EFFECT OF DIFFERENT MESOSTRUCTURED MATERIAL BASED ON SILICA (TiO_2, SBA-15 AND CAB-O-SIL) AS COBALT SUPPORTS FOR FISCHER-TROPSCH SYNTHESIS

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EFFECT OF DIFFERENT MESOSTRUCTURED MATERIALS BASED ON SILICA (TiO_2, SBA-15 AND CAB-O-SIL) AS COBALT SUPPORTS FOR FISCHER-TROPSCH SYNTHESIS

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ABSTRACT

The research was about the synthesis of active and selective for syngas processing via Fischer–Tropsch synthesis (FTS) producing clean and best fuel. A series of 20 wt. % cobalt catalysts be prepared by impregnation of a mesoporous molecular sieve based on silica as 75 wt. % of cobalt catalytic supporters (SBA-15, TiO_2 and Cab-O-Sil) with 5 wt. % Zn promoter for comparison purposes. All materials used characterizing by several analysis equipments which are SEM, TGA and FTIR. The characterization results achieve gave a great influence of mesoporous support porosity on the structure, reducibility of cobalt oxide species supported over the selected materials. Firstly, the experiment was started from the synthesis of SBA-15. TiO_2 and Cab-O-Sil are commercialized support. Then, the silica as cobalt supporters were synthesized by incipient wetness impregnation method of using mixture of Cobalt (II) Nitrate and Zinc Nitrate Hexahydrate solution. Next, the prepared catalysts were calcined at 350°C for 6 h by increasing the temperature at a controlled heating rate of 2°C/min. The characterization of catalysts and catalyst studies was performed. The result from experiment was SBA-15 supporter shown the better result compared to other samples as the microscopic size captured by SEM equipment prove that SBA-15 had smoothest and smallest of mesoporous surface size. The result from FTIR showed that the peak at around 3,440 cm^{-1} have the hydroxyl groups and about 1,630 cm^{-1} is due to the bending vibrations of O-H bonds that the percentage reflectance of O-H bonds which indicates the SBA-15 can effectively restrain the loss of surface hydroxyl groups during calcinations. The peak around 1000-1200 cm^{-1} can be assigned to the siloxane or Si-O-Si stretching bands; peak appears as a broad and strong peaking the sample. Lastly, TGA result showed that SBA-15 can help the catalyst samples restrained more water content in the evaporation process and had high thermal stability that can prolong life at high temperature and high pressure in the Fischer-Tropsch synthesis. The new silica as cobalt supporter will be developed to enhance the performance of the best and clean fuel production. This research hopefully can be carried out successful in order to get the new invention for production of catalyst that will produce the best and clean fuel and to get rid of exceed cost of production but in the same quality of expensive product.

ABSTRAK

Penyelidikan itu kira-kira sintesis aktif dan selektif untuk syngas pemprosesan melalui sintesis Fischer-Tropsch (FTS) menghasilkan bahan api bersih dan terbaik. Satu siri 20% berat. Pemangkin kobalt disediakan oleh penghamilan liang meso molekul berdasarkan silika sebagai 75% berat. Daripada penyokong sebagai pemangkin kobalt (SBA-15, TiO_2 dan Cab-O-Sil) dengan 5% berat. Penganjur Zn untuk tujuan perbandingan. Semua bahan yang digunakan mencirikan oleh beberapa peralatan analisis seperti SEM, TGA dan FTIR. Keputusan pencirian mencapai memberikan pengaruh yang besar sokongan keliangan pada struktur liang meso, pengurangan spesis oksida kobalt yang disokong ke atas bahan-bahan yang dipilih. Pertama, eksperimen bermula dari sintesis SBA-15 tetapi TiO_2 dan Cab-O-Sil adalah penyokong yang telah dikomersialkan. Kemudian, silika sebagai penyokong kobalt telah disintesis oleh keadah pembasahan menggunakan Kobalt (II) nitrat dan Zink nitrat Hexahydrat. Seterusnya, sample yang terhasil dioksidakan pada suhu 350°C selama 6 jam dengan kadar peningkatan sebanyak 2°C/min. Pencirian dan kajian pemangkin dilakukan. Keputusan dari eksperimen adalah SBA-15 penyokong menunjukkan hasil yang lebih baik berbanding dengan sampel lain seperti saiz mikroskopik yang ditangkap oleh peralatan SEM membuktikan bahawa SBA-15 permukaan liang meso paling rata dan saiz liang meso paling kecil. Dari keputusan FTIR menunjukkan bahawa puncak dalam lingkungan 3,440 cm-1 menpunyai kumpulan hidrosil dan pada 1,630 cm-1 disebabkan bengkokan getaran ikatan O-H yang menunjukan peratusan kereflekan ikatan O-H dalam SBA-15 menolong kehilangan permukaan kumpulan hidrosil ketika pengoksidaan. Puncak pada 1000-1200 cm-1 menentukan kumpulan siloxane or ikatan kembangan Si-O-Si; puncak yang tinggi kelihatan. Akhir sekali, hasil TGA menunjukkan bahawa SBA-15 boleh membantu sampel pemangkin menahan lebih kandungan air dalam proses penyejatan dan kestabilan haba yang tinggi yang boleh memanjangkan jangka hayat pada suhu tinggi dan tekanan tinggi dalam sintesis Fischer-Tropsch. Silika baru sebagai penyokong kobalt akan dimajukan untuk meningkatkan prestasi pengeluaran bahan api yang terbaik dan bersih. Kajian ini diharapkan dapat dijalankan berjaya untuk menghasilkan ciptaan baru bagi pengeluaran pemangkin yang akan menghasilkan bahan api yang terbaik dan bersih dan mengurangkan lebihan kos pengeluaran tetapi dalam kualiti yang sama produk mahal.

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CHAPTER ONE

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 applies 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 is 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 $CH_4 + H_2O \leftrightarrow CO + 3H_2$
ii. CO_2 reforming $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$
iii. Partial oxidation $CH_4 + ½ O_2 \leftrightarrow CO + 2H_2$
iv. Water gas shift reaction $CO + H_2O \leftrightarrow CO_2 + H_2$

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 to 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. Because many disadvantage of others supporters, that’s why this research just come out with this chosen, SBA-15 supporter as the best cobalt supporter in this research.

SBA-15 have been chosen because of low price cost and it’s have advantages of high thermal & thermal stability. Limitations for other supporters like TiO_2 and Cab-O-Sil are lower stability and it just have short prolong life than SBA-15 in the FTS.

Additional to that, Zn and 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 (2009).

1.3 Research Objectives

1. To synthesis ZnCo catalyst with different supports such as TiO_2, SBA-15 and Commercialize Cab-O-Sil.
2. To identify the characteristic of ZnCo catalyst with different supports.

1.4 Scope of Research

This research is to investigate the effect of the mesostructured materials based on silica (TiO_2, SBA-15andCab-O-Sil) as cobalt supports for preparing ZnCo 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 N_2 adsorption-desorption.

The silica as cobalt catalyst supporter will run with additional of Zn 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 Zn 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.

CHAPTER TWO

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.

Figure below showed the flow process of Fischer-Tropsch synthesis. 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.

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 highest activity. 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).

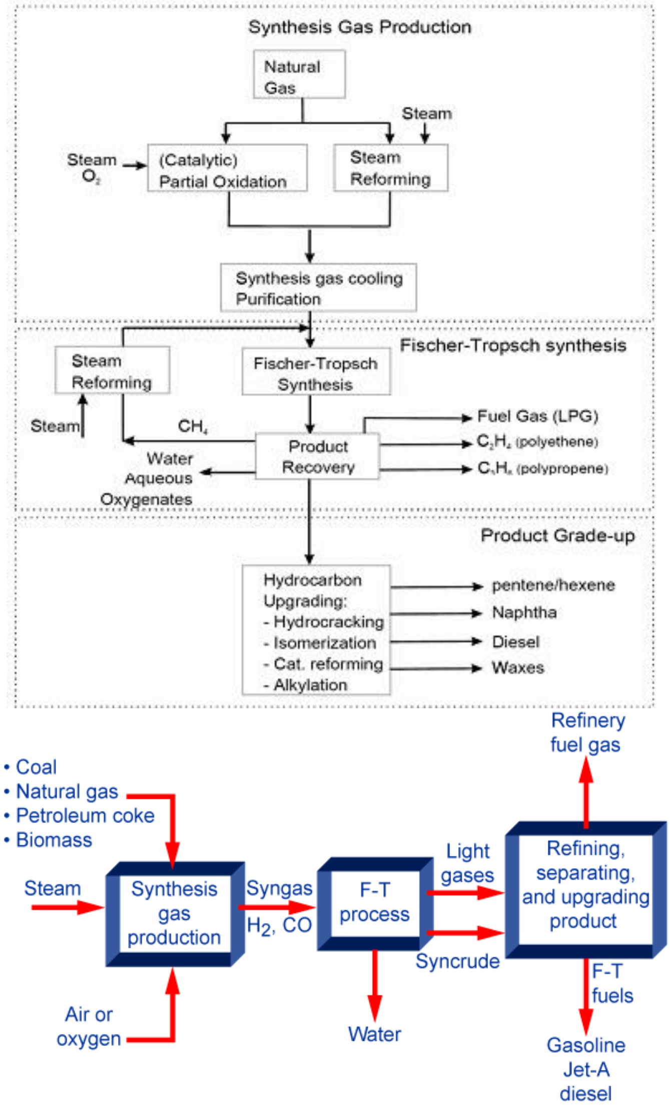


Figure 2.1 showed the Fischer-Tropsch synthesis.

2.2 SBA-15 supporter

This is a most common type mesoporous of pure silica which is a form of silica and a recent development in nanotechnology.

The SBA-15 was many used in the recent research especially about 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 O. González et al (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 FTS 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.

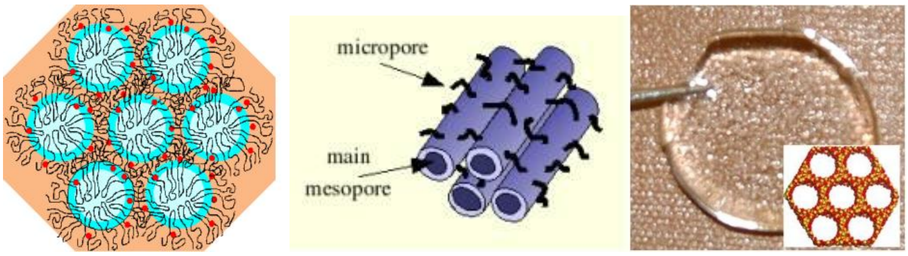


Figure 2.2 showed the structure of SBA-15.

2.3 Effects of others supporter on Co based catalysts

2.3.1 TiO_2 supporter

This is also known as titanium (IV) oxide or titania that naturally occurring oxide of titanium.

Besides of SBA-15 supporter, this research also uses for this supporter. From Antonelli et al (1999) by his thesis of Microporous Mesoporous Mater stated that the successful synthesis of stable mesoporous TiO_2 involves the application of tetra decyl phosphate surfactant as a template and removing it by calcinations.

The preparation of mesoporous TiO_2 uses dodecyl amine as the directing agent. While this solved the problem of residual phosphorous, the porous structure remained unstable after calcinations. Conclusion from his thesis was the silica of TiO_2 is the one of most stable mesoporous silica in the FTS.

