EFFECT OF PROMOTERS (Mn, Zn and ZrO_2) ON THE CHARACTERIZATION OF SBA-15 SUPPORTED COBALT CATALYST FOR FISCHER-TROPSCH SYNTHESIS

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“I hereby declare that I have read this thesis and in my opinion this thesis has fulfilled the qualities and requirements for the award of Degree of Bachelor of Chemical Engineering (Gas Technology)”

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A thesis submitted in fulfillment of the requirements for the award of the Degree of Bachelor of Chemical Engineering (Gas Technology)

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To my family
Thank you for the support, encouragement and motivation that have been given
To all my friends
Thank you for the support and assistance that have been given

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ABSTRACT

Fischer–Tropsch synthesis (FTS) is a part of gas-to-liquids (GTL) technology, which produces synthetic liquid hydrocarbons from natural gas. Recently the production of clean fuels and particularly of synthetic diesel by means of the FTS process has aroused renewed interest in both industrial and academic field. This process was shown to be catalyzed by certain transition metals, such as Co which present the highest activity. This research work is about the synthesis of SBA-15 and preparation of catalyst with different promoter Zr, Zn, Mn – Co based supported by SBA-15 by wet impregnation catalysts and characterizes all sampling. All materials were characterized by several physico-chemical techniques such as TGA, SEM and FTIR. The catalytic and characterization results show a great influence of mesoporous support porosity on the structure, reducibility and FTS catalytic behavior of cobalt oxide species supported over these ordered materials. After modification of SBA-15 by Co with different loading, the particles found to be attached closely with each other. The SEM picture shows a large number of SBA-15 particles attaching closely with one another. So this will make catalyst more efficient and effective during FT process. Then, using FTIR, the functional groups will be observed with certain wavelength in the samples such as cobalt oxides, Si-O-Si, Si-CH_3, zinc oxide, OH band, Si-C, and others. Besides that, the identification of metal inside SBA-15 was determined by comparing the pure SBA-15 with the incorporated metal on SBA-15. For this research, the characterization of the catalyst by selecting Zn as promoter have quiet similar characterization with noble metal that already investigate.

ABSTRAK

Fischer-Tropsch sintesis (FTS) adalah sebahagian daripada proses penukaran gas kepada cecair (GTL), yang menghasilkan cecair hidrokarbon sintetik dari gas asli. Baru-baru ini pengeluaran bahan api bersih terutamanya diesel sintetik melalui proses FTS telah menimbulkan minat dalam bidang industri dan akademik. Proses yang telah dimangkinkan oleh logam peralihan yang tertentu, yang menunjukkan aktiviti yang tinggi. Penyelidikan tentang sintesis SBA-15 dan penyediaan pemangkin dengan unsur penggalak yang berbeza, Zn, Mn - Co berasaskan/disokong oleh SBA-15 melalui kaedah impregnasi yang sedikit basah.Sifat-sifat mangkin di percirikan dengan menggunakan teknik fizik-kimia seperti TGA, SEM dan FTIR. Hasil keputusan pencirian menunjukkan liang meso mempunyai pengaruh yang besar pada struktur dan tingkah laku sebagai pemangkin spesis oksida kobalt disokong ke atas bahan-bahan ini yang diperintahkan. Selepas pengubahsuaian SBA-15 oleh bersama dengan unsur penggalak yang berbeza, zarah didapati rapat antara satu sama lain. Gambar SEM menunjukkan sebilangan besar SBA-15 menunjukkan zarah rapat antara satu sama lain. Jadi ini akan menjadikan pemangkin yang lebih cekap dan berkesan semasa proses FT. Kemudian, dengan menggunakan FTIR, kumpulan berfungsi akan diperhatikan dengan panjang gelombang tertentu dalam sampel seperti oksida kobalt, Si-O-Si, Si-CH3, zink oksida, OH band, Si-C, dan lain-lain. Selain itu, pengenalan logam di dalam SBA-15 telah ditentukan dengan membandingkan SBA-15 yang asli dengan SBA-15 yang telah dimpregnasikan dengan logam. Untuk kajian ini, didapati ciri-ciri mangkin dengan pemilihan Zn sebagai unsur penggalak mempunyai ciri-ciriyang sama dengan logam aktif yang telah digunakan sebelum ini.

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LIST OF ABBREVIATIONS

FTIR	Fourier Transform infrared Spectra
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy
FT	Fisher Tropsch
WGS	Water Gas Shift
TEM	Transmission Electron Microscopy
SCR	Selective Catalytic Reduction
Zn	Zinc
Co	Cobalt
Mn	Mangan
CoO	Cobalt Oxide
GTL	Gas to liquid
Al_2O_3	Alumina

CHAPTER 1

INTRODUCTION

1.1 Background of study

Nowadays, a large fraction of chemical, refinery and pollution control process involve catalyst. For example In 1993 the worldwide catalyst usage was $8.7 billion , comprising $3.1 billion for chemical,$3 billion for environmental application, $1.8 billion for petroleum refining, and $0.8 billion for industrial biocatalyst(schilling and Thayer.,1994) . So we can see that how much industry spent money for the catalyst. Fischer Tropsch process also involves more cost. The Figure below show the overall Fischer-Tropsch process.

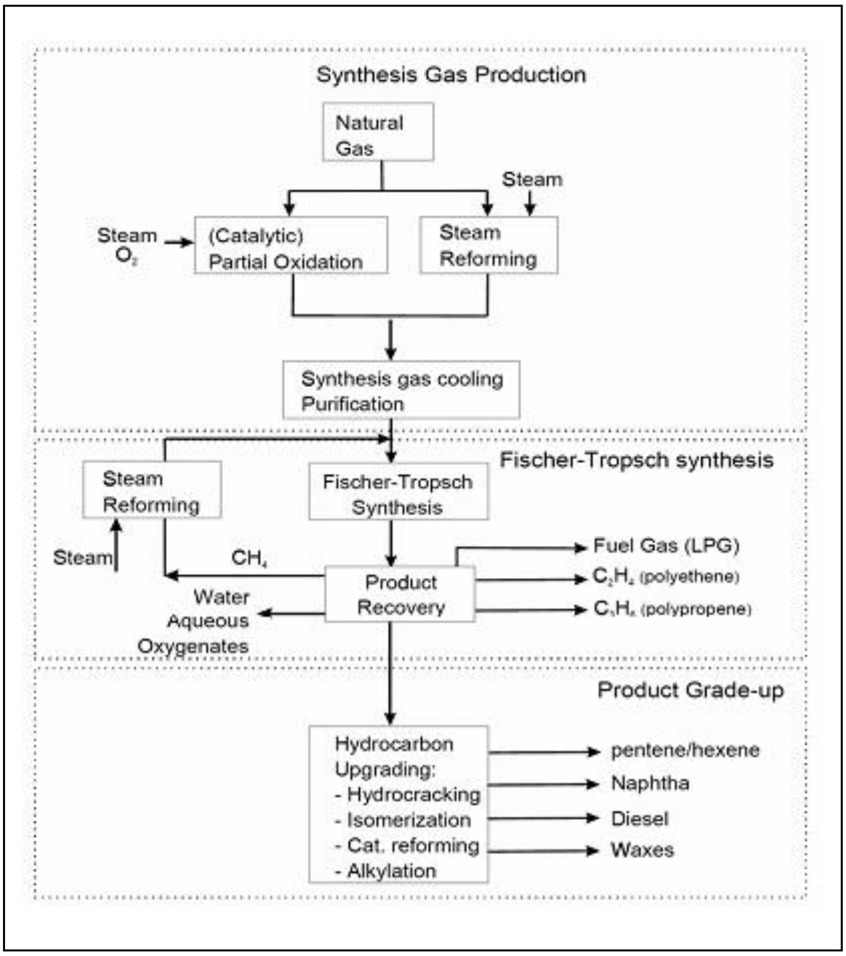
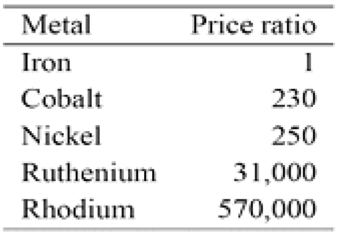


Figure 1.1: Block diagram of the overall Fischer-Tropsch process Configuration

Fischer-Tropsch(FT) synthesis is a part of gas to liquid(GTL) technology, which is a chemical process that produces high hydrocarbons chain from syngas (carbon monoxide &hydrogen). Natural gas can be converted to carbon monoxide and hydrogen (synthesis gas) via existing or newly developed processes such as steam reforming, carbon dioxide reforming, partial oxidation and catalytic partial oxidation, followed by the Fischer–Tropsch synthesis reactionin which "–CH2" represents a product consisting mainly of paraffinic hydrocarbons of variable chain length (Sie, 1999). Fischer-Tropsch synthesis is catalyzed by transition metal such as Co, Fe, and Ru.Among them, cobalt based catalyst are preferred for their high activity compared to Fe catalyst. Besides that, cobalt based catalyst produce high yield of long chain paraffin, low activity for the competing water gas shift reaction and lower price than metal like Ru(Lira et al.,2008)Usually, for catalyst support silica-based mesoporous material such as MCM-41 and SBA-15 are the common catalyst support using in GTL plant. The most common Fischer-Tropsch catalysts are group VIII metals (Co & Fe). Iron catalysts are commonly used, because of their low costs in comparison to other active metals. Iron catalysts have a high water gas shift activity, high selectivity to olefins and appear to be stable when synthesis gas with a high H2/CO ratio is converted. Table below show the price ratio of the metal.

Table 1.1: Relative prices of metals



Metal	Price ratio
Iron	1
Cobalt	230
Nickel	250
Ruthenium	31,000
Rhodium	570,000

Cobalt catalysts give the highest yields and longest life-time and produce predominantly linear alkanes. A cobalt catalyst on kieselguhr became the standard catalyst for commercial purposes in the Second World War in Germany. Disadvantages are the high costs of cobalt and low water gas shift activity. Therefore, cobalt catalysts are viable for natural-gas based Fischer-Tropsch processes for the production of middle distillates and high-molecular weight products. Cobalt catalysts are resulting in a higher productivity at a high synthesis gas conversion. In short, it can be said that Fe catalysts are more versatile yet more vulnerable to being damaged and are cheaper than cobalt catalysts. From the chemical standpoint, the Fe structure is simpler and is more easily enhanced which in turn increases its selectivity and life length.

