DEVELOPMENT OF CATALYST FOR ACETALIZATION OF GLYCEROL USING FORMALDEHYDE

BY

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CHEMICAL ENGINEERING (STD ID: 11205)

Thesis submitted in partial fulfilment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

AUGUST 2012

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CERTIFICATION OF APPROVAL

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Chemical Engineering Programme
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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 acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

TENGKU ZULFADZLY BIN T.AZIZ

ACKNOWLEDGEMENT

First and foremost, I would like to express my praises to Allah for His blessing.

My deepest appreciation and gratitude is extended to my supervisor, AP. Dr Anita Binti Ramli for being very encouraging, supportive and responsive throughout the whole process of completing this final year project to fulfill the university requirement. Without her constant supervision and guidance, I may not be able to complete this project successfully.

Apart from that, I am very thankful to the lab technicians who have helped me conduct the experimental assessment in the laboratory. Thank you to Mr Asnizam and others for their endless support and diligence providing me assistance required for the laboratory work.

Besides, thank you to the Final Year Project (FYP) coordinator, Puan Norhayati Bt Mellon and Puan Asna for being dedicated and stringent in handling the course throughout the year.

Hereby, I would like to also thank my fellow friends who have always been accommodating and cooperative whenever I am in need of ideas and opinion throughout the completion of this project.

Last but not least, I would like to acknowledge my family members for keeping me motivated throughout the year.

Thank you.

ABSTRACT

Disclosed herein is an experiment project to investigate the catalyst for acetalization of glycerol using formaldehyde to enhance the productivity. The project is conducted by exploiting the wide choice of metal for catalyst development, reporting on catalyst developed by studying the characteristic and analysis the catalytic performance in the reaction. Catalysts are all prepared by Incipient Wetness Impregnation process where to two different metal are used. Catalyst that had been develop will go to characteristic analysis using various tool to determine it surface area, porosity, metal distribution and pore volume. Then finally the catalyst will tested for its catalytic performance in acetalization of glycerol and formaldehyde.

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CHAPTER I

INTRODUCTION

As we known, world now facing the problem of decreasing in fossil fuel reserves and also global warming due to environmental pollution. As the alternative for substituting the fossil fuel and reduce global warming, the biodiesel had been chosen as the best solution since it is much more environmental friendly and also feasible (Jason Hill, 2006). Basically, biodiesel is produced using vegetable oils by trans-esterification under base catalyst condition. Besides using corn grain and soy bean as feedstock, Jatropha seed also now had been discovered as potential source of biodiesel (G. El Diwani, 2008). In biodiesel production, glycerol appeared as by product with 10% from total production. The increasing of crude glycerol in global market is worrying especially when Europe country had actively replace petroleum fuel with biofuel. Thus, many studies had been done to synthesis the crude glycerol to give add-value as alternative to disposal by incineration. Glycerol acetals from various chain of hydrocarbon are tested with animal fat biodiesel to study its performance as anti-freezing agents (Paulo H.R Silva, 2009). Another uses of glycerol are citric acid production, composite additive and bonding agent for makeup in cosmetic industry.

Acetalization of glycerol usually are carried out by processing the glycerol with aldehyde and catalyzed by homogeneous acids. Different process parameters such as ratio of glycerol and aldehyde or type or catalyst use can be adjusted to determine the composition of five and six-membered rings acetals. Since homogeneous catalyst will cost on the separation process, further study on solid acid catalyst whether in conversion or kinetic study had been done as example using mesoporous MoO_3/SiO_2 solid acid catalyst (Shubhangi B. Umbarkara, 2009), acid resin catalyst such as Amberlyst-15 (Paulo H.R Silva, 2009), and Amberlyst-47 (I. Agirre*, 2010).

In this paper, the study of development for catalyst for acetalization of glycerol with formaldehyde is carried out. Here investigation on how bi-metal catalyst can affect the conversion rate of glycerol and parameter that suitable to enhance the process.

1.1 Problem statement.

Currently, glycerol has been produce due to production of biodiesel with around 2 million gallons in year 2000 and up to 2008, 700 million gallons of biodiesel have been produced in US only (Board, 2008). This value is keep increasing due to active replacement of petroleum by biofuel done by the country. If take average of 10 wt. % of glycerol produced for every batch biodiesel produce, it mean in 2008, around 70 million gallons of glycerol produce.

Glycerol has the chemical formula of $C_3H_6O_3$ and in forms of thick, viscous and full of oxygen but hard to burn (Pollitt, 2008). Since there is a lot of hydrogen in glycerol structure rather than methane, glycerol now are actively use in production of hydrogen. Besides that, another alternative of glycerol is by adding it add-value as example by acetalization of glycerol to formed glycerol acetals that have more function.

A lot of research and experiment are done to increase the production of glycerol acetal. Reducing the cost of production by avoiding expensive material such as catalyst type, type of solvent and reaction parameters are put as first priority. Different combination of reaction can lead to different function of glycerol acetals. As example, for anti-freezing additives in biodiesel, glycerol from differect type of hydrocarbon chain will have different value of pour point (Paulo H.R Silva, 2009).

In this project, experiment on different combination of metal to form as bimetal-catalyst as studied. A number of metal are selected from catalytic group to test to know the conversion rate in order to increase glycerol production at lowest cost. The studies also include the analysis for every combination of metal regarding its physical properties such as surface area and metal distribution.

1.2 Objective and scope of study

The objectives of the project are:

1. To develop bi-metallic catalysts for acetalization of glycerol with formaldehyde.
2. To characterize the physicochemical properties of the catalyst
3. The catalytic performance of the catalyst developed.

For this particular project, the scope of study will widely covers but are certainly not limited to the metal selection, conversion, and physical properties of catalyst – chemical properties of the glycerol acetals, temperature and pressure system, types of solvent and its properties.

1.3 Background of study

Basically, background of study of the project covers the feasibility of the project – sufficient supply of metal and reagent (glycerol and formaldehyde), availability of reactor, equipment(s) needed/availability for sample(s) testing, potential of product to be commercialize.

1.3.1 Sufficient supply of metal.

In this experiment, several metal are selected to be used in catalyst development. All the metal will combine to form bi-metal catalyst by using Incipient Wetness Impregnation process. Metal are selected from range of common catalyst metal that is not harmful to human and easily find in the market.

1.3.2 Reagent/reactants.

Glycerol for this experiment is chose with 99 wt. % that suitable for synthesis work while formaldehyde are selected from the type of 37 wt% stabilized with 10% methanol. As mentioned, large amount of glycerol can be obtained easily as by-product of trans-esterification reaction to produce biodiesel. Besides that, formaldehyde can also have renewable origin as it can be obtained from methanol. Thus, all the raw materials required for this process can be obtained from renewable source and easily find in chemical market with low price.

1.3.3 Reactor

For lab scale experiment, the study will carried out using 1 litre glass jacketed stirred reactor as shown in

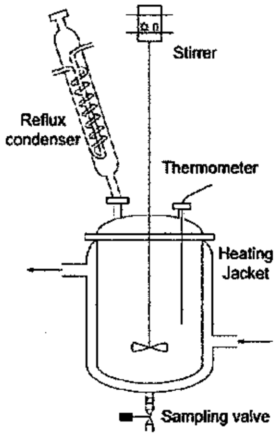


Figure 1 - Schematic diagram of 1 litre glass reactor

The reaction temperature can be controlled by external thermostat. This thermostat is connected with thermocouple that located inside the reactor to be able controlling the temperature. At the top, condenser will act to condense ad reflux all the vapors keeping the volume inside the reactor constant and avoid the evaporation.

1.3.4 Analysis

Glycerol and formaldehyde and reaction product will go through the analysis by gas chromatography using several type of analyzer method as example flame ionization detector (FID) and thermal conductivity detector (TCD). An inert gas as helium will be used as carrier gas.

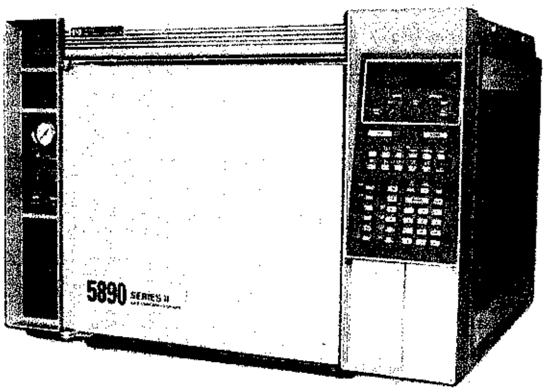


Figure 2 - Gas Chromatorgraphy

Catalyst also will be analyzed to determine the surface characteristic in order to know its surface area and metal distribution on support. All catalyst that had been developed with tested with some tools such as FTIR, XRD, BET, TPD and TPR.

CHAPTER II

LITERATURE REVIEW

Based on research done by Sharma and Chopade (Shubham P. Chopade, 1997), they suggest that the acetalization of ethylene glycol and formaldehyde consists of two reversible steps. The first reaction is where the glycol react with formaldehyde that lead to formation of hemiacetal known as 1,2-Propanediol, 3-(hydroxymethoxy). The second reaction is when two hydroxyl groups join to form dioxolone and releasing water molecule. Hemiacetalization step is fast rather than the dioxolone formation, so that the overall rate of reation are controlled by the second step. There are a lots of other research proposed the reaction mechanism of glycerol and aldehyde, but for this case, concepts proposed by Sharma & Chopade are used.

2.1 Reaction Mechanism

Glycerols with molecular formula of C3H6O3 contain 3 different hydroxyl (OH) groups. As mention by Sharma and Chopade, glycol only has two groups of hydroxyl, so only one kind of combination can happened. For glycerol, two possibilities can happened for hydroxyl depends on which group will join each other. The different formation can lead to whether 1,3-dioxan-5ol or 1,3-dioxolone-4-methanol.

In first step, glycerol will react with formaldehyde and form 1,2-Propanediol. This step is faster than the second step and does not require catalyst. The reaction is reversible and highly exothermic. In journal publish by I.Agirre and college, they found difficulties in analyzing the sample (I. Agirre*, 2010). When the sample are injected into Gas Chromatograph that in high temperature, the reverse reaction happened and most of hemiacetal disappear and no result can be obtained. Below show the flow of reaction mechanism for glycerol and formaldehyde.

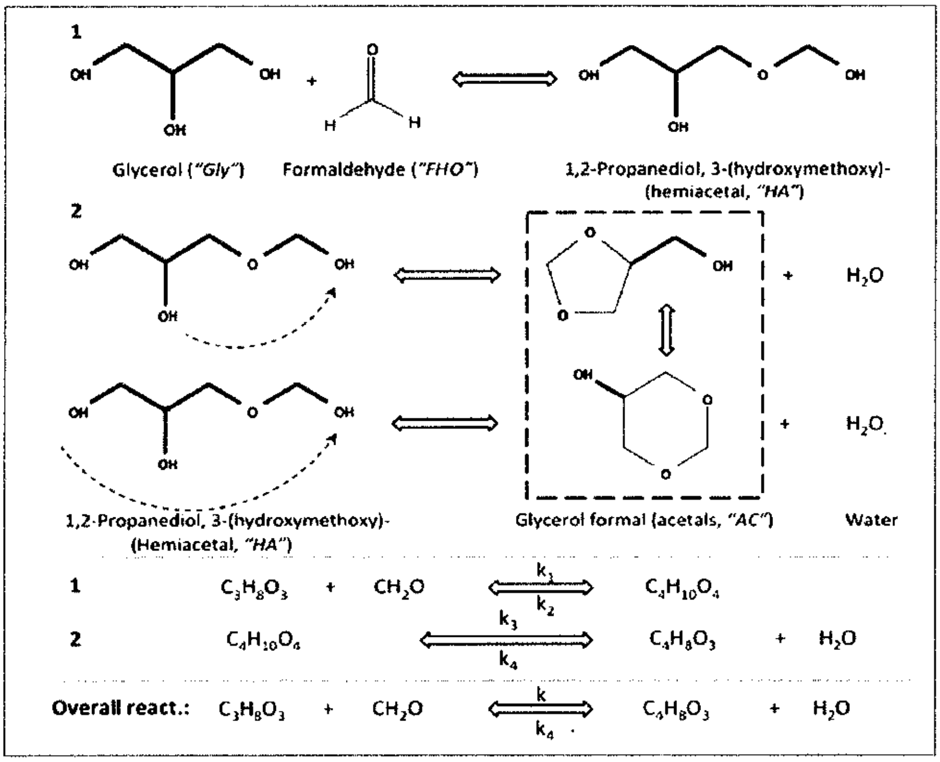


Figure 3 - Reaction mechanism of glycerol and formaldehyde

After the first step, catalyst will be added where formation of glycerol formal will occurred. Two group of hydroxyl will moved and join the other hydroxyl group to form whether 1,3-dioxan-5ol or 1,3-dioxolone-4-methanol.

