that encouraged research into the development of alternative fuels from carbon dioxide (CO_2) that would effectively reduce the level of CO_2 within the atmosphere. Main progress has been accomplished within the field of renewable energy sources over the last few years but a lot of effort still requires to be completed to rise the usage of such energy (Olabi, 2013).

Methanol is one of the alternative fuels which can be synthesis starting from carbon dioxide (CO_2) and hydrogen (H_2). In addition, methanol also important as a storage and transport medium for hydrogen. It is also has many advantages such as it is in the form of liquid in normal conditions and also can be used in conventional combustion engines. The application of a catalyst is important during the production process of methanol (Anicic, Trop, & Goricanec, 2014) for a proper conversion of the reactants. The production of methanol currently based on a $Cu/ZnO/Al_2O_3$ catalyst which was introduced by ICI in 1966 (A. Christophe, 1997). There are many reasons that caused the $Cu/ZnO/Al_2O_3$ catalysts is commercially used in methanol production such as high catalytic activity, extensive life time, high poison resistance, and the reaction temperature and pressure are low (Meshkini, Taghizadeh, & Bahmani, 2010).

Although $Cu/ZnO/Al_2O_3$ catalyst are commercially used for methanol production, research and development on the catalysts need to be done in order to increase the performance of the catalysts for the betterment of the overall methanol synthesis. Methanol synthesis via catalytic route has drawn a lot of consideration nowadays, and it is being studied broadly. Mainly, the research are focused on the support and promoter component of the catalyst to upgrade the performance of Cu-ZnO-based catalysts. This research project is focused on the catalyst support development which are silicon carbide (SiC) and Santa Barbara amorphous silica (SBA-15) at different type of promoters.

1.2 Problem Statement

There are three components for catalyst which are the active site, support and also promoters. One of the method to improve the catalytic performance is by using catalyst support. Catalyst support stands for the material that typically has a high surface area where a catalyst is affixed. The properties of the support may be inert or take part in the catalytic reactions. Carbon, alumina, and silica are the typical supports used in industry. The other method is by adding the promoters to enhance the performance of the catalyst. The function of promoters is to help the reduction of the catalyst in addition to the adsorption and dissociation of the reactant which subsequently affect the catalytic activity (Tasfy, Zabidi, Shaharun, & Subbarao, 2015).

The involvement of catalyst is significant in most of the production industries. As of now, $Cu/ZnO/Al_2O_3$ catalyst is used commercially for methanol production. However, in some cases, the total conversion of CO_2 is low. According to the research by Fujitani and his co-workers (1994), the yield of methanol production using $Cu/ZnO/Al_2O_3$ catalyst was only 11.2% and the selectivity is 52.3%. Sakurai and his co-workers (1996) also stated that the yield of methanol production for their research was only 11.7% and the selectivity is 51.3%. This is due to the strong metal-support interaction in the alumina supported catalyst that leads to the low dispersion of Cu. Moreover, the catalyst also produce copper aluminate. This problem is expected to be resolved by the development of new catalysts for the improvement of methanol synthesis, using novel resources and technologies (Anicic et al., 2014).

One of the approach to resolve the problem is by producing high metal catalyst dispersion via the use of high surface area support. Type of promoters also required to enhance the catalytic activity and performance in the reaction to produce methanol. Thus, this project is required to synthesis Cu/ZnO metallic catalyst by using SiC and SBA-15 as catalyst supports at different type of promoters and to compare the catalytic performance with the existing support such as Al_2O_3.

1.3 Objective

The objectives that need to be accomplished throughout the research process are:

i. To synthesize Cu/ZnO metallic catalyst by using Al_2O_3 at different type of promoters and to synthesize the catalyst by using SiC, SBA-15 and Al_2O_3 as catalyst supports.
ii. To characterize the properties of synthesized catalysts.
iii. To evaluate the performance of the catalyst in carbon dioxide, CO_2 hydrogenation reaction in micro-activity fixed-bed microreactor.

1.4 Scope of Study

The project is mainly focused on synthesizing new Cu/ZnO/Al_2O_3 catalyst at different type of promoters which are unpromoted, single promoter (Niobium) and double promoters (Niobium and Zirconium) and also to synthesized the Cu/ZnO metallic catalyst by using different catalyst supports which are SiC, SBA-15 and Al_2O_3 for the production of methanol. The synthesized catalyst will be characterized using SEM, EDX, TPR and TGA. The influence of the catalyst support and promoters on the performance of Cu/ZnO metallic catalyst in CO_2 hydrogenation to methanol will be studied based on the textural and morphology of the supports and catalytic performance. The result of the experiment will be compared to obtain the best catalyst performance in CO_2 hydrogenation.

1.5 Relevancy of Project

This research project is important for the development of catalysts which are capable of reducing the activation energy of the methanol production process. Besides that, this project also focus on the study of the catalyst supports and promoters which can produce a well-dispersed catalyst to enhance the deactivation rate of the catalyst. Furthermore, this research project is relevant for the development of a catalyst which can provide high methanol selectivity, high methanol yield, and high CO_2 conversion. In addition, this research project is significant because it emphases on the study of the morphologies and catalytic performance of the synthesized catalysts. The information is vital to enable the development of a novel catalyst that can improve the methanol production process.

1.6 Feasibility of Project

This research project is given to the student with condition of completing it within the stipulated time. This time frame can be divided into two parts. The first half of the project will be generally emphasis in literature review, understanding the basic concept and principle of the project. Then, in order to have the ideas on the way to set up the experiment before proceeding to the real experiment, proper planning on the experiment procedure need to be carried out. Moreover, sample preparation and some part of the catalyst preparation can be done in the first half of the research. The catalyst preparation will be continued on the second part of the research project followed by characterization of catalysts using analyzing tools. However, the characterization part of the research has been simplified to preliminary analysis whereby not all the samples will be sent for characterization due to the unavailability and limited slot given for each student to analyze their samples,. This is to make sure student is able to achieve the objectives within the short time frame given. Testing the catalysts' effectiveness in methanol production process was carried out simultaneously with the characterization process. The project is feasible within the stipulated time given with appropriate planning.

CHAPTER 2
LITERATURE REVIEW AND THEORY

2.1 Methanol Synthesis

The urgency of discovering a new alternative energy is increasing with the rapid depletion of liquid oil. Thus, methanol is become the interest for the alternative fuel energy in the future. There are many methods to synthesis methanol. In order to meet the demand for methanol production, there are two methods which focused on the reduction of carbon dioxide, CO_2 emission and operation costs which are the conventional process of methanol synthesis from synthesis gas and the hydrogenation of CO_2 for methanol production.

reaction (1) $CO_2 + 3\,H_2 \xleftrightarrow{k_1} CH_3OH + H_2O \quad \Delta H_R° = -49.57\ \text{kJ mol}^{-1}$

reaction (2) $CO_2 + H_2 \xleftrightarrow{k_2} CO + H_2O \quad \Delta H_R° = +41.27\ \text{kJ mol}^{-1}$

reaction (3) $CO + 2\,H_2 \xleftrightarrow{k_3} CH_3OH \quad \Delta H_R° = +41.27\ \text{kJ mol}^{-1}$

According to the research, the CO_2 hydrogenation was slower than the CO hydrogenation based on the defined process conditions in Table 2.1 (Pontzen, Liebner, Gronemann, Rothaemel, & Ahlers, 2011). Nevertheless, the selectivity was greater and less amount of by-products were achieved when using CO_2 as carbon source (Pontzen et al., 2011) as described in Table 2.2.

Table 2.1 Research parameters of the continuing test in the pilot plant (Pontzen et al., 2011)

Feed	Temperature, T_{jacket} [°C]	Pressure [bar]
CO_2-based	250	80
Standard syngas (C0-based)	250	70

Table 2.2 Purity of the crude methanol product from the pilot plant (Pontzen et al., 2011).

Feed	**Overall selectivity to Methanol [%]**	**Water content [%]**	**Content of other byproducts [wt-ppm]**
CO_2-based	99.96	36.1	390
Standard syngas (C0-based)	99.82	12.8	1800

Both of these technologies are using $Cu/ZnO/Al_2O_3$ catalyst to increase the rate of reaction of methanol production. Thus, this research will be focused on developing a support for Cu/ZnO catalyst in CO_2 hydrogenation.

2.2 Methanol Synthesis over Catalysts

Generally, catalyst is a material, typically in minor quantities relative to the reactants which alters and increases the rate of reaction without being used up in the process. Catalyst works by providing an alternative mechanism that lower the activation energy in a process. In order to reach the transition state, less free energy is required in the presence of catalyst. The total free energy do not change from the reactants to products.

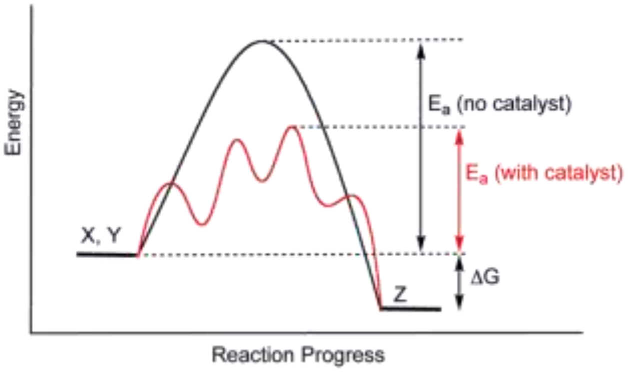


Figure 2.1 Reaction Progress vs Energy graph

Figure 2.1 shows the result of a catalyst in a theoretical exothermic chemical reaction of X + Y to produce Z. The existence of the catalyst opens a different reaction pathway (shown in red) with a lower activation energy.

The methanol synthesis was first implemented over a zinc oxide-chromium oxide catalyst that was operated under conditions at 250-350 bar and 320-450°C (Marschner & Moeller, 1983). However, in 1966, ICI introduced a highly selective copper-zinc oxide catalyst which operate at fairly mild reaction conditions which are at 50-100 bar and 200-300 °C (A. Christophe, 1997) for methanol production. This was for the sulphur-free synthesis gas which containing a high percentage of CO_2. Use of these more active catalysts was made possible because more effective synthesis gas purification processes had become available, mainly removing catalyst poisons (A. Christophe, 1997). In addition, Cu/ZnO catalyst also recognized for its high selectivity and activity for methanol production (Suhas, Prakash, Bhalchandra, & Jyeshtharaj, 2014).

Currently, the $Cu/ZnO/A1_2O_3$ catalyst is used commercially for the methanol production. Important elements that influenced the catalytic process are particle size, surface area, metallic copper surface area and composition of $Cu/ZnO/A1_2O_3$ catalyst (Mierczynski, Maniecki, Chalupka, Maniukiewicz, & Jozwiak, 2011). Basically, in $Cu/ZnO/Al_2O_3$ catalyst, Cu is usually observed as the active part but the properties of ZnO and Al_2O_3 is more than that of an inert support (Grunwaldt, Molenbroek, Topsøe, Kakumoto, Watanabe, Nakamura, & Uchijima, 2000). This is because the activity of Cu-based catalysts can be enhanced by mixtures of metal oxides MOx (M: Cr, Zn, Al) which were typically formed by co-precipitation or impregnation techniques (Mierczynski et al., 2011). Catalysts containing these metal oxides have been observed to be more active than the individual component (Shishido, Yamamoto, Ki, Tian, Morioka, Honda, & Takehira, 2006). The support also helps to further increase the activity of the catalyst and selectivity of methanol (Suhas et al., 2014).

