

Chapter 1

1 Introduction

1.1 Background of Project

Fischer–Tropsch (FT) synthesis looks back to a lively history of about seventy years. Franz Fischer founded the phenomenon of how the gases CO and H₂ enter the reactor and a hydrocarbon liquid of ordered composition exits. Today it serves as an option for clean transportation fuels and chemicals' production. (1)

Two metals have the properties to be considered as the base for catalysts for Fischer-Tropsch synthesis: iron and cobalt. During the past 75 years there have been many reports on catalysts based on these two metals. However, most of these studies have been conducted so that it is difficult to make valid comparisons among the many studies. The studies for this contract have been conducted under conditions that permit catalyst properties to be directly compared under similar process conditions. Furthermore, the process variables have been varied over a range of conditions.

The results permit comparisons of the activity and selectivity properties with catalyst composition to be made for a common process condition and this adds much reliability to the correlations that are developed. Furthermore, iron and cobalt catalysts have been compared under similar process conditions and the similarities and differences from these two catalysts have been defined. In brief, the data provide a data base that will be useful for potential process developers to make a valid selection of catalyst type and composition that will fit their specific conditions. To date, potential process developers have utilized the data base to select a catalyst composition and then to contract specific studies that fall outside the current contract to develop the optimum conditions for improvement (2).

To understand the project requires a number of literature research on the calcinations process, the potential catalysts for Fischer-Tropsch and the catalyst preparation. Since the catalytic performance of FT catalysts depends strongly on the preparation method (3), this project will study the parameters of preparing Co-based catalysts using Impregnations method with different supports.

From there, the prepared catalysts will be analyzed using several methods of characterization which includes; Temperature Programmed Reduction, X-ray Diffraction, X-ray Photoelectron Spectroscopy.

What will be observed are the different characteristics of the catalyst that will be produced from different parameters of preparation process. The project will manipulate the calcination temperature and catalytic support. Since this is an experimental project, several samples with different variables are needed to study the influence of the respective parameters to the catalyst characterizations and capabilities.

1.2 Problem Statement

The interest in Fischer-Tropsch Synthesis ignites around 1970-1980, when the forecasts of fading world oil reserves and boycotts by major oil producing countries has shaken the world fossil energy industries, specifically the reserves of natural gas and such that associated with petroleum. At that time, large reserves of coal, increasing demands for liquid fuels and less optimistic forecast for oil reserves results in major research and development in FT.

From the environmental aspects, CO emissions from various sources is being blamed for global warming, energy saving policies has made flaring of associated natural gas to be charged with taxes which might be of negative value at the place of unwanted recovery. FT on the other hand is able to convert the CO pollutant into synthetic fuels. This means instead of being emitted into the atmosphere, it can be used as a source of fuel substituting petroleum. Due to that, interest in FT synthesis has increased as a consequence of reduction in fossil energy reserves, environmental demands and technological development (1).

There are many aspects contributing to producing a catalyst. Some of the main factors contributing the catalyst preparation are the calcinations temperature, the metal loading and catalytic support. Previous experiment shows that Cobalt based FT catalyst normally has 1-20% cobalt loading, supported by carbon nanotubes (CNT) silica alumina Zirconium among others. Calcination temperature is also another factor contributing to the catalyst performance. The distribution on the support varies according to the catalytic support, calcinations temperature and the percentage metal loading itself.

To suit with this project timeframe, this experiment focuses only on producing 5% loading of Cobalt on 2 different support, namely Alumina and Silica, and calcined at 300 C, 400 C and 500 C.

Why Cobalt instead of others?

Cobalt catalyst is able to have resistant to deactivation, which means it has longer lifetime and relatively high productivity at high conversion compared with Iron. Water generated by FT synthesis slows the reaction rate on iron to a greater extent than cobalt catalysts. When compared with Ruthenium, Cobalt is much cheaper which makes it practical implementation (3).

However, further studies are needed to improvise FT so that it may achieve the great objective, which is to reduce the dependency of petroleum fully replace it. Hence this study is conducted, to come out with the best parameters for calcinations and produce high performance Cobalt based catalyst.

1.3 Objective

The objectives of the research project are:

- 1.3.1 To study the parameters of calcinations and catalyst design.
- 1.3.2 To produce catalysts of different properties by manipulating the calcinations parameters.
- 1.3.3 To come out with the optimum parameter condition for calcination process in producing high performance Co-based Fischer-Tropsch nanocatalyst.

1.4 Scope Of Study

- Catalyst used will be industrial Cobalt Nitrate as base catalyst.
- Catalysts will be prepared using Impregnation method.
- Support used in this study is alumina and silica support.
- Calcination temperature is varied 300°C, 400°C and 500°C
- Analyzing the catalyst design involves catalyst synthesis, morphology of catalyst structure and reduction temperature.
- Characterization equipment will include; X-ray Photoelectron Spectroscopy, X-ray diffraction and Temperature Programmed Reduction.

In order to achieve high surface active sites (Co^0), cobalt precursors are dispersed on porous carriers, with SiO_2 and Al_2O_3 .

A drawback of these support materials is their reactivity toward cobalt, which during preparation or catalysis results in the formation of mixed compounds that are reducible only at high reduction temperatures. To avoid these problems, the use of carbon as a support has been explored. Activated carbon has many advantages if utilized as FTS catalyst support such as resistance to acidic or basic media and stable at high temperatures. Carbon nanotubes (CNT) possess similar properties and in most cases outperform activated carbon in this respect. CNT have many unique structural properties and have attracted increasing attention as a novel support media for heterogeneous catalysis (4).

However, this paper will not covers the preparation for CNT based Fischer-Tropsch catalysts.

Chapter 2

2 Literature Review

2.1 Calcination

Calcination process is to heat (a substance) to a high temperature but below the melting or fusing point, causing loss of moisture, reduction or oxidation, dissociation into simpler substances and the decomposition of carbonates and other compounds (5).

2.2 Fischer-Tropsch Synthesis (3)

Currently, there are two FT operating modes: high and low-temperature FT processes.

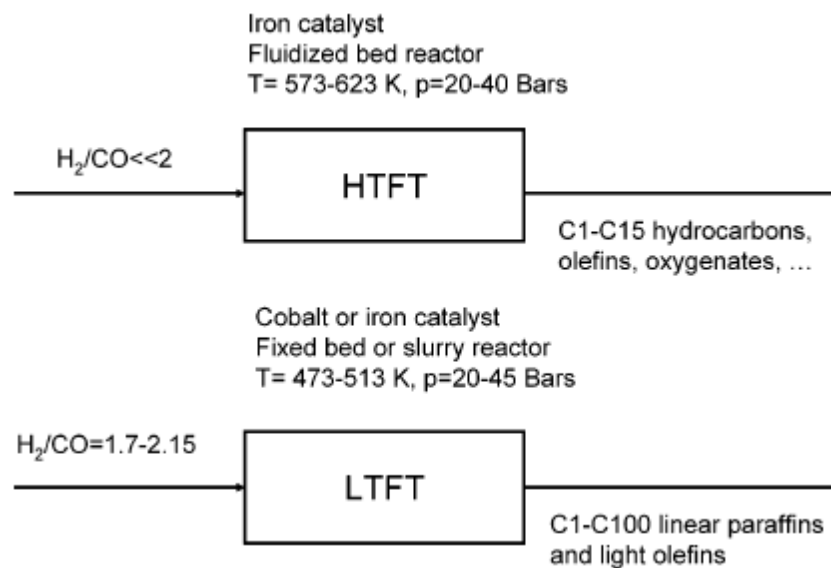


Figure 1: High and Low Temperature of FT Process

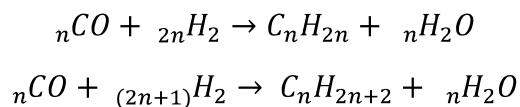
In the high temperature FT (HTFT) process syngas reacts in a fluidized bed reactor in the presence of iron-based catalyst to yield hydrocarbons in the C_1 - C_{15} hydrocarbon range. This process is primarily used to produce liquid fuels, although a number of valuable chemicals, e.g., R-olefins, can be extracted from the crude synthetic oil. Oxygenates in the aqueous stream are separated and purified to produce alcohols, acetic acid, and ketones including acetone, methyl ethyl ketone, and methyl isobutyl ketone. Both iron and cobalt (Fe, Co) catalysts can be used in the low-temperature FT (LTFT) process for synthesis of linear long-chain hydrocarbon waxes and paraffins. High-quality sulfur-free diesel fuels are produced in this process. Most of the FT