2.2 Catalyst

Catalyst is a substance that added to increase the rate of reaction by reducing the activation energy for the reaction. In acetalization reaction of glycerol, acid catalyst is needed to speed up the reaction rate. Some commercial catalyst usually used for this process is strong acid such as Hydrochloric acid HCL and Phosphorus acid H_3PO_4 (Shubhangi B. Umbarkara, 2009). But using homogenenous acid is not ideal since required separation process after that. Some solid acid catalyst like MoO_3 and divinylbenzene-styrene resin such as Amberlyst-47 can also be used as catalyst in acetalization process.

For this experiment, catalyst will be developed from a number of different types of metal. Each catalyst will be having to different metal that combine together on same catalyst support. List of metal will be use is shown below:

Copper (II)Nitrate Trihydrate
Manganese (II) Sulphate.1-Hydrate
Cerium (III) Nitrate
Nickel (II) Chloride Hexahydrate
Zinc Nitrate Hexahydrate
Cobalt (II) Nitrate Hexahydrate

Table 1 - List of metal precursor for catalyst preparation

2.3 Aldehyde

In acetalization of glycerol, aldehyde are needed to able the reaction to happened. Different type of aldehyde can be used and lead to different kind of end product. Example of commonly used aldehyde is benzeldehyde, acetaldehyde, butyraldehyde, propionaldehyde and formaldehyde. For this experiment, formaldehyde has been chosen as the aldehyde. Formaldehyde is the most basic kind of aldehyde and much cheaper than others.

CHAPTER III
METHODOLOGY

In this chapter, the method on conducting the experiment for acetalization will be described in detailed. Main process that include in this experiment are catalyst preparation, catalyst characterization and catalytic test.

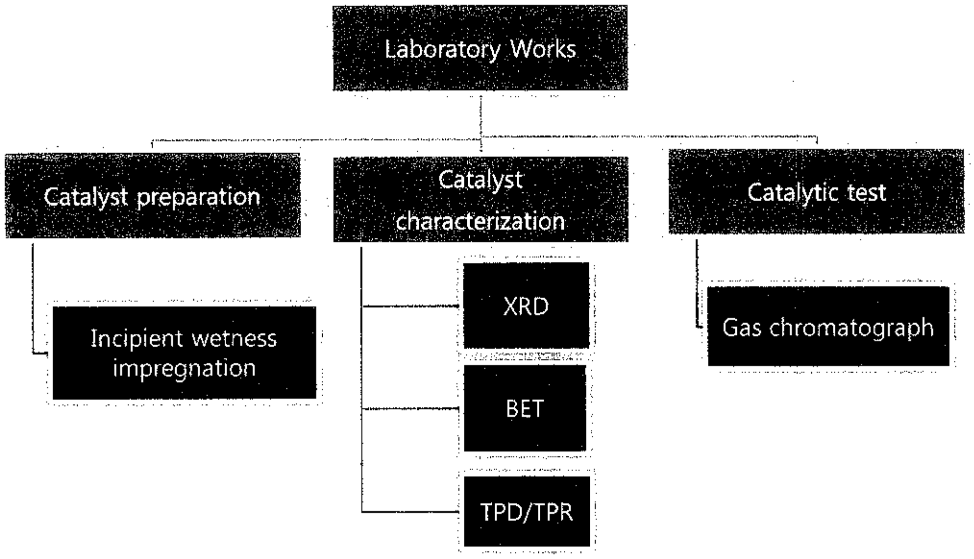


Figure 4 - Flow chart of experiment methodology

3.1 Catalyst preparation

As this experiment study on bi-metal catalyst, catalyst preparation required a number of different metals to be combined as catalyst. The process involve in catalyst preparation are called Incipient Wetness Impregnation. Zeolite (product code: CBV 2314) from Zeolyst International had been chosen as catalyst support. Firstly, catalyst support must be heated in the rotating furnace to remove any impurities and moisture. Nitrogen gas is introduced during the procedure to help the process to remove impurities out from the support. The process takes up to 10 hours of heating at 500'C in the rotating furnace.

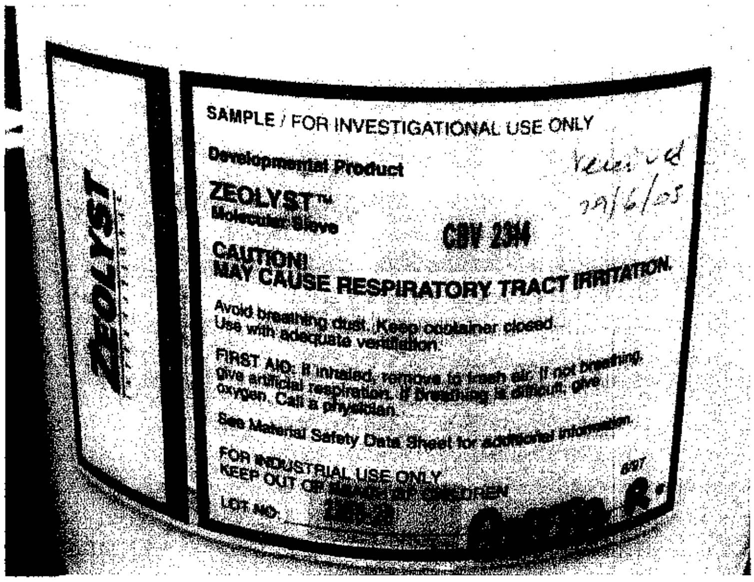


Figure 5- Label of zeolite use for experiment

This process needs us to dissolve active metal precursor into aqueous solution. Distilled water is added to metal precursor to dissolve them. After all metal have been dissolve and solution show as clear solution, catalyst support are added into solution. Capillary action draws the solution into the pores. The volume of pores must almost equal with volume of solution to avoid from diffusion action happened which is slower. 4 hours are needed to let the solution impregnated into the support and magnetic stirrer is used to help speed up the process.

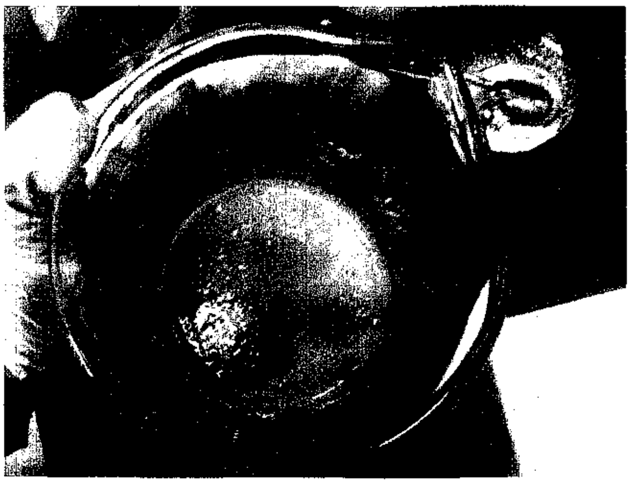


Figure 6- Impregnation process by adding metal solution with catalyst support

After 4 hours, catalyst will go through drying process in the oven with 110 degree Celsius in overnight. This process is in order to remove water content on the solution before can be moved to calcination process. Finally, the catalyst will calcined in air at 500 degree Celsius to activate the catalyst.

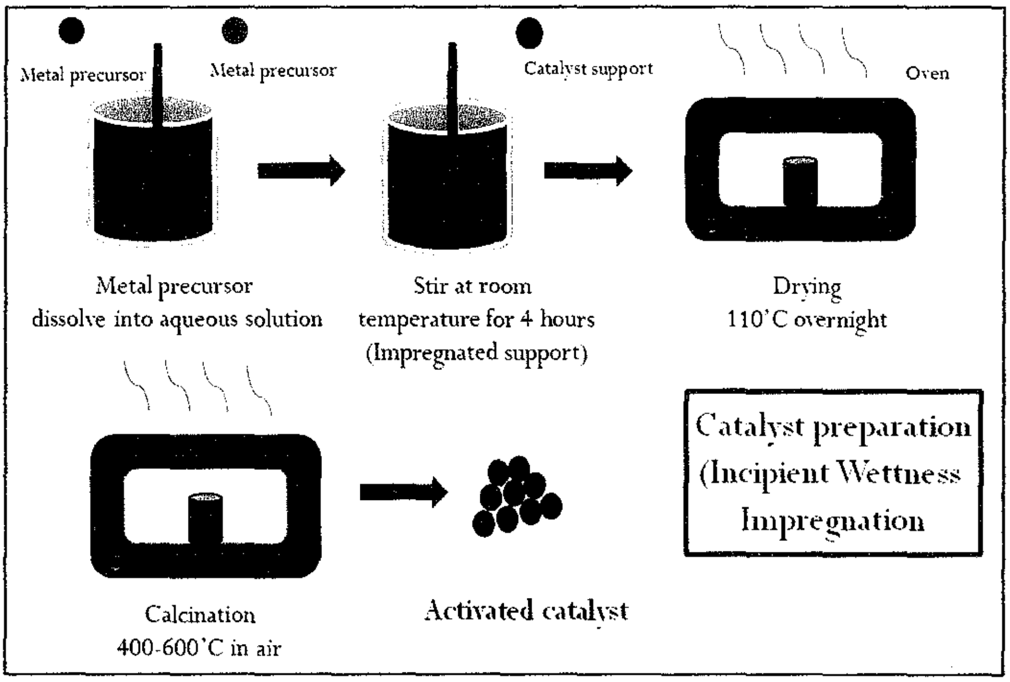


Figure 7- Process flow diagram of catalyst preparation

For this experiment, catalyst will be prepared with 5 wt% for each metal with total up of 10 wt% of bi-metal on the catalyst support. To able get the right amount of metal impregnated on the support, weight of metal precursor must be calculated first. Example of calculation to prepare copper is shown as below:

$$\frac{MW\ Cu(NO_3)_2.3H_2O}{MW\ Cu} = \frac{x\,g\ \ Cu(NO_3)_2.3H_2O}{2.5g\ Cu}$$

$$\frac{241.6g}{63.55g} x\ 2.5g\ Cu = \mathbf{9.5}g\ Cu(NO_3)_2.3H_2O$$

Equation 1 - Calculation to determine weight of metal precursor

For each catalyst prepared, it will be sent for analysis of Fourier Transform Infrared FTIR, X-ray diffraction, and BET analysis on surface area, Thermal Programmed desorption and reduction.

3.2 Catalyst Characteristic

For each catalyst prepared, it will be sent for analysis of Fourier Transform Infrared FTIR, X-ray diffraction, and BET analysis on surface area, Thermal Programmed desorption and reduction.

3.2.1 Fourier Transform Infrared FTIR

Fourier Transform Infrared is an analysis tools that use infrared beam. As the infrared passed through a sample, some of radiation is absorbed and some will passes through and detect by detector (Nicolet). This analysis is used to identify the amount of component in the mixture by studying the interferogram graph. Size of the peak indicates the amount of material present in the mixture where each peak is corresponded to the frequencies of vibration between the bonds of atom in the material. Example of interferogram graph is shown in below:

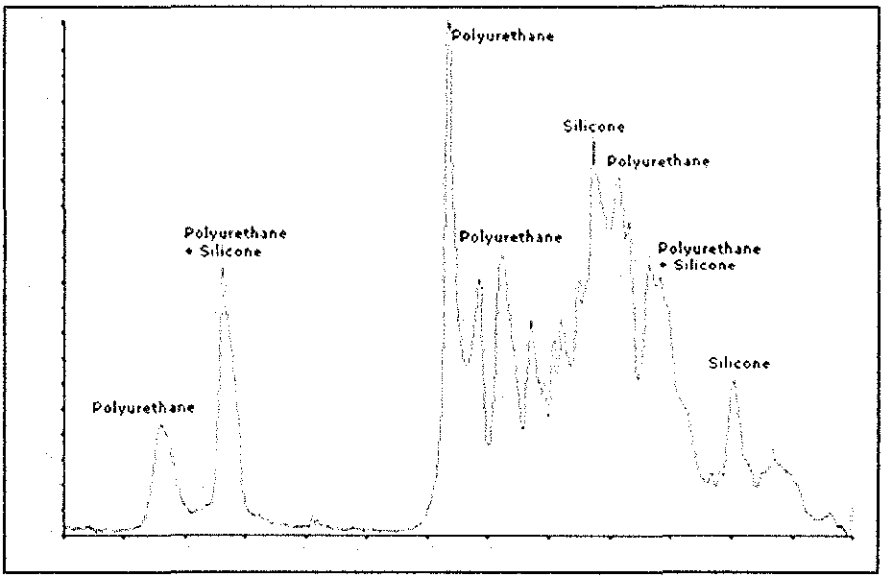


Figure 8 - Interferogram Graph

In this experiment, the FTIR will be used to analyze the characteristic of catalyst. The distribution of metal on support can be known by studying the peak of FTIR graph. Different sample of catalyst will show different result of graph. Thus, by this way, we can know the consistency of catalyst prepared.