The reactions of the FT synthesis on iron catalysts can be simplified as a combination of the

$$CO + (1 + m/2n)H_2 \rightarrow 1/nC_nH_m + H_2O \quad (FT)\ -\Delta H_{FT} = 165\ \text{kJ/mol}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad (WGS)\ -\Delta H_{WGS} = 41.3\ \text{kJ/mol}$$

Where n is the average carbon number and m is the average number of hydrogen atoms of the hydrocarbon products. Water is a primary product of the FT reaction, and CO_2 can be produced by the WGS reaction. The water gas shift (WGS) activity can be high over iron catalysts and is negligible over cobalt catalysts.

The Fischer-Tropsch product spectrum consists of a complex multi component mixture of linear and branched hydrocarbons and oxygenated products. Main products are linear paraffin's and -olefin. The hydrocarbon synthesis is catalyzed by metals such as cobalt, iron. This process operation conditions are: T: 300~350^{o}C & P:20~25 bar. Cobalt is used commercially these days for this process at a temperature of 180 to 240 °C and at 20 to 60 bar pressure. Table 1.2 below show main reactions involve in Fisccher-Tropsch synthesis.

Table 1.2: Major overall reactions in the Fisccher-Tropsch synthesis

Main reactions	
1. Paraffins	$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$
2. Olefins	$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$
3. Water gas shift reaction	$CO + H_2O \rightleftarrows CO_2 + H_2$

The siliceous SBA-15 possesses big tubular channels ranging from 3-30 nm diameters. It also possesses the greater thickness of the pore wall and the hydrothermal stability is much higher than MCM-41 (Anunziata et al., 2007) and large surface area (600 -1000 m^2/g) allowing for the dispersion of a large number of catalytically active species (Haifeng et al ., 2008). There was an obvious pore size effect on product selectivity probably due to the pores being sufficiently large for the reaction easily to proceed. Thus, SBA-15 is the better choice to be introduced as the support.

In order to gain access to the active sites, noble metal promoters are often employed. These noble metal promoters, such as Pt or Ru, reduce at a lower temperature than the cobalt oxides, and catalyze cobalt reduction, presumably by hydrogen spillover from the promoter surface (Knifton and Lin., 1982). Promoter is the site of keeping activity at the right place to optimal dispersion for active component and stabilization against sintering and gives strong impact in enhancement of cobalt FT catalyst (Wendelin et al ., 2007). Promoter are the substance that increase the catalytic activity (Chemguide., 2007).

Fourier transform infrared spectraanalysis (FTIR), N2 adsorption analysis (BET) and X-ray diffraction (XRD) were applied to analyze characterizations of the catalyst.

1.2 Problem statement

Nowadays, due to the new fuels regulation which require low sulphur content in diesel, deep hydrosulfuration is needed to remove supphur from petroleum distillates and this will drive up the cost of petroleum besed fuel. FT synthesis has become more attractive approach in producing hydrocarbon using syngas.In any industrial FT synthesis,catalyst is a vital part and one of the most important aspect during any chemical reaction.Support cobalt catalyst have been extensively used in FT synthesis when high molecular weight of hydrocarbon products is desired(Nobuntu et al ., 2005) and represent a suitable choice. Therefore, FT synthesis has become an alternative way in order to produce good and clean hydrocarbon by using syngas. In any FT synthesis for industrial application, catalyst is the main aspect and the most important part to complete the synthesis and chemical reaction.

Then, in order to gain access to the active sites, noble metal promoters are often employed. These noble metal promoters, such as Pt or Ru, reduce at a lower temperature than the cobalt oxides, and catalyze cobalt reduction, presumably by hydrogen spillover from the promoter surface (Knifton and Lin .,1982).

So, in this research research ,we manipulated the varies of the promoter like Zirconium oxide($ZrO2$),Mangan (Mn) and Zinc(Zn).The catalyst we use in this research is Cobalt(Co) and the supporter that we use is the SBA-15.We will use this three promoters to get the most efficient and increase the catalytic activity.

1.3 Objective

a) To synthesis SBA-15
b) To prepare and characterize Zr,Zn, Mn – Co based supported by SBA-15 catalysts
c) To study the activity of catalysts prepared for FT synthesis

1.4 Scope of Study

In this research, it will be focusing on the production of Co based SBA-15 catalyst by impregnation method with different loading of Zn, Mn and Zr .In this process the amount of Co is same which 20 wt % and different promoters but still the content are same which is 0.5 wt %.After that the catalyst then will be characterized by using Fourier transform infrared spectroscopy (FTIR.Then we also study the activity of different catalysts for FT synthesis to aspect the result which one the best promoters among (Zn,Mn and Zr).

CHAPTER 2

LITERATURE REVIEW

2.1 Fischer Tropsch(FT)

Fischer–Tropsch (FT) synthesis is an important catalytic process which was well-known to produce ultraclean alternative fuels from coal, natural gas and biomass via syngas . Cobalt-based catalysts have been widely applied in an FT synthesis owing to their high activity, high selectivity towards long chain *n*-paraffins, and their lower activity for the competing water gas shift reaction (WGSR). The FT synthesis activity over cobalt catalyst depended primarily on the overall amount of an exposed metallic cobalt during the reduction process, which was determined by the cobalt loading amount, metal particle size, dispersions and reduction degree. Furthermore, the chemical and texture properties of the support influenced the catalytic activity and product selectivity of cobalt catalysts via their modifications on the reducibility and dispersion of cobalt or the formation of well-fined phases. Sometimes it might be more economical to modify or change the support properties than to increase the number of active sites (Wang et al., 2011).

It has been shown that the control of hydrophilic/hydrophobic properties of supports were of importance in the preparation of catalysts and in determining the catalytic behavior. Especially, an FT synthesis is the hydrothermal reaction, because the amount of water is produced along with the main reaction. Several researchers reported the impact of support hydrophobicity on the catalyst activity in the Fischer–Tropsch synthesis. For example(Kim and team 2007) showed that the preliminary silylation of an SBA-15 support enhanced the reducibility of the cobalt oxide species due to the weaker cobalt oxide-support interaction and consequently promoted the activity for the FT synthesis. (Ojeda et al ,. 2002) reported that the CO conversion rate increased over the silylated catalyst, because the hydrophobic surface expelled the water molecules and more surface sites were available for CO adsorption and dissociation. In our previous study found that CH_3-modified $Co/Ru/SiO_2$ catalysts showed a higher selectivity towards C_5–C_{11} hydrocarbons, which should be ascribed to its hydrophobic characteristics (Jia et al ., 2011).The figure below show the one of the reactor use in Fischer-Tropsch process.

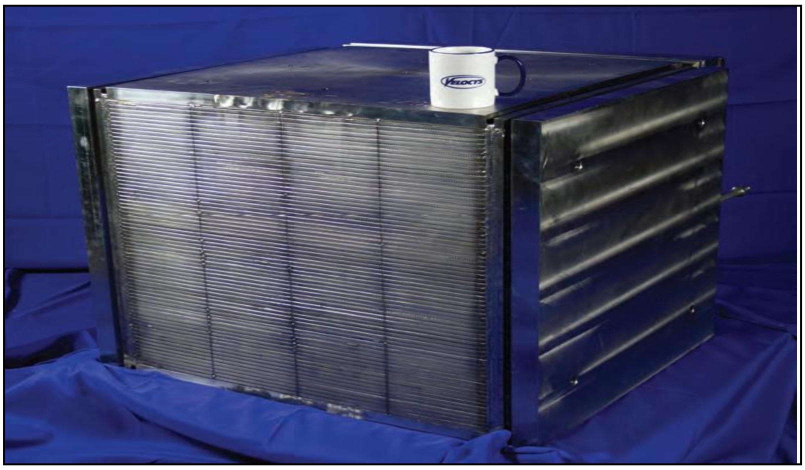


Figure 2.1: Big Daddy reactor: a full-scale microchannel Fischer-Tropsch reactor by US firm Velocys

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. An increasing demand for clean fuels and chemicals are expected to lead to an important shift from crude oil to natural gas as feedstock for chemical industries. This will certainly involve the use of Fischer-Tropsch (FT) technology, in which high molecular weight hydrocarbons are synthesized by catalytic hydrogenation of CO using cobalt-based FT catalysts. 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(Huang et al ., 2010).

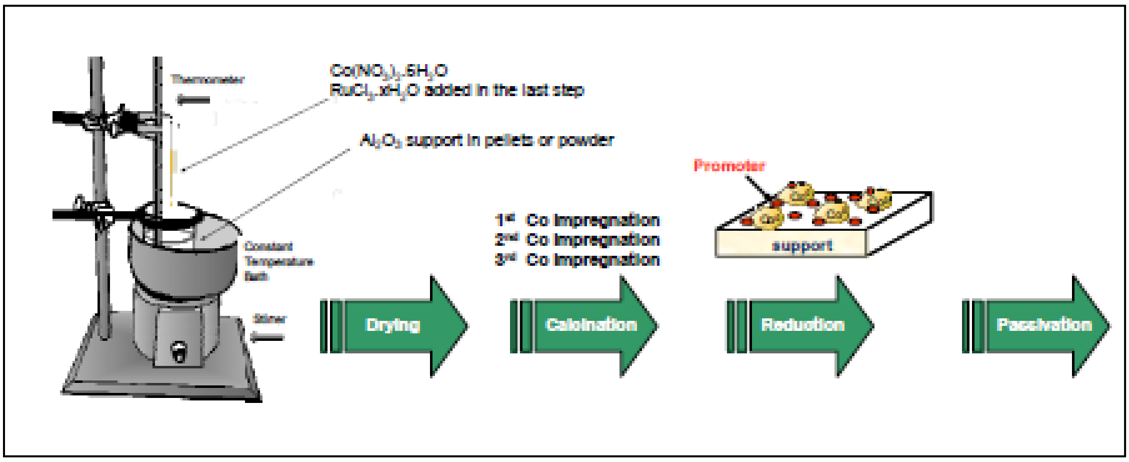


Figure 2.2: Steps preparation of catalyst

2.3 SBA-15 Supporter

The SBA-15 was many used in the recent research especially about in the Fischer-Tropsch synthesis. The recent experiment was on the Use of different mesostructured materials based on silica as cobalt supports for the Fischer–Tropsch synthesis was released by Gonza´lez and team in 2009. He published about the advantages of SBA-15 uses as cobalt supporter as saying that the use of SBA-15 as cobalt catalyst support for the FT synthesis seems to be very promising, since the Co/SBA-15 catalyst with a Dp of 5 nm has shown the best catalytic behavior in comparison with the rest of the materials tested in reaction such as Al- MCM-41 and INT-MM1.He also stated that larger surface-Co species anchored or encapsulated in the wide pore mesoporous supports showed a contrary tendency. As conclusion of his statement that SBA-15 gave more great effect on the catalyst compared with other silica such as MCM-41 and INT-MM1 in his recent research.