technologies developed in last two decades are based on the LTFT process. These new LTFT processes have involved syngas with a high H₂/CO ratio, which is generated by vaporeforming, autothermal reforming, or partial oxidation using natural gas as a feedstock.

Because of their stability, higher per pass conversion and high hydrocarbon productivity, cobalt catalysts represent the optimal choice for synthesis of long-chain hydrocarbons in the LTFT process.

2.3 Cobalt Catalysts

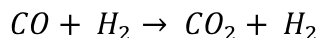
All group VIII metals have noticeable activity in the hydrogenation of carbon monoxide to hydrocarbons. Ruthenium followed by iron, nickel, and cobalt are the most active metals for the hydrogenation of carbon monoxide. The molecular average weight of hydrocarbons produced by FT synthesis decreased in the following sequence: Ru > Fe > Co > Rh > Ni > Ir > Pt > Pd. Thus, 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 Fischer and Tropsch as the first catalysts for syngas conversion. Both cobalt and iron catalysts have been used in the industry for hydrocarbon synthesis.

It has been shown that supercritical pressure conditions are beneficial only at high density conditions; but it is, only when there is a high partial pressure of a component is present in concentrations that approach the critical pressure. For Fischer-Tropsch synthesis, this means that a component that is a liquid at room temperature is required and that it is likely that the separation and recycle of the components will make the utility of supercritical synthesis of questionable benefit for commercial operations. Briefly, the gain in catalyst stability will not offset the added cost of separations and recycle. More importantly, there were only minor

differences in product selectivity among the products from the various operating reactors. Cobalt catalysts, lacking water-gas-shift activity, must operate in the presence of high partial pressure of water. In spite of this, kinetic expressions to date have not included water. Studies at various partial pressure of water while other variables were held constant have been conducted.



These studies show that the impact of water on the catalytic activity is dependent upon the support and may even vary with the properties of a particular support. Thus, for some silica supports the conversion increases with increasing water partial pressure whereas with other silica supports the conversion may decrease. These studies have provided the most extensive definition of the impact of water with the range of cobalt catalysts and under comparable reaction conditions. Kinetic expressions have been developed that include water partial pressure. More importantly, catalyst characterization studies as the material is used to affect Fischer-Tropsch synthesis have defined chemical changes that occur for the cobalt catalyst (2).

2.4 Comparison Between the FT Catalysts (3)

All group VIII metals are potentially an FT catalyst for having noticeable activity in hydrogenation of CO to hydrocarbons but only Ru, Fe, Co and Ni are suitable for commercial production. Ruthenium is too expensive while Nickel under practical condition produced too much methane.

A brief comparison of cobalt and iron catalysts is given in Table 1.

parameter	cobalt catalysts	iron catalyst
cost	more expensive	less expensive
lifetime	resistant to deactivation	less resistant to deactivation (coking, carbon deposit, iron carbide)
activity at low conversion		comparable
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 $CO + H_2O \rightarrow CO_2 + H_2$	not very significant; more noticeable at high conversions	significant
maximal sulfur content	<0.1 ppm	<0.2 ppm
flexibility (temperature and pressure)	less flexible; significant influence of temperature and pressure "on hydrocarbon selectivity	flexible; methane selectivity is relatively low even at 613 K
H ₂ /CO ratio	~2	0.5–2.5
attrition resistance	good	not very resistant

Table 1: Comparison between Cobalt and Iron Fischer-Tropsch Catalysts

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. Water generated by FT synthesis slows the reaction rate on iron to a greater extent than on cobalt catalysts. At relatively low temperatures (473-523 K), chain growth probabilities of about 0.94 have been reported for cobalt-based catalysts and about 0.95 for iron catalysts. The water-gas shift reaction is more significant on iron than on 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; they are more suitable for use in slurry-type reactors. Iron catalysts produce hydrocarbons and oxygenated compounds under different pressures, H_2/CO ratios, and temperatures (up to 613 K). Cobalt catalysts operate at a very narrow range of temperatures and pressures; an increase in temperature leads to a spectacular increase in methane selectivity. Iron catalysts seem to be more appropriate for conversion of biomass-derived syngas to hydrocarbons than cobalt systems because they can operate at lower H_2/CO ratios (3).

2.5 Cobalt Catalysts Preparation

A few number of cobalt-based Fischer-Tropsch catalysts are prepared that can be used to obtain baseline data on cobalt-based Fischer-Tropsch synthesis. Pretreatment conditions used for supported cobalt Fischer-Tropsch (FT) catalysts often have significant effect on the catalyst activity, selectivity and lifetime. A number of researchers focused on the study of pretreatment of the catalyst with hydrogen, including the effects of calcination and hydrogen reduction temperatures. Calleja et al. investigated the FT reaction over a Co/HZSM-5 catalyst, and found that the calcination and reduction temperatures did not have an effect on the catalyst activity. The results obtained by Rathousky et al., however, revealed that the calcination and reduction temperatures have a significant effect on the catalytic properties of both Co/Al_2O_3 and Co/SiO_2 catalysts.

The turnover frequency (TOF) for the F-T reaction decreased with increasing calcination temperature for both Co/Al₂O₃ and Co/SiO₂. However, the total reaction rate increased for Co/Al₂O₃ while it decreased for Co/SiO₂. Belambe et al. studied the pretreatment effects on the activity of a Ru-promoted Co/Al₂O₃ catalyst for the FT reaction. The calcination temperature was found to have a pronounced effect on the overall activity of the catalyst, but not on the TOF. The reduction temperature had only a negligible effect on the overall activity and TOF. A few studies on the effect of treatment with carbon monoxide or syngas for the supported cobalt catalysts has been reported. It has been reported that the supported cobalt catalyst pretreated with a gas containing carbon monoxide had increased activity and greater selectivity towards producing C₅₊ hydrocarbons. Older work indicates that Co₂C is formed by low temperature activation with CO. Supported cobalt that were reduced in hydrogen, carburized with CO at 208°C and then hydrogenated at 208°C, the carbide was quickly converted to cobalt metal. Below about 240°C, treatment of cobalt catalysts with CO led to Co₂C with little, if any, free carbon.

In this study, wet impregnation method is applied on alumina and silica support. Even though pretreatment is highly suggested to obtain better selectivity, catalyst activity and lifetime, the experiment timeframe does not permits pretreatment.