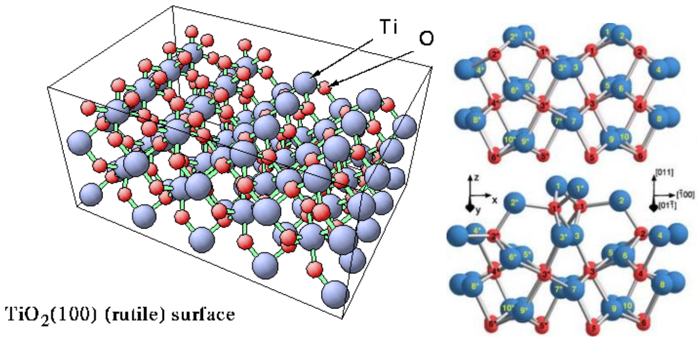


Figure 2.3 showed the structure of TiO_2.

2.3.2 Cab-o-Sil supporter

This is also known as fumed silica which consists of microscopic droplets of amorphous silica fused into branched, chainlike, three-dimensional secondary particles which then agglomerate into tertiary particles.

Cab-o-sil is still new supporter operating with Fischer-Tropsch synthesis. However, there already a lot of recent research that produce various type of cab-o-sil which it was commercial for domestic and industry uses. Amama et al (2005) stated that catalysts synthesized from Cab-O-Sil were more stable and maintained their high mesoporous structural integrity after the reaction better than those synthesized from HiSil.

Amama et al also stated that the N_2 adsorption-desorption isotherm of the former still showed a distinct capillary condensation step at p/po of 3.5 while the latter showed an inconspicuous step. As the result of these thesis statements, Cab-O-Sil was more stable than HiSil and gives more effect to catalyst reactivity in the Fischer-Tropsch synthesis.

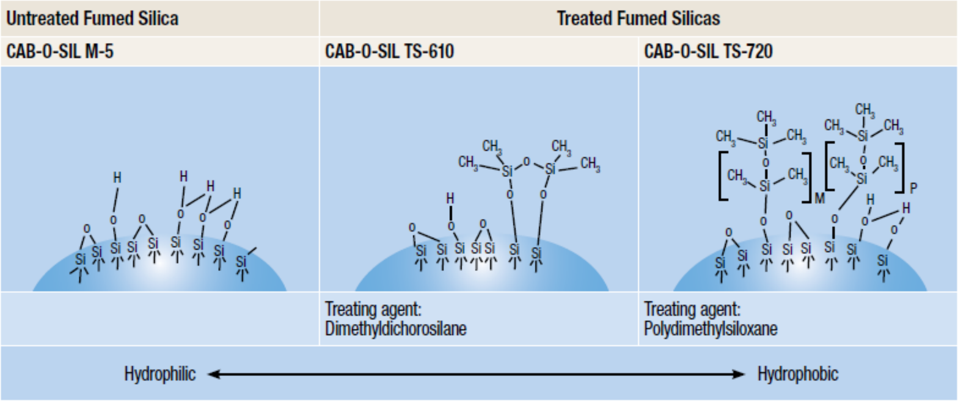


Figure 2.4 showed the structure of Cab-O-Sil.

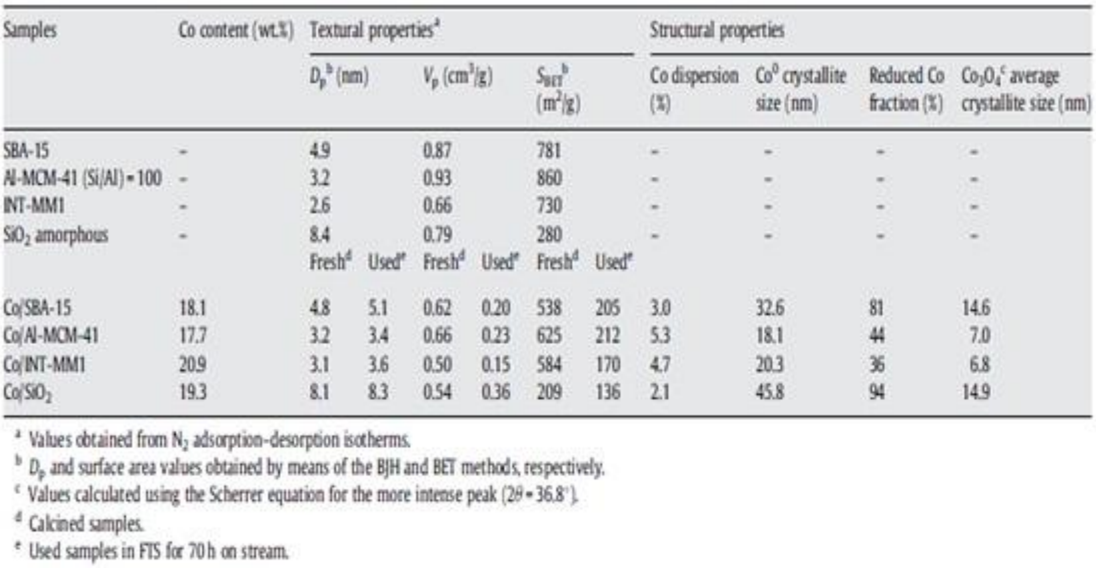
2.4 Characterization of catalyst

2.4.1 BET

a) SBA-15

The chemical analysis results are presented in Table 2.1. Nominal and real cobalt contents were too similar. Cobalt introduction on supports based on silica leads to a sharp decrease in S_{BET} in all cases. The S_{BET} in all periodic mesoporous silicas (Al-MCM-41, SBA-15, and INT-MM1) was higher than 730 m_2/g, whereas the S_{BET} of the commercial amorphous silica was much lower (280 m_2/g).

Table 2.1: Chemical and physical properties of supports based on silica and Co-supported catalysts calcined at 350°C, (O. Gonza´ lez a, 2009).



Samples	Co content (wt.%)	Textural properties[a]						Structural properties			
		D_p[b] (nm)		V_p (cm^3/g)		S_{BET}[b] (m^2/g)		Co dispersion (%)	Co^0 crystallite size (nm)	Reduced Co fraction (%)	Co_3O_4[c] average crystallite size (nm)
SBA-15	-	4.9		0.87		781		-	-	-	-
Al-MCM-41 (Si/Al) = 100	-	3.2		0.93		860		-	-	-	-
INT-MM1	-	2.6		0.66		730		-	-	-	-
SiO_2 amorphous	-	8.4		0.79		280		-	-	-	-
		Fresh[d]	Used[e]	Fresh[d]	Used[e]	Fresh[d]	Used[e]				
Co/SBA-15	18.1	4.8	5.1	0.62	0.20	538	205	3.0	32.6	81	14.6
Co/Al-MCM-41	17.7	3.2	3.4	0.66	0.23	625	212	5.3	18.1	44	7.0
Co/INT-MM1	20.9	3.1	3.6	0.50	0.15	584	170	4.7	20.3	36	6.8
Co/SiO_2	19.3	8.1	8.3	0.54	0.36	209	136	2.1	45.8	94	14.9

[a] Values obtained from N_2 adsorption-desorption isotherms.
[b] D_p and surface area values obtained by means of the BJH and BET methods, respectively.
[c] Values calculated using the Scherrer equation for the more intense peak ($2\theta = 36.8°$).
[d] Calcined samples.
[e] Used samples in FTS for 70 h on stream.

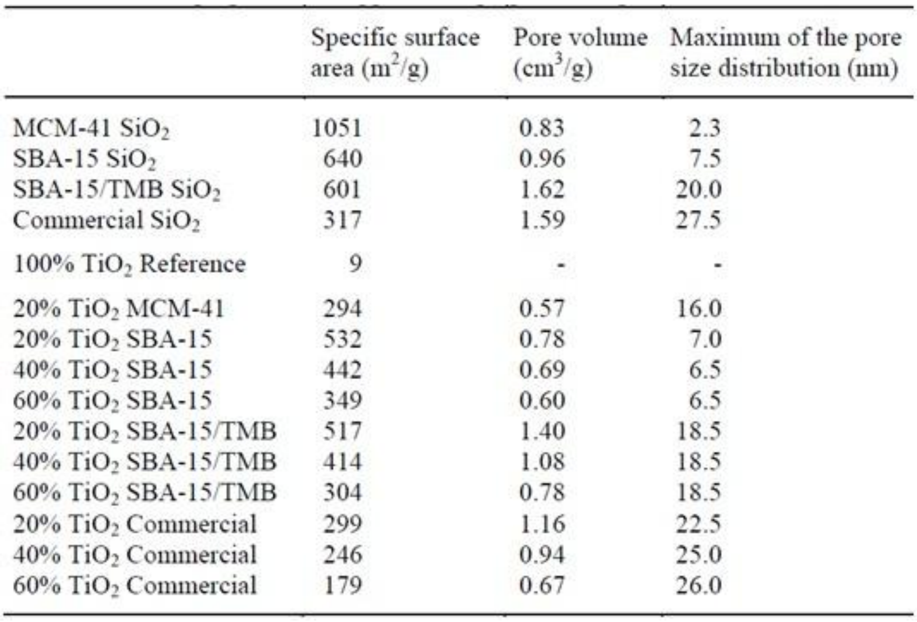
Compared to the pure mesoporous silicas, a reduction of S_{BET} and V_p is noted for all catalysts after incorporation of ~20 wt. % Co. The decrease may be attributed to the dilution effect of the support caused by the presence of the supported cobalt oxide phase or to a partial blockage of the support pores especially micropores and mesopores occurred after Co incorporation. Textural properties comparison between the fresh and used catalysts has been performed in order to evaluate their hydrothermal stability.

Other observations suggested that the ordered structures of these mesoporous materials under reaction conditions continue collapsing in varying degree depending on their hydrothermal stability and depending on the pore wall thickness of mesoporous material. Thus, according to the differences between Dp, S_{BET} and Vp noticed for fresh and used catalysts might be established a hydrothermal stability order for all mesoporous materials as follows: Co/SBA-15 > Co/Al-MCM-41 > Co/INT-MM1.These observed variations in Dp, S_{BET} and Vp attributed to the accumulation of the waxes deposited in the catalyst pores.

b) TiO_2

From Table 2.2 below 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 TiO_2 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.

Table 2.2: Textural properties of supports and prepares samples, (Rosenthal et al, 2008).



