

**SYNTHESIS AND CHARACTERIZATION OF COBALT SUPPORTED TiO₂ WITH
Mn/Zn/Zr PROMOTERS FOR FISCHER TROPSCH SYNTHESIS**

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ABSTRACT

This research about the synthesis and characterization cobalt supported TiO_2 catalyst for Fischer–Tropsch synthesis (FTS) producing clean and best fuel. In variety of type of promoters, the effect is determined. The catalytic material will be prepared by impregnation of a mesoporous molecular sieve based on silica which is TiO_2 as cobalt catalytic supporters and Zn/Zr/Mn as promoters for comparison purposes. All materials will be used characterizing by several physico-chemical techniques such as SEM, , TGA, FTIR. The catalytic and characterization results achieve give a great influence of mesoporous support porosity on the structure, reducibility and Fischer-Tropsch synthesis catalytic behavior of cobalt oxide species supported over these ordered materials. The size of supported cobalt oxide species formed during the calcination step increased with the average pore size (D_p) of the mesoporous support. Thus, the catalyst with larger Co oxide species located in wide pore silica showed to be easily reducible, more active and very selective toward the fuel fraction. The additional of promoters will be used to increase the performances of Fischer-Tropsch synthesis.

ABSTRAK

Penyelidikan tentang sintesis dan kobalt pencirian ini disokong TiO₂ pemangkin untuk sintesis Fischer-Tropsch (FTS) menghasilkan bahan api bersih dan terbaik. Dalam pelbagai jenis penganjur, kesan ditentukan. Bahan pemangkin akan disediakan oleh pencampuran molekul berdasarkan silika TiO₂ dijadikan sebagai penyokong kepada pemangkin kobalt dan Zn / Zr / Mn sebagai penganjur untuk tujuan perbandingan. Semua pemangkin akan di tentukan ciri-ciri spesifik oleh beberapa teknik fizik dan-kimia seperti SEM,, TGA, FTIR. Hasil daripada uji kaji pencirian penganjur bersama penyokong TiO₂ memberi pengaruh yang besar kepada faktor pengurangan, struktur, dan tingkah laku kobalt sebagai pemangkin Fischer-Tropsch. Saiz spesies kobalt-oksida yang terbentuk meningkat dengan saiz liang purata (Dp) dengan sokongan asas silika. Oleh itu, pemangkin dengan spesies kobalt oksida yang lebih besar yang terletak dalam silika liang luas menunjukkan dengan mudah dikurangkan, lebih aktif dan sangat selektif terhadap pecahan bahan api. Tambahan penganjur akan digunakan untuk meningkatkan prestasi sintesis Fischer-Tropsch

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CHAPTER 1

INTRODUCTION

1.1. Background of Research

The invention of the original process was released by Franz Fischer and Hans Tropsch since they were working at the Kaiser Wilhelm Institute in the 1920s and there are many refinements and adjustments have been made. The term “Fischer-Tropsch” was applied now to a wide variety of similar processes or more commonly with the name of Fischer-Tropsch. The Fischer–Tropsch synthesis (FTS) is a set of chemical reactions that use to convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons. This process is a key component of part of gas-to-liquids (GTL) technology which it produces synthetic liquid hydrocarbons from natural gas. The FTS process has received intermittent attention as a source of low-sulfur diesel fuel and be address as the supply or cost of petroleum-derived hydrocarbons.

The most important reactions are:

- i. Steam reforming $\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$
- ii. CO_2 reforming $\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2$
- iii. Partial oxidation $\text{CH}_4 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{CO} + 2\text{H}_2$
- iv. Water gas shift reaction $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$

The production of clean fuels and synthetic diesel released by the FTS process has inspired renewed interest in both industrial and academic field recently. The super clean diesel oil fraction produced through the FTS is mainly composed by linear paraffins have high cetane numbers (more than 70) and free of sulfur and aromatics pollutants. From those derived crude oil that was the quality of this diesel offers significant environmental and efficiency benefits.

1.2 Problem Statement

Due high demands and lack of fossil fuel, Fischer-Tropsch synthesis has become most important as synthesis gas can be produced from a large variety of sources such as natural gas, biomass, coal, etc. and the process can orienting towards a variety of products such as fuels, paraffins, alcohols, etc. Many types of cobalt supporter based catalysts in CO hydrogenation have been shown to depend on several factors such as particle size, nature of the support, the presence of promoters and pre-treatment conditions. Modification of preparation parameters is known to strongly affect the microstructure of cobalt supported catalysts.

TiO₂ have been chosen because of low price cost and easily made of. By using different type of promoters, it simply conclude between Zn/Zr/Mn which is suitable for producing desired product. Additional to that, Co was chosen as precursors because it will enhance the reducibility, dispersion and influencing the stability of the cobalt catalyst in order to achieve highly stable and highly active cobalt for Fischer-Tropsch catalyst was released from E. L. Viljoen et al.'s thesis in 2009.

1.3 Research Objectives

There are 3 objectives of this study:

- a) To synthesis Co/ TiO₂ supported catalyst with different promoters. (Mn/Zn/Zr)
- b) To identify the characteristic of Co catalyst with different promoters.
- c) To study the effect and activity of Co catalyst with different promoters

1.4 Scope of Research

This research is to investigate the effect different promoters of the mesostructured materials based on silica TiO₂, as cobalt supports for preparing Co based FTS catalysts. It's had explored based on recently similar research since this material represent an efficient tool to control the sizes of supported cobalt particles. For the characterization and catalytic measurements of catalyst in this research, the

apparatus that will be used such as AAS, XRD, BET surface area, TPR, TGA, FTIR SEM and N₂ adsorption-desorption.

The silica as cobalt catalyst supporter will run with additional of Zn/Zr/Mn promoter that well known as function of an electron donor to metal that can prolong life of the catalysts and has a great effect on the catalyst. Additional of promoter will be effect both of the reduction rate and the density of active cobalt catalyst sites. It also lowers the temperature of the two-step conversion of cobalt oxide to cobalt metal observed in temperature programmed reduction.

The limitation of cobalt supporter will present the uniform pore size distribution in the ordered mesoporous materials that allow a better control on the cobalt crystallite size and catalytic properties and the narrow pore size distribution of the support also could prevent the sintering effect of the cobalt particles will be recorded and analyzed to compare with different cobalt supporter the level of reactivity of reaction in FTS.

1.5 Rationale & Significance of Research

Among the industrial nowadays, they mostly spend more cost to get the highly reactivity catalyst. The rationale and significance in this research is to achieve the most effective and low cost silica as cobalt supporters in the Fischer-Tropsch synthesis process. The utilization of such novel materials as supports of Co catalysts makes it possible to design new catalysts with higher productivity for C₁₀ – C₂₀ paraffins as the main component of diesel oil.

The effect of periodic mesoporous silica as supports for heterogeneous metal catalysts has caused a great interest nowadays in a wide range of catalytic reactions such as photo catalysis, hydrogenation, hydrodesulphurization, oxidative dehydrogenation and more recently in the FTS. One of them is TiO₂ materials that have only surface area of 94-350m²/g. However, TiO₂ materials also have nanoporous structures with pore sizes between 3.2-4.0 nm in diameter. Besides that, Cab-O-Sil or well known as fumed silica has a very strong thickening effect and hardness since antiquity. Its primary

particle size is 5–50 nm. Its particles are non-porous and have a surface of 50–600 m²/g also. This information was also from Wikipedia.org.

In order to achieve low cost production for catalyst, this new silica will be commercialized if the silica fulfills the condition of synthesis that needed in the fixed temperature and fixed pressure to produce catalyst in the Fischer-Tropsch synthesis. This new catalyst produced will be uses in the industrial and commercial customers are for synthesized using conventional sol–gel methods. Besides that, it will be used as a universal thickening agent, in milkshakes and an anticaking agent whom is free-flow agent in powders. This information was from Wkipedia.org. Additionally, it is used as a light abrasive, in products like toothpaste. Other uses include filler in silicone elastomer and viscosity adjustment in paints, coatings, printing inks, adhesives and unsaturated polyester resins.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The development of new silica use as a cobalt supporter to produce a clean and good fuel in the industry has been improved time by time. This is because the cost of silica use for now was too expensive and they need to spend on it to get the best product of fuel. Due to the fumble economic problem, the new cobalt supporter has been developed from various type of silica in order to enhance the Fischer-Tropsch synthesis performance as well as low energy use and lower capital cost. In this research study, the new type of silica been focused in order to develop a new commercialize silica that can replaced the old silica that use in the industry nowadays.

Fischer-Tropsch synthesis is a set of chemical reactions changes a mixture of carbon monoxide and hydrogen into liquid hydrocarbons which a master key component of gas to liquids technology produces a petroleum substitute from coal, natural gas, or biomass that uses as synthetic lubrication oil and synthetic fuel.

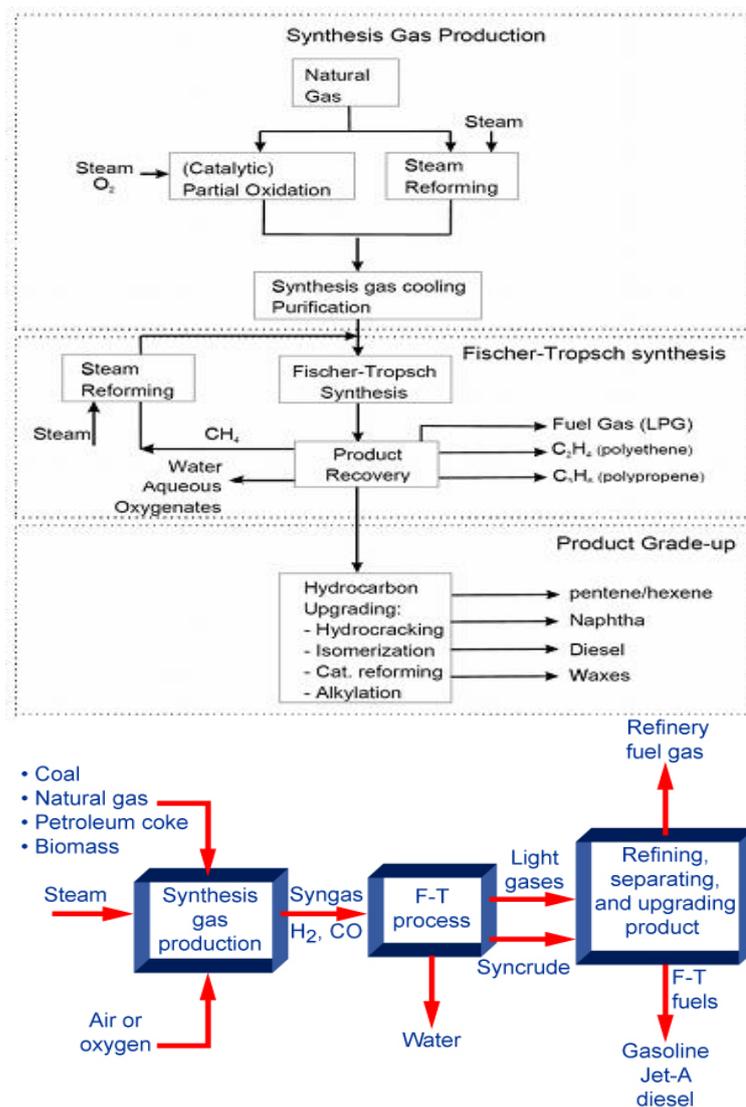


Figure 2.1: Fischer-Tropsch synthesis

(Josh ,2008)

The precursor will be used are Zn and Co. Among several example of transition metals usually use in the Fischer-Tropsch synthesis such as Co, Fe and Ru, these three types of metals which it's present the high estactivity. However, Co is considered the most favourable metal for the synthesis of long-chain hydrocarbons from synthesis gas due to its high activity per weight of metal compared to Fe, high selectivity to linear paraffins, high stability toward deactivation by water which it's a by-product of the FTS process, low water–gas shift activity and low price compared to noble metals such as Ru, Re, or Pt was released by O. González et al. (2009).