2.6 Characterization Equipment

2.6.1 X-Ray Diffraction (XRD)

XRD is used to characterize thickness, crystallographic structure, and strain in thin epitaxial films. It employs parallel-beam optics. It is a non-destructive analytical technique which reveals information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy.

It is also used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. XRD is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data. It may also be used to characterize heterogeneous

solid mixtures to determine relative abundance of crystalline compounds and, when coupled with lattice refinement techniques, can provide structural information on unknown materials. XRD also a common method for determining strains in crystalline materials. An effect of the finite crystallite sizes is seen as a broadening of the peaks in an X-ray diffraction as is explained by the Scherrer Equation.

2.6.2 Temperature Programmed Reduction (TPR)

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

A simple U-tube container is filled with a solid or catalyst. This sample vessel is positioned in a furnace with temperature control equipment. A thermocouple is placed in the solid for temperature measurement. To remove the present air the container is filled with an inert gas either nitrogen or argon. Flow controllers are used to add hydrogen. The composition of the gaseous mixture is measured at the exit of the sample container with appropriate detectors. Then, the sample in the oven is heated up on predefined values.

Heating values are usually between 1 K/min and 20K/min. If a reduction takes place at a certain temperature, hydrogen is consumed which is recorded by the detector. In practice the production of water is a more accurate way of measuring the reduction. This is due to the potential for varying hydrogen concentrations at the inlet, so the decrease in this number may not be precise, however as the starting concentration of water will be zero, any increase can be measured more accurately.

2.6.3 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that

escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra high vacuum (UHV) conditions.

XPS is a surface chemical analysis technique that can be used to analyze the surface chemistry of a material in its "as received" state, or after some treatment, for example: fracturing, cutting or scraping in air or UHV to expose the bulk chemistry, ion beam etching to clean off some of the surface contamination, exposure to heat to study the changes due to heating, exposure to reactive gases or solutions, exposure to ion beam implant, exposure to ultraviolet light.

Detection limits for most of the elements are in the parts per thousand range. Detection limits of parts per million (ppm) are possible, but require special conditions: concentration at top surface or very long collection time (overnight).

XPS is also known as ESCA, an abbreviation for Electron Spectroscopy for Chemical Analysis. XPS detects all elements with an atomic number (Z) of 3 (lithium) and above. It cannot detect hydrogen ($Z = 1$) or helium ($Z = 2$).

XPS is routinely used to analyze inorganic compounds, metal alloys, semiconductors, polymers, elements, catalysts, glasses, ceramics, paints, papers, inks, woods, plant parts, make-up, teeth, bones, medical implants, bio-materials, viscous oils, glues, ion modified materials and many others.

XPS is used to measure:

- elemental composition of the surface (top 1– 10 nm usually)
- empirical formula of pure materials
- elements that contaminate a surface
- chemical or electronic state of each element in the surface
- uniformity of elemental composition across the top surface (or line profiling or mapping)
- uniformity of elemental composition as a function of ion beam etching (or depth profiling)

A typical XPS spectrum is a plot of the number of electrons detected (sometimes per unit time) (Y-axis, ordinate) versus the binding energy of the electrons detected (X-axis, abscissa). Each element produces a characteristic set of XPS peaks at characteristic binding energy values that directly identify each element that exist in or on the surface of the material being analyzed. These characteristic peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc. The number of detected electrons in each of the characteristic peaks is directly related to the amount of element within the area (volume) irradiated. To generate atomic percentage values, each raw XPS signal must be corrected by dividing its signal intensity (number of electrons detected) by a "relative sensitivity factor" (RSF) and normalized over all of the elements detected.

To count the number of electrons at each kinetic energy value, with the minimum of error, XPS must be performed under ultra-high vacuum (UHV) conditions because electron counting detectors in XPS instruments are typically one meter away from the material irradiated with X-rays.

It is important to note that XPS detects only those electrons that have actually escaped into the vacuum of the instrument. The photo-emitted electrons that have escaped into the vacuum of the instrument are those that originated from within the top 10 to 12 nm of the material. All of the deeper photo-emitted electrons, which were generated as the X-rays penetrated 1– 5 micrometers of the material, are either recaptured or trapped in various excited states within the material. For most applications, it is, in effect, a non-destructive technique that measures the surface chemistry of any material.