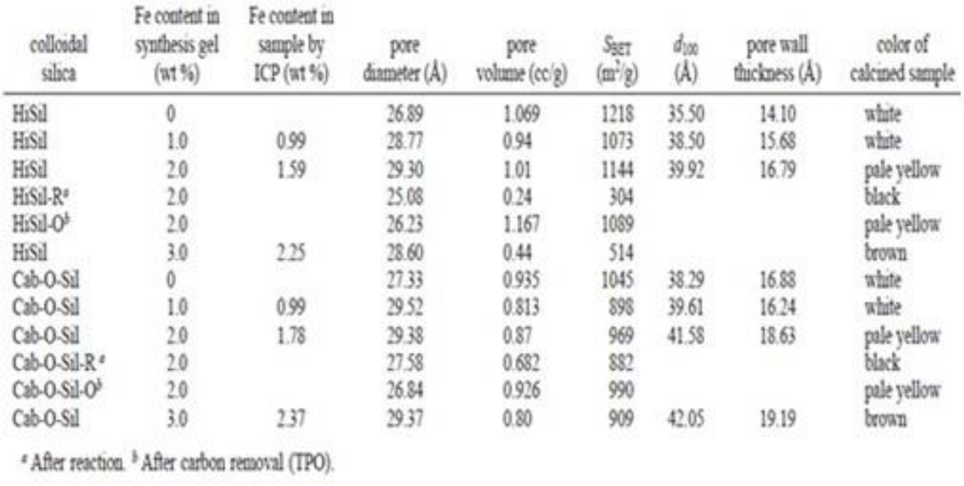
	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Maximum of the pore size distribution (nm)
MCM-41 SiO_2	1051	0.83	2.3
SBA-15 SiO_2	640	0.96	7.5
SBA-15/TMB SiO_2	601	1.62	20.0
Commercial SiO_2	317	1.59	27.5
100% TiO_2 Reference	9	-	-
20% TiO_2 MCM-41	294	0.57	16.0
20% TiO_2 SBA-15	532	0.78	7.0
40% 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

The average pore size of 7.5 nm of the hexagonal mesoporous silica structure SBA-15 was modified by the addition of trimethyl benzene 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.

c) Cab-o-sil

From Table 2.3 below, the physical properties of the catalysts used in this study presented in figure above. The results of data above as shown in figure above revealed that Cab-o-Sil had larger pore diameter and pore wall thickness but had smaller S_{BET} and pore volume compared to HiSil. So that the reactivity of silica supporter will limited by these criteria in order to get into the maximum level. However, Cab-o-sil had just small different of all the textures properties and just got difference in range of 0.08-2.50 in pore diameter, 0.36-0.442 in volume, 175-578 in S_{BET} and 0.56-1.83 in pore wall thickness .

Table 2.3: Textural Properties of the Various Catalysts Synthesized from Hisil and Cab-O-sil, (Amama et al, 2005).



colloidal silica	Fe content in synthesis gel (wt %)	Fe content in sample by ICP (wt %)	pore diameter (Å)	pore volume (cc/g)	S_{BET} (m^2/g)	d_{100} (Å)	pore wall thickness (Å)	color of calcined sample
HiSil	0		26.89	1.069	1218	35.50	14.10	white
HiSil	1.0	0.99	28.77	0.94	1073	38.50	15.68	white
HiSil	2.0	1.59	29.30	1.01	1144	39.92	16.79	pale yellow
HiSil-R[a]	2.0		25.08	0.24	304			black
HiSil-O[b]	2.0		26.23	1.167	1089			pale yellow
HiSil	3.0	2.25	28.60	0.44	514			brown
Cab-O-Sil	0		27.33	0.935	1045	38.29	16.88	white
Cab-O-Sil	1.0	0.99	29.52	0.813	898	39.61	16.24	white
Cab-O-Sil	2.0	1.78	29.38	0.87	969	41.58	18.63	pale yellow
Cab-O-Sil-R[a]	2.0		27.58	0.682	882			black
Cab-O-Sil-O[b]	2.0		26.84	0.926	990			pale yellow
Cab-O-Sil	3.0	2.37	29.37	0.80	909	42.05	19.19	brown

[a] After reaction. [b] After carbon removal (TPO).

2.4.2 N_2 adsorption–desorption isotherms

a) SBA-15

From Figure 2.5, the shapes of these isotherms are typical for mesostructured materials and occur on porous adsorbents possessing pores in the diameter range from 2 to50 nm. The isotherms for the SBA-15 presented a sharp inflection in the range of relative pressure from 0.7 to 0.8 indicative of good-quality SBA-15 material with uniform mesopores. This reveals a wide pore size distribution that corresponds to a macroporous material.

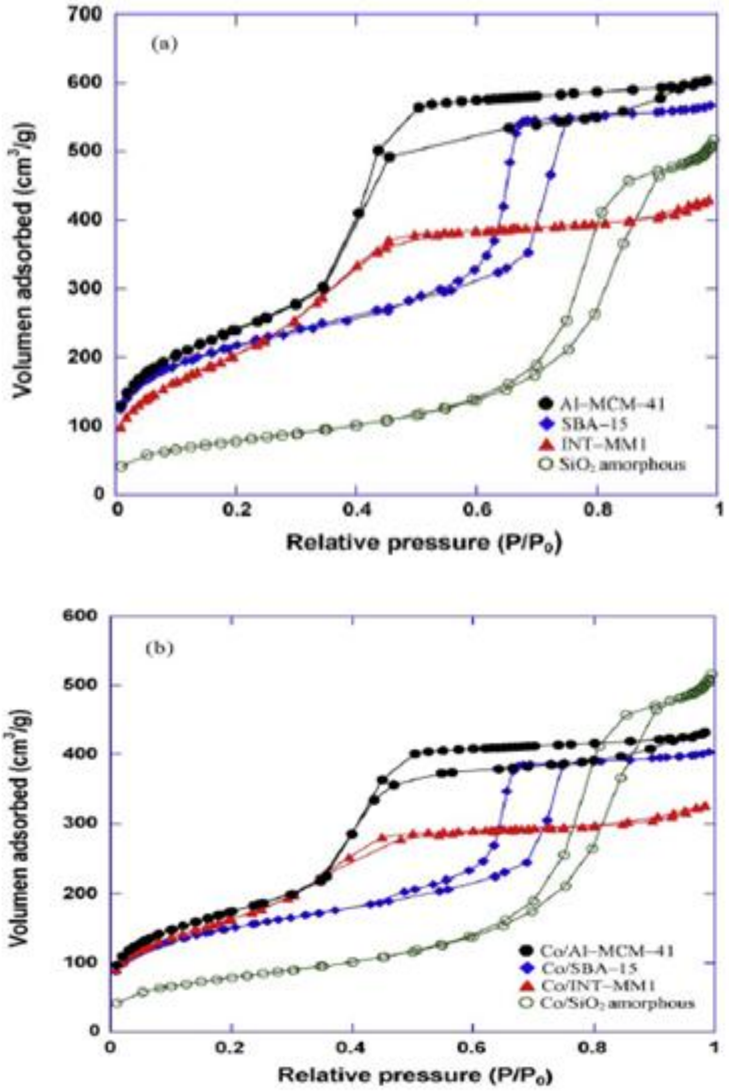


Figure 2.5: Nitrogen adsorption–desorption isotherms obtained at 196°C, (a) Supports based on silica and (b) Co catalysts supported on silica supports, (O. Gonza´ lez a, 2009).

For the Al-MCM-41, the sharp increase observed in adsorbed volume at 0.3–0.4 relative pressure. The previous results obtained from the density function theory (DFT) method for the INT-MM1gave a Dp of 2.5 nm and a bimodal pore distribution, with approximately 55% mesoporosity and 45% microporosity contributing to the total surface area of this material. The bimodal pore supports such as SBA-15 and INT-MM1 contain large and small pores simultaneously. The small pores could yield the sites for anchoring smaller cobalt oxide particles, while the large pores could provide a network for fast diffusion of reacting molecules and products.

The shapes of the N_2 adsorption isotherms of Co supported samples are similar to their corresponding siliceous supports which it's suggesting that the mesoporous structure was mostly retained upon Co impregnation in all cases. This observation is in agreement with previous reports in the recent researches.

b) TiO_2

From Figure 2.6, 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 TiO_2 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.

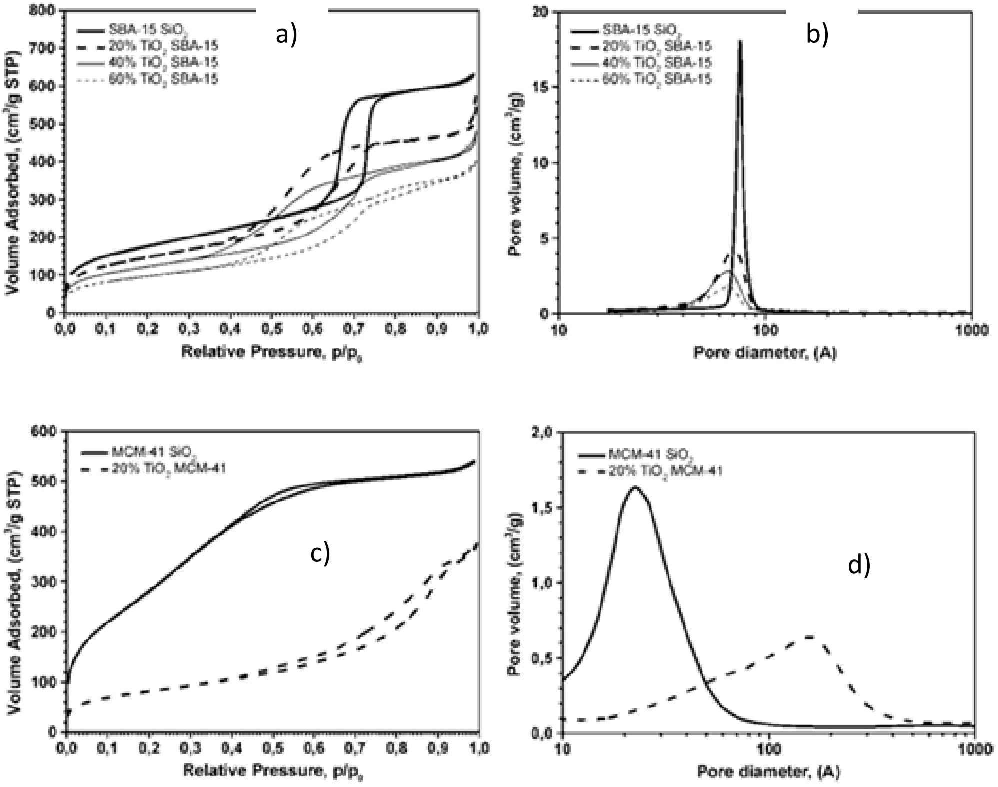


Figure 2.6: (i) Nitrogen adsorption isotherms of: a) 0 – 60 % TiO_2& SBA-15 and b) 0 – 20% TiO_2& MCM-41 samples. (ii) Pore size distributions of: c) 0 – 60 % TiO_2& SBA-15 and d) 0 – 20% TiO_2& MCM-41 samples, (Zhang et al, 2005).

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%TiO_2&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 2.6 d) indicates the breakdown of the structured pore arrangement.

c) Cab-o-sil

From Figure 2.7, the isotherm corresponding to $p/po < 0.3$ represents the monolayer adsorption of N_2 on the walls of the mesopore, while that with $p/po > 0.4$ represents the multilayer adsorption on the outer surface of the particles. The point at which the inflection begins is related to the capillary condensation within the uniform mesopores and their diameter. There was a slight shift in the inflection step toward higher p/po upon the introduction of Fe.