3.2.2 Brunauer-Emmet-Teller (BET) adsorption analysis

BET adsorption is used to study the specific surface area that catalyst have. The analysis will use nitrogen and let it adsorb into the catalyst at 77K. Nitrogen that acts as absorbate will form the layer on the catalyst surface. The volume required for nitrogen to form monolayer on the surface will be calculated with equation below:

$$v = \frac{VmC\left(\frac{P}{Po}\right)}{(1-\frac{P}{Po})(1-\left(\frac{P}{Po}\right)+C\left(\frac{P}{Po}\right)}$$

Equation 2 - BET equation

S= specific surface area [m2/g]

V_m= the amount of adsorbate required to form one monolayer over the entire adsorbent surface [cm3/g]

N_A = the Avogadro number

A_m = the surface area occupied by one molecule, 16.2 for N2

After obtaining the required volume to form monolayer, Vm, the value will be used to calculate the surface area using the equation below:

$$S = \frac{Vm}{22414} NaAm \times 10^{-20}$$

Equation 3 - Surface Area of catalyst equation

3.2.3 Temperature Programmed Desorption and Reduction.

These two tools help in order to analyze the reduction condition of catalyst prepared and analyze the active acid site on the catalyst.

3.2.4 X-Ray Diffraction

X-ray diffraction analysis is one of the tools use to determine the phase and composition of catalyst that had been prepared. This tool also can analyze the particle size of metal of the catalyst support. Silicone powder will be used as comparison with the observed data which is catalyst itself.

$$\boxed{B_d^2 = B_{observed}^2 - \boxed{B_{instrument}^2} \longleftarrow \boxed{\text{Silicone powder}}}$$

Equation 4 - X-ray diffraction equation

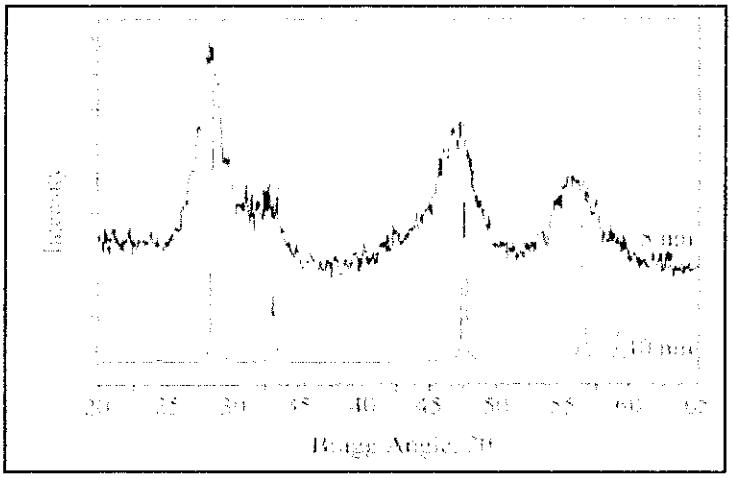


Figure 9 - Example graph of X-ray diffraction

3.3 Catalytic test

For catalytic test, catalyst which has been prepared will be test for reaction between glycerol and formaldehyde. Firstly, reactant will be charged into the reactor with total initial volume is 0.5 Liter. After the temperature has been stabilized to required temperature for reaction, the catalyst will be added into the reactor. At certain intervals of time, the sample will be collected from the sampling valve. The sample will be tested with Gas Chromatograph to analyze the component of product.

CHAPTER IV
RESULT AND DISCUSSION

4.1 Catalyst preparation result

Before the catalyst was begun to be prepared, the catalyst support has to be calcined in order to ensure all the impurities inside the support are removed. Zeolite, which is the catalyst support that used during the experiment are calcined in rotating furnace under temperature of 500C for 16hours. Along the process, nitrogen gas is introduced to help in removing the impurities. In every batch, 100g of zeolite can be prepared and the process is repeated up to 5 batches which is equivalent to 500g of zeolite. After the calcination, the support will be let to cool down and stored in airtight container to avoid from any impurities. To prepare up to ten (10) different type of catalyst, 45g of zeolite are needed in order to prepare one combination of catalyst.

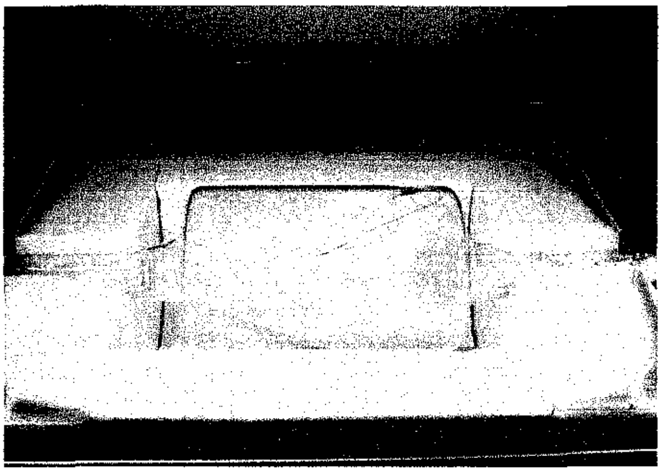


Figure 10 : Catalyst support heated in rotating furnace

In order to prepare the catalyst, metal precursor must be dissolve into aqueous solution using distilled water. A small aluminum weighing cup is weighed and the electronic scale is set to 0 before the metal can be weight. Each catalyst will have 10% w/w of metal. Since the objective is to prepare bi metallic catalyst, 5% of each metal will be impregnated into the catalyst support. Calculation must be done to identify how much metal are needed to ensure every metal precursor represent 5% of total catalyst weight. Metal that have been weighed will be moved into 100ml to be dissolved with distilled water. Then, proceed weighing process with zeolite which is 45g needed to prepare 50g of catalyst. After that, slowly add the zeolite into the metal aqueous solution while slowly stir to ensure the support are blend well together with the solution.

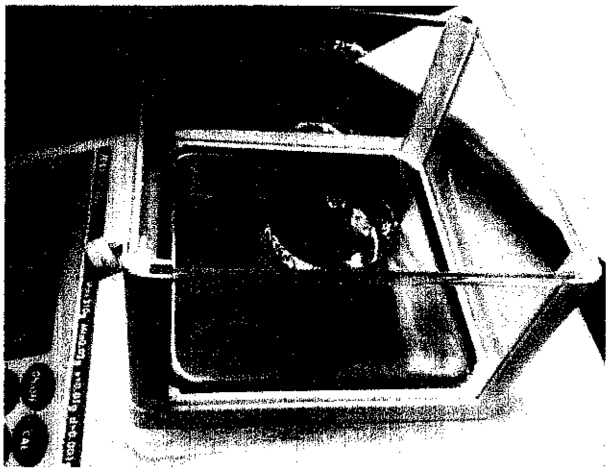


Figure 11 : Metal are weighed for catalyst preparation

Table 2 : List of catalyst prepared

Catalyst	Metal A loading %	Metal B loading %	Catalyst support
Cu-Ag	5	5	Zeolite (CBV 2314)
Cu-Ba	5	5	Zeolite (CBV 2314)
Cu-Ce	5	5	Zeolite (CBV 2314)
Cu-Mn	5	5	Zeolite (CBV 2314)
Cu-Ti	5	5	Zeolite (CBV 2314)
Cu-Co	5	5	Zeolite (CBV 2314)
Mn-Ba	5	5	Zeolite (CBV 2314)
Ba-Zn	5	5	Zeolite (CBV 2314)
Mn-Ag	5	5	Zeolite (CBV 2314)
Ce-Ni	5	5	Zeolite (CBV 2314)

The solution with zeolite will be let under normal condition for 4 hours to give time for impregnation process. During this process, capillary action will happen where metal solution penetrated into pores of support. If there are too much water are added during dissolving the metal, the capillary action will change to diffusion action which is much slower and lead to ununiformed distribution of metal inside the support pores. After 4 hours, the solution now can be proceeding to drying process in the oven for 16 hours. This process are done under temperature of 100-110C to remove all water content within the solution. The beaker opening is wrapped with aluminum foil with small hole to let water evaporated to the air during drying process

Figure 12 : 1.catalyst during impregnation process 2. Catalyst crushed after drying process

After drying process for 16 hours, the solution will in solid form where water contains had been totally remove. The solid need to be crushed into small and grind to turn it into powder form. The fine powder of catalyst then will be calcine with furnace under 500C for 16 hours. This process is to remove nitrate and activate catalyst to be ready for use. Commonly catalyst will change its color into black or grey colored powder. Catalyst will be put into small crucibles and place inside furnace for overnight. After that, the catalyst preparations are all done and catalysts are stored in air tight container. Catalysts now are ready to move for second step which is catalyst characterization to analyze it physiochemical properties.

Figure 13 : Catalyst after calcination process for 16 hours under 500C temperature

4.2 Catalyst Characterization result

4.2.1 Fourier Transform Infrared Analysis

Here is the result of catalyst characterization using FTIR analyzer tool. This will be executed in the future experimental work as well as thorough discussion. The analyses are done on the catalyst before and after calcination process in order to determine all molecules available inside the catalyst and also to see the effectiveness of calcination process to remove other molecules. Example of compound that need to be remove is Mostly nitrate compound are determine to be removed from the catalyst since almost all the metal salt had been use consist of nitrate compound. List of some metal salt used are as below:

- Copper (II)Nitrate Trihydrate
- Manganese (II) Sulphate.1-Hydrate
- Cerium (III) Nitrate
- Nickel (II) Chloride Hexahydrate
- Zinc Nitrate Hexahydrate
- Cobalt (II) Nitrate Hexahydrate

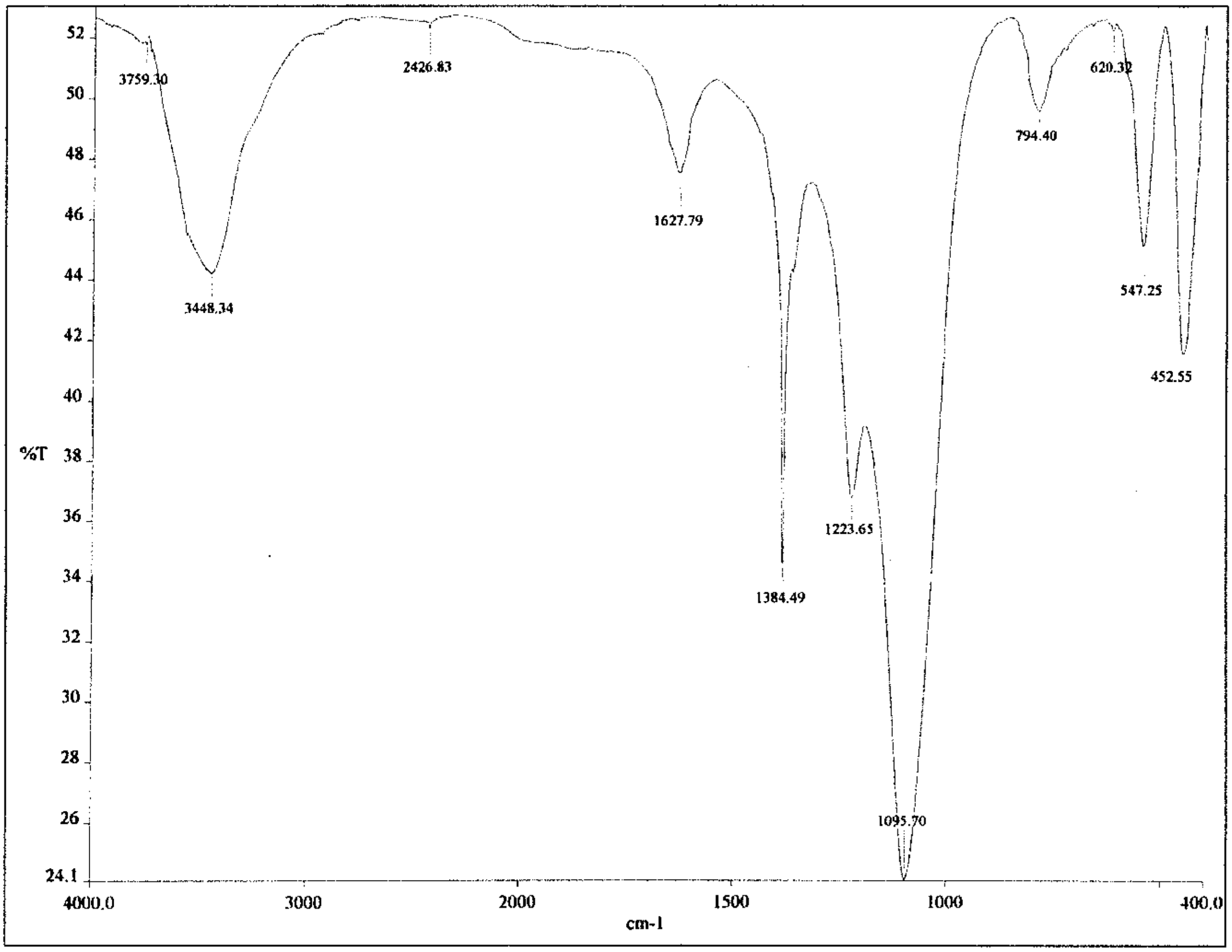


Figure 14:Fourier Transform Infrared Spectroscopy: Barium-Zinc catalyst (before calcination)

