

**PREPARATION OF Fe/SiO<sub>2</sub> SPHERICAL MODEL NANOCATALYST USING  
COLLOIDAL METHOD**

by

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**CHEMICAL ENGINEERING**

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## **CERTIFICATION OF APPROVAL**

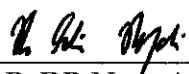
### **Preparation of Fe/SiO<sub>2</sub> Spherical Model Nanocatalyst by Using Colloidal Method**

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Atikah Binti Awang

A project dissertation submitted to the  
Chemical Engineering Programme  
Universiti Teknologi PETRONAS  
in partial fulfilment of the requirement for the  
BACHELOR OF ENGINEERING (Hons)  
(CHEMICAL ENGINEERING)

Approved by,

  
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(AP. DR Noor Asmawati Mohd Zabidi)

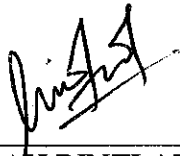
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January 2010

## **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.



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ATIKAH BINTI AWANG

## ABSTRACT

Fischer-Tropsch synthesis is a catalyzed chemical reaction in which synthesis gas, a mixture of carbon monoxide and hydrogen, is converted into liquid hydrocarbons of various forms. The most common catalyst used in the synthesis are cobalt and iron. In this project colloidal method approach is used to synthesize mono dispersed iron silica based nanocatalyst. The iron loading was kept at 6 wt%. The nanocatalysts are then characterized by using FESEM and TPR. There are several parameters are taken into account in order to produce a uniform distribution iron on the silica support which are aging time, temperature and ratio between surfactant and precursor.

## **ACKNOWLEDGEMENT**

First and foremost, I would like to give my sincere thanks to ALLAH SWT, the most almighty God, the source of my life and hope for giving me the strength and wisdom to complete the research.

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# CHAPTER 1

## INTRODUCTION

### 1.1 BACKGROUND OF STUDY

This project involves the preparation and characterization of the iron nanoparticles using colloidal synthesis method. Iron catalyst is the preferred choice for the Fischer Tropsch (FT) synthesis. The major problem with iron catalyst in slurry bubble column reactor (SBCR) reactor is the catalyst attrition. The addition of silica as the binder improved the attrition resistance of the catalyst. Studies from Goodwin Group [7,10] have shown that the type and the content of  $\text{SiO}_2$  incorporated into iron catalysts have significant effects on catalyst attrition property [1].

Loss of catalyst activity is associated with changes of iron into a mixture of iron oxide and iron carbide during the FT synthesis. The relation between deactivation and changes in composition and morphology are not fully understood for iron catalyst. The size and morphology of catalyst particles affect the product selectivity in the FT reaction. The application of electron microscopy techniques on supported nanoparticles are well suited to investigate morphological changes that occur on these catalyst.

In order to perform fundamental study on the catalytic reaction, spherical model catalysts well define properties will be fabricated. Various synthesis methods for the nanocatalyst particles will be investigated. The resultant spherical model catalysts will be characterized using various microscopy and spectroscopy techniques such as transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

### 1.2 PROBLEM STATEMENT

Colloidal synthesis has been widely used as an efficient route to control metal particle size, shape, crystallinity, and crystal structure. Metal colloids displayed remarkable catalytic performance in a wide range of reaction. Stabilization of colloidal systems is a crucial issue in the synthesis of metal colloids and colloid-based supported

catalyst. Thus, research has primarily focused on immobilization of surfactant-stabilized colloids on catalytic supports but it usually tends to agglomerate even under mild conditions. Thus, during synthesis of the colloids the presence of surfactant is essential to disperse and stabilize nanoparticles in the solvent [2].

### **1.3 OBJECTIVES & SCOPE OF STUDY**

At the end of this project, the author should be able to:

1. Synthesize monodispersed nanocatalyst particles.
2. Characterize the spherical model nanocatalysts.

This project focuses on several parameters in order to produce a uniform distribution of iron on the silica support and to control the size of nanoparticles :

1. Aging time.
2. Temperature.
3. Ratio between surfactant and precursor.

### **1.4 FEASIBILITY OF THE PROJECT**

Chemical engineering students need to complete the project within 2 semesters. It is presume that the project is feasible within the scope and time frame if there are no issues with regard to equipment function and material availability. Research work was done in first semester while the experimental work is already started from in the beginning of the semester.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Fischer-Tropsch Synthesis

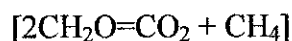
A catalyzed chemical reaction in which synthesis gas, a mixture of carbon monoxide and hydrogen, is converted into liquid hydrocarbons of various forms. The most common catalysts are based on iron and cobalt, although nickel and ruthenium have also been used. The principal purpose of this process is to produce a synthetic petroleum substitute, typically from coal, natural gas or biomass, for use as synthetic lubrication oil or as synthetic fuel. This synthetic fuel runs trucks, cars, and some aircraft engines. The use of diesel is increasing in recent years.

Good data are matters of fact and stand the test of time; reaction mechanisms are more a matter of opinion and are subject to change. This is certainly the situation with the mechanism for the Fischer-Tropsch reaction.[11]

#### 1. Period Following Introduction (discovery to 1940) [11]

The possibility of reaction mechanism or the Fischer-Tropsch:

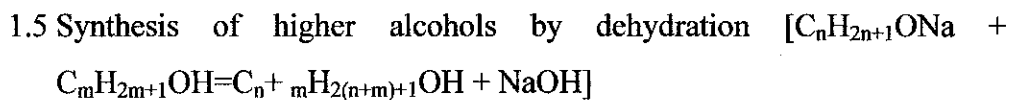
1.1 Formation of formaldehyde in contact with metallic hydrogen carriers



1.2 Modification of reaction 1.1 – in the presence of bases or salts the following is possible:  $[2\text{CH}_2\text{O}=\text{CH}_3\text{OH} + \text{CO}]$

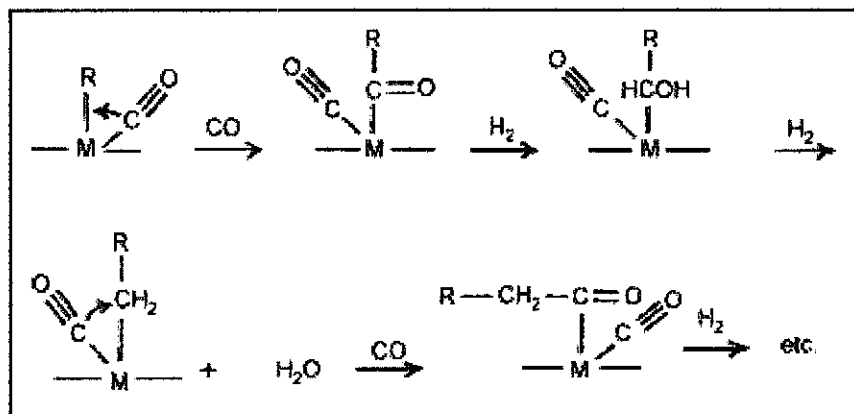
1.3 Synthesis by condensation of aldehydes- higher alcohols analogous to aldol condensation as is known to be especially favored by the presence of alkali.

1.4 Synthesis by CO addition to alcohols. Just as CO combines with water to produce formic acid, it might unite with methanol to give acetic acid and, by analogy, higher alcohols.



2. The Oxygenate Mechanism (1940-1970) [11]

Mechanism work on the Fischer-Tropsch synthesis was nearly eliminated during the WWII years. The commercial operations, using a cobalt-based catalyst, continued during the war years but building new plants was terminated in Germany before 1940. By 1945 there was a perception that western countries were facing a critical shortage of petroleum. This led Percival "Dobbie" Keith to form hydrocarbon by commercializing the Fischer-Tropsch process in the US.



