PREPARATION OF Co/SiO_2 SPHERICAL MODEL NANOCATALYST USING REVERSE MICROEMULSION METHOD

by

SIVERANJINI RAJAN THIRAN

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

JANUARY 2010

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Preparation of Co/SiO_2 Spherical Model Nanocatalyst Using Reverse Microemulsion Method

by

Siveranjini Rajan Thiran

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,

(Assoc. Prof. Dr. Noor Asmawati Binti Mohd Zabidi)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2010

ACKNOWLEDGEMENT

I would like to thank numerous individuals for their tremendous support in performing this project. Deepest gratitude goes to my Final Year Project (I and II) supervisor, Dr. Noor Asmawati for her tremendous support and technical guidance throughout the experimental process and preparation of this report.

I would also like to thank all the lecturers of Chemical Engineering Program of UTP, who have been very helpful and resourceful while guiding me. My deepest gratitude is also dedicated to the postgraduate student, Ms.Aishah for her guidance and assistance, through which without, this study might not have come up to the completion level.

I would like to also extent my gratefulness to all the technicians at Block 3, 4 and 5 for their kindness in assisting me to operate the laboratory equipments throughout the project and as well all my friends who have directly or indirectly aided me in completing this project.

ABSTRACT

Fischer-Tropsch (FT) synthesis is one of the components of Gas-to-Liquid (GTL), Biomass-to-Liquids (BTL) and Coal-to-Liquids (CTL) technologies. Catalyst is a very important part of a Fischer-Tropsch process. This FT process also uses Cobalt as the catalyst. Cobalt is usually favored for lower temperature Fischer-Tropsch synthesis because it has higher stability, higher per single pass conversion, higher yield, smaller negative effect on water conversion and higher resistance to erosion compared to iron. There are few ways of preparing the Cobalt catalyst; colloidal method, impregnation method, deposition-precipitation method, sol-gel method and also microemulsion method. The most common method is incipient wetness impregnation using cobalt salt.

There are many studies, methods and techniques that have been developed to synthesize catalysts with the catalytically active material in the required size range. Catalyst performance can be improved by tuning the crystallite size distribution for the required reaction. In order to achieve the desired size, it needs a control of the crystallite size distribution and also understanding of the fundamental principles and process variables in the synthesis of these materials. Microemulsion method allows formation of particles in nano-size range with a small size distribution. The water-to-surfactant molar ratio (W_0) can also be changed to vary the size of the reversed microemulsions by using the water-in-oil microemulsion method. This method can be used to control the particle size.

The catalyst is prepared using reverse microemulsion method and studies were conducted on the effect of various amount cobalt loading content and various calcination temperatures. Apart from that, several techniques are used to characterize the properties of the prepared catalyst which includes TPR, FESEM and XRD. Experimental results indicated that high calcination at 450°C and higher cobalt loading at 6wt% produces good nanocatalyst.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Fischer-Tropsch (FT) synthesis is one of the components of Gas-to-Liquid (GTL), Biomass-to-Liquids (BTL) and Coal-to-Liquids (CTL) technologies. This process produces clean alternative fuel from sources such as biomass, natural gas and coal. FT synthesis produces hydrocarbon from syngas. This reaction takes place at 473-623K. [1]

Catalyst is a very important part of a Fischer-Tropsch process. Usually, for the production of lighter hydrocarbons and olefins, iron catalysts are used. This FT synthesis takes place at a high temperature and is necessary for the conversion of syngas with low H_2/CO ratio. A more recent type of FT synthesis needs lower temperature to take place. This FT synthesis is useful in the production of middle distillate fractions and waxes. This FT process also uses Cobalt as the catalyst. Cobalt is usually favored for lower temperature Fischer-Tropsch synthesis because it has higher stability, higher per single pass conversion (60%-70%), higher yield, smaller negative effect on water conversion and higher resistance to erosion. [1]

1.2 Problem Statement

Cobalt is a transition metal that is used as a catalyst in Fischer-Tropsch synthesis process. There are few ways of preparing the Cobalt catalyst; colloidal method, impregnation method, deposition-precipitation method, sol-gel method and also microemulsion method. The most common method is incipient wetness impregnation using cobalt salt. However, when using these methods, the desired nano size of the catalyst particle could not be achieved. In this project study, reverse microemulsion method will be focused on to get the nanocatalyst in desired size.

1.3 Objective and Scope of Study

The objectives and scope of study of this project are:

- Preparing Co/SiO_2 spherical model nanocatalyst using reverse microemulsion method.
- Characterization of spherical Co/SiO_2 model catalyst.
- Performing experimental analysis on the topic.
- Collecting, analyzing and documenting data obtained.

CHAPTER 2

LITERATURE REVIEW AND/OR THEORY

2.1. Fischer-Tropsch Process

The most important reaction in the Fischer-Tropsch process is the formation of alkanes. The most important reactions are[2]:

$nCO + 2nH_2 \rightarrow CnH_2n + nH_2O$

$(2n+1)\underline{H_2} + n\underline{CO} \rightarrow \underline{C_nH_{(2n+2)}} + n\underline{H_2O}$

$CO + H_2O \rightarrow CO_2 + H_2$ (Water gas shift reaction)

This process is also known as hydrogenation of carbon monoxide to hydrocarbons.

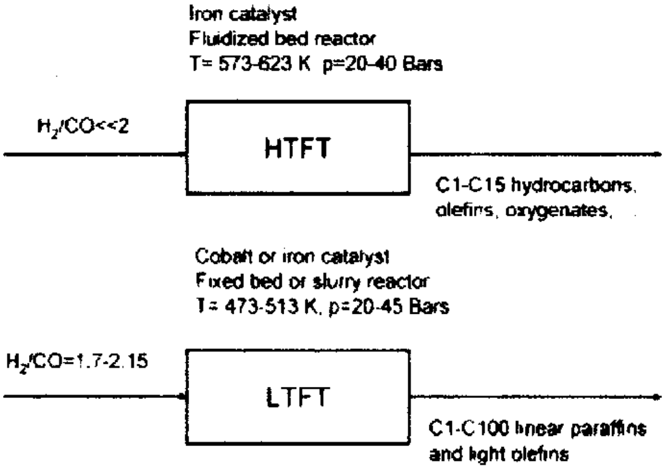


Figure 2.1: High- and low-temperature FT processes [1]

Generally, all the elements of group 9 from the periodic table have evident activity in the hydrogenation of carbon monoxide to hydrocarbons.[1] However, the most suitable catalysts were narrowed down to cobalt and iron as they appear economically reasonable on an industrial scale. Controlling selectivity is also an important aspect of Fischer-Tropsch Synthesis (FTS) catalyst development. Cobalt catalyst has a high activity for hydrogenation and tends to produce linear alkanes[2] The productivity at higher conversion is more significant with cobalt catalysts compared to other metals. Oxide supports are mostly used for cobalt catalysts.[3] However, cobalt catalyst functions at a very constricted temperature and pressure range. This means that a slight raise in temperature or pressure can cause drastic increase in methane's selectivity.

The history of the Fischer-Tropsch Synthesis dates back to 1902 where methane was synthesized from hydrogen and carbon dioxide. The first catalyst that was used is nickel and later cobalt was used. The first catalyst that produced higher hydrocarbons at atmospheric pressure was a mixture of iron oxide and zinc oxide. However, it found later that a mixture of cobalt oxide and chromic oxide is more active. Nickel was also found to be an active component as a catalyst. Iron catalysts show high water shift activity and are preferred when synthesis gas from coal with a low H_2/CO ratio is used.

Cobalt and ruthenium catalyst have a low water shift activity. Cobalt is by far the cheaper of the two metals. Nickel catalyst is not appropriate because of high methane selectivity.

Today, the researches on Fischer Tropsch Synthesis are focused more on catalysts, reactor design and process development. In the past years, new techniques and methods for catalyst surface have been derived. This is very important in getting better knowledge of the catalyst properties and structure-function relationships. A better understanding of the mechanisms will make it easier to design desired catalyst. [18]

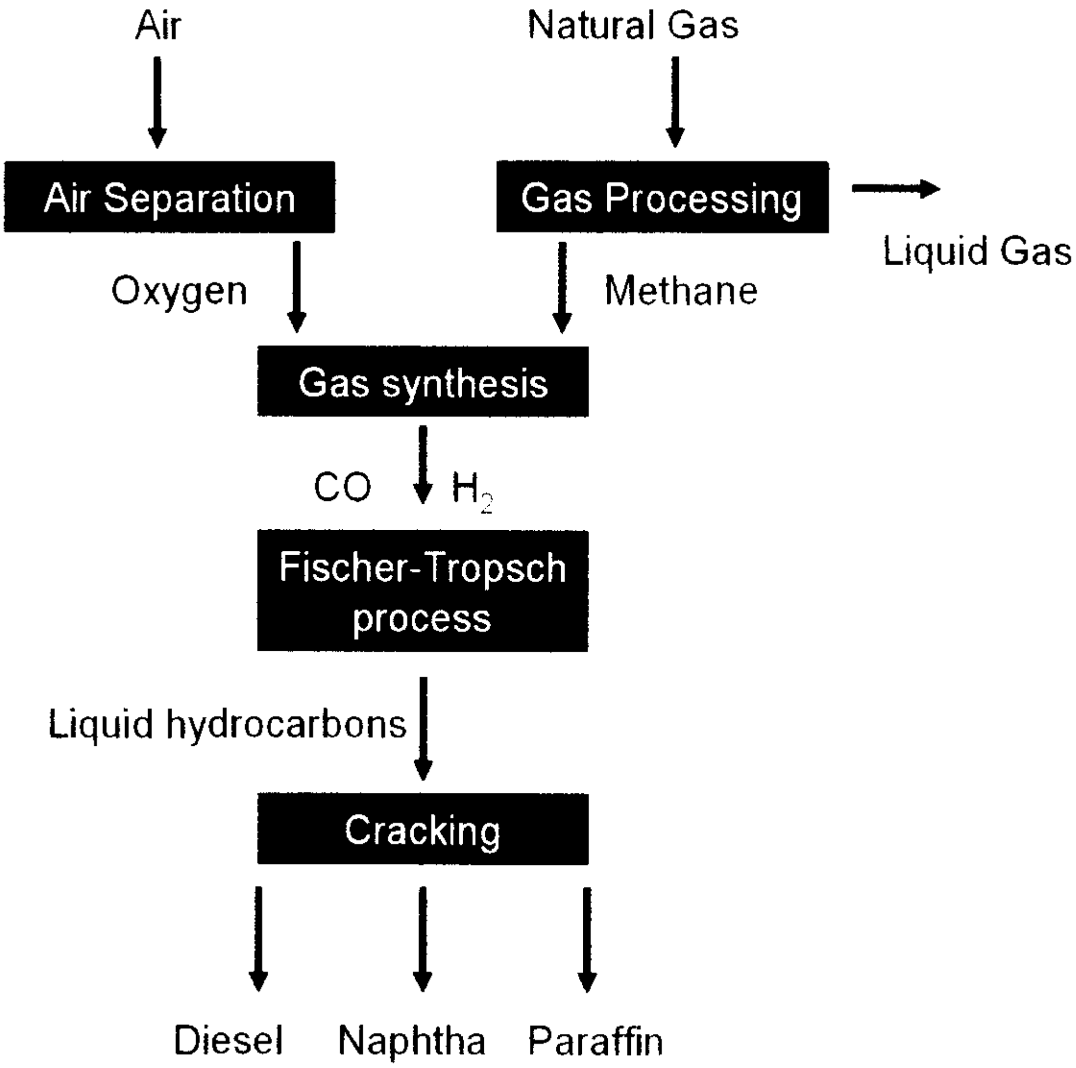


Figure 2.2 : Fischer-Tropsch process block diagram

2.2. Cobalt

COBALT			
Name	Cobalt	**Standard State**	Solid at s.r.t
Symbol	Co	**Standard Atomic Weight**	58.93 g.mol^{-1}
Atomic Number	27	**Element Category**	Transition Metal
Group in Periodic Table	9	**Density**	8.9 g.cm^{-3}
Group Name	None	**Electron Configuration**	[Ar] $4s^2 3d^7$
Block in Periodic Table	D-block	**Color**	Grey metallic
Melting Point	1495 °C	**Boiling point**	2927 °C
Thermal Conductivity	100 W m^{-1} K^{-1}	**Coefficient of Liner Thermal Expansion**	13.0 x 10^{-6} K^{-1}
Specific Heat @ 20°C	0.456 J/g mol	**Evaporation Heat**	389.1 kJ/mol
Fusion Heat	15.48 kJ/mol	**Heat of Vaporization**	377 kJ/mol

Table 2.1: basic information about and classifications of cobalt. [19]

It is alloyed with iron, nickel and other metals to make Alnico, an alloy of unusual magnetic strength with many important uses. Stellite alloys, containing cobalt, chromium , and tungsten , are used for high-speed, heavy-duty, high temperature cutting tools, and for dies.