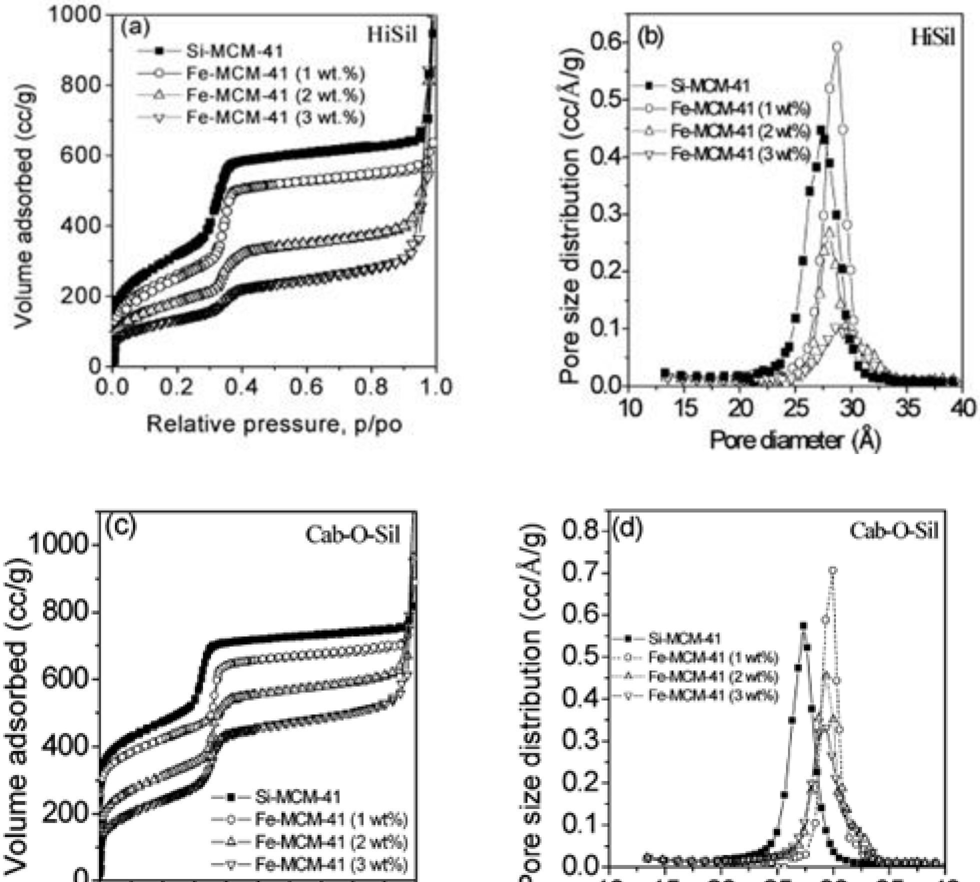


Figure 2.7: N_2 adsorption-desorption isotherms of Si-MCM-41 and Fe-MCM-41 (1, 2, and 3 wt %) and their respective pore size distributions synthesized from HiSil (a) and (b) and Cab-O-Sil (c) and (d), (Amama et al, 2005).

This signifies an increase in pore size, in consonance with XRD results. There was no noticeable shift in the inflection step ofFe-MCM-41 upon incorporation of more Fe^{3+}cations. The value of the slope increased upon the initial introduction of Fe (1 wt %) into the silica framework because of the knitting effect in consonance with previous observation. Further increase in the amount of Fe (>1 wt %) resulted in a decrease in the value of slope, which could be attributed to the oversaturation of Fe^{3+} in the pore walls of MCM-41. The effect of Fe loading on the full width at half-maximum (fwhm) of the pore size distribution (PSD) curve is shown in figure above. There is a general decrease in the fwhm of the PSD curve upon the incorporation of 1 wt% of Fe. However, as the Fe amount in MCM-41 is increased beyond 1 wt %, the fwhm increases suggesting a decrease in the structural order. The behaviors of the fwhm of the PSD curves and of the slopes of the capillary condensation steps upon incorporation of different concentrations of Fe into MCM-41were in consonance.

Therefore, its conclude as follows: (i) there is a significant structural improvement upon the incorporation of 1 wt % of Fe into MCM-41, but a decrease in the structural integrity is observed upon incorporation of higher Fe concentrations, (ii) siliceous MCM-41 and Fe-MCM-41 synthesized from Cab-O-Sil have higher structural order in comparison to those synthesized from HiSil, as evidenced by their higher values for capillary condensation slopes and lower fwhm of the PSD curves. It can just be assumed that the type and the amount of impurities present in these colloidal silica and their synthesis routes may rationalize this observation.

2.4.3 XRD

a) SBA-15

From Figure 2.8, the XRD patterns for all cobalt catalysts supported on mesoporous silicas are presented in figure above. These show five sharp signals characteristic of Co_3O_4 spinel (PDFWIN 42-1467) and one broad signal with low intensity located at 2ϴ = 238 typical of siliceous materials. The latter signal is attributed to diffuse dispersion caused by the lack of long-range order of Si atoms located on the walls of the channels in the materials based on silica. The XRD peaks become narrower and more intense for the Co/SiO_2 and Co/SBA-15 catalysts, indicating the presence of larger and easier to reduce Co_3O_4 crystallite size in these materials in comparison with the Co/Al-MCM-41 and Co/INT-MM1 solids.

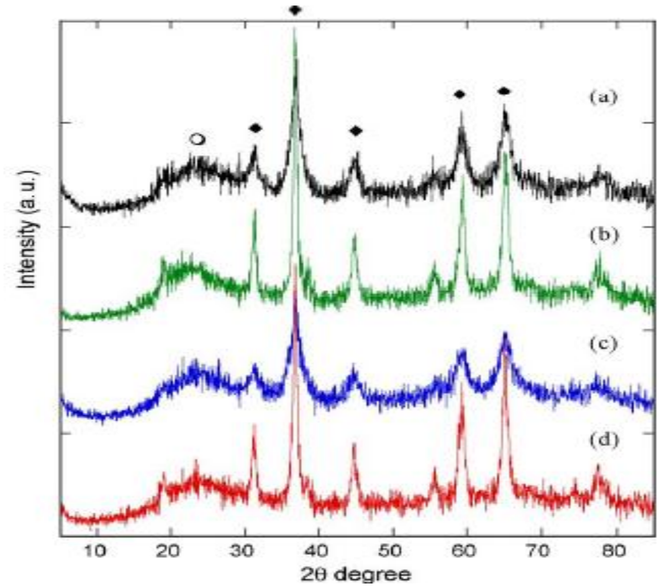


Figure 2.8: XRD patterns of cobalt-supported catalysts, (a) Co/Al-MCM-41, (b) Co/SiO_2 amorphous, (c) Co/INT-MM1, and (d)Co/SBA-15. Identified phases: (○) amorphous SiO2 and (◆) Co_3O_4 spinel, (O. Gonza´ lez a, 2009).

This observation can be correlated with the Co_3O_4 average crystallite size data and supported the results of reduced Co fraction presented in previous Table 2.1, where is clearly showed that the Co/SiO_2 and Co/SBA-15 samples exhibit the largest Co_3O_4 average crystallite size (~15 nm) and the higher reduced Co fraction (>80%). In this sense, strong metal-support interactions and consequently higher Co dispersion percentages are expected to be found in the Co/Al-MCM-41 and Co/INT-MM1 catalysts. On the one hand, Table 2.1 shows that the sizes of the supported Co_3O_4 crystallites depend on silica porous structure, specifically from Dp since larger Co_3O_4 crystallite sizes are found in the catalysts prepared from the support with wider pores (SBA-15 and commercial SiO_2) and vice versa (Al-MCM-41 and INT-MM1). On the other hand, Table 2.1 also shows in all cases that the Co_3O_4 crystallite size values estimated for the catalysts exceed the Dp values calculated for their corresponding supports.

Therefore, these results suggest that a portion of larger Co_3O_4 particles could be located on the external surface of the support while another portion (the smallest ones) could be encapsulated inside the mesoporous channels. This statement is consistent with previous works. Additionally, those small Co_3O_4 particles in narrow pores are expected to be more difficult to reduce than those larger ones deposited in wider pores, suggesting in a certain sense that differences in Co_3O_4 crystallite sizes lead to differences in Co reducibility. This argument is in line with the reduced Co fraction results shown in Table 2.1 and with the results previously reported by other authors.

It must be noted that in Table 2.1 were shown notable differences between the Co_3O_4 average crystallite size values obtained for all the catalysts and their corresponding Co0 crystallite size values. In all cases the second ones values are larger than the first ones. These lacks of compatibility could be explained by sintering effects of reduced metal species or by considering the limitations and approximations of the characterizations techniques used for this type of analysis.

b) TiO_2

From Figure 2.9, 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 particles[13]. On this basis, the reference 100% TiO_2 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 stabilized them as anatase against phase transition following identical thermal treatment.

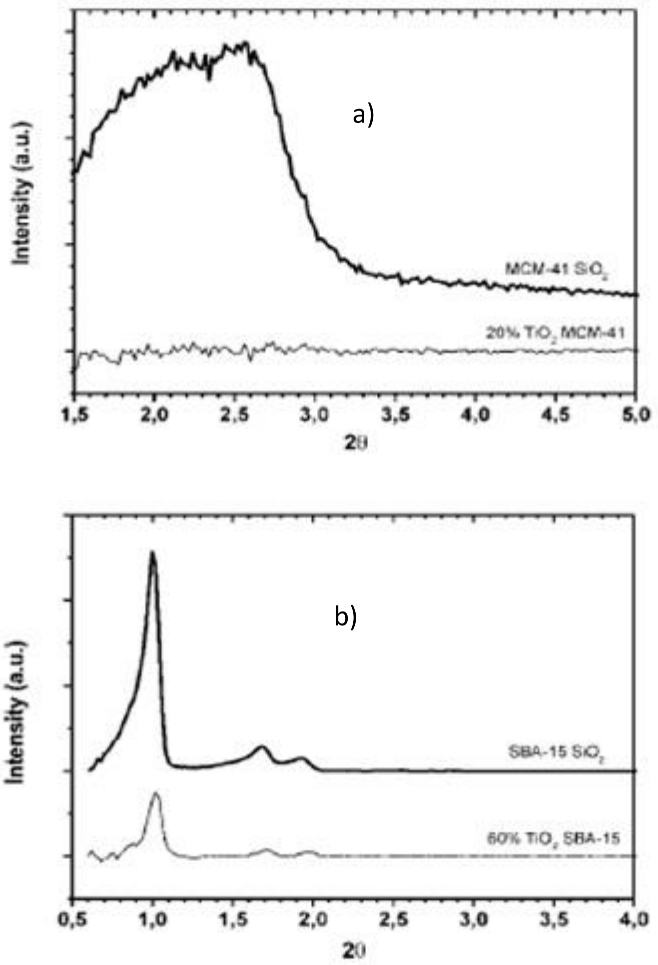


Figure 2.9:XRD patterns at low angle of: a) MCM-41 and 20% TiO_2& MCM-41 samples and b) SBA-15 and 60% TiO2 & SBA-15 samples, (O. Gonza´ lez a, 2009).

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 2ϴ~25.3º associated with anatase (101) diffraction. No rutile phase was detected in any case according to the absence of the (110) rutile reflection at 2ϴ~27.4º. 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.

c) Cab-o-Sil

From Figure 2.10, the results of XRD above use to characterize the two dimensional-hexagonal structures of the catalysts. While XRD characterizes only the ordered portion of the material, N_2 physisorption gives a volume average measure of order and thus gives a complementary picture of the overall structure of the material. The N_2 adsorption-desorption isotherm and PSD of siliceous MCM-41 and Fe-MCM-41 (1, 2, and 3wt %) synthesized from HiSil are presented in figure above, while those synthesized from Cab-O-Sil are shown in figure above c and d. All samples (except Fe-MCM-41, 3 wt %) exhibited relatively high surface areas and pore volumes. The mesopore diameter observed for all samples containing Fe was about 29 Å and was unaffected by the introduction of more Fe^{3+}cations.