**Figure 1:** Hydroformylation mechanism for FT reaction.

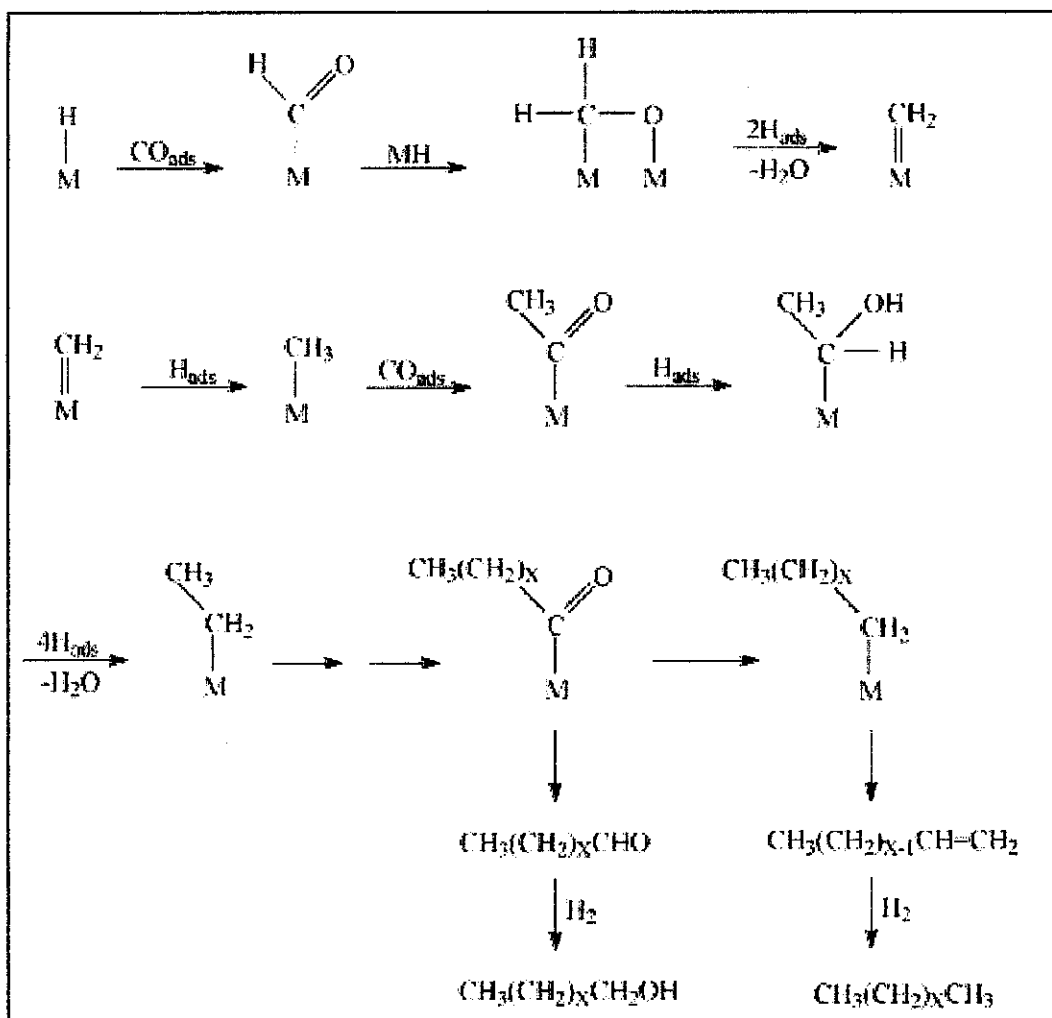


Figure 2: The Pichler-Schulz mechanism.

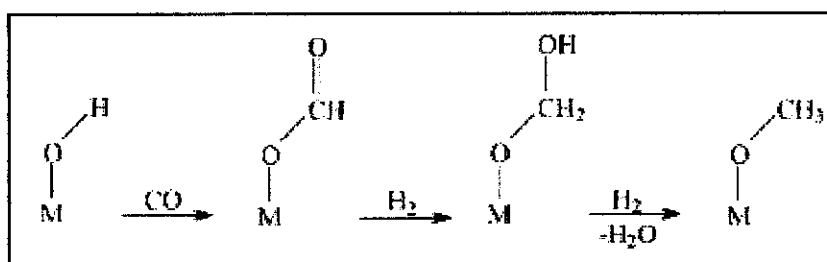
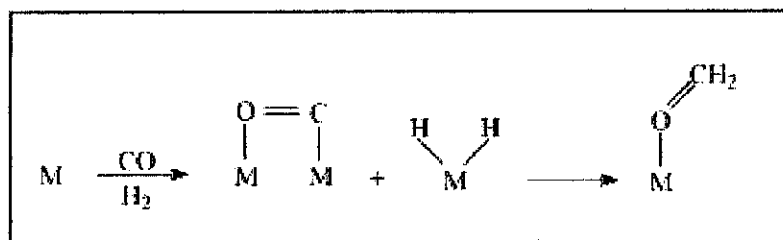


Figure 3: Advanced mechanism by Deluzarche et al.



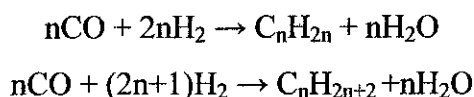
**Figure 4:** Advance mechanism by Sapienza et al.

### 3. The Surface Carbide Mechanism (1970 to present) [11]

With the advent of the surface science instrumentation, the view shifted from the oxygenate to once again the carbide mechanism. A reason for this was the observations made using surface science instruments that show essentially the absence of oxygen on the catalyst surface but an abundance of carbon. This led to the view that it was a surface, or near surface, metal carbide that was the initial surface species in the formation of carbenes. Maitlis indicated that this mechanism should be named the Fischer–Tropsch–Brady–Pettet–Biloen–Sachtler mechanism.

## 2.2 Catalysts for Fischer-Tropsch Synthesis [2]

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. But only ruthenium, iron, cobalt, and nickel have catalytic characteristics which allow considering them for commercial production. Nickel catalysts under practical conditions produce too much methane. Ruthenium is too expensive; moreover, its worldwide reserves are insufficient for large-scale industry.

Cobalt and iron are the metals which were proposed by FT as the first catalyst for syngas conversion. Both cobalt and iron catalysts have been used in the industry for hydrocarbon synthesis. 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.

Parameter	Cobalt Catalysts	Iron Catalysts
Cost	More expensive	Less expensive
Lifetime	Resistant to deactivation	Less Resistant to deactivation
Productivity at high conversion	Higher; less significant effect of water on the rate of carbon monoxide conversion	Lower; strong negative effect of water on the rate of carbon monoxide conversion
Maximal chain growth probability	0.94	0.95
Water gas shift reaction	Not very significant; more noticeable at high conversions	Significant
Flexibility (temperature and pressure)	Less flexible; significant influence of temperature and pressure on hydrocarbon selectivity	Flexible; methane selectivity is relatively low even at 613K
Atrition resistance	Good	Not very resistant
H <sub>2</sub> /CO ratio	~2	0.5-2.5
Maximal sulfur content	<0.1 ppm	<0.2 ppm

**Table 1:** Comparison of Cobalt and Iron FT Catalysts

## **2.3 Synthesis of Fischer-Tropsch Catalysts [2]**

The catalytic performance of FT catalysts strongly depends on the methods of catalyst preparation. Preparation of supported catalysts involves several important steps:

- Choice of appropriate catalyst support
- Choice of appropriate catalyst support
- Choice of active phase
- Catalyst promotion
- Oxidative and reductive treatments

The goal of active phase deposition is to spread the metal onto porous support and provide the precursors of metal clusters. Properties of the catalysts, number of cobalt metal sites, their characteristics and localization on the support could be controlled by promotion with noble metals and oxides. The catalytic performance of FT catalysts is usually strongly affected by different oxidizing and reducing pretreatments. The catalytic support could also influence the performance of FT catalysts.