2.2 Cobalt catalyst

Fischer–Tropsch (FT) synthesis is one major step for the transformation of nonpetroleum feedstocks, such as naturalgas, coal, and biomass, into gasoline or diesel fuel bysyngas (CO/H₂). Fischer–Tropsch synthesis has received greater attention recently among scientific community and industry because of the worldwide demand for a decreased dependence on petroleum. To date, much attention has been paid to cobalt-based catalysts Supported cobalt catalysts are well known for their activity and selectivity in the FT reaction. Optimization of cobalt dispersion and cobalt reducibility seems to be the most obvious goals in the design of efficient cobalt catalysts for FT synthesis. It has been demonstrated that catalyst preparation method, support, and promoter have important effects on the catalytic performance and structure. Strong interaction between support and cobalt species leads to high dispersion and low reducibility. A drawback of porous supports (SiO₂, Al₂O₃) is their reactivity toward cobalt, which during preparation of catalysts results in the formation of mixed compounds such as aluminates or silicate. These cobalt-support compounds are irreversible, and it is difficult to be reduced even at 1000 K. Low degree of reduction of cobalt species on the support surface results in decreasing the number of active sites, and thus degrades the catalytic properties of the catalyst(Z. Huang, et al,2010).

2.3 TiO₂ supporter

This is also known as titanium (IV) oxide or titania that naturally occurring oxide of titanium was got from Wikipedia.org.

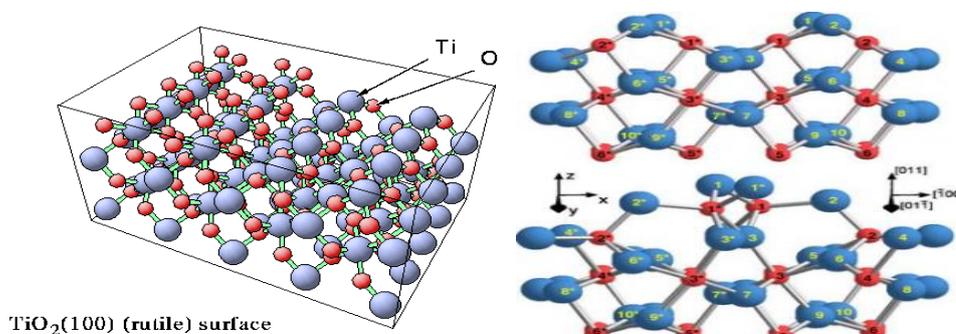


Figure 2.2: Structure of TiO₂
(Antonelli ,1999)

This research is focusing on optimize the product by experimenting TiO₂ supporter using different type of promoter. From Antonelli et al research in 1999 by his thesis of Microporous Mesoporous Mater stated that the successful synthesis of stable mesoporous TiO₂ involves the application of tetradecylphosphate surfactant as a template and removing it by calcinations.

The preparation of mesoporous TiO₂ uses dodecyl amine as the directing agent. While this solved the problem of residual phosphorous, the porous structure remained unstable after calcination. Conclusion from his thesis was the silica of TiO₂ is the one of most stable mesoporous silica in the FTS.

2.4 Promoters

The goal of promotion is to enhance cobalt FT catalysts by the addition of small amounts of noble metals and metal oxides. Numerous studies have shown that introduction of a noble metal has strong impact on the structure and dispersion of cobalt species, FT reaction rates and selectivities. The promoting metal is typically introduced via co-impregnation or subsequent impregnation. Analysis of the literature data suggests that introduction of noble metals could result in the following phenomena:

- easing cobalt reduction.
- enhancement of cobalt dispersion.
- better resistance to deactivation.
- formation of metallic alloys.
- high concentration of hydrogen activation site.
- modification of intrinsic activity of surface sites.

In this research the goal is about to find out what are the effects of addition of promoter (noble metals) on the enhancement of Co/TiO₂ catalyst for FT synthesis and to find the best promoter for catalyst. The metal will be introduced as promoter the catalyst by impregnation method. This is example the effect the reaction use promoter and not.

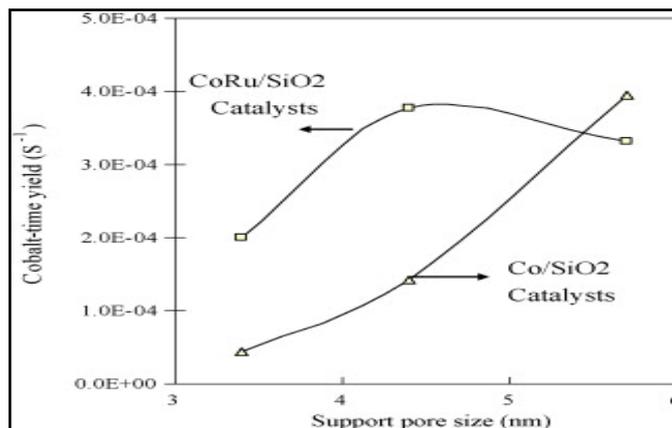


Figure 2.3:Relation between cobalt time yield and pore size of support

(J.Hong,2009)

The addition of ruthenium not only improved the reducibility of cobalt compounds into Co but also significantly increased the concentration of active sites and improved catalytic performance in FT synthesis. For another example Ni-based catalysts supported on SiO₂ aerogel that is unpromoted (Ni/SiO₂) or promoted (Ni/ZrO₂-SiO₂) with ZrO₂ are prepared by the incipient-wetness impregnation method. It is found that the Ni/ZrO₂-SiO₂ catalyst shows higher catalytic activity, over which CO can be completely converted into CH₄ at 240 °C (Y.Wang, et al,2010)

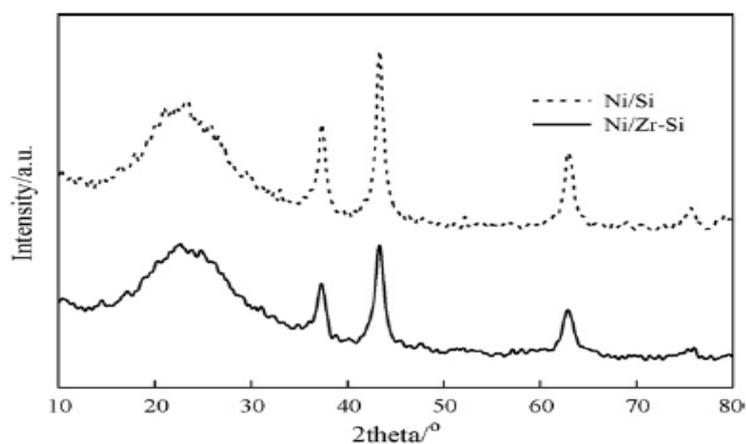


Figure 2.4: XRD patterns of the Ni/Si and Ni/Zr-Si

(J.Hong,2009)

The addition of ZrO₂ promoter enhances the dispersion degree of NiO species in the Ni/Zr–Si catalyst, which is generally consistent with our TEM observation.

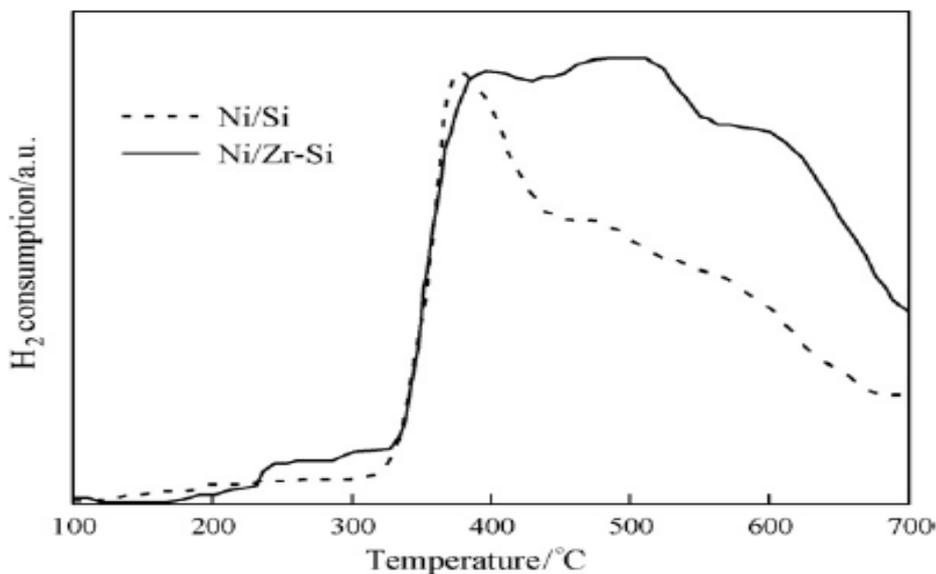


Figure 2.5: XRD patterns of the Ni/Si and Ni/Zr–Si

(J.Hong,2009)

The total peak area of the Ni/Zr–Si catalyst has a progressive increase due to the addition of ZrO₂ promoter, indicating that NiO species has a higher reduction degree. Therefore, it is concluded that the Ni/Zr–Si catalyst possesses higher Ni dispersion and more active Ni species after reduction, which is generally consistent with the results of H₂-TPD. So we can conclude that smaller Ni crystallite size, higher Ni dispersion, more active Ni species and stronger adsorption ability for H₂ may contribute to higher catalytic activity of the Ni/ZrO₂–SiO₂ catalyst for CO methanation (Y.Wang, et al,2010)