Cobalt is also used in other magnetic steels and stainless steels, and in alloys used in jet turbines and gas turbine generators. The metal is used in electroplating because of its appearance, hardness, and resistance to oxidation.

The salts have been used for centuries to produce brilliant and permanent blue colors in porcelain, glass, pottery, tiles, and enamels. It is the principal ingredient in Sevre's and Thenard's blue. A solution of the chloride is used as a sympathetic ink. Cobalt carefully used in the form of the chloride, sulfate, acetate, or nitrate has been found effective in correcting a certain mineral deficiency disease in animals. [20]

2.4. Nanoparticles

A nanoparticle is defined as a particle having one or more dimensions of the order of 100nm or less. [23] It is also said that the properties that differentiate nanoparticles from the bulk material can be developed at a critical length scale which is under 100nm. The properties of nanoparticles are different compared to the properties of the bulk material.

There is not a definite boundary between the definitions of nanoparticles and non-nanoparticles. It is more difficult to define a different shape nanoparticle, for example carbon nanotubes. Usually these materials are grown into long tubes which may be argued as not nano-sized. However, the diameter of these tubes is often nano in size.

Many of these nanomaterials are made directly as dry powders, and it is a common myth that these powders will stay in the same state when stored. In fact, they will rapidly aggregate through a solid bridging mechanism in as little as a few seconds. Whether these aggregates are detrimental will depend entirely on the application of the nanomaterial.

If the nanoparticles need to be kept separate, then they must be prepared and stored in a liquid medium designed to facilitate sufficient interparticle repulsion forces to prevent aggregation. In catalyst studies, it is very essential to synthesize nanosize particles and controlling their properties. Furthermore, the size of the nanosized particles can affect the electronic and optical properties.[24] There are many methods that are being studied for spherical ultrafine particles. These methods include colloids, polymers and micelles which can be used to control aggregation.

Recent studies showed that aqueous synthesis can lead to growth control which can be used to prepare fine particles. Solution-based particle synthesis can result in higher levels of chemical homogeneity. Besides that, in a solution system, mixing of the starting materials is achieved at the molecular level which is vital in preparation of multi-component oxides. The size of the micelles particles are controlled by varying the ratio of the water to surfactant.

2.5. Reverse Microemulsion Method

Microemulsion is a system of water, oil and surfactant liquid. The differences between emulsions and microemulsions are shown at the table below:

Emulsions	**Microemulsions**
High shear condition is required for formation	Can be formed by simple mixing
Common size of particle 1 to 10 μm range (radius)	Particle size with radius 10 nm range.
Colloidally instable	Colloidally stable
Thermodynamically unstable	Thermodynamically stable

Table 2.2: Differences between emulsions and microemulsion.[4]

Microemulsions are thermodynamically stable, have low viscosity, isotropic dispersion of aqueous and hydrocarbon liquids (oil) that are stabilized by an interfacial film of surfactant molecules.[4] There are three types of microemulsions; oil-in-water (O/W) where water is the continuous medium, water-in-oil (W/O) where oil is the continuous medium, and water and oil continuous microemulsion where both exist in equal amount. Water-in-oil microemulsion is also known as reverse microemulsion. Microemulsions are often monodispersed spherical droplets.

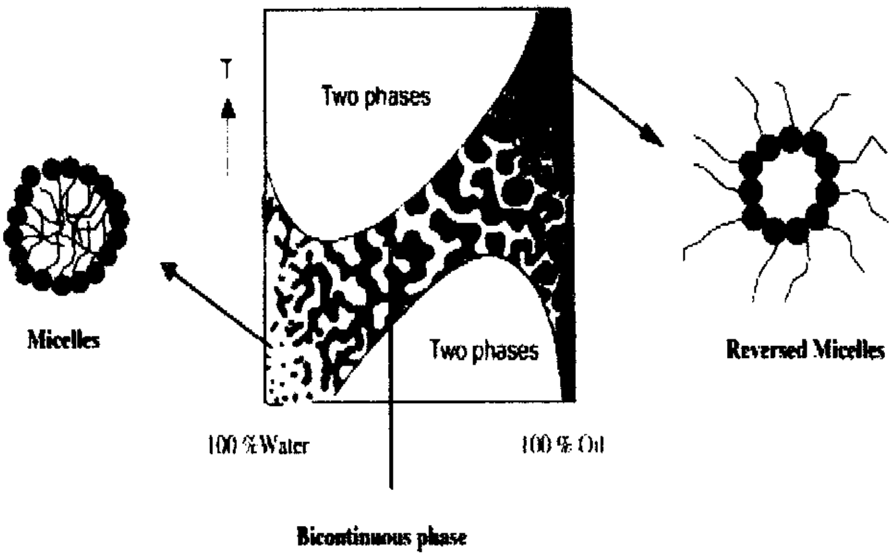


Figure 2.3: The microscopic structure of a microemulsion at a given concentration of surfactant as function of temperature and water concentration. [7]

The type of the microemulsion (W/O) or (O/W) depends on the composition of microemulsion (the volume fraction of water and oil) and also the character of surfactants (surfactant interfacial film).[4] Droplets of water-in-oil microemulsions (reversed microemulsion) form when water fraction is lower den oil and oil in water microemulsions form when oil volume fraction is lower than water volume.

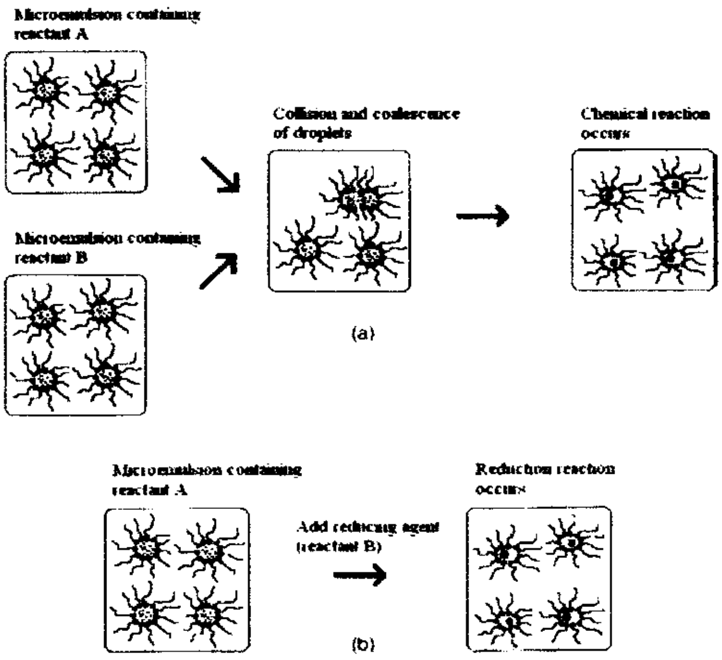


Figure 2.4: Modes of particle preparation from microemulsion: (a) mixing of two microemulsions; (b) direct addition of precipitating (reducing) agent to the microemulsion[3]

2.6. Water-in-Oil Microemulsion Method for Nanocatalyst

Catalyst often [6] consists of small metal particles distributed on an inert support. Metal particle is the vital component of the catalyst. They are responsible for the activity and selectivity of the catalyst. Size of the metal particles usually will affect the activity of the catalyst. From previous studies it said that catalysts with small particles will give high activity. This is because a large amount of atoms are available on the metal particles' surfaces. Besides that, for some type of catalysts, the selectivity depends on the nature of the catalytic sites on the surface of the metal particles. The type of sites present is varied depending on the particle size. There are also structure sensitive reactions where the activities depend on metal size particle.

Microemulsion method[6] allows formation of particles in nano-size range with a small size distribution. The water-to-surfactant molar ratio (W_0) can also be changed to vary the size of the reversed microemulsions by using the water-in-oil microemulsion method. This method can be used to control the particle size.

There are also few catalytic processes which use more or less homogeneous materials as catalysts. Usually they are metal oxides. For these processes, the catalytic activities are proportional to the specific surface area. In another word, the active stage of the catalyst is compromised of the entire surface area of the material. Preparation of the metal oxide catalyst using the reverse microemulsion method has its advantages. This is because this method can have a better control of the composition of the material on nanoscale level and may also increase the specific surface area.

Generally, for Fischer-Tropsch Synthesis, the most common method to prepare supported catalyst is the wet impregnation method. Usually, the support powder is impregnated by an aqueous solution of metal precursors. This is to fill the pores of the support. Next, the impregnated support material is dried, calcined and reduced. The metal particles are formed in the pores of the support. [6]

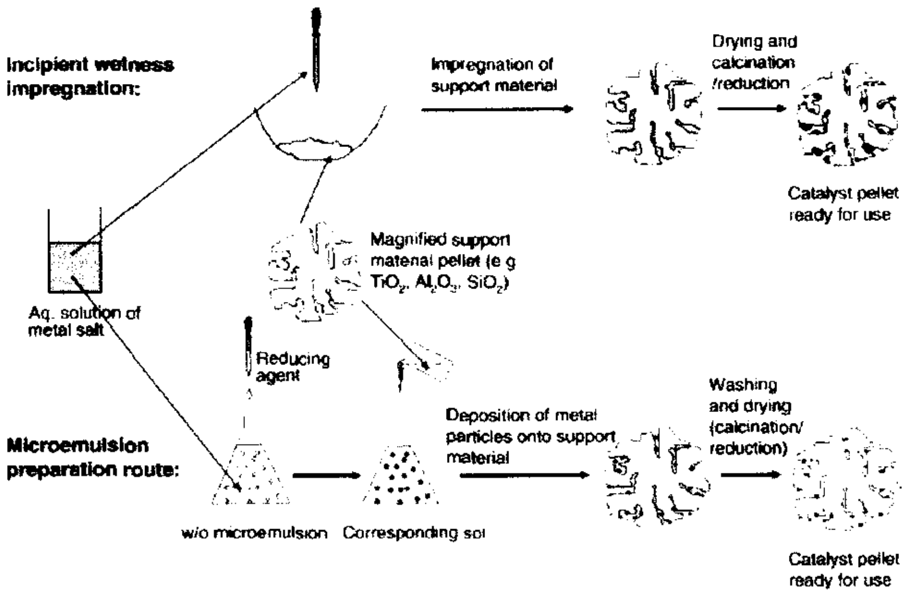


Figure2. 5 : Schematic presentation of two preparation routes for supported metal catalyst [6]

By using the microemulsion method for the catalyst preparation, formation of the metal particles occurs at room temperature in the microemulsion after the addition of a reducing agent. Next, the particles which were formed are deposited onto the support from the microemulsion. The downside of the impregnation technique is the size of the metal particles formed will be controlled by the pore size and structure of the support. This often leads to a broad size distribution. However, for microemulsion route, the size of the particles will be based on the nature of the microemulsion, which usually results in fine particles size allocation.

There are various after-treatments used needed on the microemulsion prepared catalyst depending on the application of the catalyst. They include calcination, reduction and washing. Catalysts that are to be used at higher temperatures have to be completely removed of surfactant by washing and calcination. This should be done so that the excess decomposed surfactant does not cover the catalysts active sites. Besides that, in low-temperature liquid-phase catalytic processes, the surfactant should also be removed so that reactant molecules reach the active sites of the catalyst. However, the selectivity of the desired products has improved when the surfactant is attached to the metal particles in some cases.

Normally, metals will be oxidized if contacted with air after microemulsion preparation method. There is more probability of an oxide to form if calcination process in air is done. So, there will be a need for extra reduction before the catalytic process if the metallic state playa a major role in the activity. Precipitation method is favored for the preparation of bulk oxide materials in microemulsions. Usually, the conventional precipitation in water solution is used. Compared to the conventionally prepared precipitate, extra washing procedure is needed for microemulsion method. This extra washing is needed to remove the surfactant. Then, the materials are dried and calcined resulting in formation if the specific oxide.