Chapter 3

3 Methodology

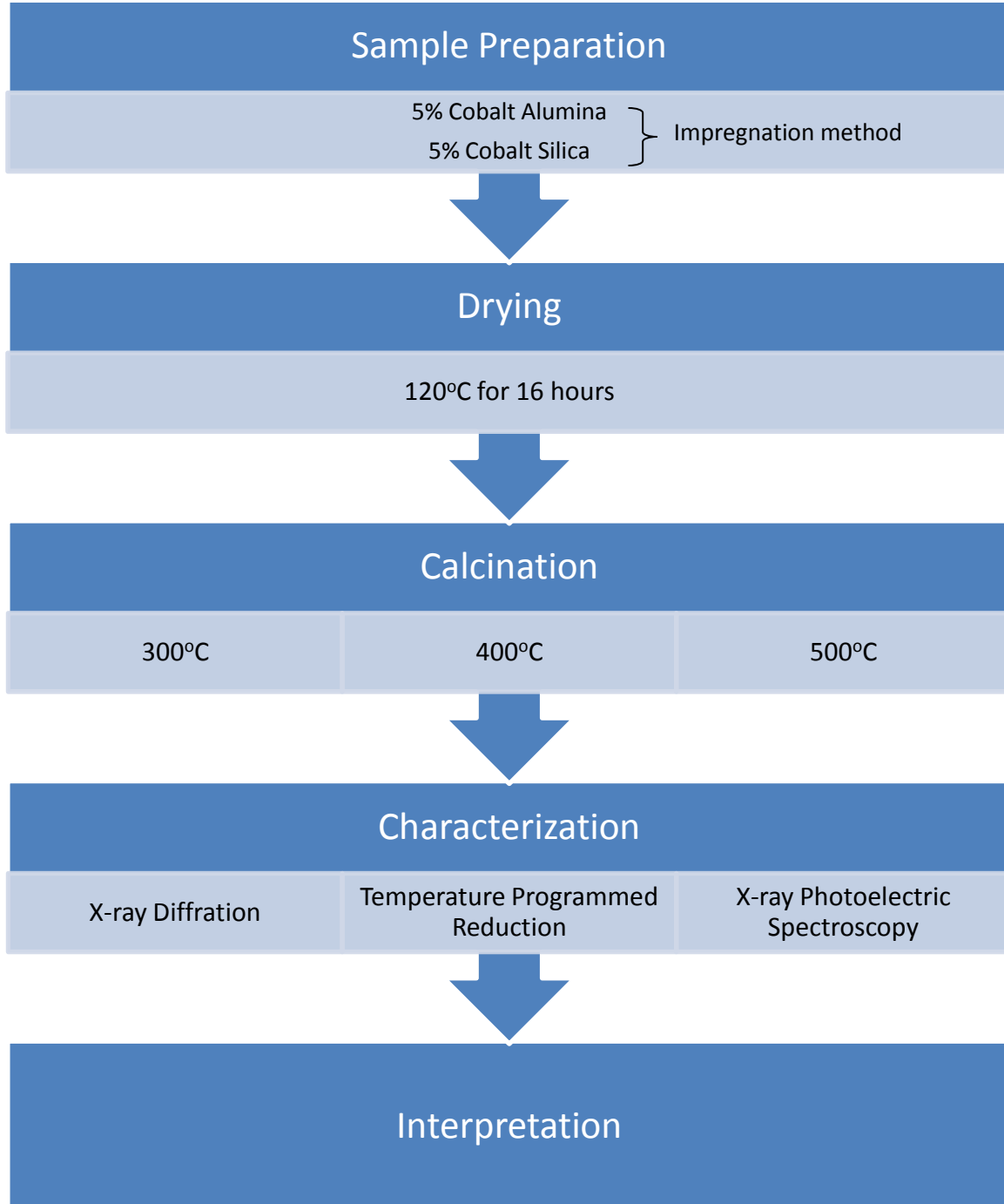


Figure 2: Flowchart of Methodology

3.1 Sample Preparation

5 g 5wt % cobalt loading for Co/Al₂O₃ and Co/Si₂O using impregnation method

The catalysts were prepared by the wet impregnation technique using OX-50 alumina. To produce 5g of the catalysts, 0.25 g of cobalt is needed, therefore 1.2319 g of Cobalt nitrate Co(NO₃)₂ · 6H₂O is measured. Sample calculation is shown in Appendix A. Cobalt nitrate is dissolved in water and drop little by little on the stirred support until all of the precursor solution is mixed together with the support. The mixture is stirred for 24 hours at room temperature. The same procedure was repeated using Silica as support.

3.2 Drying

The sample was dried in 120°C for 16 hours to make sure any water trapped inside the mixture is completely evaporated. The sample was crushed and stirred after the first 1 hour of drying.

3.3 Calcination

The produced 5 g sample will be calcined at 300°C, 400°C and 500°C heating rate is set at 5°C min⁻¹ and dwell at the setpoint temperature for minimum 5 hours before cooled down to 30°C at 3°C min⁻¹.

3.4 Interpretations

All together 6 samples were made: 3 samples for each support with varying calcinations temperature and currently being characterized using Temperature Programmed Reduction, X-ray diffraction and X-ray Photoelectron Spectroscopy. The results for each sample are compared in term of calcinations temperature and catalytic support on how they perform from the other samples.

X-Ray Diffraction

XRD is used to characterize thickness, crystallographic structure, and strain in thin epitaxial films. It employs parallel-beam optics. It is a non-destructive analytical technique which reveals information about the crystallographic structure, chemical composition, and physical properties of materials. On this research, emphasis will be on recognizing the catalytic structure whether crystalline or amorphous.

Temperature Programmed Reduction

TPR profiles for the catalysts is estimated to show two apparent peaks and these are attributed to the reduction of Co_3O_4 to CoO , which then reduces at higher temperatures to metallic Co^0 . If the calcination shifted the position of the high temperature peak to a lower temperature, it is indicating a larger cluster size and therefore a decreased interaction of the cluster with the support.

X-Ray Photoelectron Spectroscopy

This equipment is used to study the changes of the catalyst in exposure to heat to monitor the reduction temperature. The element to be studied is Cobalt, Aluminum and Oxygen. Since these characteristic peaks correspond to the electron configuration of the electrons within the atoms, the reduction temperature of the element studied can be obtained. The number of detected electrons in each of the characteristic peaks is directly related to the amount of element within the area (volume) irradiated.

Chapter 4

4 Results and Discussion

All samples will be labeled as Table 2 below. As previously mentioned, these samples will be characterized using TPR, XRD and XPS. The results from the characterization equipment will be compared in term of support and calcinations temperature as the modified variables of this experiment.

Table 2: Sample labeling and the criteria

Sample	Criteria
A	Co/Al ₂ O ₃ 500 °C
B	Co/Al ₂ O ₃ 400 °C
C	Co/Al ₂ O ₃ 300 °C
D	Co/SiO ₂ 500 °C
E	Co/SiO ₂ 400 °C
F	Co/SiO ₂ 300 °C

Temperature Programmed Reduction

Support Comparison

The results will be grouped together according to the calcined temperature to see the effect of support to the reduction temperature. What will be observed is the reduction temperature to the lower metal oxides. Lower reduction temperature will indicate lower activation energy which is favorable for a catalyst.

Detailed table for this result is attached in the appendix

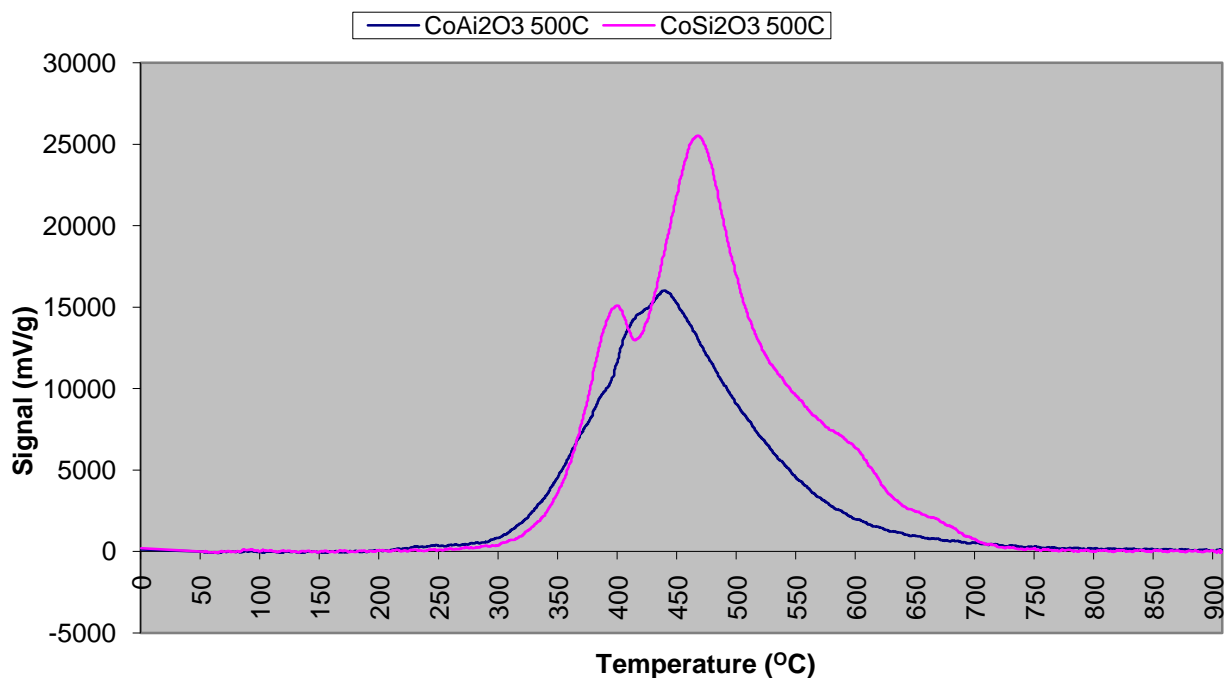


Figure 3: TPR result for Cobalt /Alumina and Cobalt /Silica calcined at 500 C

The peaks for Cobalt /Alumina is at 440 C and Cobalt Silica at 474 C, which shows in figure 3 that Cobalt /Alumina has lower activation energy compared to Cobalt /Silica for this sample.

