CHAPTER 1

INTRODUCTION

1.1. Background of Study

Various processes are carried out in the industry to produce clean and high purity diesel fuels and lubricating oil. One common environmentally friendly method used is the Fischer-Tropsch synthesis (FTS) which converts syn gas (mixture of CO and H_2) to a range of hydrocarbons. The first FTS experiment was conducted in the 20th century in which methane was synthesized from carbon monoxide and hydrogen. Catalysts play a vital role in producing reasonably good FTS as they enhance the rate and selectivity of chemical reaction and they will be regenerated. The catalyst productivity and selectivity towards hydrocarbons is an important criteria in the design of FTS catalysts. At present, cobalt-based catalyst is favored for the FTS because of their performance in terms of high selectivity, high activity and they are cheap as well.[1] In addition, several supports like SiO_2, Al_2O_3 and TiO_2 are needed as the textural and chemical properties of the supports influence the catalytic performances and selectivity of Co-based catalyst. This happens by modification on reducibility and dispersion of cobalt catalyst. Metal promoters are introduced to the catalyst to improve the catalytic performance. These promoters contribute impact to the adsorption intensity, FT reaction rates and the structures and dispersion of catalyst. The FTS can be optimized by selecting the suitable promoter for the cobalt-based catalyst, the support as well as the promoter.

1.2.Problem Statement

The problem revolves around preparing the best obtainable or optimum Co/SiO_2 Fischer-Tropsch nanocatalyst that enhances the FTS with the addition of a promoter. zirconium(Zr) and manganese (Mn) have been chosen as the capable promoters to this case.

Effects of Zr and Mn on Co/SiO_2 properties such as high selectivity, reducibility and the interaction between the nanocatalyst and support as well as the particle size and morphology have to be identified or studied and compared in order to know the effectiveness for selecting that particular promoter. This is because different promoters give different effects on the structure and catalytic performance of the Co/SiO_2. Furthermore, the effect of promoter can be studied in terms of the loadings and other experiment parameters. Besides, from the various preparation methods of FT catalysts, a particular method has to be chosen to prepare Co/SiO_2 nanocatalyst and the promoter.

1.3. Objective and Scope of Study

The main goal of the project is to study the effect of metal promoter on the properties of Co/SiO_2 nanocatalyst. Zirconium and manganese are used as the promoter. Both the promoters are from the same group which is promotion with metal oxides but the different effects on the catalyst is studied.This project covers the following:

i. Prepare Co/SiO_2 with the promotion of Zr and Mn
ii. Perform characterization and comprehend the properties of the catalyst prepared using several characterization techniques(TPR,XRD and FE SEM)
iii. To relate the physical and chemical properties of the promoters used and the effects on the properties of Co/SiO_2

1.4. Feasibility of Project

This project requires carrying out experiments to prepare Co/SiO_2 nanocatalyst with the addition of Zr and Mn followed by characterization studies on the morphology, reducibility of cobalt spesies and interaction between the nanocatalyst and the support. The chemicals required for this project are currently available at the laboratory while the characterization study has to be sent outside. However these can be accomplished within the time given which is close to a year.

CHAPTER 2
LITERATURE REVIEW

2.1. Fischer-Tropsch Synthesis

The decreasing of oil propelled an improved production of liquid hydrocarbons from Carbon Monoxide and Hydrogen via metal catalyst also known as Fischer-Tropsch Synthesis. This method was founded by Franz Fischer and Hans Tropsch eight decades ago. The hybdrocarbons synthesized from this process are mainly paraffin and the by-products are olefin and alcohol. Coal gasification and Fischer-Tropsch Synthesis combination leads to production of liquid fuels. This effort led to the operation of Fischer-Tropsch plants using mainly cobalt-based F-T catalyst. Cobalt and iron were the metals initially or first proposed in this process. The Group VIII metals as well have significant affect on this process; ruthenium, iron, cobalt, nickel. The hydrogenation of carbon monoxide to hydrocarbon:

$$n\mathrm{CO} + 2n\mathrm{H}_2 \rightarrow \mathrm{C}n\mathrm{H}_2n + n\mathrm{H}_2\mathrm{O}$$
$$n\mathrm{CO} + (2n + 1)\ \mathrm{H}_2 \rightarrow \mathrm{C}n\mathrm{H}_2n{+}2 + n\mathrm{H}_2\mathrm{O}$$

Although the FT technology was of less importance or applied by people after the world war due to the economics, the FTS has picked up in recent years. This is because of the increase in crude oil price and the need to produce environmentally friendly automotive fuels. Therefore in the future natural gas will be a major source to produce fuels and chemicals as currently crude oil is the feedstock used. The drawback of FTS is that its selectivity is towards the production of methane and the back conversion of methane to syngas is not economic.[3] Hence the selection of the right catalyst is vital in helping the FTS to decrease the methane production. Supported cobalt catalyst and its nanoparticles are favoured for the FTS as they are generally not too expensive, possess high –yields of long chain paraffins, low activity for the competing water-gas shift reaction and high activity or performance compared to other catalyst suitable for the reaction. Besides the types of reactor is taken into consideration too when selecting the catalyst materials to be used for the plant operations. However in this case study, reactor types will not be considered as the effect of metal promoter on the nanocatalyst is the main objective.

2.2. Catalyst, Nano-Catalyst, FT Catalyst

Basically catalyst is another substance than reactants added to a chemical reaction which enhances the rate and selectivity of a chemical reaction and is regenerated cyclically. A catalyst that is in the same phase as the reactant and product is known as homogenous catalyst while that is in a separate phase from them is called heterogeneous catalyst or contact catalyst. This type of catalyst is material that has the capability to adsorb gas and liquid molecules onto their surfaces and regenerated.

A catalyst reduces the activation energy E_a, which is the energy barrier, necessary for electron exchange in a reaction by providing an alternate pathway for the reaction, thus speeding the reaction rate. The rate and rate constant k of a reaction are related to E_a as shown below:

$$\text{Rate of reaction} = k * \text{function of concentration}$$

$$k = A \exp\left({}^{-E}{}_{a} / {}_{RT}\right)$$

where A is a constant related to collision rates.

Thus, change in E_a changes/affects the rate of a reaction.

Nano- catalyst from the name itself can be explained as catalyst that exists in small particles, usually less than 100nanometres (nm). The nanoparticles’ properties are different from the properties of bulk material. Researchers observations states that using nanoparticles or nanocatalyst in catalytic processes gives dramatic effects. Use of nanocatalyst also gives much desired results due to the larger surface area contact.

Fischer-Tropsch Synthesis is the production of hydrocarbons with broad range of chain length from syn-gas or can be explained as the catalytic hydrogenation of carbon monoxide.[4] Group VIII transition metals are known to be the active metal for FTS but not all of the metals from that group gives effect to the carbon monoxide hydrogenation activity. The few active metals from Group VIII that is suitable for this reaction are nickel, cobalt, iron and ruthenium. The active FT metal choice for a catalyst is based on few parameters which include the price of the metal element, the carbon source used in producing the syn gas and the products desired.[2]

2.3. Cobalt catalyst

Cobalt and iron were the metals initially or first proposed by Hans Fischer and Franz Tropsch for the syn gas conversion or hydrocarbon synthesis. Cobalt catalysts are more expensive compared to iron catalysts but they were known to be active for the hydrocarbons production, possess higher resistance to deactivation and oxidation. G.R. Moradi et. al.[3] mentioned that cobalt catalysts are more preferred for this reaction as they possess high yields of long chain paraffins, low activity for the competing water-gas shift reaction and high activity or performance compared to iron catalysts. Besides, due to the environmental considerations, cobalt is believed to be less harmful than iron because of its high water-gas shift activity which contributes to greenhouse effect. The productivity of syn gas at high conversion is significant with cobalt and the water-shift reaction is less significant with cobalt. *Table 2.1* below displays the performance comparison between cobalt and iron catalysts in terms on their selectivity and activity. It can be seen that for both promoted and unprompoted catalyst, cobalt is much more active than iron on per gram catalyst and on a site basis. Also the C_{5+} selectivities of cobalt catalyst are approximately 20-30% higher.[1] Cobalt is very sensitive to sulfur and this could contaminate them easily, hence the amount of sulfur in syn gas should be much lesser than 0.1ppm in order to avoid contamination. Cobalt catalysts operate at a very low temperature and pressure ranges and an increase in the temperature leads to increase in methane selectivity. F.Diehl et al.[5] studies explain that to have an effective FTS, certain criteria of the cobalt catalyst has to be followed:

- high density of cobalt surface metal sites
- cobalt metal particles larger than 6-8 nm
- low fraction of barely reducible cobalt compounds (cobalt silicate, etc.)
- the cobalt metal surface sites and catalyst structure should be stable at FT reaction conditions;
- the cost of cobalt catalysts should be reduced.

Table 2.1: Co vs. Fe Catalysts Performance Comparison[1]

Catalyst composition^a	TOF x 10^3 $(s^{-1})^b$	$-r_{CO}$ (μmol/$g_{cat.b}$)	$T(P_{tot})^c$ Select. data	Sco_2 (at C%)^d	S_{CH4} (at C%)^d	Sc_{5-} (at C%)^d	α^c
Co/support(18)	23±4		200(20)	-	6.8± 1.1	84.8±3.1	0.93-0.95
12Co/Ti	18	2.7	200(20)		7.0	84.5	0.945
12Co0.1Ru/Ti	56	10	200(20)	0.1	5.0	93	0.946
15Co/Al	13	11	220(20)	0.6	11	76	0.91
12Co/Al		24	195(1)		10	$90(C_{2+})$	
12Co0.5Re/Al		61	195(1)		12	$88(C_{2+})$	
40Co2.0Re/Al		114	195(1)		16	$84(C_{2+})$	
12Co/Al		16	195(1)		10	$90(C_{2+})$	
12Co0.1Pt/Al		40	195(1)		16	$86(C_{2+})$	
20Co0.17Pt/Al		54	195(1)		17	$83(C_{2+})$	
99Fe/1%Al	5.8±1.7		240(10)	16	61	9	0.70
98Fe1.3K/1Al	15± 1		240(10)	10	39	25	0.79
90Fe/10Zn	7.4	1.8	220(32)	2.3	4.8	82	> 0.90
Fe-Zn-K_4-Cu_2	18	6.0	220(32)	17	3.8	81	> 0.90
Fe/K/Cu/Si	4.4	4.8	220(20)	18	5.6	69	0.91
1.1%Ru/TiO_2	16		200(20)	-	3.5	93	0.96

2.4 Silicon Dioxide/Silica – Catalyst Support

Both the structure and catalyst performance depend on the catalyst support and the types of support used are oxide supported cobalt, novel mesoporous and carbon supports. These supports function is to ease cobalt dispersion and produce stable cobalt particles after reduction process. Furthermore, the support materials provide mechanical strength and thermal stability to the cobalt catalyst. The catalyst support texture affects the strength of the FT catalyst and also the diffusion and capillary condensation of products from a reaction in the catalyst particles.[6] Generally cobalt catalysts supported on oxide are more resistance to attrition. Different cobalt oxide support gives different results on the number of active cobalt metal sites after reduction and also the amount of supported cobalt oxide that is reduced to its metal state. This is because the interaction between the cobalt catalyst and its support varies. For example, titania or alumina supported cobalt which has strong interactions, gives rise to the dispersion of the cobalt particles but reduces their reduction capability which leads to the reduced number of active cobalt metal sites. On the other hand, silica supported cobalt has weaker interaction comparatively and this facilitates to higher reducibility of cobalt catalyst.[4] However, the disadvantage is that, the dispersion of cobalt in silica supported catalyst is low thus it will be a challenge during the designing stage. Saib et al.[7] studies show that "the effect of silica-supported cobalt varies by the particle sizes and in general the catalyst with particle sizes between 6-10nm shows high FT performance and C5+ selectivity." This information will be useful when conducting the experiment as the correct sizes of catalyst and its support will give the desirable result.

