REFERENCES

Adesina, A.A. Hydrocarbon synthesis via Fischer-Tropsch reaction: travails and triumphs. Appl. Catal. A: General 138 (1996): 345-367.

Arakawa, H. Dubois, J.L., and Sayama, K. Selective conversion of CO_2 to methanol by catalytic hydrogenation over promoted copper catalyst. Energy Convers 33 (1992): 521-528.

Baca, et al. Characterization of mesoporous alumina prepared by surface alumination of SBA-15. Microporous and Mesoporous Mat. 110 (2008): 232–241.

Backman, L.B., Rautiainen, A., Krause, A.O.I., and Lindblad, M. A novel Co/SiO_2 catalyst for hydrogenation. Catal. Today 43 (1998): 11-19.

Choi, J.G. Reduction of support cobalt catalysts by hydrogen. Catal Lett. 35 (1995): 291-296.

Chu, W., et al. Cobalt species in promoted cobalt alumina-supported Fischer–Tropsch catalysts. J. Catal. 252 (2007): 215-230.

Dagle, R.A., et al. Selective CO methanation catalysts for fuel processing applications. Appl. Catal. A: General 326 (2007): 213-218.

Daniell, W., et al. Enhanced surface acidity in mixed alumina–silicas: a low-temperature FTIR study. Appl. Catal. A: General 196 (2000): 247–260.

Dry, M.E. Practical and theoretical aspects of the catalytic Fischer-Tropsch process. Appl. Catal. A 138 (1996): 319-334.

Evans, K.A.; 1993. Properties and uses of oxides and hydroxides. Downs, A. J.; Chemistry of aluminium gallium indium and thallium 248. 1st ed. :Blackie Academic and Professional.

Frohlich, G., et al. Activation and deactivation of cobalt catalysts in the hydrogenation of carbon dioxide. Appl. Catal. A: General 134 (1996): 1-19.

Grzechowiak, J.R., Szyszka, I., and Masalska, A. Effect of TiO_2 content and method of titania–silica preparation on the nature of oxidic nickel phases and their activity in aromatic hydrogenation. Catal. Today 137 (2008): 433–438.

Gu, F.N., Zhou, Y., Wei, F., Wang,Y., and Zhu, J.H. Creating the adsorptive sites with high performance toward nitrosamines in mesoporous silica MCM-41 by alumina modifier. Microporous and Mesoporous Mat. 126 (2009): 143–151.

Iglesia, E. Design, synthesis, and use of cobalt-based Fischer-Tropsch synthesis catalysts. Appl. Catal. A: General 161 (1997): 59-78.

Jacobs, G., et al. Fischer-Tropsch synthesis: support, loading, and promoter effects on the reducibility of cobalt catalysts. Appl. Catal. A 233 (2002): 263-281.

Jongsomjit, B., Wongsalee, T., and Praserthdam, P. Catalytic behaviors of mixed TiO_2-SiO_2 supported cobalt Fischer-Tropsch catalysts for carbon monoxide hydrogenation. J. of Mat. Chem. and Phys. 97 (2006): 343-350.

Khodakov, A.Y., et al. Reducibility of Cobalt Species in Silica-Supported Fischer-Tropsch Catalysts. J. Catal. 168 (1997): 16-25.

Khodakov, A.Y. Fischer-Tropsch synthesis: Relations between structure of cobalt catalysts and their catalytic performance. Catal. Today 144 (2009): 251–257.

Kogelbauer, A., Weber, J.C., and Goodwin, J.G., Jr. The formation of cobalt silicates on Co/SiO_2 under hydrothermal condition. Catal Lett. 34 (1995): 259-267.

Kusuma, H., Okabe, K., and Arakawa, H. Characterization of Rh-Co/SiO2 catalysts for CO_2 hydrogenation with TEM, XPS and FT-IR. Appl. Catal. A: General 207 (2001): 85-94.

Lahtinen, J., Anraku, T., and Somorjai, G.A. CO and CO hydrogenation on cobalt foil model catalysts: evidence for the need of CoO reduction. Catal. Lett. 25 (1994): 241-255.

Lebedev, O.I., Tendeloo, G.V., Collart, O., Cool, P., and Vansant, E.F. Structure and microstructure of nanoscale mesoporous silica spheres. Solid State Sci. 6 (2004): 489–498.

Liu, H., Ning, G., Gan, Z., and Lin, Y. A simple procedure to prepare spherical α-alumina powders. Mat. Research Bulletin 44 (2009): 785-788.

Liu,S., et al. The Influence of the Alcohol Concentration on the Structural Ordering of Mesoporousm Silica: Cosurfactant versus Cosolvent. J. Phys. Chem. B 107 (2003): 10405-10411.

Marie, A.J., Constant, A.G., Khodakov, A.Y., and Diehl, F. Cobalt supported on alumina and silica-doped alumina: Catalyst structure and catalytic performance in FischereTropsch synthesis. C. R. Chimie 12 (2009): 660-667.

Martínez, A., López, C., Márquez, F., and Díaz, I. Fischer–Tropsch synthesis of hydrocarbons over mesoporous Co/SBA-15 catalysts: the influence of metal loading, cobalt precursor, and promoters. J. Catal. 220 (2003): 486-499.

Okabe, K., Li, X., Wei, M., and Arakawa, H. Fischer–Tropsch synthesis over Co-SiO_2 catalysts prepared by the sol–gel method. Catal. Today 89 (2004): 431–438.

Panagiotopoulou, P., Kondarides, D.I., and Verykios, X.E. Selective methanation of CO over supported noble metal catalysts: Effects of the nature of the metallic phase on catalytic performance. Appl. Catal. A: General 344 (2008): 45-54.

Riedel, T., et al. Comparative study of Fischer-Tropsch synthesis with H_2/CO and H_2/CO_2 syngas using Fe- and Co-based catalysts. Appl. Catal. A: General 186 (1999): 201-213.

Saib, A.M., claeys, M., and Steen, E.V. Silica supported cobalt Fischer–Tropsch catalysts: effect of pore diameter of support. Catal. Today 71 (2002): 395-402.

Somorjai, G.A. Introduction to Surface Chemistry and Catalysis, NewYork, Wiley, 1994.

Son, D., and Li, J. Effect of catalyst pore size on the catalytic performance of silica supported cobalt Fischer-Tropsch catalysts. J. of Molecule Catal A: Chem. 247 (2006) 206-212.

Storsæter, S., Borg, Ø., Blekkan, E.A., and Holmen, A. Study of the effect of water on Fischer–Tropsch synthesis over supported cobalt catalysts. J. Catal. 231 (2005): 405–419.

Suzuki, T., Mayama, Y., Hirai, T., and Hayashi, S. Preliminary attempt to enhance the hydrogenation of carbon dioxide to methane on cobalt oxide catalyst by adding $CuO\text{-}ZnO\text{-}Cr_2O_3$. Int. J. Hydrogen Energy 18 (1993): 979-983.

Sun, X., Zhang, X., Zhang, Y., and Tsubaki, N. Reversible promotional effect of SiO_2 modification to Co/Al_2O_3 catalyst for Fischer–Tropsch synthesis. Appl. Catal. A: General 377 (2010): 134–139.