There are several methods in producing catalysts for Fischer Tropsch (FT) synthesis that have been reported by several literatures. The methods include:-

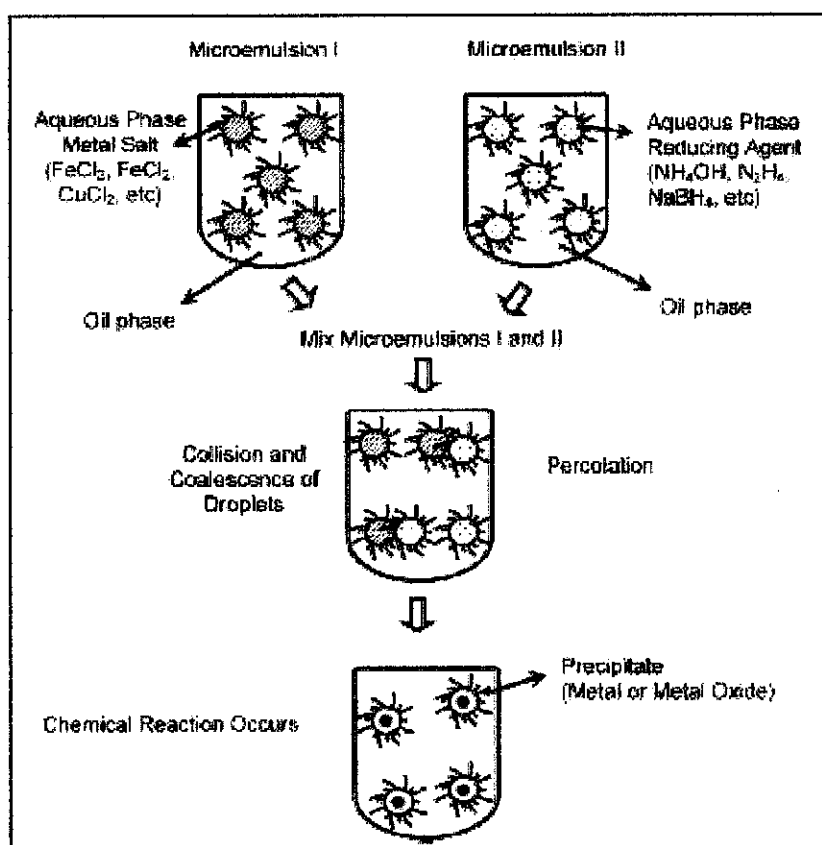
## **2.4 Sol-Gel Method [2]**

Sol-Gel method is another technique to prepare catalyst for FT synthesis. It allows mastering and adjusting the surface area, porosity, and particle size of prepared catalyst. It also has been known as one of the easiest way to obtain uniform structure; the microscopic feature strongly depends on the preparation method.



## 2.5 Microemulsion Method [2]

The method usually involves microemulsion stabilizer. A stabilizer (emulsifier) is a molecule that possesses both polar and non-polar moieties. In diluted water (or oil) solution, emulsifier dissolves; it is present in the form of monomer. A particle size in the range of 5-50 nm depends on the size of microemulsion droplets and can be controlled by adjusting the water to surfactant ratio or concentration of reagents. The metal particles produced by this method usually have a spherical shape.



**Figure 5:** Principal stages of metal nanoparticle preparation using the microemulsion approach.

## 2.6 Colloidal Method [2]

It is an efficient route to control metal particle size and shape, crystallinity and crystal structure. Several methodological approaches have been developed to prepare metallic heterogeneous catalysts from colloidal system.

#### 1) Polyol Process

- boiling alcohol is used as both reductant and a solvent. 1,2-dodecanediol is added into hydrated cobalt acetate solution dissolved in diphenyl ether containing oleic acid and trioctylphosphine. The cobalt particle size is controlled by changing the relative concentration of both precursor and stabilizer.

#### 2) Ethylene Glycol Method

- is based on complexation of colloidal metal particles by carboxylic species produced via oxidation of ethylene glycol.

#### 3) Coordination Capture Method

- involves capture of colloidal metal particles onto the surface of functionalized silica by ligand coordination.

#### 4) Pseudo-colloid method

- prepared cobalt nanoparticles supported by faujasite zeolites.

### **2.7 Precipitated Iron Based Catalyst [9]**

All precipitates iron based catalyst were prepared by precipitation from an aqueous nitrate solution by adding an aqueous solution of  $(\text{NH}_4)_2\text{CO}_3$ . The precipitates were filtered and washed with distilled water several times. The washed filter cakes were dried in air over the range of 373-393 K and subsequently calcined in air over the range 653-693 K.

### **2.8 Impregnations [2]**

Impregnation is a method of cobalt deposition on porous support in which a dry support is contacted with a solution containing dissolved metal precursor. There are two types of impregnation techniques:

- *Impregnation Using Solutions of Cobalt Salts*

Incipient wetness impregnation is the most common method to prepare cobalt-supported catalysts. In the incipient impregnation method a solution of cobalt salt, typically cobalt nitrate is contacted with a dry porous support. After being contacted, the solution is aspires by 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.

- *Impregnation with Cobalt Carbonyl Solutions*

Impregnation is one of the simple techniques for immobilizing transition-metal carbonyls on porous oxides. Impregnation with carbonyls could also lead to bimetallic catalysts. Bimetallic particles were obtained on alumina using co-adsorption of dicobalt octacarbonyl and diruthenium hexacarbonyl tetrachloride complexes from pentane solutions.

## **2.9 SiO<sub>2</sub> Support [4]**

SiO<sub>2</sub> was found to be the most preferable one in terms of both activity and selectivity. SiO<sub>2</sub> was chosen as the principal structural promoter for the preparation of iron-based catalyst with high attrition resistance using co-precipitated method and popular spray-drying technology.

Although SiO<sub>2</sub> as structural promoter has been widely used and investigated, the effects of SiO<sub>2</sub> on the iron-based catalyst still keep some inconsistent conclusion, because these studies were conducted under different conditions or over different catalyst systems.ok

Incorporation of SiO<sub>2</sub> to precipitated iron-based catalyst was found to have significant influences on the surface basicity, reduction and carburization behaviors, as well as catalytic activity. SiO<sub>2</sub> stabilizes the iron oxide crystallites from sintering, facilitates the high dispersion of Fe<sub>2</sub>O<sub>3</sub> and CuO and further enhances the contact between Fe<sub>2</sub>O<sub>3</sub> and CuO

No	Reference	Preparation Method	Reaction Studies	Characterization	Remarks
1.	J. Huo, H.Song, X. Cheln, S. Zhao, C. Xu, Structural transformation of carbon-encapsulated iron nanoparticles during heat treatment at 1000°C, Materials Chemistry and Physics 101, (2007) 221-227	<ul style="list-style-type: none"> <li>Carbon-encapsulated iron nanoparticles is synthesized by co-carbonization of an aromatic ferrocene at 495°C under autogeneous pressure.</li> </ul>	<ul style="list-style-type: none"> <li>Mixture of YD and ferrocene (proportion 62.5 wt%) was introduced into a 200ml autoclave and heated with the rate of 3°C min<sup>-1</sup> up to 495°C under an environment of pure N<sub>2</sub>.</li> </ul>	<ul style="list-style-type: none"> <li>Using TEM, HREM and XRD</li> <li>TEM &amp; HREM result: nanoparticles become larger and exhibited various morphologies, e.g. hollow carbon cages and carbon nanotubes.</li> <li>XRD result: the structure of the carbon shell was turbostratic and the iron carbide increased after heat treatment.</li> </ul>	<ul style="list-style-type: none"> <li>No application stated in the article.</li> </ul>
2.	K. Pansanga, N. Lohitharn, A.C.Y Chien, E. Lotero, J.Pampranot,	<ul style="list-style-type: none"> <li>Preparation of reference 1% Cu on</li> </ul>	<ul style="list-style-type: none"> <li>For the reference cat., of</li> </ul>	<ul style="list-style-type: none"> <li>Using N<sub>2</sub> physisorption,</li> </ul>	<ul style="list-style-type: none"> <li>The % conversion is</li> </ul>