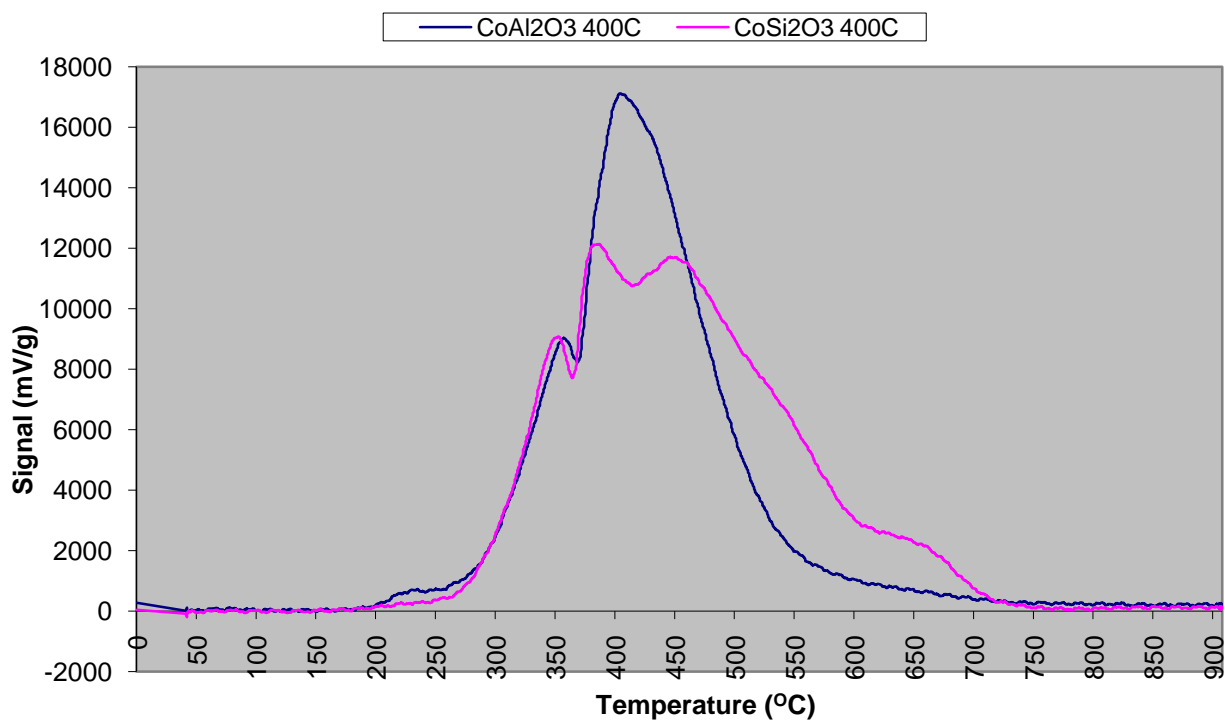


Figure 4: TPR result for Cobalt /Alumina and Cobalt /Silica calcined at 400 C

The first peaks for both samples shows that reduction from Co_3O_4 to CoO at 355 C, which then reduces at higher temperatures to metallic Co^0 at the second peak. The second peaks for Cobalt /Alumina is at 401 C and Cobalt Silica at 415 C, which shows in figure 4 that Cobalt /Alumina has lower activation energy compared to Cobalt /Silica for this sample.

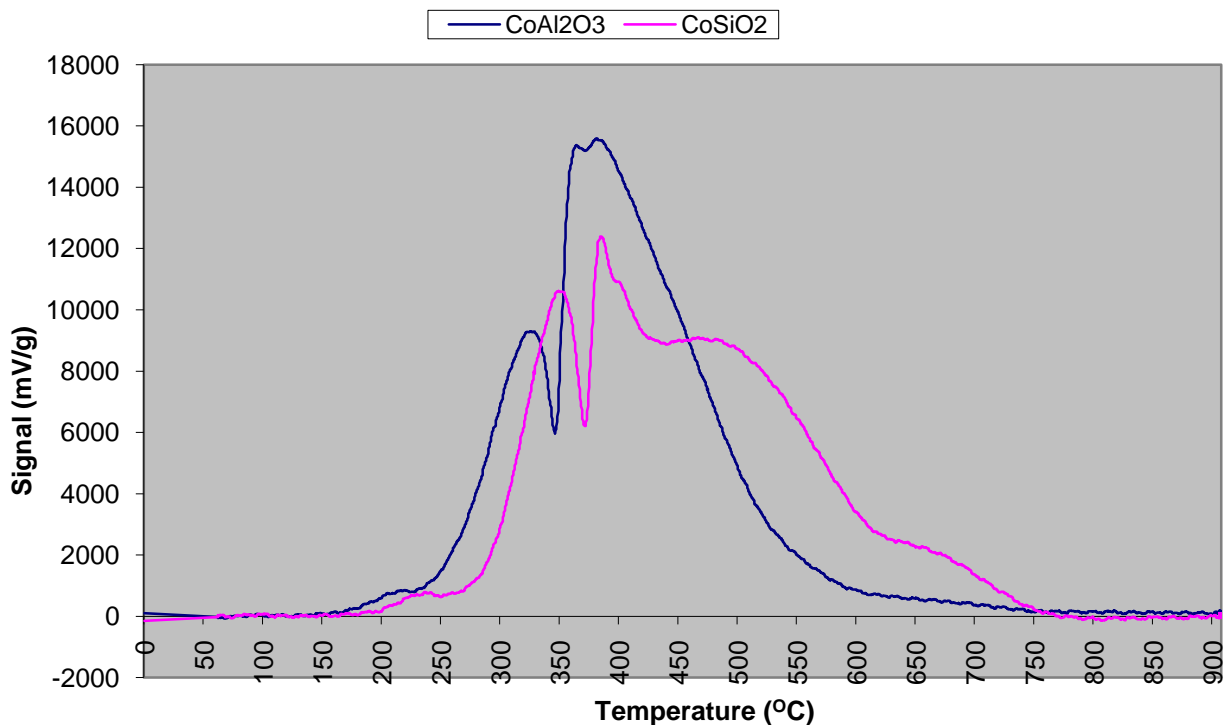


Figure 5: TPR result for Cobalt /Alumina and Cobalt /Silica calcined at 300 C

Similar to figure 4, the first peaks for both samples shows that reduction from Co_3O_4 to CoO at 323 C for Cobalt /Alumina and 350 C for Cobalt /Silica, which then reduces at higher temperatures to metallic Co^0 at the second peak. The second peaks for Cobalt /Alumina is at 385 C and Cobalt Silica at 390 C, which shows in figure 5 that Cobalt /Alumina has lower activation energy compared to Cobalt /Silica for this sample.

The support comparison shows Cobalt /Alumina has lower activation energy than Cobalt /Silica. Therefore, Cobalt /Alumina is more favorable than Cobalt /Silica.

Temperature Comparison

The results will be grouped together according to the catalytic support to see the effect of temperature to the reduction temperature. What will be observed is also the reduction temperature to the lower metal oxides. Lower reduction temperature will indicate lower activation energy which is favorable for a catalyst.