2.4.1 Zirconium Promoter

ZrO₂ has also been widely used as a promoter due to its redox and acid–base properties (X.F. Dong, et al,2004). reported that the addition of ZrO₂ promoter in CuZnAlO catalyst could increase the conversion of methanol and selectivity of H₂ in the

methanol steam reforming reaction. The addition of ZrO_2 promoter could inhibit the deactivation of Co/SiO_2 catalyst and improve its stability for F-T synthesis that had been reported by Zhou et al.2006 . Rana et al,2004 also found that incorporation of ZrO_2 with SiO_2 strengthened the weak interaction of active phases with SiO_2 support, overcame poor dispersion on the support surface, and therefore efficiently improved the activity of the $MoCo(Ni)/ZrO_2-SiO_2$ catalyst through enhanced number of active sites as well as activity per site. However, to our knowledge Ni-based catalysts supported on SiO_2 aerogel promoted by ZrO_2 are studied less for CO methanation. In this work, the Ni/SiO_2 and Ni/ZrO_2-SiO_2 catalysts were prepared by the incipient-wetness impregnation method using SiO_2 aerogel support unprompted or promoted with ZrO_2 . Their catalytic activities and the effect of ZrO_2 promoter on structure and catalytic activity of the Ni/SiO_2 catalyst for CO methanation were investigated. Combined with characterizations, a possible reason for higher catalytic activity of the Ni/ZrO_2-SiO_2 catalyst has been given.(Y.Wang, et al,2010)

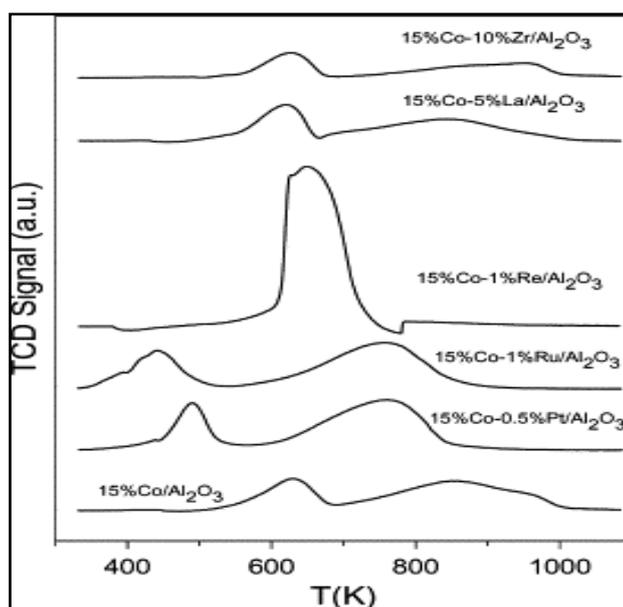


Figure 2.6: TPR comparison of Al_2O_3 supported Co catalysts with and without metal and metal cation promoters

(G.Jacobs, et al,2002)

2.4.2 Mangan Promoter

The improved efficiency of the FT-process has been driven by the addition of promoter elements, such as Mn, which have been shown to improve the selectivity and activity of Co-based FT-catalysts. Recently, the effects of the catalyst synthesis on the promoter-catalyst interaction has been examined in an attempt to gain a better understanding of the role of the promoter's involvement. Morales et al. studied Mn-promoted Co/TiO₂ FT catalysts synthesized by incipient wetness impregnation (IWI) and homogeneous deposition precipitation (HDP). The authors found by using extended X-ray absorption fine-structure (EXAFS) analysis that the observed increase in activity and selectivity was the direct result of a Mn-Co compound formed on the surface of the catalyst. In addition, it was reported that the distribution of MnCoO_x is governed by the initial Mn distribution, and thus depends on the catalyst synthesis method. However, we have recently shown that strong electrostatic adsorption (SEA) and IWI methods exhibit different initial Mn distributions in Mn-promoted Co/TiO₂ catalysts, but after calcinations and reduction of the different catalysts, the Mn migrated towards the Co/Ti interfaces in both systems, which indicates that two different starting points could lead to systems with similar catalytic properties.

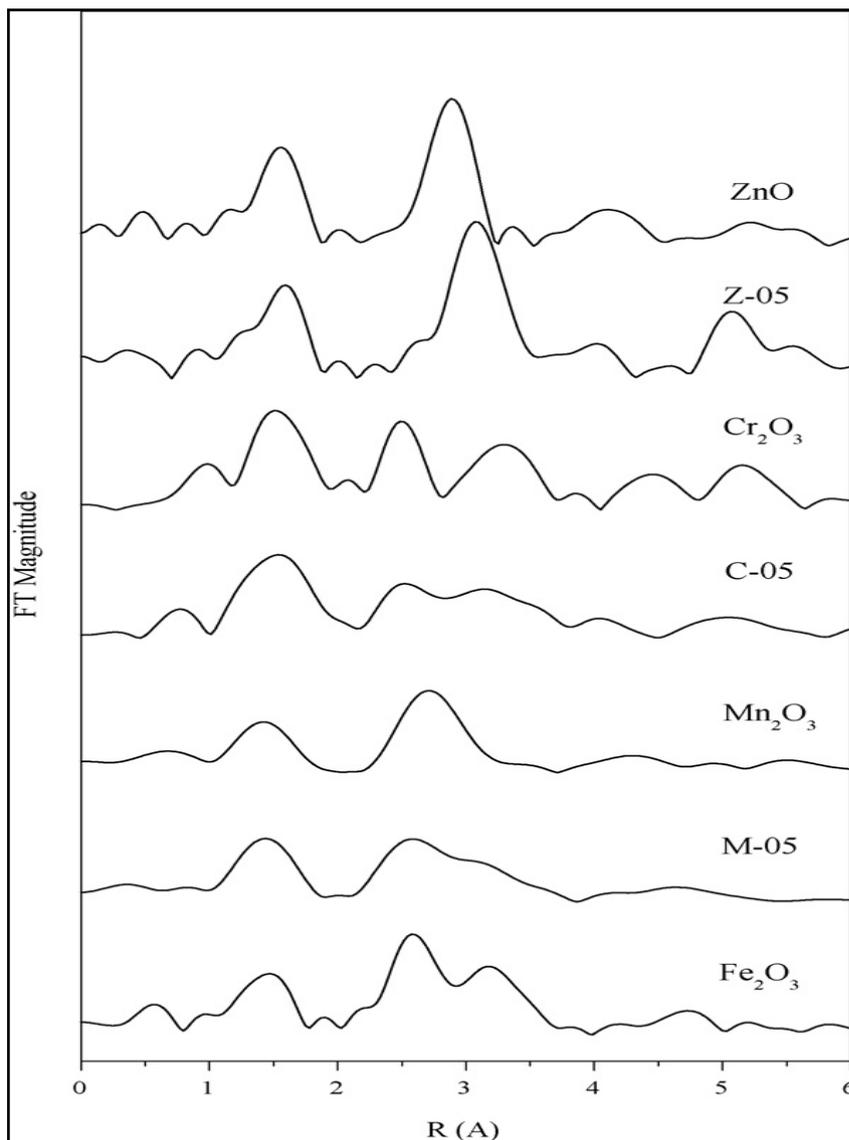


Figure 2.7: Fourier transform magnitudes of EXAFS spectra of the as prepared catalyst and reference compounds

(H. Wang, et al, 2010).

2.4.3 Zinc Promoter

In this research, addition of Zn promoter gives a lot of effect in the Fischer-Tropch synthesis. According to E. L. Viljoen et al in his thesis of 'Rate of Oxidation of a Cobalt Catalyst in Water and Water/Hydrogen Mixtures: Influence of Platinum as a Reduction Promoter' in 2009 said that '...Promoters are added to cobalt catalysts to

enhance the reducibility and dispersion'. Therefore, factors like the addition of promoters, possibly influencing the stability of the cobalt catalyst, have to be investigated in order to tailor highly stable, highly active cobalt based Fischer–Tropsch catalyst was added more details by E. L. Viljoen et al. As the conclusion, Zn promoter can affect the level of activation energy and reaction reactivity of catalyst in the FT synthesis

2.5 Characterization of catalyst

2.5.1 BET

BET is crucial in determining the pore size and surface area of catalysts..

Table 1. Textural properties of supports and prepared samples.

	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Maximum of the pore size distribution (nm)
MCM-41 SiO ₂	1051	0.83	2.3
SBA-15 SiO ₂	640	0.96	7.5
SBA-15/TMB SiO ₂	601	1.62	20.0
Commercial SiO ₂	317	1.59	27.5
100% TiO ₂ Reference	9	-	-
20% TiO ₂ MCM-41	294	0.57	16.0
20% TiO ₂ SBA-15	532	0.78	7.0
40% TiO ₂ SBA-15	442	0.69	6.5
60% TiO ₂ SBA-15	349	0.60	6.5
20% TiO ₂ SBA-15/TMB	517	1.40	18.5
40% TiO ₂ SBA-15/TMB	414	1.08	18.5
60% TiO ₂ SBA-15/TMB	304	0.78	18.5
20% TiO ₂ Commercial	299	1.16	22.5
40% TiO ₂ Commercial	246	0.94	25.0
60% TiO ₂ Commercial	179	0.67	26.0

Figure 2.8: TiO BET analysis 2

(J.Hong,2009)

Figure above shows the textural properties of the silica supports and the titania loaded samples: S_{BET} , specific surface area; V_P , pore volume, and pore size corresponding to the maxima of the plotted pore size distributions. The TiO₂ supports within a range of 2 to 25 nm of pore size tested in order to get the influence of the silica pore size in the growth of the titania particles. The mesoporous ordered material MCM-41, which presented the higher BET surface area which it's had a mean pore size of 2.3 nm. The average pore size of 7.5 nm of the hexagonal mesoporous silica structure SBA-15 was modified by the addition of trimethylbenzene in the synthesis as it has been explained above. The resulting material that SBA-15/TMB presents the pore size value

of 20.0 nm whereas the BET surface area was slightly lower than the presented by the unmodified SBA-15 silica. Finally, it can be observed that the non-structured commercial silica offered the highest pore size value (27.5 nm) and the smaller surface BET area.

