Synthesis & Characterization of Zirconia Promoted $Cu/ZnO/Al_2O_3$ Catalyst for Methanol Synthesis Via Hydrogenation of CO_2

By

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Dissertation submitted in partial fulfillment of

The requirements for the

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CERTIFICATION OF APPROVAL

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JULY 2010

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.

(NIK AHMAD ROMZI BIN NIK ABDUL AZIZ)

ABSTRACT

Nowadays, issues on global warming of the world atmosphere have continously become more and more important. Due to global warming, our environment encounter the problem called climate change that will result in very catasthropic event and diseases. This CO_2 are the primary cause of global warming. The atmospheric concentration of CO_2 has steadily increased owing to human activity and this accelerates the green house effect. One of the best route to remedy CO_2 is by tranforming it to reusable hydrocarbon such as methanol that is very usefull in our routine life (Jeffrey, 2005). A number of studies on this reaction have been reported over copper, Cu-based catalysts. $CuO/ZnO/Al_2O_3$ catalyst, a very typical methanol synthesis catalyst from CO_2, is being investigated very actively for this reaction, but the investigations of other ternary catalysts are comparatively few (Naofumi Nomura, 1998). This paper is mainly a study on development of $Cu/ZnO/ZrO_2$ for CO_2 hydrogenation for methanol process. The author is focusing on the effect of catalyst composition. Mainly, in this paper the author were to study the catalytic system comprising copper-based hydrogenation catalyst and solid acid catalyst. Besides that, the job is to characterize the physical properties of the catalyst. In order to complete this project, the author will need some tools and apparatus to characterize the catalyst. The equipments used are Field Emission Scanning Electron Microscopy (FESEM) and FESEM – Energy Dispersed X-ray (EDX).

ACKNOWLEDGEMENT

The author would like to thank all team members that have contributed to the success in finishing the project. With the assistance and guidance in the project, two semesters of hard works and sacrifices was paid off through the satisfaction of experiencing team work.

The author greatest gratitude goes to his supervisor, Dr Maizatul Shima Shaharun who assisted in providing relevant data and information regarding the project while guiding in the process of doing the catalyst preparation and characterization.

The author would like to thank the Final Year Project committee for arranging various seminars to provide support and knowledge. The seminars were indeed very helpful and insightful to the author. The author would like to thank all lecturers from Universiti Teknologi Petronas who had given the guidance throughout the period of the project.

Last but not least, not to forget family members and fellow friends who gave moral support to motivate and allowed the author to pursue to greater heights in this project.

Thank You.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Issues on global warming of the atmosphere have continously become more popular and got attention in this recent years. The awereness is triggered due to man-made emissions of greenhouse gases which are feared to harm the ozone layer badly. Since the industrial revolution around 250 years ago, fossil fuel consumption has increased rapidly. This led to the increment in the global concentration of carbon dioxide, which amounts to 370 ppm [Keeling, C. D, 1997]. Predictions about global climate change with the overall rise of about plus 0.5°C during the 20th century is often support of global warming [Hansen, J., 1996; Hansen, J., 1987; Hansen, J., 1988]. Thus, for nowdays how much this number is already gain at our atmosphere. Furthermore, the major source of carbon dioxide is mainly from oil and gas processing industries. This is very relevant to this project since the author need to find a way in mitigating the carbon dioxide into the hydrocarbon type of product. One possible approach of the above mention problem is by recyle the carbon in a chemical process to form products as methanol [Bill, A., 1998].

1.2 PROBLEM STATEMENT

Almost 87 years now since Badische Anilin-und Soda-Fabrik (BASF) has invented methanol synthesis process from syngas using ZnO-Cr_2O_3 catalyst in 1923, but still there is no ultimate process which produces methanol from CO_2 itself. It is mainly because of hydrogenation of CO_2 is much more thermodynamically unfavorable compared to CO under operating condition of interest [Inui, 1997]. Furthermore, it provides a low conversion of CO_2 due to the chemical equilibrium and poor selectivity due to the water-gas shift reaction on the same copper containing catalyst [Park, 1995]. Hence, many trials have been made not only to increase activity but also to facilitate the consecutive reactions of the primarily formed products for the diminution of CO selectivity [Park, 1995]. The challenge is to choose the most suitable and appropriate type of catalyst in CO_2 hydrogenation process that is capable to achieve high conversion of CO_2 and at the same time giving low formation of CO.

1.3 OBJECTIVE AND SCOPE OF STUDY

The main objectives of this study are:

1) To develop the Zr promoted $Cu/ZnO/Al_2O_3$ catalyst
2) To characterize the physical properties of the developed catalyst
3) To study the effect of catalyst composition.

Based on the proposed objectives, there are a few scope of work that need to be done through this paper work. It include the development of $Cu/ZnO/Al_2O_3$ catalyst using zirconium nitrate as promoter. Besides, the author has to study the effects of catalyst preparation such as effect of catalyst composition. On the other hands, the author would do the comparison between the commercial catalyst using the Zirconium (Zr) promoter and without using it to show a clear picture of this two catalysts. Present study, characterizations as well as catalysts testing were performed to investigate the relationship between the characteristics. Some tools or equipments need to be used in order to do the characterizations. They are including FESEM and FESEM-EDX.

1.4 METHANOL

Methanol (CH_3OH) also known as methyl alcohol, is one type of the simplest example of an alcohol. It is a light, volatile, colourless, flammable and poisonous liquid. Methanol is a valuable commodity due to its wide range applications. It provides for a diversity of final applications ranging from adhesive manufacture, agricultural chemical production, paint and varnish production, the manufacture of synthesis resins, synthetic fiber fabrication and even for cardiac disease medications. It also can be used to produce methyl-tertiary-butyl-ether (MTBE), which is blended with gasoline to enhance the octane number and create cleaner burning fuel.

Methanol has the advantage of being a liquid under normal conditions and can be stored and transported as easily as gasoline. It can also be used in convensional combustion engines without requiring any major modifications. The benefits of using methanol as fuel include lower emissions, higher peformance, and lower risk of flammabiliy than gasoline. In addition, methanol can easily be made into hydrogen as it has twice the energy density of liquid hydrogen [Bill, A., 1998]. Some researchers are currently working to overcome the barriers in using methanol as a hydrogen fuel source. Therefore, methanol may potentially be used as a hydrogen carrier for hydrogen fuel cell vehicles in the future.

World methanol demand during the last five years had shown steady growth (temps of the growth were about 3% per year) as depicted in Figure 1.2. It is expected that in 2008 average annual growth of demand will be about 2% and world methanol consumption will reach 36 million metric tons.

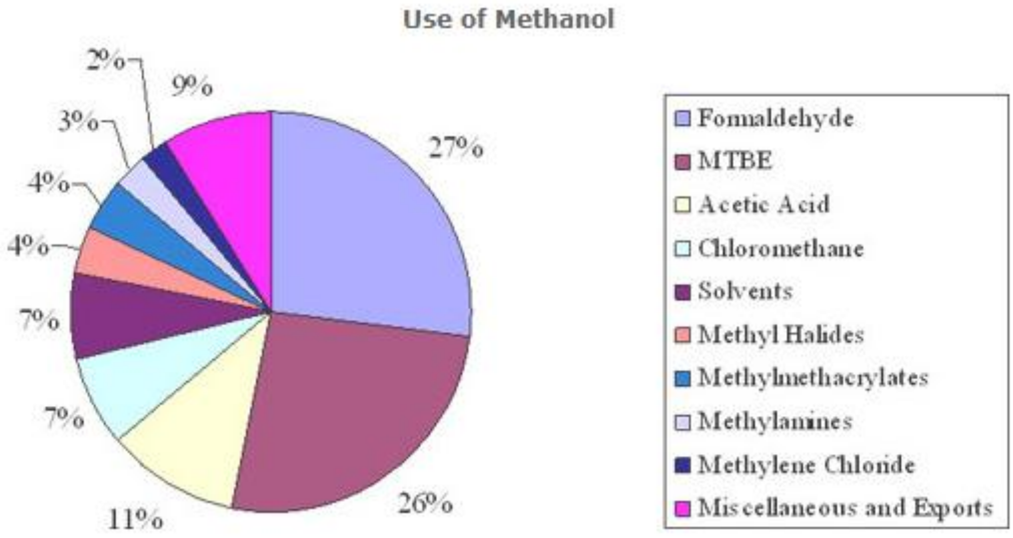

Figure 1.1: Wide range of methanol usage

(Source: http://www.metcallcompany.com/methanol.htm)

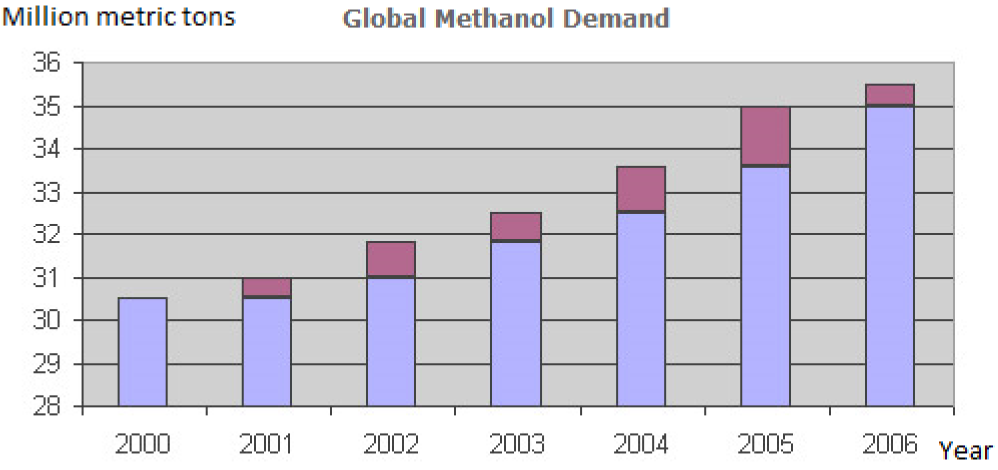

Figure 1.2 Global Methanol Demand

(Reproduced source: http://www.metcallcompany.com/methanol.htm)

Methanol synthesis technology has evolved from organic feedstock to hydrocarbon sources. In the 20th, methanol is synthesized industrially from synthesis gas (syngas) feedstock comprising carbon monoxide (CO), hydrogen (H_2) and CO_2 through well-known high pressure process which was operated at temperatures ranging from 200 – 300°C and pressure at 30 – 80 bar over MK-101 type Haldor Topsoe catalyst [PFK, 2000]. In modern technology, the process is carried out via low-pressure and low-temperature reactions on copper-based catalyst.

This catalyst is thermally stabilized with alumina and added with zinc oxide to provide protection against impurities such as chlorine and sulfur that are present in the syngas which can poison the catalyst and causing it to deactivate. Because this copper-based catalyst system is extremely and well known active and selective, methanol synthesis could be carried out at 220 – 230°C and 50 bar with methanol purity up to 99.5% [Reinhard Rauch,2003]. More importantly, public awereness of clean technology in chemical processing industries in the recent years has created an interest in developing methanol synthesis technology using industrial byproducts. Issues on global warming led to climate change associated with CO_2 are the main reason for developing a direct hydrogenation process for conversion of pure CO_2 into methanol product.

1.5 METHANOL SYNTHESIS VIA CO_2 HYDROGENATION

Methanol is produced from natural gas or coal via syngas commercially containing CO and H_2 along with the portions of CO_2. Many investigations have reported that the conversion of CO_2 into hydrocarbons has been gained a little attention. This is due to the fact that carbon dioxide is a thermodynamically very stable compound. The equilibrium value for methanol synthesis from CO_2 is about one third of that from CO. Moreover, at temperature below 250°C, the yield of methanol is hardly reaches the equilbrium [Inui, 1992]. The high concentration of CO_2 in flue gas, which comes out from large facilities in the electric power generation plants, the steel, petrochemical and petroleum and cement industries occupies about one third of total CO_2 emissions by fossil fuel combustion, therefore it is considered as the material for hydrogenation [Saito, 1996].