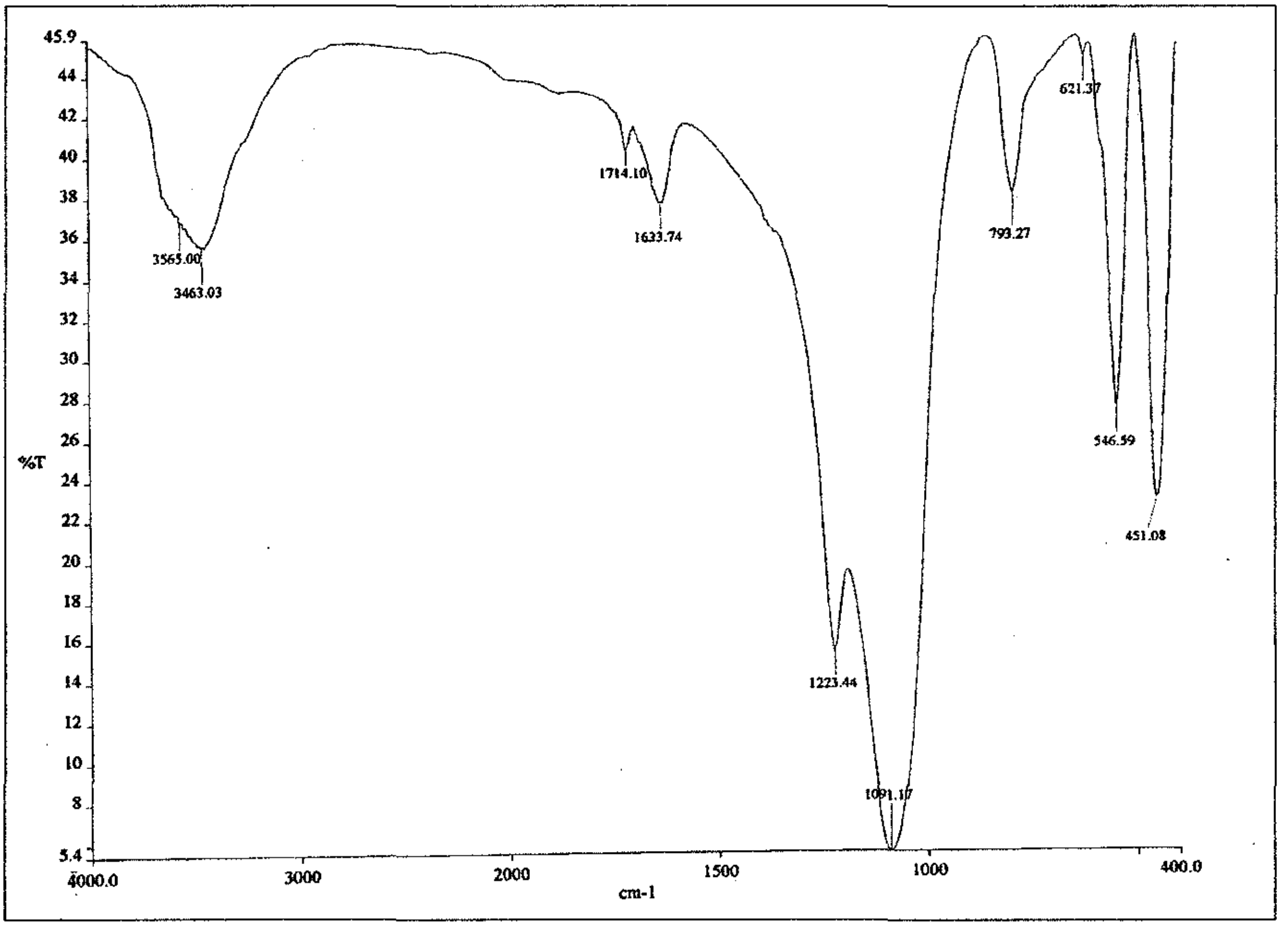


Figure 15:Fourier Transform Infrared Spectroscopy: Barium-Zinc catalyst (after calcination)

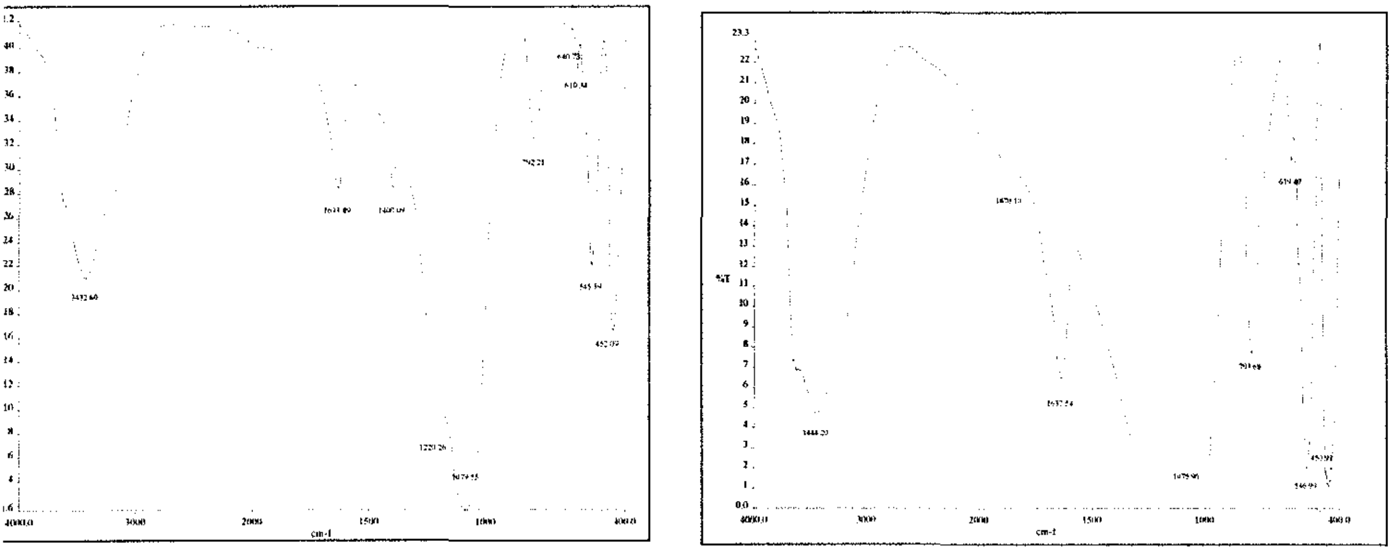


Figure 16: Fourier Transform Infrared Spectroscopy: Manganese-Barium catalyst (Before calcination: left), (after calcination: right)

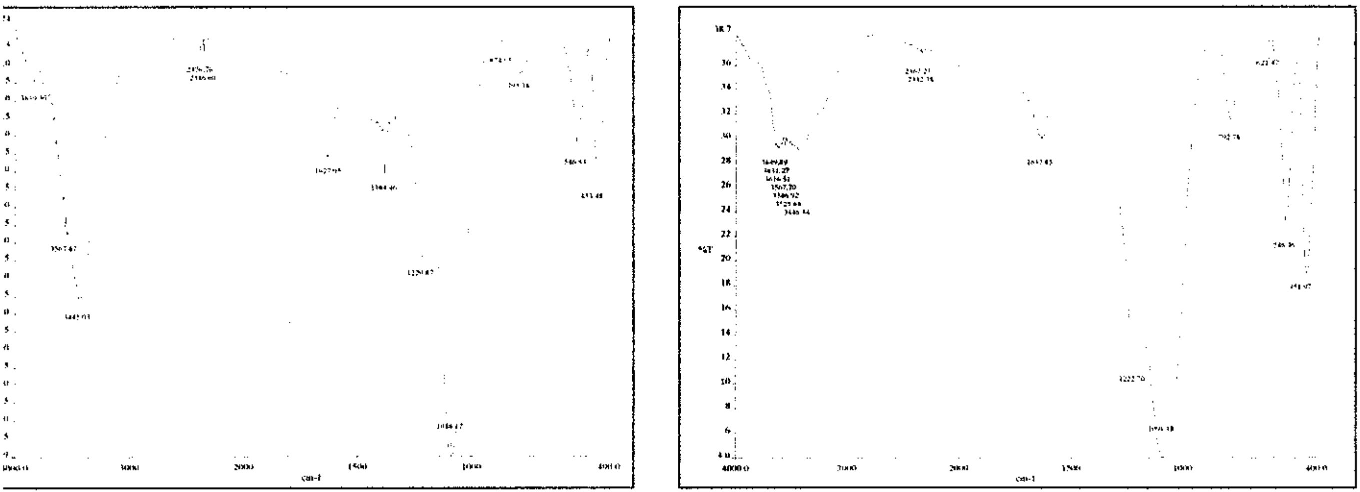


Figure 17: Cerium-Nickel catalyst (Before calcination: left), (after calcination: right)

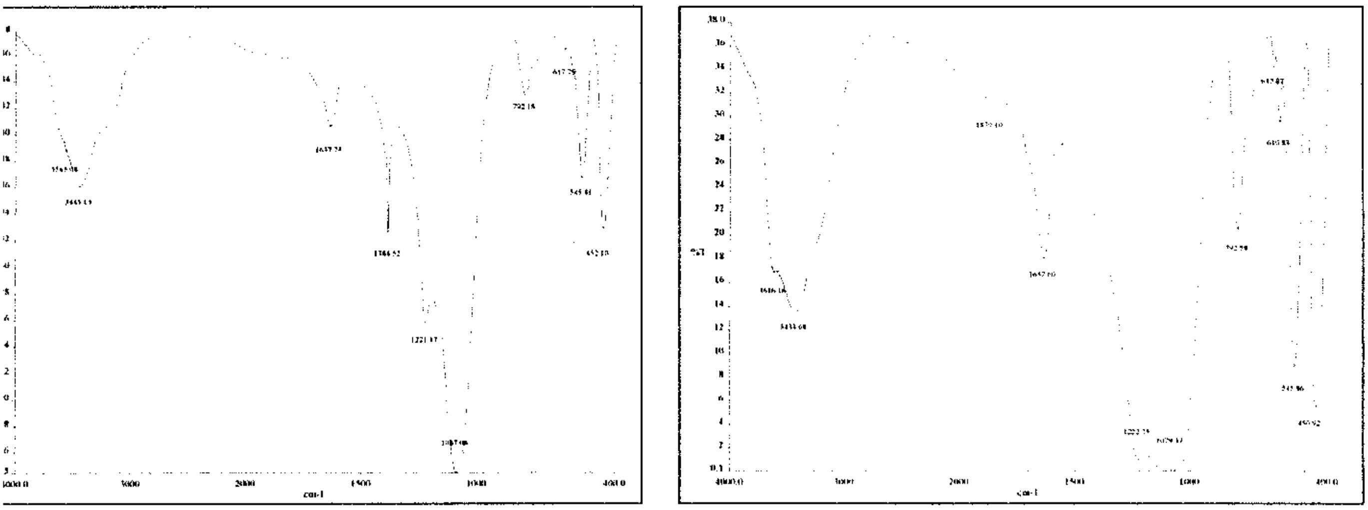


Figure 19:Manganese-Argentum catalyst (Before calcination: left), (after calcination: right

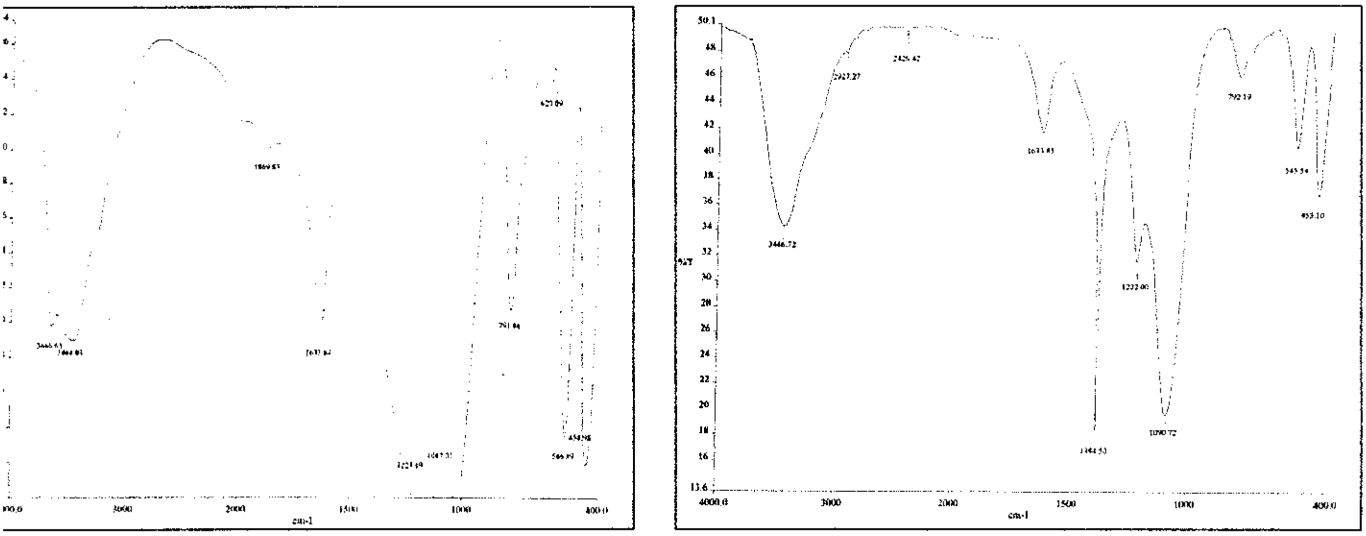


Figure 18: Copper-Cereum catalyst (Before calcination: left), (after calcination: right)