Moreover, in order to modify the activity of the $Cu/ZnO/A1_2O_3$ catalyst, some transition metals have been used as promoters (Nitta, Suwata, Ikeda, Okatomo, & Imanaka, 1994). However, the structural promoters are assumed to increase the number of active sites but only for electronic promoters that influenced on the activation energy and reaction order of a catalytic reaction (Schumann, Eichelbaum, Lunkenbein, Thomas, Álvarez Galván, Schlögl, & Behrens, 2015).

In other hands, the catalytic activity also depend on the kind of support used in methanol synthesis (Mierczynski et al., 2011). The research on the catalyst’s support is still being widely studied.

2.3 Heterogeneous Catalyst Support and Promoter

After decades of research, catalytic reaction also has some limitations and one of the major limitation is separation and distribution (Hu, Yang, & Dang, 2011). Thus, heterogeneous catalyst are now optimized for the maximum reaction rate, which resulted in optimal selectivity (Shibasaki-Kitakawa, Honda, Kuribayashi, Toda, Fukumura, & Yonemoto, 2007). By using various catalyst supports to immobilize the particle for the heterogeneous catalyst, the problem of catalyst separation and recovery from the reaction matrix are addressed (Uysal & Oksal, 2013).

In recent times, there are huge interest in the significance of a suitable catalyst support material. The key point is that the main catalyst should be distributed well on an appropriate support to create the stable catalytic nanoparticles, achieve optimal performance and minimize the amount of costly metal being utilized, which consequently minimize the total catalyst expenses (Shibasaki-Kitakawa et al., 2007). Moreover, support materials with porous characteristics provide a high dispersion of nanoparticle catalyst and simplify electron transfer, both of which result to better catalytic performances (Planeix, Coustel, & Coq, 1994, Kent, Mondloch, & Finke, 2014, Dobrzeniecka & Kulesza, 2013, Astruc, Lu, & Aranzaes, 2005).

However, sometimes, the heterogeneous catalyst support may use a structural effect which brought about by textural and active phase-linked effect (Kent et al., 2014). Thus, the selection on support heterogeneous catalyst must preserve its specific properties, such as dispersion, porosity, selectivity, surface area, and activity (Dobrzeniecka et al., 2013, Astruc et al., 2005, Crudden, Sateesh, & Lewis, 2005). In order to enhance the heterogeneous catalyst’s stability and performance, the morphology and pores size of the selected support materials play an important role (Astruc et al., 2005). They typically help to increase the dispersion of the active phases by rendering more difficult its sintering or aggregation (Marc & Pham-Huu, 2001). Based on the previous research, the support of the heterogeneous catalyst can be alumina (Solsona, Edwards, & Landon, 2006), zeolites (Corma, Iglesis, Pino, & S´anchez, 1991), carbon nanofibers (Dobrzeniecka et al., 2013), active carbon (Planeix et al., 1994), and metal oxides (Leng, Liu, Jiang, & Wang, 2014).

In this research project, the basic interest SiC arose because it exhibits a high thermal conductivity, a high mechanical strength, chemical inertness, a high resistance towards oxidation, and a low specific weight (Addamino & Sprague, 1984, Marchand, Laurent, Guyader, L'Haridon, & Verdier, 1991). These all properties required for a good heterogeneous catalyst support.

SBA-15 also provide thick silica wall, high surface area and large pore diameter which are the good characteristics of catalyst support. Figure 2.2 below is the morphological structure for the SBA-15.

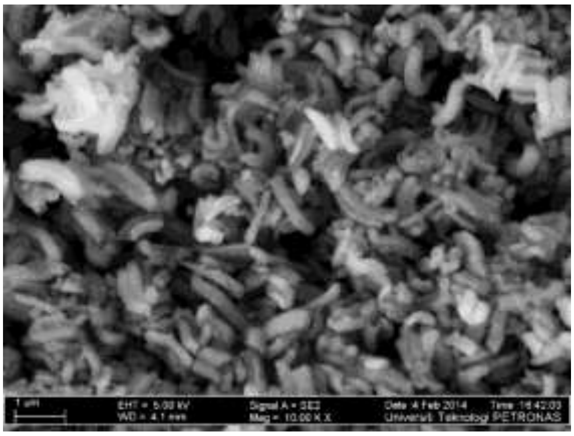


Figure 2.2 Morphological structure of SBA-15

Promoters also plays an important role in the development of catalyst. It enhance the activity and performance of the catalyst for methanol production (Suhas et al., 2014). Zirconia has attracted much attention because it shows a good activity for both CO/H_2 and CO_2/H_2 reactions. Addition of ZrO2 increased the dispersion of Cu particle and changes the surface area of Cu. Niobium has getting higher interest due to its redox property, acidic property and/or photosensitivity thus enhance its catalytic activity and prolong their life time (Tasfy et al., 2015).

CHAPTER 3

METHODOLOGY AND PROJECT WORK

3.1 Chemical

Throughout the experimental works, all the laboratory gas and chemicals needed are listed below:-

I. Laboratory Gas
   a) Carbon monoxide
   b) Hydrogen
   c) 5%hydrogen/nitrogen
   d) Nitrogen
   e) Carbon dioxide
   f) Helium
   g) RGA standard gas
   h) Scott specialty gas
   i) Methanol mixture

II. Chemicals
   a) Tetraethyl orthosilicates (TEOS)
   b) Aluminum oxide
   c) PURALOXSBa-200/Zr20
   d) Copper nitrate tri-hydrate
   e) Zinc nitrate trihydrate
   f) Zirconia (IV) oxynitrate hydrate
   g) Ammonium niobate (V) oxalate hydrate
   h) Ethanol
   i) Hydrochloric acid

j) Pluronic P123 triblock copolymer
k) Ammonia

3.2 Experimental

3.2.1 Synthesis of Catalyst

There are a lot of synthesis methods that can be applied to synthesize the Cu-based methanol synthesis catalysts. The techniques are precipitation, impregnation, sol-gel, colloidal and micro-emulsion. Thus, in this project, impregnation method are the most suitable one to synthesis the supported Cu/ZnO nanocatalyst. Cu/ZnO-based catalysts supported by SiC, Al_2O_3 and SBA-15 supports were promoted by Zr and Nb and the result of the supports on the catalytic performance will studied. After that, the effect of the synthesis conditions on the catalytic performance will be studied.

There are two sections in the preparation of catalyst which are the synthesis of catalyst supports and the preparation of supported Cu/ZnO-based catalysts by impregnation method.

i. Preparation of the Catalyst Supports

a. Silicon carbide (SiC)

Silicon carbide was purchased from the chemical vendors as it is available commercially.

b. Aluminium oxide (Al_2O_3)

The support of catalyst which in this experiment is aluminium oxide (γ-alumina) was pre-treatment in air using furnace chamber at 673K for 5 hours with an temperature increment at 5°K/min.

c. Santa Barbara amorphous silica (SBA-15)

The SBA-15 was synthesized based on the procedure proposed by Dacquin et al in 2012.

Mesoporous SBA-15 was prepared (Dacquin, Lee, Pirez, & Wilson, 2012) by dissolving 10 g of Pluronic P123 triblock copolymer which is a structure directing agent in 260 mL of water. In order to achieve the desired pH 2, different quantity of 10% of HCl solution was added. After that, 22.5 mL of tetraethyl orthosilicate (TEOS) was added to the pluronic acid solution and the synthesis temperature was varied between 313.15K under continuous stirring. Turbid solution was obtained before the addition of TEOS which could be attributed to the formation of the precipitate. The influence of synthesis duration was achieved by stirring the pre-solution for 10 hours. The mixture was aged at 353.15K for range of aging duration of 48 hours. The white mixture was washed using ethanol after the aging step is completed. The solid product was recovered through filtration of the washed mixture and then dried at ambient temperature 298.15K for 24 hours. Removing of the template was accomplished by calcining the sample in air at 823.15K for 4 hours (Thielemann, Girgsdies, Schlögl, & Hess, 2011).

3.2.2 Preparation of the Methanol Synthesis Catalyst

i. Supported Cu/ZnO-based catalysts

By using impregnation technique, catalyst with bimetal (Cu and Zn) with ratio Cu:Zn is 70:30, loadings of 15 wt% was synthesized. A metal precursor that was used in this method are copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) and zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$). The total of each precursor was calculated in order to produce 5 g of the total catalyst with 15% metal loading over different type of supports. The calculation is attached in the Appendices.

The required amount of $Cu(NO_3)_2.3H_2O$ and $Zn(NO_3)_2.6H_2O$ were dissolved in a beaker filled with deionized water to produce a desired 0.5M aqueous solution. After that, in order to form a homogeneous mixture, the solution was stirred by using hot plate stirrer for 1 hour. After the mixture is formed, the ready aqueous solution was added drop by drop using pipette into the beaker containing support (SiC) under continuous stirring for 24 hours. The pH of the mixture was altered to pH 2 using 10M ammonia solution during the addition of the precursor solution. The paste was air-dried in an oven at 393.15K for 12 hours. Z Then, followed by calcination in an Al_2O_3/quartz boat using furnace chamber at 623.15K for 4 hours. The experiment was repeated by using Al_2O_3 and SBA-15 catalyst supports to compare the result.

ii. Supported Cu/ZnO-based catalysts incorporated with promoter

The silicon carbide (SiC) support was placed in a beaker filled deionized water and stirred for 1 hour using hot plate stirrer. After that, the pH of the solution was altered to pH 7 by using 10M ammonia. 22 mL of deionized water was prepared to produce 0.5M solution. Then a 2.00 g of copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) and 0.82 g of zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) were dissolved in that deionized water using beaker (Calculation of the required amount of catalyst is included in Appendices). Under intense stirring using the hot plate stirrer, the nitrates precursors of Cu and Zn was impregnated in slight portions onto the support (SiC) solution. Next, an aqueous solution of $C_4H_4NNbO_9.xH_2O$ was deposited into the Cu-Zn mixture using pipette under continuous stirring for 24 hours. The resultant slurry was dried at 393.15K for 12 hours in an oven. Lastly, the sample was calcined in air using furnace chamber at 623.15K for 4 hours. The experiment was repeated by using Al_2O_3 and SBA-15 catalyst supports to compare the result. After that, the experiment was repeated again by using double promoters which are $C_4H_4NNbO_9.xH_2O$ and $ZrNO_3.xH_2O$. Table 3.1 below represent the composition of the synthesized promoted catalysts.

Table 3.1 Composition of promoted catalyst

Catalyst support	Metal loading (15%)		
	Unpromoted	Promoted (1 wt%)	
SiC	Cu:ZnO 70:30	Cu:ZnO 70:30 Nb	Cu:ZnO 70:30 ZrNb
Al_2O_3			
SBA-15			

3.2.3 Characterization Techniques

The syntehsized catalysts was characterized using Scanning Electron Microscopy (SEM) which used to determine the morphological change by scanning the sample with a high-energy beam of electrons. Moreover, Energy Dispersive X-ray Spectroscopy (EDX) analysis is used to investigate the copper metal dispersion on the surface of the catalyst support and temperature-programmed reduction (TPR) which is a technique to characterize the solid material and finding the most efficient reduction condition and studying the metal-support interaction. Thermo Gravimetric Analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of the catalysts are measured as a function of increasing temperature and time.

3.2.4 Catalytic Performance Evaluation

The performance of the prepared catalyst for the methanol synthesis in CO_2 hydrogenation was evaluated over reaction system which is two-phase (microactivity fixed-bed reactor). The two phase system consists of three components namely the gas supplying system, microactivity fixed-bed reactor and gas chromatograph (GC) system.

3.2.5 Catalyst Testing

The performance of Cu/ZnO bimetallic supported catalysts in the hydrogenation of CO_2 to methanol was conducted in a micro-activity fixed-bed microreactor as shown is Figure 3.1. Catalytic activity screening test was performed on the two form of reaction systems for all the synthesized catalyst under the same reaction conditions in order to examine the superiority.