Under proper conditions, methanol made from atmospheric CO_2 by its reaction with hydrogen is regarded as the “most economic way after oil and gas” [Olah, 2004]. Currently, methanol is produced industrially using ternary catalyst system comprising Cu/Zn/Al oxide at 5-10 bar and 250-300^{o}C with syngas feedstock. However, the ternary catalyst system that is used is active for CO-rich feedstock, then it is not so active for CO_2-rich sources under operating conditions of interest [Saito, 1996 & Inui, 1997].

The hydrogenation of CO_2 is shown in reaction {3}. Generally, reverse water gas shift reaction (RWGS) also forms simultaneously in CO_2 hydrogenation that led to the formation of CO {4}. Nevertheless, CO could also be formed from methanol decomposition {5}. Hence, a combination of both reactions gives high concentration of undesired CO. In addition, water is formed as a by-product from both methanol synthesis and the RWGS. The presence of water in CO_2 hydrogenation is one of the main differences between the hydrogenation of CO_2 and that of CO. So, the reaction activity may be affected by the presence of water. To overcome this problem, a third reaction can be added to shift the equilibrium to higher conversion of methanol. The improvement is in per-pass conversion can be achieved by transforming methanol into dimetyl ether on soild acid catalyst {6} [Ki-Won Jun, 1999].

$$CO_2 + 3H_2 \leftarrow\rightarrow CH_3OH + H_2O \qquad \{3\}$$

$$CO_2 + H_2 \leftarrow\rightarrow CO + H_2O \qquad \{4\}$$

$$CH_3OH \leftarrow\rightarrow CO + 2H_2 \qquad \{5\}$$

$$2CH_3OH \leftarrow\rightarrow CH_3OCH_3 + H_2O \qquad \{6\}$$

Combination of methanol synthesis catalyst with solid acid have been proven to form dimethyl ether and hydrocarbon with improved of CO_2 and lower CO selectivity due to the consecutive conversions of methanol to DME [Park, S-E., 1997]. Nowadays, DME is considered as a clean fuel for the 21th century because it can be applied in automotive, power generation, fuel cell and as a domestic gas replacing LPG, with low pollutant emissions [Rouhi, A. M., 1995; Jia, M., 2002]. It has recently received much attention as an alternative diesel fuel due to its low no emissions, near-zero smoke and less engine noise compared with those of traditional diesel fuels [Xu, M., 1997; Jun, K. W., 2004; Xu, M., 1997]. In addition, it has been used as an aerosol propellant to replace chorofluoro carbons which can destroy the ozone layer of the atmosphere [Bohaeun, L. J. M., 1979]. The CO_2 conversion to a clean liquid fuel such as methanol and DME could provide a way to produce a secondary energy carrier for using renewable energy more efficiently as alternative to elctricity [Ki-Won Jun, 1999].

CHAPTER 2
LITERATURE REVIEW

Literature review is the analytical, critical and objective review of written materials on the chosen topic and area. It provides the background information on the research question and to identify what others have said and/or discovered about the question. It contains all relevant theories, hypotheses, facts and data which are relevent to the objective and the findings of the project.

2.1 CATALYST FOR CO_2 HYDROGENATION

Recently, hundreds of papers concerning methanol synthesis from CO_2/H_2 mixture have been presented and the results were reviewed (Saito, 1993) and (Ohyama, 1995). The majority of the catalyst used is still contain Cu and Zn as the main components together with different modifiers as well as using different preparation methods. For this project, the author is actually dealing with the $Cu/Zn/Al_2O_3$ with Zr promoter as the catalyst for methanol CO_2 hydrogenation as well as using the co-precipitation method.

Various types of catalyst with their modifiers have been widely investigated. The reasons for those improvements were due to weak basicity, increasing both the adsorption capacity for CO_2 and the effect of hydrogen spillover. The hydrogen spillover gives an influence not only on the proper transportation rate of hydrogen as the reactant but also on the control of the intermediate oxidation state of the catalyst surface during the reaction giving the highest space-time-yield of methanol. As for example, proper addition of certains amounts of ZnO to the

Cu/ZrO_2 catalyst could greatly enhanced its activity (Nitta, 1994). Moreover, it was reported that CO2 kept the copper surface partially oxidized or preventing an over-reduction of the ZnO components (Denise, 1987). (Koppel, 1992) have also investigated a Cu/ZrO_2 catalyst using series on the influence of preparation variables on catalytic behavior and obtained a high activity and selectivity for methanol synthesis from CO_2 hydrogenation. However, the presence of zirconia bears the disadvantages of low surface area and poor thermal stability compared to the alumina counterparts.

2.1.1 $Cu/ZnO/Al_2O_3$ Catalyst (Commercially Catalyst)

Currently, methanol synthesis is run mostly on $Cu\text{-}ZnO/Al_2O_3$ catalyst at 493-573K and a pressure of 5-10 Mpa with a syngas feed containing typically 5% CO-5% CO_2 and H_2 (G. C. Chincen, 1988). $CuO\text{-}ZnO\text{-}Al_2O_3$ catalyst have been widely used for methanol synthesis from syngas ($CO + H_2$); however they exhibited a poor catalytic performance for the hydrogenation of CO_2 (F. Arena, 2007). The reasons can be ascribed to the negative effect of water on the rate of methanol formation and the strong hydrophilic characteristic of alumina (F. Arena, 2007). In the end of 1960's, a pressure-low temperature methanol synthesis catalyst was introduced by ICI (B. M. Colleens, 1973), which was based on copper-containing system such as $Cu/ZnO/Al_2O_3$ with various compositions. Since then, many studies and discussions focus on the role of copper, on which the catalytic reaction of $CO(CO_2)$ hydrogenation to form methanol could take place. It was found that the particle size, surface area, metallic copper surface area and composition of $Cu/ZnO/Al_2O_3$ catalyst are important factors to the catalytic process. A linear relationship between the catalytic activity and the metallic copper surface area of the catalyst was proposed by Chincen et al. (G. C Chincen, 1986). It was observed that the catalytic activity of methanol synthesis from carbon dioxide hydrogenation increased with increased with increasing metallic copper surface area for $Cu/ZnO/Al_2O_3$ ternary catalyst until it reaches a maximum and decrease at Cu/ZnO = 8 (molar ratio) (Jingfa Deng, 1996).

In recent years, various methods have been developed to prepare $Cu/ZnO/Al_2O_3$ catalyst with larger surface area and copper surface area, fine particle size and optimized compositions, which was believed to have a high catalytic activity for methanol synthesis from CO (CO_2) hydrogenation. Tanaka and co-workers (Y. Tanaka, 1983) prepared Cu/ZnO binary catalyst from a solution of copper zinc nitrates dissolved in ethylene glycol. It was found that the selectivity to methanol was highest when the ratio of copper to zinc was 1. The active site were concluded to be copper atoms in contact with crystallites (Y. Zhang, 1996).

2.1.2 $Cu/ZnO/ZrO_2$ Catalyst

Zirconia-supported copper catalysts, which show an interesting catalytic behavior for CO_2 hydrogenation, have been well documented (F. Arena, 2007). Among them, $CuO\text{-}ZnO\text{-}ZrO_2$ (CZZ) or modified-CZZ has gained an increasing interest for its high activity in recent years (F. Arena, 2007). It is well known that materials as supports in supported-metal-catalyst not only provide large surface area for metal dispersion, but also effect the activity and/or selectivity of such catalyst. One of the most important support effects having attracted considerable attention is the strong interaction between metal and support evidenced from encapsulation , electron interaction, diffusion and morphology modification (Guisheng Wu, 2003). Among the various support investigated, zirconia is particularly interesting because it can enhance the activity of copper for CO/CO_2 hydrogenation (H. W. Chen, 1986). Generally, the high catalytic activity of Cu/ZrO_2 is unanimously ascribed to the special active sites, but the precise role of these active sites is difficult to be understood and still controversial in the literature. Shibata (Shibata, 1985) and Baiker (Baiker, 1993) proposed that copper was incoporated in ZrO_2 with high surface area and the decrease of the methanol synthesis rate was due to the crystallization of the initial amorphous zirconia.

Furthermore, Chen (H. W. Chen, 1986) claimed that the high activity of Cu/ZrO_2 might be attributed to copper to zirconia electron transfer. In-situ FT-IR results showed the formation of formate species by CO adsorption on ZrO_2/SiO_2 or $Cu/ZrO_2/ZrO_3$ and methoxide species adsorbed on zirconia under H_2 atmosphere (I. A. Fisher, 1998). The presence of Cu greatly accelerates the hydrogenation of formate to methoxide species. Therefore, methanol synthesis over $Cu/ZrO_2/SiO_2$ is envisioned to occur on ZrO_2 and the spillover of the species activated on copper to zirconia was critical to the methanol synthesis activity. In additon to the extensive experimental investigations, high-level theoritical studies can also provide useful supports to understand the microscopic aspects of this interaction. However, quantum chemical description of the interaction between metal atoms or clusters and the support surface is still in the very beginning stage, only few studies in this direction were done so far (N. Lopez, 1999).

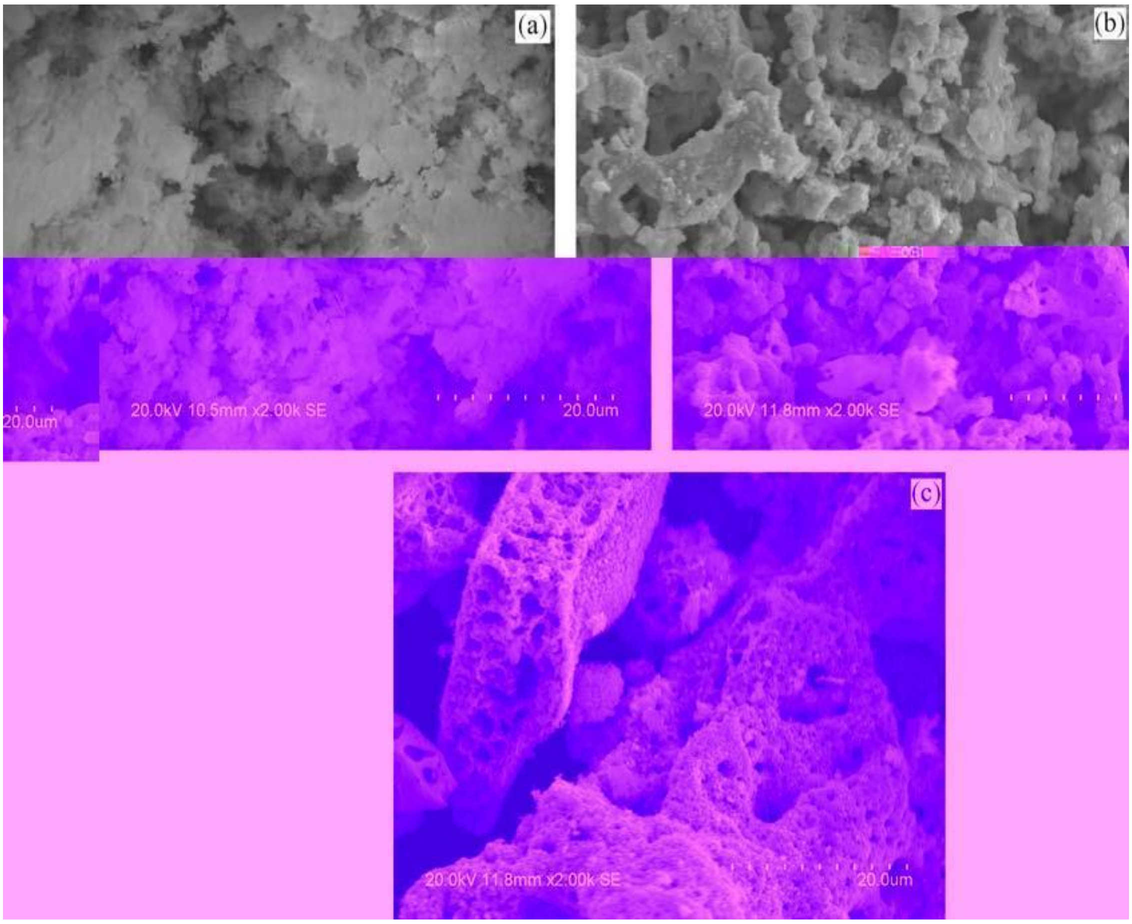

Figure 2.1: SEM mircographs of CuO-ZnO-ZrO_2 catalyst: (a) 50-CZZ; (b) 100-CZZ; (c) 150-CZZ

2.2 CO-PRECIPITATION METHOD

Conventional precipitation method is frequently used in the preparation of single and multi-component catalyst. This method provides a good dispersion of catalytic component in the support. In precipitation, the objective is to achieve a reaction of the type:

$$\text{Metal Salt Solution} + \text{Support Powder Particle} \xrightarrow{\substack{Precipitating\ agent \\ Hydroxide\ ,carbonate}} \text{Metal hydroxide/ carbonate on support}$$

The aims for employing a precipitation process in catalyst manufacturing are the intimate mixing of the catalyst components and the formation of very small particles for high surface area. The necessary degree of mixing can be achieved either by the formation of very small crystallites, in close proximity, for the different components or by the formation of mixed crystallites containing the catalsyt constituents. Hydroxide, carbonates or basic carbonates are the favored precipitating agents for the following reasons:

1. The solubilities of these transition metal salt and other catalytic components are very low. Consequently, very high supersaturations, leading to very small precipitate particle sizes, can be reached.
2. The solubilities of the precursors, typically metal nitrates and sodium hydroxide or carbonate, are high, so concentrated solutions can be used, again giving high supersaturations.
3. Hydroxide and carbonates area readily decomposed, by heat, to oxides of high area without leaving catalyst poisons as, for example, sulfur residues from the calcination of sulfates.
4. Many hydroxides, carbonates and hydroxycarbonates are known, so there is good chance of getting a mixed compound of the required composition for given components.
5. Environmental difficulties arising from the calcination of hydroxide and carbonates are minimal.