<p>P. Praserthdam, J.G. Goodwin Jr., Copper-modified alumina as a support for iron Fischer-Tropsch synthesis catalyst, Appl. Catal. A, 332 (2007) 130-137</p>	<p>Fe/Al<sub>2</sub>O<sub>3</sub> catalyst: A solution of iron(III) nitrate nanohydrate was first impregnated into the <math>\gamma</math>-alumina support using the incipient wetness method. Final catalyst composition: ca. 20 wt% Fe</p> <ul style="list-style-type: none"> <li>• The impregnated cat. Was dried at 110°C for 24 h followed by calcinations in air at 350°C for 3 hr.</li> <li>• 1 wt% Cu was impregnated unto the sample using a solution of</li> </ul>	<p>iron(III)nitrate nanohydrate was impregnated into the <math>\gamma</math>-alumina support. Final catalyst composition: ca. 20 wt% Fe. Then the cat. Was dried at 110°C for 24 h followed by calcinations in air at 350°C for 3h.</p> <ul style="list-style-type: none"> <li>• Then 1 wt % Cu was impregnated unto the sample using a solution of copper (II) nitrate trihydrate, then dried at</li> </ul>	<p>XRD, SEM, EDX &amp; TPR</p> <ul style="list-style-type: none"> <li>• N<sub>2</sub> physisorption result: BET surface areas, pore volumes, and pore sizes of the 1% Cu promoted Fe on Cu-modified Al<sub>2</sub>O<sub>3</sub> cat. Prepared with calcinations pretreatment after the last metal impregnation were in range of 107-113 m<sup>2</sup>/g &amp; were not significant different from the base 1- 0*CC catalyst (115m<sup>2</sup>/g)</li> </ul>	<p>not stated, therefore it is difficult to compare with other journals.</p>
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	<p>copper(II) nitrate trihydrate and incipient wetness.</p> <ul style="list-style-type: none"> <li>The catalyst was dried at 110°C for 24h &amp; then calcined again in air at 460°C for 3h.</li> <li>Preparation of 10% Cu-modified Al<sub>2</sub>O<sub>3</sub> support: copper(II) nitrate trihydrate was impregnated to <math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub> by IW.</li> <li>The samples were dried at 110°C for 24h &amp; calcined in air with ramping of the temperature at 10°C/min up to</li> </ul>	<p>110°C for 24 h &amp; then calcined again in air at 460°C for 3h</p>	<ul style="list-style-type: none"> <li>XRD result: The XRD patterns for all the supported Fe cat. Do not show any characteristic peaks of Fe<sub>2</sub>O<sub>3</sub> or any other Fe compound suggesting that Fe was present in a highly dispersed form.</li> <li>SEM&amp;EDX result: The alumina and Cu-modified alumina supports consisted of irregular shaped particles/granules formed by</li> </ul>	
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	<p>300°C for 1 h.</p> <ul style="list-style-type: none"> <li>The temperature was thereafter increased by 10°C/min up to 500°C &amp; held for 6 h.</li> <li>Then iron(III) nitrate nanohydrate was used to impregnate the Cu-modified alumina supports to produce 20wt% Fe cat. Followed by drying &amp; calcining at 350°C</li> </ul>		<p>agglomeration of nanocrystalline alumina.</p> <ul style="list-style-type: none"> <li>TPR result: the reduction temperature decreased significantly or the Cu modified alumina supported iron cat. With calcining pretreatments after the final impregnation step.</li> </ul>	
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## CHAPTER 3

### METHODOLOGY / PROJECT WORK

#### 3.1 Synthesis methods for iron nanoparticles [3].

- Colloidal synthesis approach by using Modified “One-pot” synthesis method.

##### *Mixture A*

- 1) SiO<sub>2</sub> spheres (0.2g) are added to a surfactant mixture containing 1 ml oleic acid, 1 ml oleyl amine, 5 ml cyclohexane.
- 2) The mixtures are then placed in a bath sonicator for 3 hours or for 1 hour in the horn sonicator with amplitude of 30%.
- 3) 5 ml of phenyl ether or octyl ether solvent is then added into the sonicated mixture. The sonicator mixture is transparent and changed to cloudy upon addition of phenyl ether and remained clear if octyl ether is added.
- 4) This mixture is poured into the reaction vessel (shown in Figure 1) and heated to 265<sup>0</sup>C under nitrogen flow.
- 5) This slurry is stirred at 200 rpm throughout the synthesis period.

##### *Mixture B*

- 1) 0.104g of Fe(acac)<sub>3</sub>, 0.0516g 1,2 hexadecanediol, 38 μl oleic acid, 39 μl oleylamine and 5 ml phenyl ether are mixed together.(Amount of Fe(acac)<sub>3</sub> varried according to the desired loading)
- 2) The molar ratio of Fe(acac)<sub>3</sub> to 1,2 hexadecanediol is kept at 1:5 and molar ratio of Fe(acac)<sub>3</sub> to surfactant is kept at 1:3.
- 3) This mixture is placed in the bath sonicator for about 20 minutes to prevent crystallization of phenyl ether solvent.



### *Mixture A + Mixture B*

- 1) Mixture B is added dropwise to Mixture A once the temperature of Mixture A reached 150<sup>0</sup>C. It takes about 10 minutes to add all of Mixture B into the reaction vessel.
- 2) The temperature rose to 209<sup>0</sup>C when the last drop of Mixture B is added to the reaction vessel.
- 3) The black mixture is heated for 30 minutes at 265<sup>0</sup>C and is cooled under nitrogen flow until the temperature decreased to about 90<sup>0</sup>C.
- 4) Ethanol (25 ml) is then added to the cooled reaction mixture to precipitate the nanoparticles.
- 5) The solid is then separated by centrifugation at 7000rpm for 90 minutes.
- 6) The precipitates obtained after centrifugation is then calcined in air at 450<sup>0</sup>C for 2 hours in the oven.

## **3.2 Characterization of nanoparticles.**

### **-Field Emission Scanning Electron Microscopy (FESEM)**

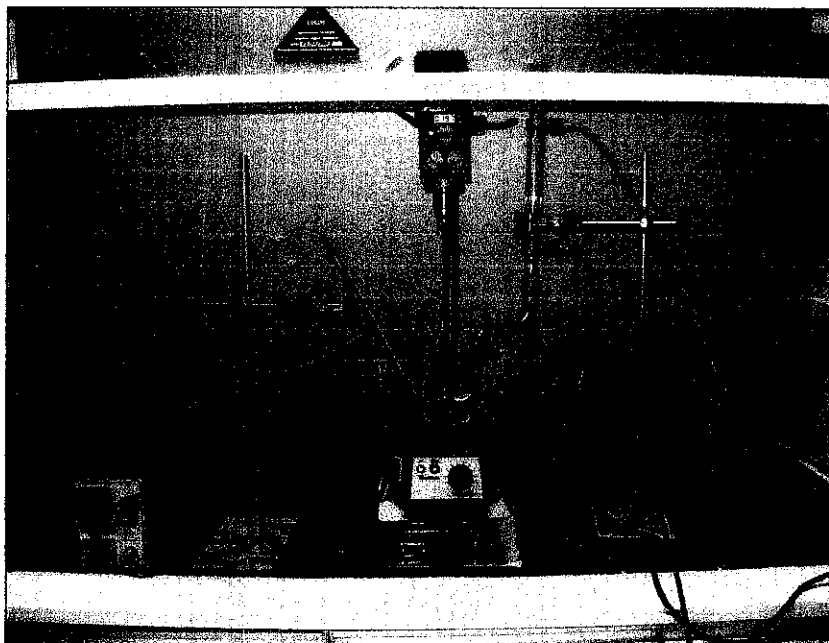
A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. Applications include:

- Semiconductor device cross section analyses or gate widths, gate oxides, film thickness, and construction details.
- Advanced coating thicknesses and structure uniformity determination.
- Small contamination feature geometry and elemental composition measurement.