2.5 Promoters

Promoters are not catalyst themselves but they are doping agents that are added in small amounts to improve the performance or effectiveness of a catalyst in terms of their selectivity, activity and stability. Promoter element assists the cobalt nanoparticles' reduction and leads to the number of active cobalt sites being increased. There are two common metal promotions used for cobalt catalyst and they are promotion with Noble

Metals and promotion with oxides. Promoter's effects can be classified into few categories and the common ones for cobalt based FT catalysts are structural promoters and electronic promoters. Structural promoters have an effect on the cobalt dispersion as it controls the cobalt-support oxide interaction and increases the active sites in a catalyst.[8] The increased active sites in a catalyst are achieved by hindering metal-support formation and avoiding cobalt particles from clustering hence smaller supported cobalt particles can be formed. An electronic promoter influences the turnover rate of a catalyst material and it can happen only when there is direct contact of the promoter and catalyst active site. In general this type of promoter increases the catalyst stability against deactivation. It is also important to note that the Co FT performance differs greatly towards the preparation method and the operating conditions. The addition of metal promoters to a catalyst leads to a few conditions such as[4]

i. Water-gas shift reaction

Water-gas shift (WGS) reaction is an undesirable reaction and with the addition of WGS reagent promoters, the ratio of the syn gas converting to CO_2 decreases. With this the activity and selectivity of the catalyst can be altered. Usually transition metal oxides acts as WGS reagents

ii. Hydrogenation/Dehydrogenation

As the main desired product of FTS is paraffins, adding a promoter affects the ratio of the alkanes to alkenes produced to a more desirable value.

iii. Coke burning during regeneration

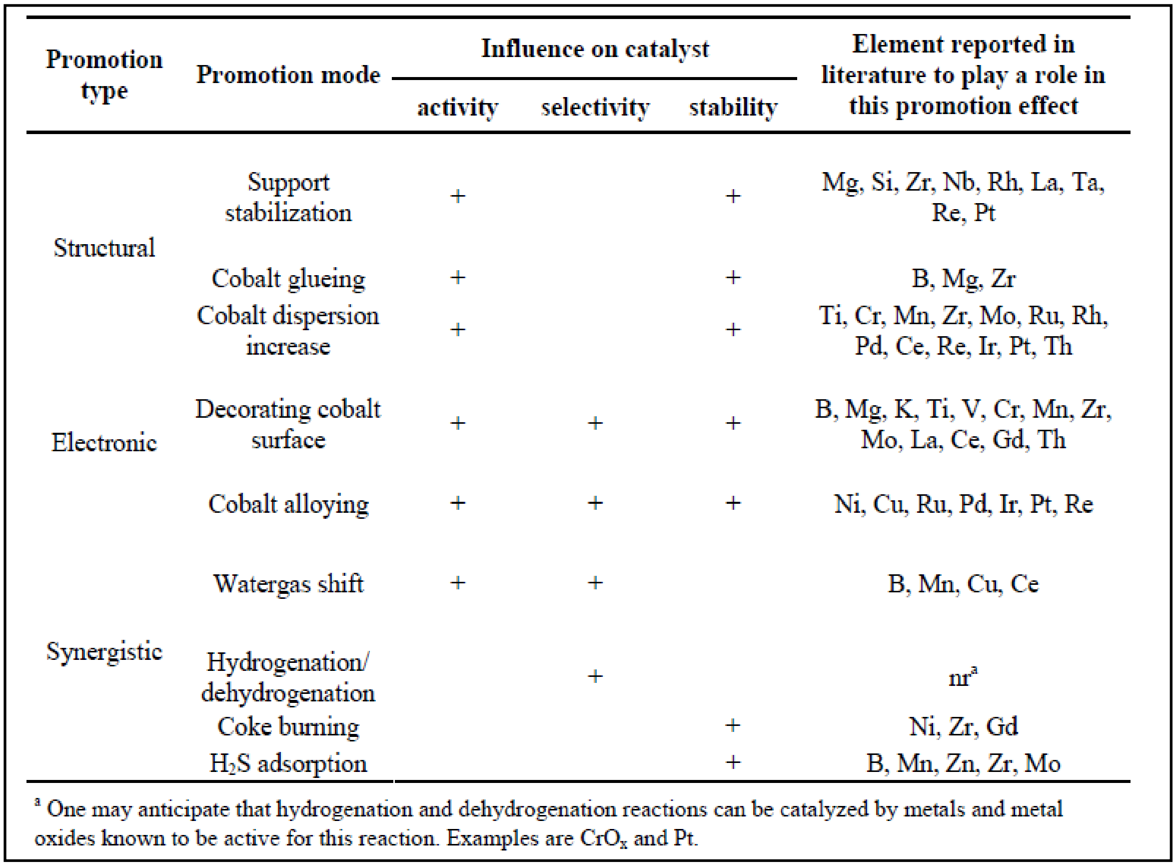
The formation of carbonaceous residue which is known as coke deactivates the FTS catalyst by blocking the actives sites. The formation of coke can be overcome by an oxidative treatment which may be conducted at high temperatures. Hence the addition of promoter elements may help in decreasing the temperature which directly prevents the clustering of the cobalt catalyst.

iv. *H_2S adsorption reaction*

As cobalt FT catalyst is known to be prone to H_2S poisoning, adding specific promoter elements would aid in reducing the effect of H_2S on the catalyst. For H_2S tolerance metal promotes like Boron and Zinc are used.

It can be seen that different metal promoters has different effects on a Fischer Tropsch catalyst. Promoters are added according to what is required of the catalyst. In this study where promotion with metal oxides is given the concentration, the common metal promoters such as zirconia and manganese are used. Promotion with metal oxides alters the catalyst texture, increases cobalt dispersion and reducibility as well as improves the chemical stability of the catalyst support. *Table 2.2* below shows an overview of the different metal promoters' effect.

Table 2.2 : The Promotion Effects Displayed By The Different Elements For The Co Fischer-Tropsch Catalytic Performances



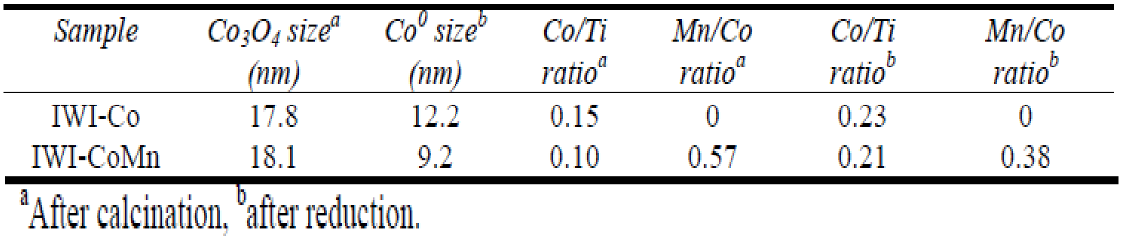
Promotion type	Promotion mode	Influence on catalyst			Element reported in literature to play a role in this promotion effect
		activity	selectivity	stability	
Structural	Support stabilization	+		+	Mg, Si, Zr, Nb, Rh, La, Ta, Re, Pt
	Cobalt glueing	+		+	B, Mg, Zr
	Cobalt dispersion increase	+		+	Ti, Cr, Mn, Zr, Mo, Ru, Rh, Pd, Ce, Re, Ir, Pt, Th
Electronic	Decorating cobalt surface	+	+	+	B, Mg, K, Ti, V, Cr, Mn, Zr, Mo, La, Ce, Gd, Th
	Cobalt alloying	+	+	+	Ni, Cu, Ru, Pd, Ir, Pt, Re
Synergistic	Watergas shift	+	+		B, Mn, Cu, Ce
	Hydrogenation/ dehydrogenation		+		nr[a]
	Coke burning			+	Ni, Zr, Gd
	H_2S adsorption			+	B, Mn, Zn, Zr, Mo

[a] One may anticipate that hydrogenation and dehydrogenation reactions can be catalyzed by metals and metal oxides known to be active for this reaction. Examples are CrO_x and Pt.

2.5.1 Manganese, Mn

Manganese is known to be a perspective promoter as it improves the CO conversion rate and the hydrocarbon selectivity which is what needed of a Fischer Tropsch catalyst.[5] According to Zhang et al. A small amount of manganese in the catalyst can improve the dispersion of cobalt active phase. Based on the studies conducted it was found that addition of manganese to Co/SiO_2 increases the metallic state of cobalt as the most active Mn-Co/SiO_2 consists of a large amount of cobalt in its metallic state.[9] This takes place as the oxidized manganese attracts more oxygen allowing Cobalt to remain in its metallic state. Hence when the metallic state is increased, the activity of the catalyst is improved as well.[4] However there is not much concentration on manganese effect on silica supported catalyst as mostly are on titania supported catalyst. *Table 2.3* shows the properties of the catalyst after calcination and reduction. Based on the Mn/Co ratio, it seems that Mn is dispersed on top of Co_3O_4 and TiO_2. This is due to the high metal-support bond. Also noticed is that, after reduction, the Mn/Co ratio decreased from 0.57 to 0.38 and this is probably because of the increase of the Co signal. Meaning the Mn is dispersed on TiO_2 even before the reduction without much interaction with Co. Hence the increase in Mn/TiO_2 ratio due to the migration of Mn from the Co particles to the TiO_2 as the metal is reduced to its metallic state

Table 2.3:XRD and XPS results obtained for the calcined and reduced Co/TiO2 catalysts.



Sample	*Co_3O_4 size^a (nm)*	*Co^0 size^b (nm)*	*Co/Ti ratio^a*	*Mn/Co ratio^a*	*Co/Ti ratio^b*	*Mn/Co ratio^b*
IWI-Co	17.8	12.2	0.15	0	0.23	0
IWI-CoMn	18.1	9.2	0.10	0.57	0.21	0.38

^{a}After calcination, ^{b}after reduction.

Figure 2.1 below shows the TPR results of manganese promoted Co/TiO_2 catalyst which was prepared via incipient wetness impregnation method.

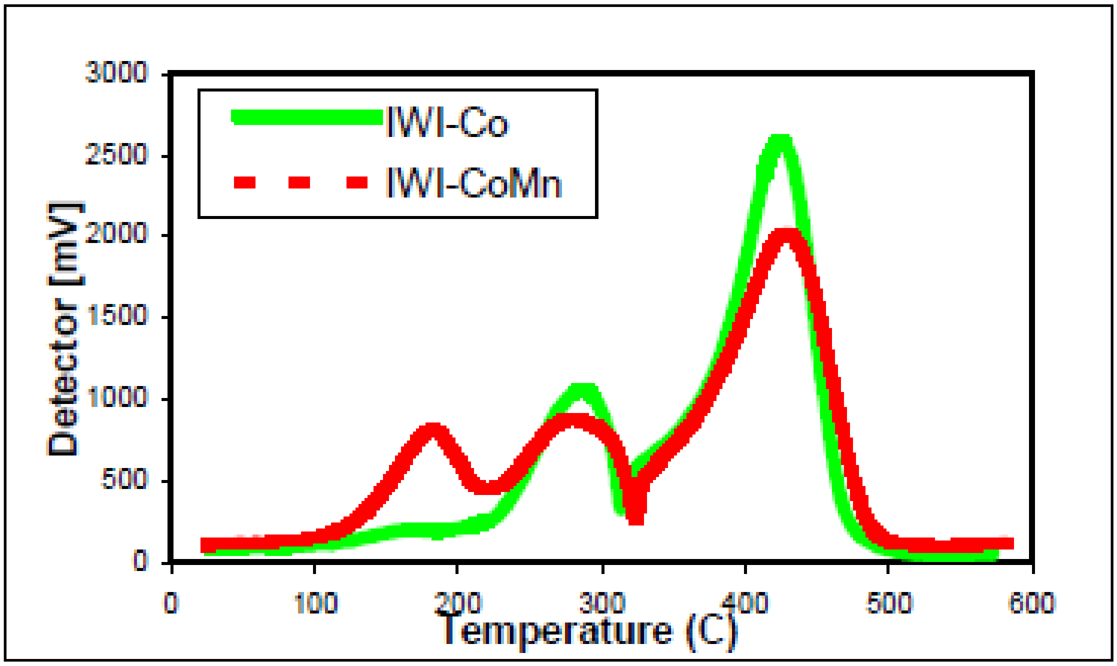
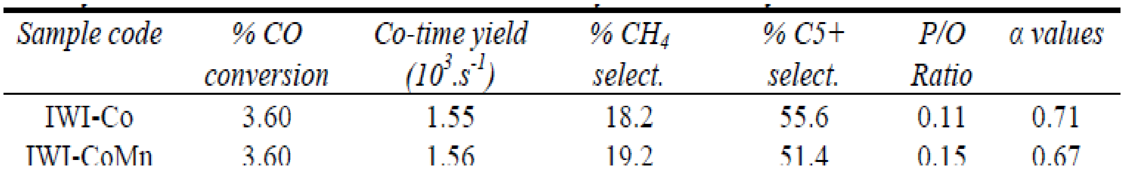


Figure 2:1: TPR profile of unpromoted and Mn-promoted Co/TiO_2 catalyst

The TPR profile shows that, with the manganese addition a new reduction peak is seen at a lower temperature but this is due to the reduction of the Maganese compound itself. The new peak has no effect on the reduction temperature of the Co as based from the XRD and XPS results, there is not much interaction between Mn and Co.