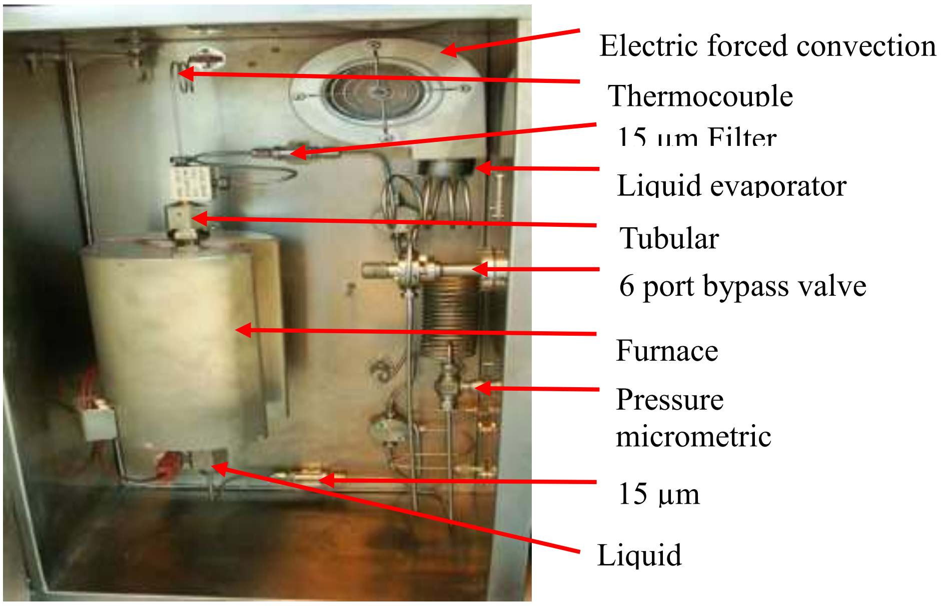


Figure 3.1 Micro-activity fixed-bed microreactor

0.2 g of the catalyst was held in the middle of the reactor tube between two layers of quartz wool. Next, the reactor tube was placed in the electrical furnace. The reactor was purged with helium at flow rate of 1.2 L/h for 15 mins. This step is required to purge the air out of the reactor tube and the line that was connected to the gas chromatography (GC). The calcined catalyst was reduced in 5 vol% H_2 in He at 20 mL min^{-1} at 523.15K for 4 hours under atmospheric pressure prior to reaction. After the reduction step is done, the reactor was purged again with helium at 1.2 L/h for 20 mins until the temperature changed from 523.15K to reaction temperature. Then, the inert gas flow was switched to a mixture of H_2 and CO_2 with desired feed ratio. The reactant was flowed directly to the reactor tube without further purification. Typically the methanol synthesis reactions was conducted for 10 hours. All post-reactor lines, valves, and hot box was heated to 453.15K to prevent product condensation. Effluent gases from the reactor was periodically analyzed by computer-controlled an on-line gas chromatograph (Agilent 7890A). At every 30 mins, sampling was conducted. The evaluation of the CO_2 conversion and product selectivity was made based on the average of the 10 reaction hours.

3.2.6 Reaction Condition

The catalytic screening test was done in the reaction system under mild reaction condition of 523.15K, 2.25 MPa, H_2/CO_2 ratio of 3:1. The range of the operation conditions is illustrated in Table 3.2.

Table 3.2 Operation condition for CO_2 hydrogenation

Variables	**Two phase**
Mass of catalyst (g)	0.2
Temperature (K)	523.15
Pressure (MPa)	2.25
H_2/CO_2 ratio (molar)	3:1

3.3 Project Flow Chart

Below is the process flow for the research project in order to achieve the objectives of the project. The methodology explains in brief the activities that been carried out throughout this research work which is illustrated in the Figure 3.2 below:

Problem Statement and Objectives

Identifying the objective of conducting the project.

Literature Review

Reading and collecting the information regarding the project from various sources e.g. journals.

Experiment Methodology and Design

Deciding the experiment method and tools, materials and procedures needed to conduct the project. This is including the preparation of catalyst, characterization and reaction study.

Data Gathering and Analysis

The data obtained from the experiment was interpreted critically and the results was discussed in more detail.

Documentation and Reporting

All findings will be documented and reported. Conclusion and recommendations will be made at the end of the report.

Figure 3.2 Process flow chart for the research project

This project is mostly experimental based research whereby different types of catalyst need to prepare at the beginning stage of experiment after a thorough literature review has been done. A reference catalyst which is $Cu/ZnO/Al_2O_3$ was prepared to compare with the new developed catalysts. Followed by characterization of prepared catalysts to analyze the porosity, surface area, structure, and other properties of the catalysts and compared with the reference catalyst. After that, reaction study was carried out for methanol production using the synthesized catalyst. Analysis of results was carried out after all the experimental works have been done to observe the catalyst with the best reaction performance for methanol production. Continuous reviewing literature throughout the experimental process was needed in discovery the explanation on the results found.

3.4 Gantt Chart and Key Milestone

Below is the Gantt chart which is the scheduled project activities and key milestone in order to complete the project.

Table 3.3 Gantt chart and key milestones for FYP 1

No	Details/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Selection of the project title	🟩	🟩												
2.	Preliminary Research Work and Literature Review • Search and collecting information from various sources		🟩	🟩	🟩	🟩	🟩								
3.	Submission of Extended Proposal (first draft)						🟩								
4.	Submission of Extended Proposal (final draft)							🟨							
5.	Preparation for Proposal Defence								🟩						
6.	Proposal Defence									🟨					
7.	Experimental Work • Prepare the $Cu/ZnO/Al_2O_3$ catalyst • Characterization and testing of the catalyst											🟩	🟩		
8.	Submission of Interim Draft Report												🟨		
9.	Submission of Interim Report													🟨	

Table 3.4 Gantt chart and key milestones for FYP 2

No	**Details/Week**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1.	Synthesized of of SBA15			🟩	🟩										
2.	Synthesis of catalysts		🟩	🟩	🟩	🟩	🟩								
3.	Characterization of catalysts				🟩	🟩	🟩	🟩							
4.	Reaction performances of Catalysts				🟩	🟩	🟩	🟩							
5.	Preparation for Progress Report						🟩	🟩							
6.	Submission of Progress Report								🟨						
7.	Continue for Experimental Work, Characterization and Reaction performances								🟩	🟩	🟩	🟩	🟩		
8.	Pre-SEDEX											🟨			
9.	Submission of Draft Report											🟨			
10.	Submission of Dissertation (Soft bound)												🟨		
11.	Submission of Technical Paper												🟨		
12.	Viva Oral Presentation													🟨	
13.	Submission of Project Dissertation (Hard bound)														🟨

🟩 **Process** 🟨 **Suggested Milestone**

CHAPTER 4

RESULT AND DISCUSSION

4.1 Characterization of synthesized catalysts

Characterization of catalysts is important as it supports the researchers to have a well insight on the physical and chemical characteristic of the catalysts. The physical characteristic of the catalysts including the surface area, pore size, morphology of the carrier and the geometry and strength of the support while the chemical characteristic may include the structure, composition, the active catalytic components and nature of the carrier. The catalysts which is investigated in this project is categorized as listed in Table 4.1.

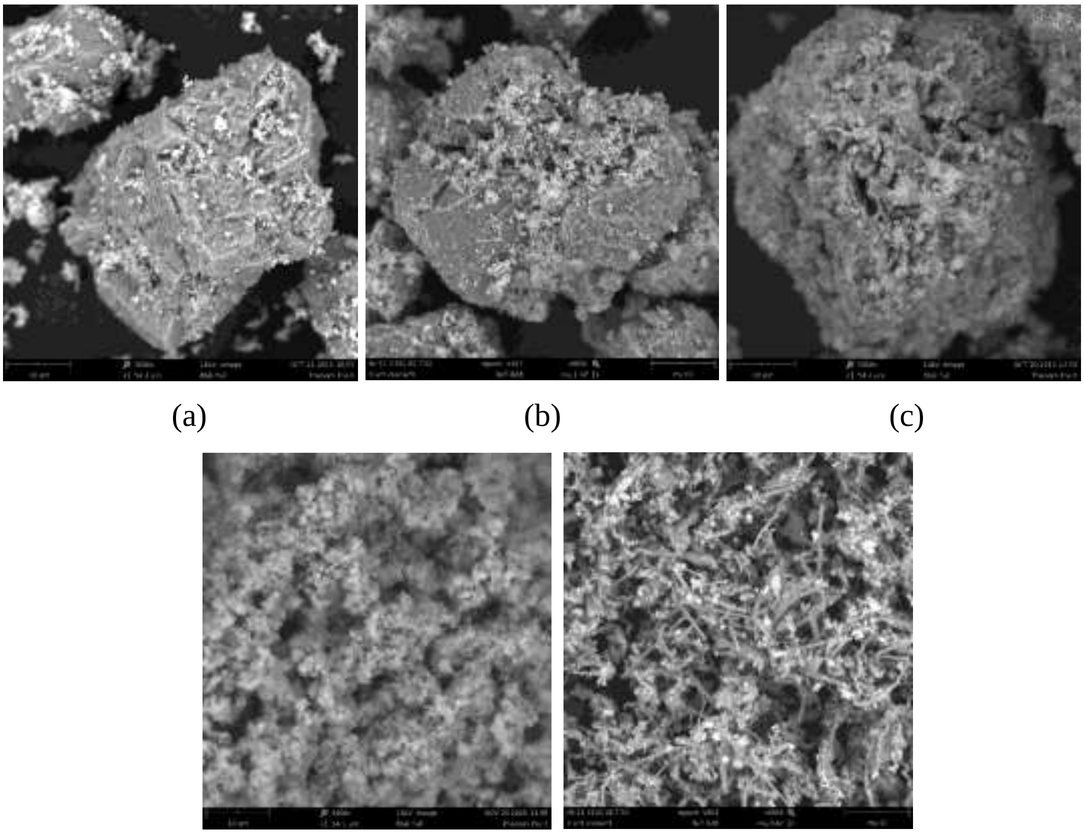
Table 4.1 Labelling of synthesized catalyst

Label of Catalyst	Description of Catalyst	Composition of Catalyst
CAT-1	Support: Al_2O_3	10.5% Cu, 4.5% ZnO, 85% Al_2O_3
CAT-2	Support: Al_2O_3 Promoter: Nb	10.5% Cu, 4.5% ZnO, 1% Nb, 84% Al_2O_3
CAT-3	Support: Al_2O_3 Promoter: Nb and Zr	10.5% Cu, 4.5% ZnO, 1% Nb, 1% Zr, 84% Al_2O_3
CAT-4	Support: SBA-15	10.5% Cu, 4.5% ZnO, 85% SBA-15
CAT-5	Support: SiC	10.5% Cu, 4.5% ZnO, 85% SiC

4.1.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) images were recorded on a Philips XL30/FEI ESEM operating at an accelerating voltage from 5 to 10kv. Before the SEM images were taken at 500x, 1000x, 1500x, 3000x, and 5000x magnification, the samples were coated with graphite. From SEM analysis, the clear image or the morphology of the catalyst's surface will be obtained.

The synthesized catalysts that have been analyzed by using SEM are CAT-1, CAT-2, CAT-3, CAT-4 and CAT-5. The results shown in Figure 4.1 with 5000 magnification as follows.