2.5.2 N₂ adsorption–desorption isotherms

(i) TiO₂

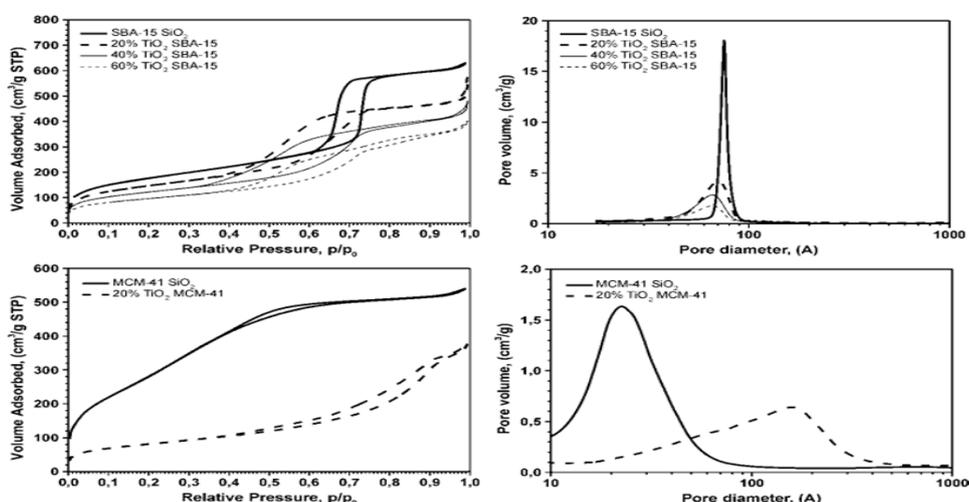


Figure 2.9: (i) Nitrogen adsorption isotherms of: a) 0 – 60 % TiO₂& SBA-15 and b) 0 – 20% TiO₂& MCM-41 samples. (ii) Pore size distributions of: c) 0 – 60 % TiO₂& SBA-15 and d) 0 – 20% TiO₂& MCM-41 samples.

From figure above, the isotherms of the SBA-15 based samples kept the features of the isotherm exhibited by the unloaded support. Therefore, it is concluded that the mesostructure is maintained upon TiO₂ addition. Moreover, it is interesting to note that the calculated pore size distribution (Figure above c) is slightly modified even for the sample with the highest titania loading, suggesting a porous structure similar to that present in the unloaded support. Similar results were obtained in the case of the SBA-15/TMB based samples. On the other hands, it can be observed in the 20% TiO₂ & MCM-41 sample how the titania loading significantly changes the isotherm shape of the support, which is indicative of structure modifications. In addition, the shift of the pore

size distribution maximum too much higher values and the wider pore size distribution (Figure above d) indicates the breakdown of the structured pore arrangement.

2.5.3 XRD

(i) TiO_2

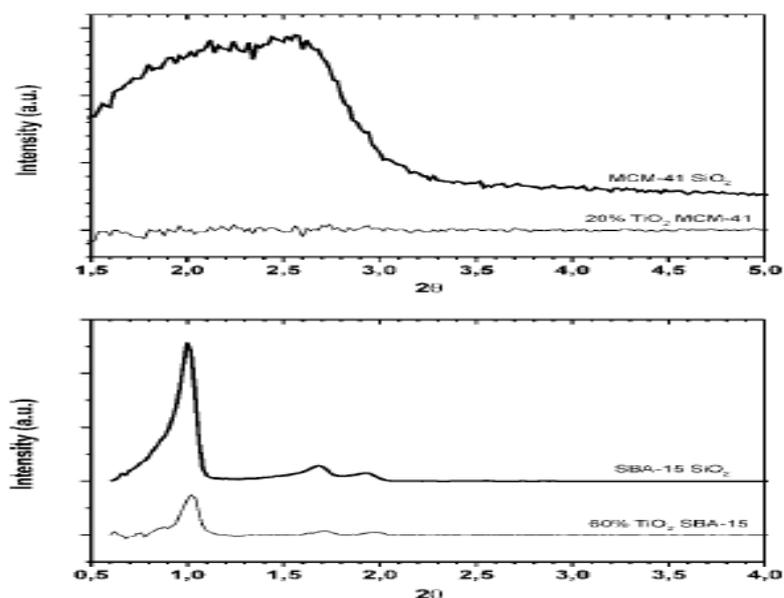


Figure 2.10: XRD patterns at low angle of: a) MCM-41 and 20% TiO_2 & MCM-41 samples and b) SBA-15 and 60% TiO_2 & SBA-15 samples

The X-ray powder diffraction patterns at higher angles of the supported TiO_2 samples evidenced that anatase was the only titania crystalline phase present in all prepared materials, as indicated by the peak emerging at $2\theta \sim 25.3^\circ$ associated with anatase (101) diffraction. No rutile phase was detected in any case according to the absence of the (110) rutile reflection at $2\theta \sim 27.4^\circ$. By contrast, the 100% TiO_2 reference material showed two crystalline phases, anatase and rutile, with a higher proportion of the latter (64%). The average crystallite sizes ϕ_{XRD} were determined from the Scherrer's equation using the broadening of the (101) anatase peak reflection with the usual assumption of spherical crystallites.

It can be observed the much higher particle size presented by the reference 100% material as compared with the supported materials. This may be explained in terms of the formation of big TiO_2 agglomerates whose development seems to be

limited in the presence of the silica support. It has been previously suggested that a critical size in the range of 40-50 nm must be achieved for the phase transition from anatase to rutile in titania particles¹³. On this basis, the reference 100% TiO₂ material would accomplish that required size and so, some rutile formation is induced upon calcination. By contrast, the particle size of the supported titania samples must stabilize them as anatase against phase transition following identical thermal treatment.

2.6 Catalytic study

(i) TiO₂

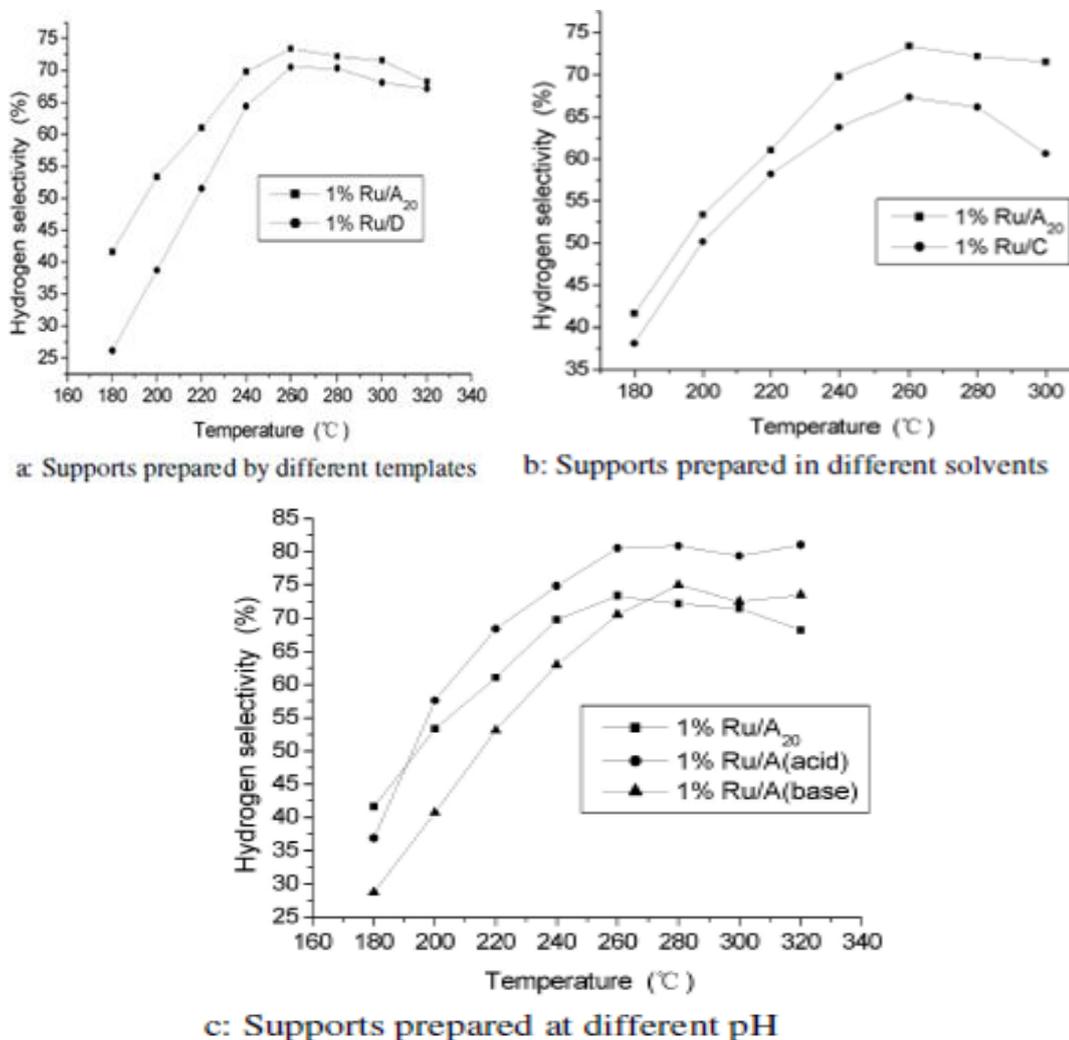


Figure 2.11: the relationship between the reaction temperature and the catalytic activity.

The catalytic activity results of Ru/m-TiO₂ synthesized by easy-operating method for methanol decomposition are given in figure above. The activity curves of all catalysts have the similar variation rule, that is, below 260 °C, the activity increases with the increase of reaction temperature, whereas the activity reduces slowly above 260 °C, which might be due to the formation of a fraction of TiO_x after being reduced using H₂. Then at high temperature, ruthenium particles are mantled partly or space blockage is formed around ruthenium particles because TiO_x species are easily migrated. Comparing to mesoporous 1% Ru/A20 and 1% Ru/D, the activity of the catalysts decreases in the following order: 1% Ru/A20 > 1% Ru/D. This result was consistent with the order of the BET surface areas at 400 °C for 2h (two of them are 174.3 and 139.1 m₂/g, respectively). It is concluded that mesoporous material with high surface areas helps to generate the very small ruthenium particles with better distributions, dispersion and stability on the surface of the mesoporous oxide supports.

From the curves in Figure 10b, the effect of solvents on the activity is contrary to the order of surface areas of samples. After being calcined at 400 °C for 2h, the BET surface areas of 1% Ru/A₂₀ and 1% Ru/C catalysts are 174.3 and 225.9 m₂/g, respectively. It is concluded that the catalytic activity is not completely depended on dispersion of active components. It may be due to the strong interaction between Ru and TiO_x in 1% Ru/A₂₀, which leads to improve the ability of adsorption hydrogen, so the activity increases. As shown in figure above c, the effect of pH on catalytic activity was investigated.

The results indicate that the BET surface areas of 1% Ru/A (acid) (pH = 3-4), 1% Ru/A₂₀ (pH = 7-8), 1% Ru/A (base) (pH =9-10) calcined at 400 °C for 2 h are similar (173.0, 174.3 and 170.0 m₂/g, respectively). However, the differences in activity is clearly observed, particularly 1% Ru/A (acid). This can be explained by the different crystal structure of supports, which lead to different strong interaction between ruthenium nanoparticles and oxide species, which may reduce the activation energy of the rate determining step in the methanol decomposition such as decomposition of the surface methoxyl group into surface carbon monoxide and hydrogen. According to these results, it is concluded that the surface area is not the only factor correlated with catalytic activity.