The catalytic activity was tested via CO conversion and *Table 2.4* shows the results of it. Both the samples have the same conversion however the promoted sample does not have any improvement on the catalytic activity. In fact it lowers the selectivity. Nevertheless the promotion of Mn enhanced the catalytic stability.

Table 2.4 : Steady state FTS results for the Co/TiO_2 catalysts under study.



Sample code	*% CO conversion*	*Co-time yield ($10^3.s^{-1}$)*	*% CH_4 select.*	*% C5+ select.*	*P/O Ratio*	*α values*
IWI-Co	3.60	1.55	18.2	55.6	0.11	0.71
IWI-CoMn	3.60	1.56	19.2	51.4	0.15	0.67

This results show that a promoter does not have the same result for all the catalyst, the effect varies as some enhances the catalytic performance and some do not have any effect at all or lowers the performance. Therefore in this project further studies can be done on promotion of manganese on Co/SiO_2 and comparison can be made with the present studies on manganese promotion on titania supported catalyst.

2.5.2 Zirconium, Zr

Promotion with metal oxide is via transition metal oxides and these metal oxides are regarded as electronic promoters. Hence it affects the intrinsic activity and/or selectivity of the cobalt sites.[10] Zirconium is generally used to test the promotion with oxides in which zirconium dioxide or also known as zirconia is added to the silica –supported cobalt catalyst. Promotion with zirconium leads to higher FT reaction rates as well as increase in C5+ selectivity.[6] By increasing zirconia, the interaction of Co-SiO_2 depreciates and is gradually replaced by Co–Zr interaction which favours the reducibility of the catalyst at much lower temperatures. GR Moradi et. al[3] claims pre-impregnated zirconia forms cobalt silicate and makes a protecting layer to prevent major interaction between SiO_2 and Co which can only be reduced at high temperatures approximately 800K and above. Besides that the reaction between Zr and the catalyst also depends on the preparation method of the catalyst.

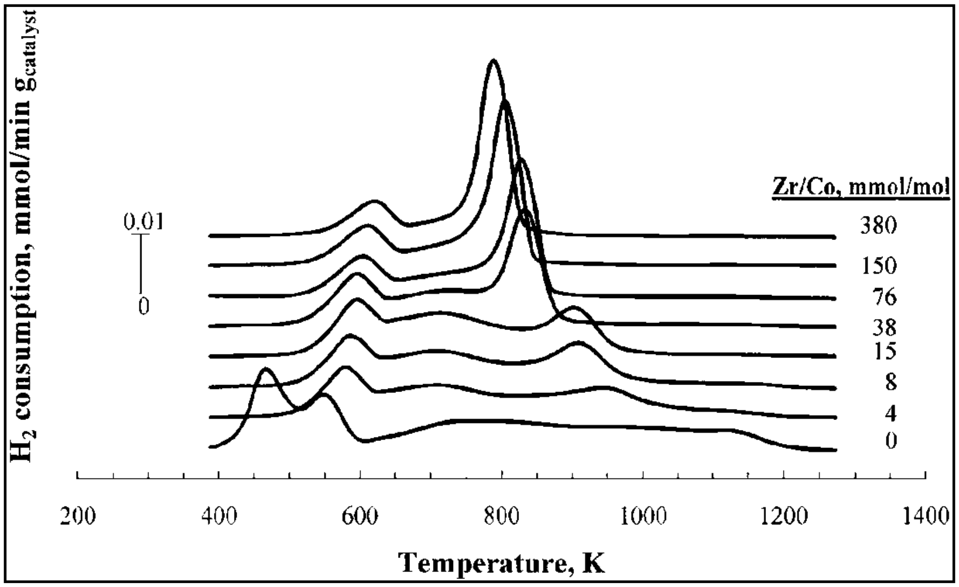


Figure 2.2: Influence of Zr loading on the reduction behaviour of Zr promoted Co/SiO_2

Andreas Feller et al. conducted a study on Zr promotion to Co/SiO_2 and based on the TPR that was conducted, *(Figure 2.1)* it was mentioned that the hydrogen consumption is between 1.04 and 1.4 mol $H_{2consumed}$/mol Co. However it decreases with the increase in Zr loading while the sample without Zr displays typical reduction behavior of the Co/SiO_2. The maximum points at somewhat lower temperatures can be related to the reduction process of and this reduction process is followed by broad region of hydrogen;

$$Co_3O_4\ (Co(III)_2Co(II)O_4 \rightarrow\ Co(II)\ O \rightarrow Co$$

The observations from TPR also shows that once the Zr was added to the catalyst, the low temperature peak disappears, which contribute to the possibility that the promoted Co/SiO_2 contains lesser Co_3O_4. The most important observation from the TPR would be the high temperature region in which the broad regions of hydrogen consumptions narrow up to a sharp maximum. This is where the interaction between Co-Zr replaces the Co/SiO_2 interaction.

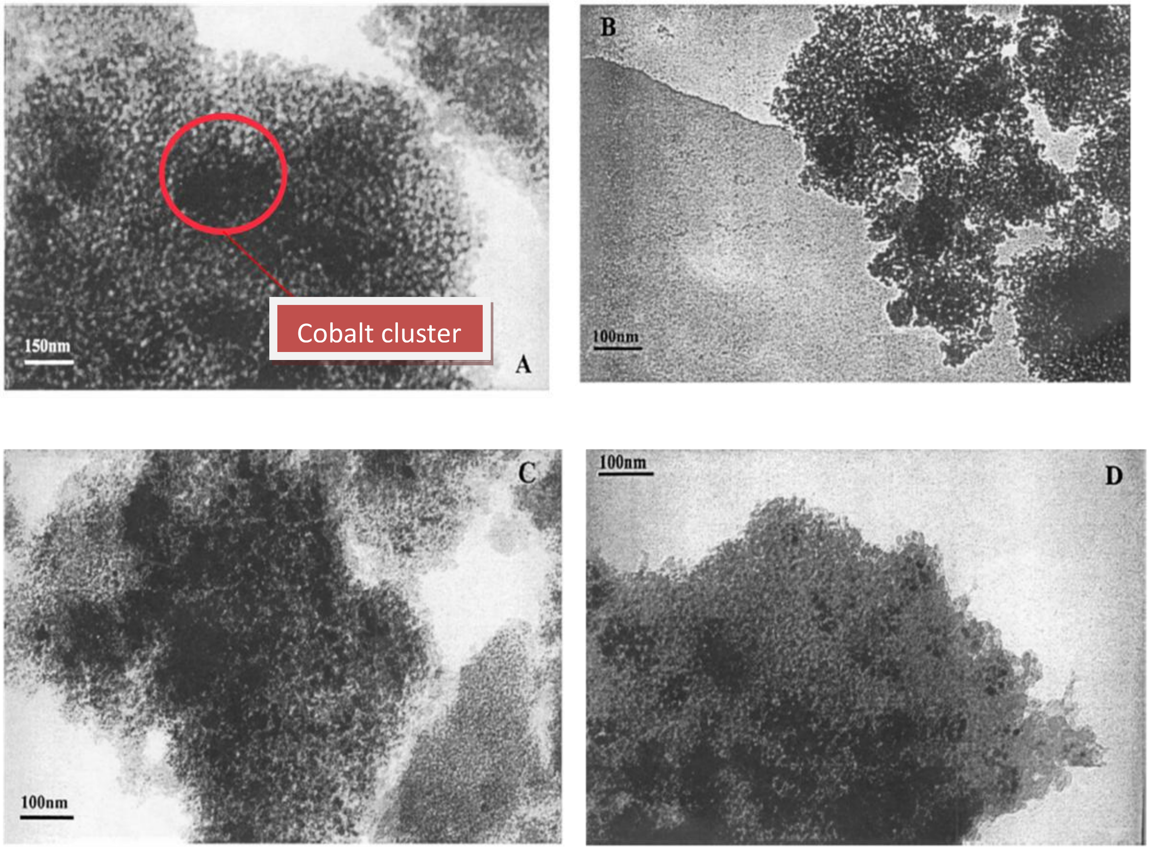


Figure 2.3 : TEM images of reduced samples (Co/SiO2=0.085 g/g) with varying zirconium content. (A) 0 mmol Zr/mol Co; (B) 15 mmol Zr/mol Co; (C) 38 mmol Zr/mol Co; (D) 76 mmol Zr/mol Co;

Based on Andreas Feller et al. studies, the cobalt particles are present in clusters in Co/SiO_2 and this can be seen from the TEM results in *Figure 2.2*. The TEM images showed that the cobalt cluster size decreases with increasing zirconium but the size of the cobalt particle itself increases. This is due to the strong interaction between zirconium and cobalt, Zr/Co and Co-SiO_2 interaction is reduced. The promoted catalyst also shows a better dispersion of the metal. It was also mentioned that the cobalt cluster formation affects the selectivity of Fischer Tropsch synthesis. Meaning when there is formation of the metal clusters, the distribution of the metal on its support or the catalyst itself is inhomogeneous.

2.6 Catalyst Preparation- Impregnation

Heterogeneous catalysts are frequently defined as solids or mixtures of solids which accelerate chemical reaction without themselves undergoing changes. There are various methods in producing the cobalt catalyst which includes precipitation, sol-gel, impregnation, deposition-precipitation, eggshell catalyst, colloidal method, adsorption etc. Among the methods mentioned above, the impregnation method is opted for the project**.** Impregnation is generally divided into two sub-method which are wet impregnation and incipient wetness impregnation. As for wet impregnation excess solution is used to contact the metal on the support fully or in other words to fully absorb in the pores of the support hence the volume of solution used is greater than the pore volume of the support. Whereas for incipient wetness impregnation the solution used is corresponding to the pore volume of the support either the same volume or smaller volume. Impregnation is basically contacting the precursor of the active phase with the solid support whereby the succeeding step is to remove the imbibed solvent by drying. The main purpose of the usage of this method is due to the fact that it is the most versatile technique which can be controlled to give good dispersion and known loading of reagents or support. In this method a metal is contacted with an oxide of high surface area in so that small metal particles with large surface area can be created followed by drying the remaining absorbed solvent and this method is commonly used to prepare cobalt-supported catalyst. However when selecting an oxide support, it must be ensured that the support is compatible with the corresponding catalyst material and according to the point of zero charge (PZC) of the oxide. PZC is the pH at which the net surface charge is zero. A.Y. Khodakov et. al[6] state that “at pH below the PZC, the surfaces of the corresponding oxides are charged positively, at pH higher than the PZC, the surface of the support is charged negatively.” Therefore at pH higher than PZC, the Co cations are distributed more homogeneously

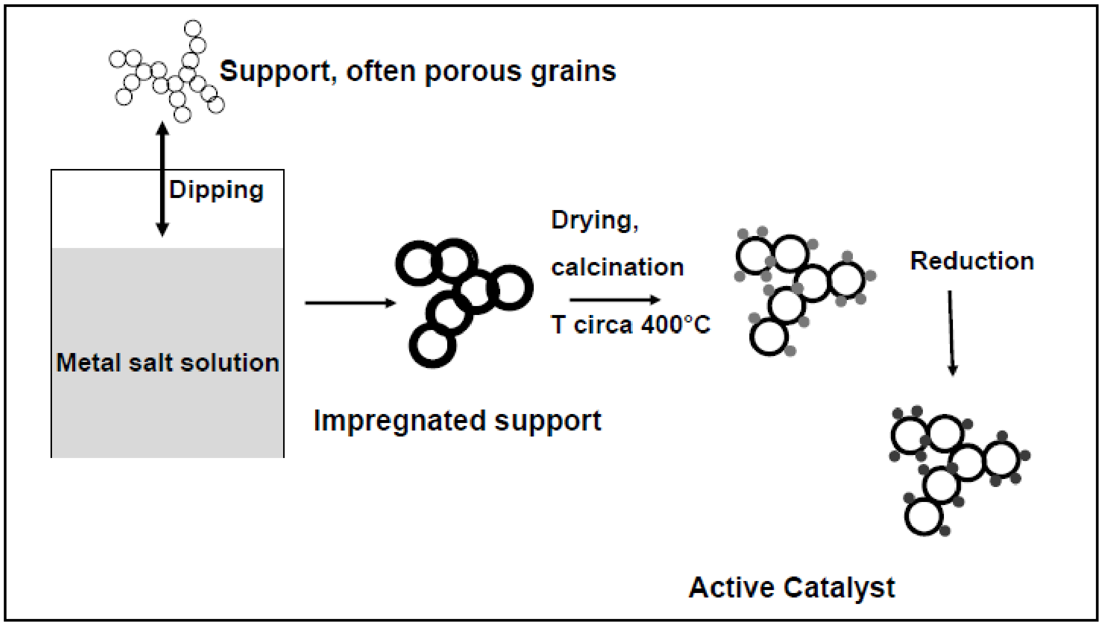


Figure 2.4: Catalyst Preparation Method- Impregnation

2.7. Characterization Method

Characterization of heterogeneous catalyst refers to the measurement of its characteristics in terms of the physical, chemical and catalytic properties, the catalyst structure, and identification of the active sites as well as the morphology of the catalysts. The characterization methods that are useful in this project include TPR, XRD and FE-SEM.

