SYNTHESIS AND CHARACTERIZATION OF SPHERICAL MODEL Co-Fe NANOCATALYST

by

MOHD ANIS BIN MOHD SHARIFF

FINAL PROJECT REPORT

Submitted to the Chemical Engineering Programme
in Partial Fulfillment of the Requirements
for the Degree
Bachelor of Engineering (Hons)
(Chemical Engineering)

Unversiti Teknologi PETRONAS
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CERTIFICATION OF APPROVAL

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Approved:

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Project Supervisor

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TRONOH, PERAK

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 that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MOHD ANIS BIN MOHD SHARIFF

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ABSTRACT

Iron and Cobalt are the commonly used catalysts for the Fischer-Tropsch reaction in the industries. This project explores the potential of combining Iron and Cobalt as a bimetallic catalyst for the Ficher-Tropsch reaction. This report discusses the synthesis and characterization of spherical model Cobalt-Ferum nano-catalyst on Silica (SiO_2). The objective of the project is to study the properties of the mixture of Cobalt-Ferum bimetallic nanoparticles supported on Silica (SiO_2). In this project, two methods of preparation had been tested namely the Impregnation and Precipitation methods. These two methods used precursor salts which were deposited on Silica (SiO_2). In precipitation method, Ammonium hydroxide was used as the precipitating agent. The preparation of nano-scale materials with desired properties represents a significant challenge. Samples were characterized using Transmission Electron Microscopy (TEM) and Temperature Program Reduction (TPR). Average particle size for samples prepared using the impregnation method was 9.3nm while the precipitation method resulted in particle size average of 3.1nm. The precipitation method is better than impregnation method as it produced rather than uniform particle shape and narrow particle size distribution.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

This research is based on the study of heterogeneous catalysis. Heterogeneous catalysts provide a surface on which the reaction may take place. In order for the reaction to occur, one or more of the reactants must diffuse to the catalyst surface and adsorb onto it. After reaction, the products must desorb from the surface and diffuse away from the solid surface. Basically, this production of nanocatalyst aims to enhance the production of oil. In theory, Cobalt and ferum are both from VIII metal which is noticeable in the hydrogenation of carbon monoxide to hydrocarbon. [1]

$$n\mathrm{CO} + 2n\mathrm{H2} \rightarrow \mathrm{C}n\mathrm{H2}n + n\mathrm{H2O}$$

Cobalt and iron are the metals which were proposed by Fischer and Tropsch as the first catalysts for syngas conversion [1]. Both cobalt and iron catalysts have been used in the industry for hydrocarbon synthesis. Briefly, in nano-scale, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties. It is further classified according to size in terms of diameter which is the range between 1 and 100 nanometer [2]. Cobalt catalysts are more expensive, but they are more resistant to deactivation. Although the activity at low conversion of two metals is comparable, the productivity at higher conversion is more significant with cobalt catalysts Iron catalysts usually produce more olefins. Both iron and cobalt catalysts are very sensitive to sulfur, which could readily contaminate them. For iron-based catalysts, the syngas should not contain more than 0.2 ppm of sulfur. For Co catalysts, the amount of sulfur in the feed should be much less than 0.1 ppm.

Cobalt catalysts supported on oxide supports are generally more resistant to attrition than iron coprecipitated counterparts as they are more suitable for use in slurry-type reactors. Iron catalysts produce hydrocarbons and oxygenated compounds under different pressures, H2/CO ratios, and temperatures (up to 340 ^{o}C) [4]. Cobalt catalysts operate at a very narrow range of temperatures and pressures; an increase in temperature leads to a spectacular increase in methane selectivity. Ferum catalysts seem to be more appropriate for conversion of biomass-derived syngas to hydrocarbons than cobalt systems because they can operate at lower H2/CO ratios [5].

1.2 PROBLEM STATEMENT

In nano technology, for catalysis, it provides far larger surface area. Naturally, Cobalt and Ferum are synthesized separately to form a catalyst for the application of fuel production. Cobalt is hard and brittle in its pure form compared to Ferum which is silvery white, very lustrous metal. These two elements have differences in parameters of cost, lifetime, productivity at high conversion, maximal chain growth probability and attrition resistance [11]. For catalyst synthesis, it is known that, cobalt is better in performance than Ferum. But, it is very expensive to use cobalt all along to produce the catalyst. The modification has to be made by mixing Iron element which is a bit cheaper even though it is less effective in performance compared to Cobalt. The suggested modification is to use bimetallic comprising Cobalt and Iron element on Silica Support.

1.3 OBJECTIVE

Objectives of this project are primarily to discover the potential of the mixture of Cobalt-Ferum bimetallic chemical to synthesize a spherical model of catalyst following nano-scale (1-100 nano-metre). In order to complete this project, the following tasks have to be performed:

i. Synthesize bimetallic Co-Fe on Silica support by using Impregnation and Precipitation Method.
ii. Characterization by Transmission Electron Microscopic (TEM) and Temperature Reduction Programme (TPR).
iii. Relate the preparation methods to the results obtained.

1.4 SCOPE OF STUDY

The study is divided into 4 major parts as follows:

1. Literature Review

In the literature review stage, the existing research that using Cobalt and Ferum as nanocatalyst is referred and reviewed. The activation method, characterization of Cobalt and Ferum and experimental method on these two elements by other researchers are the important highlights to be studied during this stage.

2. Laboratory Set Up

Tools and equipment to be used will be identified and familiarized prior to the laboratory tests to avoid malfunctioning of the equipments. Accuracy of equipments used in the tests also will be checked in order to get accurate results.

3. Laboratory Tests

A series of laboratory tests on the supporting compound will be performed, characterization of the mixture produced and as well as the experimental to see the effectiveness of the mixture on the sample.

4. Analysis of Results

Results obtained from the laboratory tests will be analyzed and interpreted. The result is important in order to achieve the objective of the project.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.0 INTRODUCTION

This section contains the literature reviews that have been taken from the books, journals and papers. Nanocatalyst is a small particle which speeds up a chemical reaction without itself being one of the reactants or products and finally remains constant. In Periodic Table, all group VIII metals have noticeable activity in the hydrogenation of carbon monoxide to hydrocarbons Ruthenium followed by iron, nickel, and cobalt are the most active metals for the hydrogenation of carbon monoxide. Thus, only ruthenium, ferum, cobalt, and nickel have catalytic characteristics which allow considering them for commercial production. Both cobalt and iron catalysts have been used in the industry for hydrocarbon synthesis [4].

Fischer-Tropsch (FT) synthesis is a process which deals with the conversion of syngas derived from coal-, biomass- and natural gas into diesel fuels consisting of paraffins, olefins, alcohols and aldehydes with a high cetane number and is environmentally friendly [1]. As a matter of fact, due to limited petroleum reservoirs and environmental restrictions, Fischer-Tropsch (FT) synthesis is gaining more attention nowadays than ever [2]. The Fischer-Tropsch (FT) synthesis is considered as surface catalyzed polymerization reaction. During this process CO is adsorbed on transition metal surface and hydrogenated producing CH_x monomers which consequently propagate to produce products consisting of hydrocarbons and oxygenates with a broad range of functionalities and chain lengths [3].

All the group VIII elements show considerable activity for this process. Among them Co, Fe and Ru present the highest activity [4]. Due to high activity for Fischer-Tropsch (FT) synthesis, high selectivity to linear products, more stability towards deactivation, low activity towards water-gas shift (WGS) reaction and low cost as compared to Ru, cobalt based catalysts are considered preferred choice for Fischer-Tropsch (FT) synthesis as compared to the other transition metals [5].

In many heterogeneous reactions the active phase are dispersed on a support which not only act as a carrier but may also contribute to the catalytic activity [6]. Al_2O_3, SiO_2 and TiO_2 are the commonly used supports for cobalt and ferum based catalysts by different companies commercially.

Industrially supported bimetallic catalysts are very important. The incorporation of second metal component to the catalysts may result in the geometric or electronic modification of the catalysts which may result in the modification of absorption characteristics of the catalysts surface and in some cases alter the reduction and deactivation behavior [7].

This paper deals with the detail study of synthesis and characterization of cobalt and ferum as monometallic and bimetallic nano-catalysts supported on Silica. Effect of incorporation of Ferum to cobalt catalysts in terms of reducibility, dispersion, and particle size distribution is studied in details.

2.1 COBALT CATALYST [4]

Cobalt catalysts are promising catalysts for the synthesis of fuels and chemicals via the Fischer–Tropsch process. In order to expose as many metal atoms as possible to gaseous reactants, the relatively precious metal cobalt is normally deposited on a high surface area carrier to obtain a high metal dispersion. Commonly used high surface area carriers are silica, alumina, and to a lesser extent, carbon, titania and magnesia. The supported metal catalyst has significant advantages over their bulk metal counterparts. They are drastically cheaper as the activity per weight of active metal is increased due to high dispersions on high surface area carriers that maximise metal usage. They also show enhanced thermal stability due to interaction between the active metal and support which leads to a decrease in sintering and an extended catalyst life. Cobalt catalysts are more expensive, but they are more resistant to deactivation [11]. Although the activity at low conversion of two metals is comparable, the productivity at higher conversion is more significant with cobalt catalysts. For Cobalt catalysts, the amount of sulfur in the feed should be much less than 0.1 ppm. Cobalt catalysts supported on oxide supports are generally more resistant to attrition Cobalt catalysts operate at a very narrow range of temperatures and pressures. An increase in temperature leads to a spectacular increase in methane selectivity. Temperature recommended for cobalt catalysis is in range 200-250 ^{o}C.