2.7. Catalyst Characterization

There are various ways of characterizing the catalyst sample that is obtained. Among them are Temperature-programmed Reduction (TPR), Transmission Electron Microscope (TEM), Field Emission Scanning Electron Microscope (FESEM), and X-Ray Diffraction (XRD).

2.7.1. Temperature-programmed Reduction (TPR)

Temperature-Programmed Reduction (TPR) is an experimental method for the investigation[7] of gas-solid reactions for the characterization of solid materials. Often, this technique is used for competent reduction conditions of heterogeneous catalysis. TPR method is straightforward and simple. A container, usually a U-Tube is loaded with the solid material or specific catalyst. Then, appropriate gas is flowed through the container. Firstly, temperature is set to low so there are practically no reactions taking place. Next, temperature is then increased at a constant rate. When this happens, the reaction rate also increases but depending on the activity [7] and the actual degree of reduction of the solid material. This will take place until the material is entirely reduced.

Concentration measurement of the gaseous reaction products is generally measured at the outlet with a high sampling velocity. Usually the experiment's method is repeated by changing the feeder gas composition or heating rates. TPR is known as a very reliable method; however the results can differ in a big range. This is maybe due to the variation of the composition and size of the particles because of the different preparation method, gas impurities and also variation of temperature ranges in the TPR method.

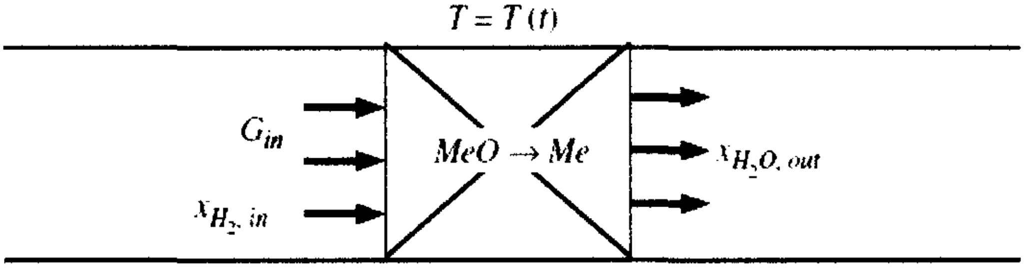


Figure 2.6: TPR Method in diagram.[7]

The data obtained from the TPR method is analysed using an ordinary differential equation:

$$\frac{dx}{dt} = k_o.\exp\left[-\frac{E_A}{RT}\right].f(x)$$

Where T, temperature is obtained from a linear function of time:

$$T = To + b.(t - to)$$

When using temperature programmed analysis, the catalyst can be studied under conditions that are close to the catalytic reaction system conditions. The reduction rate is measured continuously by monitoring the composition of the reducing as at the outlet of the reactor. Perks appear when the reduction rate passes through a maximum value. The interpretation of the TPR spectra is usually confined to the discussion of peak maximum temperatures, the number of peaks and to the total reactant consumption from which the extent of reduction can be determined. Shift in peak temperatures depend on metal support interactions, metal-metal oxide interactions and also on metal-oxide particle size. [24]

Few assumptions are to be made in the TPR method: [7]

- The solid material is made of oxides of different metals and they are being reduced separately in a single reduction step without depending on each other.
- The solid material is being reduced in a single reaction step only.
- In TPR method the next step will only take place after the previous one is completed as a metal oxide will be reduced in several steps.

The data obtained are then used to make the TPR curves.

2.7.3. Field Emission Scanning Electron Microscope – FESEM

FESEM is a microscope where minuscule structures as small as 1 nanometer can be viewed.[15] FESEM works with electrons which are generated in an emission. Then, these electrons are accelerated under the power of a strong electrical voltage gradient which is called the field. An electron beam is then formed from an electron beam. This beam is the used to scan the object and there is also production of secondary electrons by interaction with the atoms at the surface of the object. These [illegible] the

2.7.4. X-Ray Diffraction –XRD

X-Ray diffraction (XRD) [16] is a rapid analytical technique primarily used for phase identification of a crystalline material and can be used to provide information on unit cell dimensions. XRD is built from constructive interference of monochromatic X-rays and a crystalline sample. A cathode ray tube is often used to produce the X-rays. These rays are then filtered to produce monochromatic radiation, concentrated and focused towards the sample. When the incident rays touches the sample, a diffracted ray is produced. These diffracted rays are then detected, processed and analysed.

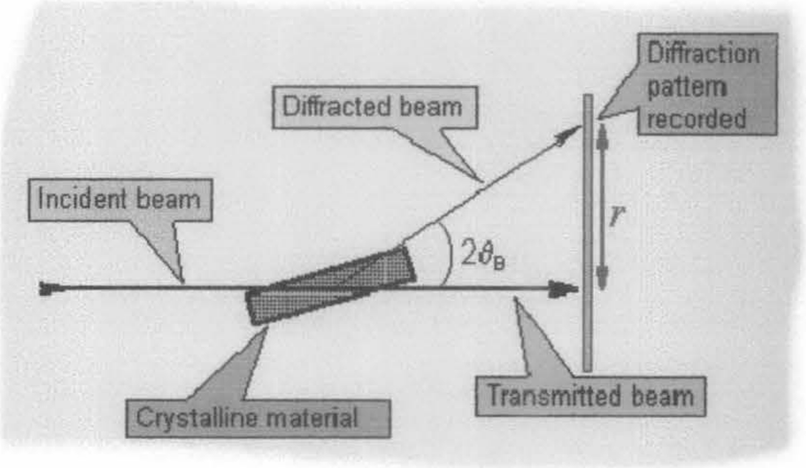


Figure 2.7: XRD Technique. [17]

XRD is generally used to identify unknown crystalline materials and also the characterization of crystalline materials. Besides that, XRD can also be used in determining unit cell dimensions and the measurement of sample purity. XRD method is a very short and powerful method in identification of an unknown mineral. Most of the time, this method gives indefinite mineral determination and the data interpretation is straight forward. Only a minimal sample preparation is required. However, for the identification on an unknown material, homogeneous and single phase is the best for this method. This method also requires a tenth of a gram material and need to be grounded into powder.

2.8. Expected Results from Literature Review

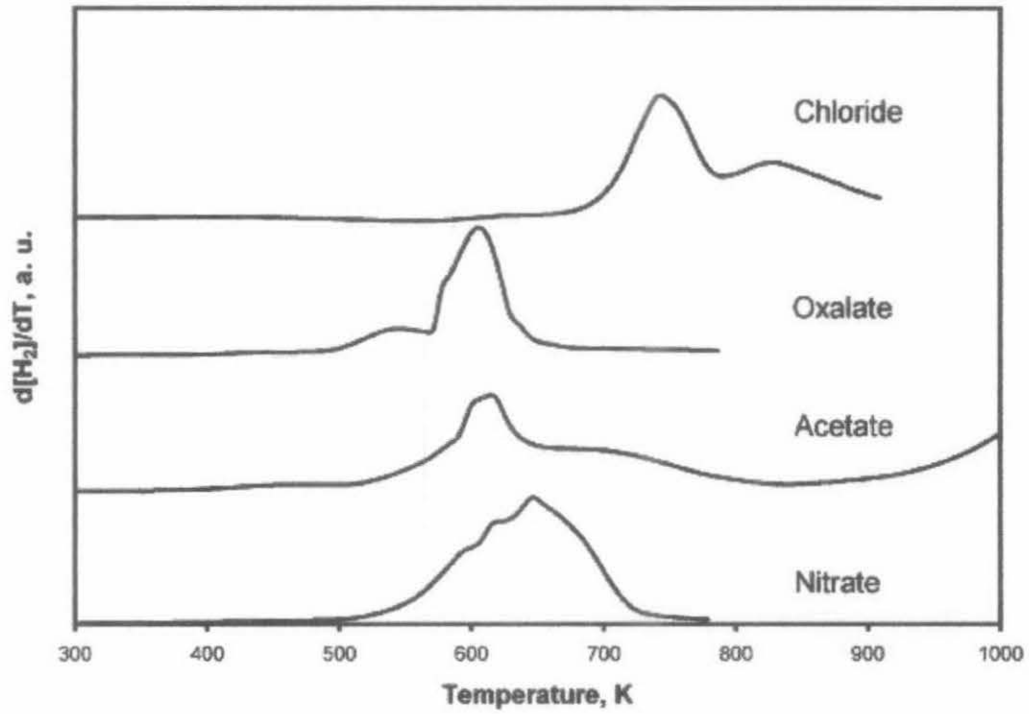


Figure 2.8: An example of TPR curve.[1]

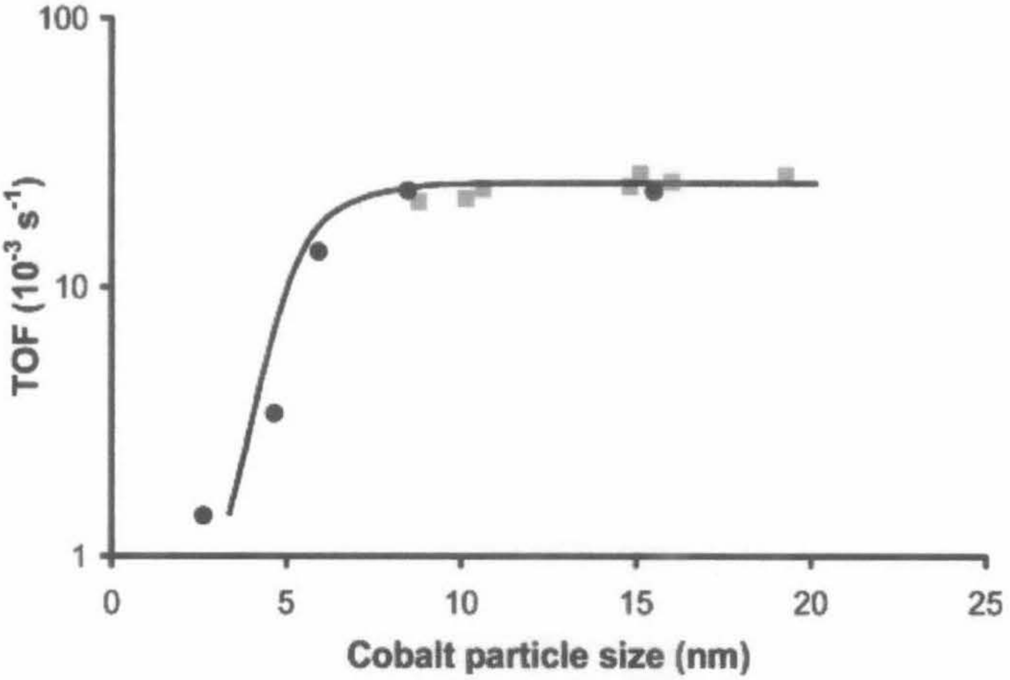


Figure 2.9: Influence of cobalt particle size on turnover frequency[1]

In some model system study, the effect of cobalt particles sizes on FT turnover frequency. From the result obtained, the turnover frequency is almost independent on cobalt particle size with sizes larger then 6-8 nm. When smaller cobalt particle sizes are used, Fischer-Tropsch reaction rates were lower and major changes in hydrocarbon selectivities were observed.