Wittayakhun, J.; Krisdanurak, N.; 2004. Catalysis: Fundamentals and Applications, 1st ed., Thammasart university publishing.

Xiong, H., Zhang, Y., Wang, S., and Li, J. Fischer-Tropsch synthesis: the effect of Al_2O_3 porosity on the performance of Co/Al_2O_3 catalyst. Catal. Comm. 6 (2005) 512-516.

Zhang, Y., Jacobs, G., Sparks, D.E., Dry, M.E., and Davis, B.H. CO and CO_2 hydrogenation study on supported cobalt Fischer–Tropsch synthesis catalysts. Catal. Today 71 (2002): 411–418.

Zhang, Y., Nagamori, S., Hinchiranan S., Vitidsant T., and Tsubaki, N. Promotional Effects of Al_2O_3 Addition to Co/SiO_2 Catalysts for Fischer-Tropsch Synthesis. Energy & Fuels an American Chem. Society J. 20 (2006) 417-421.

APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Calculation of Al_2O_3- SiO_2 composites supports

Preparation of alumina-silica composites support with 25% ratios of Alumina (Al_2O_3) by sol gel method was shown as follows:

Reagent: - Aluminium isopropoxide 98% ($Al(OPr^i)_3$)

Molecular weight = 204.25 g/mol

Alumina (Al_2O_3), formula weight = 101.9614 g/mol

- Support : SiO_2

- For 25%wt of Alumina (Al_2O_3) was shown as follow:

  Based on 75 g of silica (SiO_2) used, the composition of the catalyst would be as follows:

  Al_2O_3 = 25 g

  101.9614 g of Al_2O_3 required 204.25 g of $Al(OPr^i)_3$

  25 g of Al_2O_3 required $25 \times \frac{204.25}{101.9614}$ g of $Al(OPr^i)_3$

  = 50.08 g of $Al(OPr^i)_3$

  $Al(OPr^i)_3$ 98 g provide 98% Aluminium isopropoxide solution 100 g

  $Al(OPr^i)_3$ 50.08 g provide 98% Aluminium isopropoxide solution $\frac{50.08}{0.98}$

  = 51.10 g

Calculation of cobalt loading

Preparation of 20%wtCo/SiO_2 by the incipient wetness impregnation method was shown as follow:

Reagent: - Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$)

Molecular weight = 291.03 g/mol

Cobalt (Co), Atomic weight = 58.933 g/mol

- Support: - spherical silica support

Based on 1.00 g of catalyst used, the composition of the catalyst would be as follows:

Cobalt = 0.20 g

SiO_2 = 1.00 – 0.20 = 0.80 g

Cobalt 0.20 g was prepared from Cobalt (II) nitrate hexahydrate

$$\text{Cobalt (II) nitrate hexahydrate required} = \frac{0.20}{58.933} \times 291.03$$

$$= 0.9877 \text{ g}$$

APPENDIX B

CALCULATION FOR TOTAL CO CHEMISORPTION AND DISPERSION

Calculation of the total CO chemisorption and metal dispersion of the catalyst, a stoischiometry of CO/Co = 1, was assumed. The calculation procedure was as follows:

Let the weight of catalyst used	=	W	g
Integral area of CO peak after adsorption	=	A	unit
Integral area of 100 µl of standard H_2 peak	=	B	unit
Amounts of CO adsorbed on catalyst	=	B-A	unit
Concentration of Co	=	C	%wt
Volume of H_2 adsorbed on catalyst	=	100 × [(B-A)/B]	µl
Volume of 1 mole of CO at 30 °C	=	24.86×10^6	µl

Mole of CO adsorbed on catalyst = [(B-A)/B]×[100/24.86] µmole

Total CO chemisorption =

[(B-A)/B]×[100/29.93]×[1/W] µmole /$g_{catalyst}$

= N µmole /$g_{catalyst}$

$$\%Co\ dispersion = \frac{\text{The amount of cobalt equivalent to CO adsorption after reduction} \times 100}{\text{Total amount of cobalt active sites expected to exist after reduction}}$$

Molecular weight of cobalt = 58.93

Metal dispersion (%) = $\dfrac{1 \times CO_{tot} \times 100}{\text{No. µmole Co}_{tot}}$

= $\dfrac{1 \times N \times 100}{No.\ \mu mole\ Co_{tot}}$

= $\dfrac{1 \times N \times 58.93 \times 100 \times 100}{\left[C \times 10^6\right]}$

= $\dfrac{0.59 \times N}{C}$

APPENDIX C

CALCULATION FOR REDUCIBILITY

For supported cobalt catalyst, it can be assumed that the major species of calcined Co catalysts was Co_3O_4. H_2 consumption to reduce Co_3O_4 was calculated as follows:

Molecular weight of Co = 58.93

Molecular weight of Co_3O_4 = 240.79

Calculation of the calibration of H_2 consumption using cobalt oxide (Co_3O_4)

Let the weight of Co_3O_4 used = 0.1 g

= 4.153×10^{-4} mole

From equation of Co_3O_4 reduction;

$$Co_3O_4 + 4H_2 \rightarrow 3Co + 4H_2O \qquad (E.1)$$

Mole of hydrogen consumption = 4 Mole of Co_3O_4 consumption

= $4 \times 4.153 \times 10^{-4}$

= 1.661×10^{-3} mole

Integral area of hydrogen used to reduce Co_3O_4 0.1 g = 115.63 unit

At 100 % reducibility, the amount of hydrogen consumption is 1.661×10^{-3} mole related to the integral area of Co_3O_4 after reduction 115.63 unit.

Calculation of reducibility of supported cobalt catalyst

$$\% \text{ Reducibility} = \frac{\text{Amount of } H_2 \text{ uptake to reduce 1 g of catalyst} \times 100}{\text{Amount of theoretical } H_2 \text{ uptake to reduce } Co_3O_4 \text{ to } Co^0 \text{ for 1 g of catalyst}}$$

Integral area of the calcined catalyst = X unit

The amount of H_2 consumption =

$$\left[2 \times 1.661 \times 10^{-3} \times (X)/115.63\right] \text{mole}$$

Let the weight of calcined catalyst used = W g

Concentration of Co = Y %wt

Mole of Co = $[(W \times Y/100)/58.93]$ mole

Mole of Co_3O_4 = $[(W \times Y/100)/(3 \times 58.93)]$ mole

Amount of theoretical = $[(W \times Y/100) \times 4/(3 \times 58.93)]$ mole

Reducibility (%) of supported Co catalyst =

$$\frac{\left[2 \times 1.661 \times 10^{-3} \times (X)/115.63\right] \times 100}{[(W \times Y/100) \times 4/(3 \times 58.93)]}$$

Example for 20Co/ Z

Integral area of the calcined catalyst = *6.016 unit*

The amount of H_2 consumption = $\left[2 \times 1.661 \times 10^{-3} \times (X)/115.63\right]$ *mole*

Let the weight of calcined catalyst used = *0.1 g*

Concentration of Co = *20 %wt*

Mole of Co = $[(0.1 \times 20/100)/58.93]$ *mole*

Mole of Co_3O_4 = $[(0.1 \times 20/100)/(3 \times 58.93)]$ *mole*

Amount of theoretical = $[(0.1 \times 20/100) \times 4/(3 \times 58.93)]$ *mole*

Reducibility (%) of supported Co catalyst =

$$\frac{\left[2 \times 1.661 \times 10^{-3} \times (6.016)/115.63\right] \times 100}{[(0.1 \times 20/100) \times 4/(3 \times 58.93)]} = 34.6\ \%$$

APPENDIX D

CALIBRATION CURVES

This appendix showed the calibration curves for calculation of composition of reactant and products in CO hydrogenation reaction. The reactant is CO and the main product is methane. The other products are linear hydrocarbons of heavier molecular weight that are C_2-C_4 such as ethane, ethylene, propane, propylene and butane.