(a) (b) (c)

(d) (e)

Figure 4.1 SEM images of catalysts at 5000x magnification (10 μm scale): (a) CAT-1, (b) CAT-2, (c) CAT-3, (d) CAT-4 and (e) CAT-5

From the SEM results, it shows the morphological structure for different type of supports. The SEM images revealed that the morphological structure for CAT-1, CAT-2, and CAT-3 which are Al_2O_3 catalyst support and CAT-4 which is SBA-15 catalyst support demonstrated spherical geometry while CAT-5 which are the SiC support demonstrated needle geometry. From the morphological structure view, it can be clearly seen that the geometry of the SBA-15 is different from the literature. It could affect the performance of the catalyst in the reaction as the morphology and pores size of the selected support materials play an important role to improve the catalytic performance (Astruc et al., 2005).

Furthermore, it can be seen that the copper particles were dispersed on the surface of the Al_2O_3 support. One of the main aspects that has been considered for the development of catalysts for methanol production is the smaller particles size. It is due to the large particles dispersion may encourage to the formation of carbon on the surface of the catalysts, thus resulted in deactivation and sintering of the copper metal.

In addition, the SEM images shows that CAT-1, CAT-2 and CAT-3 catalyst's surfaces have high homogeneous morphology. In contrast, CAT-4 and CAT-5, demonstrated an uneven surface, which means that they are not in homogenous morphology. It would also effect the dispersion of copper and hence resulted in low catalytic performance. However, Energy Dispersive X-ray Spectroscopy (EDX) mapping has to be employed to discover the dispersion of copper particles on the surface of γ-Al_2O_3 support.

4.1.2 Energy Dispersive X-ray Spectroscopy (EDX) Analysis

EDX analysis was performed to determine the actual and uniform copper dispersion. The atomic percentage of the individual elements were determined from the EDX mapping to evaluate whether accurate amount of metal precursors have been incorporated into the synthesized catalysts.

The synthesized catalysts that have been analyzed by using EDX are CAT-1, CAT-2, CAT-3, CAT-4 and CAT-5. The results for the EDX analysis were indicated as follows.

Table 4.2 Determination of weight percentage of Al, O, Cu and Zn element for CAT-1 (10.5% Cu, 4.5% ZnO, 85% Al_2O_3)

Atomic Number	Element	Atomic Percentage
13	Aluminium	39.3
8	Oxygen	19
29	Copper	26.9
30	Zinc	14.8
	TOTAL	100

Table 4.3 Determination of weight percentage of Al, O, Nb, Cu and Zn element for CAT-2 (10.5% Cu, 4.5% ZnO, 1% Nb, 84% Al_2O_3)

Atomic Number	Element	Atomic Percentage
13	Aluminium	26.7
8	Oxygen	39.2
29	Copper	27.4
30	Zinc	6.3
41	Niobium	0.5
	TOTAL	100

Table 4.4 Determination of weight percentage of Al, O, Nb, Zr, Cu and Zn element for CAT-3 (10.5% Cu, 4.5% ZnO, 1% Nb, 1% Zr, 83% Al_2O_3)

Atomic Number	Element	Atomic Percentage
13	Aluminium	27.2
8	Oxygen	33.8
29	Copper	34.1
30	Zinc	4.4
41	Niobium	0.4
40	Zirconium	0.2
	TOTAL	100

Table 4.5 Determination of weight percentage of Si, C, O, Cu and Zn element for CAT-4 (10.5% Cu, 4.5% ZnO, 85% SBA-15)

Atomic Number	Element	Atomic Percentage
13	Silicon	52.4
8	Oxygen	16.6
29	Copper	18.7
30	Zinc	7.8
6	Carbon	1.5
	TOTAL	100

Table 4.6 Determination of weight percentage of Si, C, O, Cu and Zn element for CAT-5 (10.5% Cu, 4.5% ZnO, 85% SiC)

Atomic Number	Element	Atomic Percentage
13	Silicon	46.2
38	Strontium	10.0
8	Oxygen	23.3
29	Copper	16.3
30	Zinc	3.3
6	Carbon	0.9
	TOTAL	100

Based on the EDX mapping results, it can be clearly seen that the copper is nicely dispersed on the surface of Al_2O_3 support. The uniform dispersion of active catalyst helps to strengthen the catalysts and thus enabled effective methanol conversion process to take place.

The atomic percentage shows the distribution of each element in selected spots of the catalysts. The EDX analysis also showed that the amount of oxygen element is higher than the amount which is expected to be incorporated onto the catalysts due to the oxidation reaction. Moreover, there are one contaminant element which is the strontium (Sr) in SiC’s catalyst sample which affect the catalytic performance.

4.1.3 H_2-TPR Analysis

The reducibility performance of the synthesized catalysts will be determined by H_2-TPR analysis technique on a Thermo Finnigan (TPDRO 1100) instrument fitted out with a thermal conductivity detector (TCD) in two-stage processes which are pretreatment and analysis. 0.2 g of the prepared catalyst was placed between two layers of quartz wool inside a conventional atmospheric quartz flow reactor. After that, the quartz cell was positioned inside the electrical furnace that is equipped with a programmable temperature controller. The sample was pretreated under flow pure N_2 and temperature was set to increase from the room temperature to 250^{o}C at 10^{o}C/min. Then, the sample was held at 250^{o}C for one hour in order to remove the impurities and the moisture. After carrying out the pretreatment step, the flow was switched to 5%H_2/Ar (20ml/min) which was used as the reducing gas and temperature was ramped to 500^{o}C at 10^{o}C/min. Lastly, the sample was hold at 500^{o}C for 4 hours. The tail gas was directly passed to the thermal conductivity detector (TCD) to determine the hydrogen consumption in the gas stream. Distinct reducible species in the catalyst were shown as peaks in the H_2-TPR profile. The synthesized catalysts that have been characterized by using H_2-TPR are CAT-1, CAT-4 and CAT-5.

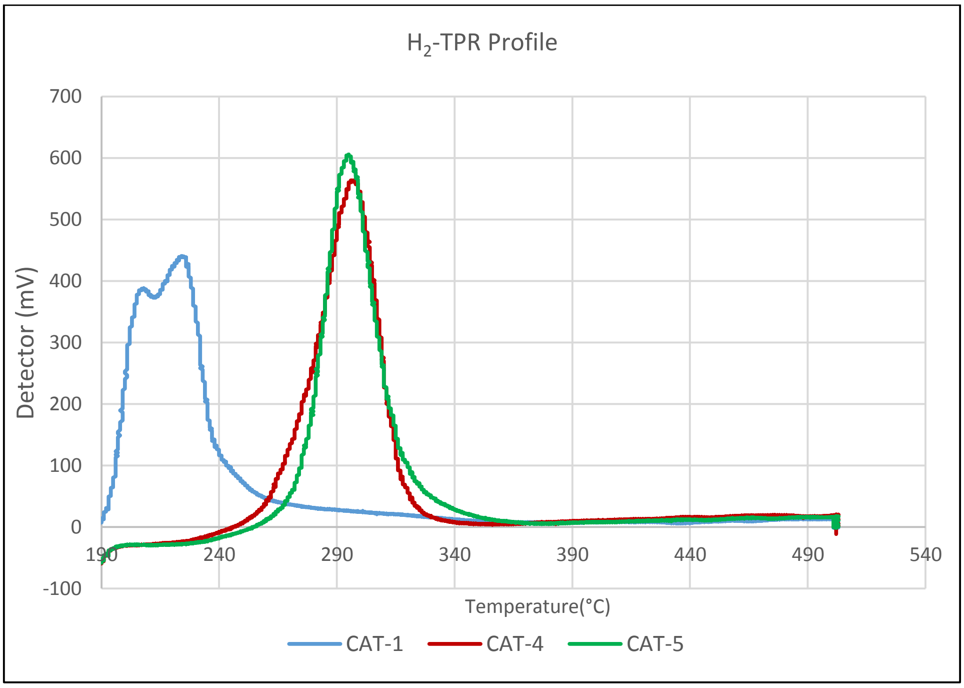


Figure 4.2 TPR Profile for CAT-1, CAT-4 and CAT-5

Figure 4.2 above shows the H_2-TPR profile for the three synthesized supported catalyst. Based on the figure, CAT-1 have two peaks. The first peak indicates the reduction of $Cu^{2+} \rightarrow Cu^0$ and the second peak indicates the reduction of $Cu^{2+} \rightarrow Cu^+ \rightarrow Cu^0$. The red peak and the green peak which are the CAT-4 and CAT-5 respectively indicate the reduction of $Cu^{2+} \rightarrow Cu^0$. Table 4.7 below represent the exact peak temperature for each catalyst.

Table 4.7 Peak temperature of synthesized catalysts

Type of catalyst	Peak temperature (°C)
CAT-1	205°C, 224°C
CAT-4	300°C
CAT-5	296°C

4.1.4 Thermal Analysis for Synthesized Catalyst

In order to investigate the thermal behavior, structural decomposition and weight loss of the synthesized catalysts, Thermogravimetric Analysis (TGA) was carried out at a heating rate of 10°C/min until the temperature going up to 800°C. 0.1 g of synthesized catalyst were used and the TGA was conducted under sweeping air atmosphere at 10mL/min.

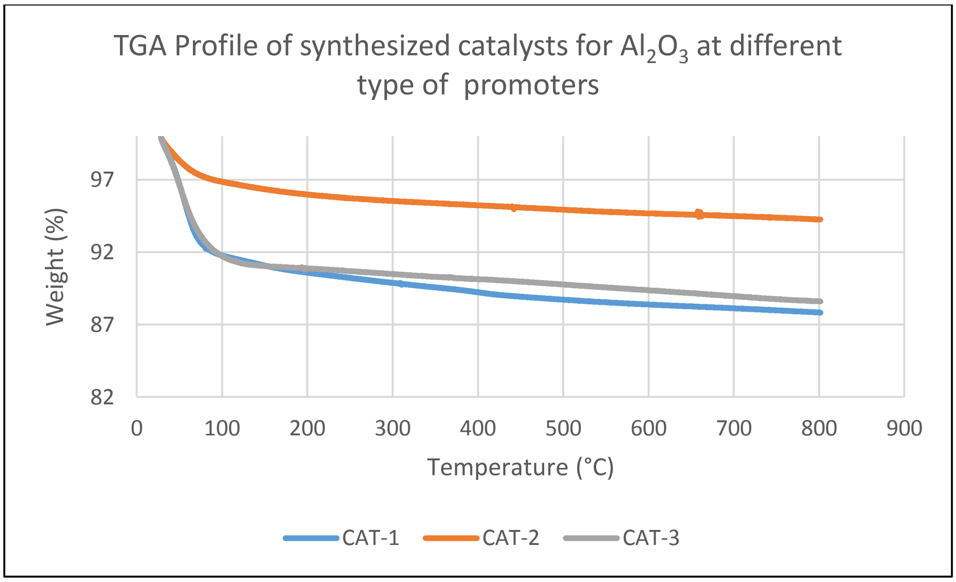


Figure 4.3 TGA Profile for CAT-1, CAT-2 and CAT-3

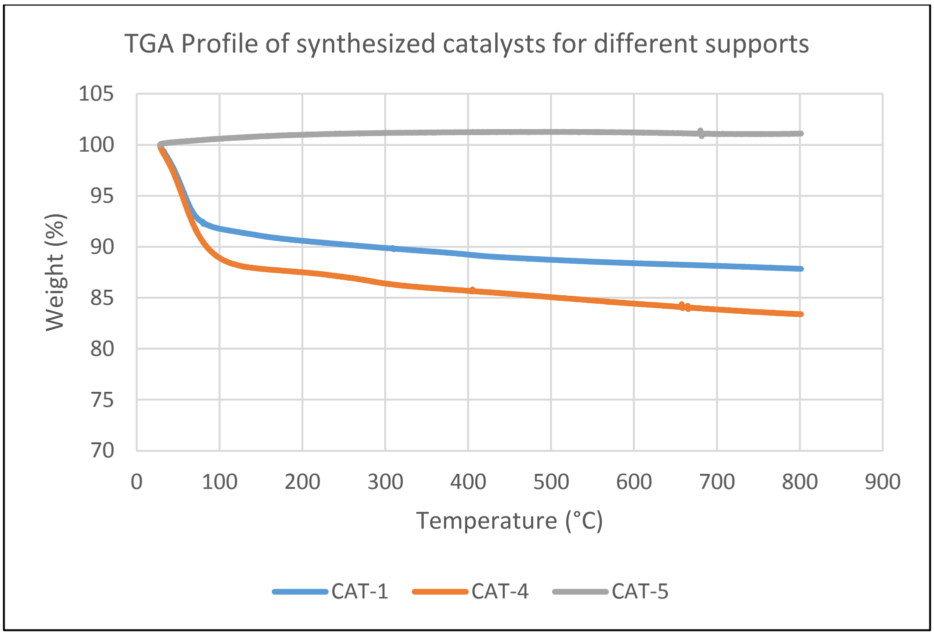


Figure 4.4 TGA Profile for CAT-1, CAT-4 and CAT-5

Figure 4.3 represents the relationship between the weight percentages with the decomposition temperature of the Al_2O_3 catalysts support at different type of promoters and Figure 4.4 represents the relationship between the weight percentages with the decomposition temperature of the synthesized catalysts at different type of support which are Al_2O_3, SBA-15 and SiC. Based on the graph, it can be seen clearly that all the synthesized catalyst demonstrated good resistances towards decomposition at temperature as high as 800℃. This is due to the ability of the synthesized catalyst to exhibit high thermal and long term stability to avoid decomposition of catalyst when the CO_2 hydrogenation takes place.