Conceivably, co-precipitation may occur by either adsorption of one material by another, or formation of a solid solution of microcomponent in the host lattice. In other words, co-precipitation can lead to either adsorption compounds, with the microcomponents free to diffuse through the interior of solid phase. Precipitated catalyst are generally prepared by rapid mixing of concentrated solutions of metal salts. Other procedures involved are filtration, washing, drying and calcination.

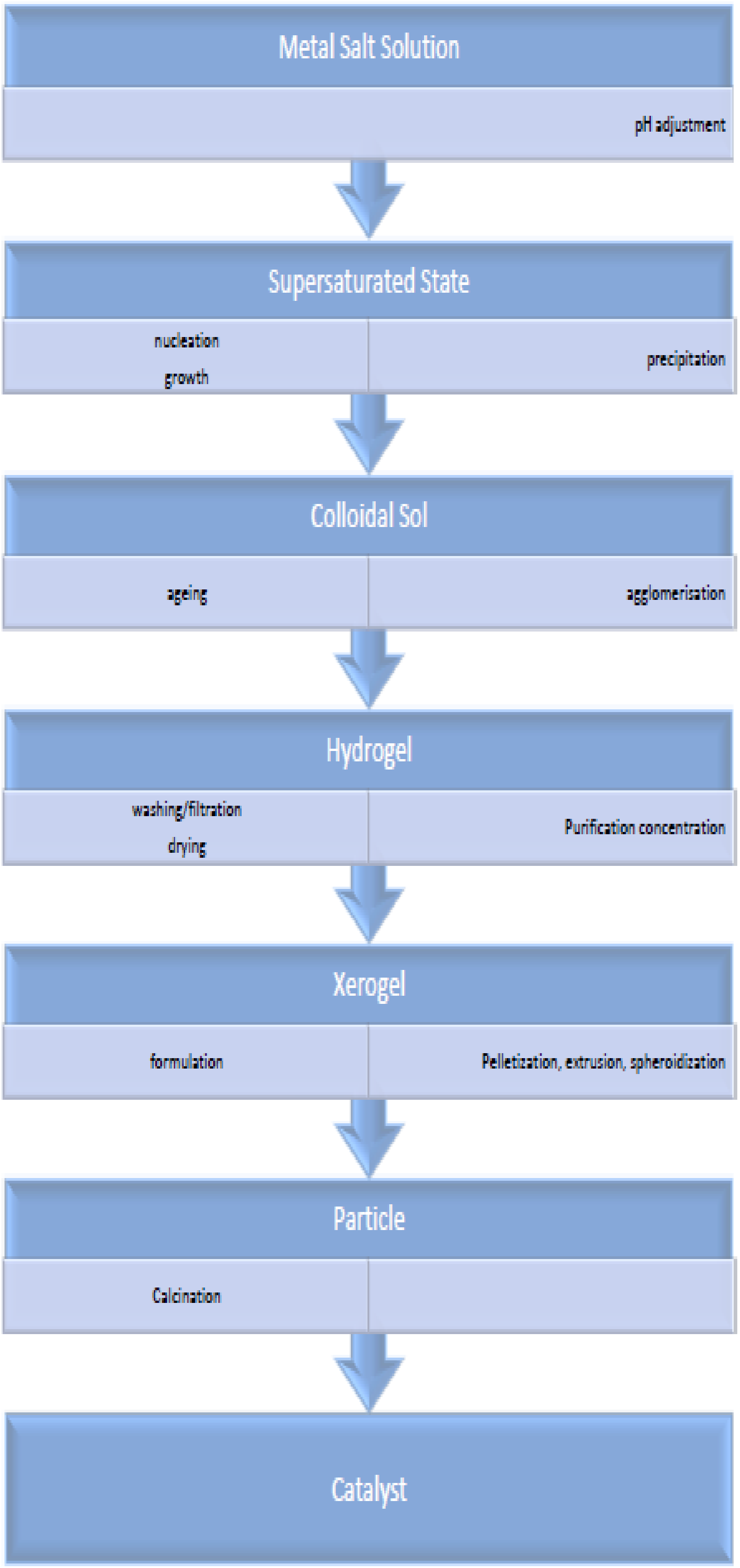

Figure 2.2: Catalyst preparation using co-precipitation method

2.3 CATALYST CHARACTERIZATION

Characterization of the catalyst is necessary at every stage of development. Critical parameters are measured not only to check the effectiveness of each operation but also to provide specifications for future products. The typical characterization methods such as FESEM (actually it is similar with SEM but with advance technology).

2.3.1 Scanning Electron Microscopy (SEM)

SEM is one of the characterization methods used to study the surface properties of the catalyst. Crystallite shape, size and size distribution are easily obtained using this method. The primary reasons for the SEM usage is the high resolution (100 Å) and mignification of 50 – 100 000X which can be obtained when bulk objects are examined. This range overlaps considerably with the light microscope at low end, and with the electron microscope at high end. It scans over a sample surface with a probe of electron ranging from 5 – 50 kV. Electrons from a tungsten or lanthanum hexaboride cathode are backscattered or emitted to produce an image on a cathode-ray tube, scanned synchorinously with the beam. Another important feature of SEM images is the three dimensional appearance of the specimen, which is a direct result of the large depth of focus.

CHAPTER 3

METHODOLOGY

Methodology refers to methods/procedure used by the author to achieve the objective(s) of the project. The author need to develop the the catalyst comparision in terms of catalyst preparation;

1) effect of catalyst composition

3.1 MATERIALS & APPARATUS

Table 3.1: List Of Chemicals Used In This Study

Chemical	**Supplier**	**Purity (%)**	**Usage**
Sodium Carbonate	R & M Chemicals	99.5%	Precipitating Agent
Zinc Nitrate hexahydrate	MERCK	98.5%	Catalyst Precursor
Aluminium Nitrate Nonahydrate	SYSTERM	98%	Catalyst Precursor
Copper (II) Nitrate trihydrate	MERCK	99.5%	Catalyst Precursor
Zirconia Nitrate *n*hydrate	Fisher Acros	99.5%	Catalyst Precursor

Table 3.2: Glassware And Equipment Used

Glassware/Equipment	**Capacity**	**Quantity**
Beaker	1000 ml	1
Beaker	500 ml	1
Beaker	250 ml	1
Porcelin	-	4
Cyclinder	500 ml	1
Cyclinder	100 ml	1
Pipet/Buret	250 ml	1
Hot Magnetic Stirrer	-	1
Oven	-	1
Furnace	-	1
Membrane Filter	-	1
Volumetric Flask	500ml	1
Volumetric Flask	100ml	1
pH Meter	-	1
Thermometer	-	1

3.2 EXPERIMENTAL PROCEDURE

3.2.1 Preparation of catalyst for different catalyst composition

The source for copper, zinc, aluminium and zirconia was obtained from copper nitrate trihydrate [$Cu(NO_3)_2.3H_2O$], zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$], aluminium nitrate nonahydrate [$Al(NO_3)_3.9H_2O$] and zirconia nitrate *n*hydrate [$Zr(NO_3)_2.nH_2O$], respectively. Precipitating agent used was sodium carbonate [Na_2CO_3].

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Oven	-	1
Furnace	-	1
Membrane Filter	-	1
Volumetric Flask	500ml	1
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Table 3.3: List of chemical composition (wt%)

SAMPLE	**COMPOSITION (wt%)**			
	$Cu(NO_3)_2$	**$Zn(NO_3)_2$**	**$Al(NO_3)_2$**	**$Zr(NO_3)_2$**
A	60.0	30.0	10.0	0.0
B	60.0	30.0	7.5	2.5
C	60.0	30.0	5.0	5.0
D	60.0	30.0	2.5	7.5
E	60.0	30.0	0.0	10.0
CC	-	-	-	-

Table 3.4: List of chemical weight composition (g)

SAMPLE	**COMPOSITION (g)**			
	$Cu(NO_3)_2$	**$Zn(NO_3)_2$**	**$Al(NO_3)_2$**	**$Zr(NO_3)_2$**
A	30.0	15.0	5.0	0.0
B	30.0	15.0	3.75	1.25
C	30.0	15.0	2.5	2.5
D	30.0	15.0	1.25	3.75
E	30.0	15.0	0.0	5.0

Precipitating agent use: Sodium Carbonate (Na_2CO_3)

0.5M, 500ml

Amount of salt required: 0.5L x 0.5moles/L x 105.99g/moles = 26.4975gram

Catalyst with different weight percentage based on the table above were prepared by using co-precipitation method.An aqueous solution (ca. 100ml) of copper, zinc, aluminium and zirconia nitrate and 0.5 M sodium carbonate, were added dropwise under vigorous stirring. Temperature and pH were maintain at 40^{o}C and 7.0-7.3, respectively during the precipitation. Vigorous stirring of the resulting slurry was continued for 20 minutes. After precipitation was completed, the suspension was kept for two hours in the mother liquid followed by filtering and washing with warm water several times to remove sodium residue. The precipitate was dried at $120^{o}C$ overnight in the oven and calcined in air at $280^{o}C$ for 12 hours in the furnace. Repeat this procedure for different chemical composition as stated in the Table 3.4.