The thermal conductivity detector, gas chromatography Shimadzu model 8A was used to analyze the concentration of CO by using Molecular sieve 5A column.

The thermal conductivity detector (TCD), gas chromatography Shimadzu model 8A was used to analyze the concentration of CO_2 by using porapack-Q column.

The VZ10 column are used with a gas chromatography equipped with a flame ionization detector, Shimadzu model 14B, to analyze the concentration of products including of methane, ethane, ethylene, propane, propylene and butane. Conditions uses in both GC are illustrated in Table C.1.

Mole of reagent in y-axis and area reported by gas chromatography in x-axis are exhibited in the curves. The calibration curves of CO, methane, ethane, ethylene, propane, propylene and butane are illustrated in the following figures.

Table D.1 Conditions use in Shimadzu modal GC-8A and GC-14B.

Parameters	Condition	
	Shimadzu GC-8A	Shimadzu GC-14B
Width	5	5
Slope	50	50
Drift	0	0
Min. area	10	10
T.DBL	0	0
Stop time	50	60
Atten	0	0
Speed	2	2
Method	41	41
Format	1	1
SPL.WT	100	100
IS.WT	1	1

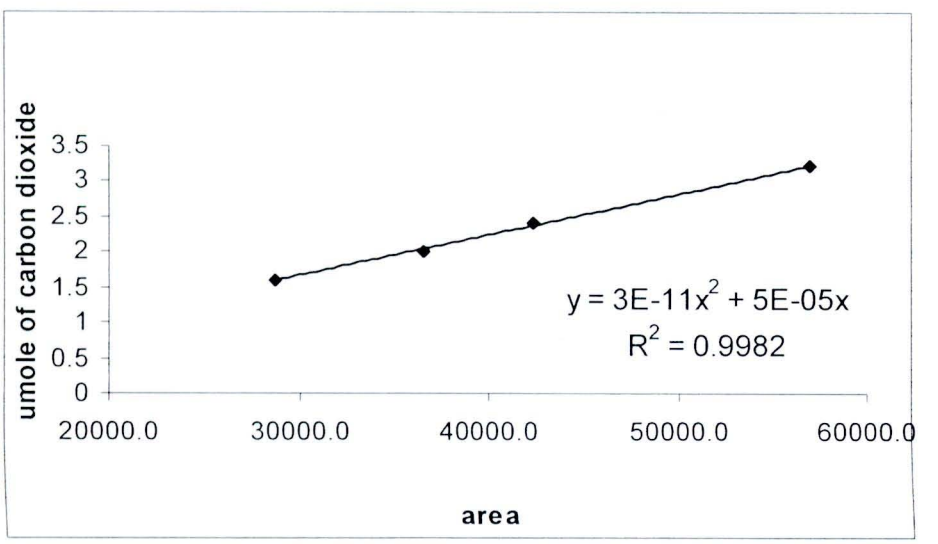


Figure D.1 The calibration curve of carbon dioxide.

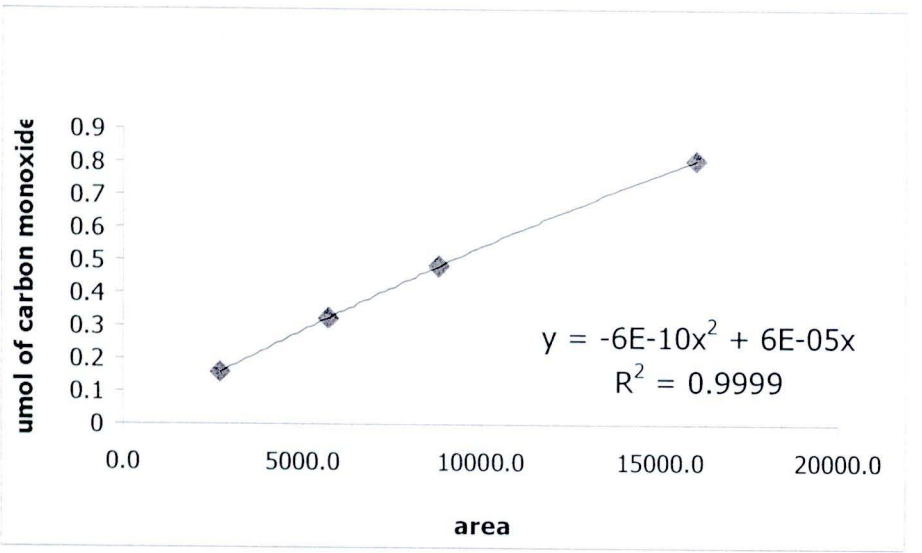


Figure D.2 The calibration curve of carbon monoxide.

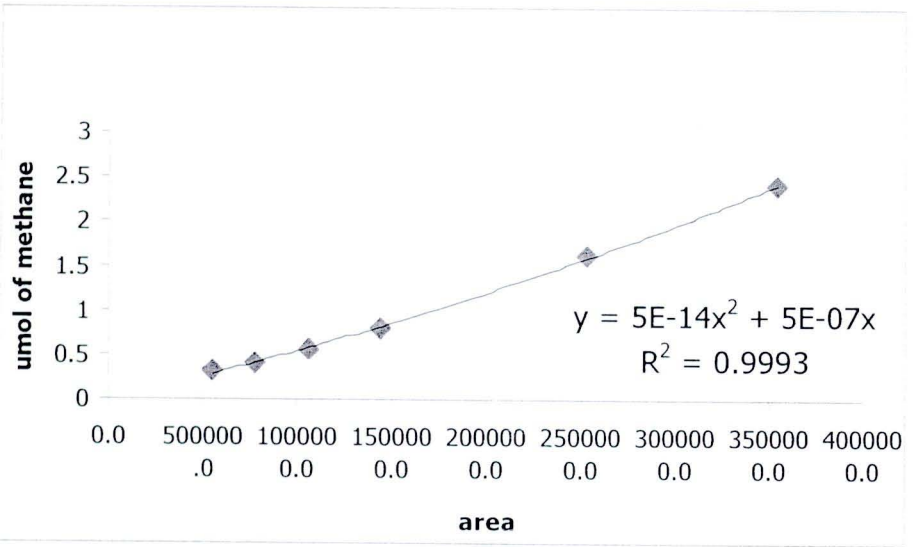


Figure D.3 The calibration curve of methane.