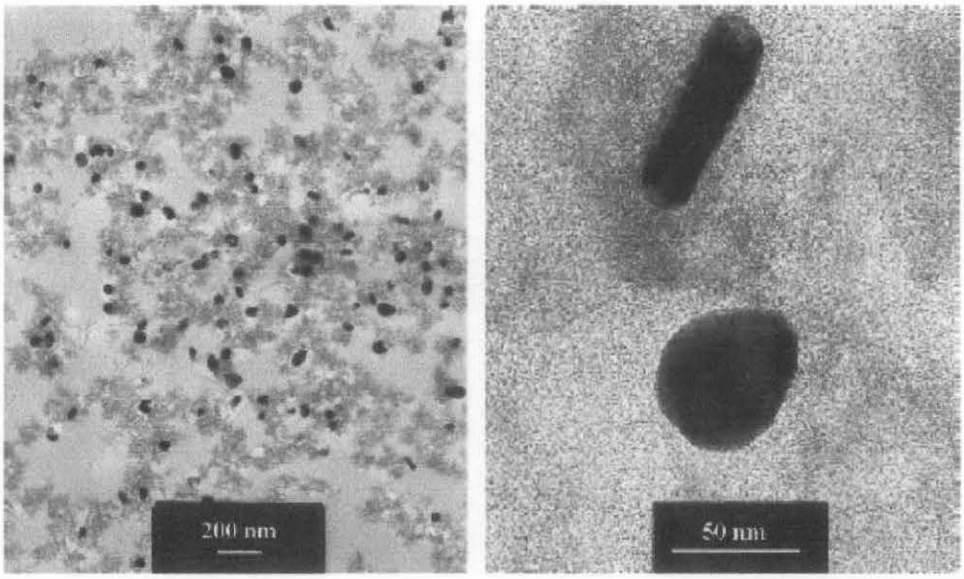


Figure 2.10: An example of image using the FESEM method.[8]

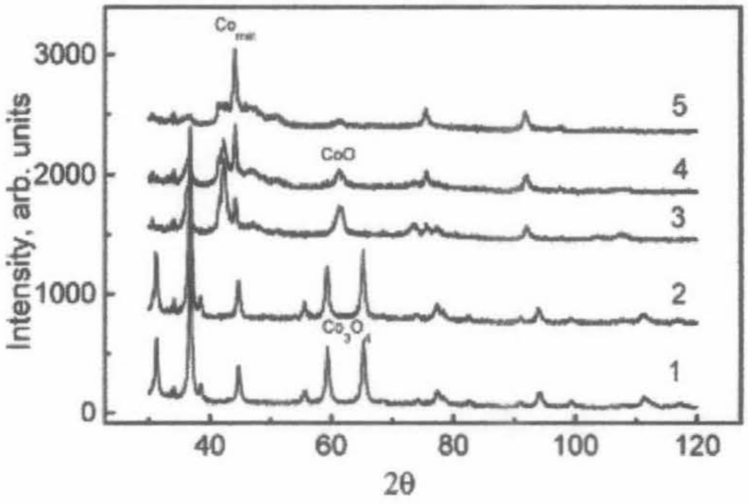


Figure 2.11: An example of XRD curve.[1]

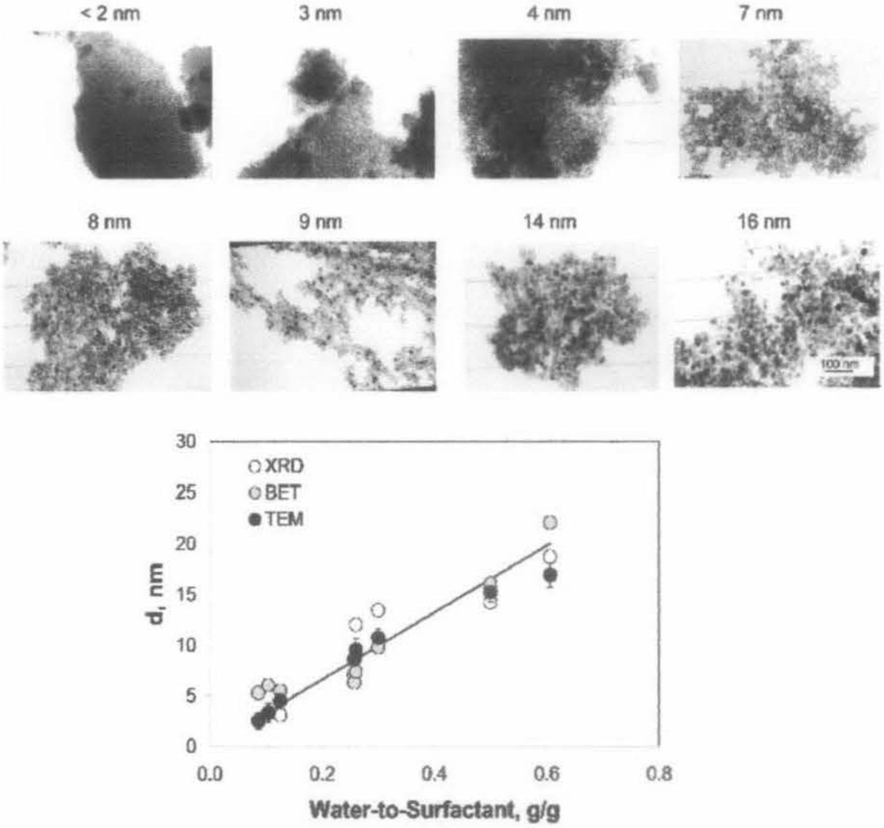


Figure 2.12: Effect of the water-to-surfactant ratio on the average volume-based crystallite size on unsupported Fe_2O_3 crystallites prepared by precipitation from reverse micelle solutions (scale identical on each photograph). [9]

Figure 12 shows the TEM micrographs of the calcined and reduced catalyst samples. In this study, Fe_2O_3 is used. The Fe crystallites are mainly found on the support material, and not as unsupported clusters, signifying that this method of crystallite deposition onto the support was successful. In general, a more homogeneous distribution of crystallites was observed with alumina as a support, especially in the samples containing small crystallites.

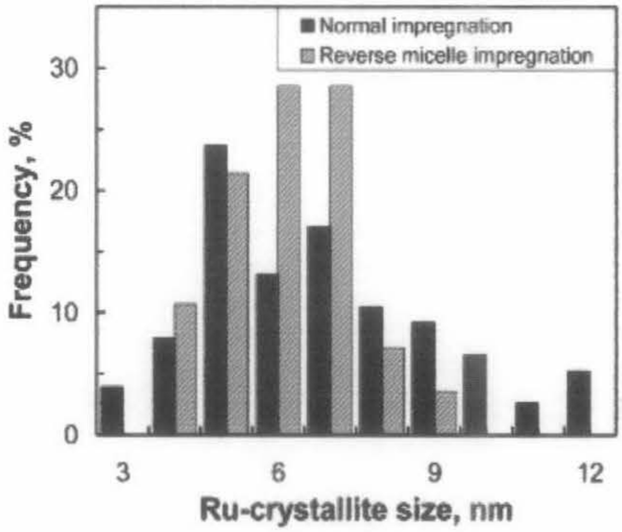


Figure 2. 13: Crystallite size distribution in calcined Ru/γ-Al_2O_3 catalysts prepared using a conventional impregnation technique (μ=6.9 nm; σ=2.3 nm; n=76) and impregnation of a reverse micelle solution (μ=6.1 nm; σ=1.2 nm; n=50). [9]

Figure 2.13 shows the crystallite size distribution in the calcined catalyst prepared using conventional impregnation and reverse micelle impregnation as determined as determined by counting the crystallites on TEM images. The catalyst prepared by conventional impregnation shows a wide crystallite size distribution. It may be assumed that the origin of the sharper crystallite size distribution results from the collision of microemulsion vesicles with the support and the consequent rapid uptake of ruthenium from the solution by the support.

CHAPTER 3

METHODOLOGY

Investigations of the preparation of Co/SiO_2 spherical model nanocatalyst using reverse microemulsion method are to be done. A detailed and thorough research will be made from the internet, journals, library and books to collect all available information on the topic. The collection of all data and information are essential in this project. Experiment on the effectiveness of the catalyst prepared by the microemulsion method will be done. Analysis will be carried out on the product obtained. The results of the analysis will be objectively compared with the already available data.

3.1 Research

Many important references were obtained from journals that were published by Science Direct website. After collecting journals, interpretations of the journal contents need to carry out in favor of to select the useful information.

3.2 Analysis

Various methods are to be used to analysis the catalyst that are obtained. Among them are, X-Ray Diffraction –XRD, Transmission Electron Microscope – TEM, Temperature-programmed Reduction (TPR) and Field Emission Scanning Electron Microscope – FESEM.

3.3. Method to be used in Preparation of Nanocatalyst

i. 2 g Co/SiO_2 nanocatalyst with cobalt loading of 2% is to be prepared.

ii. A microemulsion I (ME I) was prepared by first dissolving 8.89 g of AOT in 40.0 ml of n-heptane to form the first solution.

iii. Next, 1.2ml of H_2O and 6.0 ml of $Co(NO_3)_2$ containing 0.1975g of cobalt nitrate (2% loading) were added and the mixture is stirred vigorously to form ME I. A light pink mixture is formed.

iv. In a separate glassware, a microemulsion II (ME II). Similarly to ME I, 8.89 AOT is dissolved in 40.0 ml of n-heptane to form the second solution.

v. 3.2 ml of H_2O and 4.0 ml of hydrazine hydrate was then added to the second mixture. Then this mixture is stirred vigorously for 30 minutes to form ME II.

vi. Then, 1 ml of TEOS (Tetraethyl orthosilicate) was added to ME II and the mixture is stirred for 2 hours.

vii. A clear, colorless visible microemulsion is formed.

viii. 2 ml Tetrahydrofuran (THF) of is added to the mixture.

ix. Using a syringe, ME II was slowly added to ME I and the mixture is stirred for 24 hours.

x. Gradual color change of the mixture from light pink to rusty brown is observed.

xi. After 24 hours of stirring, the sample is then filtered twice using vacuum filter. During this, the remaining solid is washed few times with ethanol to wash away impurities.

xii. Next, the remaining solid is dried in an oven at 120^0C for 24 hours.

xiii. The dried sample is the grinded manually.

xiv. The dried sample is then calcined in a furnace for 4 hours at a temperature of 450^oC.

xv. Above steps are repeated by varying the cobalt loading, surfactant concentration and calcination temperature.

xvi. Characterizations of the catalysts by FESEM, XRD and TPR method.

xvii. The results are then analyzed.

Calculations

The amount of Cobalt metal used for 2 %wt to prepare 2g of catalyst:

$$\frac{2}{100} \times 2g = 0.04g$$

Hence Support (Silica) = 2g – 0.04g

= 1.96g

Therefore amount of $Co(NO_3)_2.6H_2O$:

$$\frac{0.04}{58.933} \times 291.03 = 0.1975g$$

The calculations are repeated for cobalt loading of 4%, 6% and 8%.

Cobalt Loading (%)	**Weight of Cobalt Nitrate (g)**
2%	0.1975
4%	0.3951
6%	0.5926
8%	0.7901

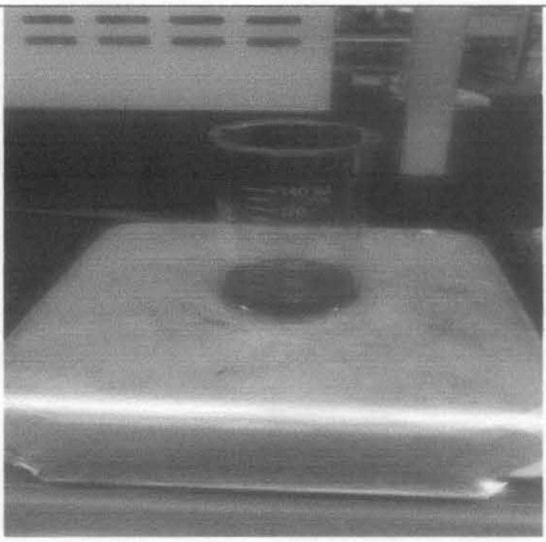
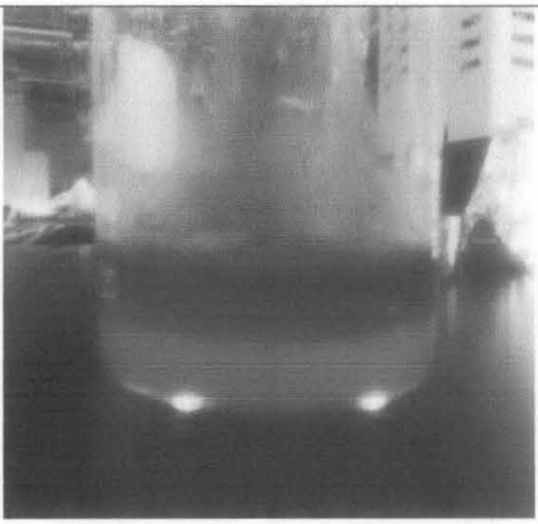
Table 3.1: Cobalt loading and the respective weight of cobalt in catalyst