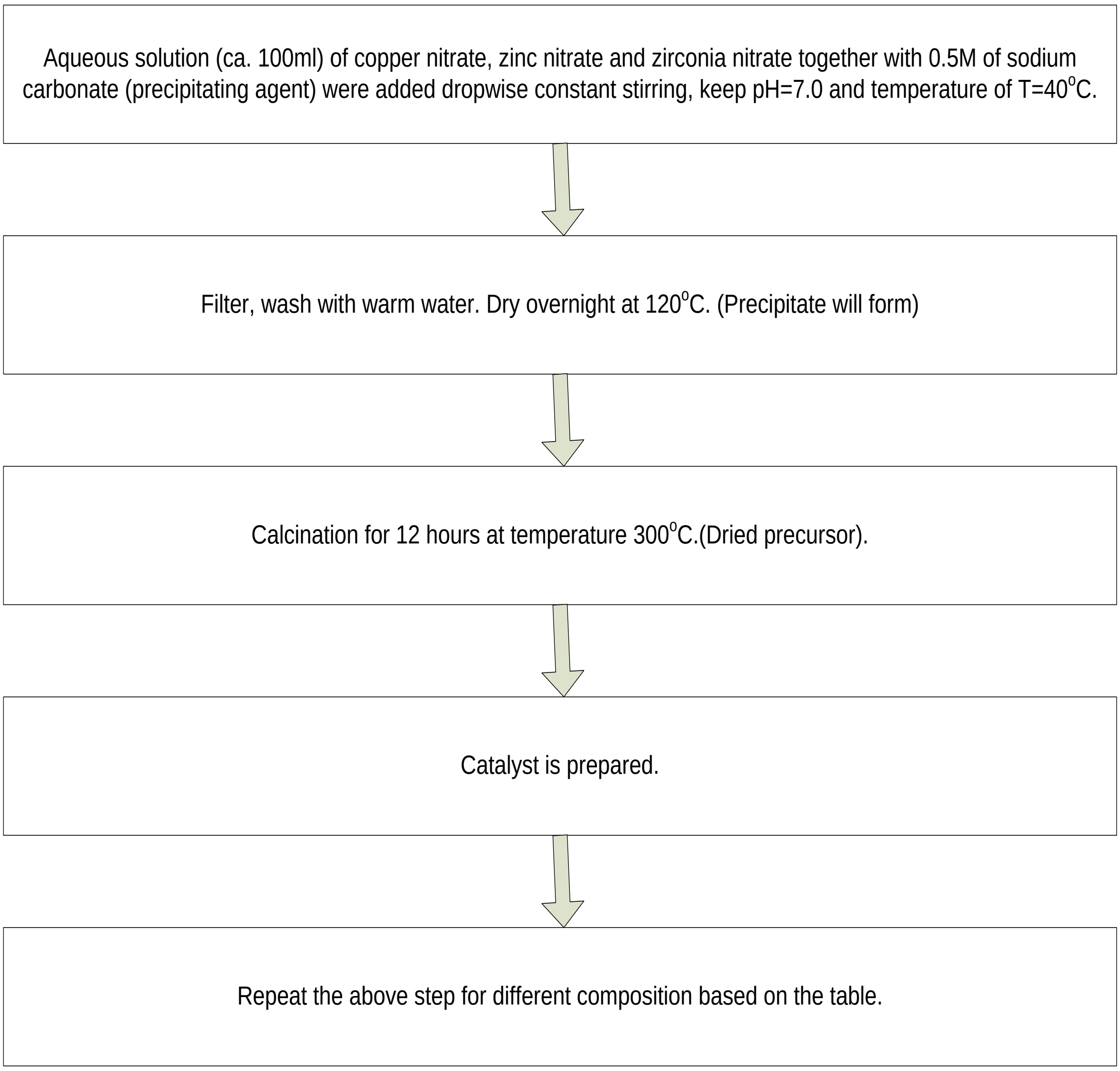


Figure 3.1: Preparation method for different composition of chemical use

3.3 CATALYST CHARACTERIZATION

The prepared catalyst were characterized by typical characterization methods such as the Field Emission Scanning Electron Microscopy (FESEM) and FESEM - EnergyDispersed X-ray (EDX).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 FIELD EMISSION SCANNING ELECTRON MICROSCOPY(FESEM)

Shape and size are two important features of morphology. Information of this nature is necessary for complete knowledge of all catalyst components. It is especially significant for higly dispersed systems such as mutli-component catalysts.

Field Emission Scanning Electron Microscopy – Energy disperse X-ray (FESEM - EDX) is a combined technique that is commonly used for characterizing solids. High resolution electron microscope provides a visualised image of the solid surface. Moreover, identification of elements and their dispersion can also be obtained. The FESEM-EDX analyses were performed to study the surface properties of the catalyst such as crystallization flawlessness, crystallite shape as well as elemental identification and dispersion.