2.4 Promoters

These catalysts are often loaded with small amounts of promoter elements that enhance their overall catalytic performances and catalyst lifetime. These beneficial effects are, however, only obtained if the promoter element is added in the appropriate manner and in a limited range of promoter loading. Although catalyst promotion is heavily studied in the field of heterogeneous catalysis, not so much is known about the physicochemical origin of cobalt FT promotion effects. Over the past decades a large number of studies have been reported on supported cobalt FT catalysts. Generally, these studies indicate that the number of available surface cobalt metal atoms determines the catalyst activity and attempts to enhance the catalytic activity have been focusing on two interconnected issues: (1) to reduce the cobalt-support oxide interaction and (2) to enhance the number of accessible cobalt atoms available for FT reaction. It has been shown that the number of catalytically active cobalt atoms as well as their selectivity can be largely enhanced by the addition of small amounts of various elements, called promoters, to the catalyst material. However, the exact role of these promoters, as is the ase for many other heterogeneous catalysts as well, remains often unclear. The aim of this chapter is to give an extensive overview of the different promoters used to develop new or improved cobalt-based FT catalysts. Special attention is directed towards a more fundamental understanding of the effect of the different promoter elements on the catalytically active cobalt nanoparticles (Bezemer ., 2005).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 selectivity. 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:

(1) Easing cobalt reduction.

(2) Enhancement of cobalt dispersion.

(3) Better resistance to deactivation.

(4) Formation of metallic alloys.

(5) High concentration of hydrogen activation site.

(6) Modification of intrinsic activity of surface sites.

2.4.1 Promoters effect

The catalyst surface often contains substances that are added deliberately to modify the turnover rate for a given catalytic reaction (Z. Paal, et al,1997). The simplest case being an additive that increases the rate per site per second. It is, in this respect, useful to recall the concepts of catalyst promotion. Promoters are doping agents added to catalyst materials in small amounts to improve their activity, selectivity and/or stability (B. Cornils ,et al,2000).

2.4.2 Structural promoters

The main function of structural promoters is to influence the cobalt dispersion by governing the cobalt-support oxide interaction (B. Cornils,et al,2000). A high Co dispersion results in a high active Co metal surface and, therefore, in a high coverage by the reactants, and as a consequence an improved catalyst activity. Structural promotion may lead to an increased catalyst activity and stability, but in principle does not influence the product selectivity since it merely increases the number of active sites in a catalyst material. This increase in active sites can be achieved by a stabilization of the Co active phase due to the promoter element, which either avoids the formation of metal-support compounds, or prevents the agglomeration and sintering of the Co particles under F-T operation conditions.

2.4.2a Stabilizing the support oxide

Promoter elements can be added to the support oxide resulting in a decreased Co compound formation with the support oxide. This is illustrated in Figure 2.3. More specifically, strategies should be followed to avoid the formation of either cobalt titanate, cobalt silicate or cobalt aluminate as a result of Co solid-state diffusion under reducing or regeneration conditions in the subsurface of these support oxides. A related problem is the reduction in the support surface area. This is especially a problem in the case of titania, where the anatase polymorph is only stable under oxidative regeneration conditions from about 400°C to 750°C. The addition of Si, Zr and Ta as promoter elements may avoid or diminish surface collapse of the support oxide. The Figure 2.3 below show the structural promoters effect the compound formation.

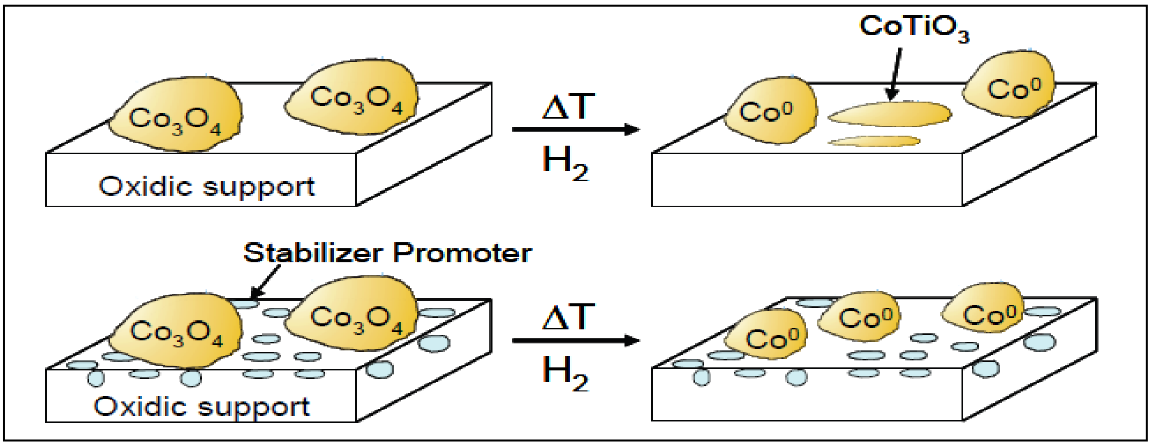


Figure 2.3: Structural promoters can lead to a decreased compound formation with the support oxide

2.4.2b Glueing the cobalt particles on the support oxide

Some promoter elements can act as an oxidic interface between the supported Co particle and the support oxide, leading to an increased stability of the cobalt particles against sintering during reduction or oxidative regeneration. A plausible schematic representation of this promotion effect is shown in Figure 2.4 below.

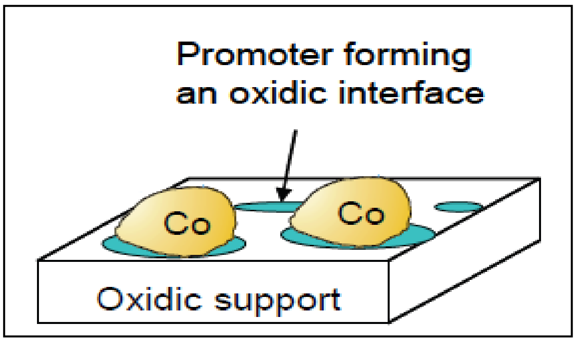


Figure 2.4: Structural promoters can act as an oxidic interface between the supported Co particle and the support oxide

2.4.2c Promoters leading to increased cobalt dispersion

The addition of promoter elements may also lead to increased cobalt dispersion after preparation. In the absence of the promoters, relatively large cobalt crystals are formed, whereas, by adding these additives, smaller supported cobalt particles can be made. Such promotion effect is illustrated in Figure 2.5 below.

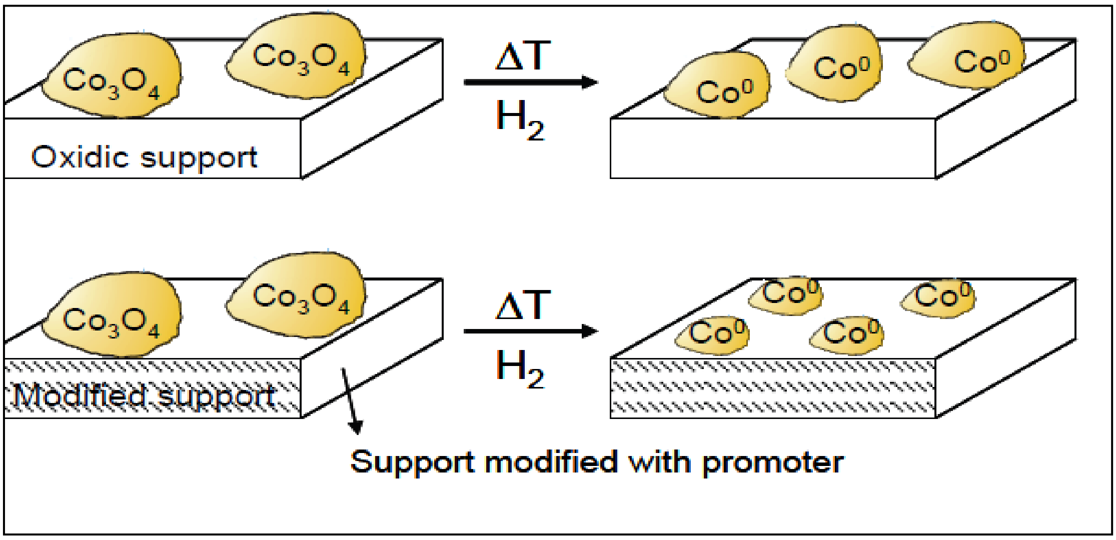


Figure 2.5: Oxide promoters can be used to modify the support leading to increased dispersions

Related to this effect it is important to mention that small metal particles composed of a promoter element can dissociate hydrogen in the neighbourhood of a supported cobalt particle leading to the formation of atomic hydrogen that may spill over by diffusion to cobalt, as illustrated in Figure 2.5.This can result in an enhanced degree of cobalt reduction and therefore a higher amount of surface cobalt metal atoms. The result of this promotion is an increase in the number of active sites and therefore a higher catalyst activity, leaving the catalyst selectivity unaltered. Noble metals, such as Re, Pt and Ru, are known to act in this manner. The Figure 2.6 below show the spill over effect by a noble metal promoter