CHAPTER 3

METHODOLOGY

3.1 Introduction

In this chapter, the procedure to synthesis TiO_2 as cobalt supporter and then, makes preparation of Co/Mn-TiO_2 , Co/Zn-TiO_2 and Co/Zr-TiO_2 . After that, the catalytic study will be done and before that, each of catalysts produce will be through the characterization techniques to analysis and identify any characteristic that can affect the result of the production of fuel.

3.2 Material List

There are lists of material that been used during conducting the experiments.

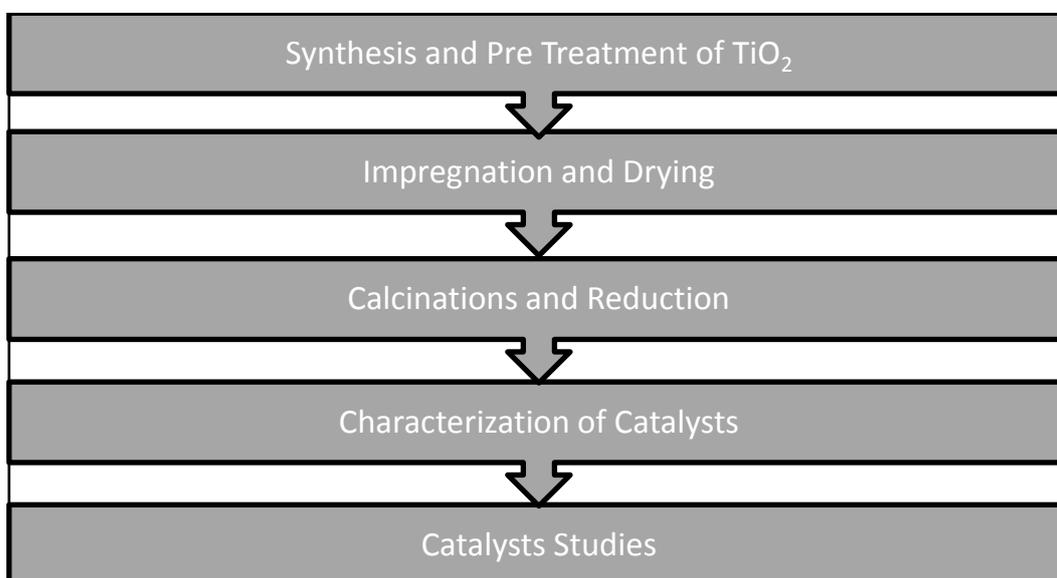
Table 3.1: List of materials

Material	Purity	Company
Zinc Nitrate Hexahydrate	98% extra pure	Sigma-Aldrich Company
Cobalt (II) Nitrate	99% purity	Sigma-Aldrich Company
Titanium (IV) Oxide	99.5% purity	Sigma-Aldrich Company
Hydrochloric acid	37% purity	Sigma-Aldrich Company

3.3 Apparatus List

1. Vacuum Pump (Rocker Company)
2. Glass Furnace (Naberthem Company)
3. Stackable Incubator Shaker (Infors AG Company)
4. Hot Plate and Magnetic Stirrer (Erla Company)
5. Glass Oven (Mettler Company)
6. Analytical Balance, maximum weighing 220g (Shimadzu Company)

3.4 Flow of Experimental Procedure



3.5 Synthesis of TiO_2

TiO_2 was synthesized by diluting in isopropanol (ROH, Baker, Aldrich). A deionized $\text{H}_2\text{O} + \text{HNO}_3$ (Baker) mixture was drop-wise added to the alkoxide solution kept under vigorous stirring at 273 K (Ts). ROH/alk., $\text{H}_2\text{O}/\text{alk.}$ and $\text{HNO}_3/\text{alk.}$ mol ratios used were 65, 20 and 0.05 respectively. After alkoxide hydrolysis, the alcogels submerged in the mother liquor were submitted to post treatments at different conditions (353 or 513 K for 1 or 4 days) in a stainless steel hermetic autoclave (Parr 4560) under autogenic pressure.

3.6 Catalyst Preparation

3.6.1 Wet Impregnation and Drying

All catalysts with a Co loading ~20 wt. % were prepared by incipient wetness impregnation using a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, 98% purity) dissolved in excess of ethanol with respect to the pore volume of each silica material used as support (liquid/solid ratio ~5 cm^3/g), followed by with slow evaporation of the solvent in a rotary evaporator at 35°C until dryness.

3.6.2 Calcination and Reduction

The samples were further dried at 60°C overnight and milled at 250 r.p.m. for 15 min by means of a centrifugal ball mill. Finally, the catalysts were calcined in air at 350°C for 6 h by increasing the temperature at a controlled heating rate of 2°C/min. This catalyst was reduced in flowing hydrogen for 2 h at 623 K to produce the Mn/Zn/Zr-promoted catalyst.

3.7 Characterization Techniques

3.7.1 FTIR (Fourier Transform Infrared)

The supports surface acidity ($T_c = 773 \text{ K}$) was analyzed by pyridine thermodesorption studied in the infrared region (Fourier Transform Infrared Nicolet 710 spectrophotometer) in the 473–773 K temperature range. Chemical analysis of Mo impregnated mixed oxides was carried out by AES–ICP (atomic emission spectroscopy-inductively coupled plasma) using a SPECTROFLAME-ICP model D (Spectro). Mo^{6+} coordination incalcined impregnated precursors ($T_c = 673 \text{ K}$) was studied by diffuse reflectance spectroscopy (Varian Cary 5E UV–vis-NIR spectrophotometer, praying mantis attachment). BaSO_4 (Kodak) was used as white reflectance standard to obtain a baseline at 298 K.

3.7.2 SEM (Scanning Electron Microscopy)

The surface features and morphologies of the MTx materials were investigated using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6330F) and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2000 FX II).

3.7.3 TGA (Thermogravimetric analysis)

Thermogravimetric measurements of 20 mg catalyst samples were conducted in a Perkin Elmer TGA 7 analyzer interfaced with a PE-7500 computer for data acquisition and automatic control of the experiment. Experiments were performed under a gas flow of 40 cm³/min. Mass flow controllers were used to adjust the flow rate of 10% hydrogen, 90% helium mixture. Heating rates varied from 1 to 10 K/min depending on the temperature response of the sample under study.

CHAPTER 4

EXPERIMENTAL RESULT

4.1 Introduction

These chapters are concluding the data of characteristics and measurements of catalyst from the recent research study. The main purpose on this research is to study the development of the TiO_2 as cobalt supporter in the Fischer-Tropsch synthesis. It focusing on characterizing Cobalt supported TiO_2 with varies of promoters which is Mn/Zn/Zr.

4.2 SEM

(i) Co/Mn- TiO_2

In the Figure 4.2.1 showed the SEM image of Co/Mn- TiO_2 catalyst sample. It can be seen that the sample shows an irregular pore structure with large particles and the shape of sample exhibits like pieces of ceramic microstructure with littler particles. O. Ducreux et al. (2009). This result indicates that silica component in Mn can stabilize mesostructures and inhibit the aggregation of particles. This form exhibits irregular squared shape and are clearly visible in agglomeration and homogeneous formed. Zhensong Lou et al (2008) had mentioned the same observation that reveals the irregular shape with agglomeration and homogenous. The form showed clearly visible

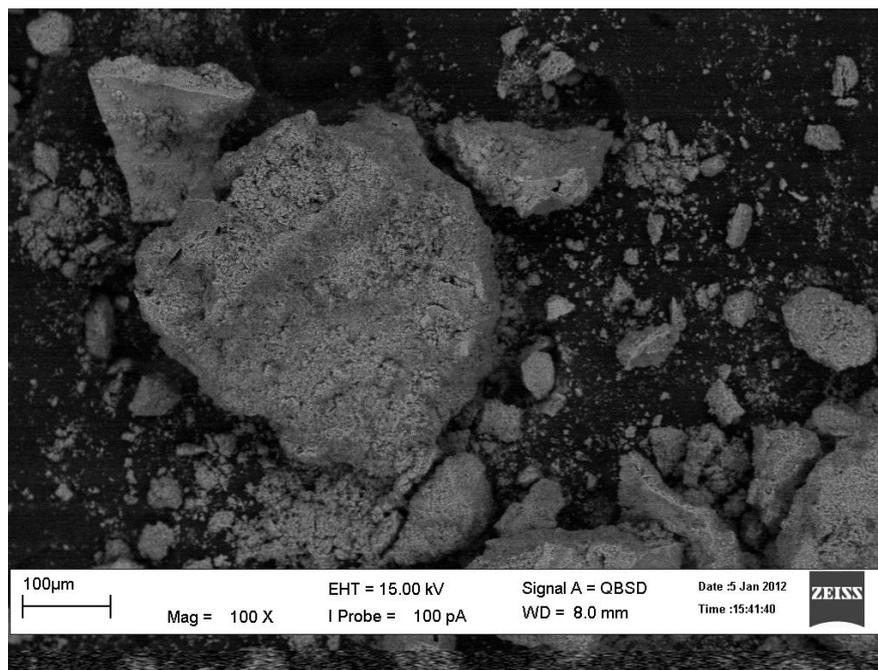


Figure 4.1(a):SEM images of the Co/Mn-TiO₂ catalyst of samples with 100 magnitude.

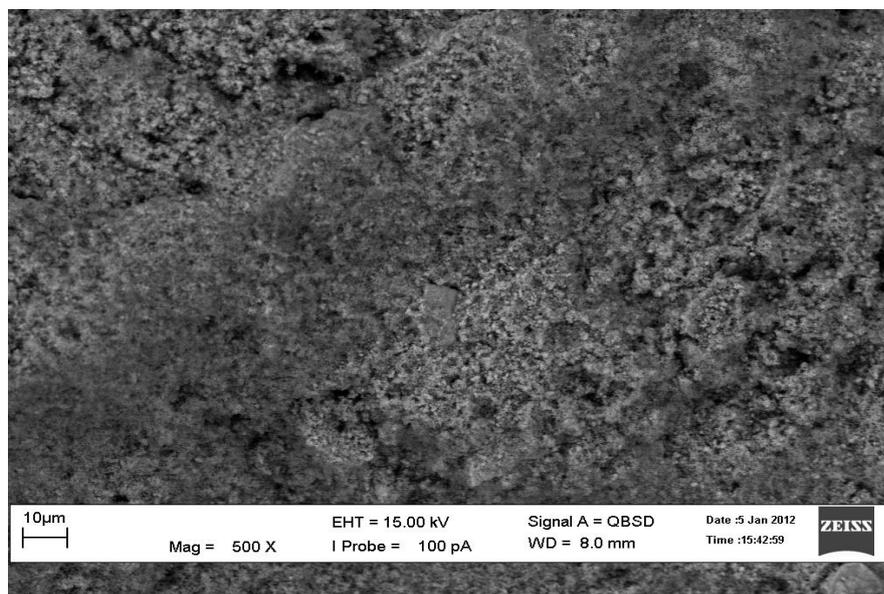


Figure 4.1(b):SEM images of the Co/Mn-TiO₂ catalyst of samples with 500 magnitude.