2.7.1. Temperature-Programmed Reduction(TPR)

TPR yields information of the reducibility of the oxide's surface as well heterogeneity of the reducible surface. TPR is commonly used to characterize heterogeneous catalysts. The characterization is done via measurement of hydrogen consumption during the heating process at constant temperature rate with continuous gas flow.[6] The flow usually consists of 5-10% of hydrogen in argon. The reduction of the catalyst with different species takes place with the interaction of the catalyst and hydrogen. Therefore the reducibility of catalyst and other information is measured based on the hydrogen consumption profile. However, there are certain limitations in using TPR as the TPR profile does not give direct information of the catalyst structure. Even the hydrogen consumption sometimes provides information on different reduction process. Furthermore the catalyst is exposed to high temperatures during the measurement which could affect the original catalyst structure.

2.7.2. X-Ray Diffraction (XRD)

XRD is used to yield reliable data about the structure of the cobalt active phases, the crystallographic structure and the chemical composition of materials. Furthermore XRD helps to measure the average spacing between layers or rows of atoms and determine the orientation of a single crystal or grain. It works via electron diffractions. When an X-ray beam hits an atom, the electrons surrounding the atom oscillate with the same frequency as the incoming beam. There will be destructive interference in all directions and constructive interference in very few directions. Hence there will be well-defined X-ray beams leaving the sample at various directions which are called diffracted beam.[11]

2.7.3. Field Emission Scanning Electron Microscope (FE-SEM)

FE-SEM is used to observe the fine surface morphology of the nanoparticles. There is a field-emission cathode in the scanning electron microscope gun which has narrower probing beams at low and high electron energy. This results in improved spatial resolution and minimized sample charging/damage. FE-SEM is used as it gives clearer and less electrostatically distorted images. The images are 3 to 6 times better than the conventional SEM.

CHAPTER 3
METHODOLOGY

3.1. Catalyst Preparation

3.1.1. Preparing Co/SiO_2 with Zr and Mn promotion via impregnation

As mentioned previously, the main objective of this project is to study the effects of metal promoter on the properties of Co/SiO_2 nanocatalyst. The promoters used in this project are the transition metal oxide, zirconium and manganese. Therefore the catalyst has to be prepared via one of the deposition methods of active phase and the impregnation method is used as it is said to be one of the successful methods in preparing the FT catalyst. Wet impregnation method is used to prepare the cobalt-supported catalysts and incipient wetness impregnation for the metal promotion. Based on S Ali et. al studies Co/SiO_2 catalysts (0-10 wt %) with different loadings of promoters were prepared within the range of 0-0.1 wt%. The detailed procedure of the experiment is as follow:

1) Total of fourteen (14) samples need to be prepared with 2g of catalyst for each sample.

2) Two metal loadings are used, 5 %wt and 7 %wt. while the promoters' loadings are 0.05 %wt ,0.1 %wt and 0.5 %wt.

3) Prior to the catalyst preparation, the support, Silica is dried in the oven at 120ºC for 12 hours to remove any moisture content.

4) Then the desired amount of the metal cobalt from $Co(NO_3)_2.6H_2O$ is dissolved in an appropriate amount of deionized water, as the method used to prepare is wet impregnation.

5) This mixture is stirred for 15 minutes, for the metal to dissolve properly in the solution.

6) Next the metal is impregnated on to the Silica via titration and this mixture is left to be stirred for 24 hours in the fume hood.

7) The steps (3) to (6) are repeated for different loadings of the metal.

8) The unpromoted samples are calcined at 450ºC for 4 hours and then sent for characterization.

9) Other samples of the catalysts are promoted with zirconia and manganese respectively.

10) The promoters are impregnated on the catalyst prepared via incipient wet impregnation. The experimental setup is similar as to the catalyst preparation and the mixture is left to stir for 4 hours.

11) The promoted catalysts are dried in the oven at 120ºC for 6 hours and calcination at 450ºC for 4 hours.

12) Steps 10 and 11 are repeated with different loadings of the metal promoter.

13) These promoted catalysts are sent for characterizations and the properties of the unpromoted and promoted catalyst are compared.

14) The characterization is done via FE-SEM, TPR, and XRD.

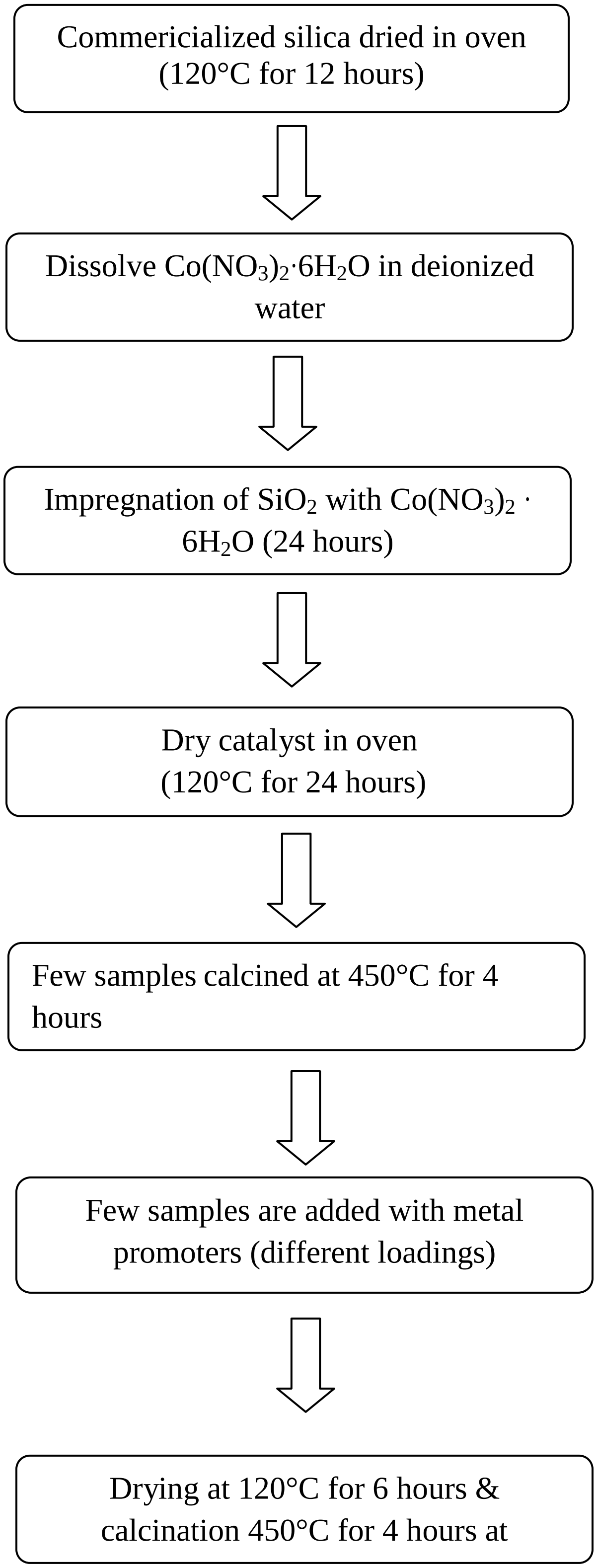


Figure 3.1 :Flow Chart of Catalyst Preparation with Metal Promotion

Table 3.1: Parameters for Catalyst Preparation

Cobalt % wt				Promoters					
				Zr(gms)			Mn(gms)		
% wt	gms	$Co(NO_3)_2.6H_2O$ (gms)	SiO_2 (gms)	0.05 %wt	0.1 %wt	0.5 %wt	0.05 %wt	0.1 %wt	0.5 %wt
5	0.10	0.49	1.9	0.0025	0.0050	0.0253	0.0046	0.0091	0.0457
7	0.14	0.69	1.86						
Drying Temperature (°C)	120°C for 24 hours								
Calcination Temperature(°C)	450°C for 4 hours								

3.1.2. Calculations

The amount of cobalt metal used for 5 %wt to prepare 2g of catalyst:

$$\frac{5}{100} \times 2g = 0.1g$$

Hence Support (silica) = 2g – 0.1g

= 1.9g

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

$$\frac{0.1}{58.933} \times 291.03 = 0.49g$$

While for the Promoter of 0.05 % wt:

e.g. Zirconia

$$\frac{0.05}{100} \times 2g = 0.001g$$

$$\frac{0.001}{91.224} \times 231.23 = 0.0025g$$

Hence for the catalyst with Zr addition

5 %wt Co	= 0.1g
0.05 % wt Zr	= 0.001g
Silica	= 2.0g – 0.1g(Co) – 0.001g(Zr)
	= 1.899g

Given;

MW of Co	= 58.933g
MW of Zr	= 91.224g
MW of $Co(NO_3)_2.6H_2O$	= 291.04g
MW of $ZrO(NO_3)_2.8H_2O$	= 231.23g

3.1.3. Analysis

The analysis is made by the characterization method in which the cobalt catalyst reducibility, selectivity, the structure, morphology, and other information is gained. The characterization methods used are TPR, XRD and FE-SEM.

3.2 Tools & Equipment

The equipments which are essential for this experiment are the characterization devices; TPR, XRD and FE-SEM while the hardware such as glassware used in the laboratory and other standard lab equipments.

3.3 Gantt Chart

Weeks Activities	1	2	3	4	5	6	7		8	9	10	11	12	13	14
Setup of experiment	🟨	🟨	🟨	🟨				**MIDSEM BREAK**							
Preparation of Catalyst				🟨 ●	🟨	🟨	🟨								
Submission of Progress Report 1			🟨	🟨	🟨 ●										
Research/Project Work Continues									🟨	🟨					
Characterization of Catalyst									🟨	🟨 ●	🟨				
Submission of Progress Report 2							🟨		🟨	🟨	🟨	🟨			
Seminar/ Poster Presentation									🟨	🟨	🟨	🟨 ●			
EDX												🟨	🟨 ●		
Final Repost Submission											🟨	🟨	🟨	🟨	🟨 ●

● Suggested Milestone

🟨 Suggested Duration

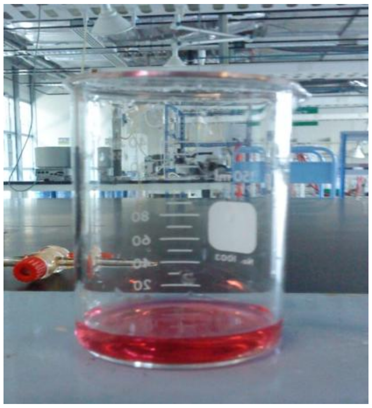
CHAPTER 4
RESULT & DISCUSSION

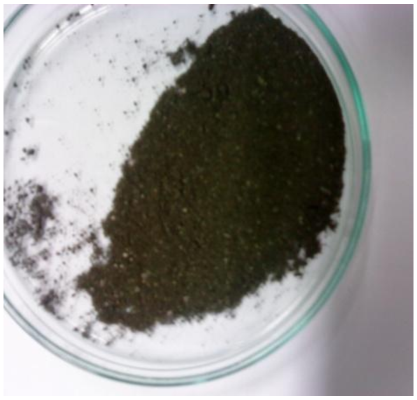
As mentioned earlier, Fischer-Tropsch Synthesis has been given much attention and developed too. The efficiency of the technology depends greatly on the performance of the catalysts used and the common plus appropriate catalyst being used is cobalt and its supported on silica. Promoters are doping agents that further improves the performance of a catalyst and only a small amount of it will be added.