4.2 Reaction Performance

The performance of the synthesized catalyst have been evaluated by conducting the reaction in the micro-activity fixed bed microreactor to produce methanol. The effect of promoters to the performance of Al_2O_3 supported catalyst and the effect of supported catalyst on the methanol selectivity is being studied.

4.2.1 Effect of promoters to the performance of Al_2O_3 supported catalyst

Tables 4.8, 4.9, 4.10 and Figures 4.5, 4.6 and 4.7 below show the products distribution of methane, methanol, methyl formate, ethanol, acetone and DME of the Al_2O_3 supported catalyst at different promoters. The synthesized catalysts that have been evaluated are CAT-1, CAT-2 and CAT-3.

Table 4.8 Products distribution for CAT-1 (Un-promoted Al_2O_3 catalyst support)

Reaction	Methane	Methanol	Methyl Formate	Ethanol	DME	Total
30	0.106764	0	0	0	0	0.106764
60	0.114505	0	147.47988	0	0	147.5944
90	1.59616	19.76837	225.55708	0	0.172767	247.0944
120	4.09196	51.19111	161.53542	0	0.097538	216.916
150	5.45683	67.89531	1.57063	0	0.135759	75.05853
180	6.39047	80.58717	3.48919	2.39431	0.144943	93.00609
210	7.04998	89.28763	3.95989	2.43484	0.157011	102.8894
240	7.47776	94.67338	4.38176	2.68394	0.163466	109.3803
270	7.81147	99.02485	4.76145	2.99913	0.178396	114.7753
300	8.05953	101.73485	4.72926	2.81116	0.183218	117.518
330	8.13725	101.85237	4.81276	3.02501	0.18371	118.0111
360	8.25202	102.19988	5.08794	3.16583	0.188582	118.8942
390	8.29322	99.70687	5.05287	3.17178	0.177284	116.402

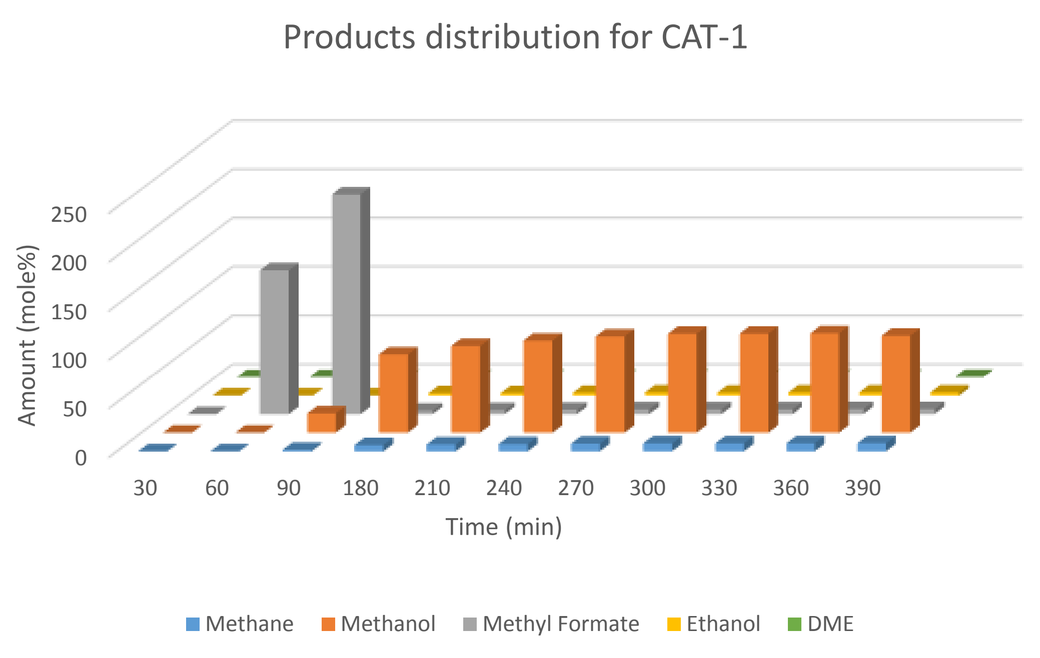


Figure 4.5 Products distribution profile for CAT-1 (Un-promoted Al_2O_3 catalyst support)

Table 4.9 Products distribution for CAT-2 (Nb-promoted in Al_2O_3 catalyst support)

Reaction	Methane	Methanol	Methyl Formate	Ethanol	DME	Total
30	0.106764	0	0	0	0	0.106764
60	0.114505	0	147.47988	0	0	147.5944
90	1.59616	19.76837	225.55708	0	0.172767	247.0944
120	4.09196	51.19111	161.53542	0	0.097538	216.916
150	5.45683	67.89531	1.57063	0	0.135759	75.05853
180	6.39047	80.58717	3.48919	2.39431	0.144943	93.00609
210	7.04998	89.28763	3.95989	2.43484	0.157011	102.8894
240	7.47776	94.67338	4.38176	2.68394	0.163466	109.3803
270	7.81147	99.02485	4.76145	2.99913	0.178396	114.7753
300	8.05953	101.73485	4.72926	2.81116	0.183218	117.518
330	8.13725	101.85237	4.81276	3.02501	0.18371	118.0111
360	8.25202	102.19988	5.08794	3.16583	0.188582	118.8942
390	8.25202	102.19988	5.08794	3.16583	0.188582	118.8942
420	8.29322	99.70687	5.05287	3.17178	0.177284	116.402

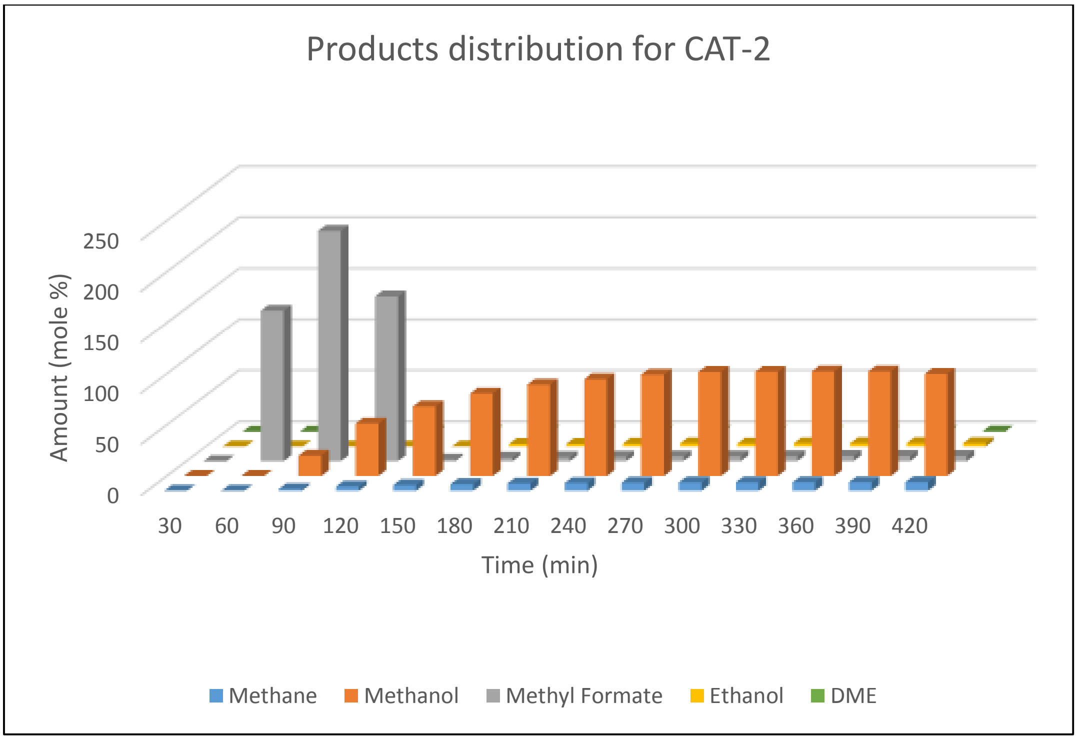


Figure 4.6 Products distribution profile for CAT-2 (Nb-promoted in Al_2O_3 catalyst support

Table 4.10 Products distribution for CAT-3 (NbZr-promoted in Al_2O_3 catalyst support)

Reaction	Methane	Methanol	Methyl Formate	Ethanol	DME	Total
30	0	0	0	0	0	0
60	0.0134071	0	0	0	0	0.013407
90	1.6365	35.23492	1.22716	0	0.309448	38.40803
120	3.04507	79.66071	2.22313	0	0.221374	85.15029
150	3.9131	106.37592	2.91847	0	0.15118	113.3587
180	4.62405	127.52189	3.99826	1.76193	0.142824	138.049
210	5.20781	144.23135	4.31954	1.75341	0.144025	155.6561
240	5.65486	156.76212	4.6475	1.80492	0.150929	169.0203
270	5.97342	166.01089	5.3036	2.0555	0.147868	179.4913
300	6.24891	173.59029	5.32286	2.07543	0.157497	187.395
330	6.4581	176.33108	5.43714	2.25818	0.16801	190.6525
360	6.60039	177.57222	5.2235	2.19105	0.169737	191.7569