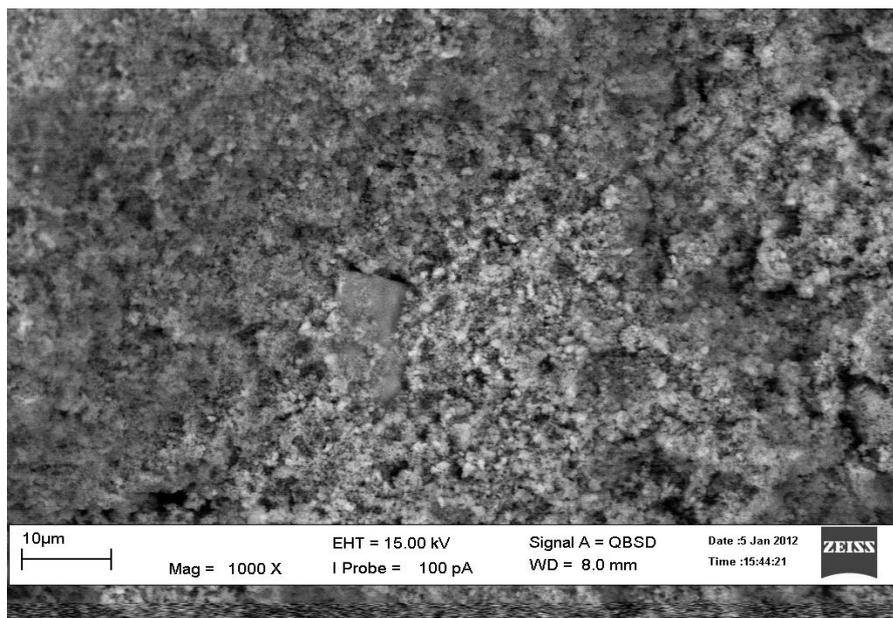


Figure 4.1(c):SEM images of the Co/Mn-TiO₂ catalyst of samples with 1000 magnitude.

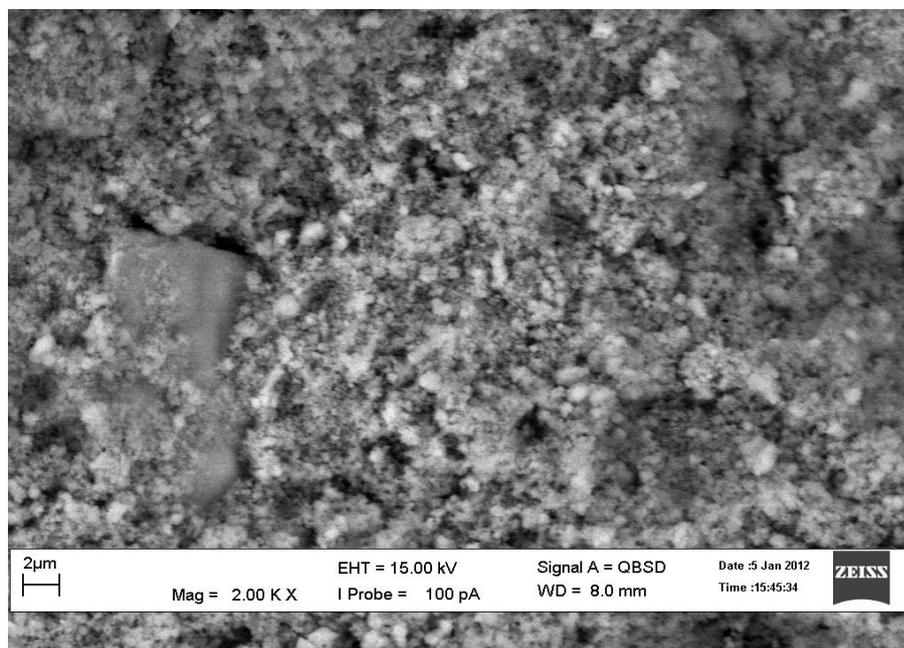


Figure 4.1(d):SEM images of the Co/Mn-TiO₂ catalyst of samples 2000 magnitude.

(ii) Co/Zn-TiO₂

In the Figure 4.2 showed the SEM image of Co/Zn-TiO₂ catalyst sample that indicating the big and several pieces of small stones-like shape that scales in microscope size. Figure (a) showed that the diameter of samples structure was about 10-100 μ m and 100-200 μ m in width. The shape of samples structure was slightly in circle and oval shape maybe insoluble of sample in Figure 3.2 (b). The structure surfaces were compact that it's hard for SEM to zoom into the porous holes. (Pavasupree et al, 2010).

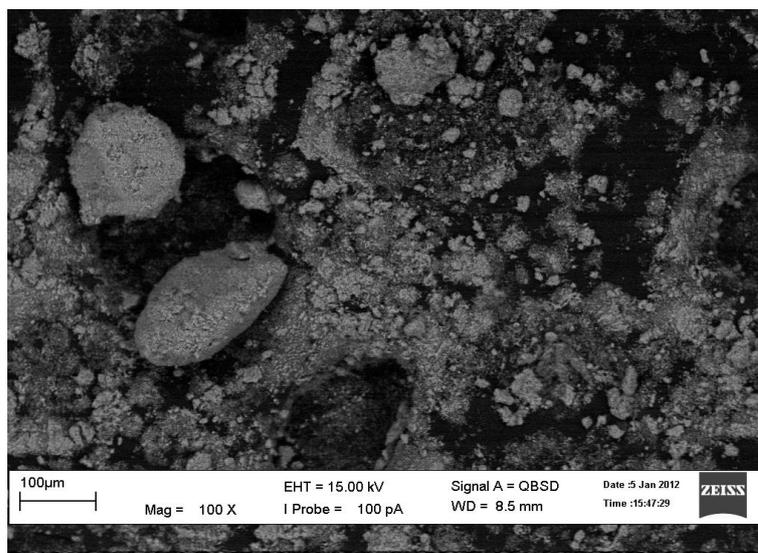


Figure 4.2(a): SEM images of the Co/Zn-TiO₂ catalyst of samples with 100 magnitude.

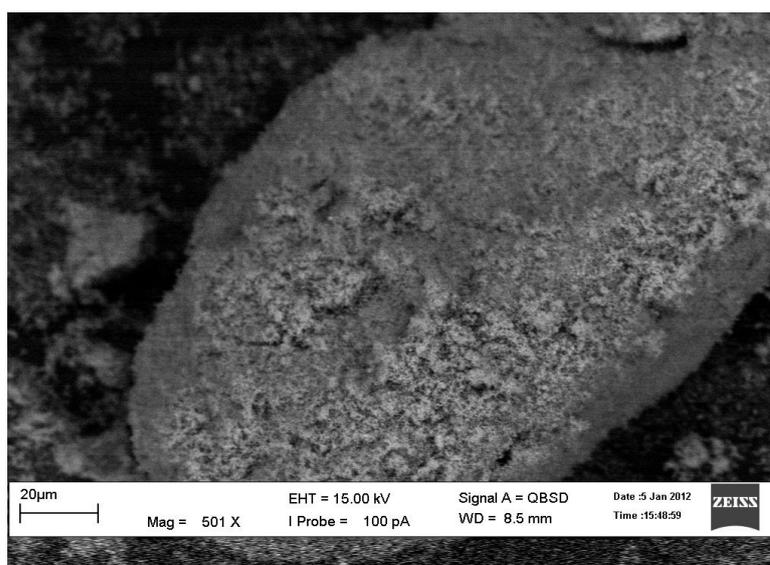


Figure 4.2(B): SEM images of the Co/Zn-TiO₂catalyst of samples with 500 magnitude.

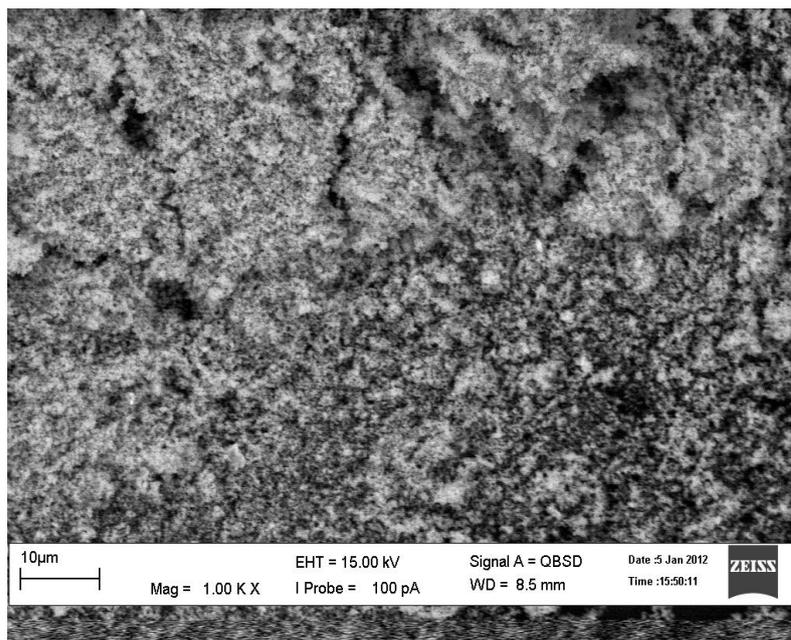


Figure 4.2(c): SEM images of the Co/Zn-TiO₂ catalyst of samples. with 1000 magnitude