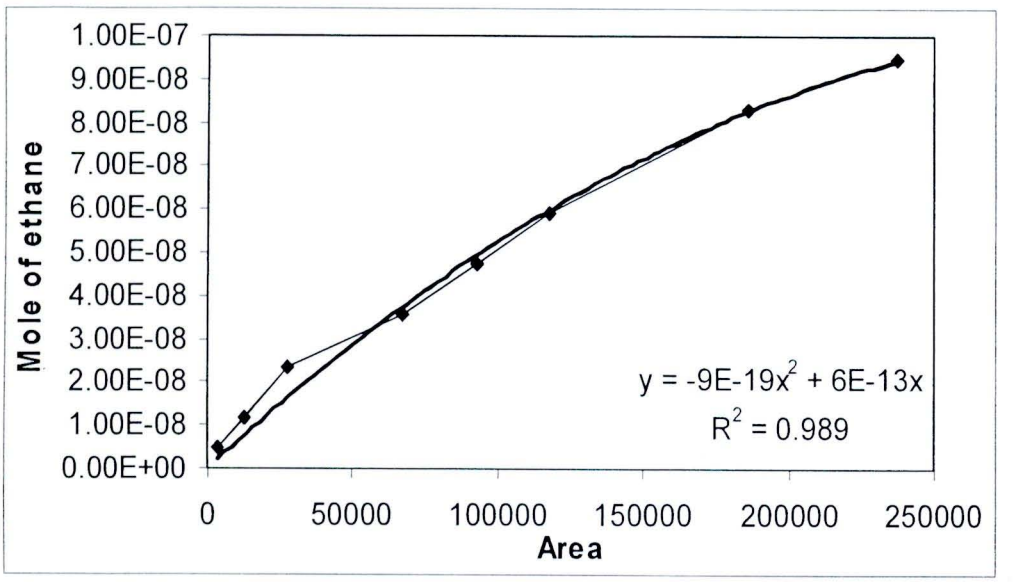


Figure D.4 The calibration curve of ethane.

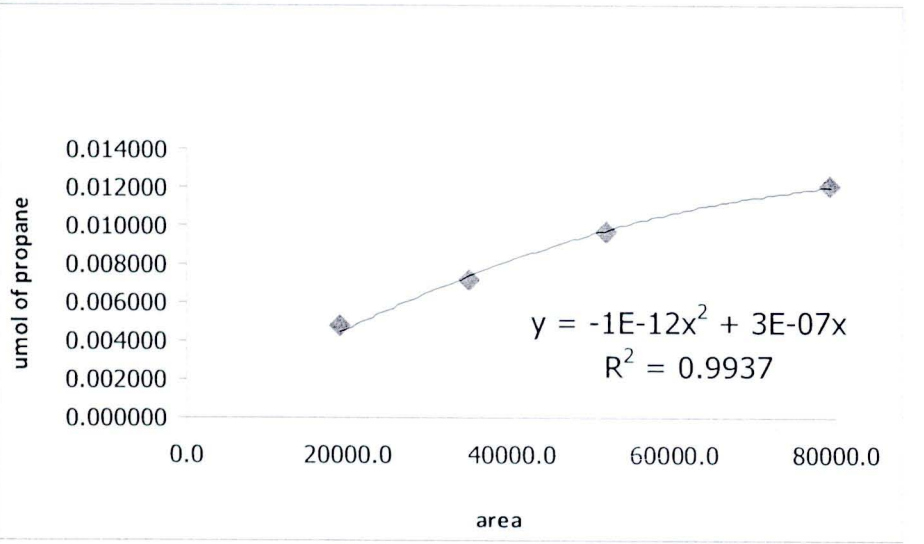
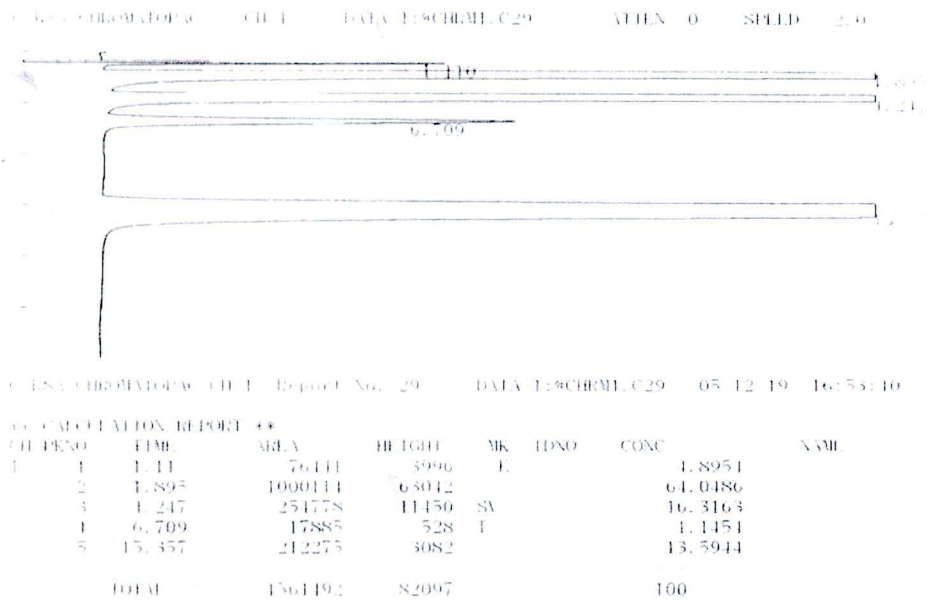


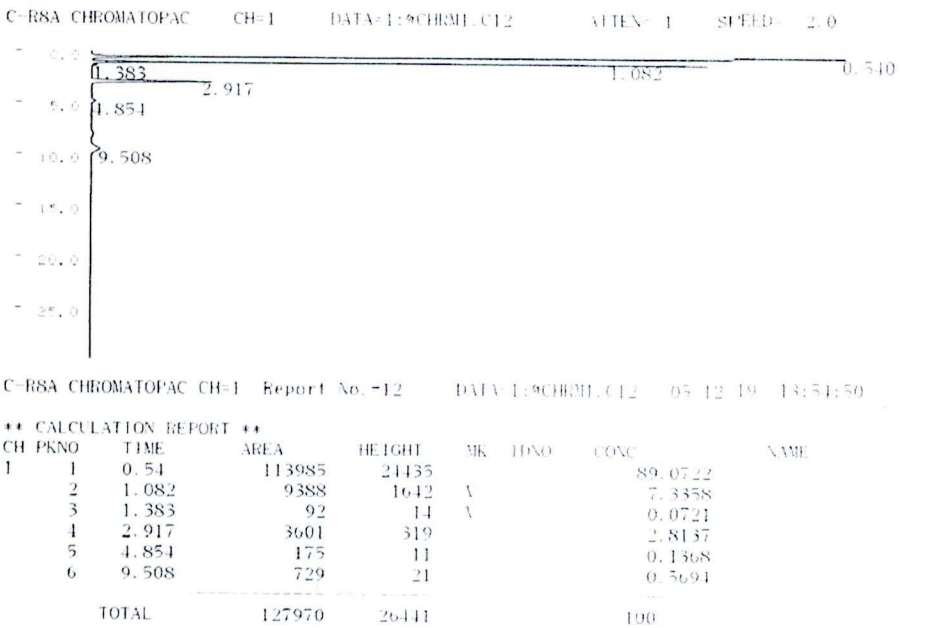
Figure D.5 The calibration curve of propane.