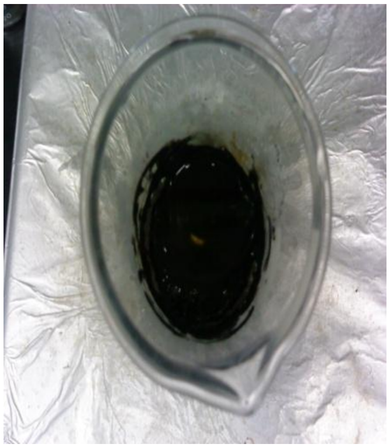
Upon carrying out this project, some observations were made. All the catalyst samples (Co/SiO_2) were prepared via the wet impregnation method, whereby excess of solution is used to ensure the metal fills the total pore volume of the solid support material hence an almost complete adsorption takes place. As for the metal promotion, incipient wetness impregnation method is used in which the metal promoter is dissolved in deionized water of a sufficient amount of it to wet the metal promoter surface with no excess solution. Fourteen samples are prepared so that comparisons can be made in terms of the metal loadings as well as the promoters.

4.1. Observations from Experiment

Table 4.1: Observations from Experiment Conducted

Observation	Discussion
	$Co(NO_3)_2$ before impregnating with SiO_2 via wet impregnation, dissolved with 15ml of deionized water.

	After titration of the metal, Co $(NO_3)_2$ to the SiO_2.Impregnation for 24 hours via stirring. After 24 hours of stirring or impregnation the mixture turns out almost like a paste as the metal has been adsorbed into the support.
	Co/SiO_2 catalyst during the drying process after 2 hours.
	Sample after 12 hours of drying at 120°C and after grinding in order to make it homogeneous before calcination.

	The unpromoted catalyst after calcination. The texture of the sample is smoother after calcination. As at the high calcination temperature the moisture content or any organic matters are removed.
	The catalyst with metal promotion is prepared via incipient wetness impregnation, dissolved in 2ml of deionized water, the mixture is in a paste form.
	After 4 hours of stirring/impregnation the sample turns to powder-like form. The consequent procedure of drying and calcination is the same as unpromoted catalyst as there is no observation can be seen with naked eye.

4.2. FE-SEM Characterization Results

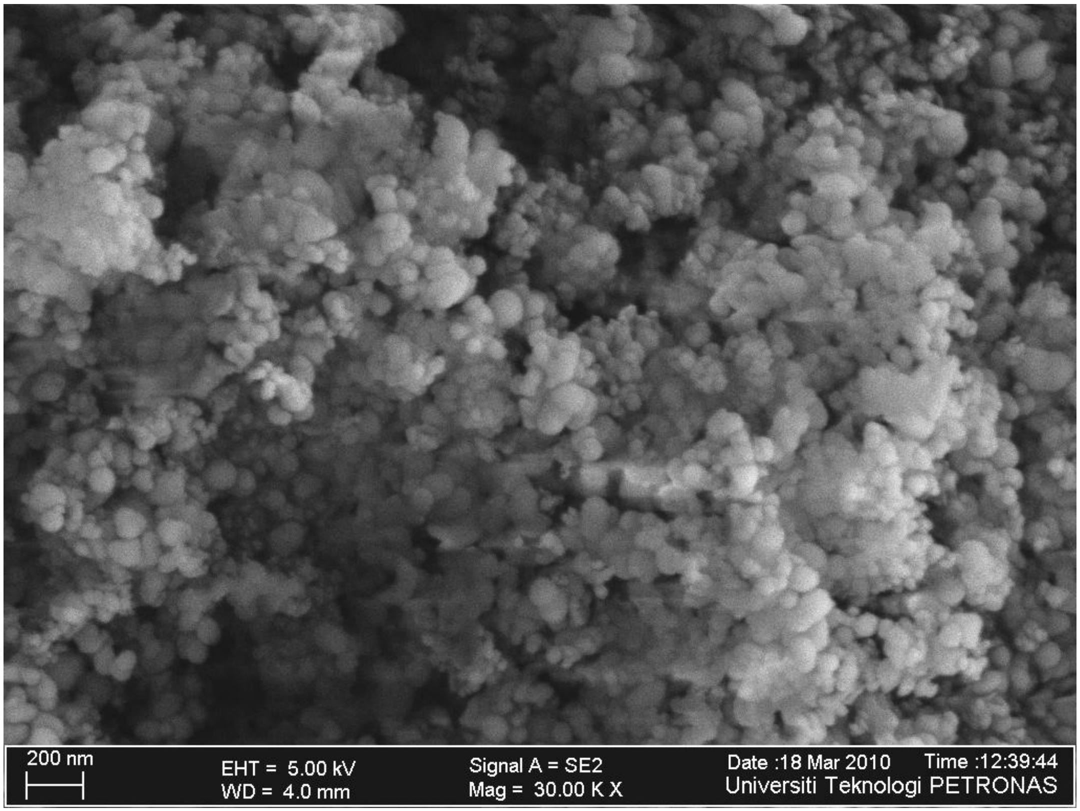


Figure 4.1a :Co/SiO$_2$ with 5wt% Cobalt

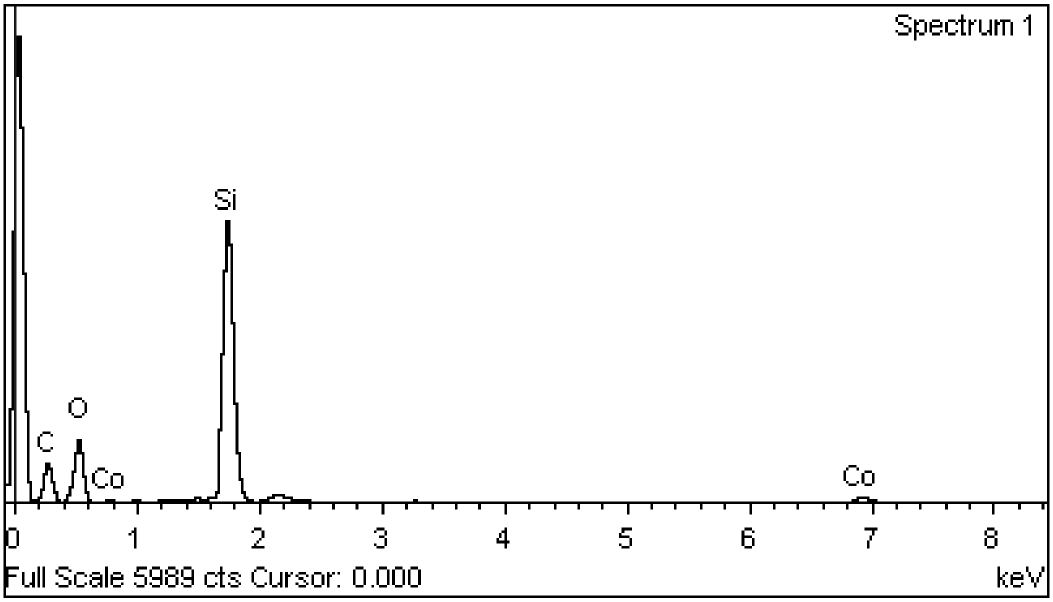


Figure 4.1b: EDX information of FE-SEM of 5Co/SiO$_2$

Figure 4.1a and *Figure 4.1b* depict the unpromoted Co/SiO_2 catalyst. From the graph it can seen be there are traces of cobalt metal found in the silica support approximately 3.14 wt % and from the FE-SEM images the cobalt can hardly be seen. This could be due to the preparation method, the wet impregnation in which the catalyst of 2g was dissolved in 10ml of deionized. The adequate amount will be slightly more than the pore volume roughly 3ml to 5ml hence the concentration of the metal in the support is very little. The other reason could be that, the cobalt has not converted to its metallic state due to the strong bond with the support hence lesser or no active site in the catalyst.