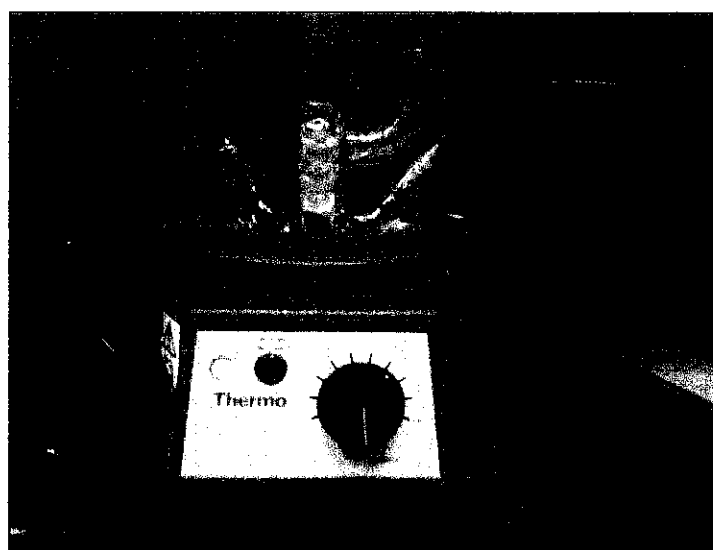
### **-Temperature-Programmed Reduction (TPR)**

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

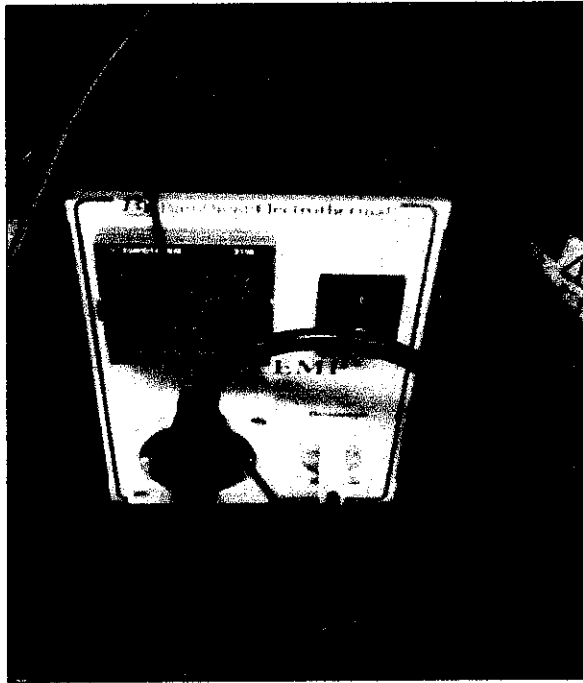
in argon. The chemical composition of the gas mixture at the reactor inlet and outlet is continuously monitored by catharometer or a mass spectrometer. Interaction of hydrogen with the catalysts leads to reduction of different species. In the TPR method all the information is extracted from hydrogen consumption profiles. This gives “fingerprints” information about the catalyst redox properties.



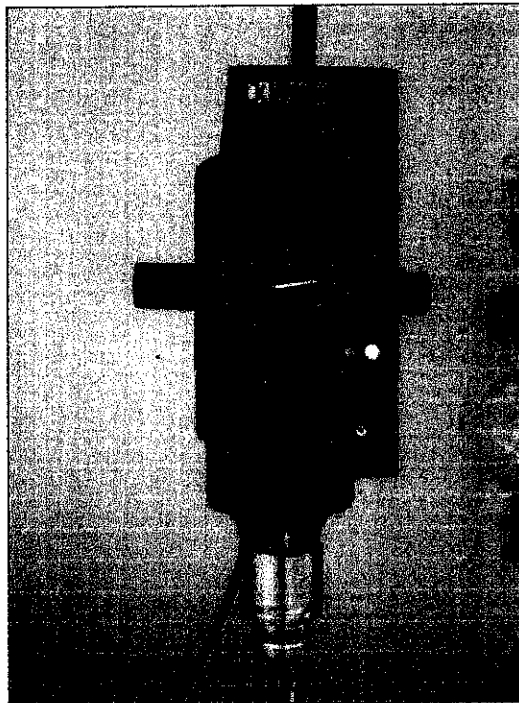
**Figure 6:** Reaction vessel setup for synthesis of nano particles.