Table 1: Table: basic information about and classifications of cobalt. [11]

Name	Cobalt
Symbol	Co
Atomic Number	27
Group in Periodic Table	9
Group Name	None
Block in Periodic Table	D-block
Melting Point	1495 °C
Thermal Conductivity	100 W m^{-1} K^{-1}

Specific Heat @ 20°C	0.456 J/g mol
Fusion Heat	15.48 kJ/mol
Standard State	Solid at s.r.t
Standard Atomic Weight	58.93 g.mol^{-1}
Element Category	Transition Metal
Density	8.9 g.cm^{-3}
Electron Configuration	[Ar] 4s^{2} 3d^{7}
Color	Grey metallic
Boiling point	2927 °C
Coefficient of Liner Thermal Expansion	13.0 x 10^{-6} K^{-1}
Evaporation Heat	389.1 kJ/mol
Heat of Vaporization	377 kJ/mol

Figure 1: Pieces of Cobalt [12]

2.2 FERUM CATALYST [13]

Ferum catalysts have been used for the commercial Fischer–Tropsch Synthesis (FTS) process, especially for synthesis of the coal-derived syngas. Many kinds of precipitated iron catalysts which contain various promoters and supports have been investigated to improve the activity, selectivity, and attrition strength. Ferum catalysts usually produce more olefins. Both ferum and cobalt catalysts are very sensitive to sulfur, which could readily contaminate them. For ferum-based catalysts, the syngas should not contain more than 0.2 ppm of sulfur. Ferum co-precipitated counterparts which they are more suitable for use in slurry-type reactors. Ferum catalysts produce hydrocarbons and oxygenated compounds under different pressures and temperatures. The temperature is usually up to 340 ^{o}C [13].

Table 2: Table: basic information about and classifications of ferum [3].

Name	Ferum
Symbol	Fe
Atomic Number	26
Group in Periodic Table	8
Sources	hematite, magnetite(oxide)
Block in Periodic Table	26
Specific gravity	7.874
Melting Point	1535°C
Thermal Conductivity	80.4 W·m−1·K−1
Specific Heat @ 20oC	0.443 J/g mol @20°C
Fusion Heat	13.8 kJ/mol
Standard State	Solid
Standard Atomic Weight	55.847
Element Category	Transition Metal

Density	7.874 g/cc
Electron Configuration	[Ar]4s23d6
Appearance	malleable, ductile, silvery metal
Boiling point	2750°C
Evaporation Heat	~340 kJ/mol
Thermal Expansion	11.8 µm·m−1·K−1 @ 25°C

2.2.1 STRUCTURE OF FERUM CATALYST

The early work on catalyst characterization was concerned with iron catalysts [3] used in the high temperature process as practiced. Thus, Dry presented a widely accepted view of the iron catalyst as shown in Figure 2. At the start of the reaction the catalyst is shown to be predominantly in the form of metallic iron. As the reaction time increases the fraction of metallic iron decreases as it is converted to Fe3O4 and iron carbides [13]. However, even after a long time-on-stream there is still metallic iron present in the catalyst. It is emphasized to the low surface area catalyst that is utilized in the high temperature process. At least two groups have presented similar data for iron catalysts used for the low-temperature process; however, in at least one of these studies, the results are based on characterization data obtained for a low surface area catalyst utilized in the La Porte, Texas pilot plant. The large particle is considered to be an iron oxide and the activation converts small nodules on the surface of the large particles to a carbide form which may become dislocated from the surface of the larger particle. This is an attractive model since it could offer an explanation for the difficulties that are found for the separation of wax from iron catalyst. However, the high surface area catalyst does not contain these large particles.

Figure 2: Chunk of 99.97% pure iron [13]

2.3 SILICA (SiO_2) [4]

The chemical compound silicon dioxide, also known as silica, is an oxide of silicon with a chemical formula of SiO_2 and has been known for its hardness since antiquity [16]. Silica is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms. It is a principal component of most types of glass and substances such as concrete. Silica is the most abundant mineral in the earth. Silica is a group IV metal oxide, which has good abrasion resistance, electrical insulation and high thermal stability. It is insoluble in all acids with the exception of hydrogen fluoride (HF). In this project, silica is used as the supported element for the preparation of Cobalt-Ferum nanocatalyst [1] [2] [3].

Table 3: Properties of Silicon Dioxide [6]

Name	Silicon Dioxide
Molecular Formula	SO_2
Molar Mass	60.0843 g/mol
Melting Point	1830°C
Thermal Conductivity	1.3 $W\ m^{-1}\ K^{-1}$
Appearance	White powder at s.r.t
Density	2.65 g/cm^3
Solubility in water	0.012 g/100 mL

Boiling point	2230oC
Coefficient of Liner Thermal Expansion	12.3x 10-6 K-1

2.4 TRANSMISSION ELECTRON MICROSCOPIC (TEM)

Transmission electron microscopic is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through [1]. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor. TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument to be able to examine fine detail even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution and semiconductor research. At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images [6]. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.

2.5 TEMPERATURE PROGRAM REDUCTION (TPR)

Temperature programmed reduction is most commonly used for characterizing heterogeneous catalysts [1]. The temperature-programmed reduction (TPR) method is a catalyst characterization method based on measuring consumption of hydrogen during heating a catalyst with a linear temperature rate under continuous gas flow. The flow typically consists of 5-10% of hydrogen in argon. The chemical composition of the gas mixture at the reactor inlet and outlet is continuously monitored by a mass spectrometer. Interaction of hydrogen with the catalysts leads to reduction of different species. In the TPR method all the information is extracted from hydrogen consumption profiles. Application of TPR techniques to different catalytic systems has been examined in several reviews [9].

The method has been largely applied for investigation of cobalt-supported catalysts. It has been shown that reduction of unsupported cobalt oxide (Co3O4) is a two-stage process which could be ascribed to successive reduction of Co3O4 to CoO and then to Co. The TPR profiles obtained for cobalt silica-supported catalysts prepared via impregnation using different cobalt salts are shown in Figure 9. Several TPR peaks have been detected usually. Though it is usually difficult to attribute these peaks unambiguously, the low-temperature peaks at 373-623 ^{o}C are commonly assigned to either partial reduction of Co3O4

$$Co_3O_4 \rightarrow CoO$$

or reduction or decomposition in hydrogen of residual cobalt precursors (cobalt nitrate, chloride, acetate, etc.) [7]. The low temperature TPR peaks could be also attributed to reduction of surface carbonate species usually present in strongly basic oxides (La2O3, ZrO2, etc.). It is assigned several low-temperature peaks to reduction of amorphous surface cobalt oxide and hydroxide species different from well-known crystalline Co3O4. Medium-temperature peaks at 673-873 ^{o}C are attributed to the emergence of cobalt metallic phases while peaks at temperatures higher than 873 ^{o}C are usually related to reduction of barely reducible mixed cobalt oxides (cobalt silicate)

$$\text{CoO} \rightarrow \text{Co}$$

TPDRO1100 MS equipped with thermal conductivity detector was used to study the reduction behaviour of the catalysts. 0.5 grams of the catalyst was placed in U-shaped quartz tube. The catalyst samples were first purged in a flow of nitrogen at 20 **°C** to remove traces of water, and cooled to room temperature. TPR was performed using 5% hydrogen in nitrogen mixture with a flow rate of 20 cm^3/min and heating from 40 **°C** to 900 **°C** keeping the temperature ramp 10 **°C** /min [8].

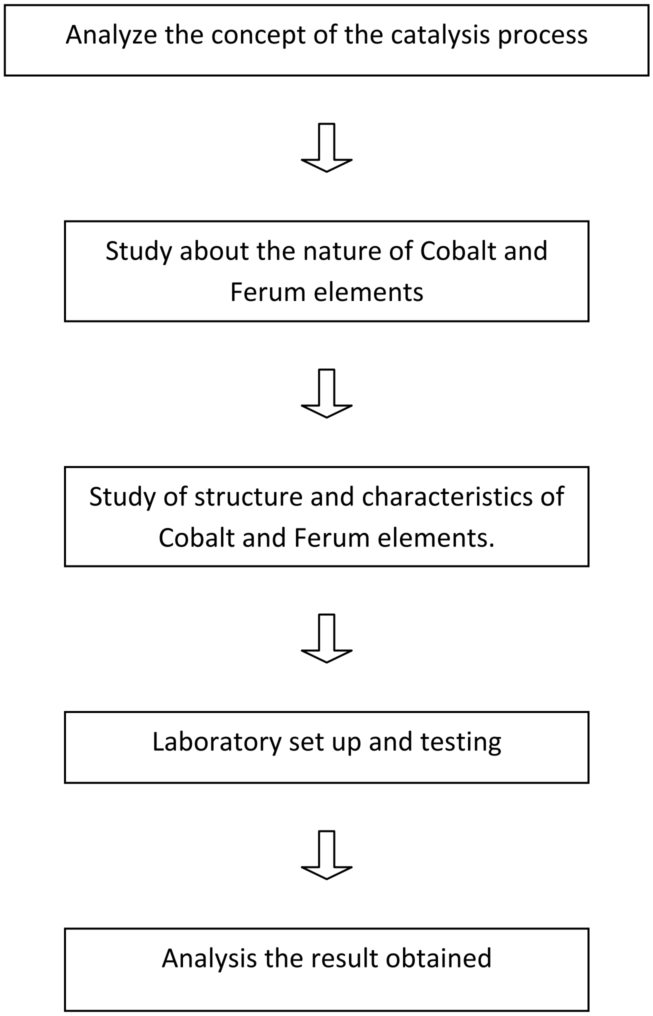
CHAPTER 3

METHODOLOGY

3.1 PROCEDURE IDENTIFICATION

The main task in this project is to bring into context the importance of nanocatalyst using Cobalt and Ferum mixture in enhancing the oil production by using Silica Dioxide (SiO2) as supporting element.