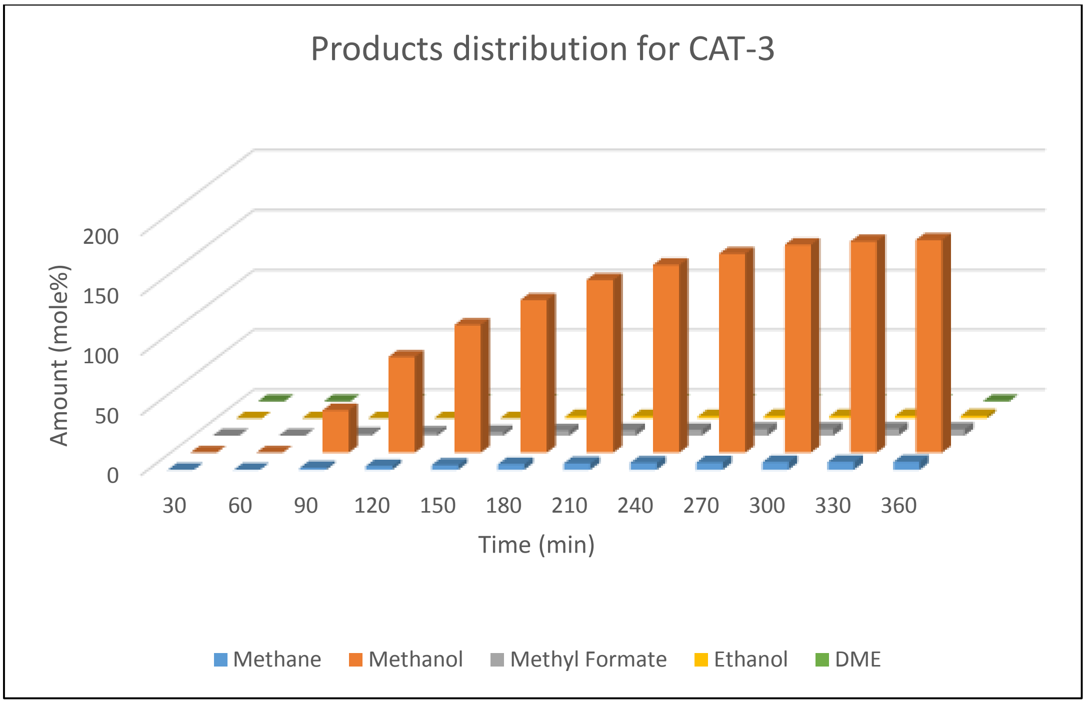


Figure 4.7 Products distribution profile for CAT-3 (NbZr-promoted in Al_2O_3 catalyst support

From the tables and figures above, it can be seen that methanol is the highest product for the reaction by using the Al_2O_3 catalyst support. In addition, those three graphs also show that the methanol produce by CAT-3 which is the Cu/ZnO/Al_2O_3-NbZr is the highest compared to CAT-1 and CAT-2. This is due to the role of promoter that enhance the reaction performance and also the methanol selectivity by preventing the Cu from sintering. Moreover, promoters also help the reduction of the catalyst in addition to the adsorption and dissociation of the reactant which successively affect the catalytic performances (Tasfy et al., 2015).

Methanol selectivity and CO_2 conversion of Al_2O_3 at different promoters are represented in Figure 4.8. The highest methanol selectivity is CAT-3 due to the presence of Nb and Zr promoters.

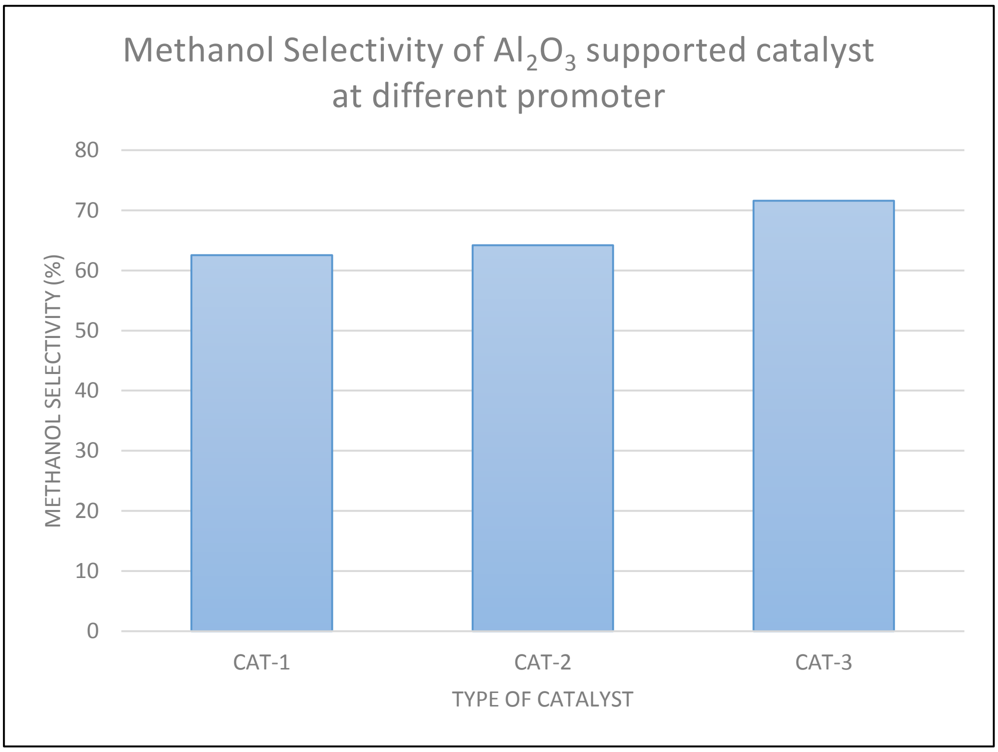


Figure 4.8 Methanol Selectivity for CAT-1, CAT-2 and CAT-3

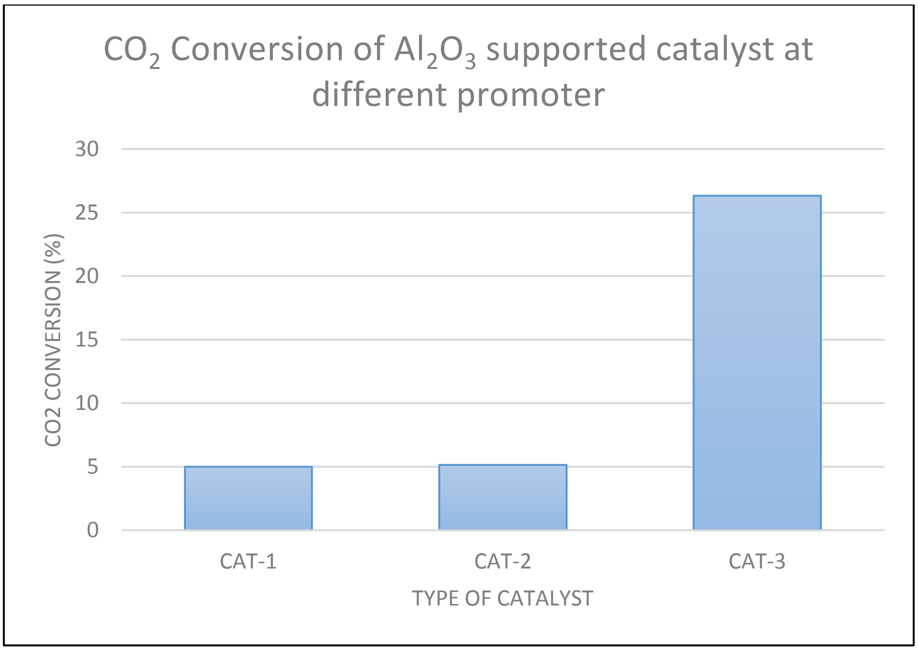


Figure 4.9 CO_2 conversion for CAT-1, CAT-2 and CAT-3

Based on Figure 4.9, it can be seen that CAT-3 has the highest conversion compared to CAT-1 and CAT-2. This shows that CO_2 is mostly converted into methanol using Cu/ZnO/Al_2O_3-NbZr catalyst.

4.2.2 Effect of Support on Catalyst Performance

Tables 4.11, 4.12, 4.13 and Figure 4.10, 4.11 and 4.12 below show the products distribution of methane, methanol, methyl formate, ethanol, acetone and DME at different type of catalyst supports which are the Al_2O_3, SBA-15 and SiC. The synthesized catalysts that have been evaluated are CAT-1, CAT-4 and CAT-5.

Table 4.11 Products distribution for CAT-1 (Un-promoted Al_2O_3 catalyst support)

Reaction	Methane	Methanol	Methyl Formate	Ethanol	DME	Total
30	0.106764	0	0	0	0	0.106764
60	0.114505	0	147.47988	0	0	147.5944
90	1.59616	19.76837	225.55708	0	0.172767	247.0944
120	4.09196	51.19111	161.53542	0	0.097538	216.916
150	5.45683	67.89531	1.57063	0	0.135759	75.05853
180	6.39047	80.58717	3.48919	2.39431	0.144943	93.00609
210	7.04998	89.28763	3.95989	2.43484	0.157011	102.8894
240	7.47776	94.67338	4.38176	2.68394	0.163466	109.3803
270	7.81147	99.02485	4.76145	2.99913	0.178396	114.7753
300	8.05953	101.73485	4.72926	2.81116	0.183218	117.518
330	8.13725	101.85237	4.81276	3.02501	0.18371	118.0111
360	8.25202	102.19988	5.08794	3.16583	0.188582	118.8942
390	8.29322	99.70687	5.05287	3.17178	0.177284	116.402

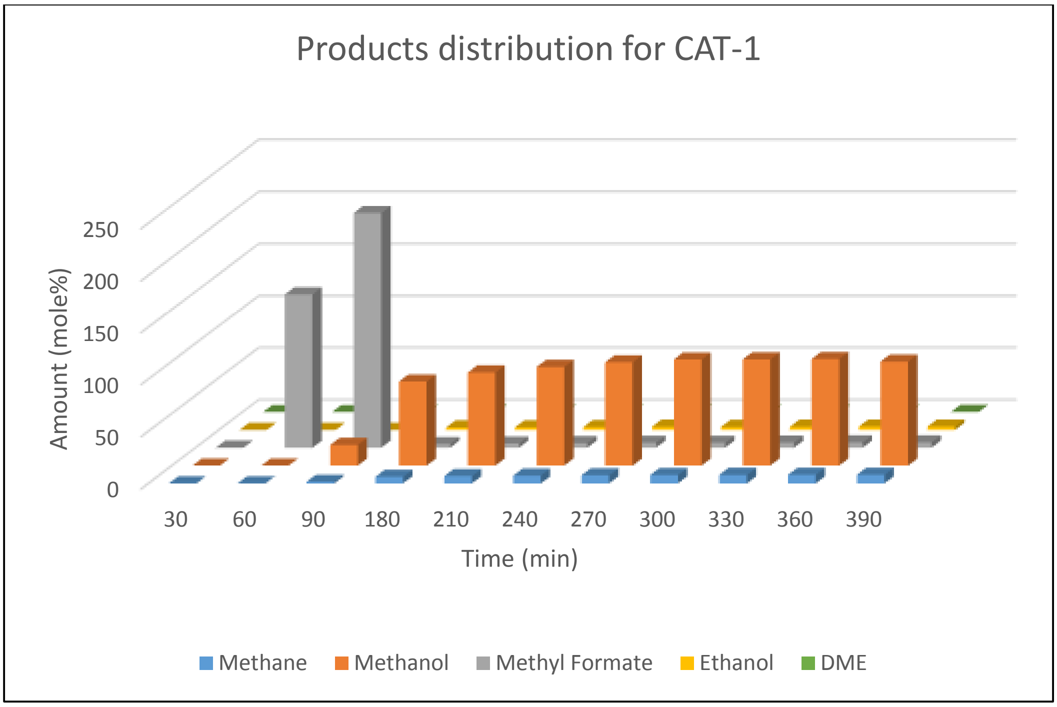


Figure 4.10 Products distribution profile for CAT-1 (Un-promoted Al_2O_3 catalyst support)

Table 4.12 Products distribution for CAT-4 (Un-promoted SBA-15 catalyst support)