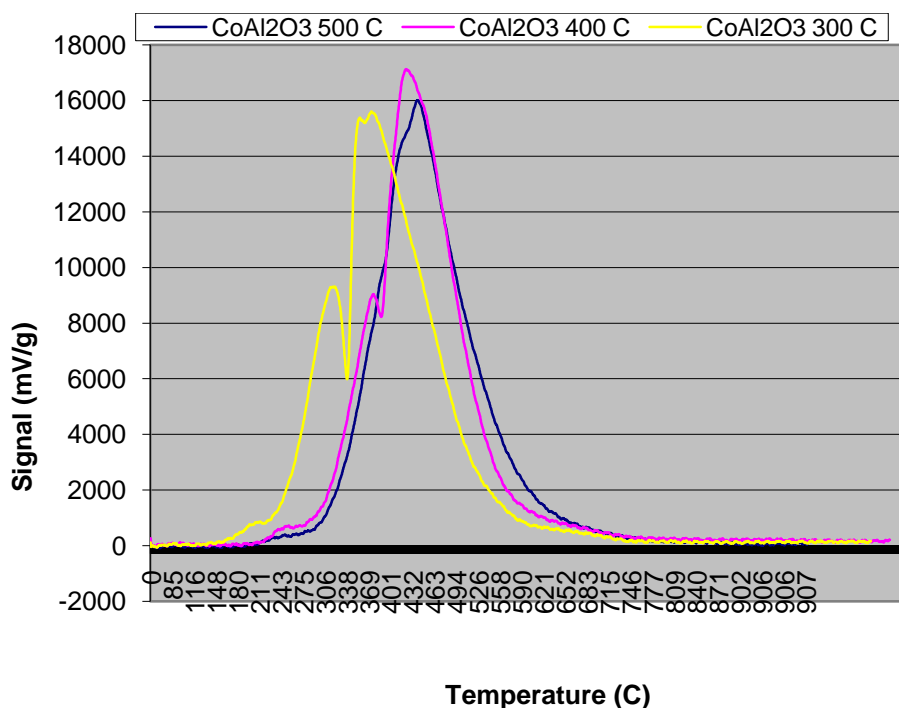


Figure 6 (a): TPR result for Cobalt /Alumina calcined at 500 C, 400 C and 300 C

From figure 6 (a), Cobalt /Alumina at 300 C has the peak shifted due to the difference in calcination temperature. Which shows that at 300 C calcined temperature, catalyst will have lower activation energy than 400 C and 500 C calcined temperature.

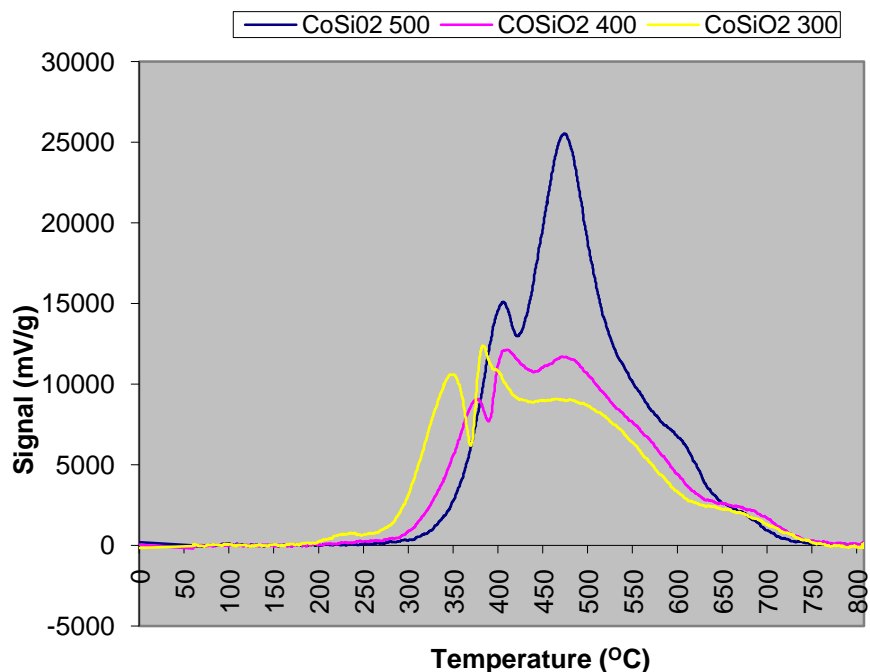


Figure 6 (b): TPR result for Cobalt /Silica calcined at 500 C, 400 C and 300 C

Similar to figure 6 (a), figure 6 (b) for Cobalt /Silica at 300 C also has the peak shifted due to the difference in calcination temperature. Which shows that at 300 C calcined temperature, catalyst will have lower activation energy than 400 C and 500 C calcined temperature.

Overall, for the temperature comparison, for all temperature, Cobalt /Alumina reduction temperature is lower than that of Cobalt /Silica. And 300 C calcinations temperature seems to yield the lowest reduction temperature than 400 C and 500 C. From this comparison Cobalt /Alumina at 300 C is more favorable compared with the rest.

X-Ray Diffraction

Support comparison

High peaks with low noise indicates a crystallite structure while low peaks and little noise indicates amorphous structure.

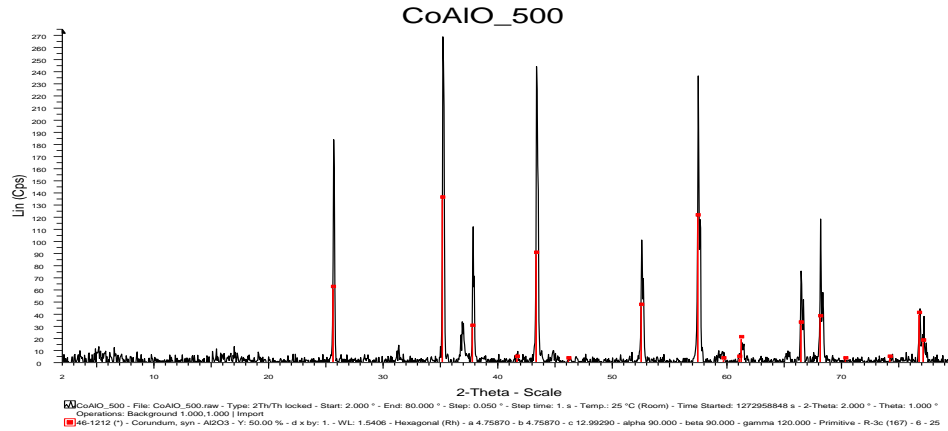


Figure 7 (a) XRD result for Cobalt/Alumina calcined at 500 C

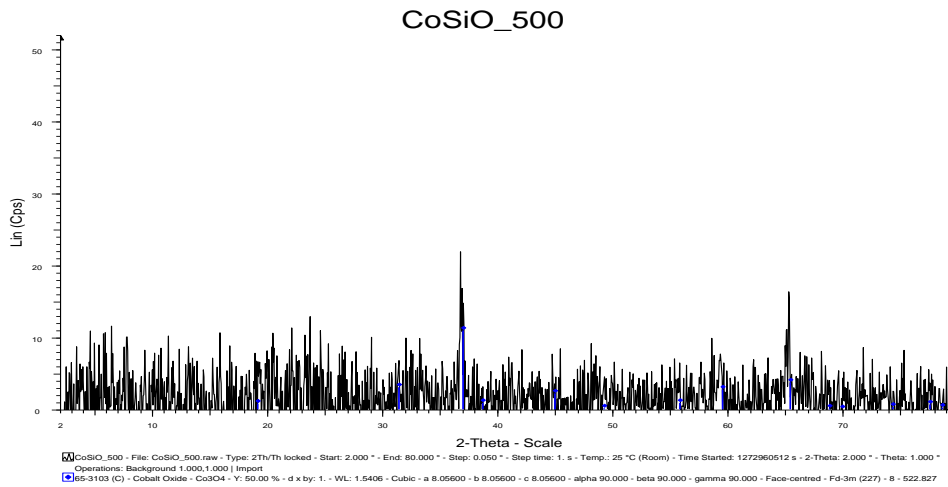


Figure 7 (b) XRD result for Cobalt /Silica calcined at 500 C

From figure 7(a) and (b), Cobalt Alumina produces crystallite while Cobalt Silica produces amorphous. Crystallite is reacts better compared to amorphous structure, thus Cobalt Alumina is more preferable than Cobalt Silica. For XRD, only sample for 500 C calcined

temperature is tested since it already yield crystallite structure for Cobalt /Alumina and amorphous for Cobalt /Silica.