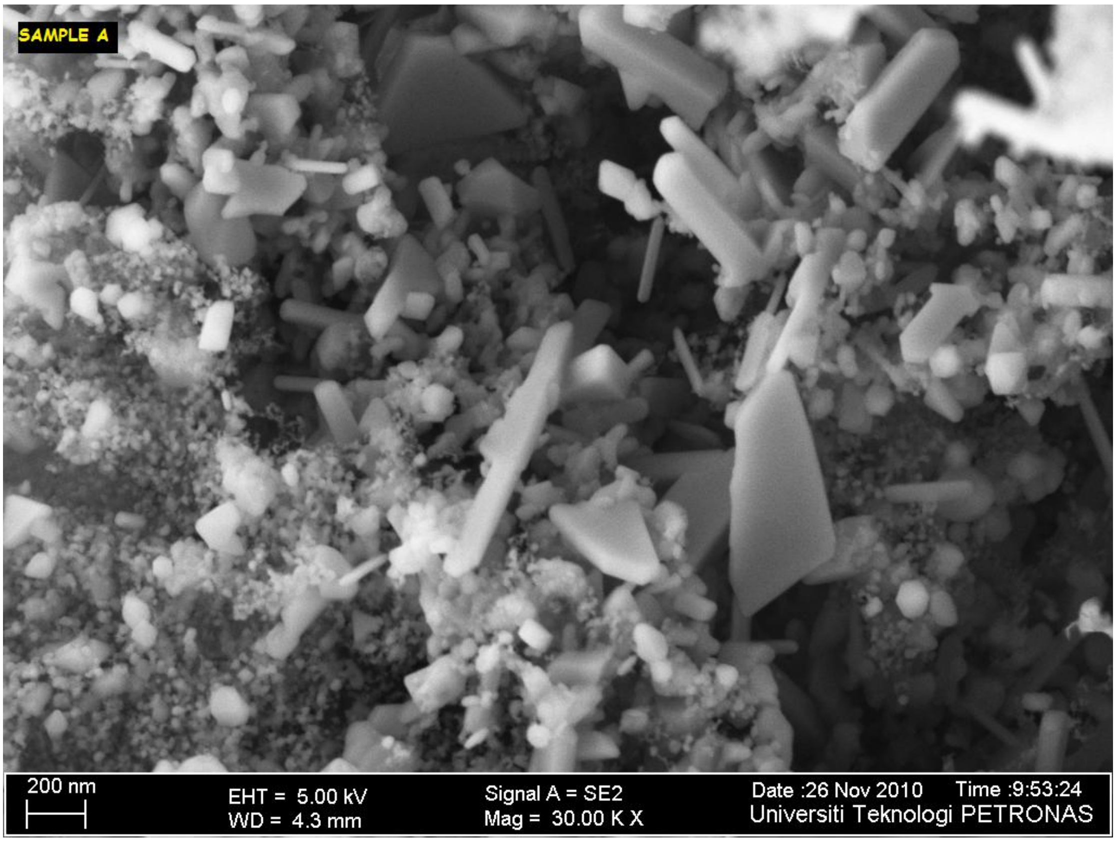


Figure 4.1: FESEM micrograph of sample A

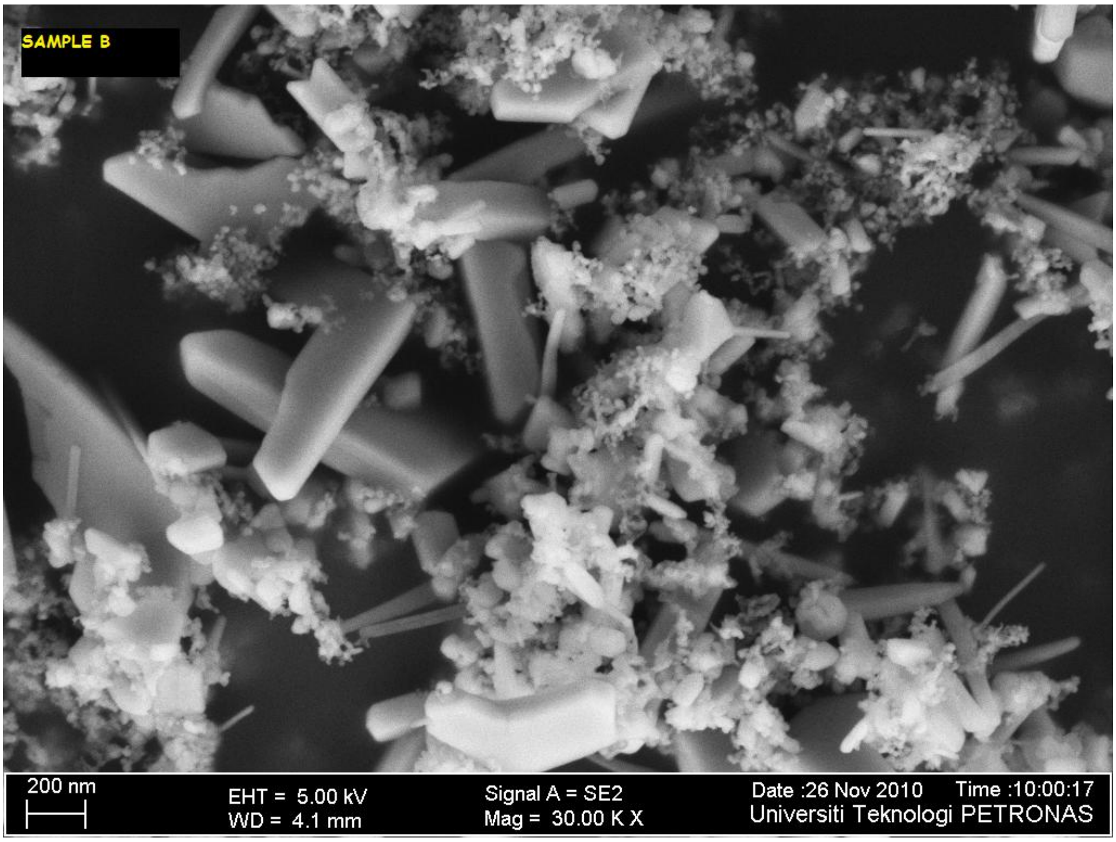


Figure 4.2: FESEM micrograph of sample B

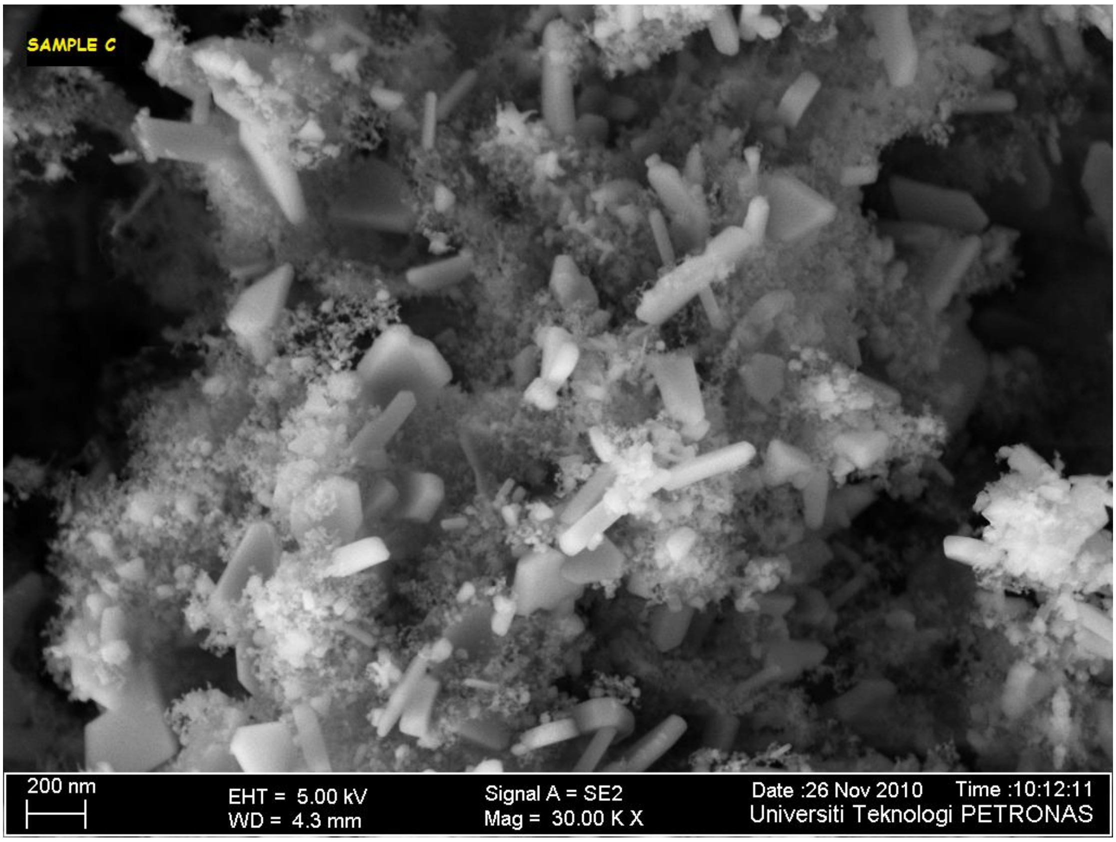


Figure 4.3: FESEM micrograph of sample C

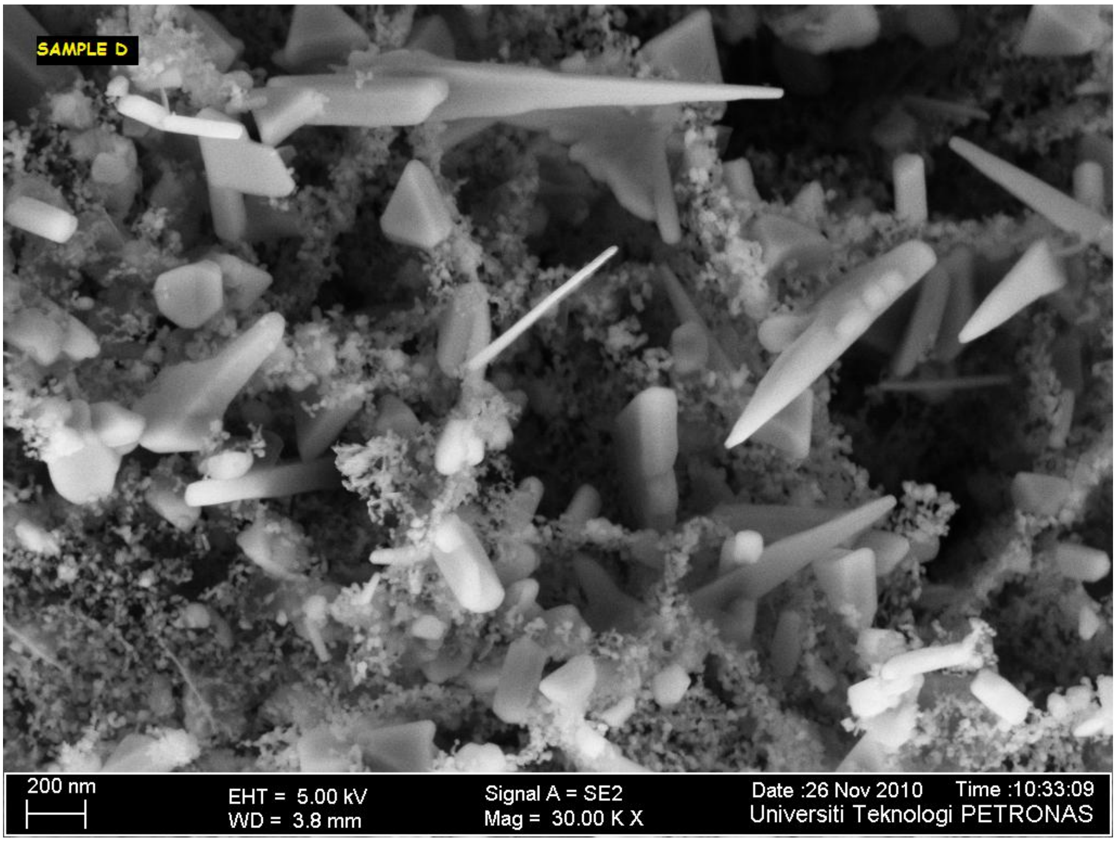


Figure 4.4: FESEM micrograph of sample D

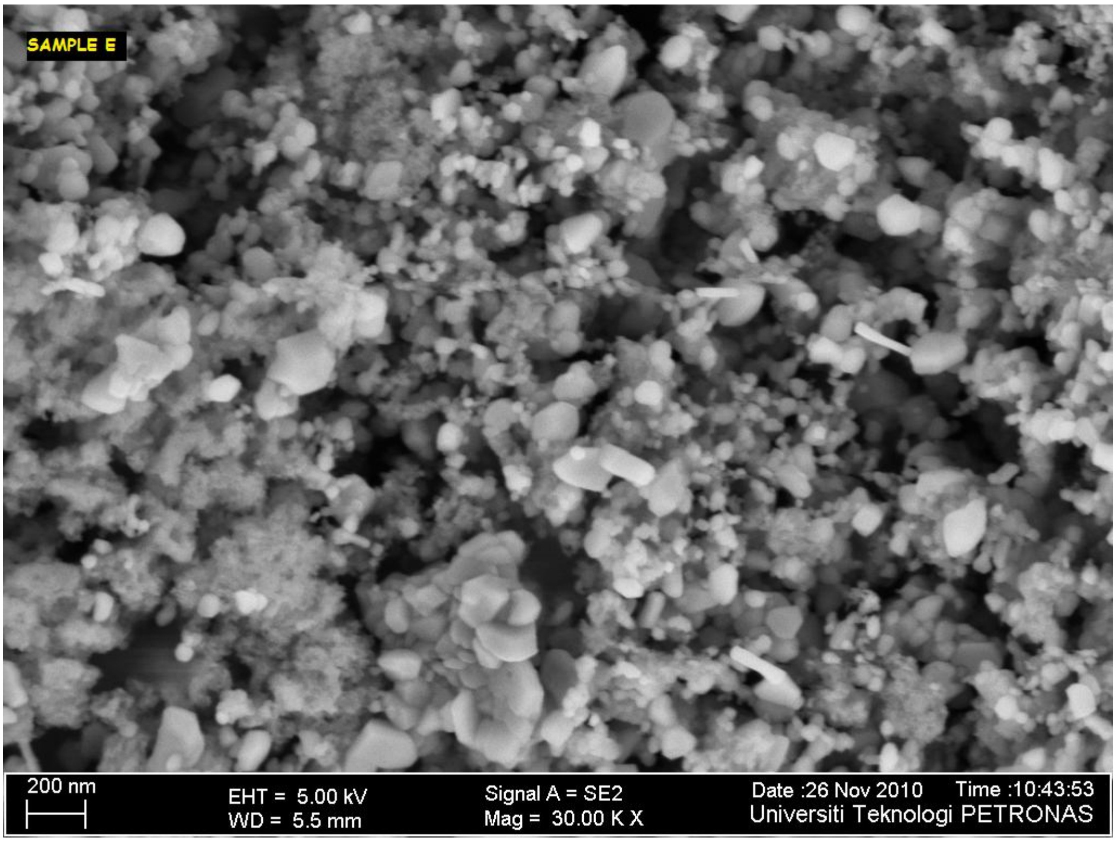


Figure 4.5: FESEM micrograph of sample E

4.1.1 Charaterization based on the crsystallite shape

Generally, a uniform crystallite shape was obtained as can be seen from the FESEM micrograph of each of the catalyst prepared, implying the crystallization perfection of the catalyst. All catalysts exhibit fibrous crystallite shape except for sample E. Sample E shows that the catalyst is plate-like microcrystal. The sample E only consist of $Cu/ZnO/Al_2O_3$. Other catalysts consists of $Cu/ZnO/Al_2O_3/ZrO_2$. Big particles of Zr crystal were uniformly mixed with small and sphere-shaped $Cu/ZnO/Al_2O_3$. This observation is in a good agreement with the density and particle size analysis. Some of the Zr particles were attached directly onto the $Cu/ZnO/Al_2O_3$ crystal surfaces and some of them were positioned solely between the structure.

A bigger size of Zr and imbalance of weight ratio result in tendency for the crystal to stick togerther. In contrast with sample C, an equal Al_2O_3 and ZrO_2 catalyst ratio had resulted in the even distribution of the catalyst particle as shown in sample C. Similar SEM results were reported by Xin An et. al. (2007) as shown in Figure 4.6. Based from Xin An et. al (2007), all the Cu/Zn/Al/Zr catalyst existed as regular one dimensional nanomaterial agglomerates. The Al/Zr ratio had a clear influence on the morphology. Catalyst sample A – sample D, whose Zr contents increased gradually, all had the fibrous structure in which the crystallites were assembled into thin nm-diameter fibers (Figure 4.6 (a) - (d)). While the sample E, which Cu/Zn/Zr, was mainly plate-like microcrystals structure. Thus, based on the author’s research it is comparable between the result obtained by Xin An et. al (2007).

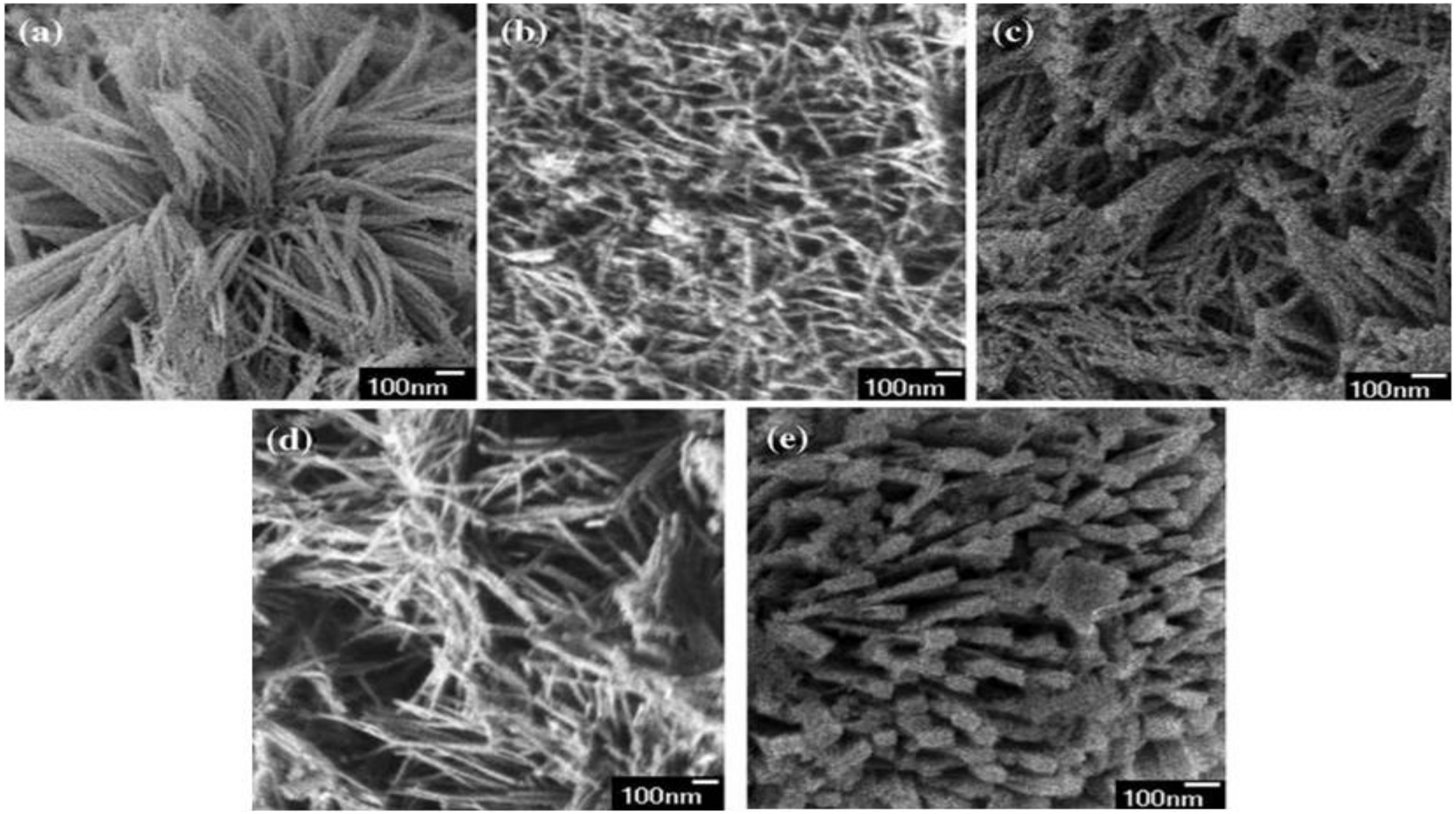


Figure 4.6: Morphology of the Cu/Zn/Al/Zr catalyst (a) Sample A (b) Sample B

(c) Sample C (d) Sample D (e) Sample E [Xin An et. Al. , 2007]