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	1.11	76111	5996	E		1.8951	
	2	1.895	1000111	68042			64.0486	
	3	4.247	254778	11450	SV		16.3163	
	4	6.709	17885	528	T		1.1451	
	5	15.457	212273	3082			13.5944	
		TOTAL	1561192	82097			100	

Figure D.6 The chromatograms of catalyst sample from thermal conductivity detector, gas chromatography Shimadzu model 8A (Molecular sieve 5A column).



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	0.54	113985	21435			89.0722	
	2	1.082	9388	1642	V		7.3358	
	3	1.383	92	14	V		0.0721	
	4	2.917	3601	319			2.8137	
	5	4.854	175	11			0.1368	
	6	9.508	729	21			0.5694	
		TOTAL	127970	26441			100	

Figure D.7 The chromatograms of catalyst sample from flame ionization detector, gas chromatography Shimadzu model 14B (VZ10 column).

APPENDIX E

CALCULATION OF CO_2 CONVERSION, REACTION RATE AND SELECTIVITY

The catalyst performance for the CO_2 hydrogenation was evaluated in term of activity for CO_2 conversion, reaction rate and selectivity.

CO_2 conversion is defined as moles of CO_2 converted with respect to CO_2 in feed:

$$CO_2 \text{ conversion (\%)} = \frac{100 \times [mole\ of\ CO_2\ in\ feed - mole\ of\ CO_2\ in\ product]}{mole\ of\ CO_2\ in\ feed} \quad \text{(i)}$$

Reaction rate was calculated from CO_2 conversion that is as follows:

Let the weight of catalyst used	=	W	g
Flow rate of CO_2	=	2	cc/min
Reaction time	=	60	min
Weight of CH_2	=	14	g
Volume of 1 mole of gas at 1 atm	=	22400	cc
Selectivity to CH_4	=	S	

$$\text{Reaction rate (g } CH_2\text{/g of catalyst.h)} = \frac{(\%\ conversion of\ CO_2 / 100) \times 60 \times 14 \times 2}{W \times 22400} \times S \quad \text{(ii)}$$

Selectivity of product is defined as mole of product (B) formed with respect to mole of CO_2 converted:

$$\text{Selectivity of B (\%)} = 100 \times [mole\ of\ B\ formed / mole\ of\ total\ products] \quad \text{(iii)}$$

Where B is product, mole of B can be measured employing the calibration curve of products such as methane, ethane, ethylene, propane, propylene and butane

$$\text{mole of } CH_4 = (\text{area of } CH_4 \text{ peak from integrator plot on GC-14B}) \times 8 \times 10^{12} \quad \text{(iv)}$$

APPENDIX F

PORE SIZE DISTRIBUTION CURVES

The pore size distribution curves derived from N_2 desorption from spherical silica and alumina-silica composites supports and their catalysts are illustrated in the following figures.

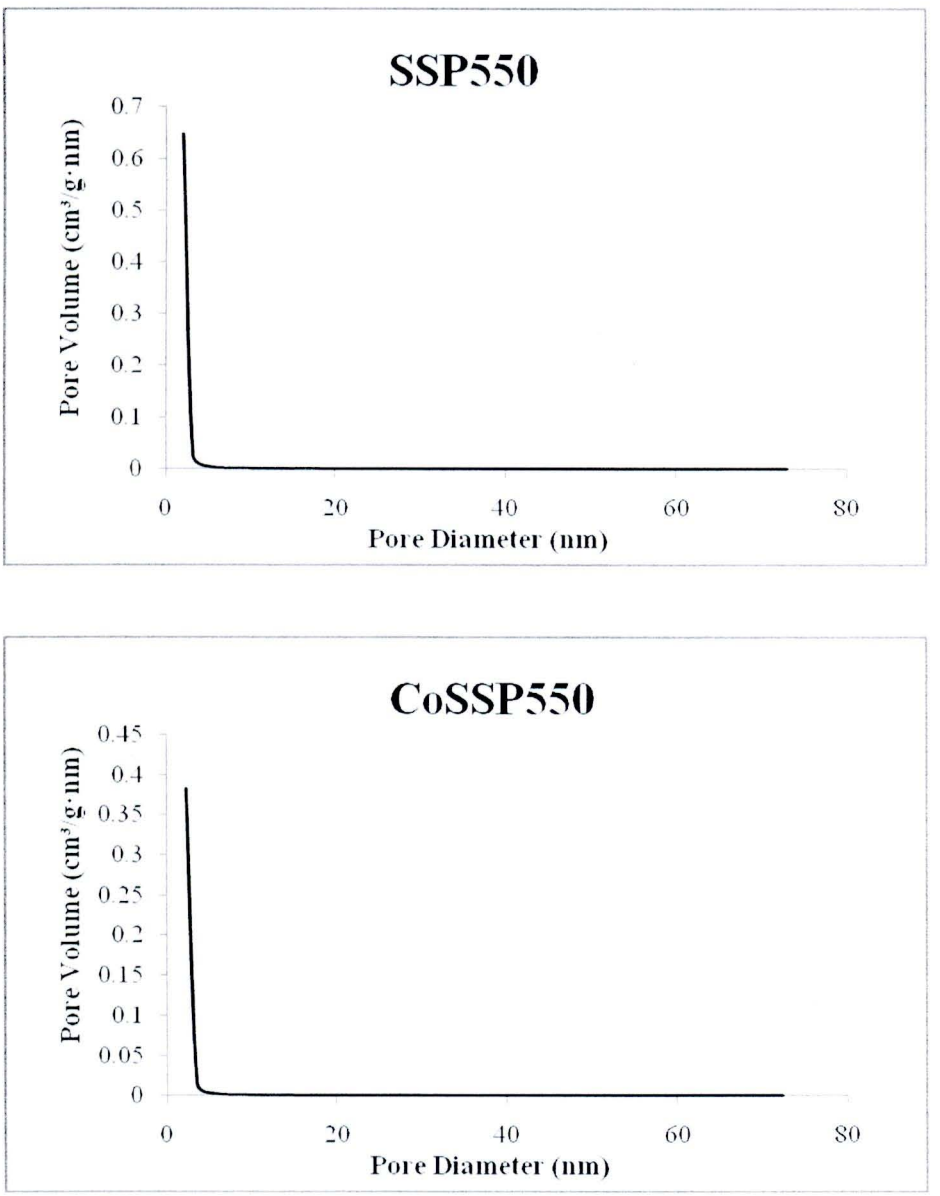
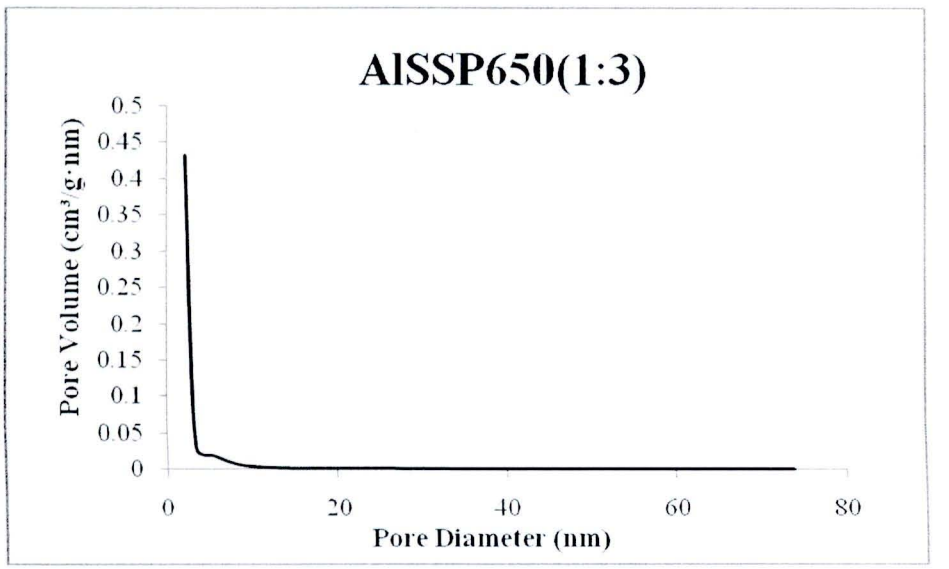