THE PROJECT FLOW :



3.2 IMPREGNATION METHOD

Cobalt-supported and ferum-supported catalysts for FT synthesis are very often prepared by impregnation. Impregnation is a method of cobalt and ferum deposition on porous support in which a dry support is contacted with a solution containing dissolved cobalt and ferum precursors. In this section we discuss impregnation techniques which involve solutions of cobalt salts and ferum salts. Impregnation method is divided into two types which are Wet impregnation and Incipient wet impregnation method:

i. Incipient wet impregnation method : 2 gram of solvent + 2-3 ml of solution
ii. Wet impregnation method : 2 gram of solvent + 5-6 ml of solution

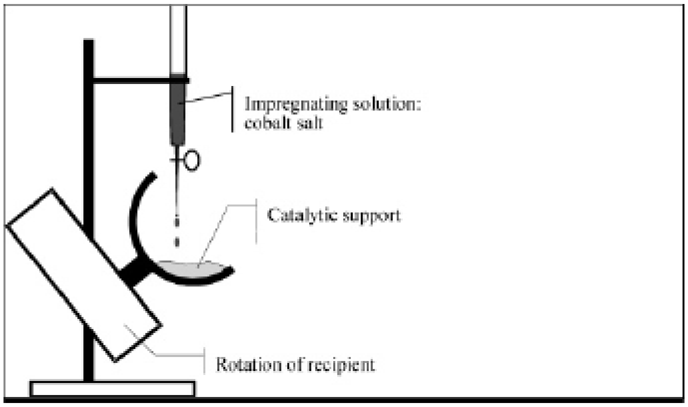


Figure 3: Scheme of experimental set up for incipient wetness impregnation [11].

3.2.1 INCIPIENT IMPREGNATION METHOD:

Incipient wetness impregnation is the most common method to prepare cobalt-supported or ferum-supported catalysts. In the incipient impregnation method a solution of cobalt and ferum salt, typically cobalt nitrate and ferum nitrate, is contacted with a dry porous support. After being contacted, the solution is aspired by the capillary forces inside the pores of the support. The incipient wetness occurs when all pores of the support are filled with the liquid and there is no excess moisture over and above the liquid required to fill the pores. Although at the first sight the practical execution of incipient wetness impregnation is simple, the fundamental phenomena underlying impregnation and drying are extremely complex. Reproducible synthesis of cobalt and ferum catalyst requires careful control of all impregnation parameters such as temperature and time of support drying, rate of addition of impregnating solution, temperature and time of drying and so on. The concentration, distribution, and nature of hydroxyl groups of the support also play an important role in the genesis of the dispersion of supported metal.

3.2.2 WET IMPREGNATION METHOD:

Slurry (wet) impregnation represents another technique of introduction of cobalt and ferum phase to the catalyst supports. Slurry impregnation entails use of an amount of impregnating liquid in excess of what can be accommodated by the total pore volume of selected porous support. The support is usually added to the impregnating solution heated at 333-363 K to yield slurry. The slurry is stirred continuously during impregnation. After removal of the excess liquid phase, the catalyst is dried at sub-atmospheric pressure or in flow of air. The initial drying at sub-atmospheric water is essential to inhibit diffusion of active component to the outer surface of catalyst grains.

3.2.3 PRECIPITATION METHOD:

The deposition-precipitation method is based on precipitation combined with deposition from a liquid medium. The method combines all the advantages of the precipitation method related to control of the size and size distribution of precipitated particles but diminishes the risk of formation of bulk mixed compounds of support and active phase. With this technique a solvated metal precursor is deposited exclusively onto the surface of a suspended support by slow and homogeneous introduction of a precipitating agent, generally hydroxyl ions, in such a way as to avoid nucleation of a solid precursor compound in the bulk solution. The most important issue in this method is to prevent precipitation far from the support surface. The process consists of two steps:

(1) Precipitation from the bulk solution both in support pores and over support and
(2) Interaction of the precipitate with the support surface.

A fine and homogeneous phase can be obtained by involving surface OH groups of the support in the precipitation process. In the deposition process, adsorption of the metal ions onto the support coincides with nucleation and growth of a surface compound. The support surface acts as a nucleating agent. The deposition-precipitation technique has been developed for preparation of highly loaded and highly dispersed oxide-supported metal catalysts. In the case of catalysts supported on SiO2 structures, the deposition-precipitation method was studied by Geus and then extensively explored by Burattin [7]. This method allows obtaining catalysts with high metal loading and dispersion.

The cobalt metal surface area measured by hydrogen chemisorption can attain 50-100 m2/g per gram of cobalt [10]. Due to the high dispersion and Co loadings, high activity in FT synthesis has been reported.

3.3 LABORATORY SET-UP:

3.3.1 Impregnation method:

i. Weigh approximately 0.5018 gm of cobalt nitrate, 0.7214gm of ferum nitrate and 0.05gm of cobalt and ferum nitrate respectively. (Calculation is based on 5% metal loading).
ii. Weigh 1.9gm of commercial Silicon dioxide.
iii. Prepare the solution of each metal in a 50 ml beaker. Add up deionized water until it reaches 10 ml measurement.
iv. Pour the Solution into buret and drop it onto supported element (Silicon dioxide).
v. Stir the mixture by using hot plate stirrer at 24 hour and cover the beaker with parafilm. [1]
vi. Dry the sample in oven at 120 degree Celcius for 12 hours [1]
vii. Calcine the sample in a furnace at 500 degree Celcius for 6 hours. [2]

3.3.2 Precipitation method:

i. Weigh approximately 0.5018 gm of cobalt nitrate, 0.7214gm of ferum nitrate and 0.05gm of cobalt and ferum nitrate respectively. (Calculation is based on 5% metal loading).
ii. Weigh 1.9gm of commercial Silicon dioxide.
iii. Prepare the solution of each metal in a 50 ml beaker. Add up deionized water until it reaches 10 ml measurement.
iv. Pour the Solution into buret and drop it onto supported element (Silicon dioxide).
v. Stir for 2 hours and the beaker is sealed with parafilm
vi. Add 100ml of Ammonium hydroxide into the solution by using a buret [6].

vii. Stir and raise the temperature to 90 degree Celcius at 6 hours. Maintain the level of the solution by adding distilled water.
viii. Dry the sample in oven at 120 degree Celcius for 12 hours [1]
ix. Calcine the sample in a furnace at 500 degree Celcius for 6 hours [2].

Table 4: Gantt chart for Final Year research project

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Project Work Continue	🟪	🟪	🟪												
2	Submission of Progress Report 1				🟦											
3	Project Work Continue				🟪	🟪	🟪	🟪								
4	Submission of Progress Report 2									🟦						
5	Seminar (compulsory)										🟪	🟪	🟪			
5	Project work continue								🟪	🟪	🟪	🟪	🟪			
6	Poster Exhibition											🟦				
7	Submission of Dissertation (soft bound)													🟦		
8	Oral Presentation														🟦	
9	Submission of Project Dissertation (Hard Bound)															🟦

🟦 Suggested milestone

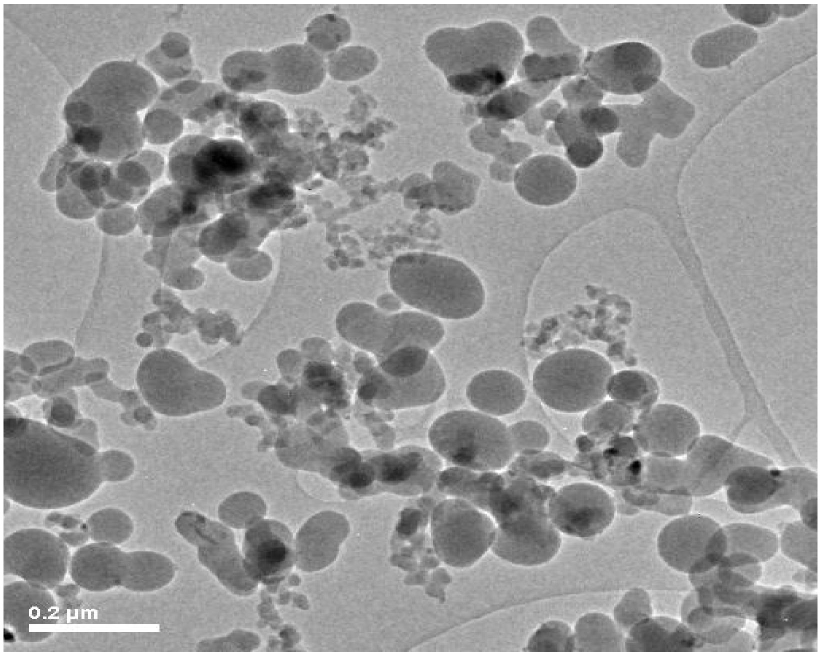
🟪 Process

CHAPTER 4

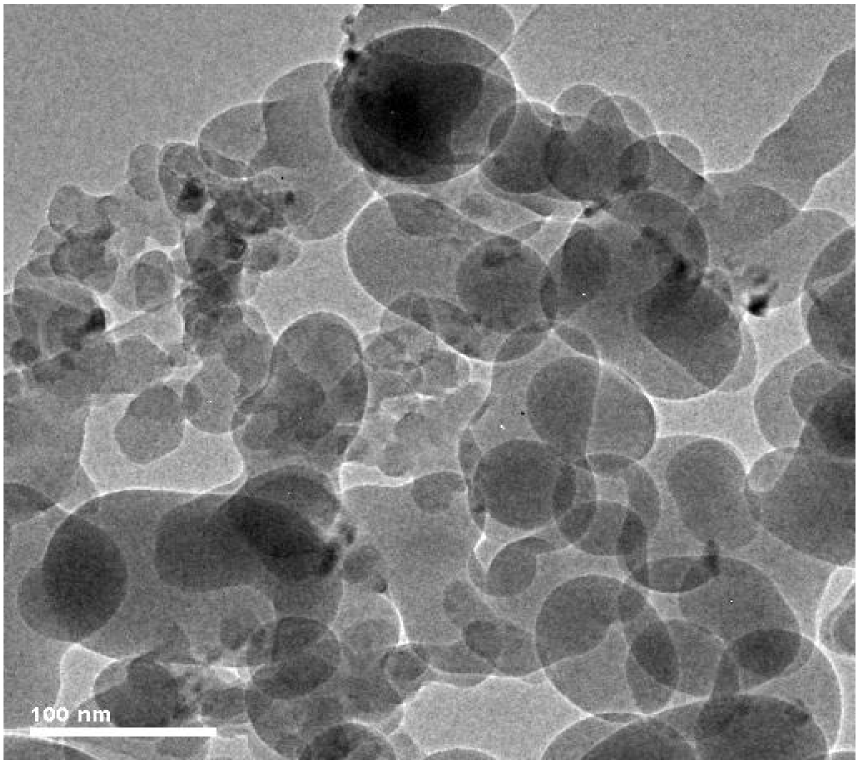
RESULTS AND DISCUSSION:

4.1 RESULTS

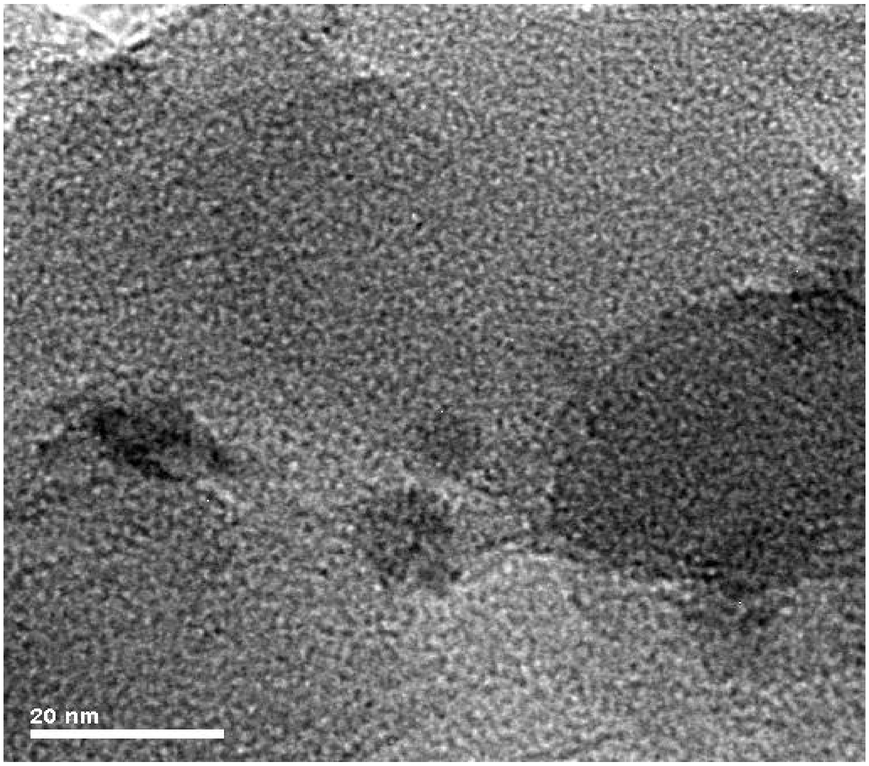
4.1.1 The images portray below are the TEM image for Co-Fe nanocatalyst for impregnation method. Morphology of the catalyst samples was characterized using Transmission electron microscopy (TEM) at AMREC SIRIM Berhad. Sample specimens of catalysts were prepared ultrasonic dispersion of the catalysts in n-hexane and the suspensions were dropped onto a copper grid [1].