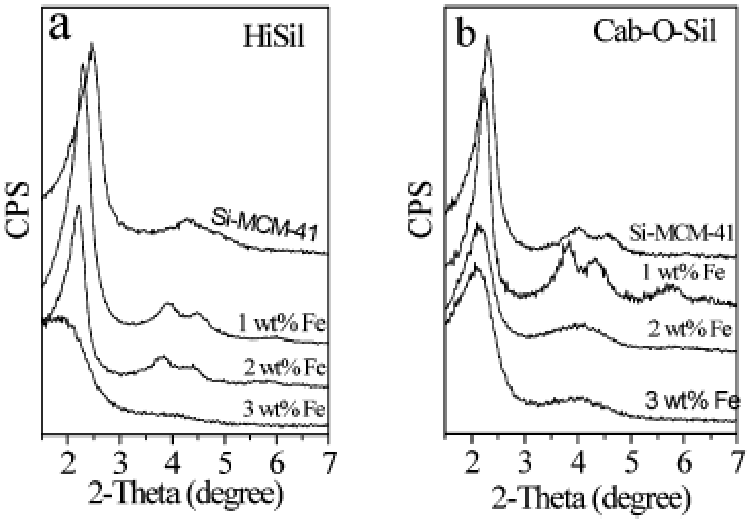


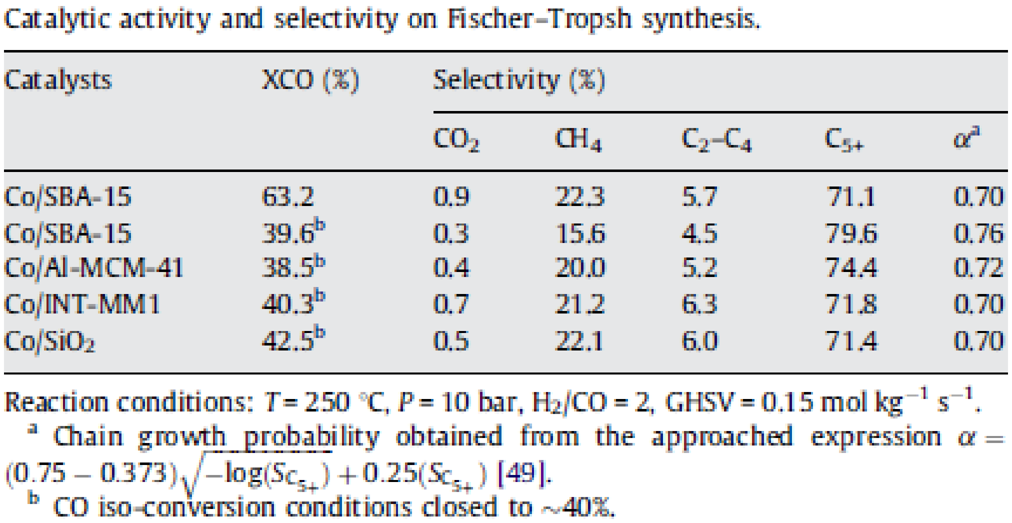
Figure 2.10: XRD patterns of calcined siliceous MCM-41 and Fe-MCM-41 containing different Fe loadings synthesized using HiSil (a) and Cab-O-Sil (b), (Zhang et al, 2005).

Siliceous MCM-41 showed pore diameters (27 Å) somewhat lower than those of Fe-MCM-41. The pore volume does not seem to be affected significantly by the incorporation of Fe. Generally, the pore wall thickness of MCM-41 increases with the Fe loading and this may be due to the longer Fe-O bond length in comparison to that of Si-O. Samples synthesized from HiSil showed greater increase in wall thickness upon the incorporation of higher Fe loadings.

2.5 Catalytic study

a) SBA-15

From Table 2.4, the results of activity in terms of syngas conversion (XCO%) and selectivity in terms of hydrocarbon product distribution (C_{5+}) and chain growth probability (a) are shown in Table 2.4. As observed, when ~0.4 g of each catalyst were used under the same FTS reaction conditions, the Co/SBA-15 catalyst displayed the highest CO conversion (~63%) than the rest of catalysts tested, showing very similar selectivity results (α~ 0.70 and selectivity to C_{5+}between 71 and 74%). It is well known that FTS selectivity could be affected by conversion. For this reason, the selectivity should be compared at similar conversion levels to evaluate any changes arising from differences in catalysts properties.



Catalytic activity and selectivity on Fischer–Tropsh synthesis.

Catalysts	XCO (%)	Selectivity (%)				
		CO_2	CH_4	C_2–C_4	C_{5+}	α[a]
Co/SBA-15	63.2	0.9	22.3	5.7	71.1	0.70
Co/SBA-15	39.6[b]	0.3	15.6	4.5	79.6	0.76
Co/Al-MCM-41	38.5[b]	0.4	20.0	5.2	74.4	0.72
Co/INT-MM1	40.3[b]	0.7	21.2	6.3	71.8	0.70
Co/SiO_2	42.5[b]	0.5	22.1	6.0	71.4	0.70

Reaction conditions: $T = 250$ °C, $P = 10$ bar, $H_2/CO = 2$, GHSV = 0.15 mol kg^{-1} s^{-1}.

[a] Chain growth probability obtained from the approached expression $\alpha = (0.75 - 0.373)\sqrt{-\log(S_{C_{5+}}) + 0.25(S_{C_{5+}})}$ [49].

[b] CO iso-conversion conditions closed to ~40%.

Table 2.4: The catalytic activity and selectivity of SBA-15 supporter on Fischer-Tropsch synthesis,(O. Gonza´ lez a, 2009).

In this sense, under CO iso-conversion conditions (40%) the Co/SBA-15 mesoporous catalyst exhibited the highest selectivity to C_{5+} (80%) and lowest selectivity to CH_4, with a higher a value than the rest of the tested solids in FTS reaction (α = 0.76). The high activity and selectivity obtained for the Co/SBA-15 catalyst can be explained by the interplay between the reducibility obtained for this catalyst and its dispersion degree, which could be controlled by the pore size of the Co/SBA-15 support.

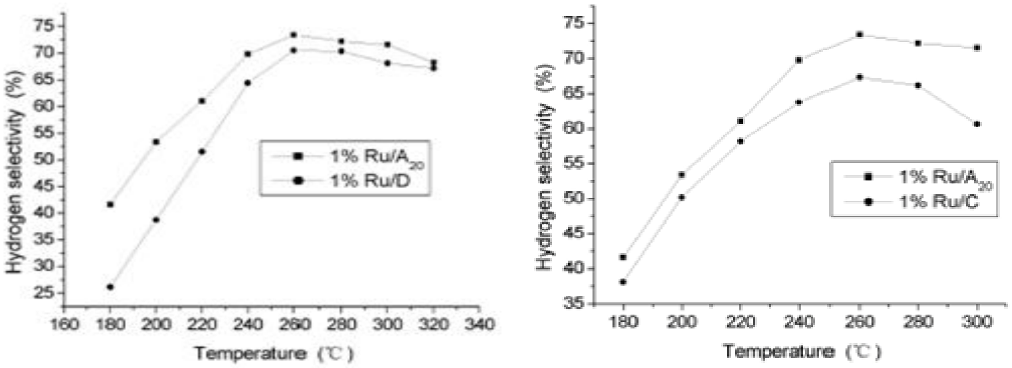
According to the textural properties results, the Co/SBA-15 material presented the highest Dp (~5 nm) of the mesostructured material series was evaluated. The shape and dimensions of these pores could yield sites appropriated for the anchoring or encapsulating of surface-Co oxide species with sizes smaller than 5 nm. Such species could be easily reduced (81%of reducibility according results shown in Table 2.1) increasing the number of active sites available for the reaction, which can be reflected on a better catalytic performance.

b) TiO_2

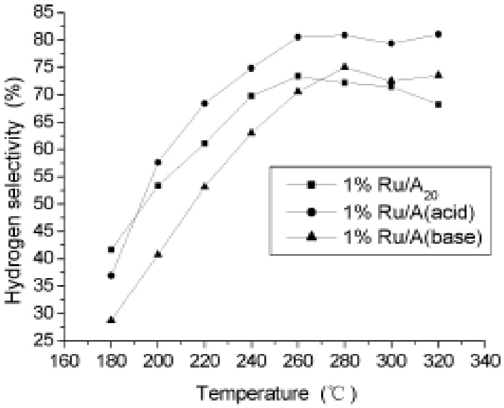
From Figure 2.11, the catalytic activity results of Ru/m-TiO_2 synthesized by easy-operating method for methanol decomposition are given in figure above. The activity curves of all catalysts have the similar variation rule, that is, below 260 °C, the activity increases with the increase of reaction temperature, whereas the activity reduces slowly above 260 °C, which might be due to the formation of a fraction of TiOx after being reduced using H_2. Then at high temperature, ruthenium particles are mantled partly or space blockage is formed around ruthenium particles because TiOx 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 m_2/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 2.11 b, the effect of solvents on the activity is contrary to the order of surface areas of samples. After being calcined at 400 °C for 2hour, the BET surface areas of 1% Ru/A_{20} and 1% Ru/C catalysts are 174.3 and 225.9 m_2/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 TiOx 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, (O. Gonza´ lez a, 2009).



a: Supports prepared by different templates b: Supports prepared in different solvents



c: Supports prepared at different pH

Figure 2.11: The relationship between the reaction temperature and the catalytic activity, **(**Duvenhage et al, 2010).

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 hour are similar (173.0, 174.3 and 170.0 m_2/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 nano particles 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.

c) Cab-o-Sil

From Figure and 2.12 and 2.13, an attempt was made to find correlations between the catalyst activity or stability and other properties of the catalysts. A plot of catalyst activity at the beginning and at the end of the reaction vs. the corresponding surface area of the catalysts is shown in Figure 2.13. As zero catalyst surface area would mean dehydrogenation through non-catalytic process only, all correlation lines pass through this value, 1%. It is revealed that their initial activities are directly proportional to their total surface areas. It should be noted also that even for similarly prepared catalysts, differences in activities cannot be directly related to their pore structure. Indeed, CrOx/SiO2xrpossesses fairly small pores but greatly surpasses in activity CrOx/SiO2xr/Cab–O–Sil sample which exhibits a significant portion of large pores, (O. Gonza´ lez a, 2009).

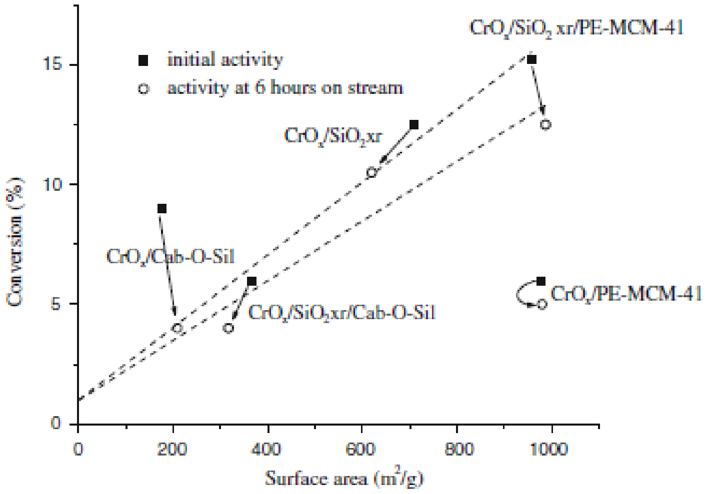


Figure 2.12: The conversion of propane at the beginning and the end (6 h on stream) of the reaction vs. surface areas of the catalysts, **(**Zhang et al, 2005).