Figure F.1 The pore size distribution of SSP550 and CoSSP550.



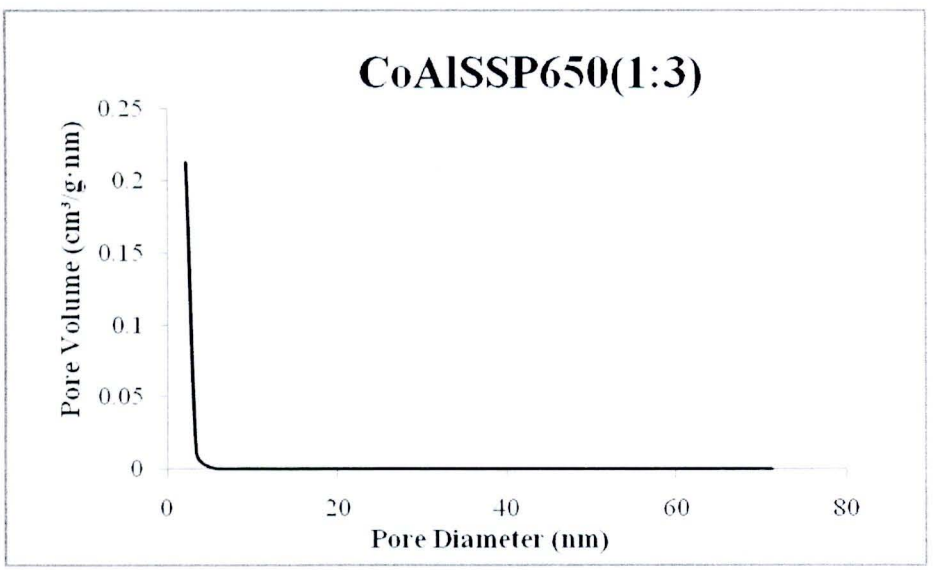
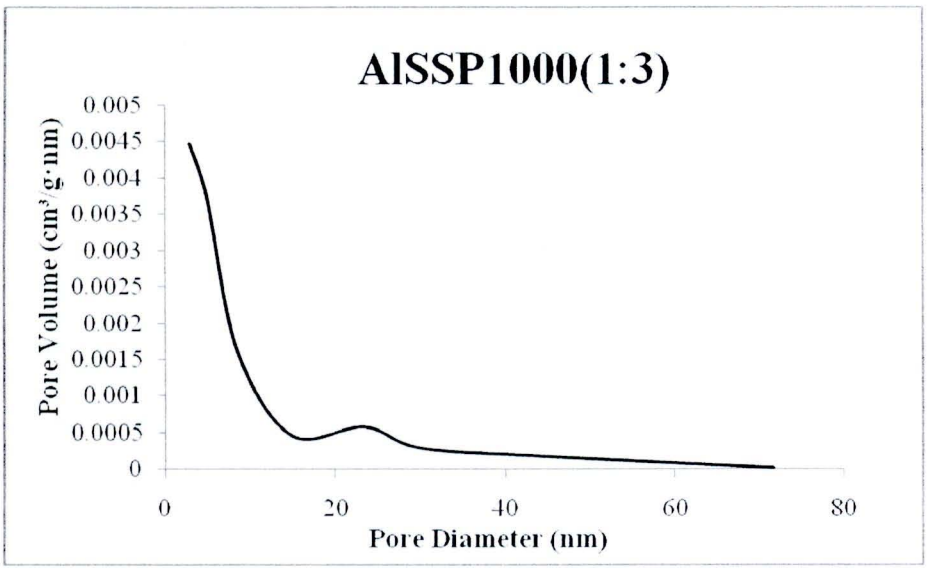


Figure F.2 The pore size distribution of AlSSP650 (1:3) and CoAlSSP650 (1:3).



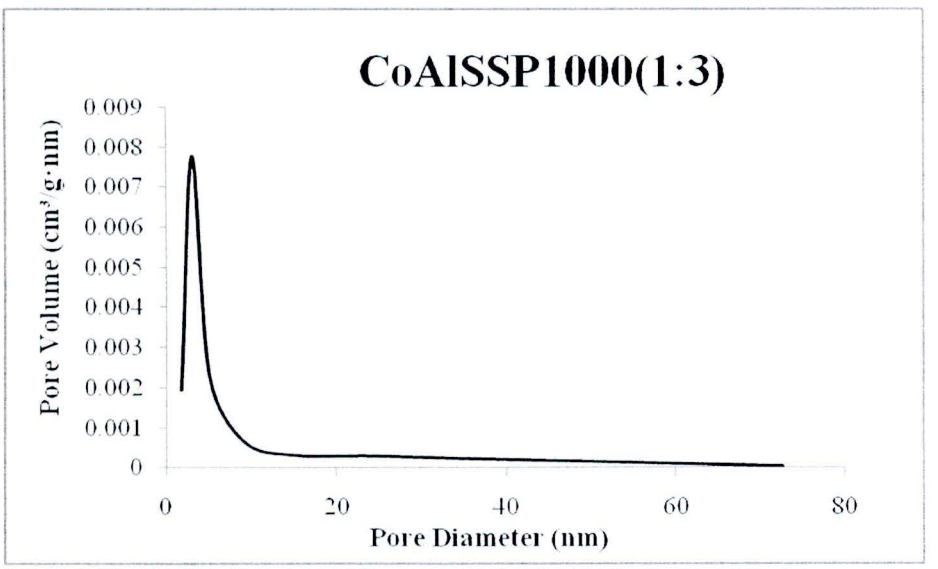
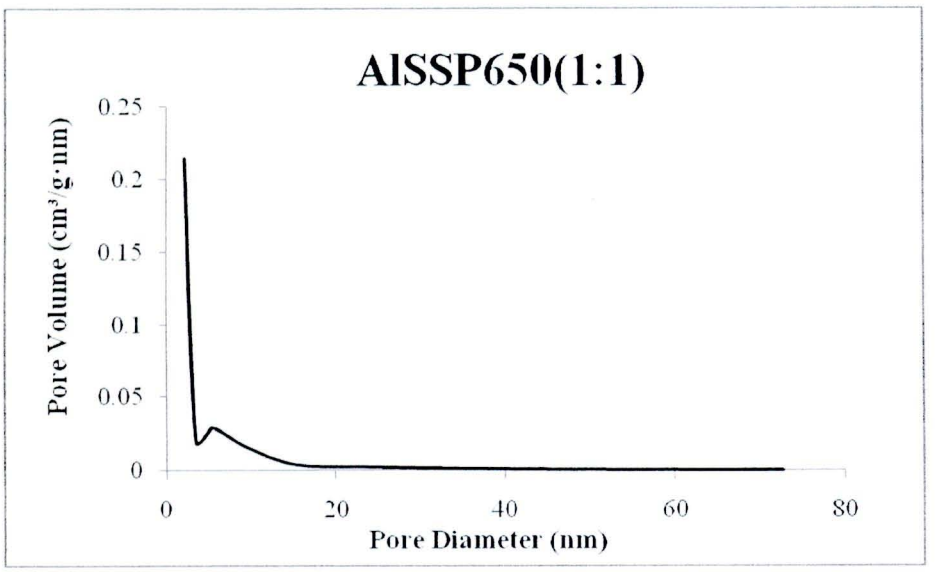