**Figure 7:** Heating mantle (Thermo Scientific)



**Figure 8:** Heating Controller (Barnstead Electrothermal)



**Figure 9:** Mechanical Stirrer (EUROSTAR digital IKA\* WERXE)

## CHAPTER 4

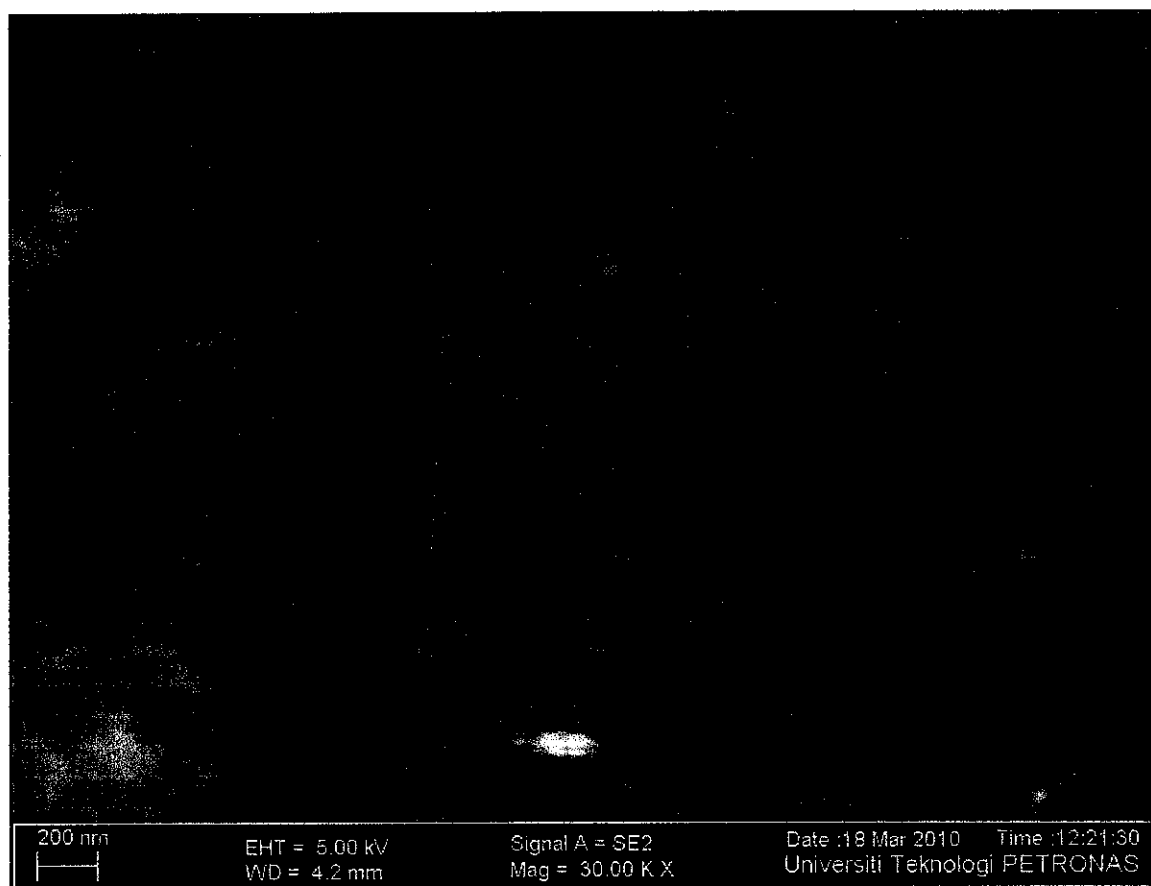
### RESULTS AND DISCUSSIONS

#### 4.1 RESULTS

##### 4.1.1 FESEM

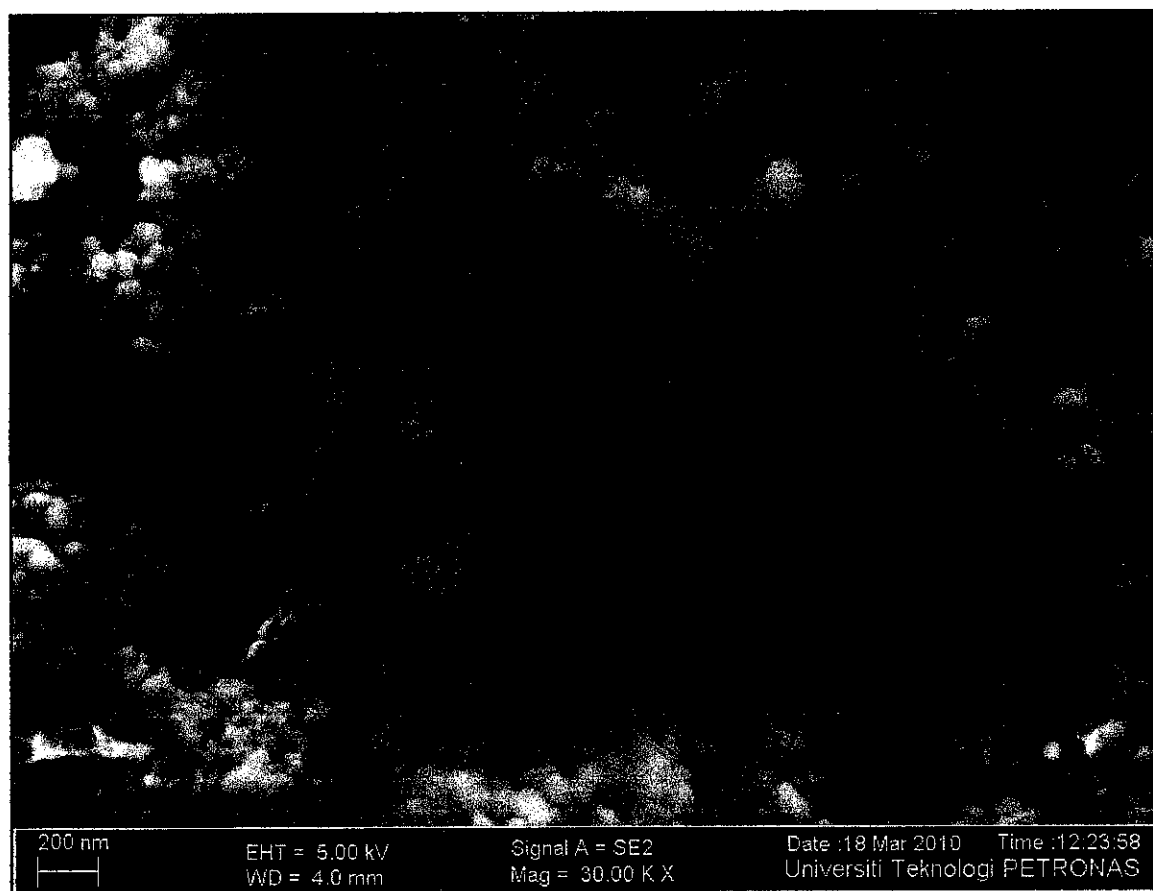
All the samples were sent for characterization test by using FESEM. The purpose of this characterization test is to find the size and distribution of the iron on the silica support. The images results are as follows:

1) At 230°C



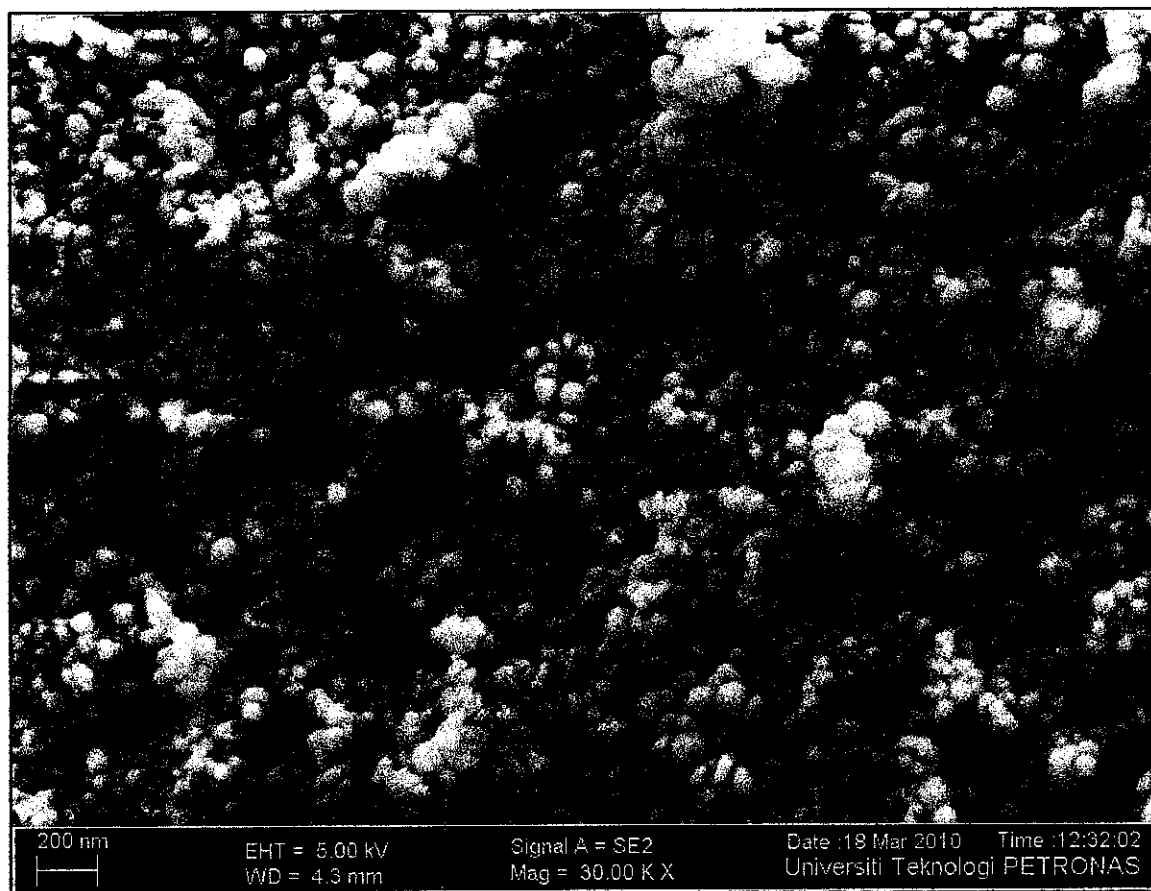
**Figure 10:** FESEM image of Fe/SiO<sub>2</sub> nanocatalyst synthesized at 230°C

2) At 250°C



**Figure 11:** FESEM image of Fe/SiO<sub>2</sub> nanocatalyst synthesized at 250°C

3) At 260°C



**Figure 12:** FESEM image of Fe/SiO<sub>2</sub> nanocatalyst synthesized at 260°C

#### 4.1.2 Temperature Programmed Reduction

Fe catalysts during FTS contain multiple phases with differing size and morphology. Detailed localized information about phase distribution and phase evolution will be helpful in understanding the nature of the metal-support interaction. This method is used to study catalyst reducibility and metal-support interactions [13].