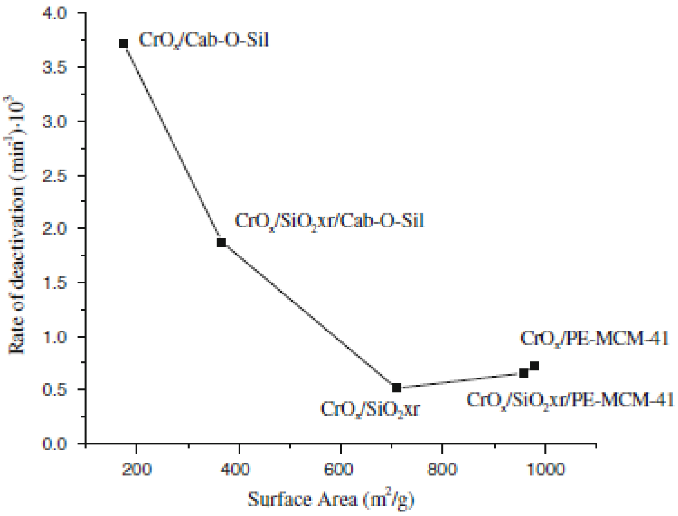


Figure 2.13: The deactivation rate vs. surface areas of the catalysts, **(**Zhang et al, 2005).

The turn over frequencies of catalysts prepared by a simple impregnation method were independent of chromium loading, implying the occurrence of similar structure of the active sites in all catalysts. The turnover frequencies were found to vary strongly among similarly prepared catalysts. One of the possible explanations to this phenomenon may lie in the variation of a structure of active sites. Deactivation of the catalysts due to coke formation is a major problem in the production of olefins via non-oxidative dehydrogenation route. The obtained deactivation rates, k, were plotted vs. surface areas in Figure 2.12 and 2.13. At the same chromium loading, the experimental data seem to indicate that catalysts with large surface areas are less prone for deactivation.

So that, the catalytic activity was found to be proportional to the catalyst surface area, whereas among all the samples tested, an increase in the surface generally entailed higher catalyst stability.

CHAPTER THREE

RESEARCH METHODOLOGY

3.1 Introduction

In this chapter, the procedure is to synthesis of SBA-15, TiO_2 and Cab-o-sil as cobalt supporter and then, makes preparation of ZnCo/SBA-15, ZnCo/TiO_2 and ZnCo/Cab-O-Sil. 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.

3.2.1 Material List

Table 3.1 showed the material lists were used in this research.

Chemical Name	Purity	Supplier Name
Tetra ethyl orthosilicate	98%	Johnson Matthey
Zinc Nitrate Hexahydrate	98%	Sigma-Aldrich
Cobalt (II) Nitrate	99%	Sigma-Aldrich
Pluronic triblock copolymer (P123)	N/A	Sigma-Aldrich
Titanium (IV) Oxide	99.5%	Sigma-Aldrich
Hydrochloric acid	37%	Sigma-Aldrich
Cab-O-Sil M5	N/A	Sigma-Aldrich

3.3 Apparatus List

Table 3.2 showed the apparatus lists were borrowed and used in this research.

Equipment Name	Brand Name
Vacumm Pump	Rocker
Glass Furnace	Naberthem
Stackable Incubator Shaker	Infors AG
Hot Plate and Magnetic Stirrer	Erla
Glass Oven	Memmert
Analytical Balance	Shimadzu

3.4 Research Flow

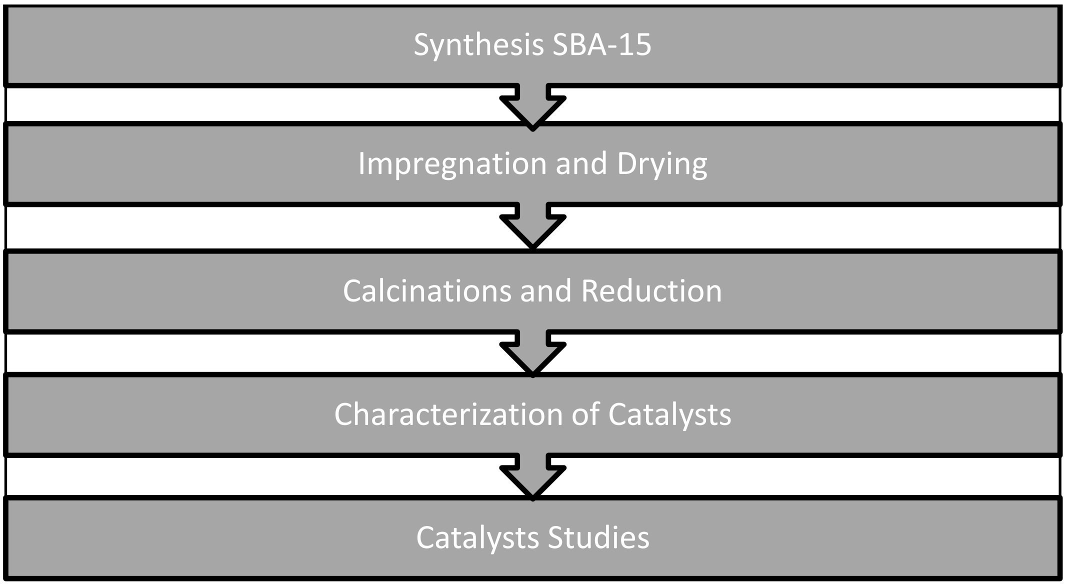


Figure 3.1 showed the research flow that was did; follow step by step in this research.

3.5 Methodology

3.5.1 Synthesis of SBA-15

SBA-15materials was start synthesized by a 150 ml HCL solution with 2M concentration was shaken in an orbital shaker at 40°C for half an hour. Then, a 4 ml Pluronic triblock copolymer (P123, Aldrich) was dissolved in the HCL solution. Later, the mixture was shaken at 40°C for an hour. 9 ml tetraethyl orthosilicate was added into the above solution and the mixture was stirred for two hours at around 40ºC. As the gel started to develop, the mixture was heated at 40ºC under slow shaking at 50 rpm for 24 hours. Furthermore, the solid forms were filtered and wash for several times with distilled water. Finally, the sample was calcined at 500ºC for 6 hour in the furnace, (Zhensong Lou, 2008).

3.5.2 Catalyst Preparation

a) Wet Impregnation and Drying

All catalysts with a Co loading ~20 wt. % were prepared by incipient wetness impregnation using a solution of Co(NO3)2.6H2O (Aldrich, 98% purity) dissolved in the distillate waters with respect to the pore volume of each silica material used as support (liquid/solid ratio ~5 cm3/g), followed by with the catalysts were dried in a rotary evaporator at 35°C until dryness, (O. Gonza´ lez a, 2009).

b) Calcinations and Reduction

The catalysts were further dried overnight in an oven at 120°C (H.Xiong,et al,2008). 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, (O. Gonza´ lez a, 2009).

3.5.3 Characterization techniques

a) FTIR

The supports surface acidity (Tc = 773 K) was analyzed by pyridine thermo desorption 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 in calcined impregnated precursors (Tc = 673 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, (O. Gonza´ lez a, 2009).

b) SEM

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), (O. Gonza´ lez a, 2009).

c) TGA

Thermogravimetric measurements of 5 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 from temperature room $25^{o}C$ until $900^{o}C$. Heating rates varied from 10 to 20 $^{o}C/min$ as the weight percentage changes depending on the temperature response of the catalyst samples,(O. Gonza´ lez a, 2009)

CHAPTER FOUR

RESULTS AND DISCUSSION

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 new silica as cobalt supporter in the Fischer-Tropsch synthesis. Besides that, this research also wants to investigate about the quality product from Fischer-Tropsch synthesis.

4.2 Scanning Electron Microscopy (SEM)

In the Figure 4.1 below showed the low and high magnification Scanning Electron Microscopy (SEM) images of the as-synthesized Co/Zn-SBA-15 catalyst sample, indicating wood-like surface that composed in microscopic size in Figure 4.1 (a). The small pieces of wood-like structure had diameter around 10µm in Figure 4.1 (a) that smoother and smaller in size compared to other silica supporters in the Figure 4.2 and 4.3. In the Figure 4.1 (b) showed the SEM image shows that the curved morphology of the Co/Zn-SBA-15 materials, many rope-like aspect of as long as several hundred micrometers, (Zhensong Lou et al, 2008).This microstructure was slightly perished and approximately 10 µm in width and 5-10 µm in thickness at Figure 4.1 (b) smaller than other silica supporters in the Figure 4.2 (a) and 4.3 (a).

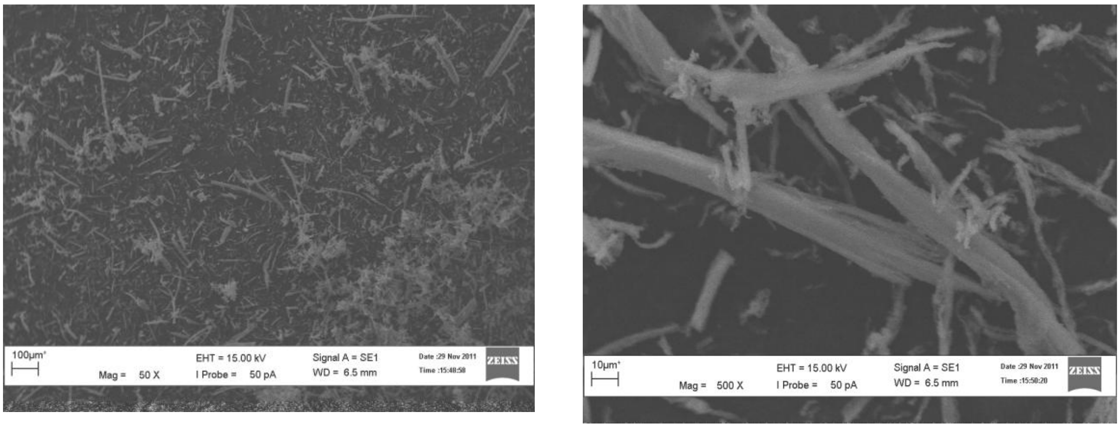

(a) Magnification at 50x (b) Magnification at 500x

Figure 4.1: SEM images of the Co/Zn-SBA-15 catalyst of samples.

In the Figure 4.2 showed the SEM image of Co/Zn-TiO_2 catalyst sample that indicating the big and several pieces of small pieces of stones-like shape that scales in microscope size. Figure 4.2 (a) showed that the diameter of samples structure was about 10-200 µm and 100-200 µm in width that bigger than SBA-15 microscopic size in Figure 4.1 (a). The shape of samples structure was slightly unsmooth circle or oval shape and bigger size than Co/Zn-SBA-15, maybe because it’s insoluble substance in the catalyst sample in Figure 4.2 (b), (Pavasupree et al, 2010). The structure surfaces were too compact that it’s hard for SEM to zoom into the porous holes.