Reaction	Methane	Methanol	Methyl Formate	Ethanol	DME	Total
30	1.90584	9.10399	839.71443	8.18402	0.076742	858.985
60	1.82312	8.7092	808.73344	7.33722	2.29E-01	826.8324
90	1.74128	8.38851	784.25743	7.54141	2.07E-01	802.1354
120	1.68687	8.20933	763.1459	7.94941	3.13E-01	781.3049
150	1.65601	7.57818	738.97484	7.0334	1.84E-01	755.4268
180	1.64806	7.21775	717.02576	7.30265	7.30265	733.4232
210	1.67461	6.82463	700.74814	6.39975	1.93E-01	715.8405
240	1.70988	6.57132	679.11743	6.38122	3.79E-01	694.1587
270	1.7719	6.17221	662.90146	6.4165	2.30E-01	677.4925
300	1.85403	6.06655	648.19046	9.09367	1.91E-01	665.3959

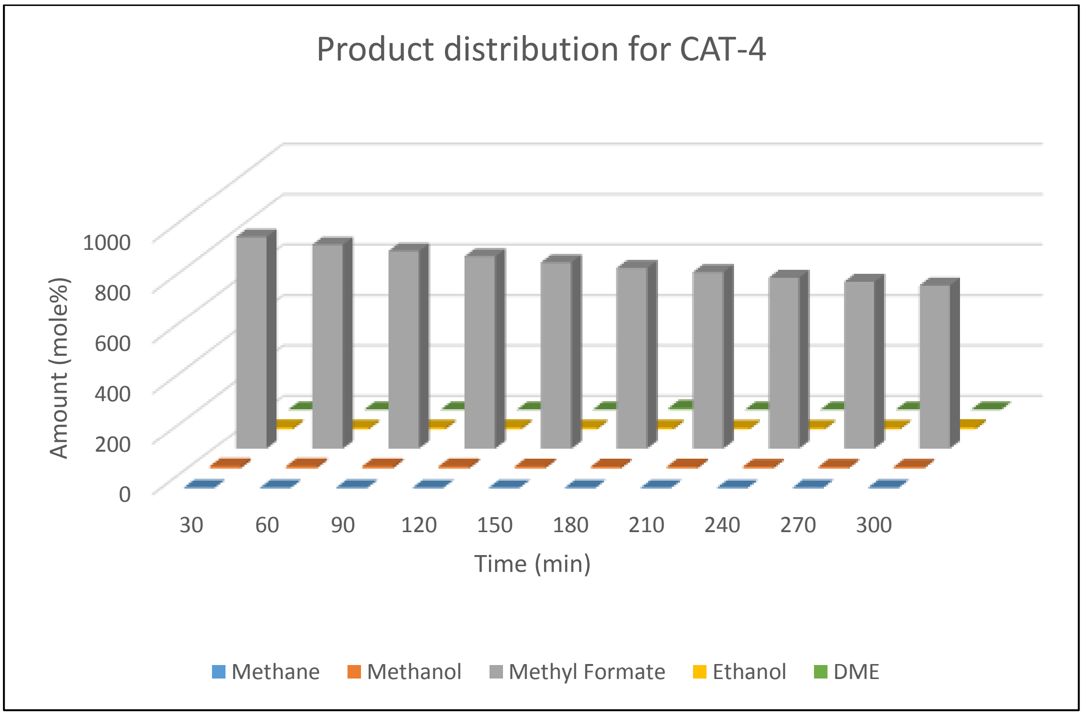


Figure 4.11 Products distribution profile for CAT-4 (Un-promoted SBA-15 catalyst support)

Table 4.13 Products distribution for CAT-5 (Un-promoted SiC catalyst support)

Reaction	Methane	Methanol	Methyl Formate	Ethanol	DME	Total
30	0	0	110.40123	0	0	110.4012
60	0	0	110.40123	0	0	110.4012
90	0.0101662	0	122.82444	0	0	122.8346
120	0.0138371	0	209.60129	0	0	209.6151
150	0.0179884	0	303.76694	0	0	303.7849
180	0.0239309	0	375.97824	0	0	376.0022
210	0.0340169	0	424.43882	0	0	424.4728
240	0.051456	1.55797	458.44131	0	0	460.0507
270	0.0739737	0	475.87276	0	0.143654	476.0904
300	0.113202	0	489.43233	0	0	489.5455
330	0.165536	1.97307	494.53976	0	0	496.6784
360	0.23259	2.04292	494.21001	0	0	496.4855
390	0.320315	0	497.12948	0	0	497.4498
420	0.425501	2.08855	496.0807	0	0	498.5948
450	2.23323	2.29566	934.18945	6.40531	0.097632	945.2213

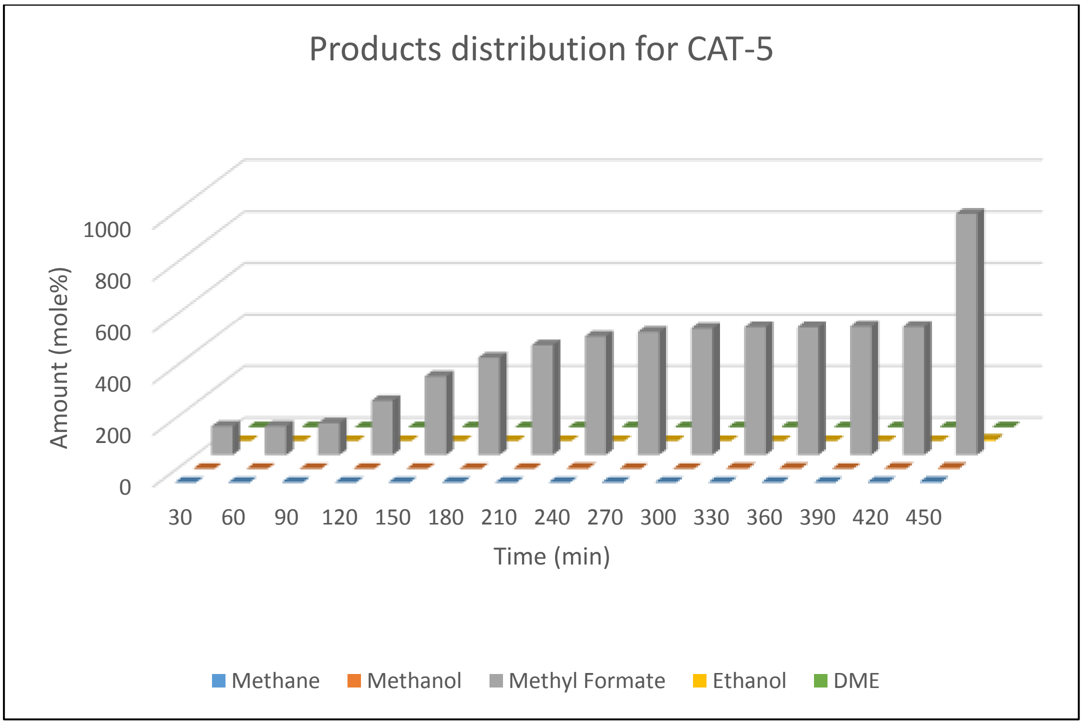


Figure 4.12 Products distribution profile for CAT-5 (Un-promoted SiC catalyst support)

Based on the tables and figures above, it represent the product distribution for the reaction at different type of catalyst support. Figure 4.10 shows that the methanol production is higher by using the Al_2O_3 catalyst support. However, figures 4.11 and 4.12 show that the production methyl formate is the highest. Figure 4.13 and Figure 4.14 below represent the methanol selectivity and CO_2 conversion of different type of catalyst supports.

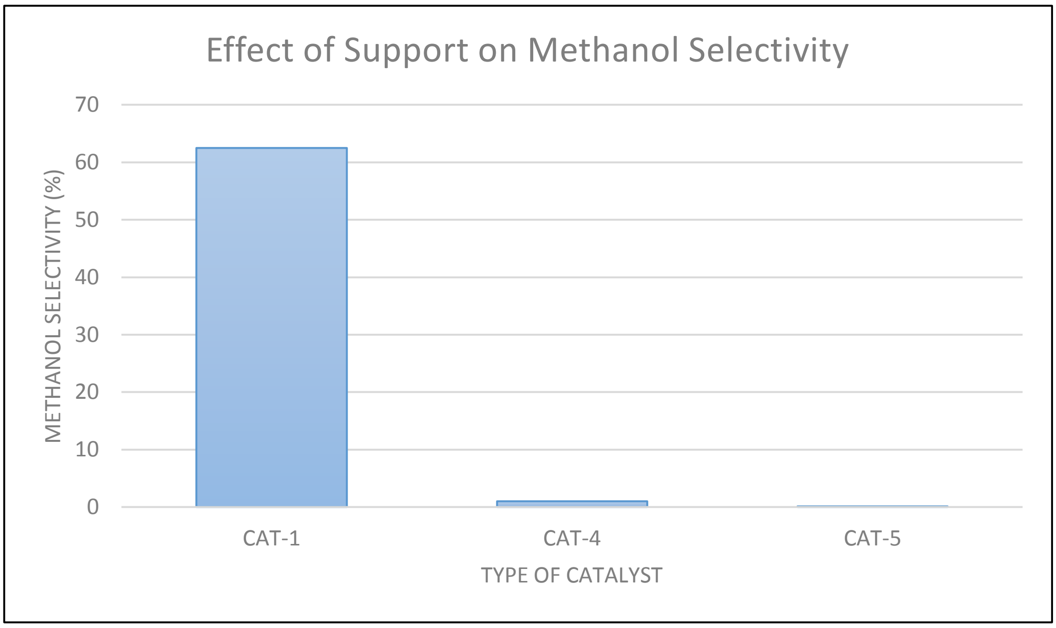


Figure 4.13 Methanol Selectivity for CAT-1, CAT-4 and CAT-5

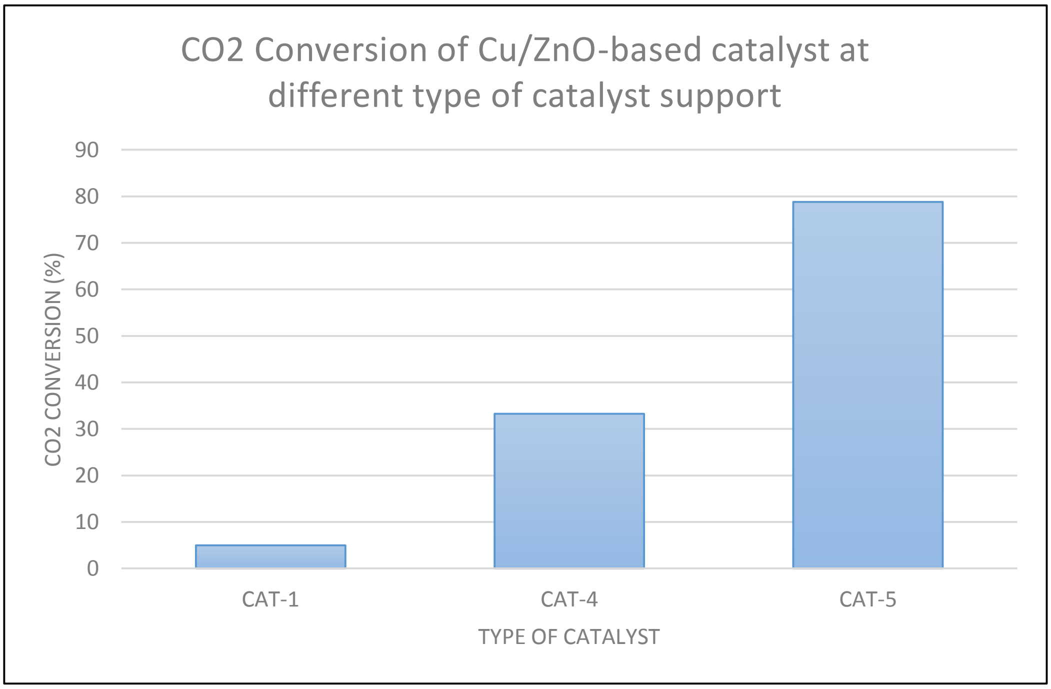


Figure 4.14 CO_2 Conversion for CAT-1, CAT-4 and CAT-5

The methanol selectivity for CAT-1 which is Cu/ZnO/Al_2O_3 is the highest compared to CAT-4 and CAT-7 which are the SBA-15 and SiC respectively. This is due to the spherical morphological structure of SBA-15 that affect the performance of the catalyst. Furthermore, the SiC support may be useful for the production of methyl formate. Nevertheless, there may be few ways to improve the performance of SiC catalyst support for methanol production such as pretreatment the catalyst support to increase the porosity of SiC. However, Figure 4.14 shows that the CO_2 conversion for CAT-3 is the highest compared to CAT-1 and CAT-2. High percentage of CO_2 is converted into methyl formate. Table 4.14 below shows the exact percentage of methanol selectivity for each synthesized catalysts.