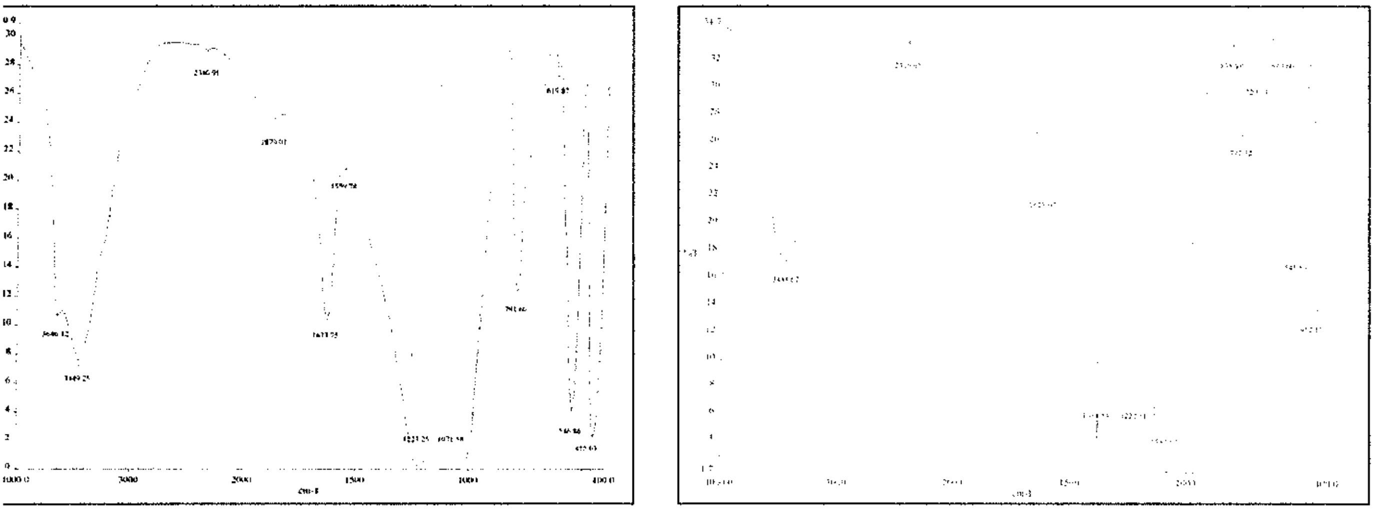


Figure 22: Copper-Barium Catalyst (Before calcination: left), (after calcination: right)

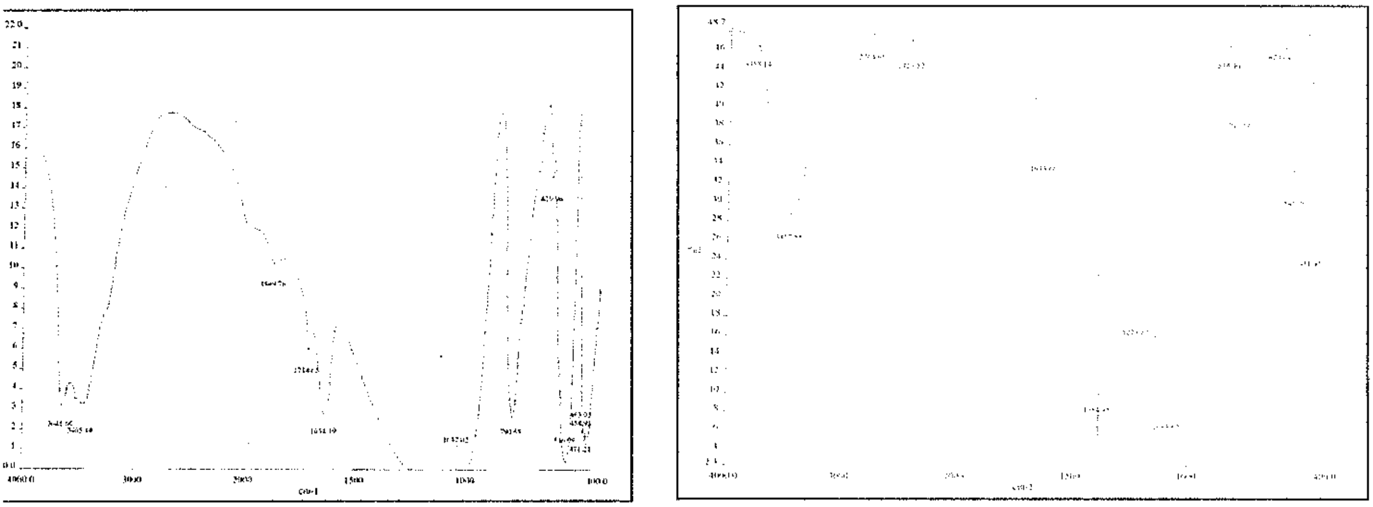


Figure 20:Copper-Argentum catalyst (Before calcination: left), (after calcination: right)

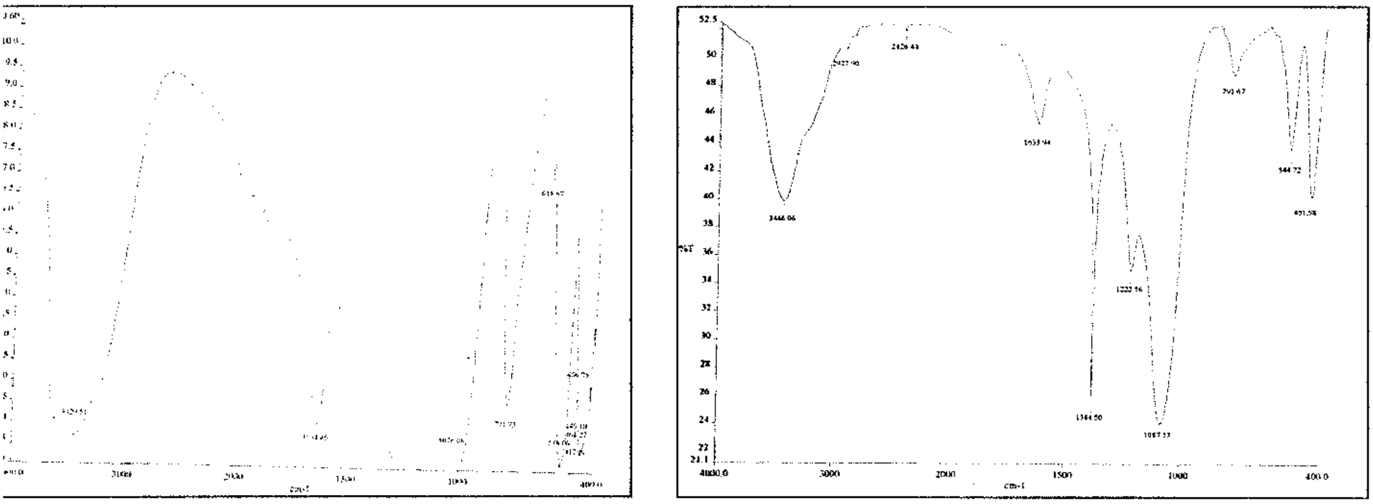


Figure 21: Copper-Manganese catalyst (Before calcination: left), (after calcination: right)

FTIR graph normally consist of number of peak that represent the compound itself. List of frequency range that refer to the representative peak are shown as below:

[illegible]	[illegible]	[illegible]
C-H	Alkanes	2960-2850(s) stretch
		1470-1350(v) scissoring and bending
	CH_3 Umbrella Deformation	1380(m-w) - Doublet - isopropyl, *t*-butyl
C-H	Alkenes	3080-3020(m) stretch
		1000-675(s) bend
C-H	Aromatic Rings	3100-3000(m) stretch
	Phenyl Ring Substitution Bands	870-675(s) bend
	Phenyl Ring Substitution Overtones	2000-1600(w) - fingerprint region
C-H	Alkynes	3333-3267(s) stretch
		700-610(b) bend
C=C	Alkenes	1680-1640(m,w)) stretch
C°C	Alkynes	2260-2100(w,sh) stretch
C=C	Aromatic Rings	1600, 1500(w) stretch
C-O	Alcohols, Ethers, Carboxylic acids, Esters	1260-1000(s) stretch
C=O	Aldehydes, Ketones, Carboxylic acids, Esters	1760-1670(s) stretch
O-H	Monomeric -- Alcohols, Phenols	3640-3160(s,br) stretch
	Hydrogen-bonded -- Alcohols, Phenols	3600-3200(b) stretch
	Carboxylic acids	3000-2500(b) stretch
N-H	Amines	3500-3300(m) stretch
		1650-1580 (m) bend
C-N	Amines	1340-1020(m) stretch
C°N	Nitriles	2260-2220(v) stretch
NO_2	Nitro Compounds	1660-1500(s) asymmetrical stretch
		1390-1260(s) symmetrical stretch

As for nitrate compound, the frequency range is 1660-1500 cm^{-1} and 1390-1260cm^{-1}. From the graph can be analyzed that the correspondent peak for nitrate and certain other peak disappear. Those show the effectiveness of calcination process in order to remove the unrelated compound inside the catalyst.

4.2.2 Temperature Programed Reduction

Temperature-programmed reduction (TPR) is a technique for the characterization of solid materials and is often used in the field of heterogeneous catalysis to find the most efficient reduction conditions, an oxidized catalyst precursor is submitted to a programmed temperature rise while a reducing gas mixture is flowed over it.

The analysis was done with flow of nitrogen gas. Samples are first pretreated with Ser.Nr.2033057. The time for every peak are collected and shown as result below:

Result:

Cu-Ag catalyst:

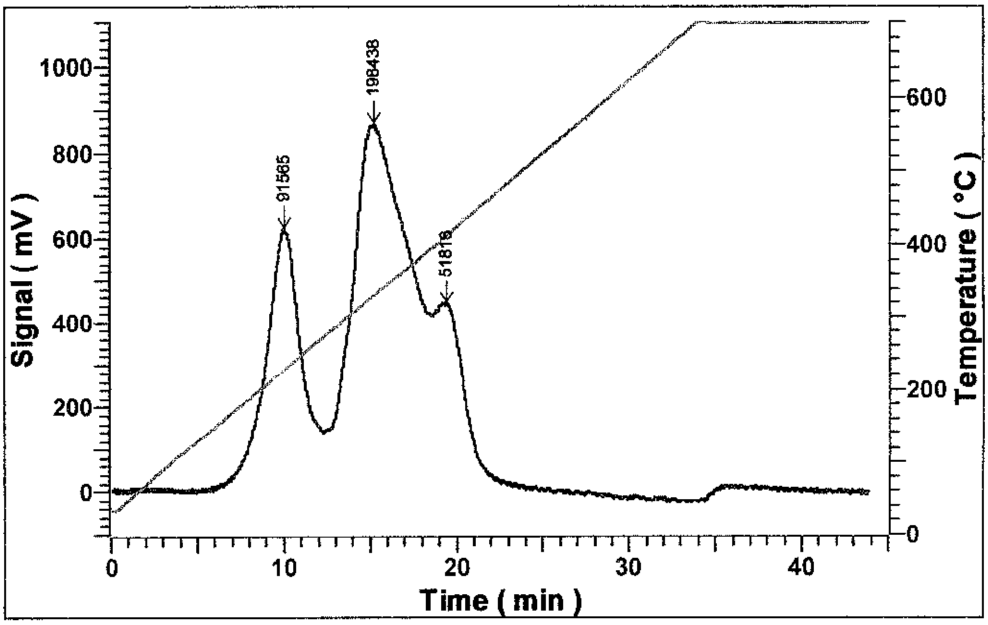
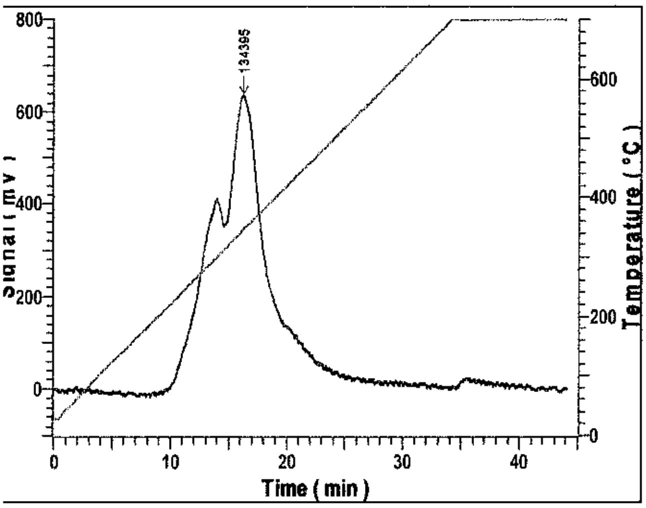