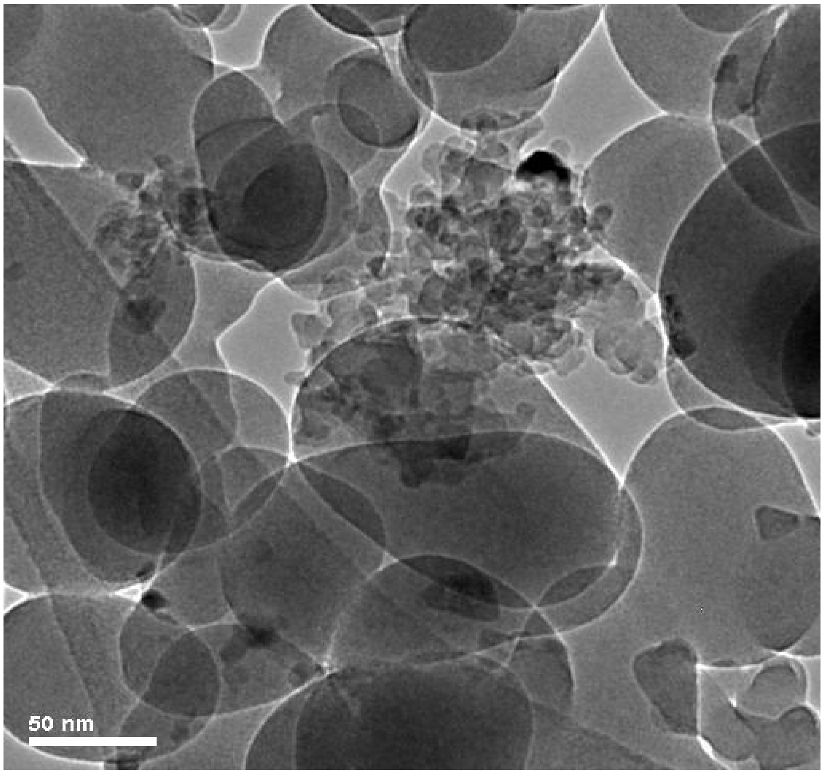
a) 1.0 µm X 1.0 µm



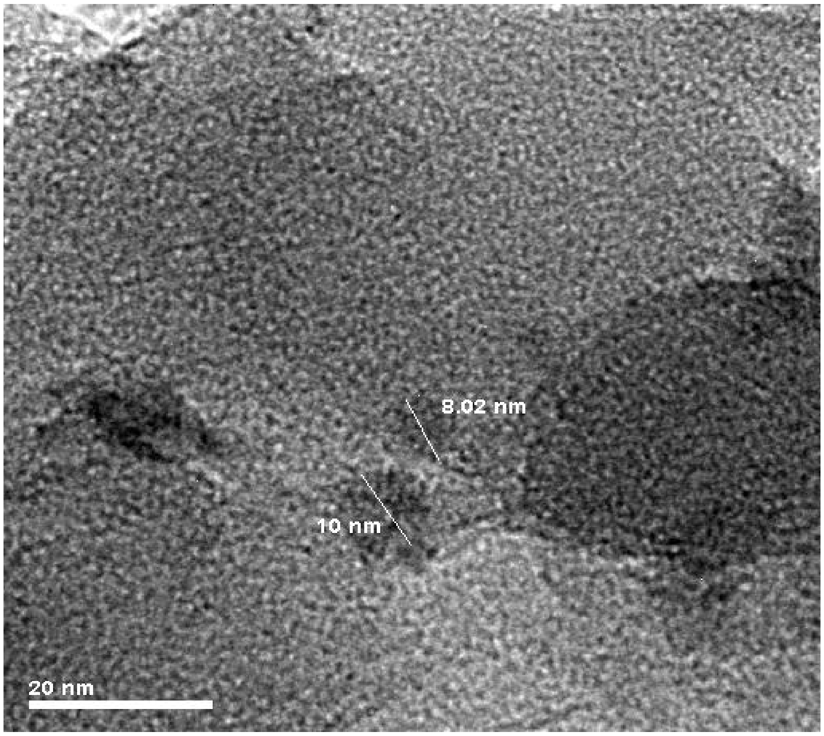
b) 500 nm X 500 nm



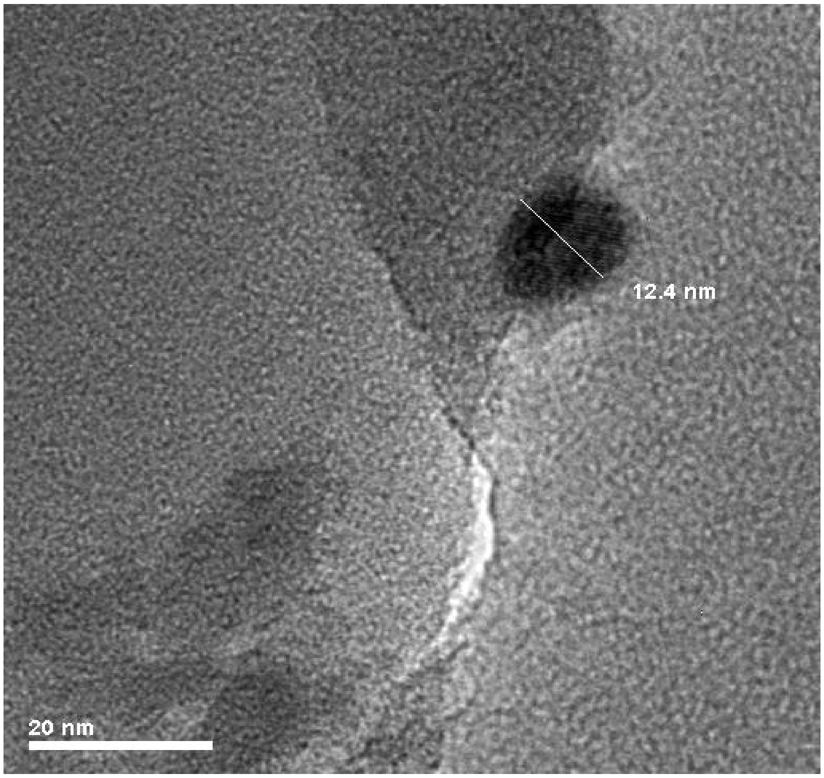
c) 100 nm X 100 nm



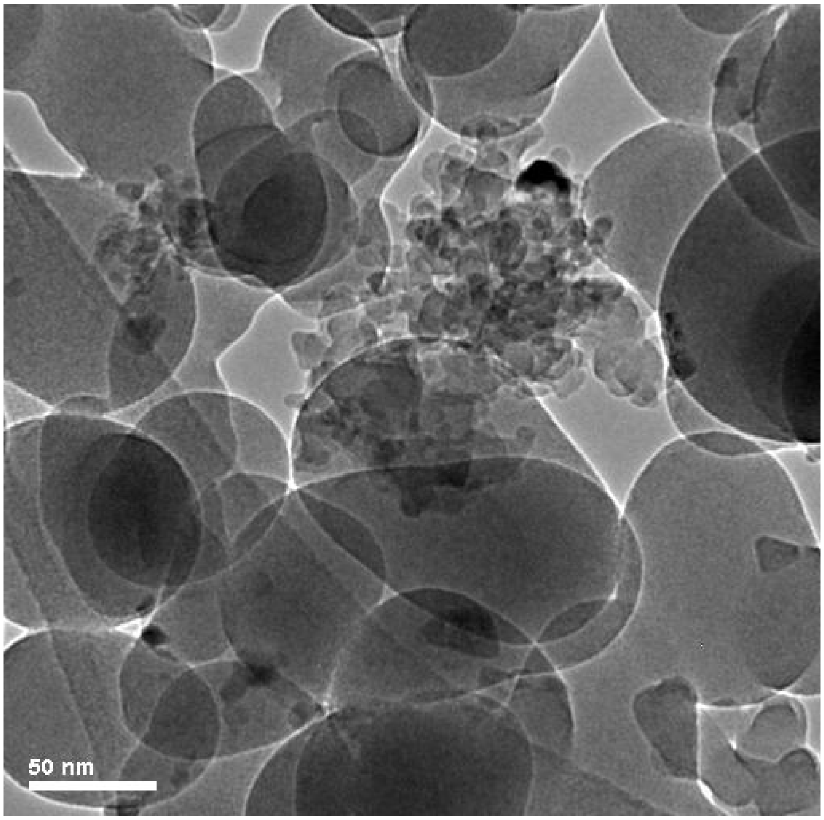
d) 250 nm X 250 nm



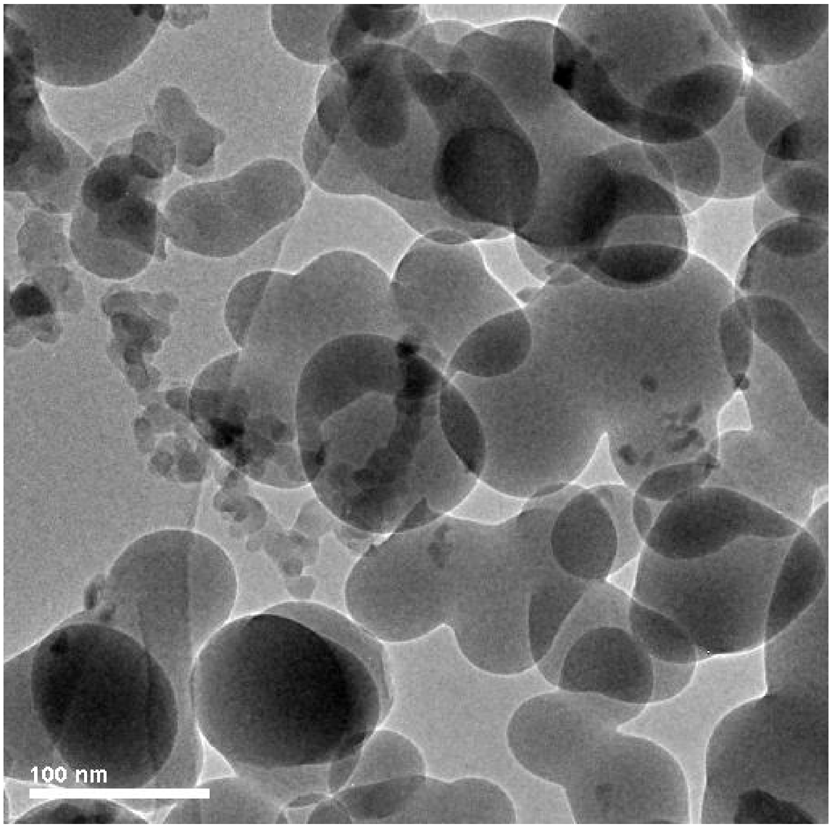
e) 100 nm X 100 nm



f) 100 nm X 100 nm



g) 250 nm X 250 nm



h) 500 nm X 500 nm

Figure 7: TEM image for Co-FE by impregnation method

Referring to the images portrayed by variety of magnification above, it shows that silica supports (grey spot) are not fully covered with metals (black spot). For more clarification, it could be obviously seen that the particle shape is different. It could be stated that the particles are unevenly distributed. Histogram has been built as shown in figure 8 for clearer description regarding the particle size distribution.

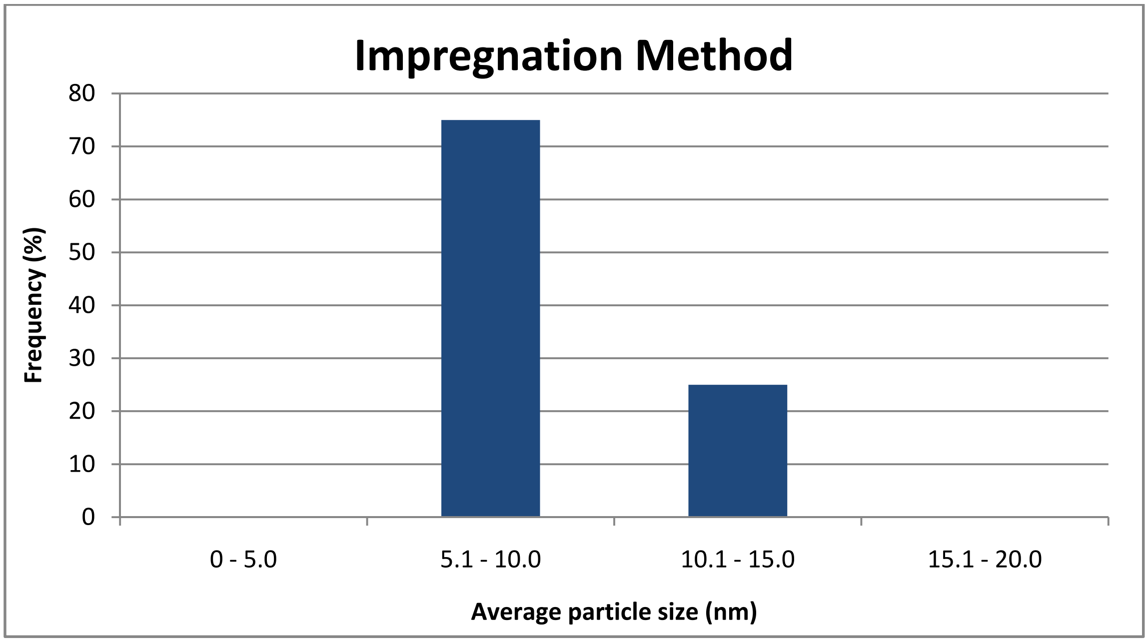
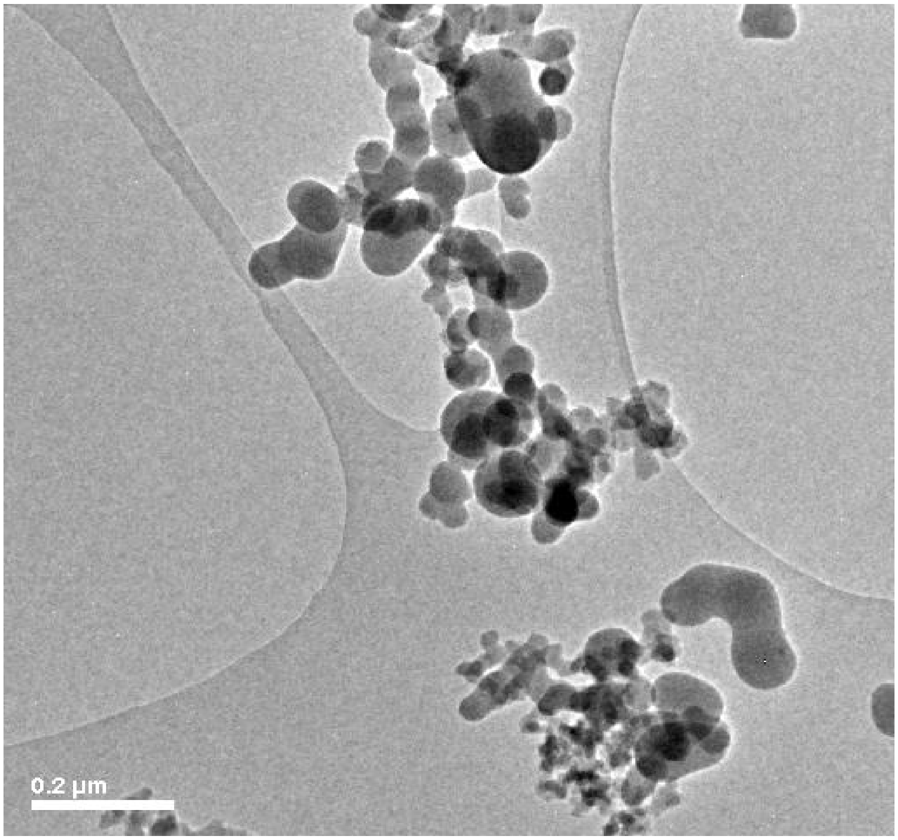