Figure F.3 The pore size distribution of AlSSP1000 (1:3) and CoAlSSP1000 (1:3).



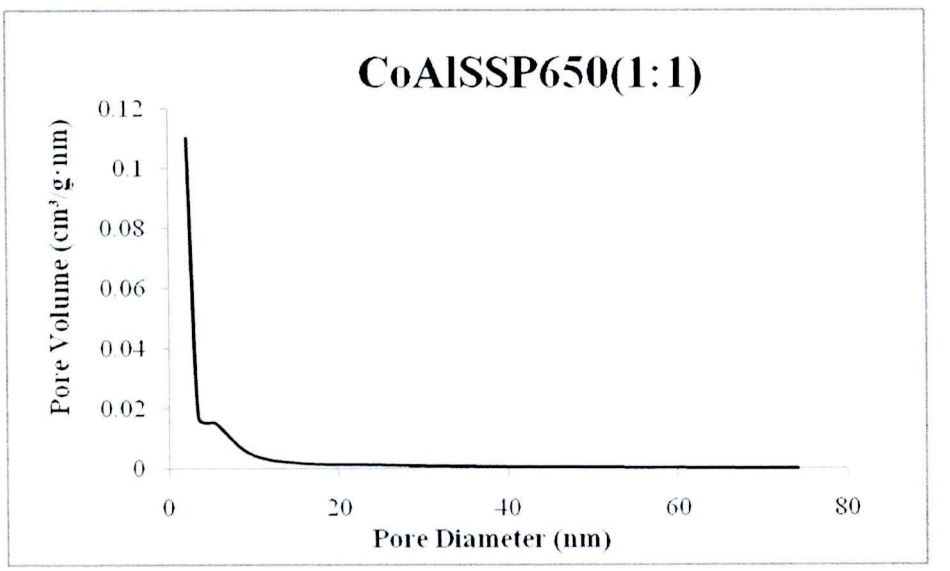
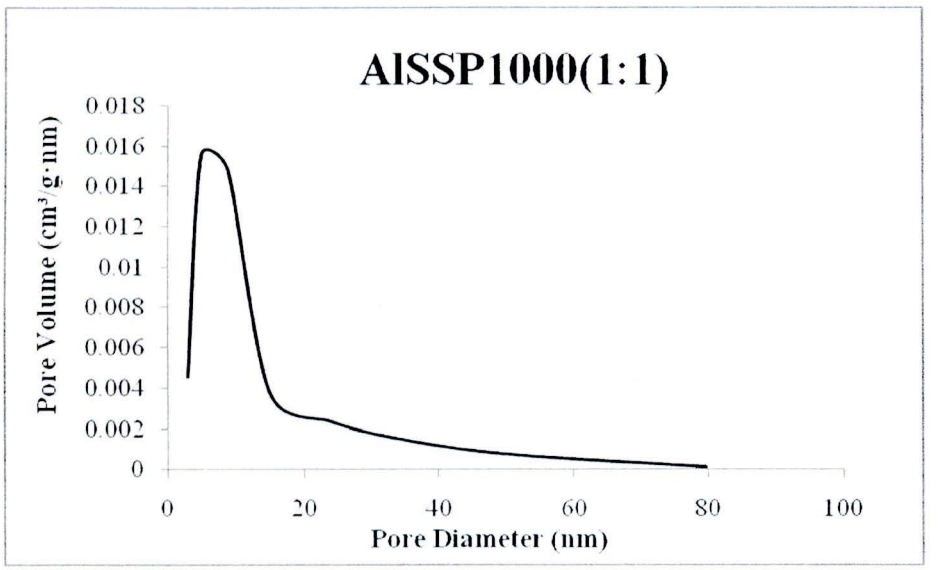


Figure F.4 The pore size distribution of AlSSP650 (1:1) and CoAlSSP650 (1:1).



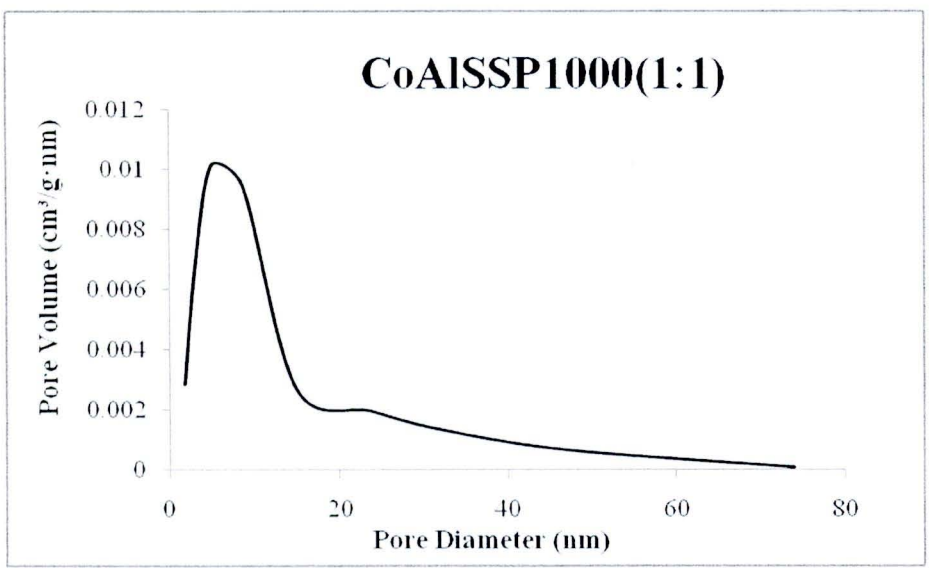
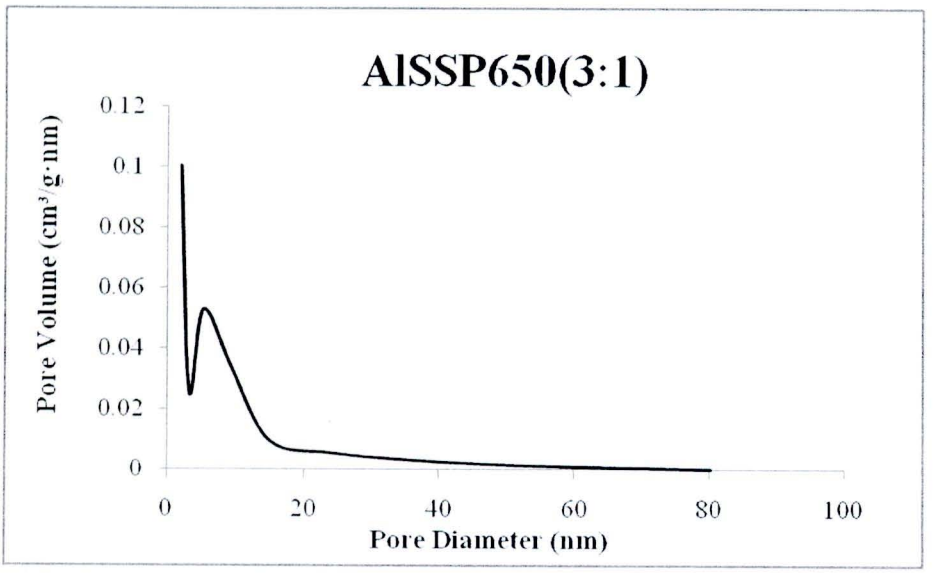