A flow of 5% Hydrogen in Nitrogen, maintained at a flow rate of 20 ccm/min, was used as the reducing gas. Hydrogen consumption was monitored by measurement of the thermal conductivity (TC) of the effluent gas. In this method, a ramp of 10°C/min was used. The temperature at the peak maximum ( $T_{max}$ ) and the temperature at the onset ( $T_{onset}$ ) in TPR profiles were used as measures of the reducibility of these iron catalysts [13].

The TPR profiles are quantified by integrating the peak areas. TPR peaks corresponding to transformations of  $Fe_2O_3 \longrightarrow Fe_3O_4$  and  $Fe_3O_4 \longrightarrow \alpha\text{-Fe}$  (iron carbide) [13].

1) At 230°C

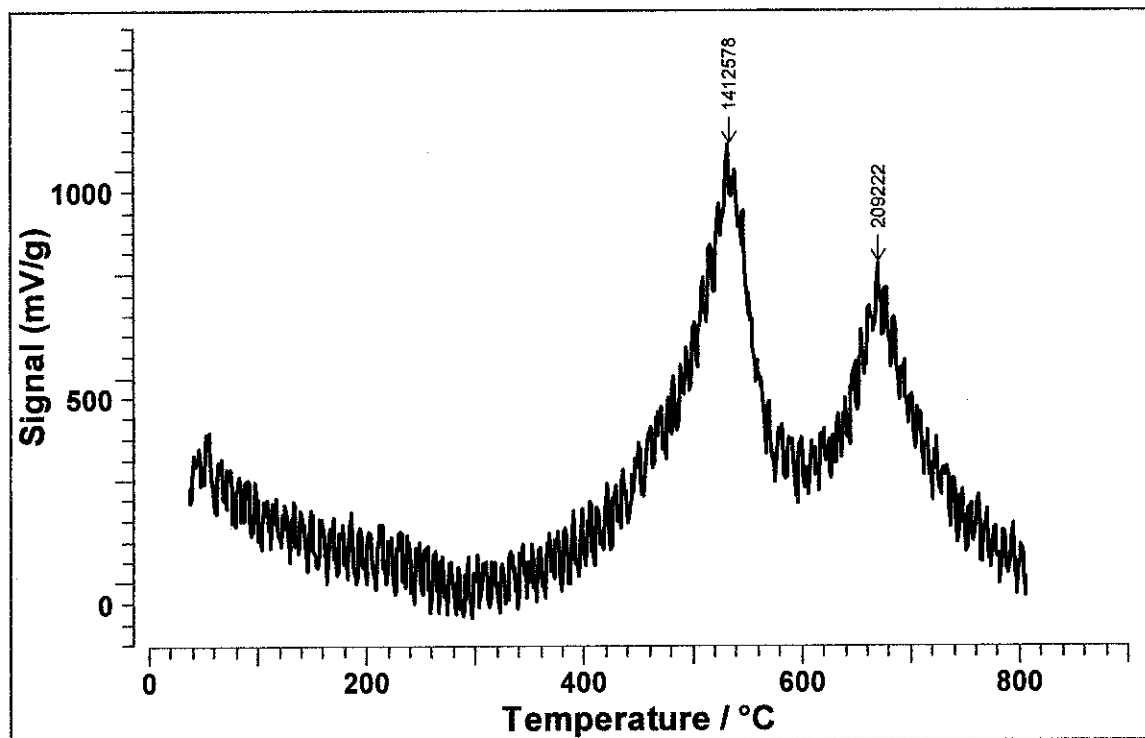


Figure 13: TPR profile of Fe/SiO<sub>2</sub> nanocatalyst synthesized at 230°C

2) At 250°C

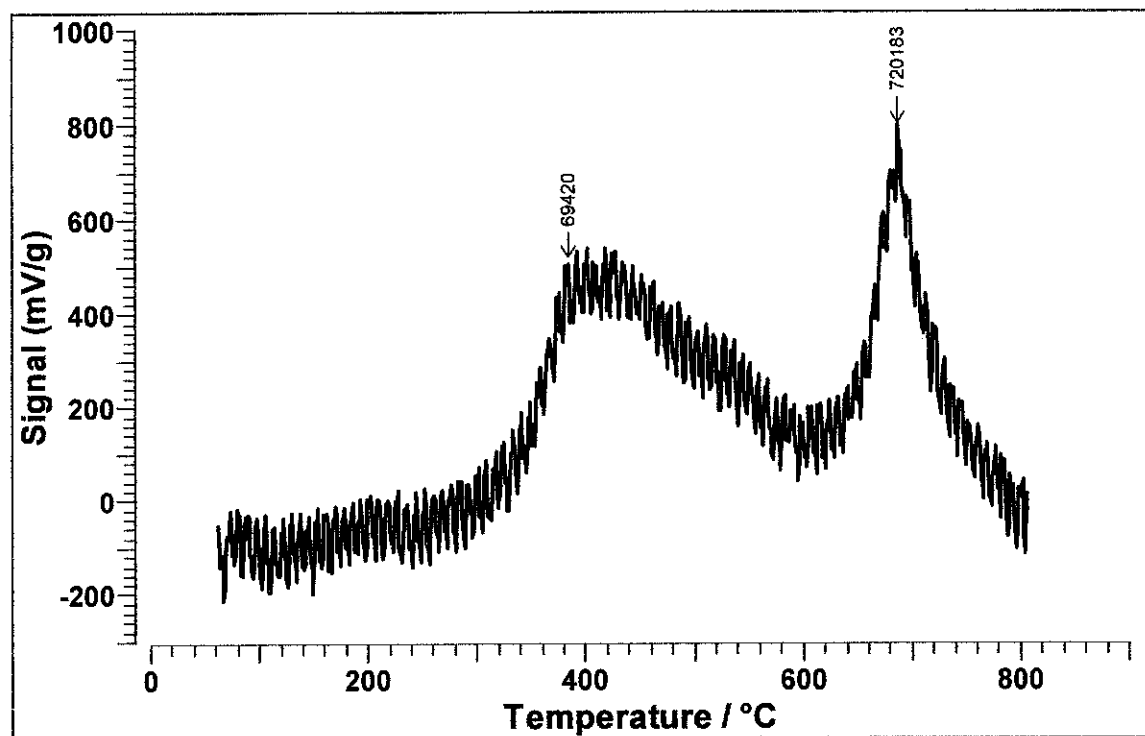
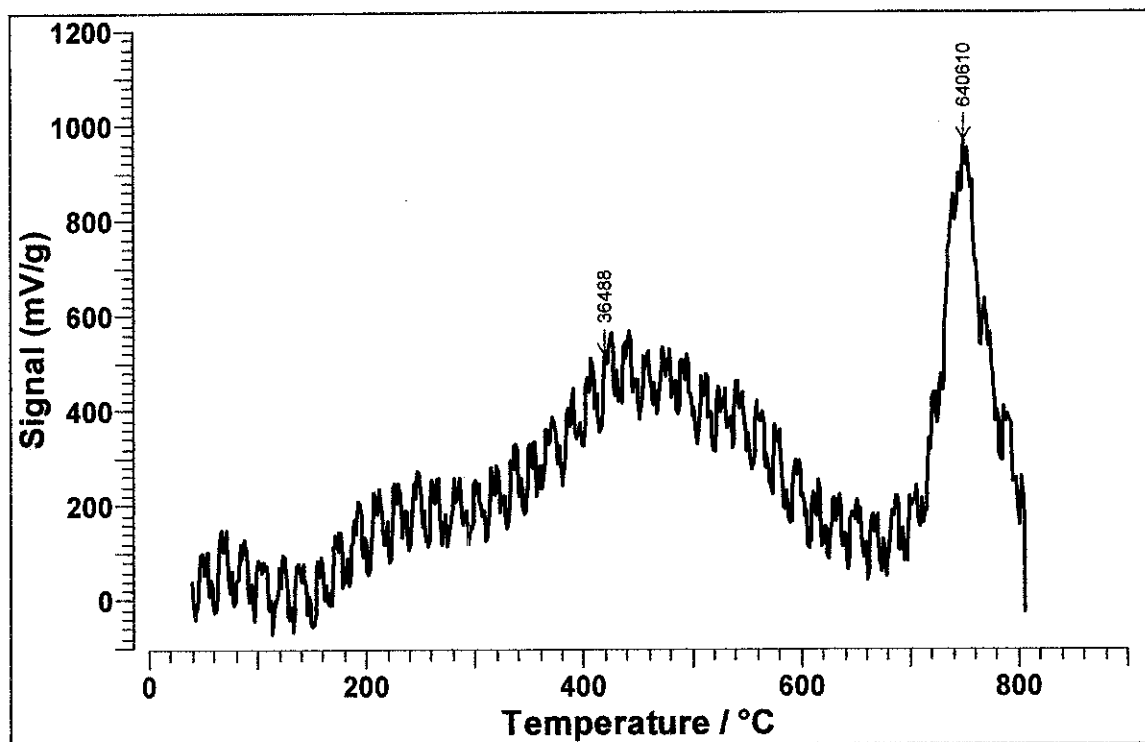