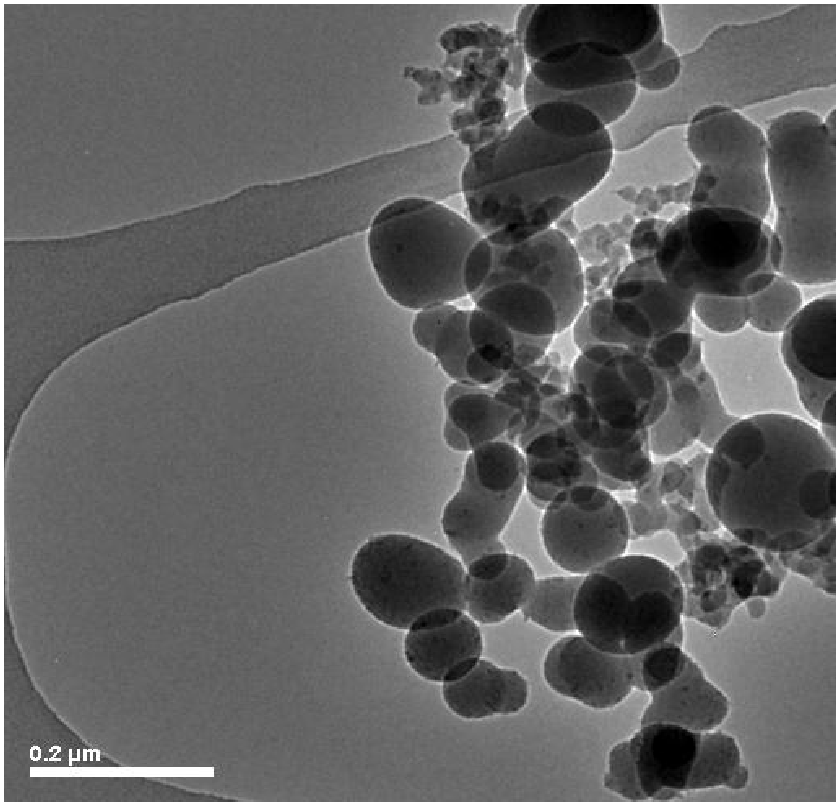
Figure 8: Shows the frequency of average particle Co-FE by impregnation method

For estimation of particle size distribution percentage, twenty (20) data had been measured manually as the images by TEM only can measure accurately three (3) data out of all images scanned. After calculation had been done, the average of the particle size is 9.34 nm. In order to view it clearer, histogram for frequency (%) versus average particle size had been made. Referring to the Histogram above, for impregnation method, CO-FE, a great percentage of the particles are in size ranging from 5-10nm which is approximately 75 %. For the range of 10-15nm, it represents about 25%. Therefore, it can be said that the particle size distribution for bimetallic oxide are slightly uniform.

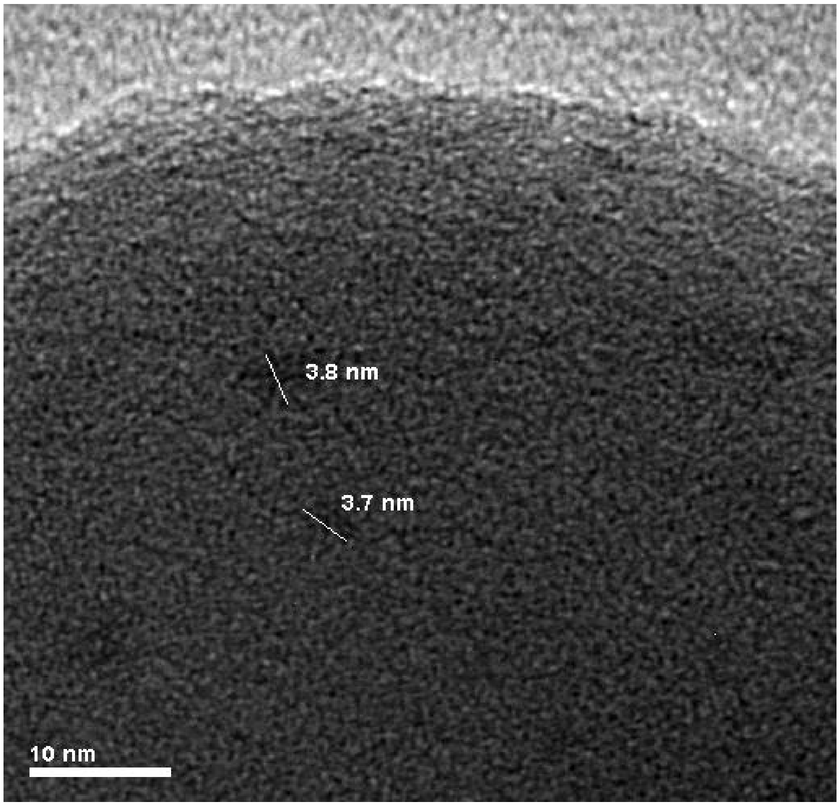
4.2.2 The images portray below are the TEM image for Co-Fe nanocatalyst for precipitation method. Morphology of the catalyst samples was characterized using Transmission electron microscopy (TEM) at AMREC SIRIM Berhad. Sample specimens of catalysts were prepared ultrasonic dispersion of the catalysts in n-hexane and the suspensions were dropped onto a copper grid