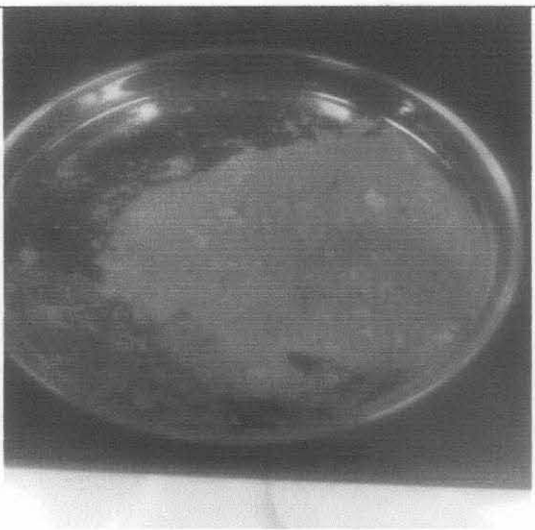
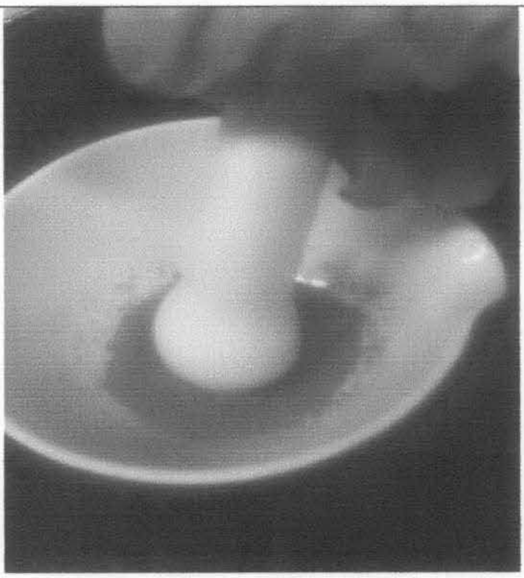
CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Observations

Diagram of Observations	Discussions
	AOT (sodium diethyl sulfosuccinate), the surfactant that is used in this reverse microemulsion method to prepare Co/SiO_2 catalyst.
	AOT (natrium diethyl sulfosuccinate), surfactant being dissolved in 40ml of n-heptane.

	6 mL of aqueous solution containing cobalt nitrate
	Microemulsion I and Microemulsion II mixed together to form this mixture which is the stirred for 24 hours. The different phases are clear in this figure.

	The Co/SiO_2 catalyst sample after drying in the oven.
	After drying the sample in the oven, manual grinding is required to make the sample more even. There are sometimes clusters formed during the drying process.

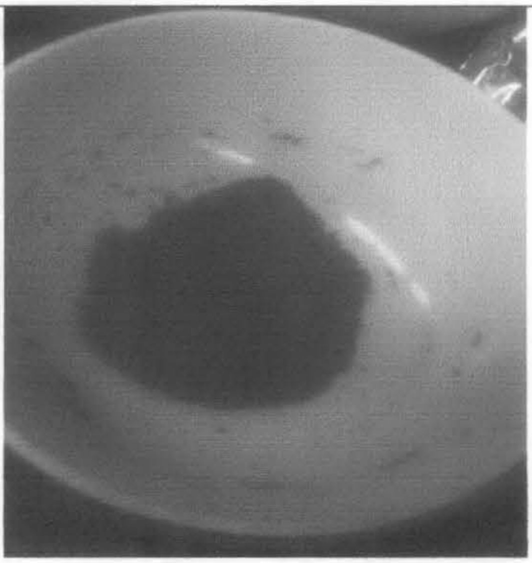
	The sample that is calcined will be black in colour if there is cobalt present in it.

Table 4.1: Observations during the experiment

4.2 FESEM Analysis

4.2.1 Varying Cobalt Loading

According to the journal, the molar water-to-surfactant ratio is set to 8. The cobalt loading in the catalyst is varied to 2%, 4%, 6% and 8%. Where else, the surfactant concentration in the organic phase was set at a constant value of 1M.

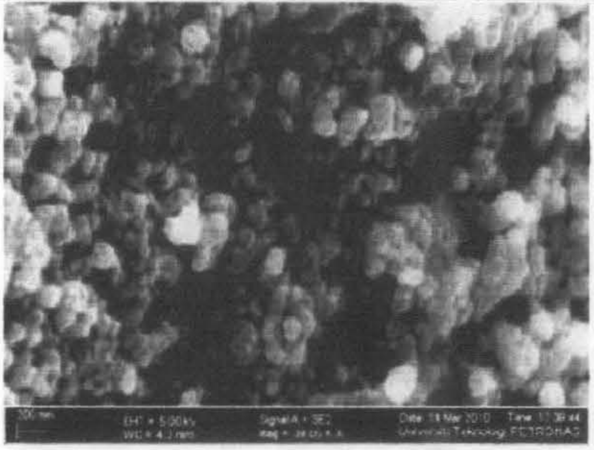
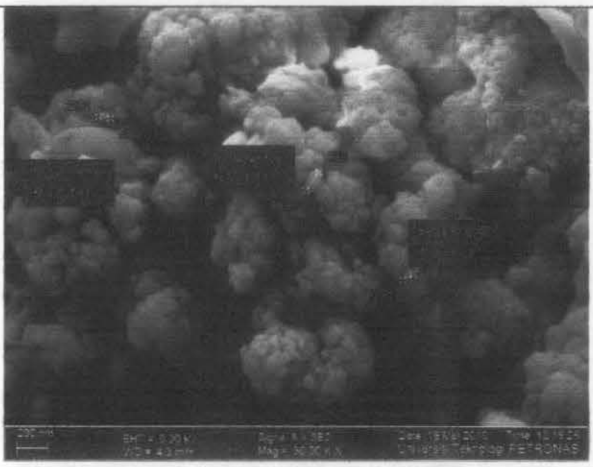
Cobalt loading (%)	FESEM image	Discussion
2%		For Co/SiO_2 catalyst with cobalt loading of 2%, the nanocatalyst is not very spherical shaped. The cobalt on the silica support is also not clearly visible.
6%		For Co/SiO_2 catalyst with cobalt loading of 6%, the nanocatalyst is more spherical in shape. Even though it is not very clear, cobalt deposits on silica support is almost visible.

Table 4.2: FESEM images for different cobalt metal loading

4.2.2 Varying Calcination Temperature

2 gram Co/SiO_2 with 6% cobalt loading is prepared. All parameters including surfactant concentration, cobalt loading, and oil volume are kept constant. The catalyst sample is then calcined using different temperature of 250°C, 350°C and 450°C.

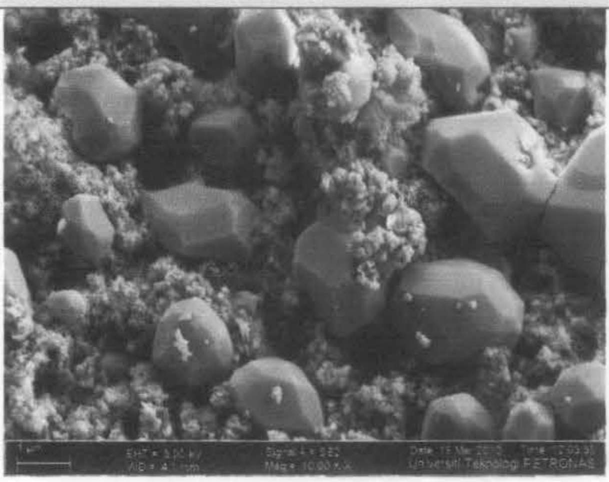
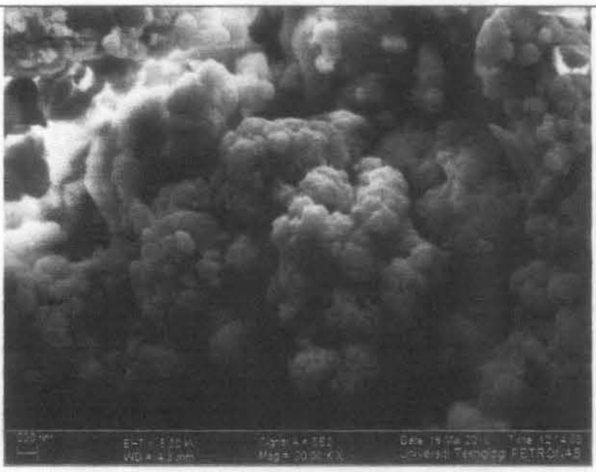
Calcination Temperature	FESEM image	Discussion
300°C		From the FESEM image, it can be seen that there are impurities in catalyst sample. It can be concluded that 300°C of calcination temperature is not enough to remove organic materials from the catalyst.
450°C		From the FESEM image, there are no impurities found in the catalyst. So it can be concluded that 450°C can be an ideal temperature for Co/SiO_2 catalyst.

Table 4.3: FESEM images for different calcination temperature

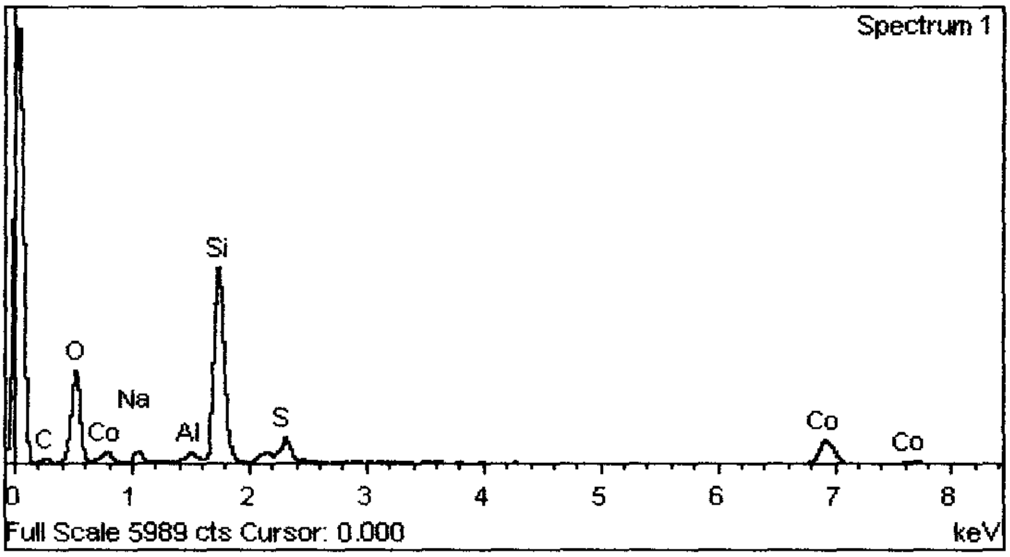


Figure 4.1 : EDX image of 6wt% cobalt loading which was calcined at 250^{0}C

EDX image of FESEM for 6wt% cobalt loading which was calcined at 250^{o}C (figure 4.1) shows the presence of SiO and Co along with other elements. Sample is contaminated. This is due to the low calcination temperature which could not eliminate the organic matters in the sample.

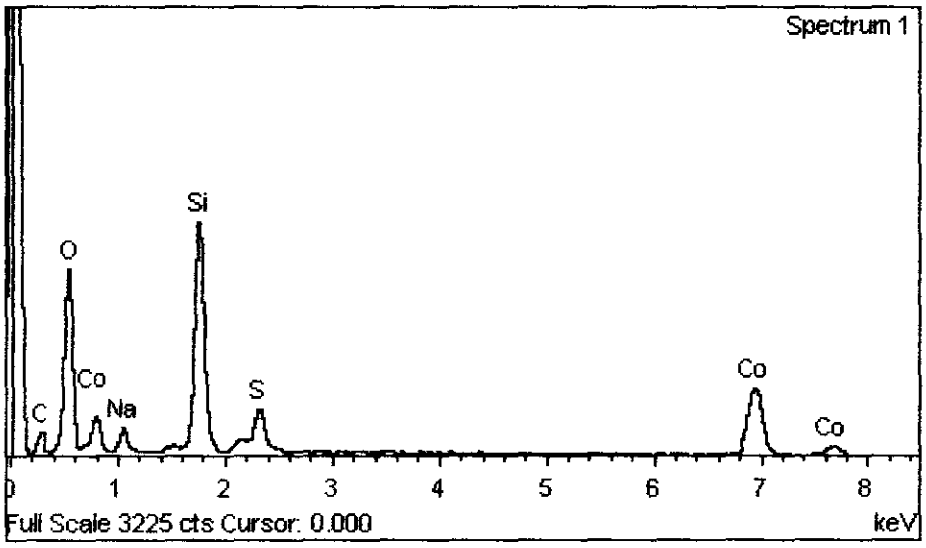


Figure 4.2 : EDX image for sample 6wt% which is calcined at 450^{0}C

The EDX image above is for sample 6wt% which is calcined at 450°C (figure 4.2). There is more cobalt and oxygen content in this sample. Besides that, there is also a high content of carbon element in this sample. This might be caused by the high calcination temperature that can contribute to the factor of carbon presence in this sample.