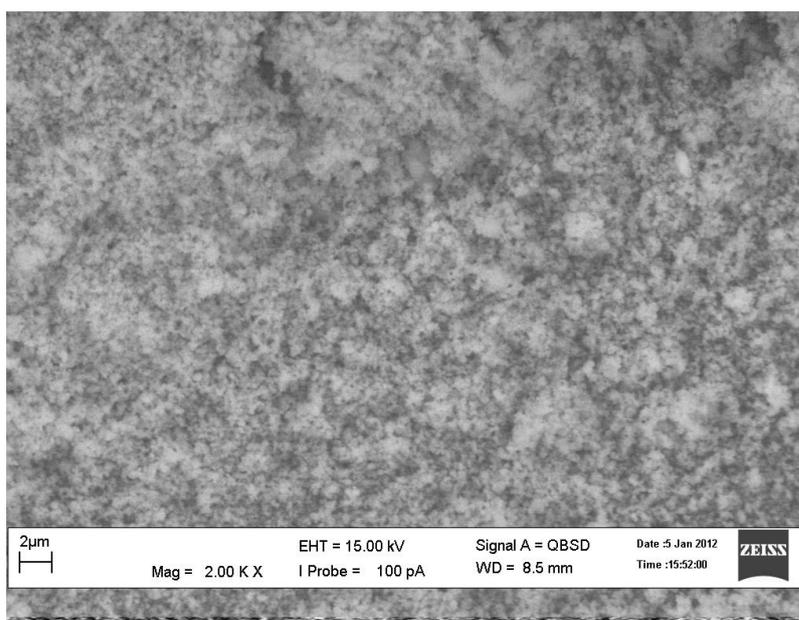


Figure 4.2(d): SEM images of the Co/Zn-TiO₂ catalyst of samples. with 2000 magnitude

(iii) Co/Zr-TiO₂

In the Figure 4.2.2 below showed the low and high magnification SEM images of the as-synthesized Co/Zr-TiO₂ catalyst sample, indicating rock-like surface that composed in microscopic size. The rock-like structure can be seen. This micro structure is

measured approximately 300-400 μm in width and 5-20 μm in thickness at (b). There are shining pieces showed in (c) and (d) explained that the metal compound in the catalyst which combining completely while the impregnation process. (Chenxu He et al, 2010)

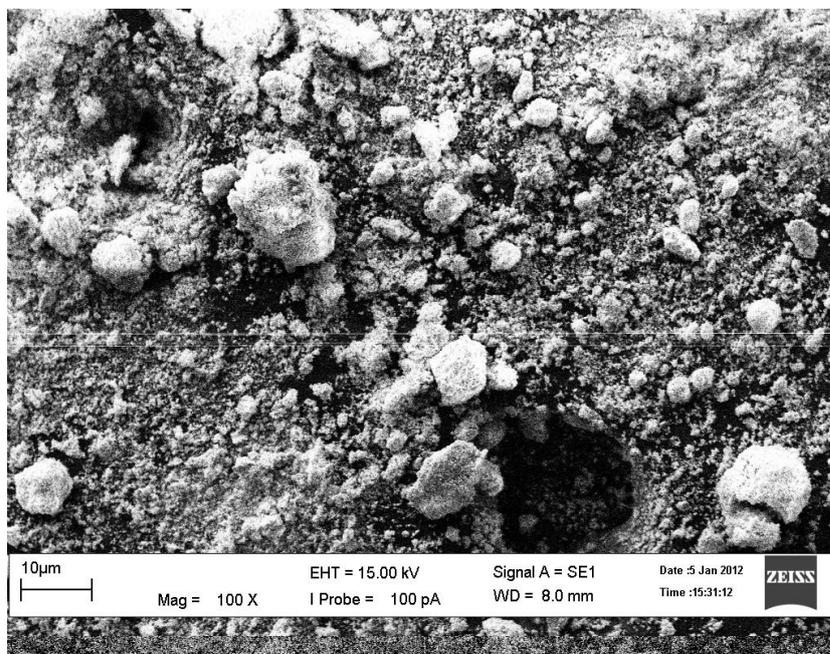


Figure 4.3(a): SEM images of the Co/Zr-TiO₂ catalyst of samples with 100 magnitude

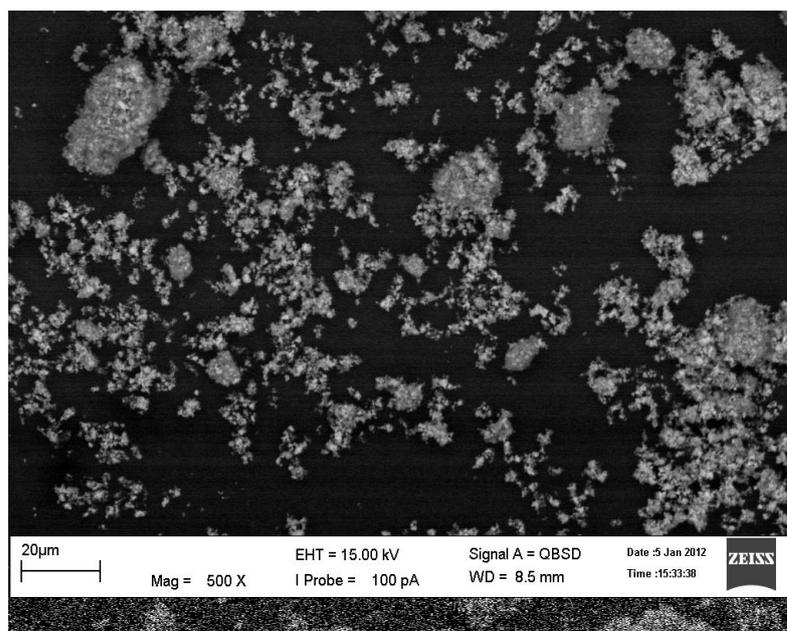


Figure 4.3(b): SEM images of the Co/Zr-TiO₂ catalyst of samples with 500 magnitude.

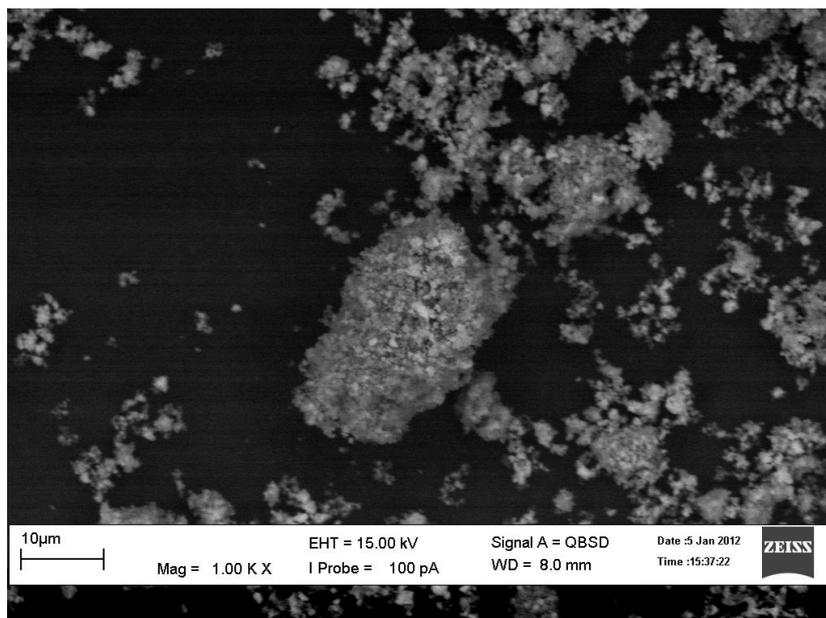


Figure 4.3(c): SEM images of the Co/Zr-TiO₂ catalyst of samples with 1000 magnitude

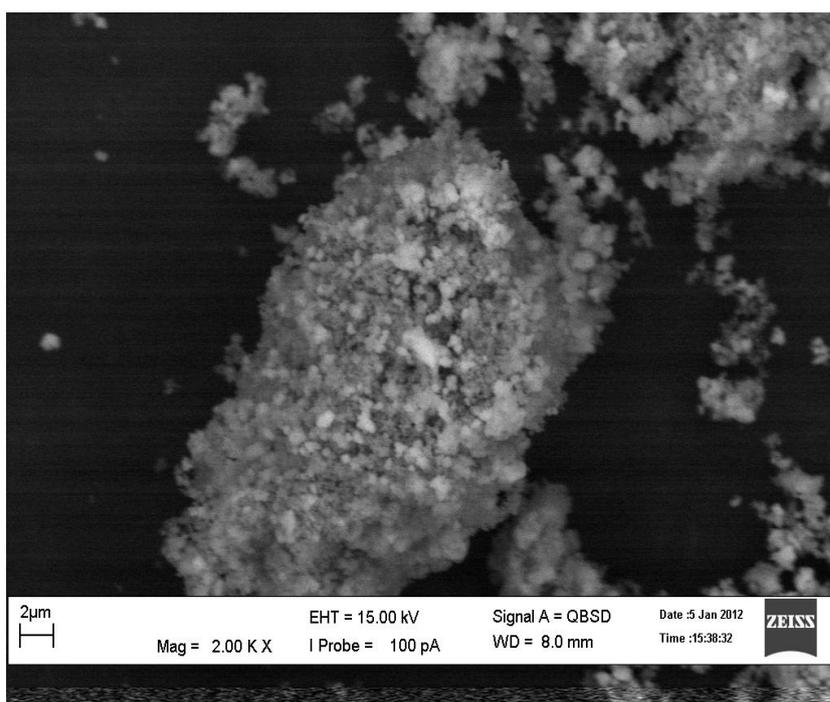


Figure 4.3(d): SEM images of the Co/Zr-TiO₂ catalyst of samples with 2000 magnitude

defects induced by high temperature treatment. The IR band at about 960 cm^{-1} is usually taken as evidence at the relevant concentration of Ti-skeleton. The intensity of this band increases with the increase in Ti content of m-TiO₂, which indicates that all the Ti of m-TiO₂ may be incorporated into the channel wall.(Chenxu He et al, 2010).