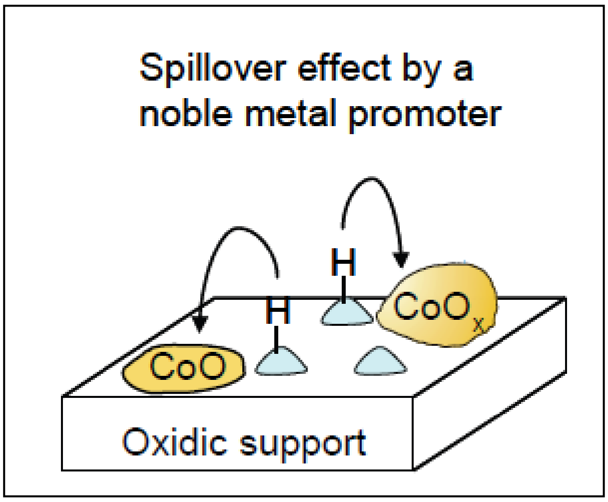


Figure 2.6: H2 spillover effect, leading indirectly to a higher dispersion of the supported Co particles

2.4.3 Synergistic promotion effect

As was already mentioned promoter elements are not considered themselves to be catalytically active, but it is fair to say that this is not always the case. This promoter activity may indirectly affect the behaviour of the catalytic active element since it will alter the local feed composition or may, due to its catalytic properties, influence the overall reaction product distribution. The following effects, illustrated in Figure 2.7 below, are expected to occur in a promoted Co FT catalyst.

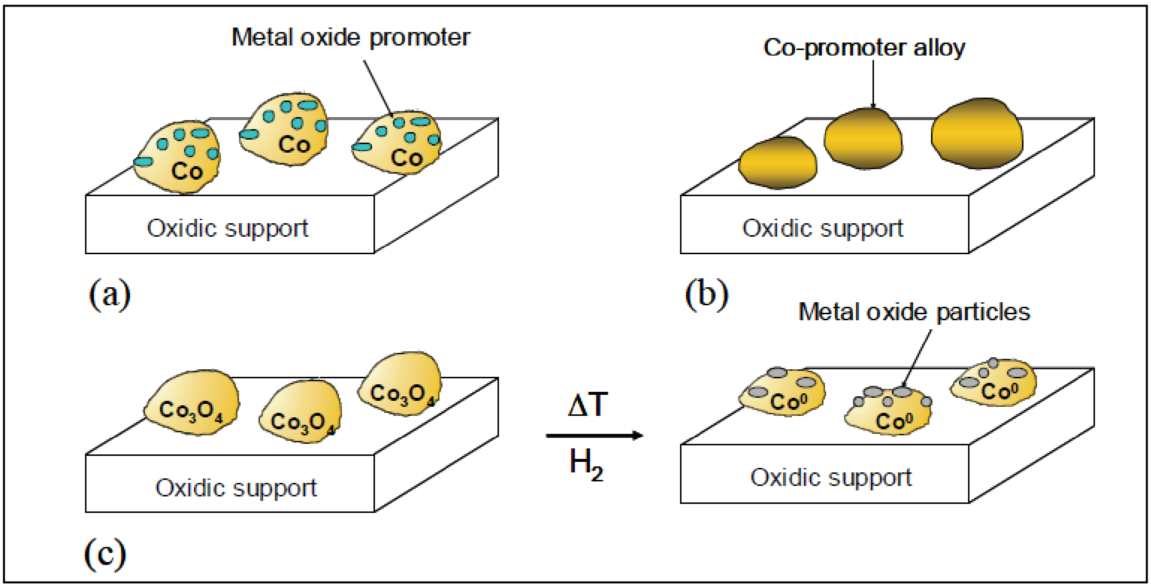


Figure 2.7: The different modes of action of electronic promoters in Co-based FT catalysts:(a) promoter metal oxide decoration of the cobalt surface;(b)cobalt– promoter alloy formation; and (c) metal oxide decoration effect occurring upon reduction with some oxidic supports.

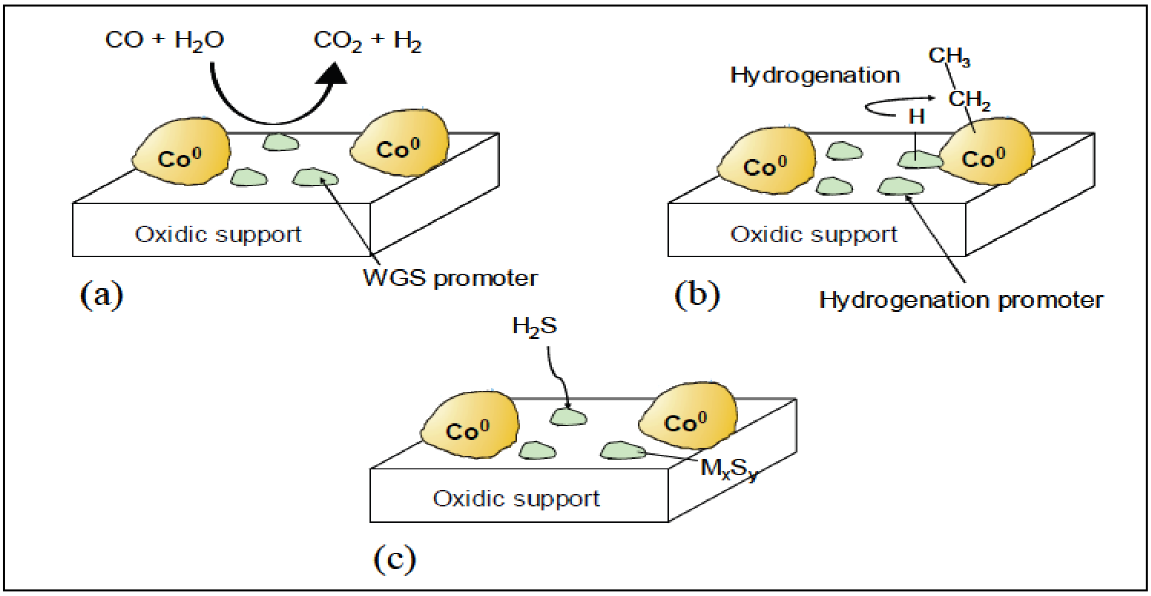


Figure 2.8: Survey of possible synergistic promotion effects occurring in Co-based FT catalysis :(a) water-gas shift reaction; (b) hydrogenation/dehydrogenation reactions; and (c) H_2S adsorption.

2.4.3a Water gas shift(WGS) reaction

The water-gas shift reaction ($CO + H_2O = H_2 + CO_2$) made by particles composed of a promoter element close to a supported cobalt particle leads to a change in the local CO/H_2 ratio, which may affect the surface coverage of cobalt. As a result, both the activity and the selectivity of the catalyst can be altered. Transition metal oxides could act as WGS reagents.

2.4.3b Hydrogenation/dehydrogenation reactions

The end products of the FT process are a mixture of higher alkanes and alkenes. The promoter elements could show under FT conditions some activities for hydrogenation or dehydrogenation reactions leading to a shift in the relative ratio of alkanes to alkenes.

2.4.3c Coke burning during regeneration

Co FT catalysts deactivate due to coke formation blocking the active sites. This coke can be burned off by an oxidative treatment. The addition of promoter elements may decrease the temperature of this oxidative treatment, preventing the possible clustering of supported cobalt particles.

2.4.3d H_2S adsorption reaction

As was already mentioned, Co FT catalysts are prone to H_2S poisoning and the addition of specific promoter elements may lead to an increased H_2S tolerance. Crucial for this are the use of promoter elements, such as B and Zn, which make stable surface compounds with sulfur.

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/SBA-15 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 Figure 2.9 is example the effect the reaction use promoter and not.

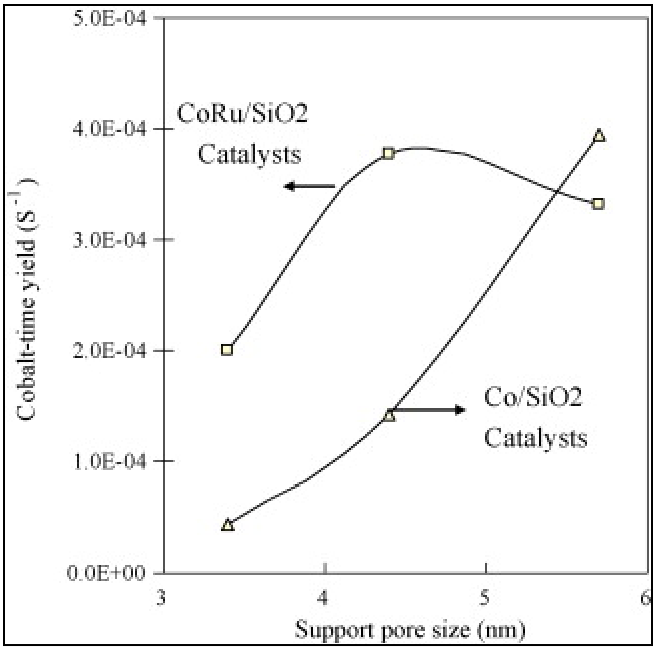


Figure 2.9: Relation between cobalt time yield and pore size of support (Hong et al ., 2009)

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 SiO_2 aerogel that is unpromoted (Ni/SiO_2) or promoted (Ni/ZrO_2–SiO_2) with ZrO_2 are prepared by the incipient-wetness impregnation method.It is found that the Ni/ZrO_2–SiO_2 catalyst shows higher catalytic activity, over which CO can be completely converted into CH_4 at 240 °C (Wang et al ., 2010).The Figure 2.10 below show the XRD patterns of the Ni/Si and Ni/Zr–Si.