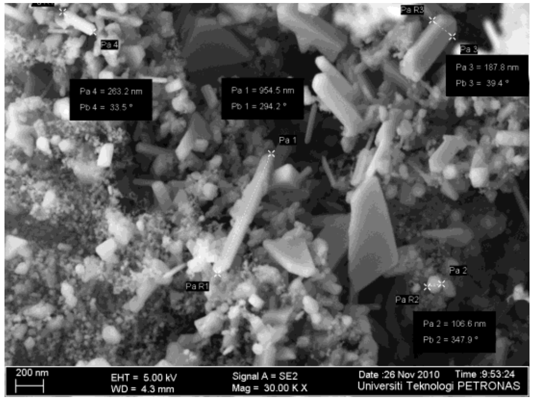


Figure 4.7: Average Diameter of sample A

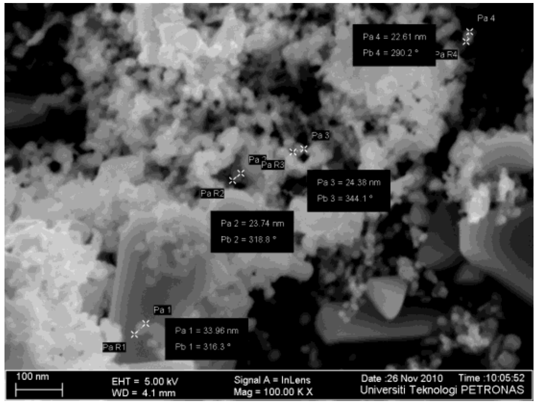


Figure 4.8: Average Diameter of sample B

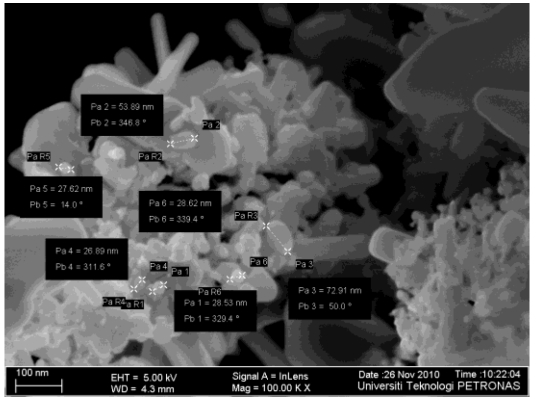


Figure 4.9: Average Diameter of sample C

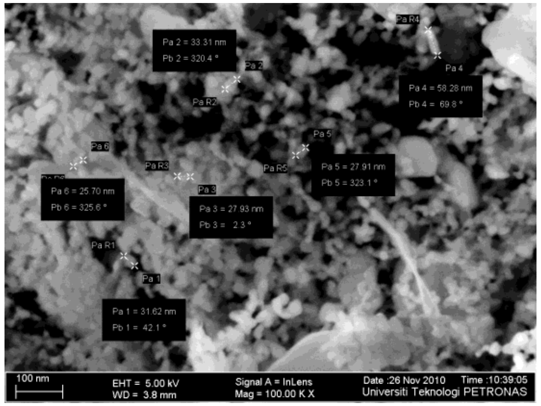


Figure 4.10: Average Diameter of sample D

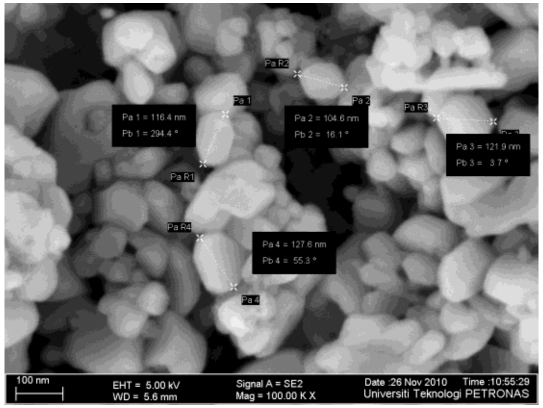


Figure 4.11: Average Diameter of sample E

4.1.2 Characterization based on the average diameter

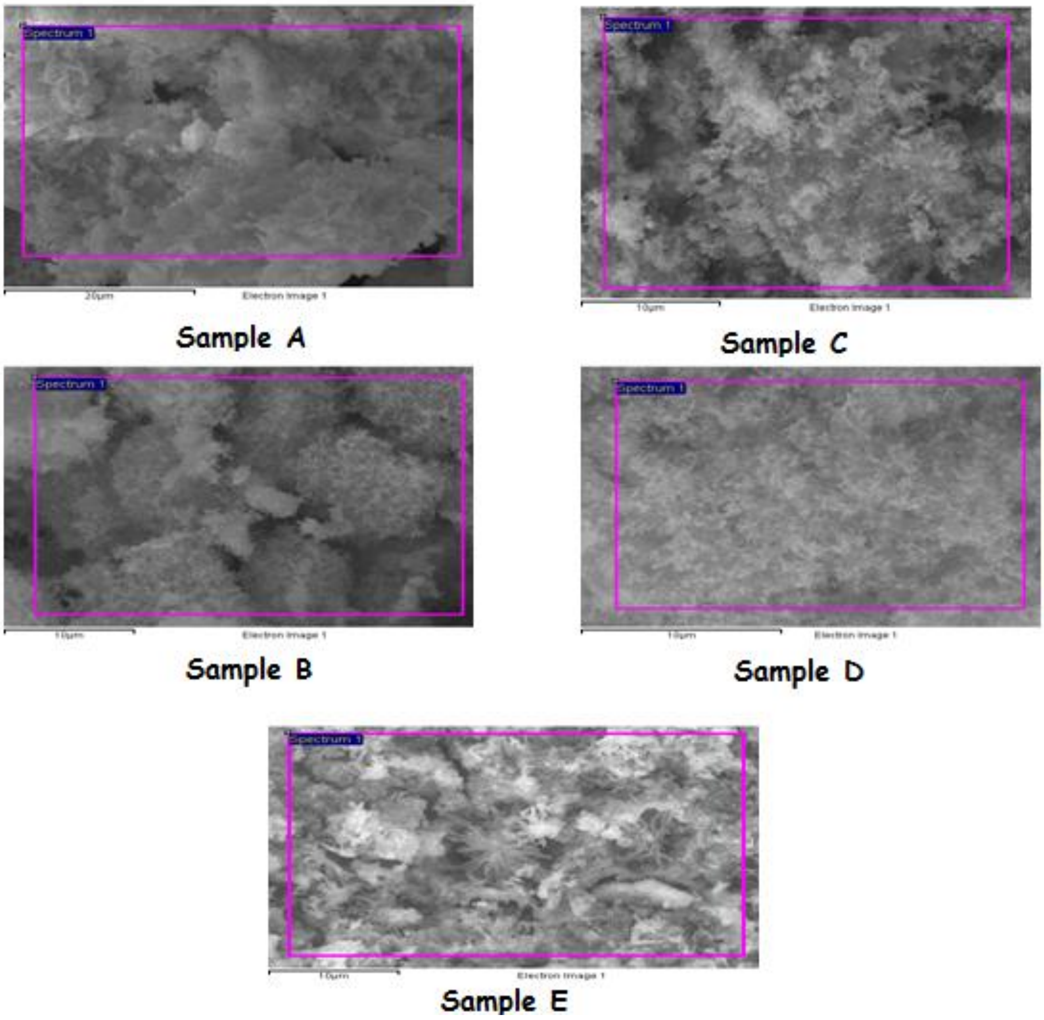
Based on the FESEM micrograph showing the diameter of several particles from the above picture, the author manage to find the average diameter of each samples. By finding the average diameter of each of the catalyst samples, we can detemined which catalyst has the largest surfaces area.

From the calculation, sample A, B, C, D and E have an average diameter of 33.3 nm, 24.13 nm, 17.5 nm, 25.8 nm and 83.7 nm. From the average diameter, we can see that the smallest average diameter is sample C with the average of 17.5 nm. From the literature [Xin An et. Al., 2007], the smallest average diameter is expected to be the best potential catalyst for methanol synthesis via CO_2 hydrogenation. Thus, sample C is predicted to bean active catalyst because it shows the smallest average diameter among others.

Based on the previous study [Xin An et. al., 2007], he claim that the fiber diameter were uniformly distributed. The resulted averaged diameter that he managed to get from his sample is 25 nm for sample A, 18 nm for sample B, 14 nm for sample C and 18 nm for sample D. For sample E which consists of Cu/Zn/Zr, the average diameter is about 70 nm, in comparion with this result, sample E is 83.7nm which is the slightly higher. By comparing with this project result, it is comparable in terms of the average diameter distribution that led to sample C is having the smallest average diameter, same with Xin An et. al. managed to get. Sample C is having the smallest average diameter, thus allowing high surface area for process reaction to occur, thus giving the result that sample C is the best potential catalyst.