4.3 XRD Study of the Catalyst

Metal dispersion in oxidised Co catalyst was studied by using XRD. The results obtained are compared to the results from the journals.[8, 10]

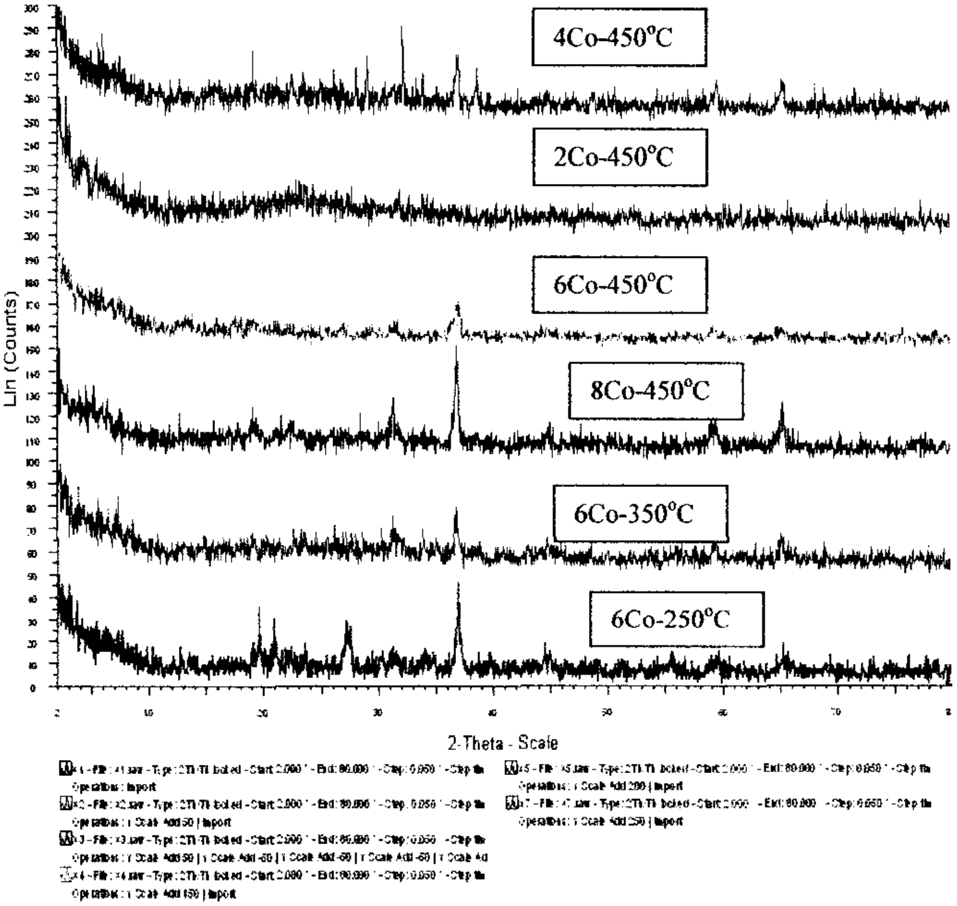


Figure 4.3 : XRD profile of all samples

4.3.1 Varying Calcination Temperature

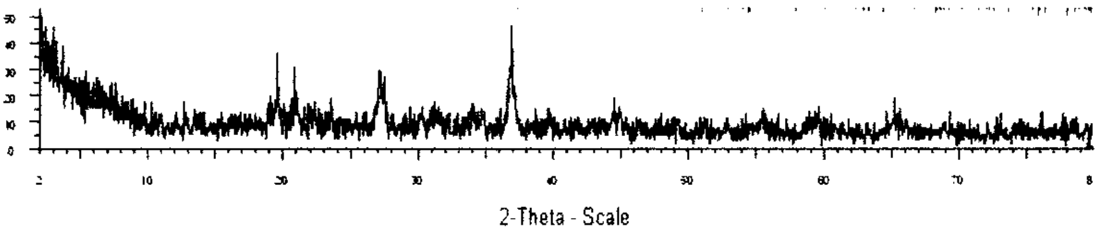


Figure 4.4: XRD profile of 6%Co/SiO₂ catalyst which is calcined at 250°C

The first sample is 6%Co/SiO_2 catalyst which is calcined at 250°C (figure 4.4). From the XRD analysis it can be seen that this sample has a very high diffraction at $2\theta=37^\circ$ and slightly lower peaks at 19-21° and 27°. This shows the presence of cobalt in the form of Co_3O_4 mainly. The presence of other peaks shows that there other elements also in the sample. This may be caused by the low calcination temperature where some organic elements could not be eliminated.

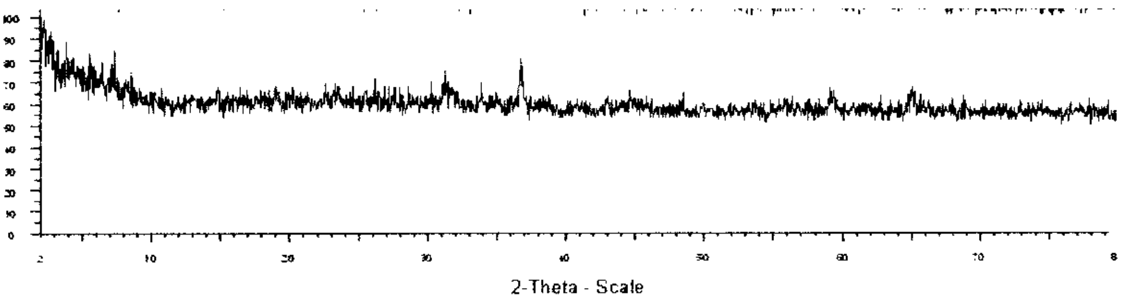


Figure 4.5: XRD profile of 6%Co/SiO₂ catalyst which is calcined at 350°C

The second sample is 6%Co/ SiO_2 catalyst which is calcined at 350°C (figure 4.5). The XRD diagram shows that there is one prominent peak which is at $2\theta=37^\circ$. This shows the presence of cobalt in the sample. The high and thin peak suggests that the cobalt in the sample still in CoO form. There are also other not so obvious peaks in the XRD diagram. This shows that are still some organic matters in the catalyst sample.

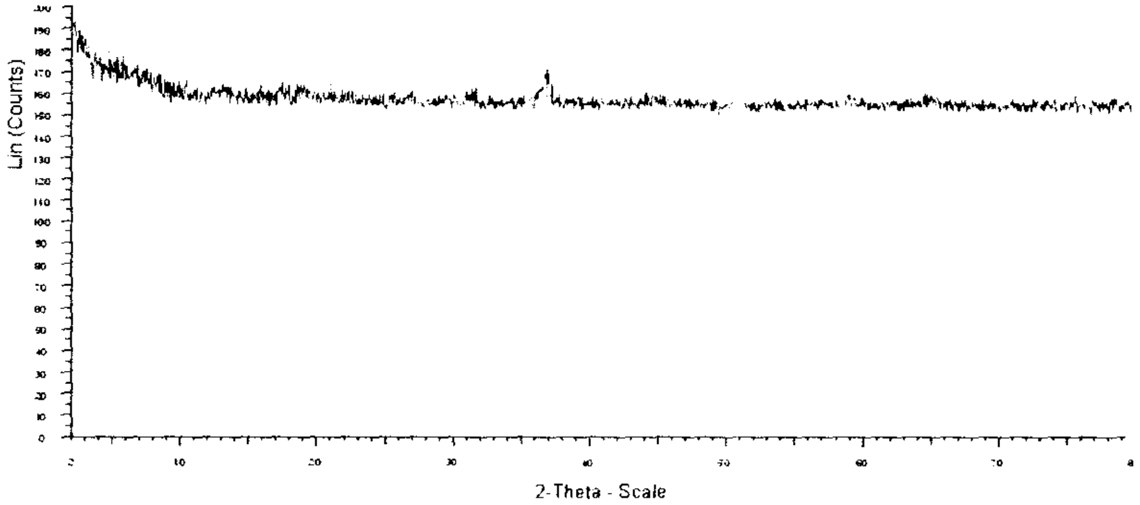


Figure 4.6: XRD profile of 6%Co/SiO$_2$ catalyst which is calcined at 450^{o}C

Next sample is 6%Co/ SiO$_2$ catalyst which is calcined at 450^{o}C. (Figure 4.6). From the XRD diagram above, it can be clearly seen there is only one weak diffraction at $2\theta=37^o$. It can be concluded that the cobalt in the sample is in the form of Co. The broad and short peak suggests that the particle size in this sample is smaller. There are no other obvious peaks suggesting that most of the organic matter that may be present in the sample is eliminated.

So, from the XRD analysis it can be said that the optimum calcination temperature is 450^{o}C for the Co/SiO$_2$ catalyst in the experiment.

4.3.2 Different Cobalt Loading

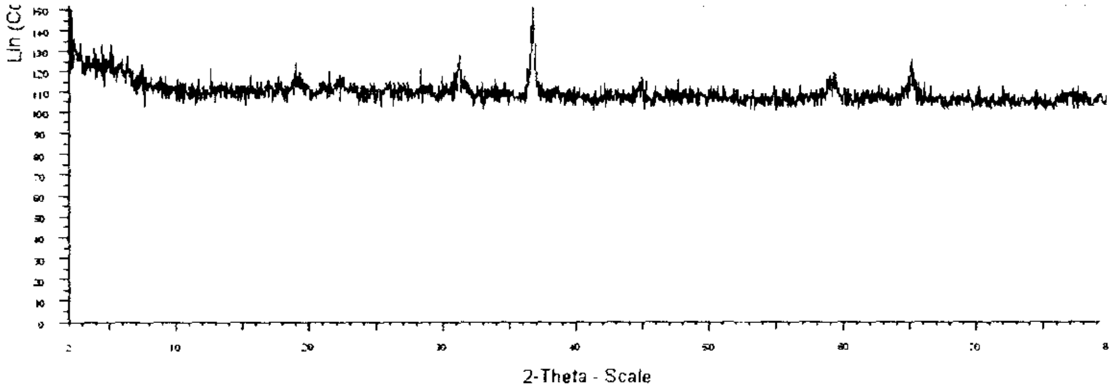


Figure 4.7: XRD profile of 8%Co/SiO$_2$ catalyst which is calcined at 450^{o}C

The sample 8%Co/SiO$_2$ which was calcined at 450^{o}C was studied under XRD analysis. From the XRD diagram (figure 4.7), it can be seen there is a high peak at 2θ=37^o. This high peak possibly means the cobalt in this sample is mainly in the form of Co$_3$O$_4$. This might be caused by the high amount of cobalt used in the sample, which is 8% loading. Some low peaks may also show the presence of cobalt in the form Co and CoO.