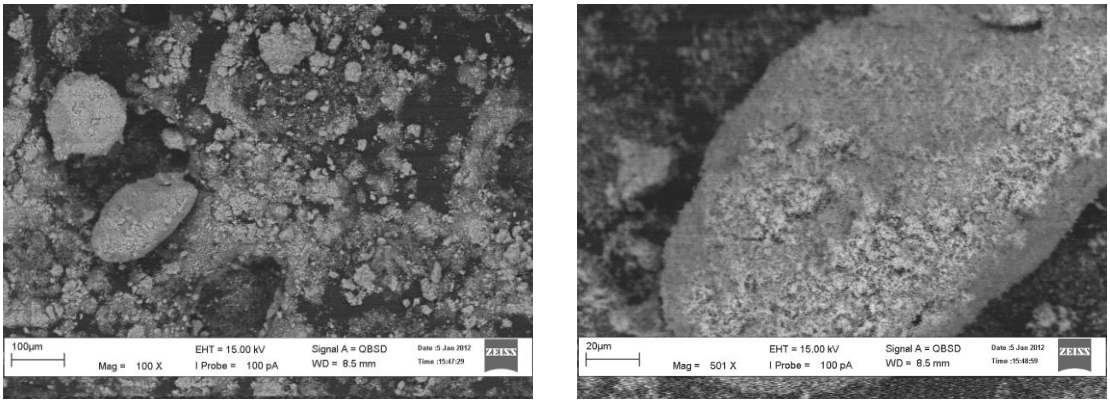
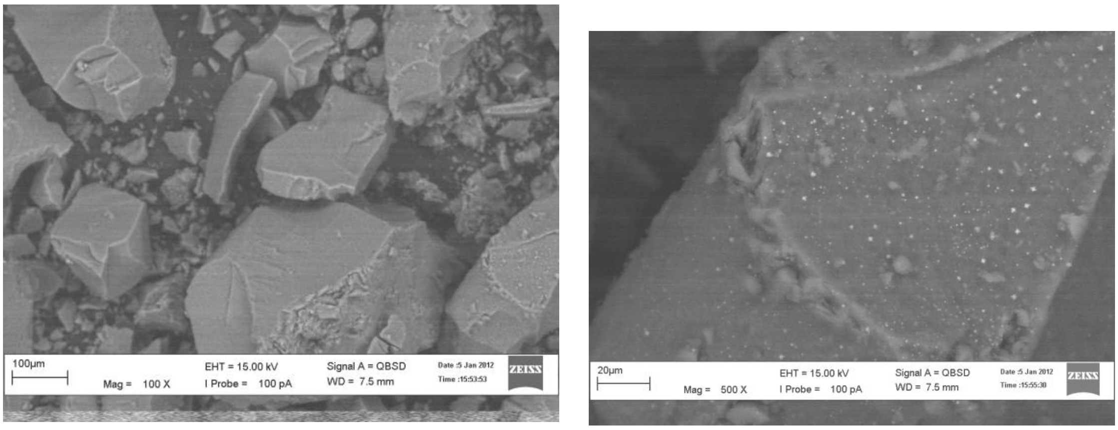

(a) Magnification at 100x (b) Magnification at 501x

Figure 4.2: SEM images of the Co/Zn-TiO2 catalyst of samples.

At the Figure 4.3 below showed that the SEM images of Co/Zn-Cab-O-Sil samples. It can be seen that the sample shows an irregular pore structure with large particles and the shape of sample in Figure 4.3 (a) exhibits like pieces of ceramic microstructure with littler particles explained by O. Ducreux et al, (2009). This result indicates that silica component in Cab-O-Sil can stabilize mesostructures and inhibit the aggregation of particles. The Figure 4.3 (b) and (c) formed that exhibits irregular squared shape and are clearly visible in agglomeration and homogeneous formed compared to other catalyst samples. Zhensong Lou et al (2008) also mentioned the same observation that reveals the irregular shape with agglomeration and homogenous. The form showed clearly visible.

(a) Magnification at 100x (b) Magnification at 500x



(c) Magnification at 2000x

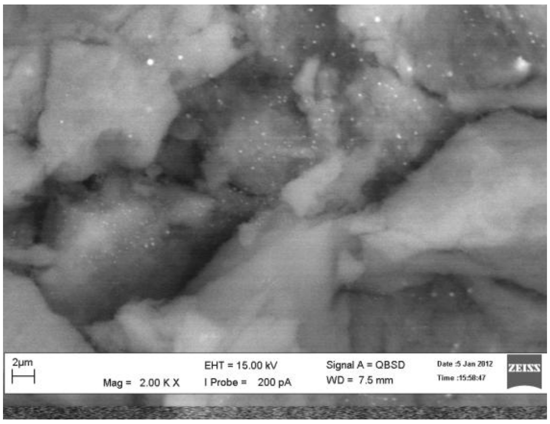


Figure 4.3: SEM images of the Co/Zn-Cab-O-Sil catalyst of samples.

In the figure 4.4, there were the comparisons of three catalyst samples of Co/Zn-SBA-15, Co/Zn-TiO_2 and Co/Zn-Cab-O-Sil. From this comparison, we could compare clearly the different of texture and microscopic size for each sample. This comparison had proved that the texture of Co/Zn-SBA-15 was the smoothest and had smallest microscopic size compared to other catalyst sample.

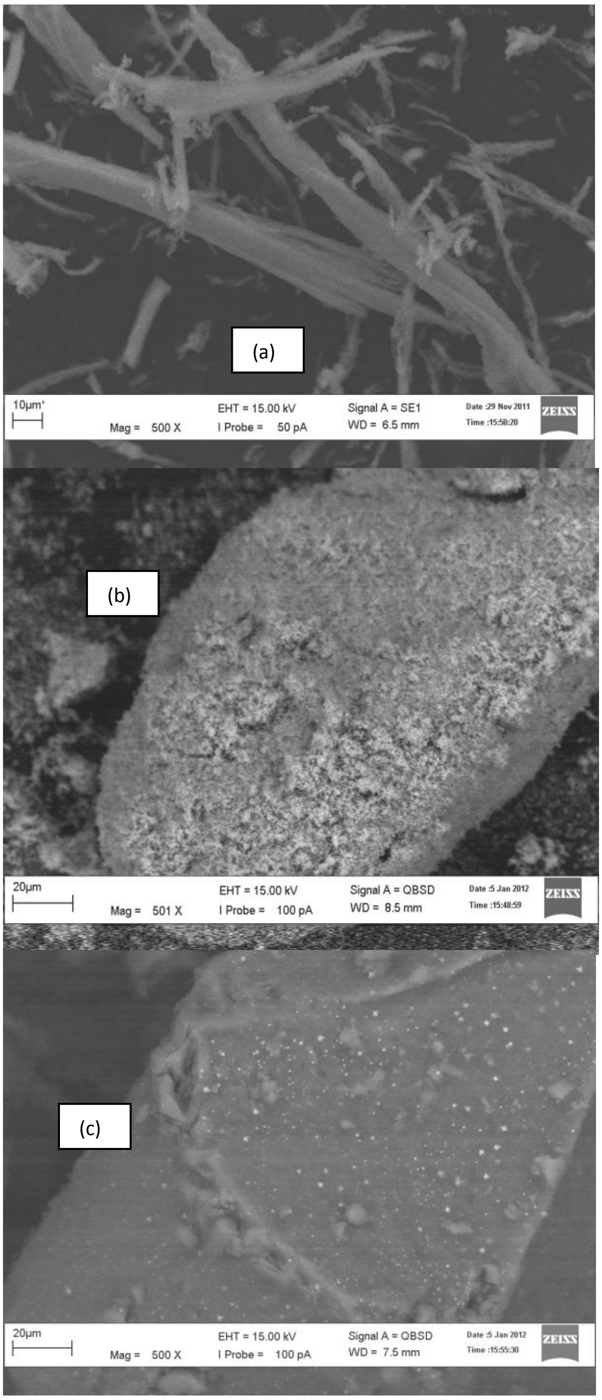


Figure 4.4: Comparison SEM images of(a) Co/Zn-SBA-15, (b) Co/Zn-TiO_2 and (c) Co/Zn-Cab-O-Sil catalyst of samples at Magnification at 500x.

4.3 Fourier Transform Infrared (FTIR)

Figure 4.5 below showed 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. Co was set to 5% loading in this experiment. For Zn promoter and other cobalt supporters were set to 20% and 75 % loading. The curves above showed that it consist of OH bond stretching's Si-O-Si, Si-CH_3 and Si-OH. There are many functional groups observed with certain wavelength in the samples such as cobalt oxides, Si-O-Si, Si-CH3, zinc oxide, OH band, Si-C, and etc.

The broad peak at around 3,440 cm^{-1} in Figure 4.5 (a) and (c) corresponds to the surface adsorbed water and hydroxyl groups, and the other peak also in Figure 4.5 (a) and (c) at about 1,630 cm^{-1} is due to the bending vibrations of O-H bonds. It can be observed that the percentage reflectance of O-H bonds which indicates the SBA-15 can effectively restrain the loss of surface hydroxyl groups during calcinations. As a result, the hydroxyl groups on the surface of the samples can be preserved, which is a benefit for reaction in the Fisher-Tropsch synthesis, (Chenxu He et al, 2010). The statement showed that the SBA-15 can hold more OH bonds in their catalyst sample compared to other catalyst samples.

The peak around 1000-1200 cm^{-1} in Figure 4.5 (a) and (c) is also present in the sample. The range of 1000-1200 cm^{-1} wavelength can be assigned to the siloxane or Si-O-Si stretching bands; peak appears as a broad and strong peaking the sample, (Kababji et al, 2009). The O-H bond stretching bands of the silanol groups were observed and absorbed at 3200-3600cm^{-1} in Figure 4.5 (a) and (c) can be assigned as the surface silanol group of SBA-15 is mainly of the hydrogen-bonded type in IR absorption bands, (Kababji et al, 2009). Furthermore, the functional groups at range 400-1000 cm^{-1} in Figure 4.5 (b) 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, (Zhensong Lou, 2008). Additional to that, formation of hydroxyl group also formed when SBA-15 is present in the sample. The hydroxyl groups were assigned around 1640 cm^{-1} in Figure 4.5, (Kababji et al, 2009).