X-ray Photoelectron Spectroscopy

For XPS, the element studied is Cobalt, Aluminum and Oxygen. Peak(s) on the graph indicates the reduction temperature of the element to the lower oxides. Catalyst with lower reduction temperature is favorable as it contributes to lower activation energy.

Co2p scan

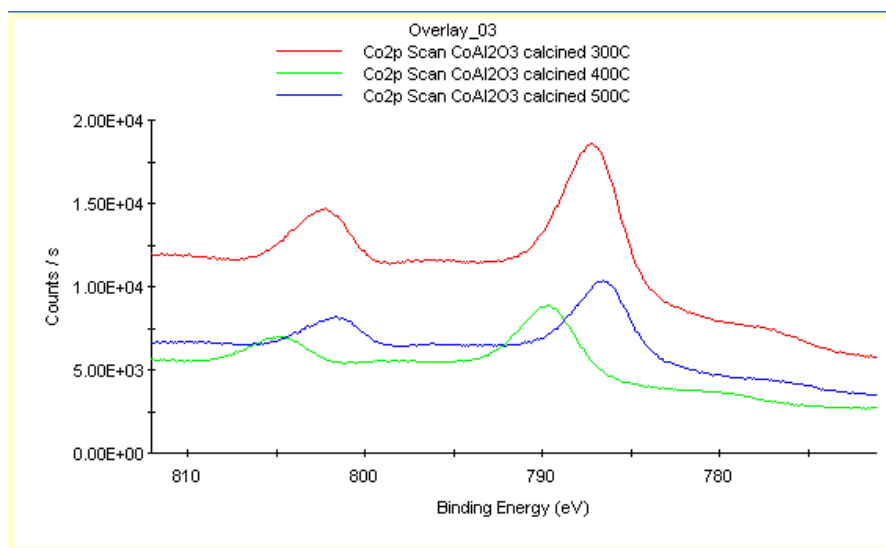


Figure 8 (a): XPS result for Co2p scan for Cobalt /Alumina

Temperature comparison

From figure 8 (a), the first peak indicates reduction to Co₂O₃ and second peak indicates reduction to Co⁰. Cobalt /Alumina at 500 C calcined temperature shows to has the lowest binding energy, 786 eV followed by 300 C and 400 C.

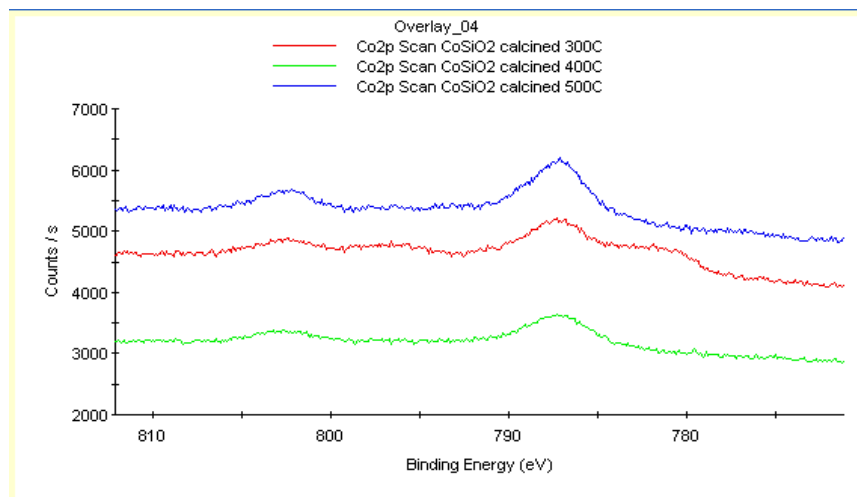


Figure 8 (b): XPS result for Co2p scan for Cobalt /Silica

Temperature comparison

From figure 8 (b), the first peak indicates reduction to Co_2O_3 and second peak indicates reduction to Co^0 . Calcined temperature difference seems to show no effect on Cobalt /Silica since both peaks are set at the same point for all three calcined temperature samples.

Support comparison

Referring to figure 8 (a) and (b), in Cobalt reduction, the reduction temperature Cobalt /Alumina sample (786 eV) is slightly lower than Cobalt /Silica (788 eV).

Al2p scan

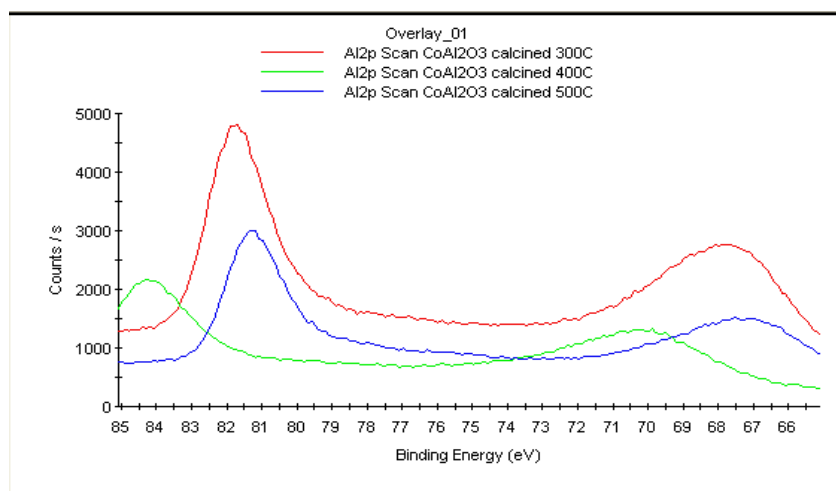


Figure 9 (a): XPS result for Al2p scan for Cobalt /Alumina

Temperature comparison

From figure 9 (a), the first peak indicates reduction to AlO_2 and second peak indicates reduction to Al^0 metallic. Cobalt /Alumina calcined at 500 C has the lowest binding energy, 67.5 eV followed by 300 C and 400 C reduction temperature

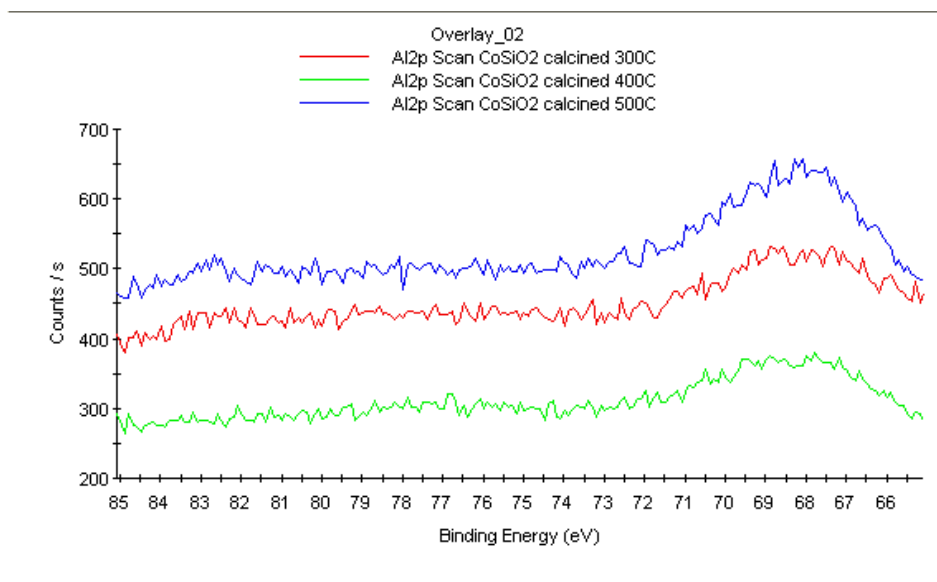


Figure 9 (b): XPS result for Al2p scan for Cobalt /Silica

Temperature comparison

From figure 9 (b), Cobalt Silica only show 1 peak for reduction to Al^0 as this samples does not contain Aluminum element. Calcined temperature difference seems to show no effect on Cobalt /Silica since the peaks are set at the same point for all three calcined temperature samples.