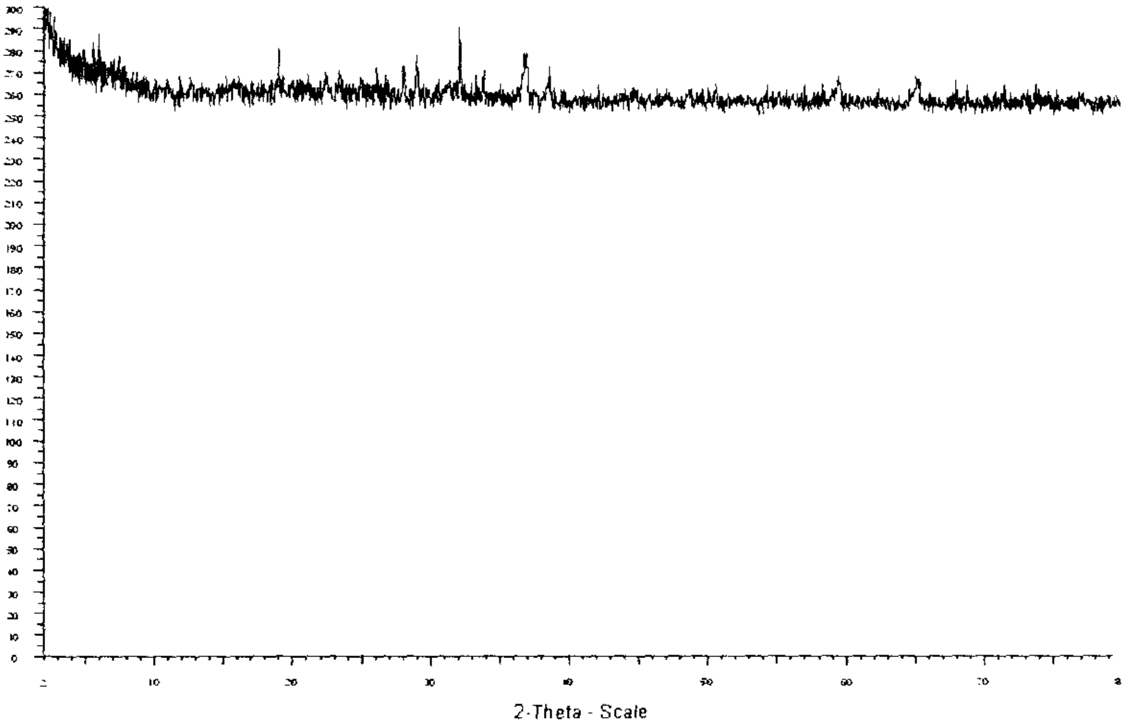


Figure 4.8: XRD profile of 4%Co/SiO$_2$ catalyst which is calcined at 450^{0}C

Next sample is 4%Co/SiO$_2$ which was calcined at 450^{0}C (figure 4.7). There is average sized diffraction at 2θ=37°. This shows that there is cobalt present in this sample. The peak size shows the particle is in smaller size compared to 8% cobalt loading sample. However, there are also a higher peak at 2θ=32°. This can mean that there is a mixture of cubic and hexagonal cobalt after the calcination.

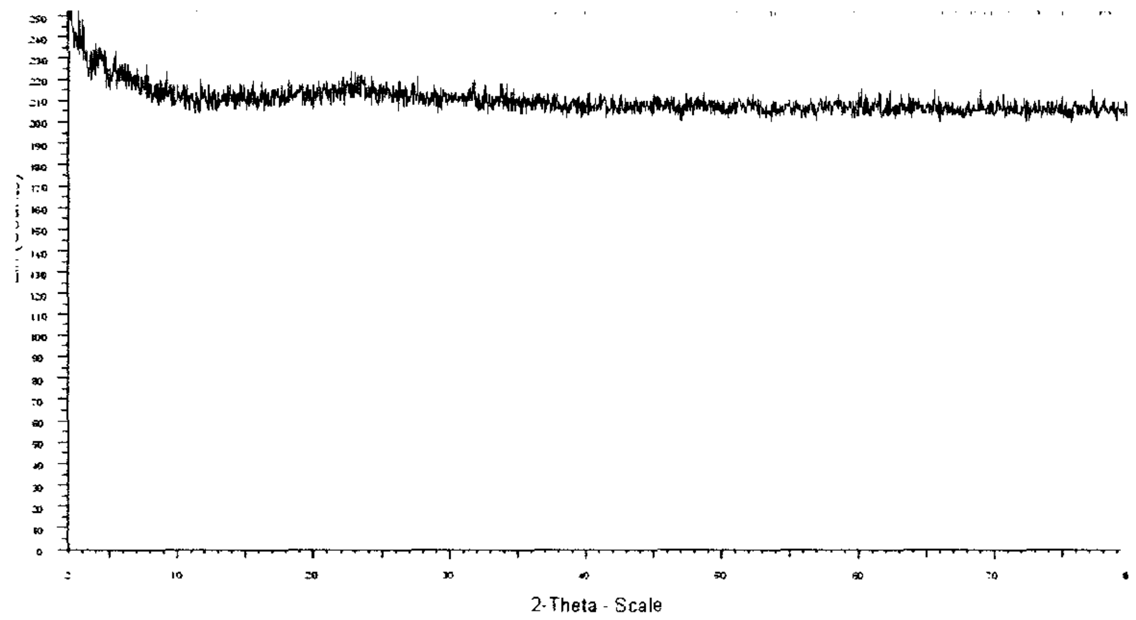


Figure 4.9: XRD profile of 2%Co/SiO$_2$ catalyst which is calcined at 450^{0}C

2%Co/SiO$_2$ catalyst sample was calcined at 450^{o}C and analysis was done by using XRD. From the XRD diagram (figure 4.9), it is clear that there are no diffractions and peaks present. So it can be concluded that there are no or too little cobalt present in the sample. This is because only 2% cobalt loading is used in this sample. There is no cobalt attached in this sample or too little to be detected by the signal.

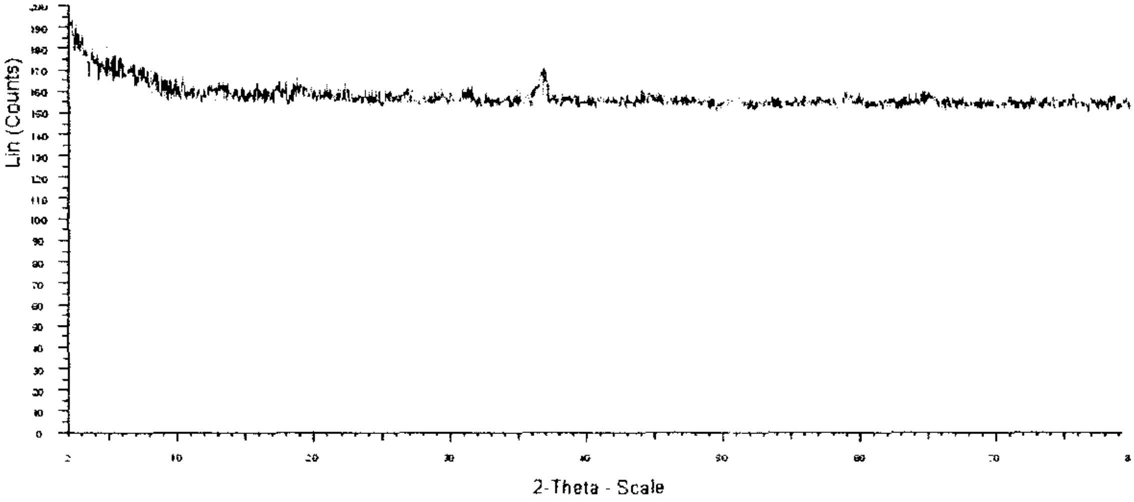


Figure 4.10: XRD profile of 6%Co/SiO$_2$ catalyst which is calcined at 450^{0}C

Next is 6%Co/SiO$_2$ catalyst sample was calcined at 450^{o}C. From the XRD diagram it can be seen that there is only one prominent peak at 2θ=37^0. The size of the peak is broad and low which shows that the particles in this sample are small sized and spherical in shape. It can be concluded that 6% cobalt loaded catalyst gives the optimum result, shape and size.

4.3.3 Scherrer Equation

This equation is a shape factor that can be used in XRD (X-Ray Diffraction) to link the size of usually nanoparticles from the broadening of a peak in a diffraction pattern. The Sherrer equation is as below:

$$\tau = \frac{K\lambda}{\beta\cos\theta}$$

where *K* is the shape factor,

λ is the x-ray wavelength, typically 1.54 Å,

β is the line broadening at half the maximum intensity in radians,

θ is the Bragg angle;

τ is the mean size of the particles.

However, this Scherrer equation can only be used in nano sized particles. It can't be used on particles larger than about 0.1 μm.

4.3.4 Bragg Equation

The Bragg equation is:

$n\lambda = 2d\sin(\theta)$
where,
d is distance,
θ is the scattering angle,
λ is the wavelength,
n is an integer determined by the order given

By using both the S Scherrer Equation and Bragg Equation, the size of the particles obtained can be determined.

4.4 TPR Analysis

4.4.1 Varying Cobalt Loading

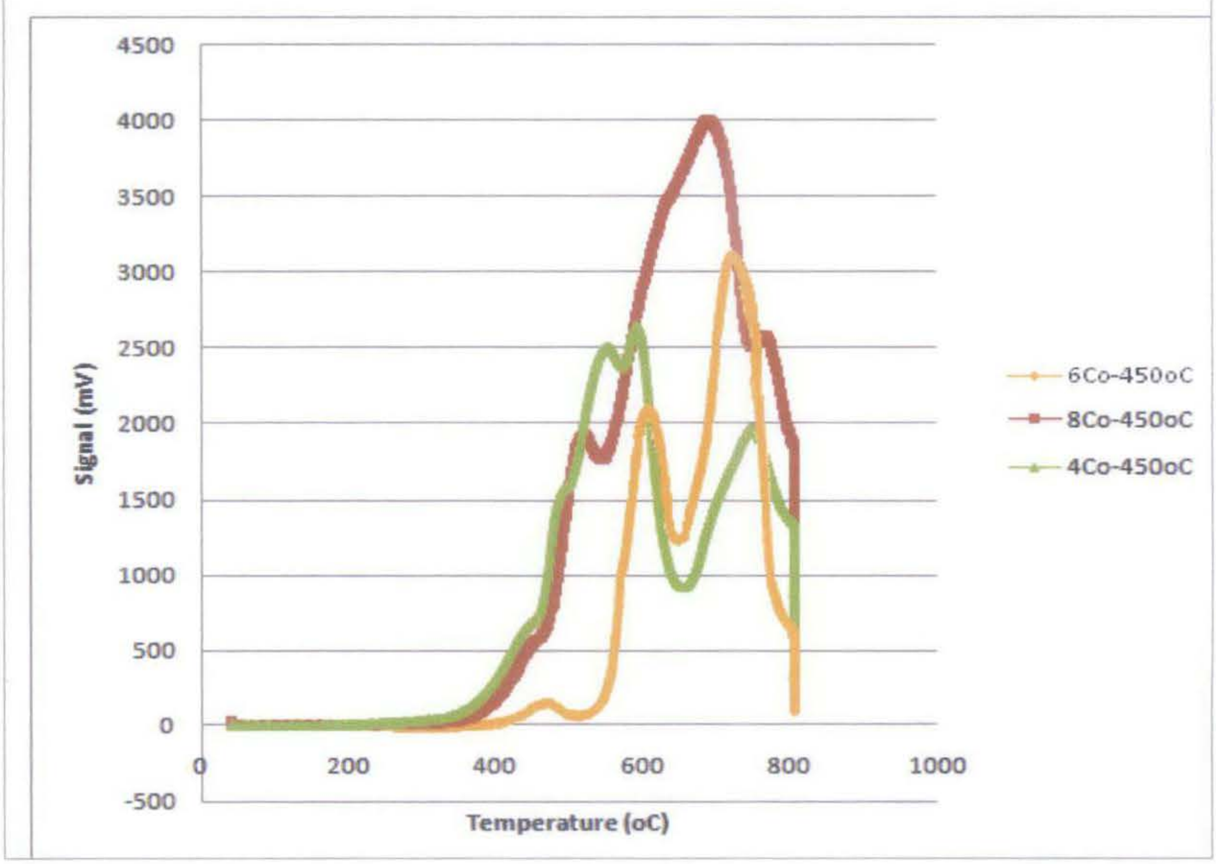


Figure 4.11: TPR profile for different cobalt loading

The TPR profile (figure 4.11) above shows the reduction temperature of 4wt%, 6wt% and 8wt% of cobalt loading catalyst samples. As observed all three sample has almost similar pattern.

For 6wt% cobalt loading, there are two main peaks on the graph which means there are two main H_2 consumptions taking place. This H_2 consumption takes place at a temperature range of 600-800°C. This corresponds to the two-step reduction of

Co_3O_4: $Co_3O_4 + H_2 \rightarrow 3CoO + H_2O$ (peak I at temperature 600 °C) and

Co : $3CoO + H_2 \rightarrow 3Co + 3H_2O$ (peak II at temperature of 750°C).

The second peak takes place at a higher temperature and consumes more H_2 compared to the first peak. This is due to the fact that it more difficult to reduce the cobalt oxide to its metallic state because of the strong bond. The sharp peaks of 6wt% cobalt loading sample shows that the reducibility of the cobalt metal is good.