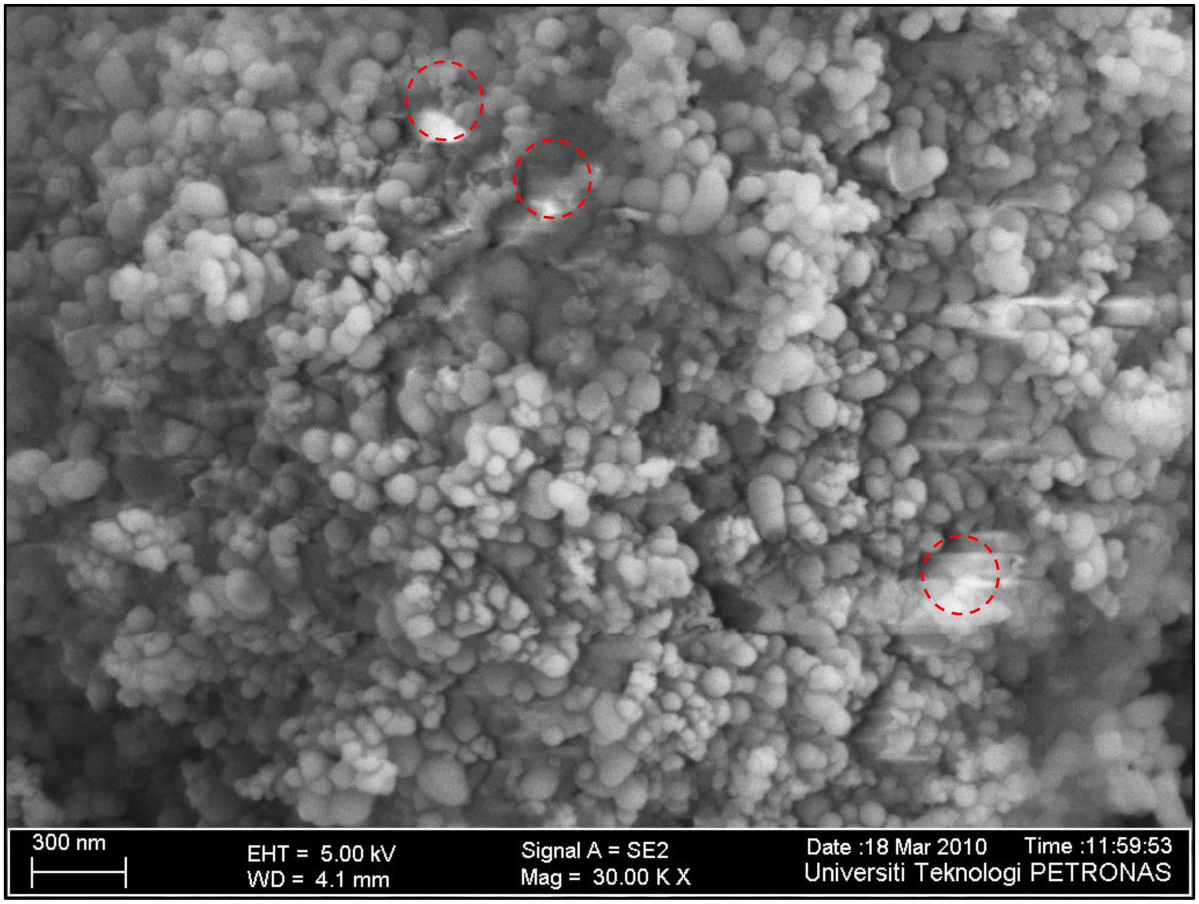


Figure 4.2a:Co/SiO2 with 7wt% Cobalt

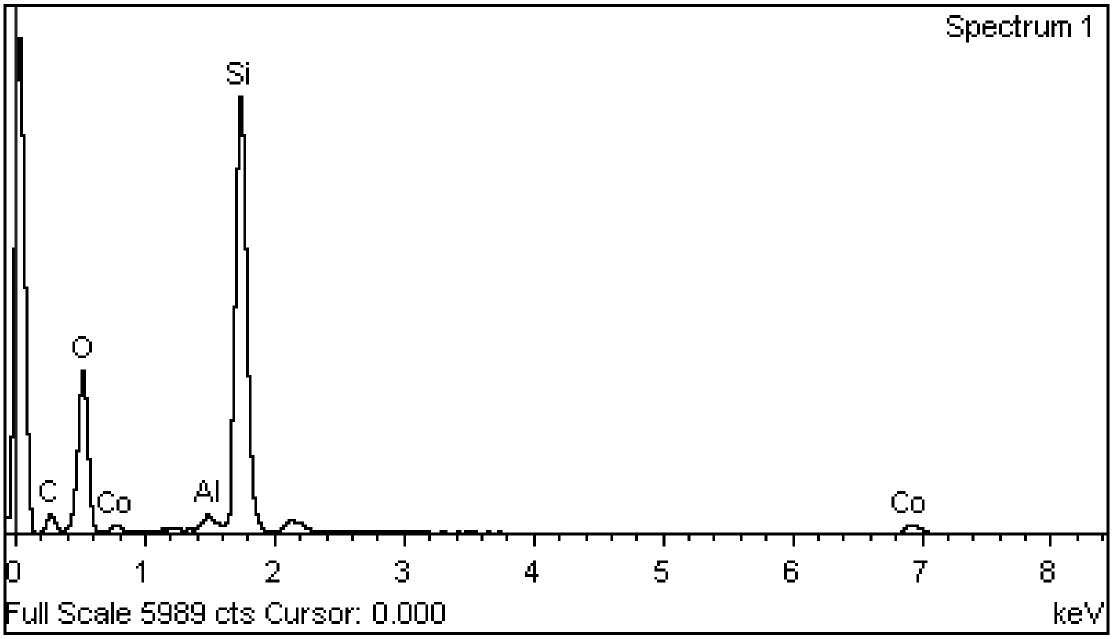


Figure 4.2b: EDX information of FE-SEM of 7Co/SiO$_2$

Based on *Figure 4.2a* and *Figure 4.2b*, it can clearly be seen that the cobalt content is more significant in this sample as the red-dotted circles shows the metal presence in the support. It can be said that the metal has been reduced to its metallic state and there is active site in the catalyst compared to the previous sample. The images do not explain anything about the dispersion of the catalyst however there is some amount of Alumina noticed in the EDX, which could be the impurities. Comparing the two samples of 5 % and 7 % cobalt, the latter seems to have a more defined shape even for the silica this could be due to the preparation method as for the 7% cobalt sample, it was dissolved in 5ml of deionized water only. Perhaps the metal has more homogeneously dispersed onto the catalyst.

4.3. Temperature-Programmed Reduction

i. *5wt% Co vs 7wt%*

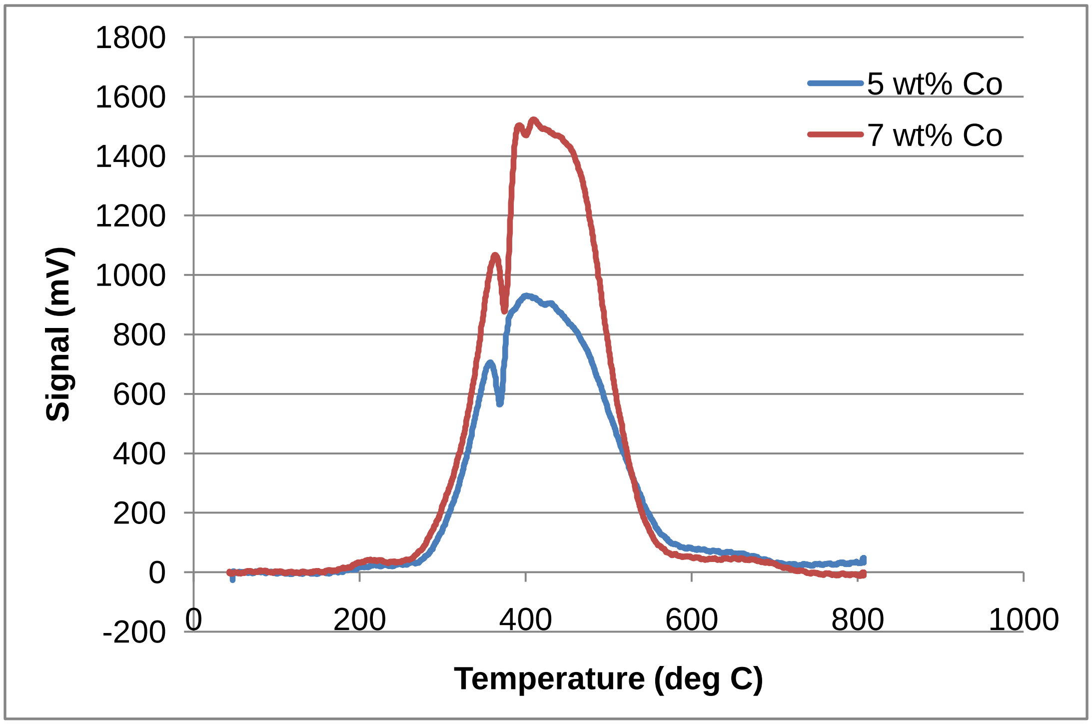


Figure 4.3: TPR profiles for 5wt% and & 7wt% Co/ SiO2 catalyst

The TPR profile for the unpromoted catalyst is seen as in *Figure 4.3* which looks reasonable as the reduction temperature is almost similar and the 7wt% Co loading consumes more hydrogen to reduce the cobalt catalyst. The increase in cobalt concentration may cause higher cobalt species formation that needs higher consumption of hydrogen to reduce to its metallic state or reduction takes place at higher temperature. The two peaks represent the two reduction steps which are

$$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O$$
$$3CoO + H_2 \rightarrow 3Co + 3H_2O$$

The second step usually consumes more hydrogen and it is reduced at higher temperature. This is because it is much harder to reduce the cobalt oxide to its metallic state and also the broad peak shows the strong metal-support mixture interaction.

ii. *5Co-0.1/0.5 Zr*

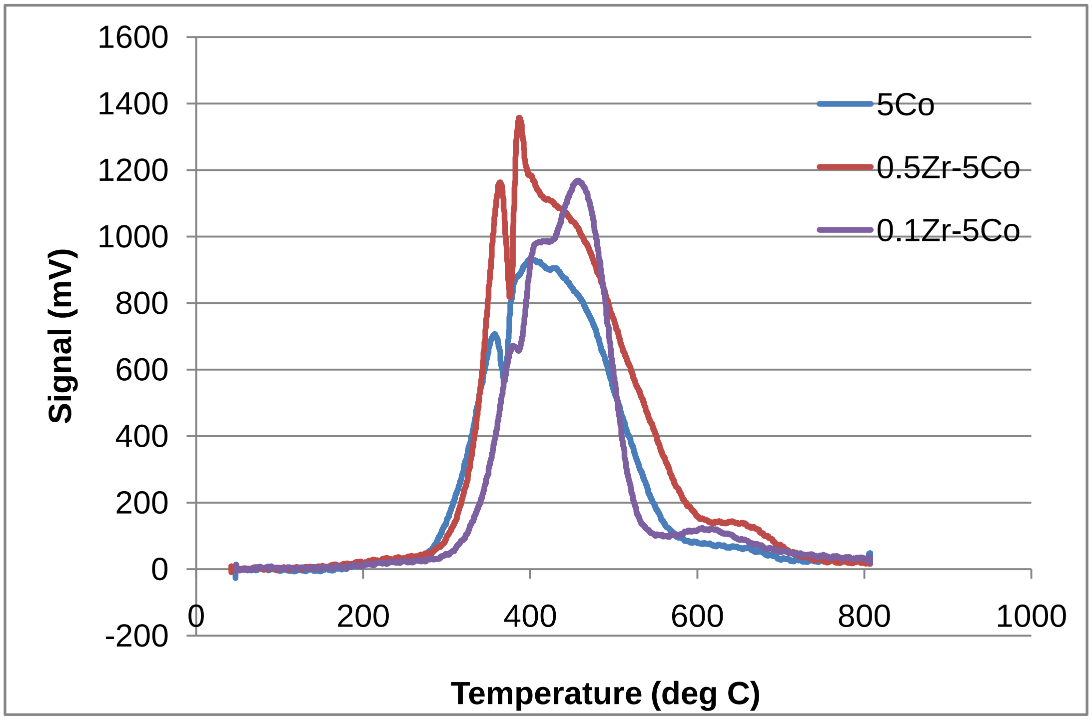


Figure 4.4:TPR profiles for unpromoted 5Co/SiO$_2$ with zirconia promoted Co/SiO$_2$

As for the TPR profiles for zirconia promoted 5Co/SiO$_2$, the lower concentration Zr of 0.1wt% shows the reduction peak is shifted to higher temperature. While with 0.5wt% addition of Zr , the reduction peak shifted to lower temperature. Based on the journals, increasing the zirconia loading, shifts the reduction temperature to lower temperature. Hence in this case, it can be said that, the very small amount of zirconia such as 0.1wt% may not have fully loaded on the catalyst or in other words it is not homogeneously dispersed onto the catalyst. As for 0.5wt% of Zr, sharp peaks are observed and this emphasizes on the presence of the reduced CoO or Co. The broader peaks show the interaction between the metal and support that is not easily reducible. The addition of

0.5wt% of Zr reduced the cobalt catalyst and lesser interaction between the metal and support is noticed.

iii. 5Co-0.1/0.5Mn

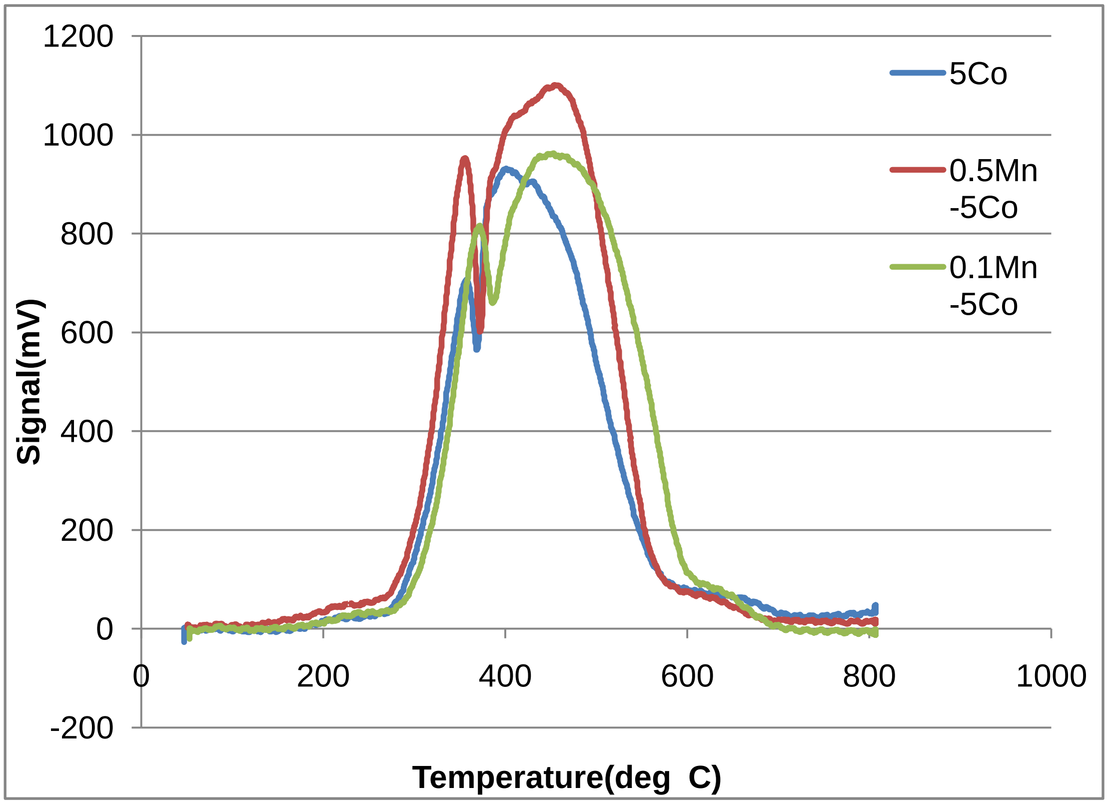


Figure 4.5:TPR profiles for unpromoted 5Co/SiO$_2$ and manganese promoted 5Co/SiO$_2$