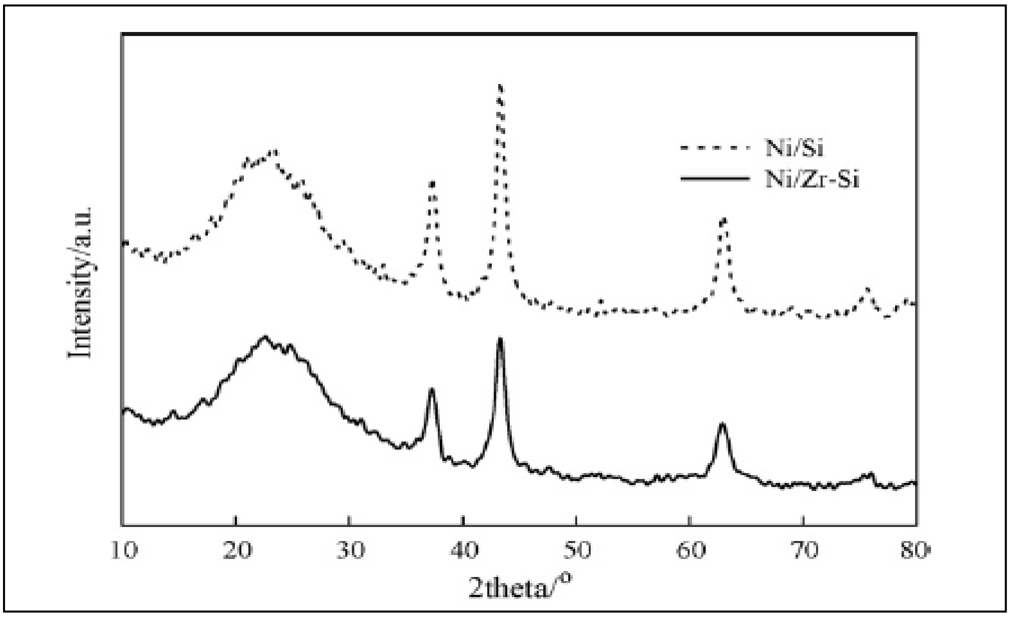


Figure 2.10: XRD patterns of the Ni/Si and Ni/Zr-Si

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. The Figure 2.11 shows the TPR profiles of the Ni/Si and Ni/Zr-Si

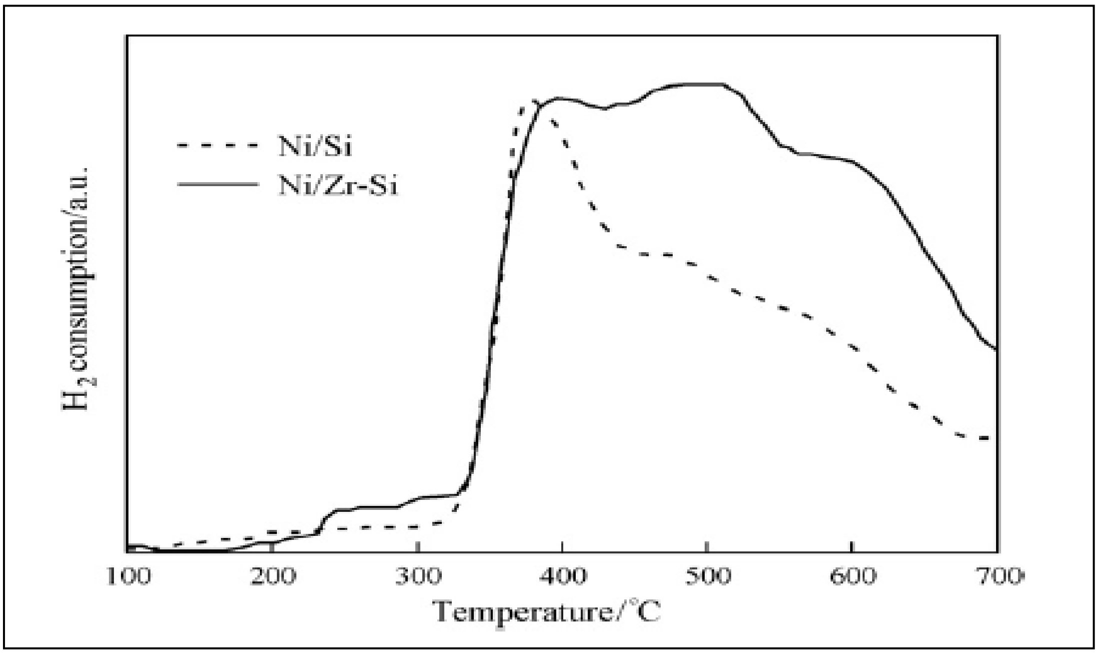


Figure 2.11: TPR profiles of the Ni/Si and Ni/Zr–Si

The total peak area of the Ni/Zr–Si catalyst has a progressive increase due to the addition of ZrO_2 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 H_2-TPD. So we can conclude that smaller Ni crystallite size, higher Ni dispersion, more active Ni species and stronger adsorption ability for H_2 may contribute to higher catalytic activity of the $Ni/ZrO_2–SiO_2$ catalyst for CO methanation(Wang et al .,2010)

2.4.4 ZrO_2

ZrO_2 has also been widely used as a promoter due to its redox and acid–base properties (Dong et al ., 2004) reported that the addition of ZrO_2 promoter in CuZnAlO catalyst could increase the conversion of methanol and selectivity of H_2 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 and team (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 (Wang et al ., 2010).Figure 2.12 show the comparison catalyst with metal and without metal.

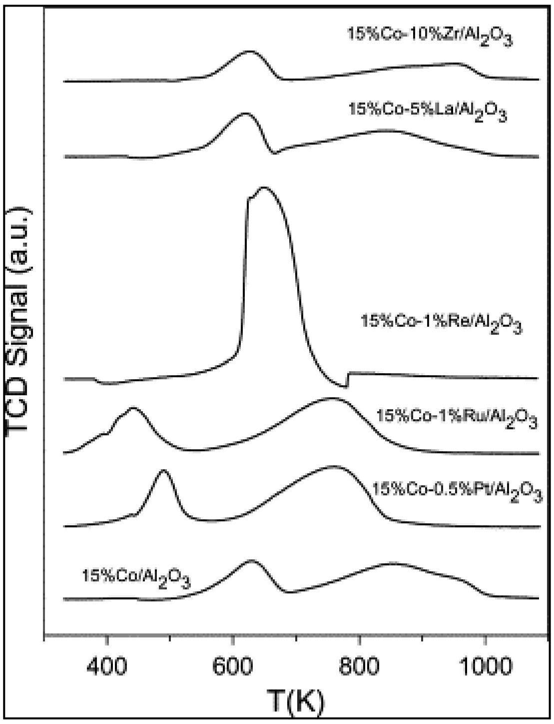


Figure 2.12: TPR comparison of Al_2O_3 supported Co catalysts with and without metal and metal cation promoters (Jacobs et al ., 2002)

2.4.5 Mn

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/TiO2FT 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-Cocompound formed on the surface of the catalyst. In addition, it was reported that the distribution of

MnCoOx 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. The Figure below show Fourier transforms magnitudes of EXAFS spectra.

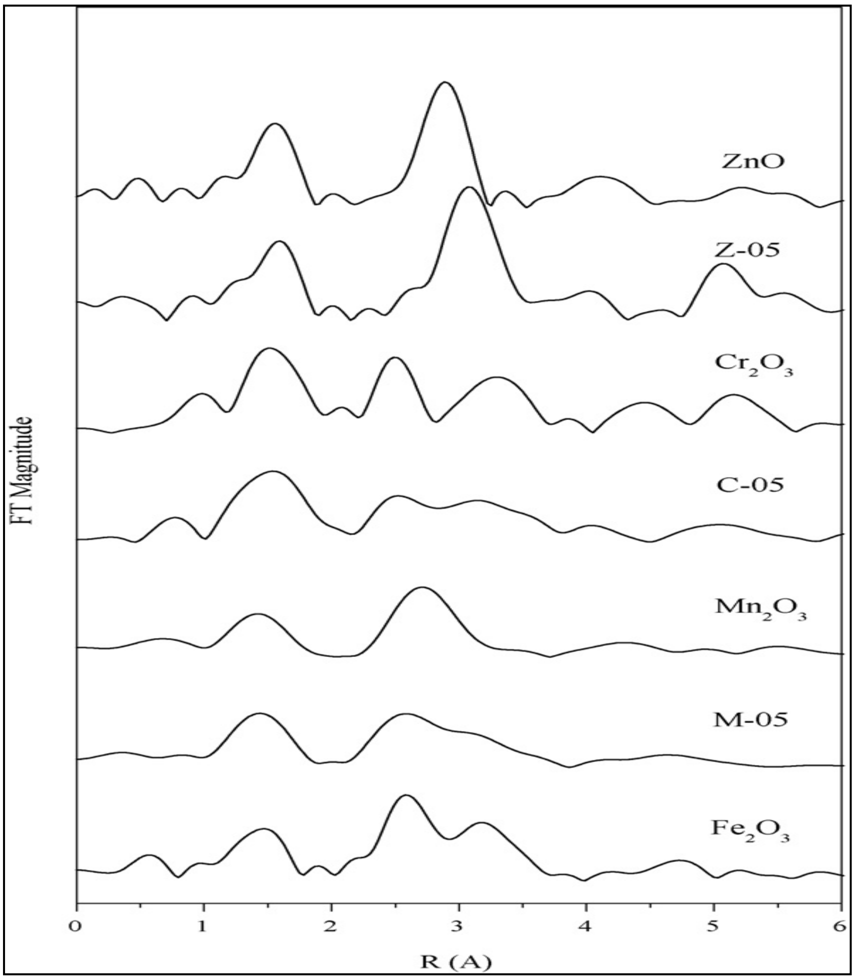


Figure 2.13: Fourier transforms magnitudes of EXAFS spectra of the as prepared catalyst and reference compounds (Wang et al .,2010).