4.4 Thermogravimetric analysis (TGA)

(i) Co/Mn-TiO₂

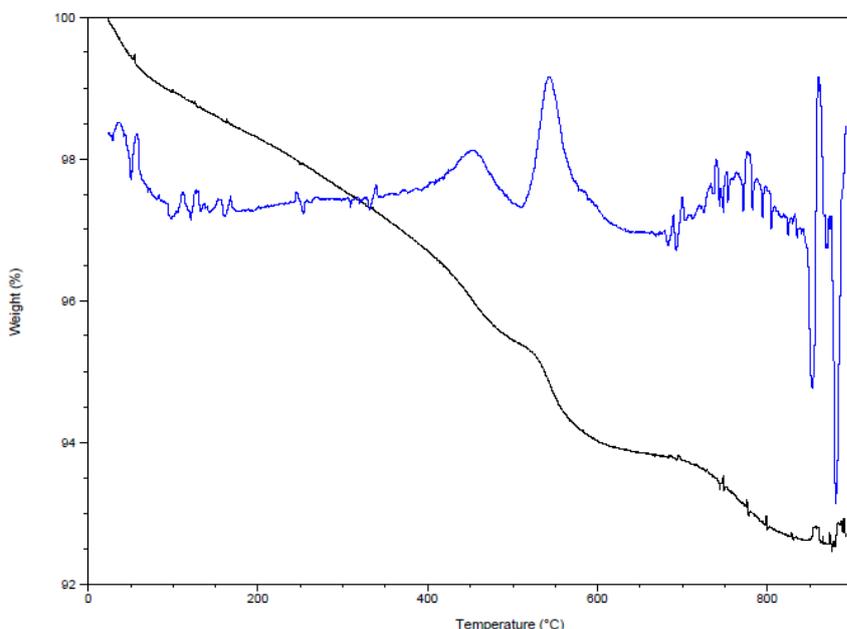


Figure 4.5: Thermogravimetric analysis (TGA) of Co/Mn-TiO₂

The Thermogravimetric analysis curve of the Co/Mn-TiO₂ catalyst sample prior to calcinations is shown in Figure 4.4.1. The TGA was performed at the temperature range between 25°–900°C with 20° C/minute of heating rate. In overall, weight percentage of sample is decreasing according the increasing of the temperature. It is because some components is burn out and decompose by the combustion process. At first significant slope, we can see around 100°C and up, sample is losing weight. It may cause of some water being removes from the sample. Then, around 500°C-600°C another decreasing slope can be seen. Some components are being decomposed during this period of time. Furthermore, almost identical slope is occur around 750-900 °C.The material with high melting point is decomposed at the period of time.In nutshell,the

sample does decompose due to increasing temperature within 900°C. Thus, we can conclude this sample has high thermal stability.

(ii) **Co/Zn-TiO₂**

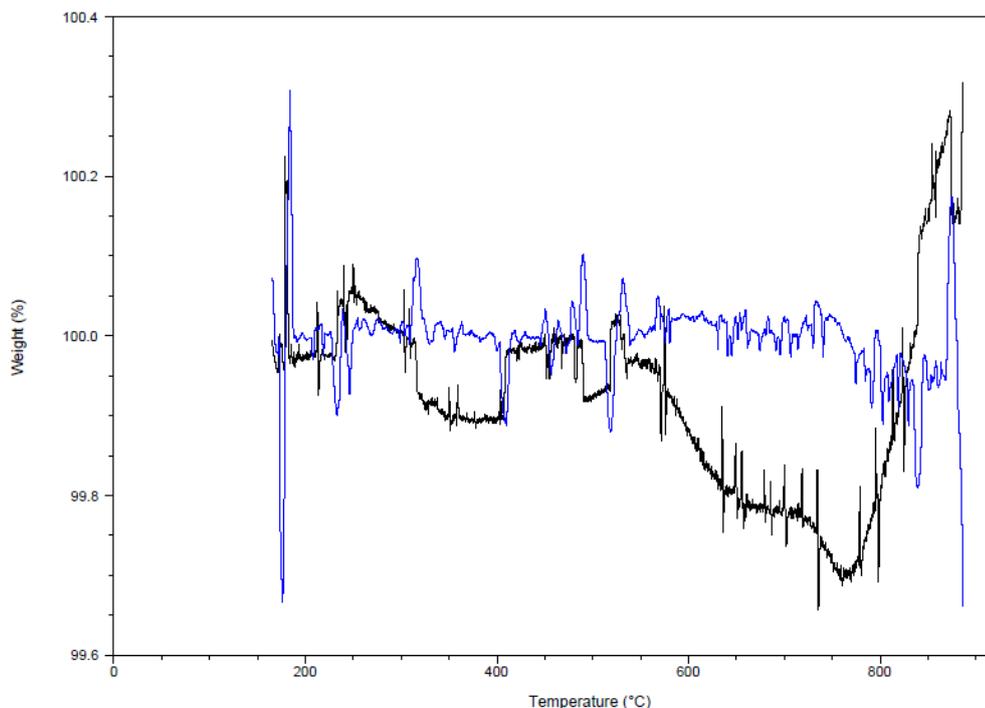


Figure 4.6: Thermogravimetric analysis (TGA) of Co/Zn-TiO₂

The Thermogravimetric analysis curve of Co/Zn-TiO₂ the catalyst sample prior to calcinations is shown in Figure 4.4.2. The TGA was performed at the temperature range between 25°–900°C with 20° C/minute of heating rate. (Zhang et al, 2005). According to analysis from TGA received, the weight loss was inconsistent. In the first step at 170°C, suddenly, the curve was decreasing from 100.25% to 99.7%. Then, the second step at 250°C, the weight becomes increase from 99.7% to 100.1%. Next, the third step, the weight loss occurred from 100% to 99%. The unstable weight increasing was happened twice until to the temperature of 770°C, which the weight was 99.67%. After that, the weight of TGA curve, becomes increasing unpredictable again to 100.3% at temperature of 900°C. As the result, we concluded that this catalyst sample had high thermal stability resulting from the unstable TGA curve.

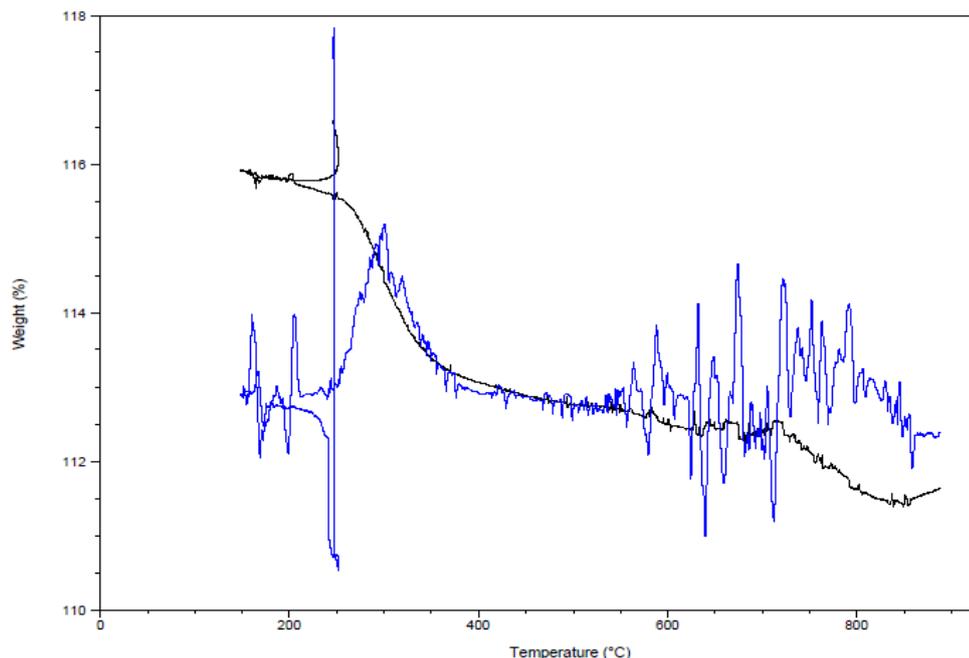
(iii) Co/Zr-TiO₂

Figure 4.7: Thermogravimetric analysis (TGA) of Co/Zr-TiO₂

The Thermogravimetric analysis curve for Co/Zr-TiO₂ of the catalyst sample prior to calcinations is shown in Figure 4.4.3. The TGA was performed at the temperature range between 25°–900°C with 20°C/minute of heating. We can clearly see that weight percent of catalyst is decreasing prior to increasing of temperature. This is because some of the catalyst is decompose as a results of combustion from furnace. As we can see, at first the weigh is increasing as a result of minor error from startup procedure. Then, it starts to decrease by step. It clearly shows decreasing from 200°C to 400°C. It cause of some materials decompose at this temperature. Then it started to flat again start from 400°C to 700 °C. Finally, after 700°C and towards 900°C it started to decrease again. It cause some other material is start to decompost when nearly 900°C. Thus we can say that, the catalyst hardly decompose by the 20-900°C range of temperature. We can say that it is has high thermal stability.

CHAPTER 5

CONCLUSION

5.1 Conclusion

From this research, Optimisation of catalyst activity in the Fischer-Tropsch synthesis will affect the best quality, valuable and clean fuel with higher chain hydrocarbon in the fuel of final product. Co and TiO₂ supported with three different promoters (Mn, Zn and Zr) were synthesized by incipient wetness impregnation method by using Cobalt (II) Nitrate as cobalt source. SEM result showed that the rock-like surface that composed in microscopic size was observed in the catalyst sample of Co/Zn-TiO₂.

From the results of FTIR, the identification of Ti-O-Zn and Ti-O-Co functional group were observed because of the present of zinc and cobalt onto silica TiO₂ support at band 1200cm⁻¹. Besides that, the identification of metal inside TiO₂ was determined by comparing the pure TiO₂ with the incorporated metal on TiO₂. The preparation of 20 wt % of cobalt loading showed a more OH group were presented.

As conclusion, the catalyst supporter with high pore size distribution also will the quality product with higher purity of fuel but for this research, the cobalt supporter. The catalyst TiO₂ supporter with high hydrothermal and thermal stability such as gives its more advantages to have a prolong life at high temperature and high pressure in the Fischer-Tropsch synthesis. So that much longer material was synthesized, more of fuel will produced with the same quality of higher price cobalt supporter such as MCM-41, INT-MM1 and etc. The new silica as cobalt supporter will be developed to enhance the performance of the best and clean fuel production.

5.2 Recommendation

After run this research project, there are a lot of recommendations that need to improve our research in future. The research should be performing by using various data analysis to get better and persistence result. I suggested that the catalyst activity studies should not limit just several characterize equipment such as Thermo gravimetric analysis (TGA), Fourier Transform Infrared (FTIR), scanning electron microscopy (SEM).. Other analysis apparatus like N₂ adsorption-desorption isotherms, Barrett–Joyner–Halenda (BJH) method, Atomic absorption spectroscopy (AAS), Transmission electron microscopy analysis (TEM analysis), and X-ray diffraction analysis (XRD) were the major component in the catalyst activity study.

We cannot neglect all these catalyst analysis apparatus because they were very useful for specific scope. For example, N₂ adsorption-desorption isotherms and BJH analysis was used to collect more details data for BET surface area, pore volume and pore diameter, cobalt dispersion on SBA-15, and XRD, AAS and TEM was used to help to get more details for surface image information about crystal structure and amorphous pore size of catalyst samples. Only SEM apparatus is not enough to check and analysis all of it. FTIR's and TGA function was limited to analyze the material contain and observed the thermal stability of catalyst samples.

Besides that, the catalyst activity from Fischer-Tropsch synthesis (FTS) also should perform for this further research. This FTS was important to obtained the catalyst activity and the stability of catalyst from this reaction. This catalytic performance of cobalt silica-supported catalysts in FT synthesis will be decided that the catalyst is possible or not for use in the industry.

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