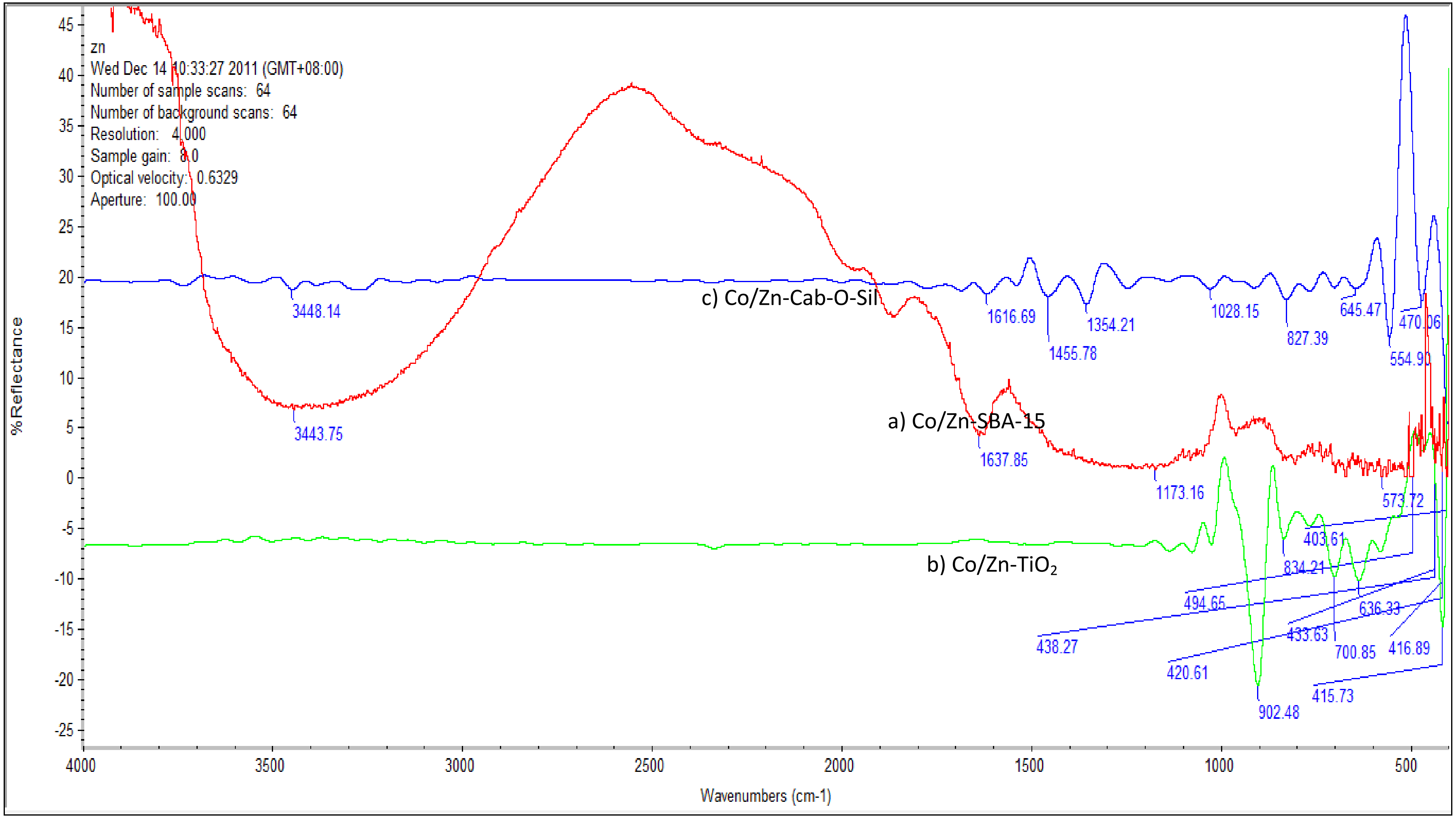


Figure 4.5: Comparison between FTIR spectra of Co/Zn-SBA-15,Co/Zn-TiO_2 and Co/Zn-Cab-O-Sil.

4.4 Thermogravimetric analysis (TGA)

The Thermogravimetric analysis curve of the catalyst sample prior to calcinations is shown in Figure4.6. All TGA was performed at the temperature range between 25–900°C with 20° C/minute of heating rate for each catalyst samples, (Zhang et al, 2005). 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, I conclude that the catalyst sample of Co/Zn-SBA-15 was one criteria of catalyst's high thermal stability, (O. Gonza´ lez a, 2009).

Furthermore, for the weight loss of Thermogravimetric analysis (TGA) of Co/Zn-TiO_2 was slightly consistent. There is no combustion occurred and the weight of catalyst sample becomes stable until 800°C.After that, the weight of TGA curve becomes increasing unpredictable like Co/Zn-TiO_2 from 800°C to 900°C but the weight increased less than 1%. As the result, we concluded that this catalyst sample had high thermal stability resulting from the stable TGA curve or we assumed that the melting point of catalyst sample was higher than 900°C.

Another TGA for the catalyst sample of Co/Zn-Cab-O-Sil, its TGA was similar to the catalyst sample of Co/Zn-TiO_2 but it's had quite weight loss at lower temperature. The weight loss at 56-85°C is due to desorption of water. The weight loss above 85°C is attributed to the combustion of organic compounds; that is to say, this weight reduction is due to the removal of templates, (Rakesh et al, 2009). The observed continuous weight loss of Co/Zn-Cab-O-Sil was 1.7%.This indicates by the fact that the amount of surfactant linked with Cab-O-Sil species is related with the chain length. At the same time, this result also shows that there are the larger amount of surfactant linked with Cab-O-Sil species, (Brian Yuliarto et al, 2010). Resulting from TGA, we concluded that this catalyst sample had high thermal stability resulting from the stable TGA curve or we assumed that the melting point of catalyst sample that higher than 900°C was just like the catalyst sample of Co/Zn-TiO_2.

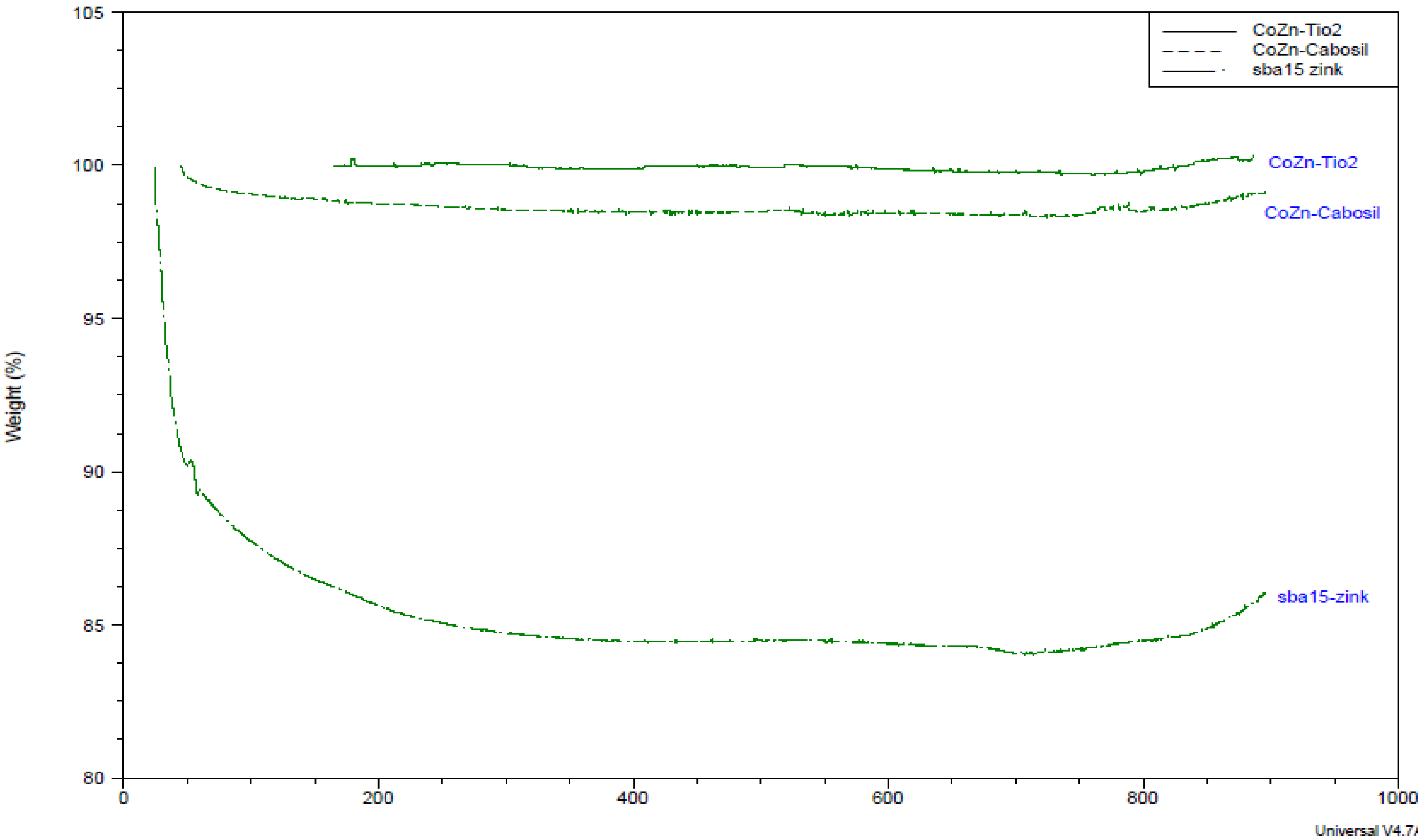


Figure 4.6: Comparison Thermogravimetric analysis (TGA) of Co/Zn-SBA-15, Co/Zn-TiO_2 and Co/Zn-Cab-O-Sil.

4.5 Limitation of the research

As a conclusion, from analysis data achieved had shown that there are many errors occurred in this research. Several factors were suspected such as the worst handling skills, wrong steps or wrong methods in the preparation of SBA-15 and synthesis of SBA-15. Besides that, the correct pretreatment of silica except SBA-15 in the catalyst preparation was needed. Additional to that, FTIR equipment analysis was in the error conditions as we were informed after we used it. Furthermore, the magnification of SEM depend on person handling skill as the data we received was too different compared to the recent similar research and some images captured had light reflects that disturbed our data to zoom into the microscopic pore size of catalyst samples.

CHAPTER FIVE

CONCLUSION

5.1 Conclusion

From this research, as well known that the Fischer-Tropsch synthesis will affect the best quality and clean fuel with higher percentage (%) purity of hydrocarbon in the fuel of final product.Co and Zn promoter with three different supporters (SBA-15, TiO_2 and Cab-O-Sil) were synthesized by incipient wetness impregnation method by using Cobalt (II) Nitrate as cobalt source and Zinc Nitrate Hexahydrate as zinc source. In the previous chapter, SEM result showed the low and high magnification SEM images of the Co/Zn-SBA-15 catalyst sample that indicating wood-like surface that composed at 50x in microscopic size in Figure 4.1 (a).

In the Figure 4.1 (b) showed the SEM image shows that the curved morphology of the Co/Zn-SBA-15 materials, many rope-like surface at 500x in microscopic size. This was showed the texture and structure of SBA-15 that produced was in the best condition and specification. Furthermore, the results of FTIR showed that the identification of Si-O-Zn and Si-O-Co functional group were observed because of the present of zinc and 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. The preparation of 20 wt % of cobalt loading showed a more OH group were presented. Besides that, TGA result showed the catalyst sample of Co/Zn-SBA-15 was one criteria of catalyst’s high thermal stability after the catalyst sample had the weight loss of Co/Zn-SBA-15 occurred at below 100 °C to the evaporation process of water, the combustion of catalyst sample between 50°C to 375°C and becomes stable as no combustion occurred until 800°C.

As a 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, Cab-O-Sil was limited by its characteristic of its non-porous. The catalyst supporter with high hydrothermal and thermal stability such as SBA-15 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.

Hopefully this research can be carried out successful in order to get the new invention for production of catalyst that will produce the best and clean fuel and to get rid of exceed cost of production but in the same quality of expensive product.

5.2 Recommendations

After running 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, more accurate and more persistence result. I suggest 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 equipments analysis such as N_2 adsorption-desorption isotherms,Barrett−Joyner−Halenda (BJH) method, Atomic absorption spectroscopy (AAS), Transmission electron microscopy analysis (TEManalysis), and X-ray diffraction analysis (XRD) were the major component in the catalyst activity studies.

These catalyst analysis method were cannot skip all because they were very useful for specific scope. For example, N_2 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 imageinformation 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 FT synthesis was important to obtain the catalyst activity and the stability of catalystfrom 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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