Figure 23: TPR graph obtained for Cu-Ag catalyst

Table 3 : Result of TPR analysis

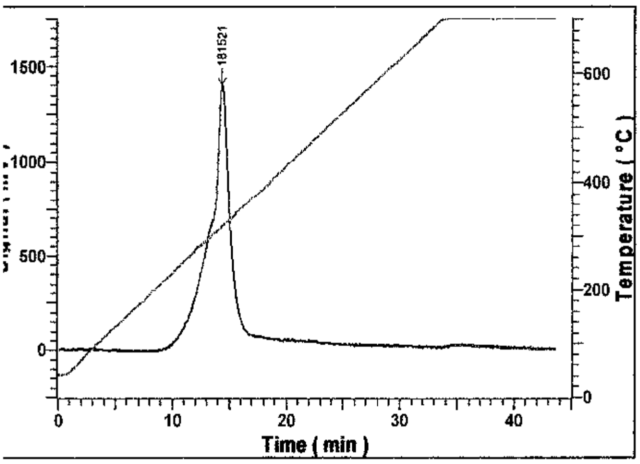
Amount gas adsorbed: µmol/g	Stoichiometric factor	Amount of metal reacted µmol/g (sample)	Total metal surface m²	Metal surface m²/g	Dispersion degree %	Mean particle diameter nm (spheres)	Total Metal %
741.73154	2	1483.46308	3.138	66.198(sample) 662.0(metal) 73.553	94.259	1.012	9.426

Cu-Ba catalyst:



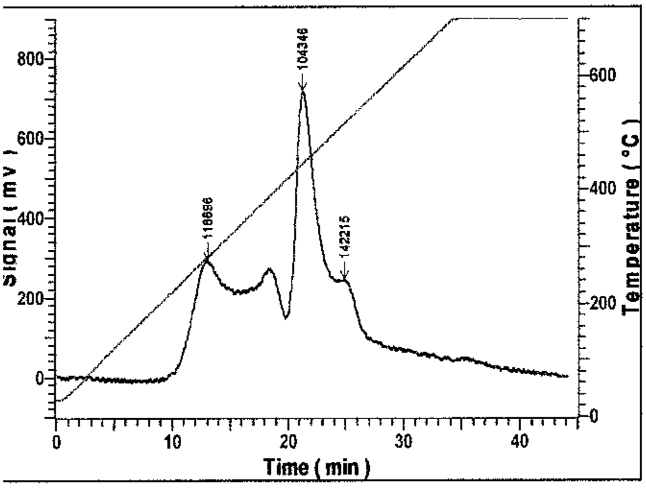
Amount gas adsorbed: µmol/g	Stoichiometric factor	Amount of metal reacted µmol/g (sample)	Total metal surface m²
364.72973	2	729.45947	1.234
Metal surface m²/g	**Dispersion degree %**	**Mean particle diameter nm**	**Total Metal %**
32.551 (sample) 325.5 (metal) 36.168	46.350	2.057	4.635

Cu-Ce catalyst:



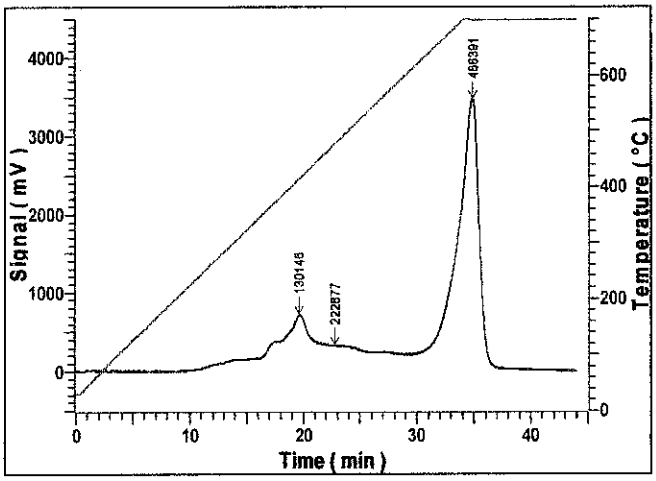
Amount gas adsorbed: µmol/g	Stoichiometric factor	Amount of metal reacted µmol/g (sample)	Total metal surface m²
552.38109	2	1104.76218	1.666
Metal surface m²/g	**Dispersion degree %**	**Mean particle diameter nm**	**Total Metal %**
49.299 (sample) 493.0 (metal) 54.777	70.197	1.358	7.020

Cu-Co catalyst:



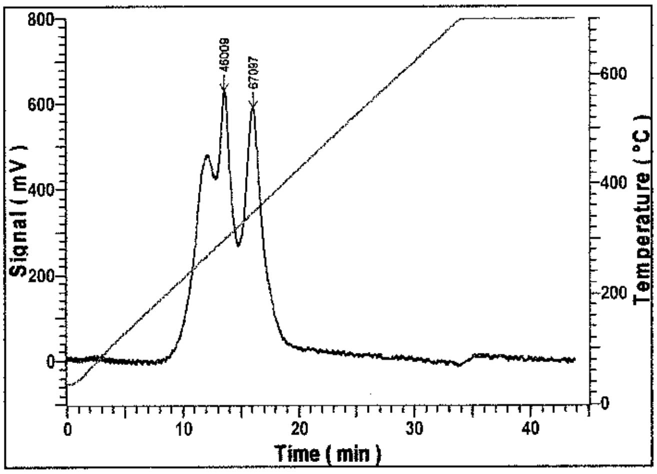
Amount gas adsorbed: µmol/g	Stoichiometric factor	Amount of metal reacted µmol/g (sample)	Total metal surface m²
552.38109	2	1104.76218	1.666
Metal surface m²/g	Dispersion degree %	Mean particle diameter nm	Total Metal %
49.299 (sample) 493.0 (metal) 54.777	70.197	1.358	7.020

Cu-Mn catalyst:



Amount gas adsorbed: µmol/g	Stoichiometric factor	Amount of metal reacted µmol/g (sample)	Total metal surface m²
2664.76562	2	5329.53124	7.706
Metal surface m²/g	Dispersion degree %	Mean particle diameter nm	Total Metal %
237.825 (sample) 2378.3 (metal) 264.250	338.638	0.282	33.864

Cu-Ti catalyst:



Amount gas adsorbed: µmol/g	Stoichiometric factor	Amount of metal reacted µmol/g (sample)	Total metal surface m²
2664.76562	2	5329.53124	7.706
Metal surface m²/g	Dispersion degree %	Mean particle diameter nm	Total Metal %
237.825 (sample) 2378.3 (metal) 264.250	338.638	0.282	33.864

4.2.3 X-ray Diffraction analysis

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials.

Result:

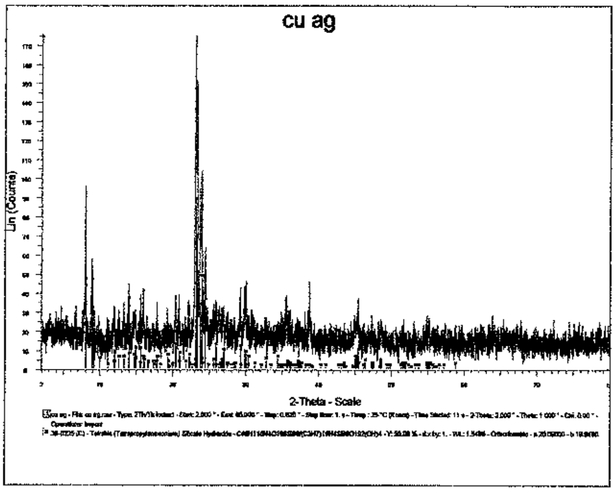


Figure 24: XRD graph for Cu-Ag catalyst

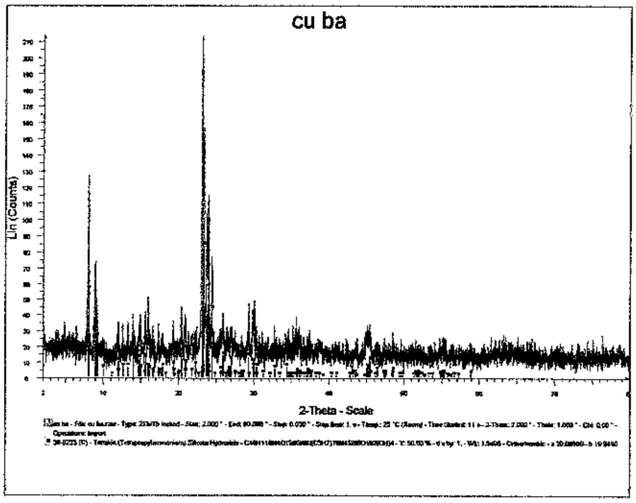


Figure 25:XRD graph for Cu-Ba catalyst

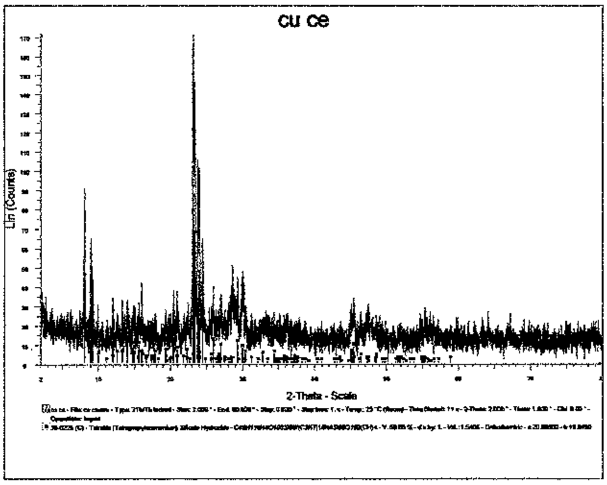


Figure 26:XRD graph for Cu-Ce catalyst

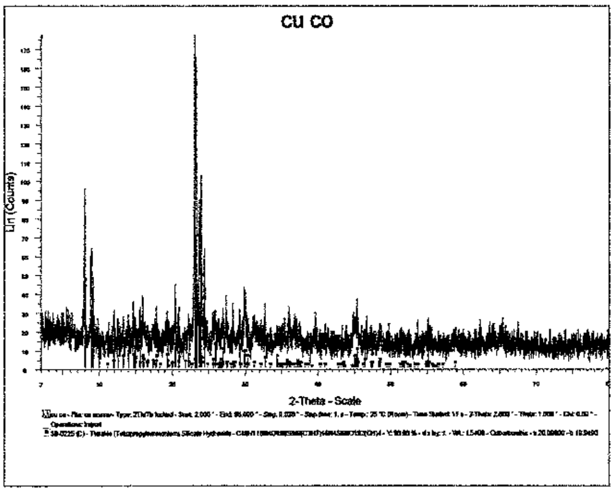


Figure 27:XRD graph for Cu-Co catalyst

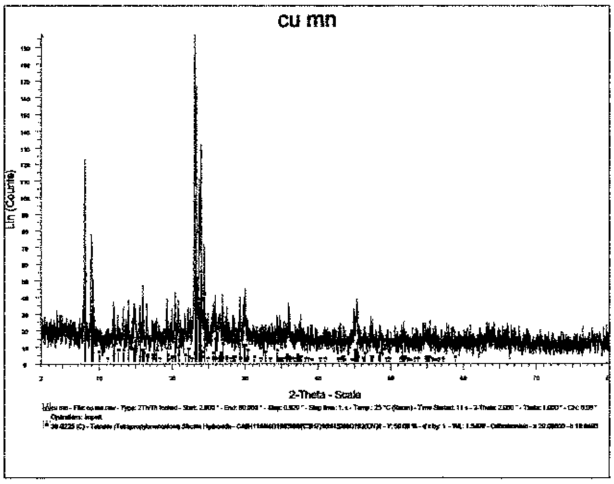


Figure 28:XRD graph for Cu-Mn catalyst

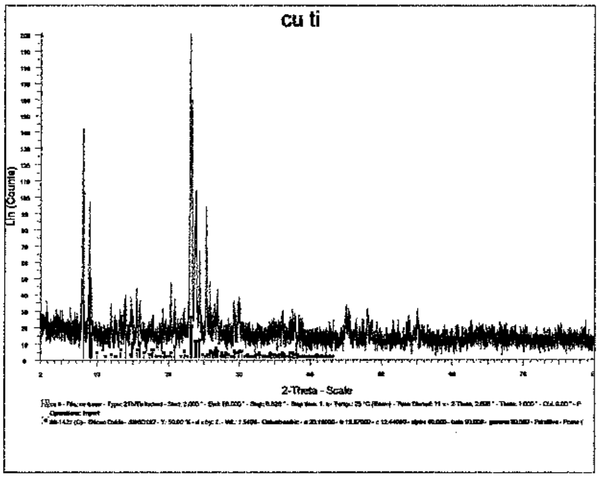


Figure 29: XRD graph for Cu-Ti catalyst

The result from XRD analysis refers to the content of the support for catalyst. In the experiment, zeolites that have been use consist of SiO_2. All the graph show the almost the same image that refer to same support that have been used in the experiment.