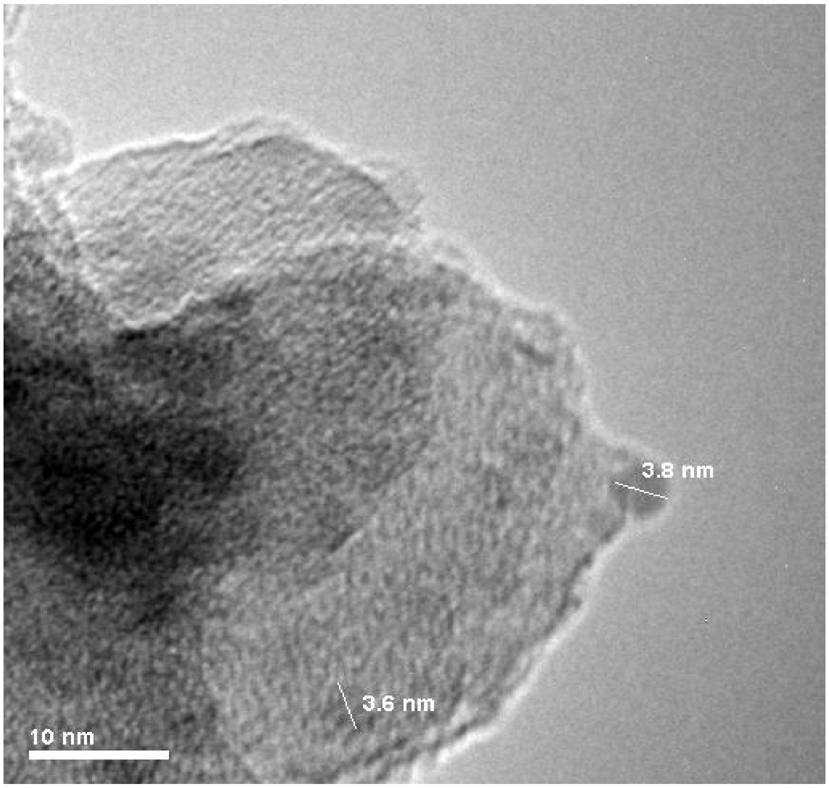
a) 1.0 µm X 1.0 µm



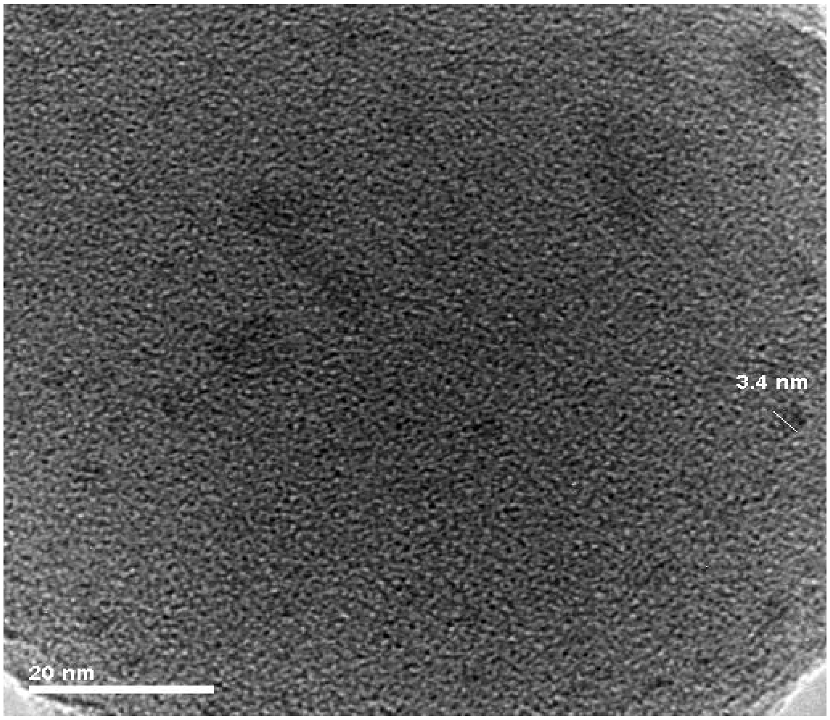
b) 1.0 µm X 1.0



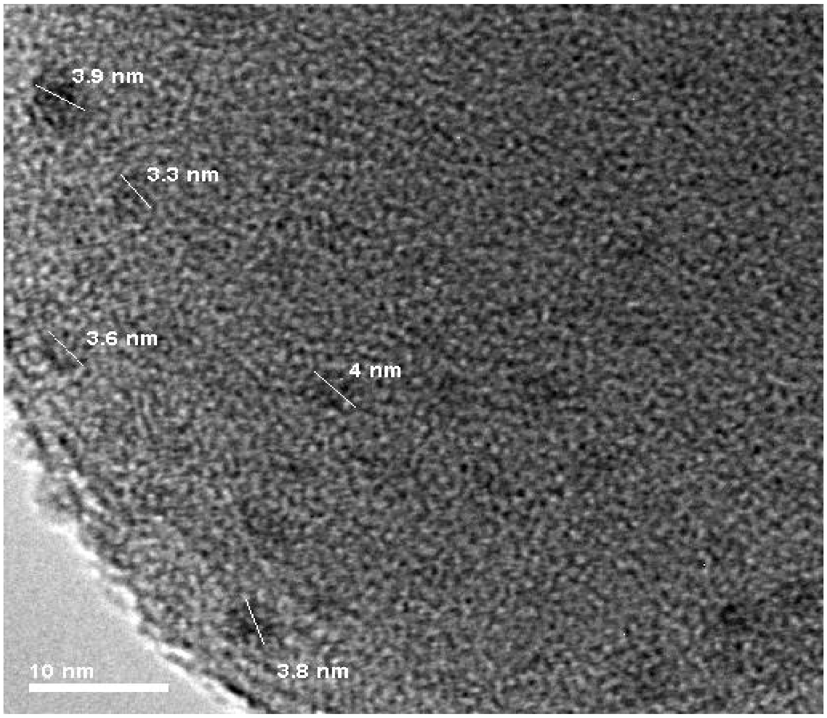
c) 50 nm X 50 nm



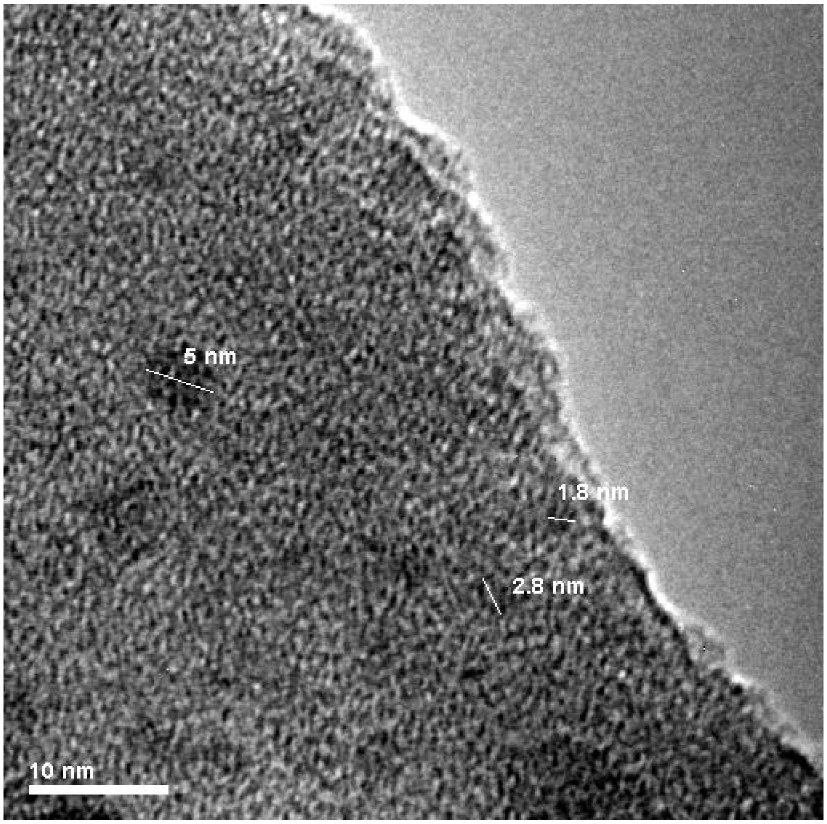
d) 50 nm X 50 nm



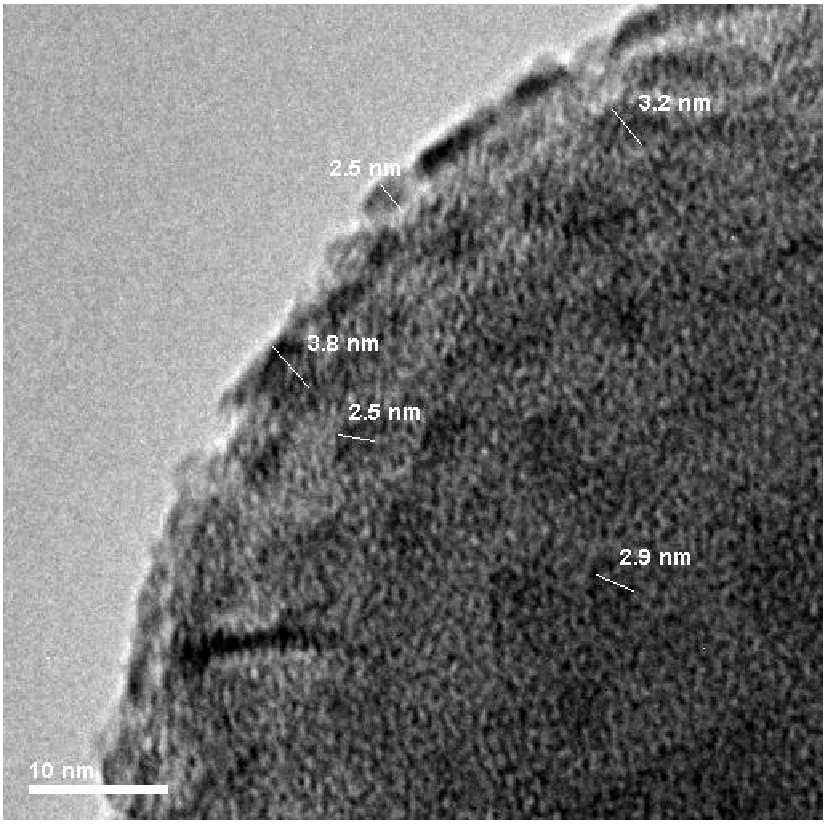
e) 100 nm X 100 nm



f) 50 nm X 50 nm



g) 50 nm X 50 nm



h) 50 nm X 50 nm

Figure 9: TEM image for Co-FE by precipitation method

Based on the images characterized using TEM characterization above, it shows that Silica supports (grey spot)are fully coated by the metals (black spot) . This proves that by using precipitation method, the interaction between the bimetallic and silica supports is higher compared to bimetallic nanocatalyst prepared by impregnation method. Therefore, the deposition by precipitation technique allowed making highly dispersed bimetallic particles. It can be seen obviously from the images above that the particle shape is approximately same to each other. It could be stated that the particles are uniformly distributed for more portrayal, Histogram had been built as shown in figure 10 for clearer analysis regarding the particle size distribution.

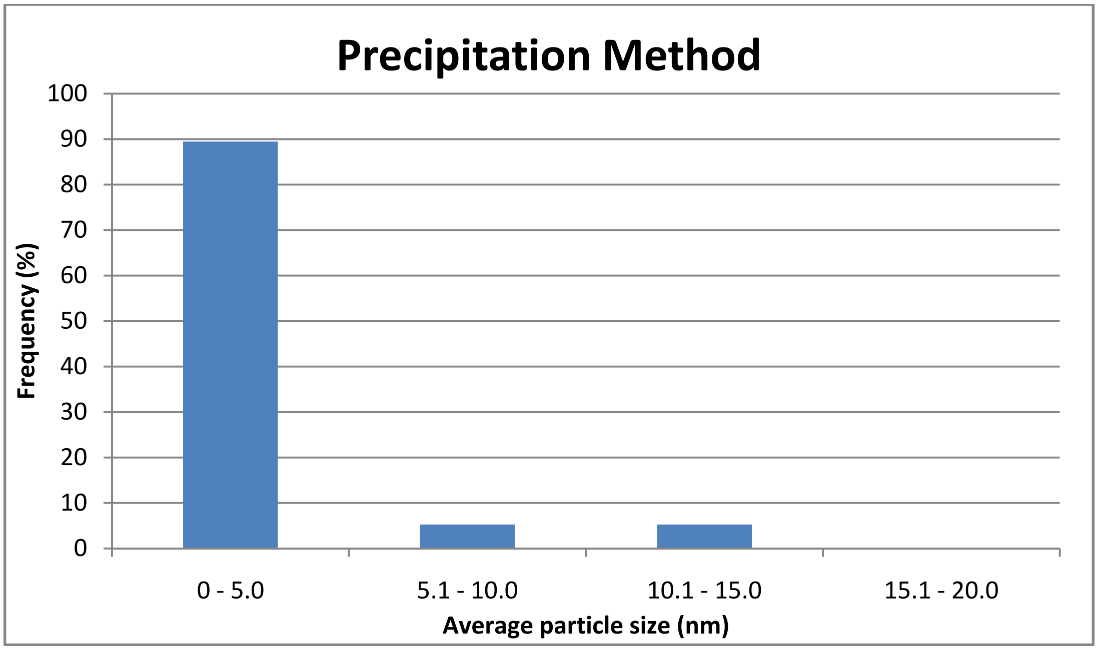
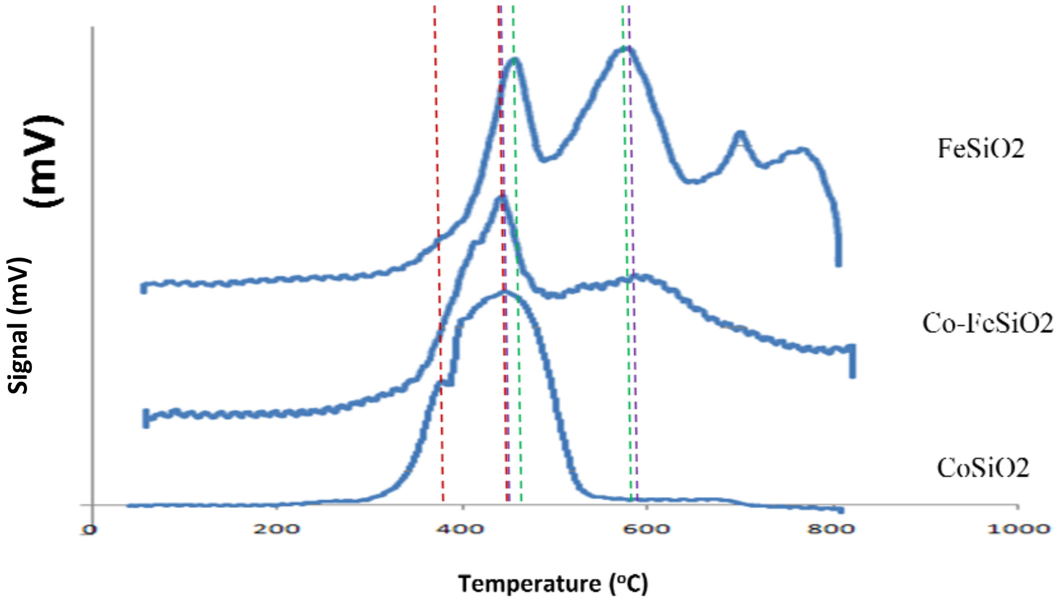


Figure 10: Shows the frequency of average particle Co-FE by precipitation method

For the calculation of particle size distribution percentage, twenty three (23) data had been measured accurately from TEM characterization. It can be seen obviously in the images above. After calculation had been done, the average of the particle size is 3.67nm. In order to view it clearer, histogram for frequency (%) versus average particle size had been made. Referring to the Histogram above, for precipitation method, Co-Fe oxides, a great percentage of the particles are in size ranging from 0-5nm which is approximately 90% and the rest are ranging from 5-10nm and 10-15nm which represented 5% each. Therefore, from this percentage, it it known that, the particle size distribution is greatly uniform. The smaller size of the particles will lead to improve the kinetics [8] of the reaction as it provides larger surface area as been stated in project background.