Figure 14: TPR profile of Fe/SiO<sub>2</sub> nanocatalyst synthesized at 250°C



3) At 260°C



**Figure 15:** TPR profile of Fe/SiO<sub>2</sub> nanocatalyst synthesized at 260°C

## 4.2 DISCUSSIONS

### 4.2.1 Sample Charging

All the images from FESEM are not clear and too small this is because of the sample charging. The sample charging is caused by the non conductive specimens that tend to charge when scanned by the electron beam, and this causes scanning faults and other image artifact. The sample must be electrically conductive, at least at the surface and electrically grounded to prevent the accumulation of electrostatic charge at the surface. The sample should be coated with an ultrathin coating of electrically conducting material that is commonly gold. The coating will prevent the accumulation of static electric charge on the specimen during electron irradiation. But for Fe/SiO<sub>2</sub> nanocatalyst, the sample cannot be coated by the ultrathin layer of gold because it will give the unclear image of the iron on the silica support. Therefore, for these samples, the FESEM is operated at low voltage which is 5.00kV. The low voltage FESEM of non-conducting specimens can be operationally difficult to accomplish in a conventional FESEM. Thus the images produced are not clear and cannot be magnified. In order to ensure the existence of the iron particles on the silica support, Temperature-Programmed Reduction (TPR) will be used for testing.

### 4.2.2 Agglomeration of SiO<sub>2</sub>

For this project, commercial SiO<sub>2</sub> spheres were used due to time constrain to synthesize the SiO<sub>2</sub> spheres. The BET surface area for commercial SiO<sub>2</sub> spheres is higher compared to the synthesized SiO<sub>2</sub> spheres. The BET surface area for synthesized SiO<sub>2</sub> is 27 m<sup>2</sup>g<sup>-1</sup> and the cumulative pore volume is 0.1 cm<sup>3</sup>g<sup>-1</sup> compared to commercial SiO<sub>2</sub> spheres which is 120 m<sup>2</sup>g<sup>-1</sup>. Agglomeration of the SiO<sub>2</sub> is due to the high BET surface area. The structure of the sample with larger specific surface area was changed is higher than that of the sample with smaller specific surface area [12].

### 4.2.3 TPR profile for the catalyst

The bulk phase reduction behavior of the catalysts is studied by H<sub>2</sub>-TPR. Figure 13, 14 and 15 illustrates the TPR spectra for Fe/SiO<sub>2</sub> colloidal method. The typical temperature range for iron catalyst first peak is 250-500°C and for second peak is between 600°C and 800°C [14,15].

From Figure 13, 14 and 15, it can be observed that the reduction process in H<sub>2</sub> occurs in two distinct stages in the temperature range of 350°C-800°C, as most of the iron-based catalyst. The first stage is ascribed to the transformation of Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub> [14,15]. It is also discovered that the first stage can be further divided into two peaks: the first peak corresponds to the reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>, and second peak corresponds to subsequent reductions of Fe<sub>3</sub>O<sub>4</sub> to FeO [15]. The reduction temperature for all sample are summarized in the table.

**Table 2:** Reduction temperatures of Fe/SiO<sub>2</sub> nanocatalyst at different reaction temperature

Fe/SiO <sub>2</sub> catalayst at	Reduction temperature (°C)	
	Fe <sub>2</sub> O <sub>3</sub> → Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub> → α-Fe
230°C	534	671
250°C	385	688
260°C	421	750

The reduction temperature for all catalyst samples are agrees with those reported in the literature [14,15].

## CHAPTER 5

### ERROR AND RECOMMENDATION

#### 5.1 ERROR

##### 5.1.1 HUMAN ERROR

- Weighing the chemical compound
  - There are some accuracy errors during weighing the chemical compound. This is due to the small decimal number of the chemical compound that needs to be weight.
- Nitrogen Flow
  - There is no regulator with flowrate indicator for the Nitrogen gas. The flow of the Nitrogen gas is based on the bubbles that come out from the tube when dipped into a beaker of water. There is possibility of the Nitrogen flow is too high.

##### 5.1.2 EQUIPMENT ERROR

- Bath Sonicator
  - The bath sonicator temperature tends to fluctuate and keep on increasing. The desired temperature for the bath sonicator is 30°C but the temperature tends to increase up to 50°C.
- Heating Mantle
  - Not enough heat supplied to reach the desired temperature. The temperature cannot reach more than 260°C.
- Furnace
  - Temperature tends to fluctuate and the timer is not function. There is no air flow for this furnace which is not suitable for the sample calcinations.
- FESEM
  - Sample charging.

## 5.2 RECOMMENDATIONS

### 1. Nitrogen Gas Regulator

- Put regulator with flow rate indicator to ensure the Nitrogen flow during synthesis is low. This is important in order to produce well distributed iron particles on the silica support and to avoid agglomeration.

### 2. Sample Calcinations

- The type of furnace used during calcinations is important. Furnace with air flow such as tubular furnace is recommended. This is because during calcinations volatile compound from the sample will evaporate and agglomerate at the top part of the furnace. When the furnace cooled down, that volatile compound will fall down and settle at the sample again. This will cause contamination to the sample and the sample not well dried.

### 3. Transmission Electron Microscopy (TEM)

- In order to get the clear view of the size and distribution of iron on the silica support, the use of TEM is suggested.

## **CHAPTER 6**

### **CONCLUSION**

In summary, there are various synthesis methods to prepare iron nanoparticles such as colloidal, reverse microemulsion and sol-gel method. In this project, it will only focus on the colloidal method because by using colloidal method the size structure sensitive crystal that can be produced is between 8-12 nm iron which is suitable for FT synthesis. The characterization of the nanoparticles can be vary by changing three parameters which are aging time, temperature and ratio between surfactant and precursor. By changing these parameters, a well distributed iron particles on the silica support will be produced.

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# APPENDIX

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)														●

Mid-Semester Break

● Suggested milestone  
 ■ Process