4.2.3 Field Emission Scanning Electron Microscopy (FESEM)

Catalysts that have been developed are sent for FESEM analysis. FESEM normally used to see the structure surface topography of sample. Field emission source generated the electron that accelerated into the field gradient under the vacuum condition. The electron beam will passed through the electromagnetic lenses to focus on the catalyst sample and as the result, different type of electron are emitted from the sample. Based on the electron beam intensity, the detector will construct the catalyst surface image.

In this experiment, huge varieties of materials are used in order to prepared the heterogeneous catalysts. Catalyst consists of three main groups which are active catalytic agents and promoters and supports. It can be developed through many type of process such as wet impregnation, drying, leaching and calcination. Support act as main component in catalyst system which it can influence the activity of active component like Argentum, Titanium, Copper and Manganese. Distribution of this metal on the support is important where high dispersion of metal.

FESEM is one of versatile method in order to characterize the heterogeneous catalyst. FESEM able to image the catalyst structure and surface with high resolution and zoom rate in order to see the nano scale of catalyst. FESEM analysis normally comes with combination with EDX-unit to provide details for microanalysis. (Thomas N. Ulaganathan, 2012)

For catalysts that have been developed for this experiment, all six catalysts are sent for FESEM analysis.

Figure 30 : FESEM image for Cu-Ag catalyst with 30 k X , 10 k X and 5 k X magnifier

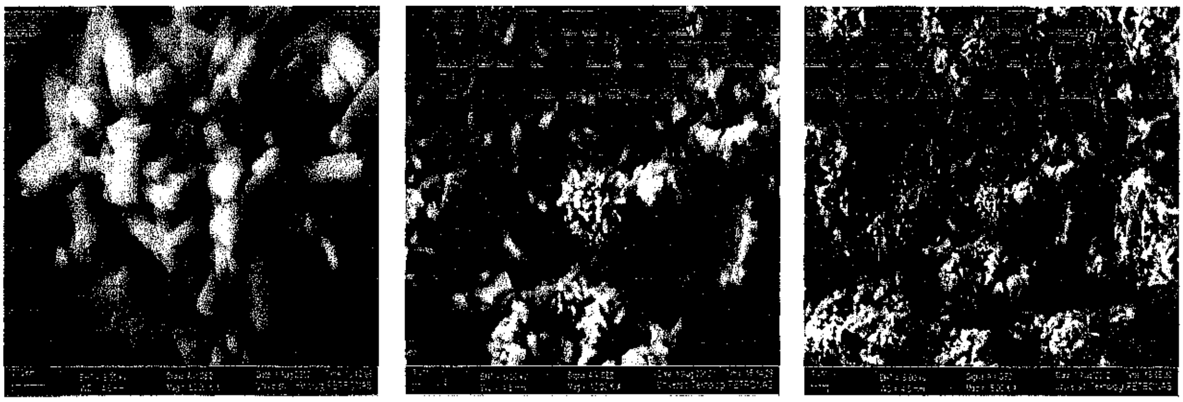


Figure 31 : FESEM image for Cu-Ba catalyst with 50 k X, 10 k X and 5 k X magnifier

Figure 32 : FESEM image for Cu-Ce catalyst with 30 k X, 10 k X and 5 k X magnifier

Figure 33 : FESEM image for Cu-Co catalyst with 50 k X, 10 k X and 5 k X magnifier

Figure 34 : FESEM image for Cu-Mn catalyst with 50 k X, 10 k X and 5 k X magnifier

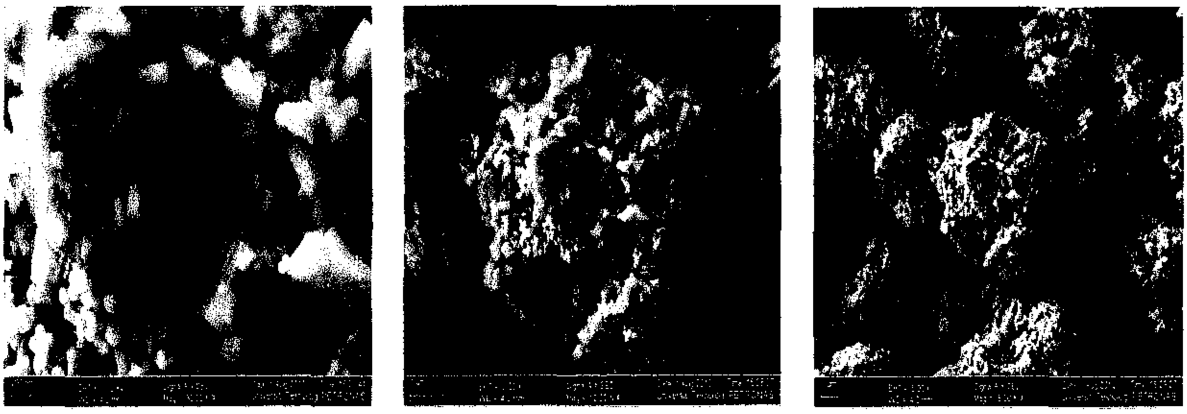


Figure 35 : FESEM image for Cu-Ti catalyst with 30 k X, 10 k X and 5 k X magnifier

From the FESEM image, we can see the structure of catalyst clearly where the catalyst consist of many pores. On the surface of support, metal that use for catalyst development crumpled together on the surface with different size. Below is the table of weight distribution for the each catalyst based on EDX information:

Table 4 : Weight % distribution based on EDX result

	C	O	Al	Si	Metal A	Metal B	Total
Cu-Ag	8.02	55.07	1.99	29.68	1.86	3.39	100.00
Cu-Ba	12.84	54.98	2.12	26.74	3.26	0.07	100.00
Cu-Ce	7.66	56.64	2.34	27.00	3.41	2.96	100.00
Cu-Co	3.89	58.18	2.38	30.12	3.04	1.34	100.00
Cu-Mn	9.25	57.79	2.17	27.36	2.21	0.82	100.00
Cu-Ti	8.79	56.93	1.90	22.89	2.77	6.72	100.00

4.3 Catalytic test and Gas Chromatograph result

The catalyst development had been going through the catalytic test in order to check the efficient in acetalization of glycerol with formaldehyde. The reactions are done for 10 hours for every batch. The setting for temperature is 354 F and pressure at 1 atm. The stirrer speed is set at 200 rpm. After one complete reaction, the sample are taken for GC-MS analysis to determine final product composition.

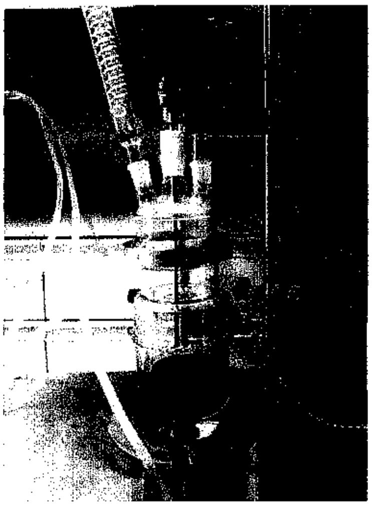


Figure 36 : Glass reactor with glycerol and formaldehyde during reaction

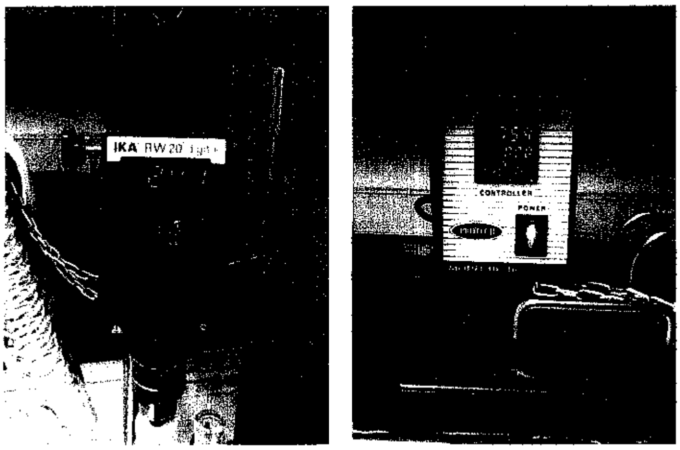


Figure 37 : Left - stirrer setting at 200 rpm right - temperature set at 80C with circulating water bath

For GC-FID analysis, the samples are prepared with methanol and use Agilent DB-1 60m x 0.53mm x 5 micrometer capillary column with helium gas as the carrier. Below is Cu-Agcatalyst product result from GC-FID:

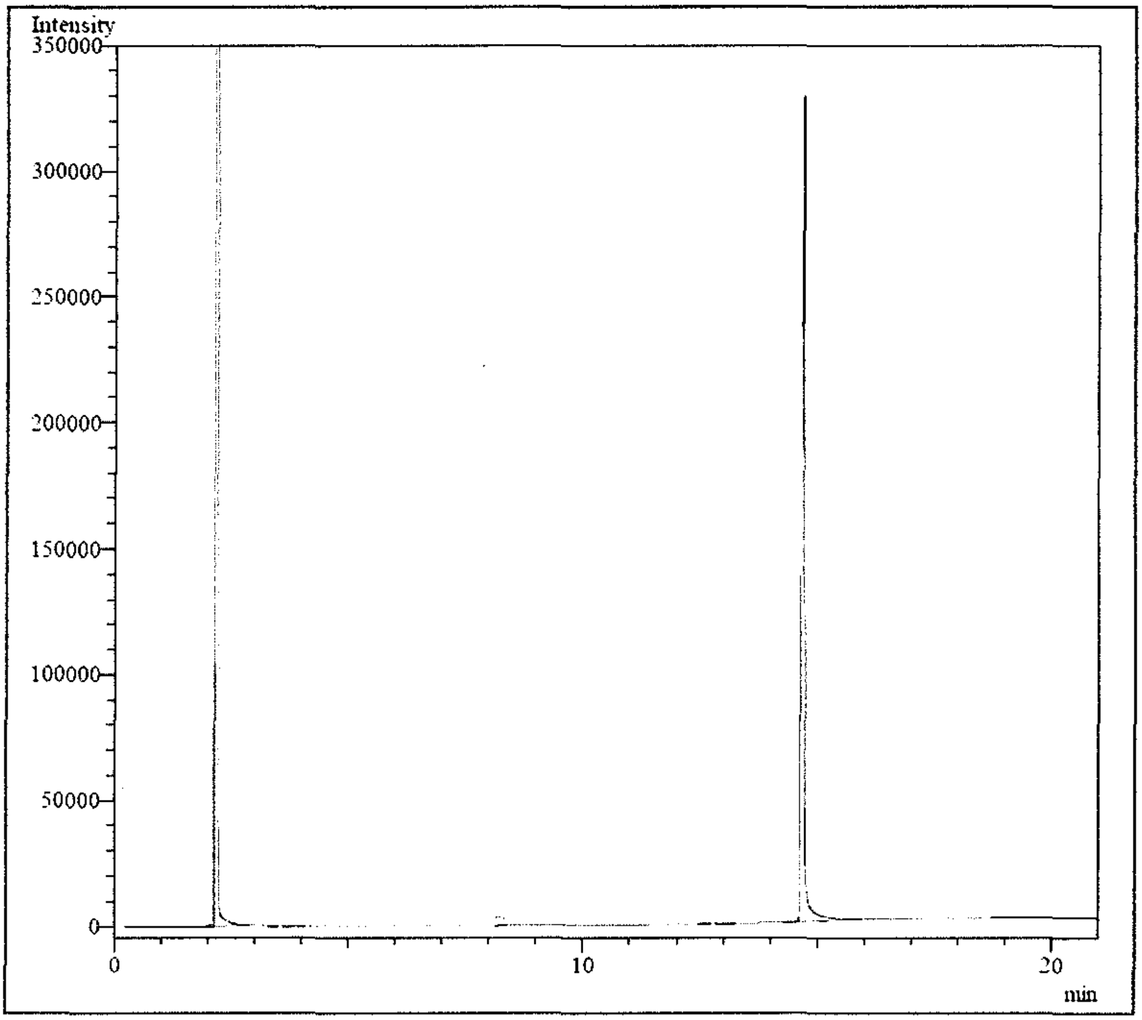


Figure 38 : GC-FID graph for Cu-Ag catalyst for product after complete reaction

Table 5 : Compound based on representative peak from GC-MS graph

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1	2.059	2242.12	820.39	0.0000	ppm	
2	2.172	11224152.25	5214666.92	0.0000	ppm	
3	8.230	1605.94	331.50	2353.9949	ppm	Glycerol formal
4	14.709	1412583.31	327722.28	0.0000	ppm	
TOTAL		12640583.62		2353.9949		

The graph shown has 4 main peaks that represent some compound that contain in the final product of acetalization. Based on the library file from GC-FID, the third peak refers to glycerol formal which determine as the final product from the reaction while the other peak refers to reactant and also solvent for the analysis that used during the experiment.