Figure 4.5 is similar to *Figure 4.4* but with manganese as the promoter. As observed in the Zr promoted catalyst, manganese with lower concentration shifts the reduction temperature to higher temperature which could possibly be due to inhomogeneous spread of the promoter onto the catalyst. However the higher concentration of manganese, 0.5wt% shifts the first peak to lower reduction temperature which is for Co_3O_4 to CoO while for the second peak the reduction temperature shifts to higher temperature. This could be because manganese does not help much in the second step reduction, which is from CoO to Co as it is usually harder. Besides it could also mean there is higher resistance against reduction which might be due to a weak interaction between cobalt and manganese. The broad peaks also show the strong interaction between Co-SiO_2 or the formation of cobalt silicate and this could be related to the literature reviews that stated the minimal interaction between Co and Mn.

iv. 7Co-0.1/0.5 Zr

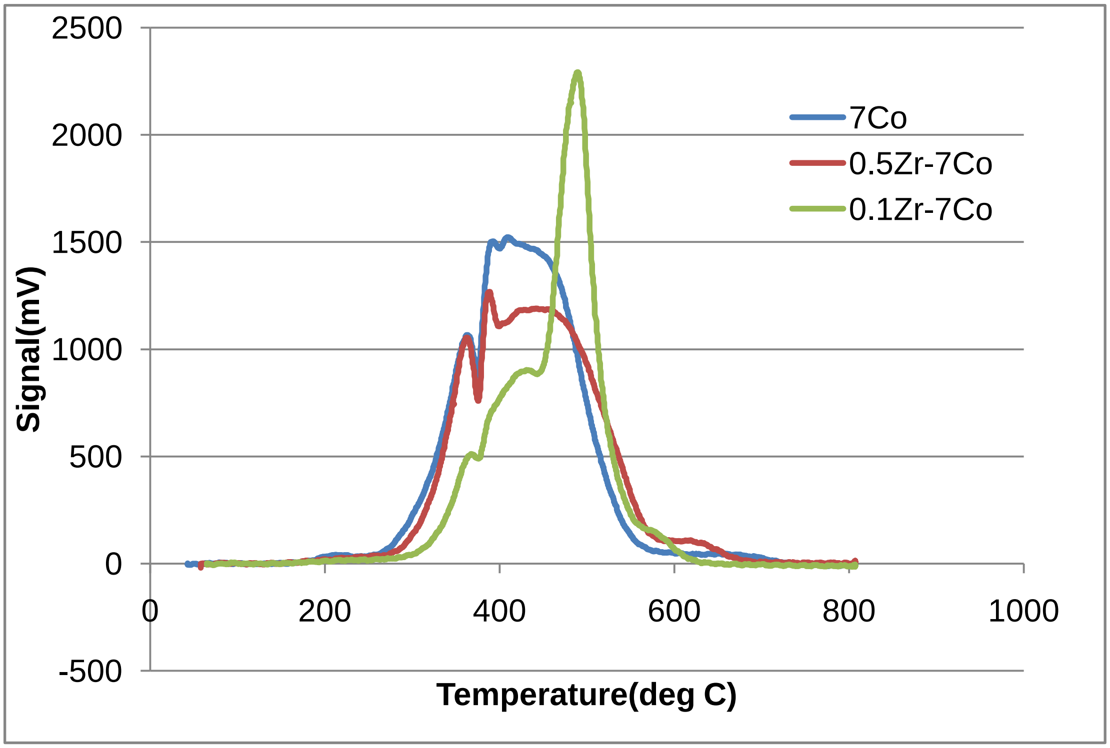


Figure 4.6: TPR profiles for unpromoted 7Co/SiO_2 with zirconia promoted Co/SiO_2

The figure above depicts the TPR profiles for 7Co/SiO_2 with the promotion of zirconia. It is noticed with the lower concentration of the promoter, the reduction temperature is shifted to a higher temperature and more hydrogen is consumed as compared to the addition with 0.5wt% Zr. Although the first and second peak has slightly shifted to lower temperatures, the hydrogen consumption is much lower. This could be due to larger loading of the cobalt which increases the cluster sizes of cobalt present and enhances reducibility. Besides, the sharp peaks for the both the promoted catalyst as compared with the broad peak of the unpromoted catalyst, shows that there are lesser interaction between the metal and support without taking into consideration of the reduction temperature. Hence adding zirconia, reduces the interaction between Co-SiO_2 which enhances the reducibility of the cobalt metal.

v. *7Co-0.1/0.5 Mn*

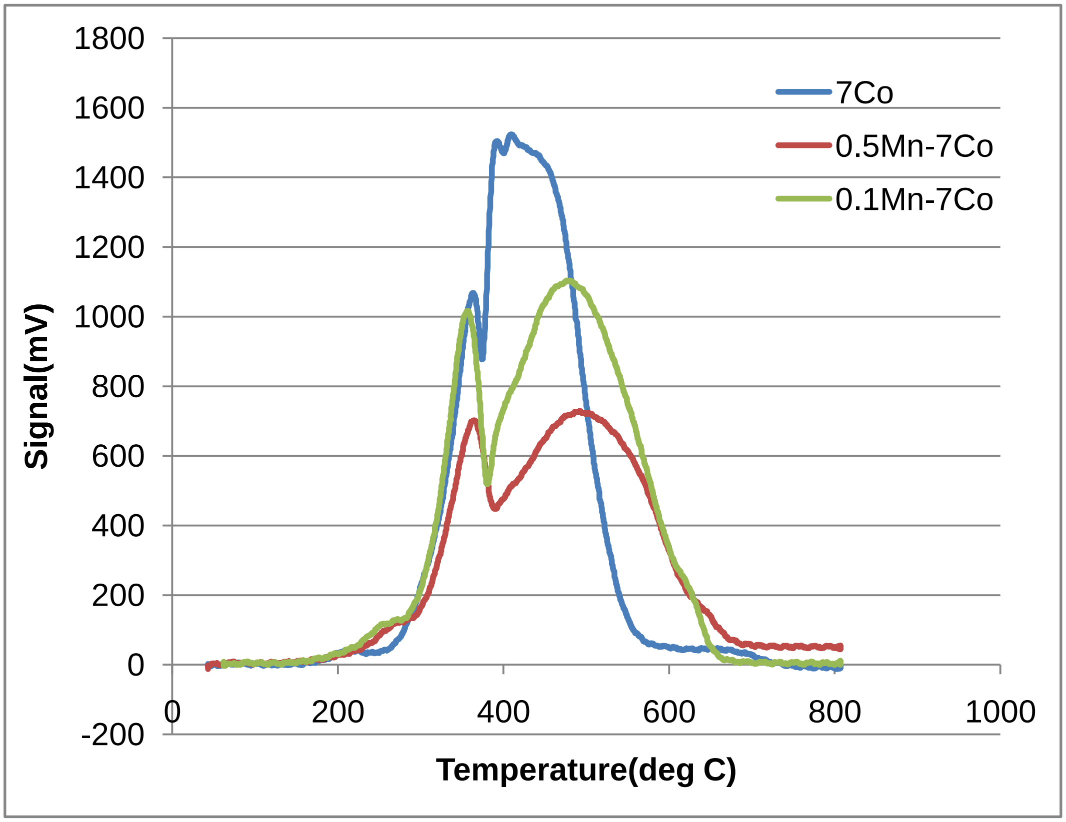


Figure 4.7: TPR profiles for unpromoted 7Co/SiO2 with manganese promoted Co/SiO_2

Figure 4.7 depicts the TPR profile for manganese promoted Co/SiO_2 with 7wt % loading of cobalt. The profile is almost similar as the 5wt% cobalt loading as at the first peak or for the first reduction step the reduction temperature is almost similar for all three profiles but with lesser hydrogen consumption. This could be related to the higher concentration of cobalt that makes the reduction easier. However manganese does not help much for the second reduction step where the reduction temperature shifts to higher temperature. This could be due to strong interaction between the metal and its support or the formation of cobalt silicate which manganese could not overcome. There could also be some parallax error while preparing the catalyst that could lead to instability of the peaks.

vi. Comparison between 5Co-0.5Mn/0.5Zr

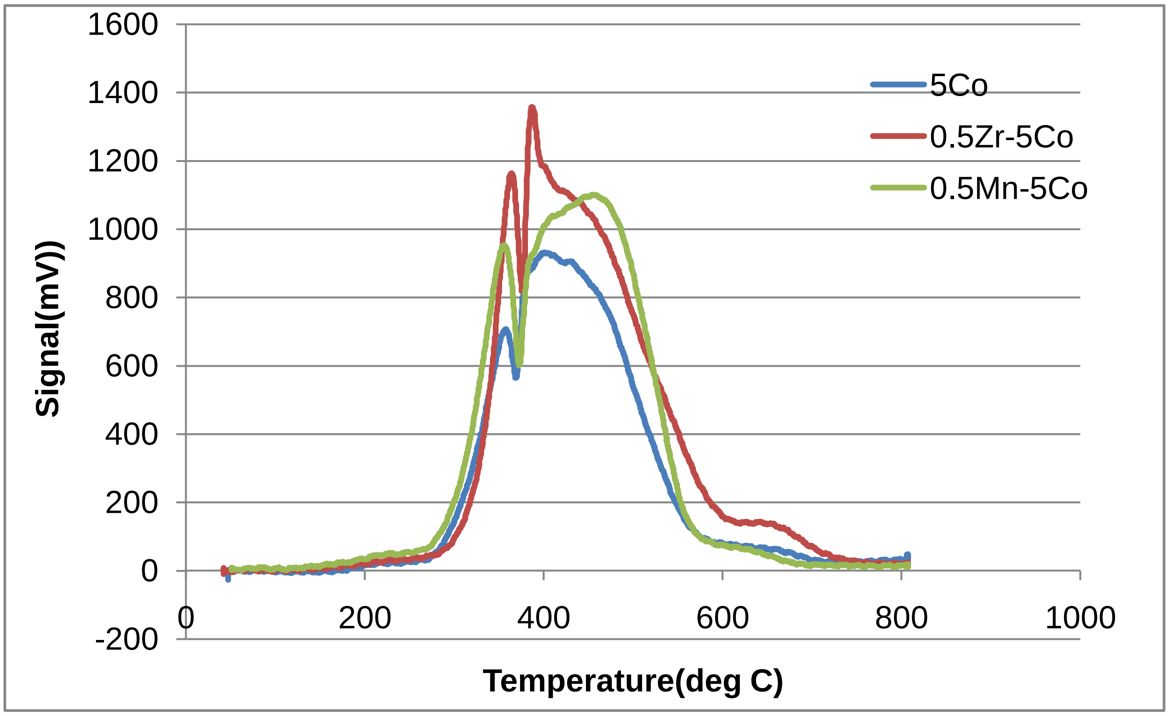


Figure 4.8: TPR profiles comparison for 5Co/SiO2 between unpromoted, Mn-promoted and Zr-promoted