Support comparison

Referring to figure 9 (a) and (b), in Aluminum reduction, the reduction temperature Cobalt /Alumina (67 eV) sample is slightly lower than Cobalt /Silica (68 eV).

O1s scan

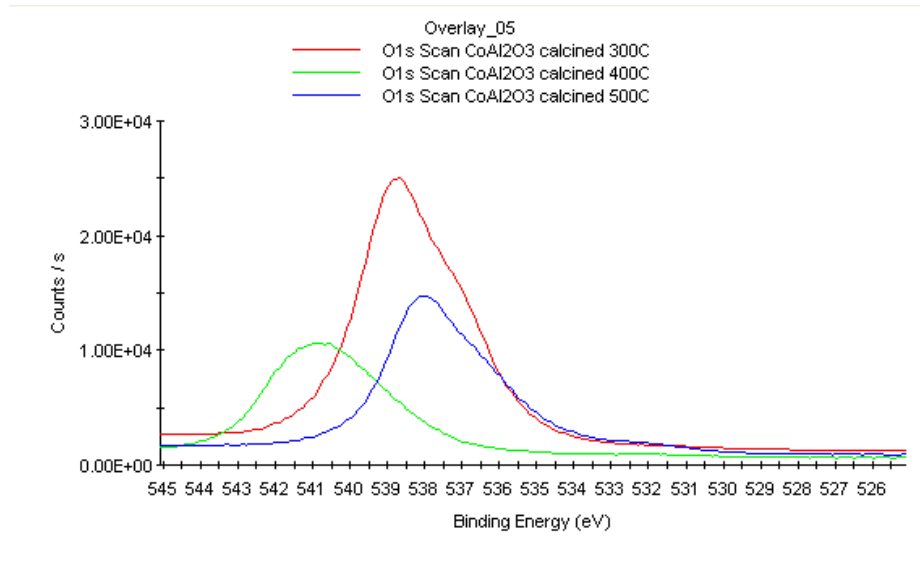


Figure 10 (a): XPS result for O1s scan for Cobalt /Alumina

Temperature comparison

From figure 10 (a), the peak indicates reduction to Oxygen atom. Sample for Cobalt /Alumina calcined at 500 C has the lowest binding energy, 538 eV followed by 300 C and 400 C. Since all XPS results for Cobalt /Alumina calcined at 400 C shifted a higher compared to 300 C sample, sample contamination is suspected for Cobalt /Alumina calcined at 400 C.

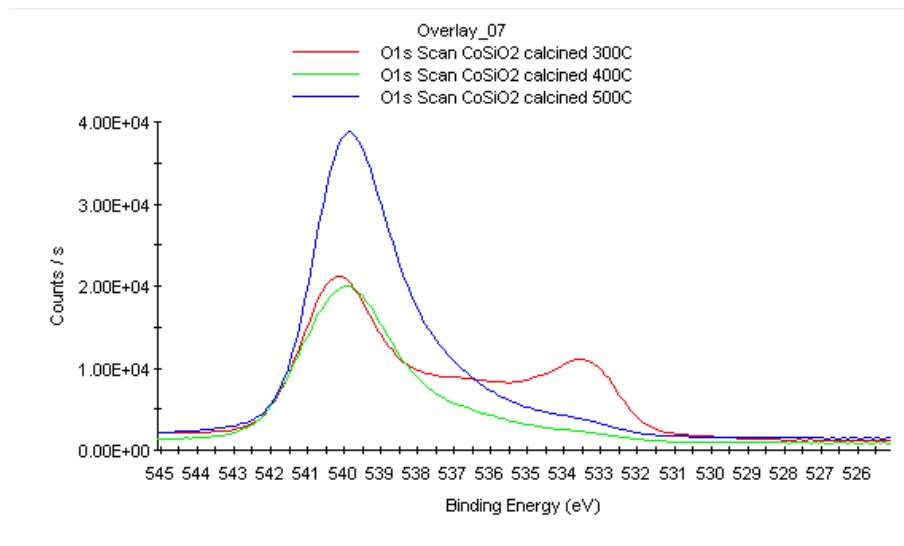


Figure 10 (b): XPS result for O1s scan for Cobalt /Silica

Temperature comparison

From figure 10 (b), the peak indicates reduction to Oxygen atom. The second peak in Cobalt /Silica calcined at 300 C may be caused by contamination as the result contradicts with 500 C and 400 C calcined samples. Calcined temperature difference seems to show no effect on Cobalt /Silica since the peaks are set at the same point for all three calcined temperature samples.

Support comparison

Referring to figure 9 (a) and (b), in Oxygen reduction, the reduction temperature Cobalt /Alumina sample (538 eV) is lower than Cobalt /Silica (540 eV).

Chapter 5

CONCLUSIONS

In all, there are several factors contributing in producing a good catalyst. In this study of calcinations parameter of Fischer Tropsch Cobalt based nanocatalysts, we have managed to study the sample preparation and the characterization method using TPR, XRD and XPS.

XRD is used to characterize thickness, crystallographic structure, and strain in thin epitaxial films. XRD results indicates that Cobalt /Alumina produces crystallite structure compared to amorphous produced by Cobalt /Silica.

TPR profiles for the catalysts is estimated to show two apparent peaks and these are attributed to the reduction of Co_3O_4 to CoO , which then reduces at higher temperatures to metallic Co^0 . From the results, it shows lower activation energy for Cobalt /Alumina in the 300 C calcined sample

XPS shows lower binding energy for Cobalt /Alumina than Cobalt /Silica which indicates lower activation energy for all three element scan; Co2p scan, Al2p scan and O1s scan. All three characterization equipment shows favorable on Cobalt /Alumina over Cobalt /Silica.

The calcined temperature comparison affects the reduction temperature of the samples and this clearly shows on the TPR results. However, the calcined temperature comparison does not show any variety on the XPS results for all element scan.

From the results and observation, it can be concluded that Cobalt /Alumina is better than Cobalt /Silica for having lower reduction temperature which contributes to lower activation energy and having crystalline structure which reacts better than amorphous shown by Cobalt /Silica. The best calcinations temperature from the comparison is 300 C. Which makes Cobalt /Alumina at 300 C calcined temperature will perform best among other samples.

The objectives of the research is achieved. The catalyst design and parameters of calcinations process has been studied, catalysts of different properties has been produced by manipulating the calcined temperature and catalytic support and the best parameter condition for Cobalt based FT catalyst has been chosen based on the parameters taken into account.

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