4.2 FIELD EMISSION SCANNING ELECTRON MICROSCOPY – ENERGY DISPERSE X-RAY (FESEM – EDX)

4.2.1 Elemental Analysis



Sample A

Sample C

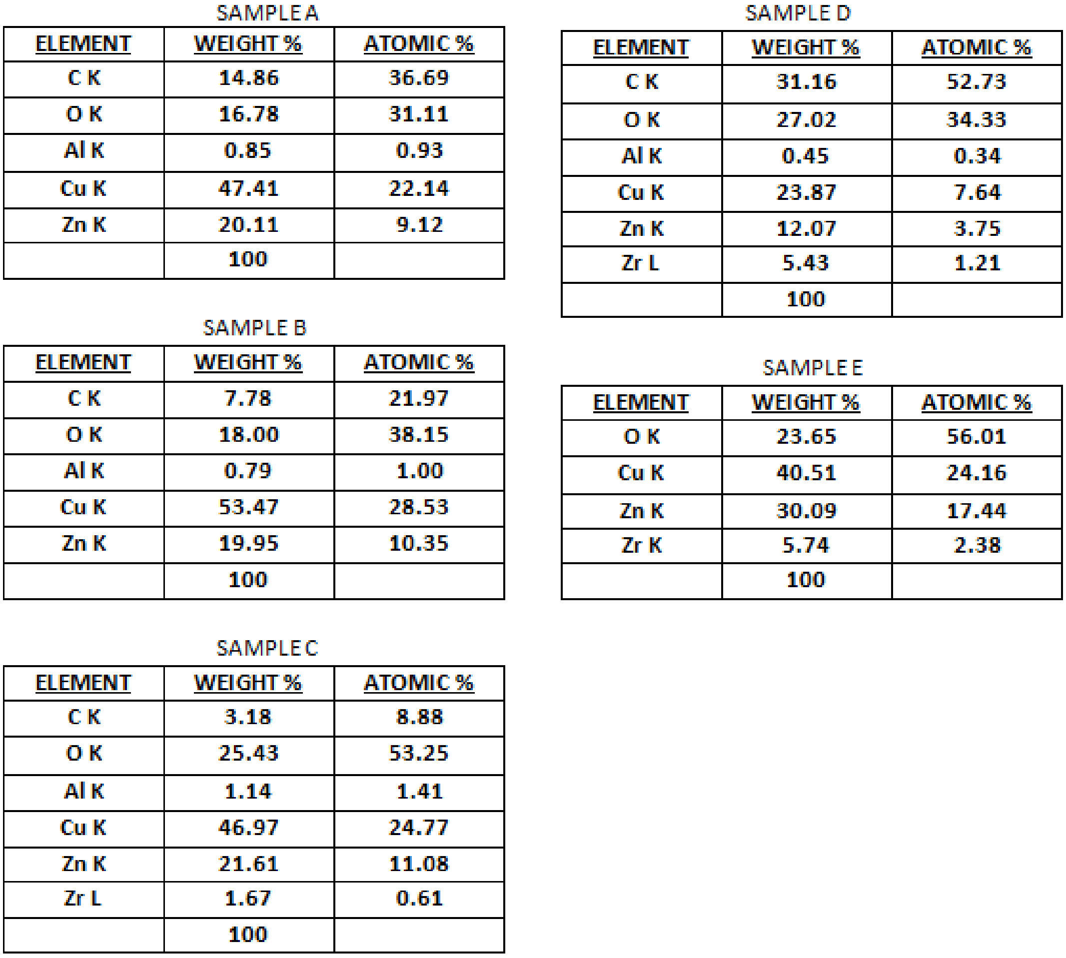
Sample B

Sample D

Sample E

Figure 4.12: EDX Samples Mapping

Table 4.1: EDX elemental analysis



SAMPLE A

ELEMENT	WEIGHT %	ATOMIC %
C K	14.86	36.69
O K	16.78	31.11
Al K	0.85	0.93
Cu K	47.41	22.14
Zn K	20.11	9.12
	100	

SAMPLE B

ELEMENT	WEIGHT %	ATOMIC %
C K	7.78	21.97
O K	18.00	38.15
Al K	0.79	1.00
Cu K	53.47	28.53
Zn K	19.95	10.35
	100	

SAMPLE C

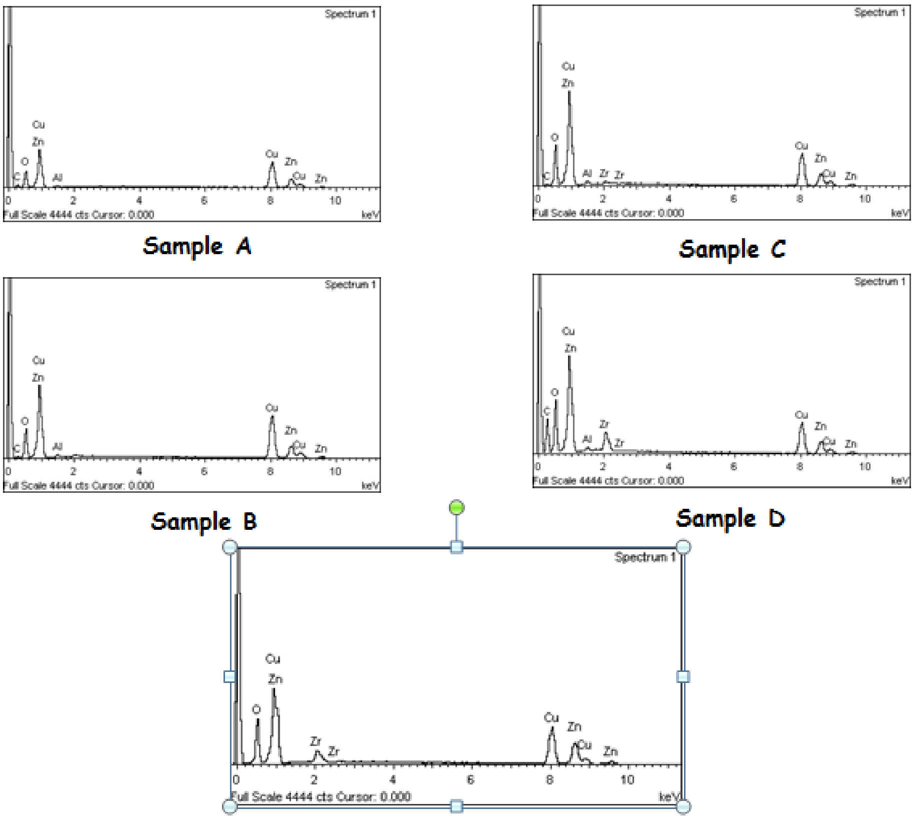
ELEMENT	WEIGHT %	ATOMIC %
C K	3.18	8.88
O K	25.43	53.25
Al K	1.14	1.41
Cu K	46.97	24.77
Zn K	21.61	11.08
Zr L	1.67	0.61
	100	

SAMPLE D

ELEMENT	WEIGHT %	ATOMIC %
C K	31.16	52.73
O K	27.02	34.33
Al K	0.45	0.34
Cu K	23.87	7.64
Zn K	12.07	3.75
Zr L	5.43	1.21
	100	

SAMPLE E

ELEMENT	WEIGHT %	ATOMIC %
O K	23.65	56.01
Cu K	40.51	24.16
Zn K	30.09	17.44
Zr K	5.74	2.38
	100	



Sample A

Sample C

Sample B

Sample D

Sample E

Figure 4.13: Graph of each sample

The FESEM – EDX method permits the elements identification and dispersion. In terms of elements distribution and dispersion, all five samples have shown fairly uniform distribution. Each element in the catalyst was well distributed dispersed evenly in the catalyst based on the mapping graph and mapping images in Figure 4.13.

From the EDX elemental analysis table, sample C shows the ratio of the Zr and Al that is most comparable. This shows that equal amount of the Zr and Al composition lead to the uniform distribution and dispersed evenly. Uniform distribution of particle will lead to the small diameter particle thus allowing high surface area of the sample. The greater the surface area of a sample, the more preferable it is to be the best potential catalyst as it can provide large surface area for reaction to occur.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 CONCLUSION

The combination or addition of zirconia promoter to the Cu/ZnO/Al_2O_3 catalyst to form Cu/Zn/Al/Zr catalyst system is found promising to catalyze CO_2 hydrogenation reaction. The catalyst is prepared by a conventional precipitation method. A uniform crystallite shape was observed from the FESEM micrograph and each element in the catalyst were well distributed and dispersed evenly except for sample E.

Based on previous study, the Sample C exhibit the most suitable catalyst for methanol synthesis via CO_2 hydrogenation. A better CO_2 hydrogenation to methanol Cu/ZnO/Al/Zr catalyst can be synthesis by taking into consideration the following factors:

1. Addition of Zr promoter
2. Morphology control by addition of Zr and Al
3. Catalyst preparation method such as successive-precipitation.

5.2 RECOMMENDATION

In order to optimize the performance of the catalyst system, one should consider seriously the physical and chemical properties of the catalyst. This is due to the fact that physical and chemical properties of the catalyst affect the reaction performance. In the case of methanol-synthesis catalyst, $Cu/ZnO/Al_2O_3$ was proven to be the best catalyst for industrial methanol production via syngas route. Therefore, improvement of this catalyst can be made in terms of varying the composition of each metal oxide present in the catalyst. One should study the effect of different composition of Cu, Zn, Al and Zr or other promoters.

Moreover, the parameter of the preparation methods can be varied. Future work can be varying the pH, precipitating temperature, calcination temperature and different types of precipitating agents. The most important thing in preparing the catalyst is, the researcher need to control the reaction parameter. For example, when dropping the precipitating agent into the beaker of metal nitrate solution, the temperature will decrease and the pH will increase. So, make sure that all the necessary equipments are well prepared and take note on this small changes. The small changes will affect the catalyst performance.