Table 4.14 Performances of Cu-based catalyst for methanol synthesis from CO_2 and H_2

Label	Catalyst	Result
		Methanol Selectivity (%)
CAT-1	**Cu/ZnO/ Al_2O_3 (10.5/4.5/85 wt%)**	**62.52**
CAT-4	**Cu/ZnO/ SBA15 (10.5/4.5/85 wt%)**	**0.99**
CAT-7	**Cu/ZnO/ SiC (10.5/4.5/85 wt%)**	**0.12**

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This chapter will discuss about the conclusion of the progress research project. In addition, further recommendations for the future work have also been discussed in this section to ensure that this research project can be extended for more significant results.

As a conclusion, this project research will be carry out to synthesis Cu/ZnO metallic catalyst by using Al_2O_3 as catalyst support at different type of promoters and to synthesis the catalysts using Al_2O_3, SBA-15 and SiC as catalyst supports. The synthesized catalysts was prepared by using impregnation method and the performance of the catalyst in CO_2 hydrogenation was evaluated using microactivity fixed-bed reactor with temperature of 250℃, pressure of 2.25 MPa and ratio of H_2/CO_2 is 3:1. The catalysts was characterized using several techniques such as SEM, EDX, TPR and TGA. The selectivity of methanol production for each synthesized catalyst is then compared and the catalyst with the highest methanol selectivity will be selected. The methanol selectivity of using $Cu/ZnO/Al_2O_3$ incorporated with Niobium and Zirconium as catalyst promoters has the highest value which is 71.61%.

The author hopes it can bring more benefits in the development of industrial production of methanol. Moreover, this research project is considered to be achievable by considering the time limitation and the competency of final year student with the guidance from the coordinator and supervisor. It is hoped that the acquiring of equipment and chemicals required for the research project runs smoothly in order to accomplish this project at the end.

5.2 Recommendation

As the research of development of catalysts for methanol production is indefinitely wide, many future works can be achieved to extend the research project to ensure more promising result. For the development of a novel catalyst which can reduce the activation energy and hence resulted in high conversion of CO_2 and high selectivity of methanol, continuous research work has to be performed in the laboratory scale to explore the possible way to optimize the methanol production process. The recommendations that are suggested for the future work are as follows:

I. Explore the effect of parameters such as temperature, concentration of solution and optimum pH value of synthesized catalysts.
II. Explore the possibility of using other types of catalyst support and promoters in the development of catalyst for methanol production.

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APPENDICES

Amount of chemical for the catalyst preparation

- **Preparation of supported catalyst**

Since the total amount of the catalyst is 5 g, the amount of the chemicals were based on the percentage of the metals.

i. For 15% Cu-ZnO/Al_2O_3 catalyst with Cu/ZnO ratio of 7:3

a) The weight of metals (Cu and ZnO) is calculated by the following equation:

$$Weight\ of\ metal\ (g) = total\ weight\ of\ the\ catalyst\ \times percentage\ of\ desired\ metal$$

$Weight\ of\ Metal = 5 \times {}^{15}/_{100}$ = 0.75 g

Weight of Cu $= 0.75 \times {}^{70}/_{100}$ = 0.525 g

Weight of ZnO $= 0.75 \times {}^{30}/_{100}$ = 0.225 g

Then the weight of precursor ($Cu(NO_3)_2.3H_2O$) is

$Weight\ of\ Cu(NO_3)_2.3H_2O = \frac{0.525 \times 241.6}{63.5}$ = 2.00 g

$Weight\ of\ Zn(NO_3)_2.3H_2O = \frac{0.225 \times 297.48}{81.41}$ = 0.82 g

b) Weight of SiC

$$Weight\ of\ Support = total\ weight\ of\ catalyst - weight\ of\ metal$$

$$Weight\ of\ \mathrm{SiC} = 5 - 0.75 = 4.25\ \mathrm{g}$$

c) Preparation of precursor solution 0.5M

$$Number\ of\ moles\ of\ Cu(NO_3)_2.3H_2O = Molarity \times Volume$$

$$Volume = \frac{number\ \text{of moles}\ (mol) \times\ liter\ of\ solution\ (ml/L)}{molarity\ (mol/L)}$$

$$Volume = \frac{number\ \text{of moles}\ \times\ liter\ \text{of solution}}{molarity}$$

$$Volume\ of\ deionized\ water = \frac{0.011 \times 1000}{0.5}$$

$$= 22\ \text{ml of}\ H_2O$$

For preparing of 15% Cu-ZnO/SiC catalyst with Cu:Zn ratio of 7:3, 2.00 g of copper nitrate and 0.82 g of zinc nitrate will be dissolved in 22 ml of deionized water and impregnated on 4.25 g of the SiC support. This calculation is the same for SBA-15 and Al_2O_3 support.

- **Preparation of promoter modified catalyst**

i. **For 15% Cu-ZnO/SiC catalyst with Cu/ZnO ratio of 7:3 modified by mixed promoter of Nb**

a) The weight of metals (Cu and Zn) is calculated by the following equation:

$$Weight\ of\ metal\ (g) = total\ weight\ of\ the\ catalyst\ \times percentage\ of\ desired\ metal$$

$Weight\ of\ Metal = 5 \times {}^{15}/_{100}$ = 0.75 g

Weight of Cu $= 0.75 \times {}^{70}/_{100}$ = 0.525 g

Weight of ZnO $= 0.75 \times {}^{30}/_{100}$ = 0.225 g

b) Weight of promoters

$$Weight\ of\ metal\ (g) = total\ weight\ of\ the\ catalyst\ \times percentage\ of\ promoters$$

$Weight\ of\ Metal = 5 \times {}^{1}/_{100}$ = 0.05 g

$Weight\ of\ Nb = 0.05 \times {}^{1}/_{100}$ = 0.0005 g

c) Weight of precursor ($Cu(NO_3)_2.3H_2O$) is

$Weight\ of\ Cu(NO_3)_2.3H_2O = \frac{0.525\times241.6}{63.5}$ = 2.00 g

$Weight\ of\ Zn(NO_3)_2.3H_2O = \frac{0.225\times297.48}{81.41}$ = 0.82 g

$Weight\ of\ C_4H_4NNbO_9.xH_2O = \frac{0.0005\times302.98}{92.9}$ = 0.0016 g

d) Weight of support

$$Weight\ of\ Support = total\ weight\ of\ catalyst - weight\ of\ metal$$

$$Weight\ of\ SiC = 5 - (0.75 + 0.05) = 4.2\ \text{g}$$

e) Preparation of precursor solution 0.5M

$$Total\ Number\ of\ moles\ of\ metales = Molarity \times Volume$$

$$Volume = \frac{number\ \text{of moles}\ (mol) \times\ liter\ of\ solution\ (ml/L)}{molarity\ (mol\,/\,L)}$$

$$Volume = \frac{number\ \text{of moles}\ \times\ liter\ \text{of solution}}{molarity}$$

$$Volume\ of\ deionized\ water = \frac{0.011 \times 1000}{0.5}$$

$$= 22\ \text{ml of}\ H_2O$$

For preparing of 15% Cu-ZnO/SiC catalyst with Cu:Zn ratio of 7:3 modified single promoters of Nb; 2.00 g of copper nitrate and 0.82 g of zinc nitrate will be dissolved in 22 ml of deionized water and impregnated on 4.2 g of the SiC support. Then 4 ml of aqueous solution contain 0.0016 g ammonium niobate (V) oxalate hydrate will be added in drop wise manner to the previous mixture. This calculation is the same for SBA-15 and Al_2O_3 support.

ii. **For 15% Cu-ZnO/SiC catalyst with Cu/ZnO ratio of 7:3 modified by mixed promoter of Zr and Nb**

a) The weight of metals (Cu and Zn) is calculated by the following equation:

$$Weight\ of\ metal\ (g) = total\ weight\ of\ the\ catalyst\ \times percentage\ of\ desired\ metal$$

$Weight\ of\ Metal = 5 \times {}^{15}/_{100}$ = 0.75 g

Weight of Cu $= 0.75 \times {}^{70}/_{100}$ = 0.525 g

Weight of Zn $= 0.75 \times {}^{30}/_{100}$ = 0.225 g

a) Weight of promoters

$$Weight\ of\ metal\ (g) = total\ weight\ of\ the\ catalyst\ \times percentage\ of\ promoters$$

$Weight\ of\ Metal = 5 \times {}^{2}/_{100}$ = 0.1 g

$Weight\ of\ Zr = 0.1 \times {}^{1}/_{100}$ = 0.001 g

$Weight\ of\ Nb = 0.1 \times {}^{1}/_{100}$ = 0.001 g

b) Weight of precursor ($Cu(NO_3)_2.3H_2O$) is

$Weight\ of\ Cu(NO_3)_2.3H_2O = \frac{0.525 \times 241.6}{63.5}$ = 2.00 g

$Weight\ of\ Zn(NO_3)_2.3H_2O = \frac{0.225 \times 297.48}{81.41}$ = 0.82 g

$Weight\ of\ Zr(NO_3)_2.3H_2O = \frac{0.001 \times 231.23}{91.218}$ = 0.003 g

$$Weight\ of\ C_4H_4NNbO_9.xH_2O = \frac{0.001\times302.98}{92.9} = 0.003\ \text{g}$$

d) Weight of support

$$Weight\ of\ Support = total\ weight\ of\ catalyst - weight\ of\ metal$$

$$Weight\ of\ SiC = 5 - (0.75 + 01) = 4.15\ \text{g}$$

e) Preparation of precursor solution 0.5M

$$Total\ Number\ of\ moles\ of\ metales = Molarity \times Volume$$

$$Volume = \frac{number\ \text{of moles}\ (mol) \times\ liter\ of\ solution\ (ml/L)}{molarity\ (mol\ /\ L)}$$

$$Volume = \frac{number\ \text{of moles}\ \times\ liter\ \text{of solution}}{molarity}$$

$$Volume\ of\ deionized\ water = \frac{0.011 \text{ x } 1000}{0.5}$$

$$= 22 \text{ ml of } H_2O$$

For preparing of 15% Cu-ZnO/SiC catalyst with Cu:Zn ratio of 7:3 modified with tri-promoters of Zr and Nb; 2.00 g of copper nitrate and 0.82 g of zinc nitrate will be dissolved in 22 ml of deionized water and impregnated on 4.15 g of the SiC support. Then 4 ml of aqueous solution contain 0.003 g zirconium nitrate and 0.003 g ammonium niobate (V) oxalate hydrate will be added in drop wise manner to the previous mixture. This calculation is the same for SBA-15 and Al_2O_3 support.

Methanol selectivity =

$$\frac{Amount\ of\ Methanol\ produce}{Total\ amountof\ products}\ x\ 100$$

CO₂ conversion =

$$\frac{CO_{2,in} - \ CO_{2,out}}{CO_{2,in}}\ x\ 100$$