Figure F.5 The pore size distribution of AlSSP1000 (1:1) and CoAlSSP1000 (1:1).



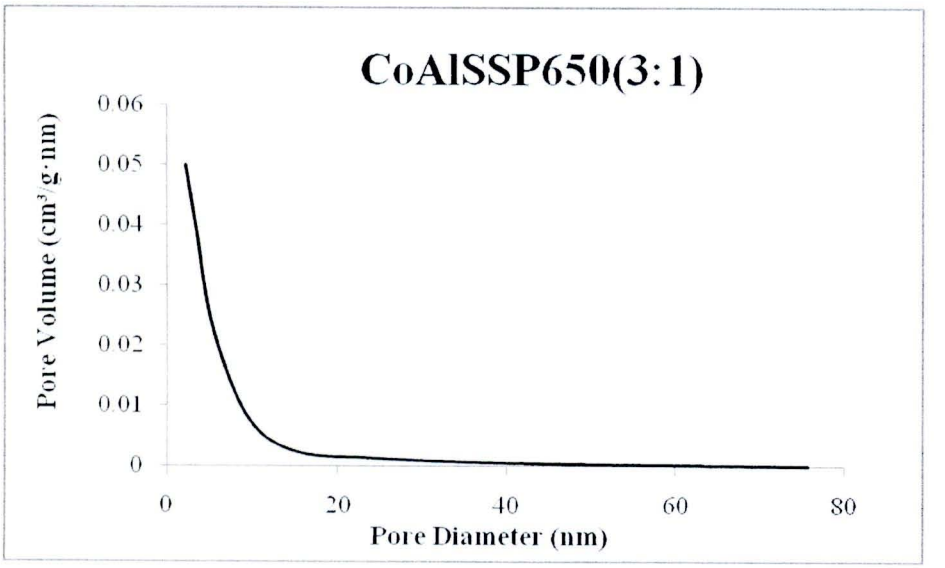
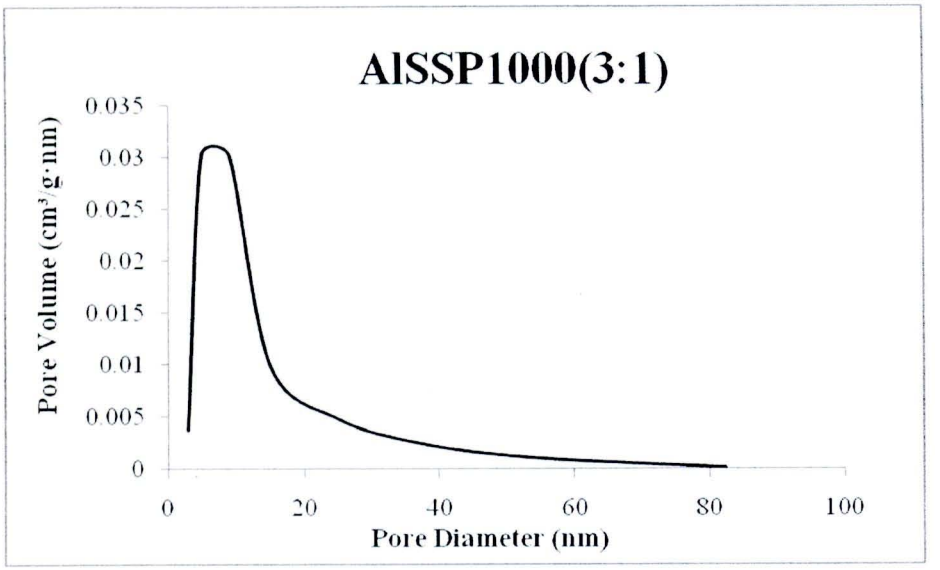


Figure F.6 The pore size distribution of AlSSP650 (3:1) and CoAlSSP650 (3:1).



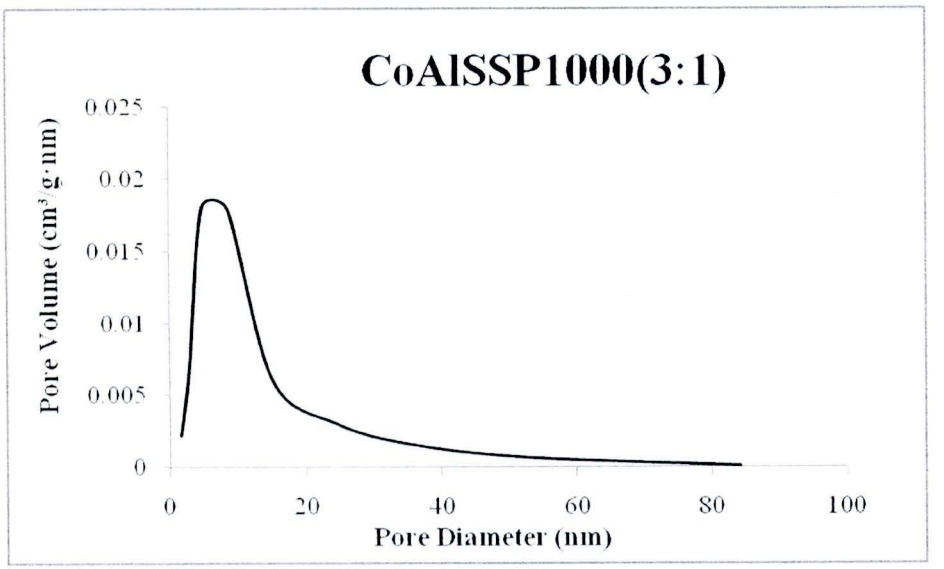


Figure F.7 The pore size distribution of AlSSP1000 (3:1) and CoAlSSP1000 (3:1).

VITA

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