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APPENDICES

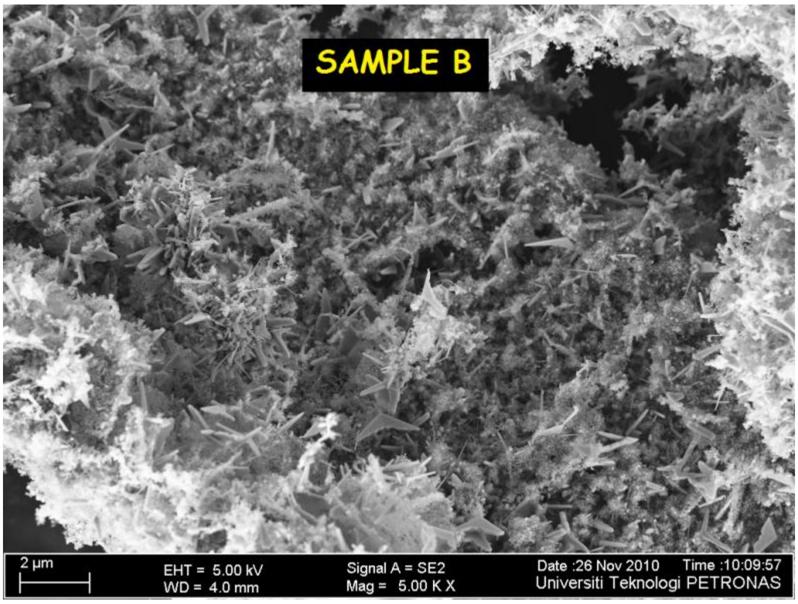


Figure A: Sample B FESEM mircograph porosity structure

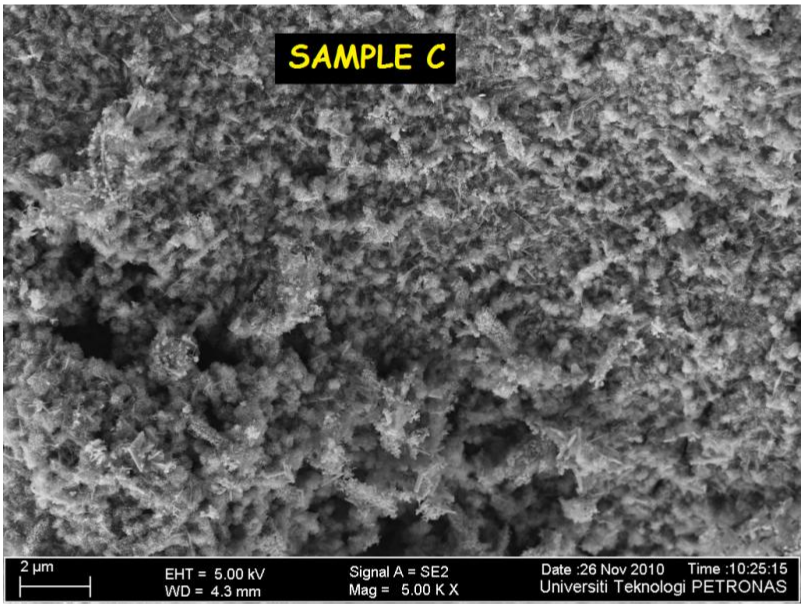


Figure B: Sample C FESEM micrograph porosity structure

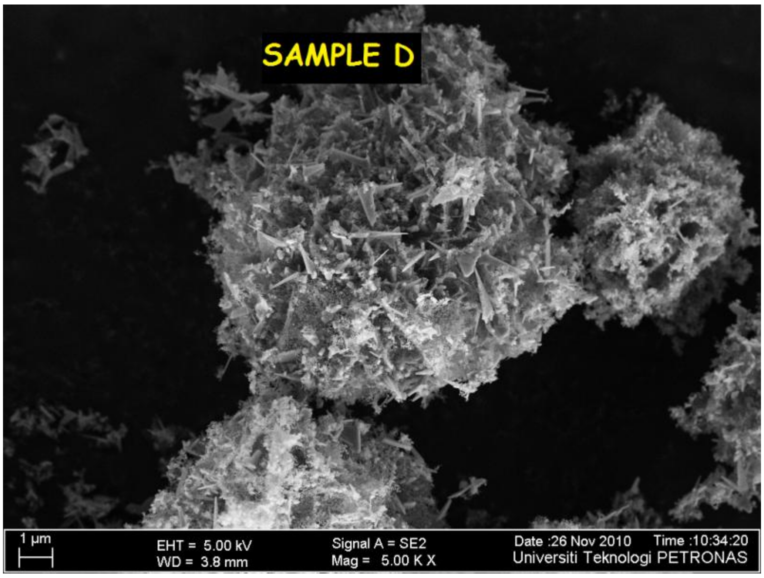


Figure C: Sample D FESEM micrograph structure

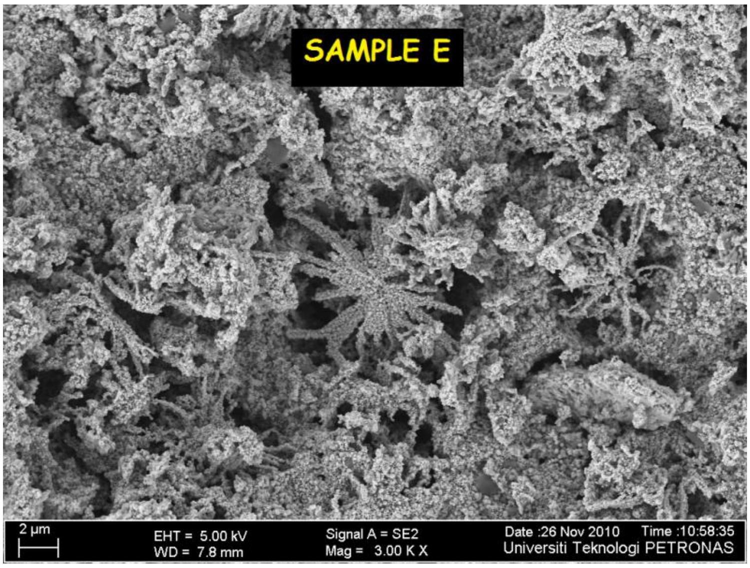
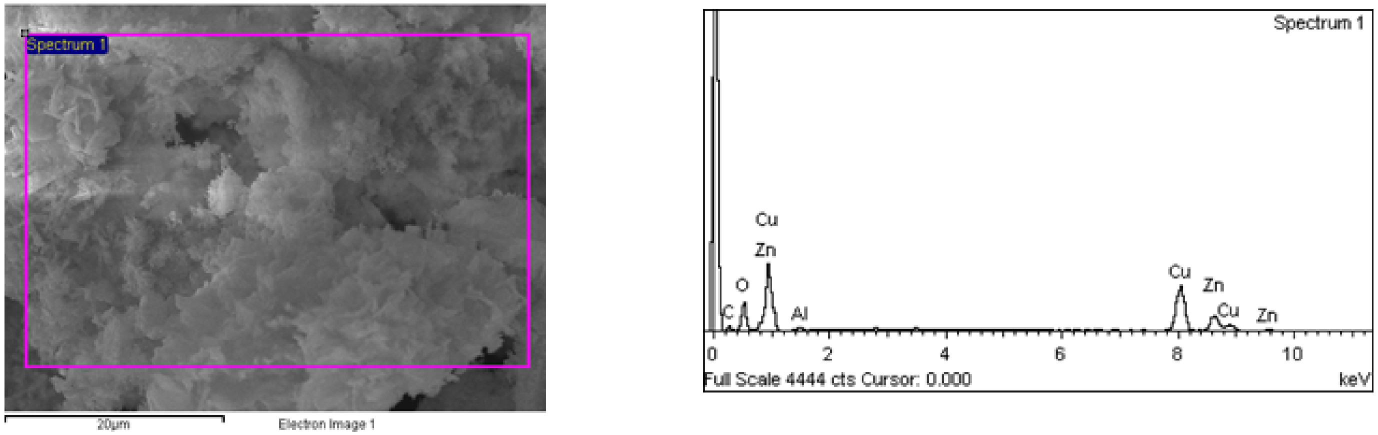


Figure D: Sample E FESEM micrograph structure

EDX ELEMENTAL ANALYSIS

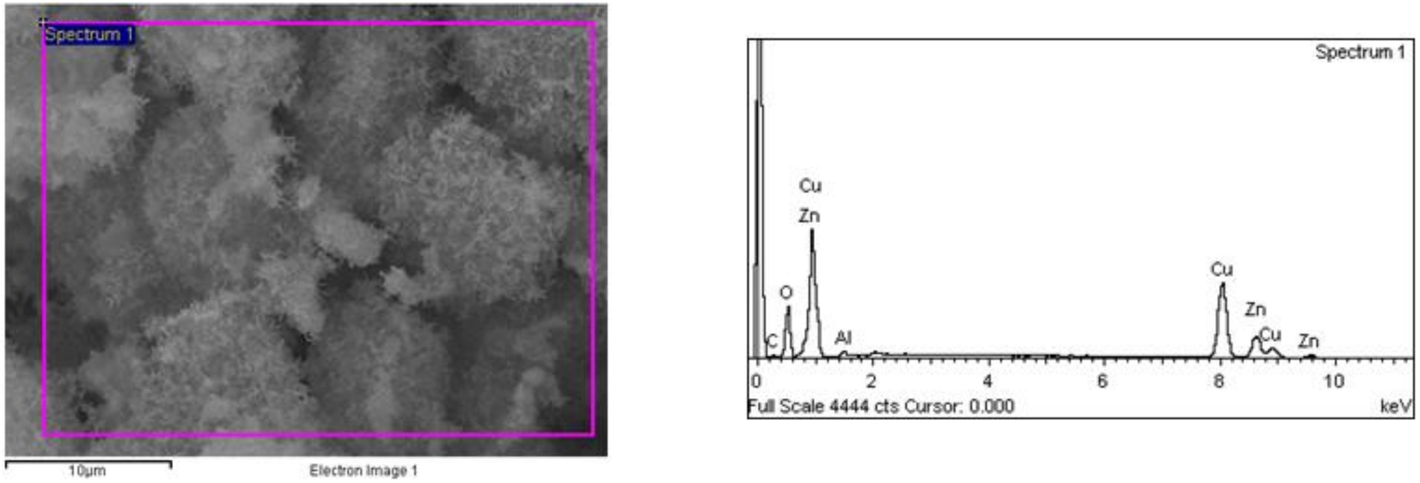
SAMPLE A



ELEMENT	WEIGHT %	ATOMIC %
C K	14.86	36.69
O K	16.78	31.11
Al K	0.85	0.93
Cu K	47.41	22.14
Zn K	20.11	9.12
	100	

Figure E: EDX elemental analysis for sample A

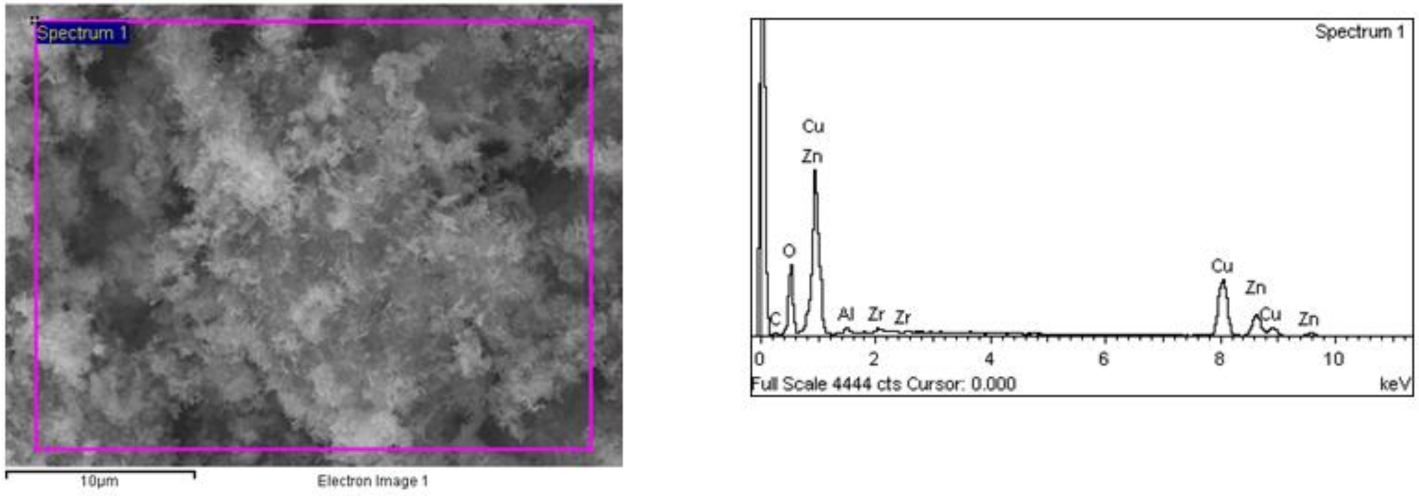
SAMPLE B



ELEMENT	WEIGHT %	ATOMIC %
C K	7.78	21.97
O K	18.00	38.15
Al K	0.79	1.00
Cu K	53.47	28.53
Zn K	19.95	10.35
	100	

Figure F: EDX elemental analysis for sample B

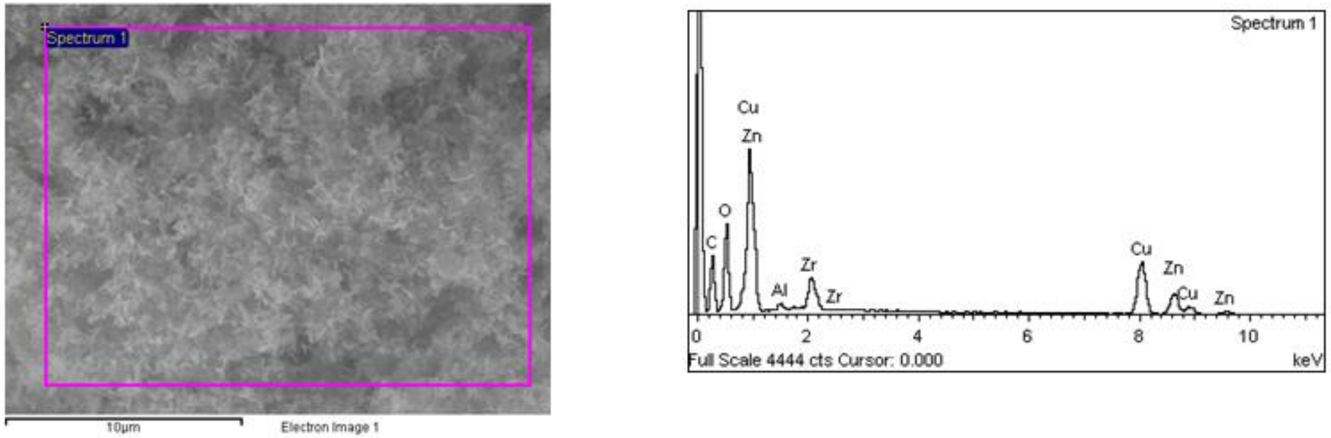
SAMPLE C



ELEMENT	WEIGHT %	ATOMIC %
C K	3.18	8.88
O K	25.43	53.25
Al K	1.14	1.41
Cu K	46.97	24.77
Zn K	21.61	11.08
Zr L	1.67	0.61
	100	

Figure G: EDX elemental analysis for sample C

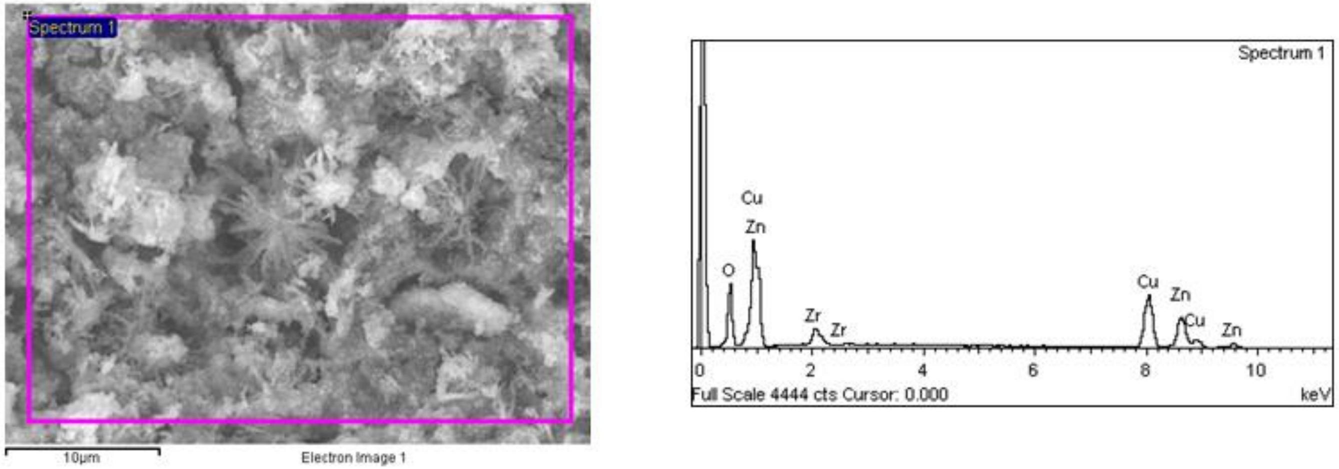
SAMPLE D



ELEMENT	WEIGHT %	ATOMIC %
C K	31.16	52.73
O K	27.02	34.33
Al K	0.45	0.34
Cu K	23.87	7.64
Zn K	12.07	3.75
Zr L	5.43	1.21
	100	

Figure H: EDX elemental analysis for sample D

SAMPLE E



ELEMENT	WEIGHT %	ATOMIC %
O K	23.65	56.01
Cu K	40.51	24.16
Zn K	30.09	17.44
Zr K	5.74	2.38
	100	

Figure I: EDX elemental analysis for sample E