2.4.6 Zn

In this research, addition of Zn promoter gives a lot of effect in the Fischer-Tropch synthesis. According to Viljoen and team (2009) 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 Viljoen and team. As the conclusion, Zn promoter can affect the level of activation energy and reaction reactivity of catalyst in the FT synthesis.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

The experiment techniques used for the preparation and characterization of the support and the catalyst through this research are summarized and presented in this chapter. The overall experimental works are summarized in the Figure 3.1 below.

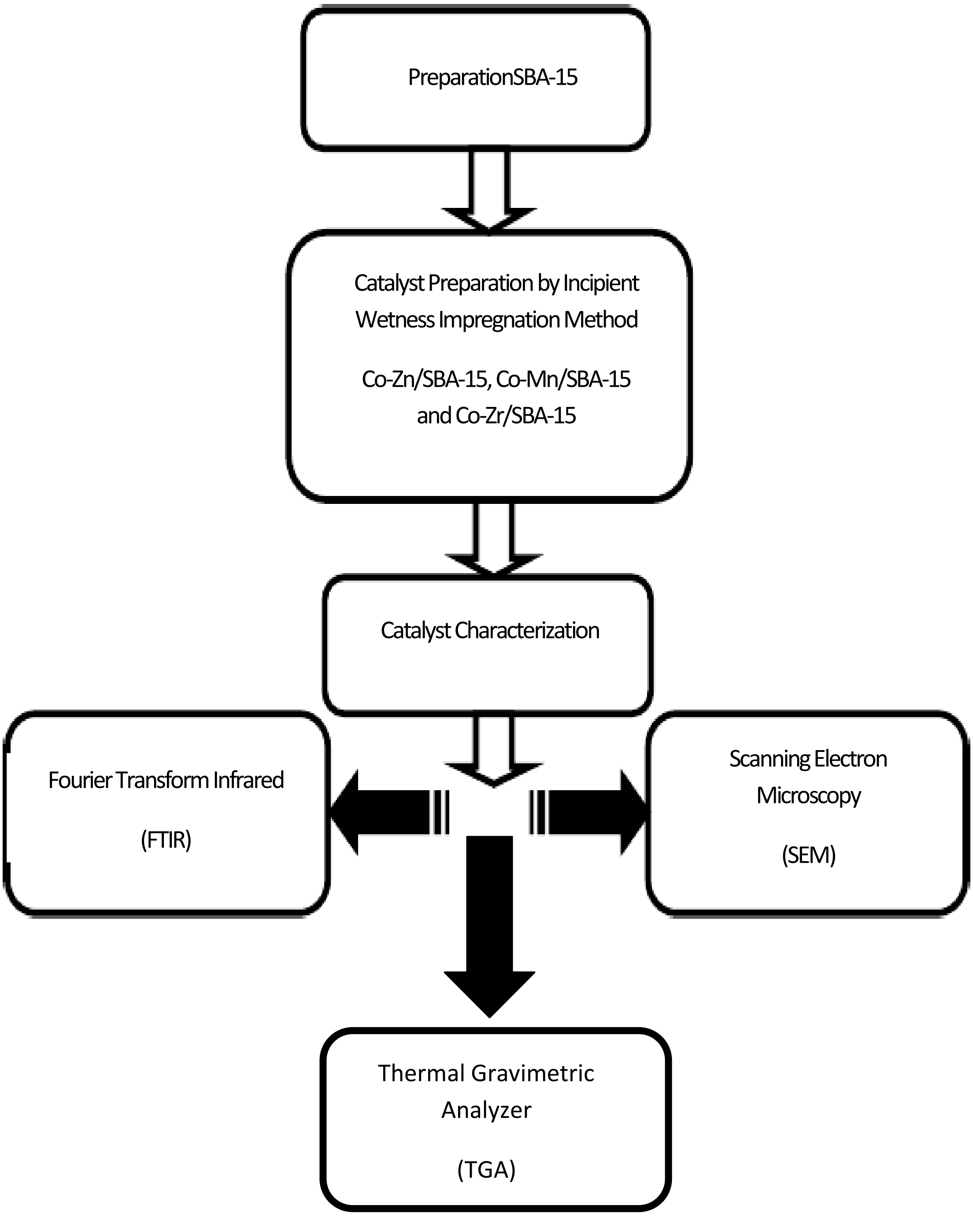


Figure 3.1: Flow chart of overall experimental work.

In this chapter, we focus on procedure how to synthesis of supporter SBA-15.The next step is preparation of catalyst ZnCo/SBA-15, ZrO_2Co/SBA-15 and MnCo/SBA. 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. The experiment will be running in the FKKSA chemical engineering laboratory with other students that also use this Fischer-Tropsch synthesis.

3.2 Materials and Chemicals

All chemicals and materials used in the present study are listed as Table 3.1 below:

Table3.1: List of chemical

Chemical	MolecularFormula	Supplier	Purity%
Cobalt Nitrate	$Co(NO_3)_2.6H_2O$	Merck	99
Zinc Nitrate	$Zn(NO_3)_2.6H_2O$	R&M Chemical	98
Manganase (II)nitrate tetrahydrate	$H_8MnN_2O_{10}$	-	97
Pluronic P-123	$HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O_{70}(CH_2CH_2O)_{20}H$	Aldrich	-
Acid hydrocloric	HCl	UMP Sources	37

3.3 Experimental procedure

3.3.1 Synthesis of SBA-15

A specific amount of HCl solution with specific concentration was shaken in an orbital shaker for half an hour at $40^{o}C$. Specific amount triblock polymer (P123) was dissolve in the HCl and shaken at the same temperature, $40^{o}C$ for another two hours and then added with Tetraethyl orthosilicate (TEOS). Here, gel started to develop so the solutions then stirred for 24hours under slow shaking about 50 rpm at $40^{o}C$. The solid formed then filtered and wash with distilled water. Lastly, the sample then calcined in furnace at $500^{o}C$ for six hours.

3.3.2 Wet impregnation

The metal oxide promoted cobalt catalyst on zirconia support with different position were prepared by wet-impregnation using cobalt (II) nitrate hexahydrate $[(Co(NO_3)_2).6H_2O]$, Calcium nitrate $[Ca(NO_3)_2.4H_2O]$ or Zinc acetate $[(CH_3COO)_2Zn.2H_2O]$. The aqueous precursors were droplet above until flooding on support prepared by flam spray pyrolysis. After wet impregnation the catalyst precursors were stirred under 70°C for 6 h and subsequently the samples were dried at 110°C overnight. All catalysts were calcined from room temperature to 500°C by temperature rate 10°C /min and kept at 500°C for 4 h under air flow. The catalysts which succeed from first calcinations were introduced to the second impregnation. The second aqueous precursor was used to wet impregnation again and followed by the second calcination in the same condition (Phattiya ., 2011).

3.4 Characterization of support and catalysts

3.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is to be used to identify the type of functional group existed because FTIR provide valuable in-situ information about different intermediates present on the catalyst surface during the FT synthesis reaction. The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum.

Figure 3.2: Overview of FTIR Unit

3.4.2 SEM

The SEM experiments were conducted in a VG Escalab MkII instrument using a non-monochromatic Al Ka source (1486.6 eV). All spectra were acquired at 20 eV pass energy, giving an overall resolution of approximately 1 eV. Binding energies were referenced to the Al2p peak at 74.5 eV. The samples were prepared by pressing powder into a 12mm sample holder. An integrated high pressure pretreatment cell allowed the catalyst samples to be pretreated and subsequently moved to the analysis chamber without exposure to air. After SEM analysis of the sample in the unreduced state, the catalyst was reduced in flowing H2 at 623K for 16 h. After reduction, the cell was evacuated and the sample was analyzed in the reduced state. The catalyst was then moved back to the pretreatment cell and exposed to a feed mixture containing different amounts H2, H2O (as steam) and inert gas (Ar). After treatment, the catalyst was again analyzed by SEM. The catalyst was moved back to the pretreatment cell and reduced in flowing H2 (623 K, 16 h) and analyzed by SEM once more. In addition to the catalyst samples, also bulk Co3O4 and CoAl2O4 were analyzed (without any pretreatment). It has been shown that the intensity ratio of the supported phase and the support SEM-peaks is related to the dispersion of the supported phase .SEM spectra of reduced catalysts were used to estimate the particle size of the metallic cobalt phase according to the method of Kerkhof and Moulijn.

Figure 3.3: SEM

3.4.3 TGA

The gravimetric measurements were performed in a high-pressure microbalance (Sartorious 4436). The catalyst was placed in a stainless steel perforated basket suspended from one arm of the microbalance and placed in a tubular, stainless steel reactor. The catalysts were dried in heat 673 K, reduced at standard conditions (623 K, 16 h) and exposed to different ratios of H2O/H2 at 523K for 16–17 h at 10 bar total pressure. All weight changes during drying, reduction and exposure to H2O/H2 could be monitored continuously.

Figure 3.4: TGA

CHAPTER 4

RESULTS & DISCUSSIONS

4.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) has been used to study on the surface morphology of structure Co/SBA-15 catalysts with different cobalt loading (Zn, Mn and Zr). The SEM images of mesoporous Co/SBA-15 catalyst for each promoter are shown in Figure 4.1 (a), (b) and (c).