TPR profile shows comparison for 5Co/SiO_2 unpromoted, Zr-promoted and Mn-promoted. Based on the profiles, it can be said that zirconia leads to catalyst reducibility at lower temperature as compared to manganese. For the first peak the reduction temperature is almost similar for all the three profiles but zirconia promoted catalyst has highest hydrogen consumption. Besides for the second reduction peak, Zr-promoted Co/SiO_2 is at 380^{o}C lower than 400^{o}C for the unpromoted catalyst. While manganese has higher reduction temperature approximately 460^{o}C and the peak for manganese is broader compared to zirconia. Meaning zirconia enhances the reducibility of the catalyst better than manganese. Besides with lower loading of the metal Co, there is higher fraction of the smaller cobalt cluster which has stronger interaction hence it is difficult to be reduced at lower temperatures

vii. Comparison between 7Co-0.5Mn/0.5 Zr

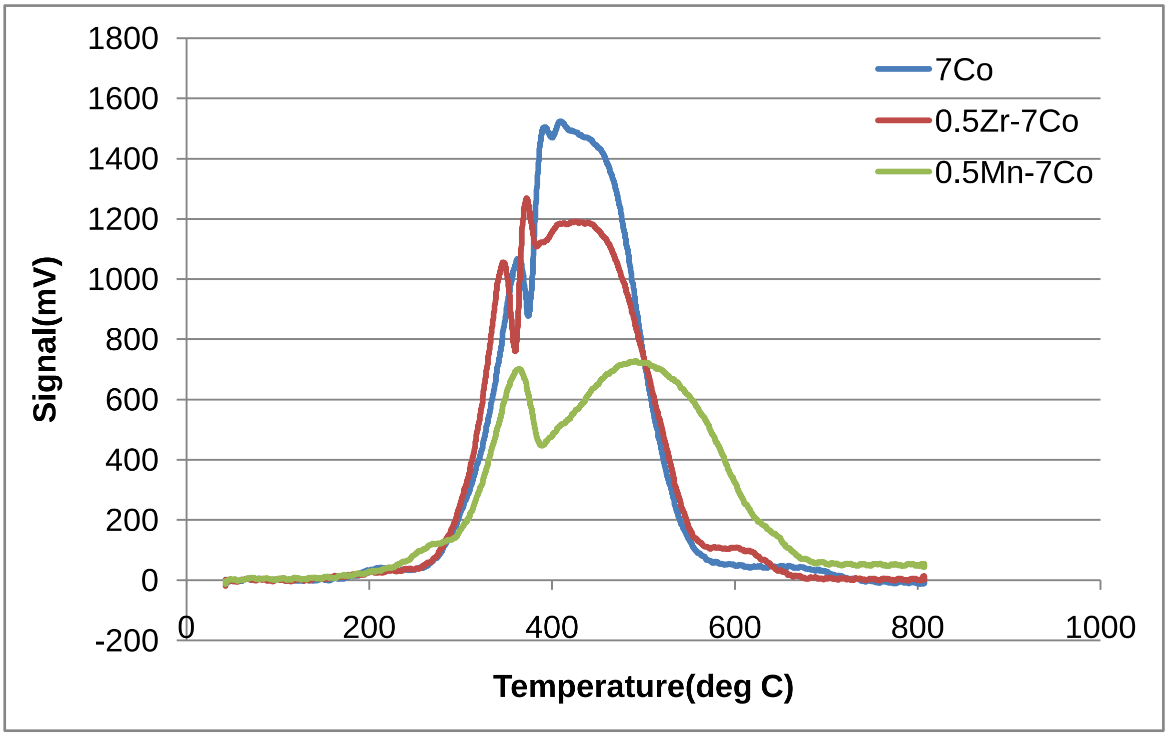


Figure 4.9: TPR profiles comparison for 7Co/SiO2 between unpromoted, Mn-promoted and Zr-promoted

Figure 4.9 shows the comparison between unpromoted, Zr-promoted and Mn-promoted catalyst. The hydrogen consumption for higher cobalt loading is noticed to be much lower and this could be due to high metal loading that has higher fraction of cobalt cluster that eases the reducibility of the catalyst, as bigger particles are easier to be reduced. The same results as 5wt% cobalt are observed here where the Zr-promoted catalyst has lower reduction temperature as compared to Mn-promoted catalyst. Also for Zr-promoted catalyst mostly the catalyst is reduced to its metal oxide state based on the peak sharpness.

In overall, based on TPR profiles obtained, it can be concluded that the promoted Co/SiO_2 enhances the reducibility of cobalt catalyst to its metallic state. However the two promoters, zirconia and manganese do not have the same effect towards the catalyst. Zirconia shifts the reduction temperature to lower temperatures for both the reduction steps. Whereas manganese only enhances the reducibility for the first step reduction. The interaction between Co-Mn is weaker that it cannot overcome the strong interaction between Co-SiO_2. The higher loading of cobalt also shows that at the same reduction temperature, lower hydrogen consumption is needed to reduce the catalyst to its metallic state. This is because higher cobalt concentration increases the cobalt cluster size which is easier to be reduced as the interaction between the metal and support is not as strong. While increasing the promoter contents leads to increase in cobalt crystallite size and the size of the cobalt clusters decreases but the number of cobalt particles in that cluster are lesser which makes it easier to be reduced.

4.4. X-Ray Diffraction Results

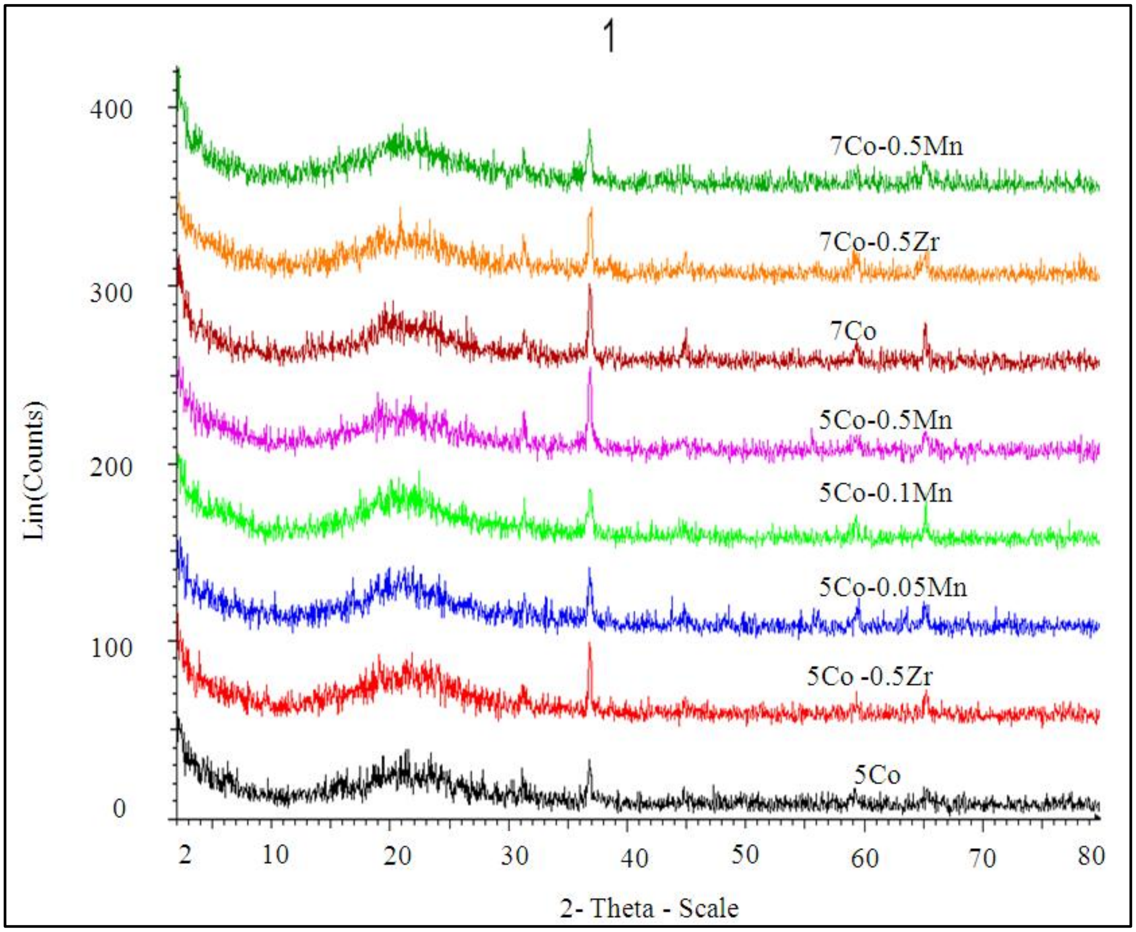


Figure 4.10: XRD patterns of unpromoted and promoted Co/SiO$_2$

Figure 4.10 depicts the X-ray diffraction patterns for unpromoted Co/SiO$_2$ and manganese and zirconia promoted Co/SiO$_2$. The presence of cobalt can certainly be seen in all the peaks as based on the literature reviews, a peak is noticed at 38- 40 2 theta scale which show the presence of cobalt in the form of Co$_3$O$_4$. As XRD patterns are usually like finger prints for every metal. It is also noticed that 5 wt% Co has lower intensity of peaks of cobalt species compared to 7wt% Co due to the lower cobalt loading contained.

XRD mainly discuses the phase of the metal and it is understood that the sharp peaks show the crystalline phase and the reducibility is higher in this phase. The silica exists as amorphous phase hence it cannot be seen in the XRD pattern. The interaction between the metal and support also exists in amorphous phase and in this case cobalt silicate is present which hinders the reducibility of the metal at lower temperatures.

Apart from that, it is observed that the promoted catalysts have peaks with higher intensity hence higher crystallinity. The XRD peak broadening represents the size of the crystallite and the broader peak means the crystallite sizes are smaller. Based on the patterns, catalysts with manganese promotion have broader peaks than zirconia promoted Co/SiO_2. When the crystallite size is smaller, it is much harder to reduce the catalyst. This information from the XRD patterns can be related to TPR profiles where Mn-promoted Co/SiO_2 does not help much in the reducibility.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1. Conclusion

Fischer-Tropsch synthesis, conversion of coal or natural gas into higher hydrocarbons has attracted attention from many due to the interest of environmentally friendly liquid fuels. Highly active catalysts are required to further enhance the process and supported cobalt catalyst has been preferred because of its high selectivity for production of long chain paraffins and low water-gas shift reaction. Metal promoters are added into the catalytic reaction to improve the performance of the catalyst thus improve the FTS too. The effect of these metal promoters is studied here, two different transition metal oxides are generally added to the catalyst in this study manganese and zirconia.

As far as this project is concern, with the studies conducted and the results obtained it can be said that the unpromoted catalyst,Co/SiO_2 does not have very significant properties in order to enhance the FTS. The promoted catalyst would present more favorable performance in terms of the reducibility which leads to the catalyst activity as when the metal is reduced to its metallic state, there are more active sites for reactions to take place.

The parameters were varied in terms of the cobalt loading, metal promoter type and metal promoter loading. The higher cobalt loading showed better results as the reduction were enhanced as for the same reduction temperature lower hydrogen were consumed. This is because larger cobalt clusters or particle sizes are easier to be reduced or in other words the interaction between cobalt and silica can be broken easily.

Next the different metal promoters were used; zirconia and manganese both of which are transition metal. However different results were obtained. Manganese did not give much favorable results in terms of the reducibility which could be related to the literature review where it was mentioned the effect of manganese can be seen more in terms of the hydrocarbon selectivity and CO conversion. In terms of reducibility the manganese is dispersed on the silica even before the reduction so there is not much of interaction with the cobalt metal. As for zirconia, the results obtained are quite similar with the ones from the studies conducted previously especially in terms of the reducibility.

Lastly for the metal promoter loading variation, it is seen that higher loading gives more significant results, where increasing the zirconia or manganese loading , decreases the interaction between Co-SiO_2 and gradually replaces it with Co-Zr or Co-Mn which favours the reducibility of the catalyst. When the interaction between Co-SiO_2 is decreased, the cluster size decreases as well but the particle size of the cobalt itself increases which enhance its reducibility. Besides increasing the promoter loading also increases the crystalline phase which is favored.

The catalyst has to be reduced to its metallic state, must be present in the crystalline phase and larger particle sizes are favored as this characteristics improves the catalytic activity. More active sites are present as reactions take place on active sites and this eventually improves the catalyst performance and as far as fisher tropsch synthesis is concerned, hydrocarbon selectivity is increased.

5.2. Recommendation

Based on the study conducted, a few suggestions have been proposed in order to enhance the performance of the experimental results further;

i. The comparison parameter should be increased in order to obtain a detailed analysis on the catalyst performance. Various methods of catalyst preparation (precipitation, sol gel method) and different calcination temperatures should be considered.

ii. More characterization method should be conducted especially microscopic ones in order to be able to correlate the profiles obtained with the microscopic images such as Tranmission Electron Microscopy (TEM) which has high resolution.

iii. Promoters from different groups should be compared as noble metals(Platinum) and transition metals(zirconia).