For 8wt% cobalt loading, there are also two peaks on the graph which means there are two main H_2 consumptions taking place. However, the second peak is more apparent than the first peak. This H_2 consumption takes place at a temperature range of 500-700°C. This corresponds to the two-step reduction of

Co_3O_4: $Co_3O_4 + H_2 \rightarrow 3CoO + H_2O$ (peak I at temperature 500 °C) and
Co : $3CoO + H_2 \rightarrow 3Co + 3H_2O$ (peak II at temperature of 700°C).

The second peak takes place at a higher temperature and consumes more H_2 compared to the first peak. This is due to the fact that it more difficult to reduce the cobalt oxide to its metallic state because of the strong bond. Compared to the 6wt% cobalt loaded sample, 8wt% cobalt loaded samples consumes more hydrogen. This is due to the higher concentration of cobalt in the sample. The broad peak of this sample shows that the bond and interaction between cobalt and silicon dioxide is very strong.

For 4wt% cobalt loading, the TPR profile has abnormal peak states. This might be caused by impurities or due to less cobalt content in the sample to be reduced.

4.4.2 Varying Calcination Temperature

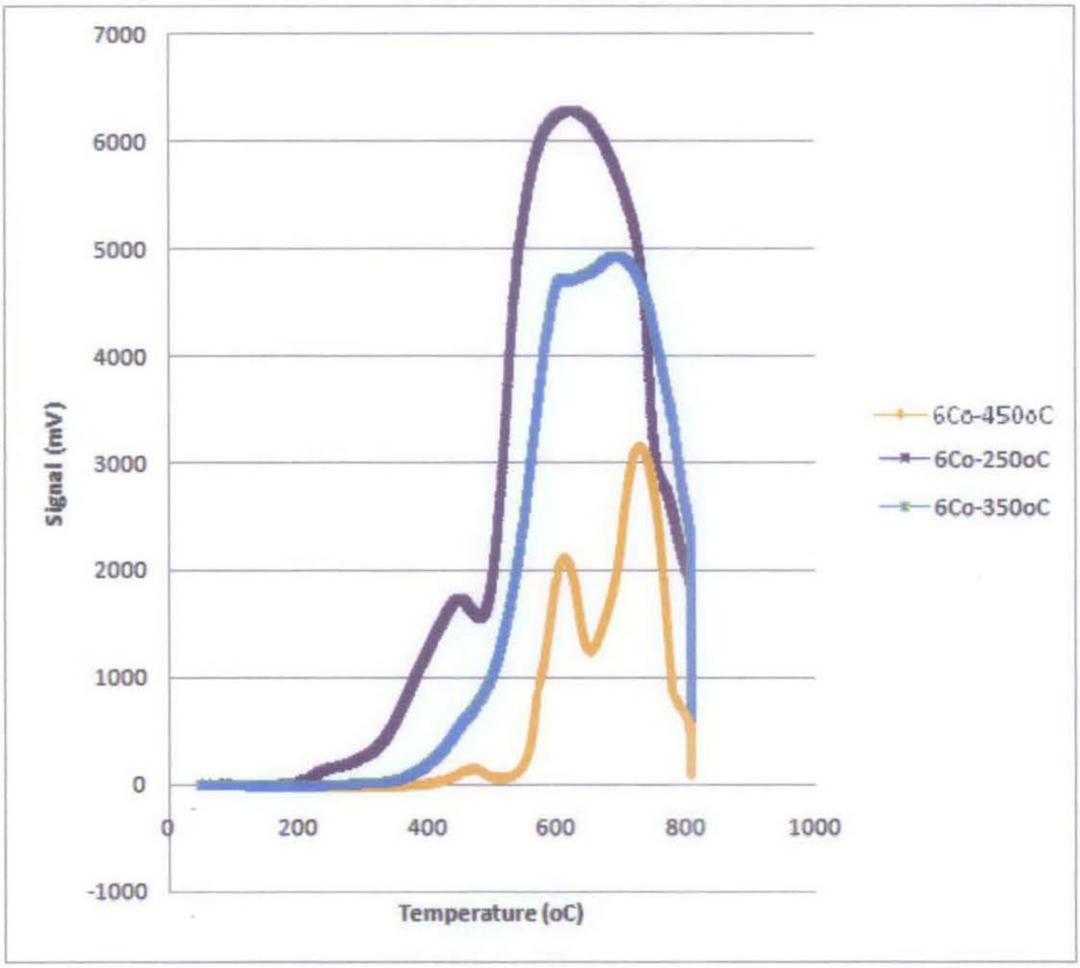


Figure 4.12: TPR profile for different calcination temperature

For 6wt% cobalt loading which was calcined at 450°C, it consumes the lowest amount of H_2 at both first and second peak. However, the temperature that is required to reduce it is higher compared to samples that are calcined at 250°C and 350°C. Samples that are calcined at lower temperature need more H_2 consumption. This may be caused by the presence of organic matter which could not be eliminated earlier.

For the sample that is calcined at 250°C, there are no sharp peaks. Instead, it has a very broad peak present. This suggests that there is a very strong bond existing between the cobalt and silica in the sample.

For 6wt% cobalt loading which is calcined at 350°C, there are no apparent peak present. The two weak peaks seem to be connected to each other. This might be caused by the difficulties to reduce the cobalt metal to its metallic state.

4.5 Surfactant Factor

In this experiment, reverse microemulsion is prepared by mixing an organic solution of AOT (sodium diethyl sulfosuccinate) in n-heptane with aqueous solution of cobalt nitrate. This must be done under stirring. AOT and tetrahydrofuran are used as ionic and non-ionic surfactant respectively. Generally, ionic surfactants are used to prepare stable metal colloids which are small in size. Where else, the non-ionic surfactants are used when ion interactions at the inner border of the reverse micelles are being avoided.

AOT is an ionic surfactant that is used in producing microemulsions. Usually, when a small amount of AOT is dissolved in an organic solvent, thermodynamically stable reverse micelles are formed. These reverse microemulsions consist of a hydrophilic core separated by the hydrophilic head group of the AOT, and with the hydrophobic alkyl tails which extends into the nonpolar continuos phase solvent.

Hydrazine hydrate, (N_2H_4) is used as a powerful reducing agent to recover metals. In this case, hydrazine hydrate is added to reduce cobalt metals. Sometimes, hydrazine hydrate is also used to nanoparticulate the cobalt phase. The reducing equation of cobalt using hydrazine hydrate is:

$2Co_2 + N_2H_4 + 4OH \rightarrow 2CoO + N_2 + 4H_2O$

4.6 Error and Recommendations

During the experiment, the results obtained might have been affected due to few reasons:

- Parallax error- error that can happen due to the equipments
- Human error- errors that are made by human during data reading and analysis
- Contamination- Samples can be contaminated by the equipments used, while transferring samples and also when drying it in the oven. During calcination also, carbon can be formed in the sample.

However, few improvements can be made to achieve better shaped and sized Co/SiO_2 nanocatalysts. The water to surfactant ration can be studied to improve the size of the particles. Besides that, the effect of the surfactant volume and surfactant type can also be used in the future research.

CHAPTER 5

CONCLUSION

Generally, heterogeneous catalysts are to be designed for specific applications. One important aspect in a heterogeneous catalyst is the choice of the size distribution of the catalytically active material. Studies have shown that the nanoparticle size of catalysts has a very important effect on the catalytic activity in many of the reactions. Hence, it is essential to be considered in the catalyst design.

There are many studies, methods and techniques that have been developed to synthesize catalysts with the catalytically active material in the required size range. Catalyst performance can be improved by tuning the crystallite size distribution for the required reaction. In order to achieve the desired size, it needs require a control of the crystallite size distribution and also understanding of the fundamental principles and process variables in the synthesis of these materials. So, more refined study and experiment are to be done on this topic as it has a lot of benefits.

For this particular study, Co/SiO_2 spherical model nanocatalysts were to be prepared by using reverse microemulsion method. From the results and analysis made, this method produces catalysts that are nanosized. In this study, both cobalt loading and calcination temperature were varied. From the results and data analysis, it can be said that 6wt% cobalt loading is the best amount for the Co/SiO_2 catalyst compared to 2%, 4% and 8%. For the calcination temperature, 450°C is the most optimum temperature compared to 250°C and 350°C.

REFERENCES

[1] A.Y.Khodakov, W.Chu, and P.Fongarland, Advances in the Development of Novel Cobalt Fischer-Tropsch Catalysts for Synthesis of Long-Chain Hydrocarbons and Clean Fuels, 2007, Vol. 107, p.5.

[2] A.Y.Khodakov, Enhancing Cobalt Dispersion in Supported Fischer-Tropsch Catalysts Via Controlled Decomposition of Cobalt Precursors, 2009, Vol. 39, p.171.

[3] B. H. Davis, Fischer-Tropsch Synthesis: Comparison of Performances of Iron and Cobalt Catalysts, 2007, Vol.46, p.8398.

[4] M. Fanun, Microemulsions : Properties Of Catalysts From Microemulsion And Applications, p.248

[5] S.Eriksson, U.Nylén, S.Rojas, M.Boutonnet, Preparation Of Catalysts From Microemulsions And Their Applications In Heterogeneous Catalysis, 2004, Vol. 265, p.207.

[6] M.Boutonnet, S.Logdberg, E.E. Svensson, Recent Development in the Application of Nanoparticles Prepared from W/O Microemulsions in Heterogeneous Catalysis, 2008, p.270.

[7] P.Heidebrechta,, V.Galvitaa, K. Sundmachera, An Alternative Method For Parameter Identification From Temperature Programmed Reduction (TPR) Data, 2008, Vol.63, p.4776-4777.

[8] K.Kouachi, G.Lafaye, C.Especel, O.Cherifi, P.Marécot, Preparation Of Silica-Supported Cobalt Catalysts From Water-In-Oil Microemulsion For Selective Hydrogenation Of Citral, 2009, Vol. 308, p.142.

[9] D. Barkhuizen, I. Mabaso, E. Viljoen, C.Welker. M. Claeyst, E.V. Steen, J.Q.C Fletchr, Experimental approaches to the preparation of supported metal nanoparticles,*Pure Appl. Chem.*, Vol. 78, No. 9, pp. 1759–1769, 2006.

[10]. A.M.Saib, A.Borgna, J.Loosdrecht P.J.Bergeb, J.W.Geus, J.W.Niemantsverdriet, Preparation And Characterisation Of Spherical Co/Sio2 Model Catalysts With Well-Defined Nano-Sized Cobalt Crystallites And A Comparison Of Their Stability Against Oxidation With Water, 2006, Vol. 239, p.326.

[11] G.Prieto, A.Martínez, P.Concepción ,R.Moreno-Tost, Cobalt Particle Size Effects In Fischer–Tropsch Synthesis: Structural And In Situ Spectroscopic Characterisation On Reverse Micelle-Synthesised Co/ITQ-2 Model Catalysts, 2009, p.11

[12] D.S. Bae, K.S. Han, J.H. Adair, Synthesis Of Cu/Sio2 Nanosize Particles By A Reverse Micelle And Sol-Gel Processing, Journal Of Materials Science Letters 21, 2002, 53– 54

[13] A.K. Datye, Electron Microscopy Of Catalysts: Recent Achievements And Future Prospects, 2003, Vol. 216, p.144.

[14] www.tech-faq.com/transmission-electron-microscope.shtml

[15] www.vcbio.science.ru.nl/en/fesem/

[16] http://serc.carleton.edu.research_education/geochemsheets/techniques/XRD.html

[17] www.micro.magnet.fsu.edu/primer/Java/interference/index.html

[18] http://www.fischer-tropsch.org/DOE/DOE_reports/95707386/de95707386_sec1.pdf

[19] http://chemistry.about.com/od/elementfacts/a/cobalt.htm

[20] http://www.radiochemistry.org/periodictable/elements/27.html

[21]http://web1.caryacademy.org/chemistry/rushin/studentprojects/compoundwebsites/2003/silicondioxide/properties.htm

[22] http://www.azom.com/Details.asp?ArticleID=1114

[23]
http://www.malvern.com/LabEng/industry/nanotechnology/nanoparticle_defiition.htm

[24] http://www.fischer-tropsch.org/DOE/DOE_reports/95707386/de95707386_sec2.pdf