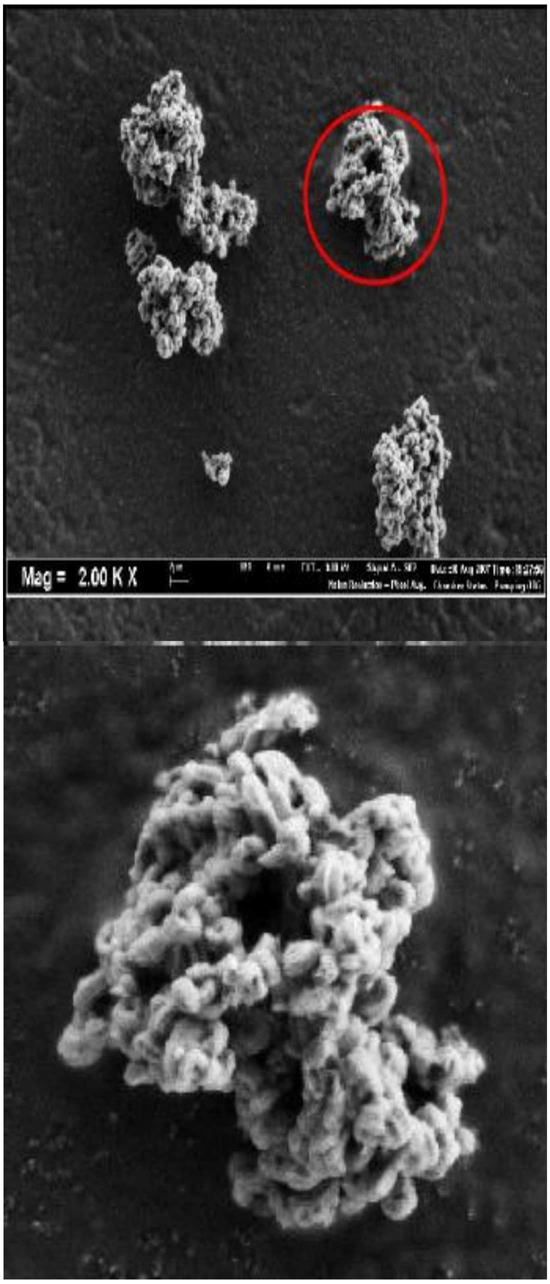


Figure 4.1(a) SEM microphotograph of SBA-15

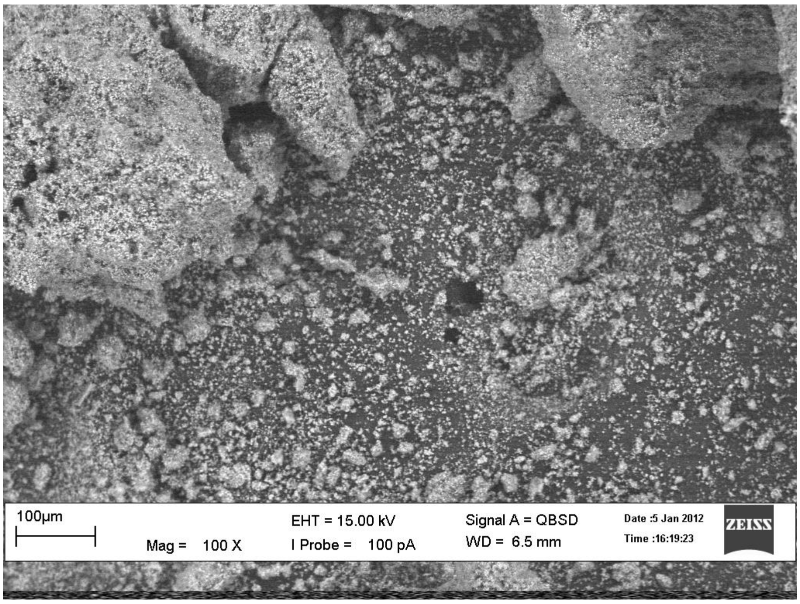


Figure 4.1(b) SEM microphotograph of Co (5wt%)-Mn (20wt %) /SBA-15

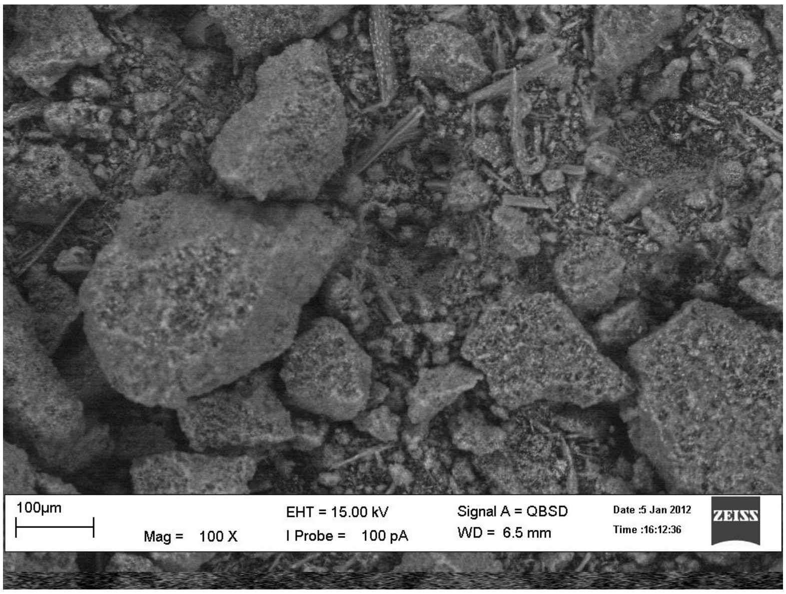


Figure 4.1(c) SEM microphotograph of Co (5wt%)-Zn (20wt %) /SBA-15

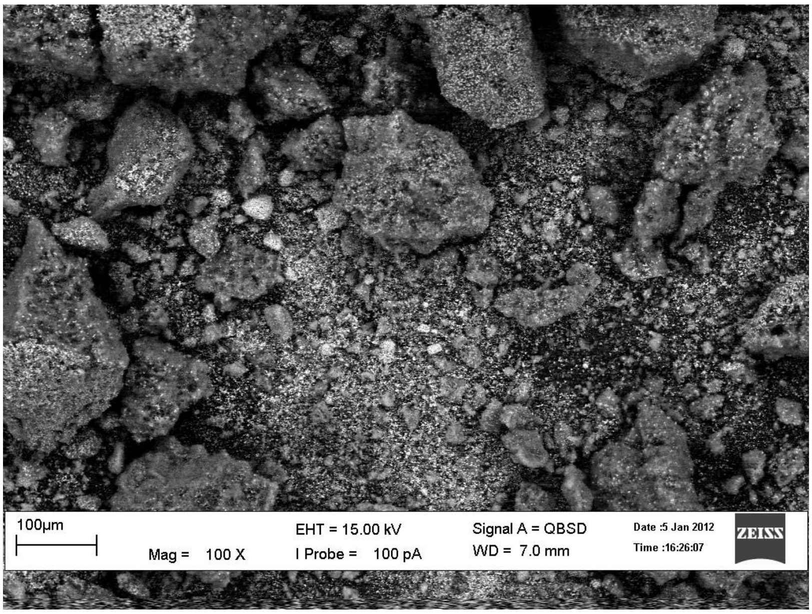


Figure 4.1(d) SEM microphotograph of Co (5wt%)-Zr (20wt %) /SBA-15

Respectively, in Figure 4.1(a) the SBA-15 reveal that it consists of many rope-like domains with relatively uniform sizes of 2 µm, which are aggregated into wheat-like macrostructures mean that rod-like primary particles aggregated to form micron-sized fibers. This finding same with Anunziata and team (2007) mentioned. The form of Co/SBA-15 also exhibits irregular spherical shape and are clearly visible in agglomeration and homogeneous formed. Recently, Mirjiet and team (2006) mentioned the same observation that reveal the spherical shape with agglomeration and homogenous .The form shown clearly visible.

After modification of SBA-15 by Co with different loading, the particles found to be attached closely with each other. The SEM picture in Figure shows a large number of SBA-15 particles attaching closely with one another. These phenomena observed both in microscopic and macroscopic scale could be due to spine (alkyl chain) like Co and promoter growth on SBA-15 (Mirji et al, 2006). Figure 4.1(b), 4.1(c) and 4.1(d) show macroscopic scale due to spine like Co and Zn, Zr and Mn growth on SBA-15. These spines of one SBA-15 particle may be caught on the spine of another SBA-15. This way the bonding of large number of SBA-15 particles may take place. On the other hand, it could be due to van der Walls and electrostatic interaction of alkyl chains between the Co and Zn, Zr and Mn of adjacent SBA-15 particles (Mirji et al., 2006). Nevertheless, the good morphology is obtained (Anunziataet et al ., 2007).

4.2 Fourier Transform Infrared (FTIR)

Figure 4.2(a), 4.2(b) and 4.2(c) show the selected FTIR spectra. All support and catalyst samples were analyze using FTIR spectra to investigate the existence of functional group were formed in the samples and provide surface information of materials for identification of chemical groups. The Figure 4.2(a) show curves of Co (5wt%)-Zn (20wt %) /SBA-15, Figure 4.2(b) Co (5wt%)-Zr(20wt %) /SBA-15, and Figure 4.2(c) Co (5wt%)-Zn(20wt %) /SBA-15 . There are many functional groups observed with certain wavelength in the samples such as cobalt oxides, Si-O-Si, Si-CH_3, zinc oxide, OH band, Si-C, and etc.