In order to find the conversion of glycerol formal, standard must be prepared to gain calibration curve. The standard is prepared with 3 different concentrations which are 3000ppm, 5000ppm and 7000ppm. The standard will be test with GC-FID to gain its calibration curve. Below is the calibration curve from standard prepared :

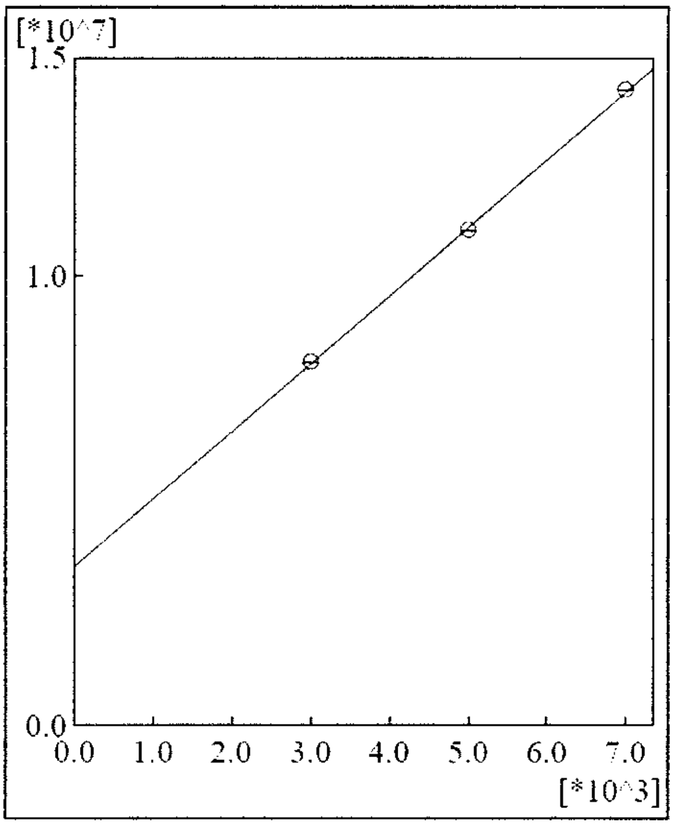


Figure 39 : Calibration curve for Glycerol formal

Based on calibration curve above, we can calculate the concentration of glycerol formal along with others compound. The functions that can be used to find the concentration are as below:

$$f(x) = 1503.89964664 * x + 3541777.98238$$

Equation 5 : Equation to calculate the concentration of final product

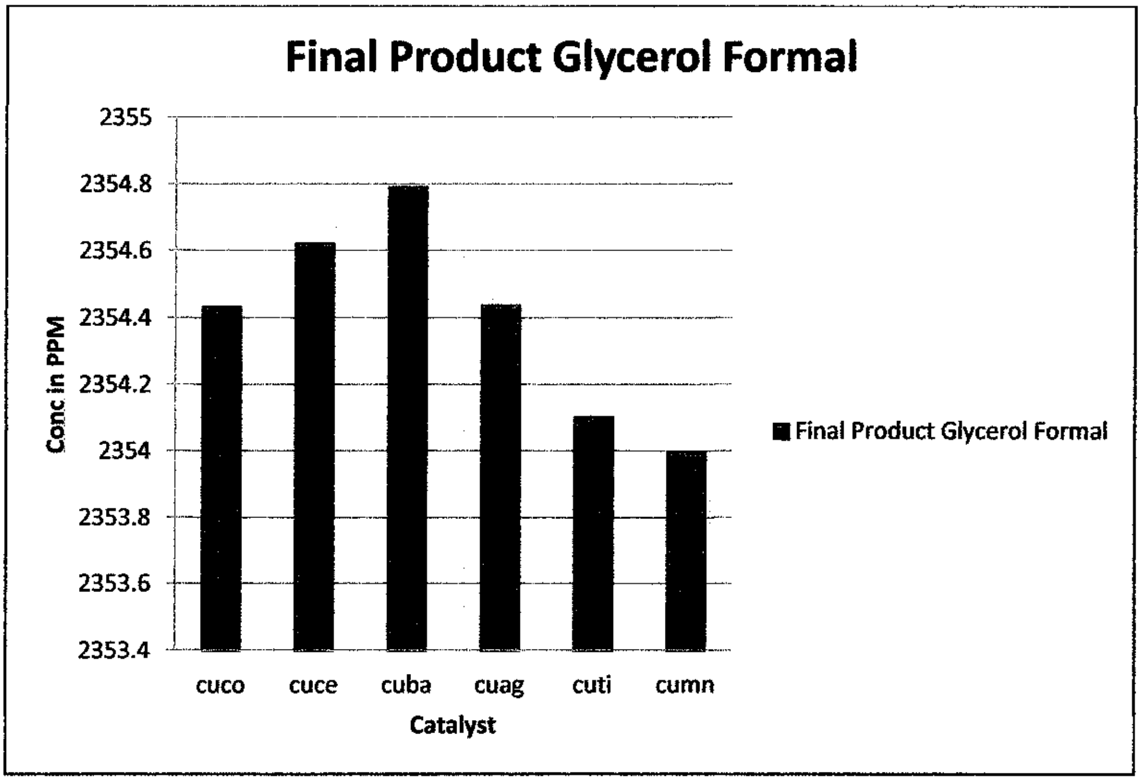


Figure 40 : Graph for concentration of glycerol formal for each catalyst

DISCUSSION

From all the result, it's clearly that these experiments are successful in developing the bi metallic catalyst from copper based metal. The other catalysts which are Mn-Ba, Ba-Zn, Mn-Ag and Ce-Ni are not able to be calcined properly. Based on previous study by researcher, it is a case where not all catalyst can be prepared using same type of procedure. Some metal or support is not suitable to be used or maybe the temperature setting is not enough to help the metal impregnated into the support. Besides that, pH of solution during impregnation also become an important parameter to able the catalyst to be prepared.

This problem is discovered after the results from TPR are obtained. The graphs of TPR for these 4 catalysts are not normal as the other graph. Besides that, the analysis report that the metal contain inside the catalyst not reach the 10 wt% of total weight of catalyst. So the all 4 catalyst are not able to proceed for catalytic test.

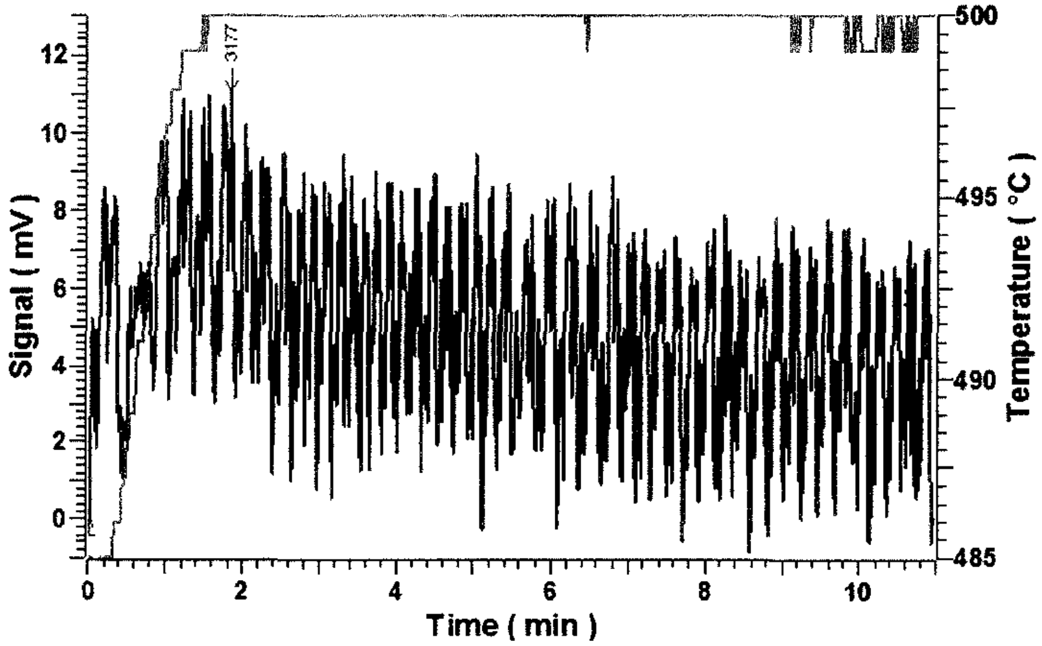


Figure 41 : Abnormal TPR graph for Ce-Ni

[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
3.05690	2	6.11379	0.026	0.239(sample) 2.4(metal) 0.266	0.359	281.700	0.036

Other characterization analysis like FESEM, XRD and FTIR for all 6 copper based catalyst are positive to say that the catalyst are successfully been developed and suitable to be used during reaction of acetalization for glycerol and formaldehyde.

In catalytic test, the result appeared only a small portion of glycerol formal which is final product for the acetalization. The highest concentration is achieved form Cu-Ba catalyst which contain up to 2354.8 ppm. Almost all the catalyst contains the same concentration with each other at around 2300ppm. The reason for only small value of concentration inside the final product must be due to short reaction time. In this experiment, we decide to run the experiment for 8 hours only instead 48 hours as suggested by previous research. It is sure that if the reaction time is increase, we able to get high conversion of glycerol.

CHAPTER V

CONCLUSION AND RECOMMENDATION

Since world now are focusing in production of bio-diesel, it has a high potential that the world will face the problem of excessive crude glycerol. So, the conversion of glycerol into glycerol formal is seen as the most interactive alternative to solve this problem. Glycerol are reacted with formaldehyde that in the end will give extra add value to the crude glycerol. By upgrading the glycerol, glycerol applicability is no longer limited due to its properties but can be used in a wide range of possible applications. So, this research are done in order to increase the understanding and also give extra view for future research that will be done based on catalyst development for reaction of glycerol and formaldehyde.

As the conclusion, these experiments are able to achieve the objectives that have been set at the beginning of the project:

1. To develop bi-metallic catalysts for acetalization of Glycerol with Formaldehyde.
2. To characterize the physicochemical properties of the catalyst
3. The catalytic performance of the catalyst developed.

Firstly, in order to achieve objective to develop bi- metallic catalysts for acetalization of glycerol and formaldehyde, up to 10 different type of catalyst are able to be developed. All the catalysts are prepared carefully by following the fixed guideline to ensure all the catalyst will have similar final result. The Incipient Wetness Impregnation of catalyst preparation is used. The process include of impregnation, drying and calcination.

Secondly, the objective to characterize he physiochemical properties of the catalyst are successfully done. All the catalyst is brought for analysis using various tools to determine the characteristic of the catalyst. The analysis include of FTIR, XRD, TPR and FESEM. All the result from analysis gives the information for the catalyst that had been developed. Finally, the catalytic test had been done to the catalyst to see their performance in order to react glycerol with formaldehyde. The final results from catalytic test show that reactions are able to convert the glycerol into glycerol formal which is the final product of the reaction. Cu-Ba catalysts are found to obtain highest conversion among the other catalyst.

Based on this research, a few recommendations can be suggested for future guideline. First, in order to develop of bi metallic catalyst, certain parameter must be revised during the preparation of catalyst. Different temperature and time setting must be checked to find the best setting to ensure the successful catalyst developed. Second, during the catalytic test for reaction, extra study can be done based on variation of temperature, pressure, stirring speed and reaction time. Extra variation done for each setting can give clearer overview to achieve the perfect setting for acetalization process using bi-metallic catalyst. On this research, only one setting are set for experiment which are temperature at 80C, pressure at 1atm and stirring speed at 200rpm. Next research can vary the temperature to higher temperature such as 90°C, 100°C, 110C and 120°C. They also can vary the reaction time to longer time than 10 hours.

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