Figure 11 shows the TPR results for CoSiO2, FeSiO and Co-FeSiO2 for impregnation method. The graph is basically obtained from TPR characterization by combining three results of TPR analysis (refer appendix 1). In order to make comparison for the temperature peak clearly, it has been summarized in the table 5 below:



Indicator:

——: CoSiO2

——: Co-FeSiO2

——: FeSiO

Figure 11: Shows TPR result in Combination of CoSiO2, FeSiO and Co-FeSiO2 for Impregnation Method

Table 5: Temperature Peak 1 and 2 for $CoSiO_2$, Co-Fe SiO_2 and $FeSiO_2$

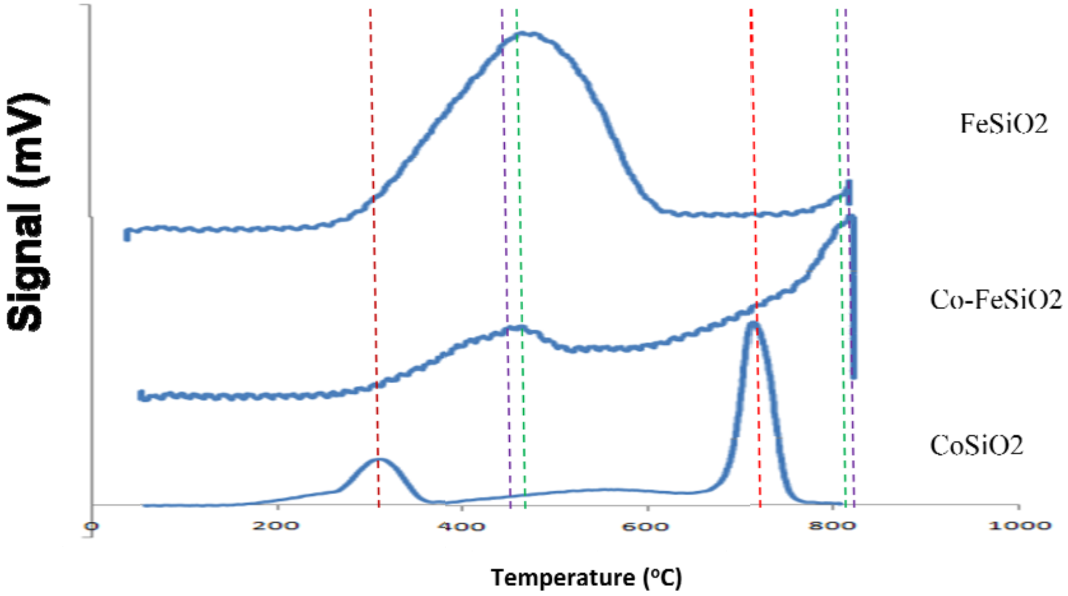
Sample	Temperature Peak 1 (^{o}C)	Temperature Peak 1 (^{o}C)
$CoSiO_2$	380	430
Co-Fe SiO_2	430	593
$FeSiO_2$	450	590

This signal versus temperature is obtained by combining three graph of TPR analysis result (refer appendix1). For Cobalt nanocatalyst, in impregnation method it shows the first peak of temperature reduction (reducibility) is at 380^{o}C and the second peak is at 430 ^{o}C. For Ferum nanocatalyst, in impregnation method it shows the first peak of temperature reduction (reducibility) is at 450^{o}C while the second peak is at 590^{o}C. For Cobalt-Ferum nanocatalyst, in impregnation method [1] it shows the first peak of temperature reduction (reducibility) is at 430^{o}C while the second peak is at 595^{o}C.

This analysis is basically emphasized on the ease of the metal oxide to undergo the reduction of temperature. By comparing Temperature peak 1, Cobalt oxide shows the lowest temperature for the monometallic while ferum shows the highest temperature. It has been stated in the literature review and it is considered to be successful as the temperature peak 1 for bimetallic oxide to be in range of these two monometallic oxides temperature peak. For the comparison of temperature peak 2, Cobalt oxide shows the lowest temperature for the monometallic while ferum shows the second lowest temperature. But, the temperature peak 2 for bimetallic oxides is slightly higher than ferum oxide temperature peak 2. This is against the expected result which the temperature for bimetallic oxides should be in range between these temperature peaks 2 for monometallic oxide.

This method of characterization has been largely applied for investigation of cobalt-supported catalysts. It has been shown that reduction of unsupported cobalt oxide (Co3O4) is a two-stage process which could be ascribed to successive reduction of Co3O4 to Co-O and then to Co. [1]. For the graph made above, it shows that Co3O4 to Co-O is for the first peak and Co-O to Co for the second peak. For Ferum monocatalyst, it shows the reduction from Fe2O3 to Fe3O4 for the first peak and Fe3O4 to Fe for the second peak [3].

Figure 12 shows the TPR results for CoSiO2, FeSiO and Co-FeSiO2 for precipitation method. The graph is basically obtained from TPR characterization by combining three results of TPR analysis (refer appendix1). In order to make comparison for the temperature peak clearly, it has been summarized in the table 6 below:



Indicator:

———: CoSiO2
———: Co-FeSiO2
———: FeSiO

Figure 12: Shows TPR result in Combination of CoSiO2, FeSiO and Co-FeSiO2 for Precipitation Method

Table 6: Temperature Peak 1 and 2 for $CoSiO_2$, Co-Fe SiO_2 and $FeSiO_2$

Sample	Temperature Peak 1 (^{o}C)	Temperature Peak 1 (^{o}C)
$CoSiO_2$	320	720
Co-Fe SiO_2	440	810
$FeSiO_2$	450	820

This signal versus temperature is obtained by combining three graph of TPR analysis result (refer appendix). For precipitation method, for cobalt catalysis, it shows the first peak of temperature reduction (reducibility) is at 320^{o}C while the second peak is at 720^{o}C. For ferum catalysis, it shows the first peak of temperature reduction (reducibility) is at 450^{o}C while the second peak is at 820^{o}C. For Cobalt-ferum catalysis, it shows the first peak of temperature reduction (reducibility) is at 440^{o}C while the second peak is at 810^{o}C.

Basically, this analysis is emphasized on the ease of the metal oxide to undergo the reduction of temperature. By comparing Temperature peak 1, Cobalt oxide shows the lowest temperature for the monometallic while ferum shows the highest temperature. It has been stated in the literature review and it is considered to be successful as the temperature peak 1 for bimetallic oxide to be in range of these two monometallic oxides temperature peak. For the comparison of temperature peak 2, Cobalt oxide shows the lowest temperature for the monometallic while ferum shows the highest temperature. For temperature peak 2 for bimetallic oxides show the slightly lower temperature than ferum oxide. This is following the expected result which the temperature for bimetallic oxides should be in range between these temperature peaks for monometallic oxide. Therefore, it could be stated that the precipitation is a better method for catalysis synthesis.

This method of characterization has been largely applied for investigation of cobalt-supported catalysts. It has been shown that reduction of unsupported cobalt oxide (Co3O4) is a two-stage process which could be ascribed to successive reduction of Co3O4 to Co-O and then to Co. [1]. For the graph made above, it shows that Co3O4 to Co-O is for the first peak and Co-O to Co for the second peak. For Ferum monocatalyst, it shows the reduction from Fe2O3 to Fe3O4 for the first peak and Fe3O4 to Fe for the second peak [3].

CHAPTER 5

CONCLUSION AND RECOMMENDATION:

5.0 CONCLUSION AND RECOMMENDATION

Catalyst synthesis, catalysts characterization, and evaluation of catalytic performance are the primary and probably most important stages in the design of cobalt-ferum nano-catalyst. The bulk and surface structure of cobalt-ferum supported catalysts could be identified by a wide range of characterization techniques. Impregnation and precipitation method are appropriate technique for catalysis process as it involves cobalt and ferum deposition on porous support in which a dry support is contacted with a solution containing dissolved cobalt and ferum precursors. TEM prove that precipitation is better than impregnation method as the particle size distribution is more uniform and the pore size is smaller. It is compared only for Co-Fe catalysis. In Temperature Reduction Program (TPR) characterization, conclusively, both methods, impregnation and precipitation method, give outstanding results for catalyst synthesis. However, the expected result has proven when single metal (Cobalt) were analyzed by TPR. The mixture (Co-FE) catalysis, if it is compared in TPR analysis, it is prone to trail on ferum character even if 1:1 in ratio mixture. The recommendation for this project:

1) Based on TEM and TPR analysis, for catalyst synthesis, precipitation method should be done rather than impregnation method.
2) Study at different ratio of Co-Fe mixture.
3) TEM should be applied for all samples done in order to obtain the information regarding the particle size distribution.
4) Surface Area characterization should be applied for more information regarding surface area and porosity.

CHAPTER 6

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6.0 REFERENCES

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