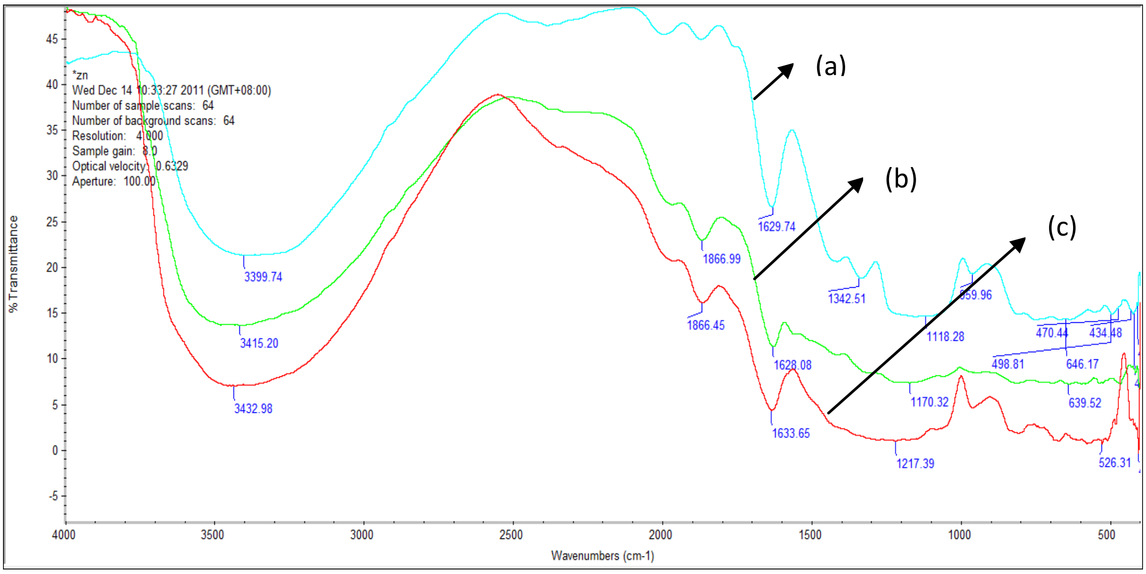


Figure 4.2: FT-IR spectra of (a) Co (5wt%)-Mn (20wt %) /SBA-15 (b) Co (5wt%)-Zr (20wt %) /SBA-15(c) Co (5wt%)-Zn (20wt %) /SBA-15

In this research, when comparing the curve on the graph the significant changes were analyses at any peak showed. Firstly, for Figure 4.2(a), the curve showed that it consist of OH bond stretching's Si-O-Si, Si-CH$_3$ and Si-OH. The O – H bond stretching bands of the silanol groups are observed at 3200-3600cm·Secondly, for Figure 4.2(b) the curve show that it consist OH bond stretching's Si-O-Si, Si-CH$_3$ and Si-OH. There are many functional group at range 400-1000 cm^{-1} which contain Si-C group. Silanol groups on the silica surface exist in several forms such as isolated, hydrogen-bonded, and germinal types of silanol groups. Lastly for the Figure 4.2(c) the results show that the it contain OH bond stretching's Si-O-Si, Si-CH$_3$ and Si-OH functional groups. surface silanol group of unmodified SBA-15 is mainly of the hydrogen-bonded type in IR absorption bands, which absorb at 3200-3600 cm^{-1}(Akcaet al,2008). The siloxane or Si-Ostretching bands, peak appears as a broad and strong peak in the range 1000-1200 cm^{-1}(centered at 1100 c^{-1}). The Si-O stretching band is clearly visible at band 1100cm^{-1}(Akcaet al., 2008).

Furthermore, formation of hydroxyl group also formed when SBA-15 are present in the sample. The hydroxyl groups were assigned around 1640 cm^{-1}(Kababji.et al, 2009). The sample on spectrum (a), (b) and (c) contains hydroxyl groups (SiOH) that mean the spectrum shows higher intensity of the bands when comparing to the other spectrum. The present of SiOH groups in spectrum (a), (b) and (c) probably favours the formation of higher amount of tetrahedrally coordinated Co^{2+} ions, interacting with the silica support. When the silica support is impregnated by an ionic solution, the adsorption of ions is strongly affected by the surface charge of the support (Agnes et al, 2009). The existence of silanol group (SiOH) on the silica surfaces also plays an important role in the formation of cobalt species (Kababji et al ,2009). As the modified of surface silanol groups of SBA-15 by present of cobalt loading, the density of the surface silanol groups decreases. Therefore, the O – H bond stretching bands of silanol groups decrease (Agnes et al, 2009).

Furthermore, FTIR spectrum also shows zinc nitrate Zn (NO3)2.6H2O, the components of zinc nitrate are attended at OH stretching vibration area. The region of OH stretching vibrations contains three major absorption bands, at 3536, 3483, and3184 cm-1, in accordance with the presence of different OH environments as evidencefrom the structural data (Eriksson et al, 1989). The broad band centred at 3184 cm-1 may be assigned to OH vibrations of water molecules whereas the bands at 3536 and3483 cm-1 may be assigned to OH vibrations of the layer hydroxyls.

4.3 Thermal Gravimetry Analyzer (TGA)

Perkin Elmer Thermogravimetric differential thermal analyzer was used to measure weight changes of the C1 sample when heated under a flow of argon (flow rate of 40 mL/min) at a constant heating rate of 10 °C/min(Tavasoli.2009).

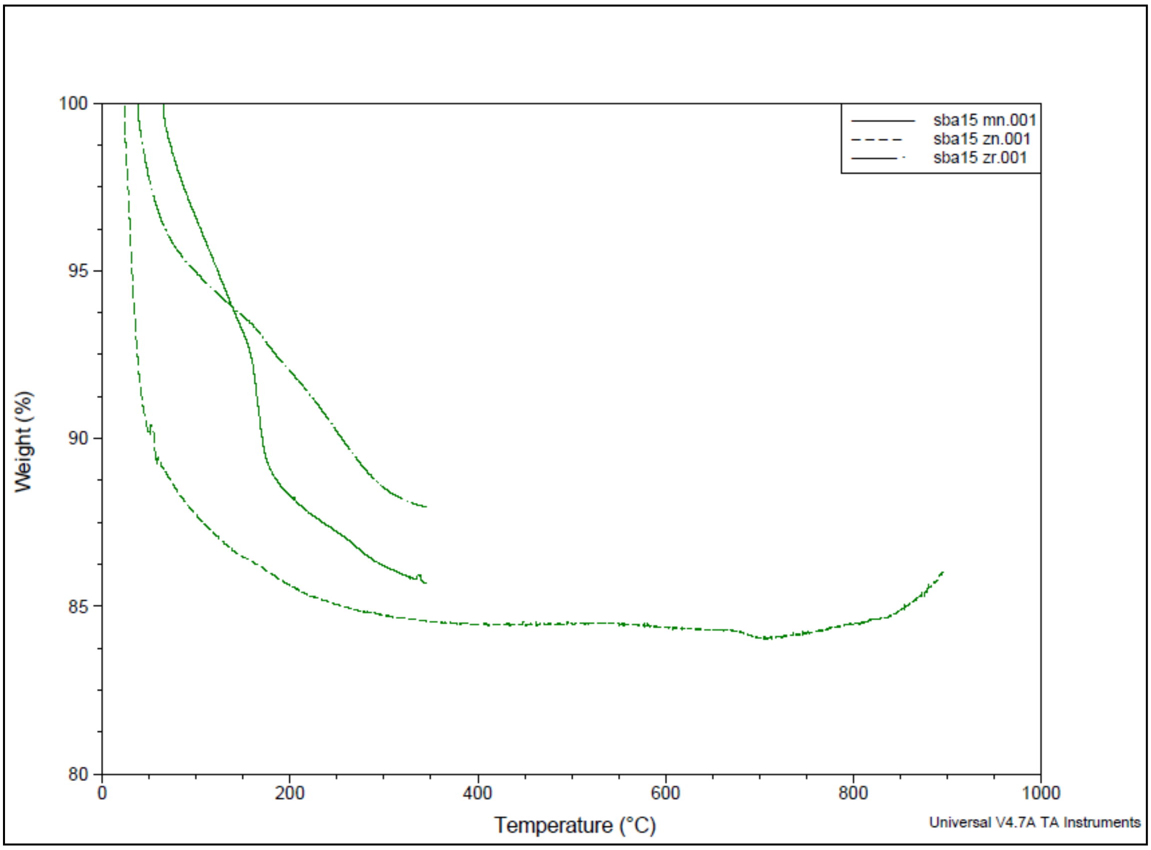


Figure 4.3: TGA

The Thermogravimetric analysis curve of the catalyst sample prior to calcinations is shown in Figure 4.3. The SBA-15 functional group is the one of the high thermal stability of the Cobalt supporter. The weight loss of Co/Zn-SBA-15 occurred at below 100 °C which it was attributed to the evaporation of water, and to the combustion of catalyst sample between 50°C to 375°C. From these results, it is showed that the weight loss was happened in 16%. After temperature at 375°C, no combustion occurred and the weight of catalyst sample becomes stable until 800°C. But, unpredicted TGA curve happened which the weight increasing around 1% at 800-900 °C. However, we conclude that the catalyst sample of Co/Zn-SBA-15 was one criteria of catalyst's high thermal stability (Gonza'lez., 2009).

For the sample Co (5wt%)-Mn (20wt %) /SBA-15 and Co (5wt%)-Zr (20wt %) /SBA-15 was performed at the temperature range between 25–350°C.This is because of technical error. However, this graph also can be analyzed. The weight loss below 350 °C which it was attributed to the evaporation of water.Both them also has high thermal stability.

CHAPTER 5

CONCLUSION & RECOMMANDATIONS

5.1 Conclusion

In the first part of this thesis, the synthesis of SBA-15 as support for FT process had been achieved according to the procedure reported. Besides, Co and promoters (Zn, Zr and Mn) incorporated SBA-15 mesoporous materials were synthesized by incipient wetness impregnation method by using cobalt nitrate as cobalt source and zinc nitrate as zinc source. The results for FTIR were identification of Si-O-Zn and Si-O-Co functional group because of the present of zinc or cobalt onto silica SBA-15 support at band 1200cm^{-1}. Besides that, the identification of metal inside SBA-15 was determined by comparing the pure SBA-15 with the incorporated metal on SBA-15. Last but not least when the preparation of 20 wt % of cobalt loading showed a more OH group were presented. For SEM analysis the rope like domain aggregated to wheat like microstructure were observed in the morphology of modified catalyst and SBA-15.TheSEM results showed that incorporation of Co and promoters did not change the morphology of the support. For this research, the characterization of the catalyst by selecting promoter have quiet similar characterization with noble metal that already investigate.

5.2 Recommendations

As a recommendation for future improvement related to our research, research should be perform by using various data analysis to get better and persist result. By using many characterize equipment such as thermo gravimetric analysis (TGA), X-ray diffraction analysis (XRD), N_2 Adsorption analysis, transmission electron microscopy analysis (TEM), we can know deeply about the character show of our samples. By using all the characterize equipment above, many information about thermal stability, cobalt dispersion on SBA-15 based on pore volume, BET surface area, cobalt surface density and give information about crystal structure of a sample. Furthermore, improvement of our research also can be better when we further by performing catalytic activity of FT reaction by using the catalyst. From the reaction condition, we will know the catalyst activity and the stability of catalyst is possible or impossible to use for FT industry. Besides, by perform regeneration of catalyst also can give improvement for our research.

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