

REFERENCES

- Adesina, A.A. Hydrocarbon synthesis via Fischer-Tropsch reaction: travails and triumphs. Appl. Catal. A 138 (1996): 345-367.
- Anderson, R. B. The Fischer-Tropsch Synthesis. San Diego: Academic Press, 1984.
- Androff, N.W., Francis, L.F., and Velmakanni, B.V. Macroporous Ceramics from Ceramic-Polymer Dispersion Methods. AIChE journal. 43 (1997): 2878.
- Backman, L.B., Rautiainen, A., Krause, A.O.I., and Lindblad, M. A novel Co/SiO₂ catalyst for hydrogenation. Catal. Today 43 (1998): 11-19.
- Backman, L.B., Rautiainen, A., Lindblad, M., and Krause, A.O.I. Effect of support and calcination on the properties of cobalt catalysts prepared by gas phase deposition. Appl. Catal. A 191 (2000): 55-68.
- Bahome, M.C., Jewell, L.L., Hildebrandt, D., Glasser, D., and Coville, N.J. Fischer-Tropsch synthesis over iron catalysts supported on carbon nanotubes. Appl. Catal. A 287 (2005): 60-67.
- Bechara, R., Balloy, D., and Vanhove, D. Catalytic properties of Co/Al₂O₃ system for hydrocarbon synthesis. Appl. Catal. A 207 (2001): 343-353.
- Bilde-Sorensen, J.B., Lawlor, B.F., Geipel, T., Pirouz, P., Heuer, A.H., and Lageribf, K.P.D. On Basal Slip and Basal Twinning in Sapphire (α -Al₂O₃)-I. Basal Slip Revisited. Acta Metall. Mater. 44 (1996): 2145-52.
- Blonski, S., and Garofalini, S.H. Molecular Dynamics Simulations of α - Alumina and γ -Alumina Surfaces. Surf. Sci. 295 (1993): 263-74.
- Bonevich, J.E., and Marks, L.D. The Sintering Behavior of Ultrafine Alumina Particles. J. Mater. Res. 7 (1992): 1489-500.
- Brindley, G.W., and Choe, J.O. The Reaction Series, Gibbsite to χ -Alumina to κ -Alumina to Corundum. I. Am. Mineral. 46 (1961): 771-85.
- Brinker, C.J., and Scherrer, G.W. Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing. San Diego: Academic Press, 1990.
- Church, J. S., Cant, N. W., and Trimm, D. L. Stabilisation of aluminas by rare earth and alkaline earth ions. Appl. Catal. A 101 (1993): 105-116.
- Cubeiro, M.L., Morales, H., Goldwasser, M.R., Perez-Zurita, M.J., Gonzalez-Jimenez, F., and de N, C.U. Hydrogenation of carbon oxides over Fe/Al₂O₃ catalysts.

- Appl. Catal. A 189 (1999): 87-97.
- Das, T., Jacobs, G., Patterson, P.M., Conner, W.A., Li, J.L., and Davis, B.H.
Fischer–Tropsch synthesis: characterization and catalytic properties of rhenium promoted cobalt alumina catalysts. Fuel 82 (2003): 805-815.
- Dawson, W.H. Hydrothermal synthesis of advanced ceramic powders. Am. Ceram. Soc. Bull. 67 (1988): 1673-1678.
- Deng, S.G., and Lin, Y.S. Microwave synthesis of mesoporous and microporous alumina powders. J. Mater. Sci. Lett. 16 (1997): 1291.
- Deng, Y., Wei, G.D., and Nan, C.W. Ligand-assisted control growth of chainlike nanocrystals. Chem. Phys. Lett. 368 (2003): 639-643.
- Doychak, J., Smialek, J.L., and Mitchell, T.E. Transient Oxidation of Single-Crystal Nickel-Aluminum (β -NiAl). Metall. Trans. A 20 (1989): 499.
- Dry, M.E. Anderson, J.R., and Boudart (Eds.), M. Catalysis Science and Technology. Vol. 1, New York: Springer-Verlag, 1981, p. 159.
- Duvenhage, D.J., and Coville, N.J. Effect of K, Mn and Cr on the Fischer-Tropsch activity of Fe:Co/TiO₂ catalysts. Catal. Lett. 104 (2005): 129-133.
- Dynys, F.W., and Halloran, J.W. Alpha alumina Formation in Alum-Derived Gamma Alumina. J. Am. Ceram. Soc. 65 (1982): 442-448.
- El-Shobaky, H.G., Mokhtar, M., and El-Shobaky, G.A. Physicochemical surface and catalytic properties of CuO–ZnO/Al₂O₃ system. Appl. Catal. A 180 (1999): 335-344.
- Ernst, B., Libs, S., Chaumette, P., and Kiennemann, A. Preparation and characterization of Fischer–Tropsch active Co/SiO₂ catalysts. Appl. Catal. A 186 (1999): 145-168.
- Ernst, F., Pirouz, P., and Heuer, A.H. HRTEM Study of a Cu-Al₂O₃ Interface. Philos. Mag. A 63 (1991): 259-77.
- Farrauto, R.J. and Bartholomew, C.H. Fundamentals of industrial catalytic processes. 1 st ed. London: Chapman & Hall, 1997.
- Gitzen W.H. Alumina as a ceramic material, 1970.
- Goellner, J.F., and Gates, B.C. Synthesis and characterization of site-isolated hexarhodium clusters on titania powder. J. Phys. Chem. B 105 (2001): 3269-3281.
- Hahn, T (Ed.). International Tables of Crystallography. Vol. A. London, U.K.: Kluwer, 1995.
- Hosseini, S.A., Taeb, A., and Feyzi, F. Evaluation of Ru-promoted Co/ γ -Al₂O₃ catalysts in Fischer–Tropsch synthesis in a CSTR. Catal. Commun. 6 (2005): 233-240.

- Iglesia, E. Design, synthesis, and use of cobalt-based Fischer-Tropsch synthesis catalysts. Appl. Catal. 161 (1997): 59-78.
- Inoue, M., Kominami, H., and Inui, T. Novel Synthesis Method for The Thermally Stable Zirconia : Hydrolysis of Zirconium Alkoxide at High Temperature With a Limited Amount of Water Dissolved in Inert Organic Solvent from The Gas Phase. Appl. Catal. A 121 (1995): L1-L5.
- Inoue, M., Kominami, H., and Inui, T. Novel Synthesis Method for The Catalytic Use of Thermally Stable Zirconia: Thermal Decomposition of Zirconium Alkoxide in Organic Media. Appl. Catal. A 77 (1993): L25-L30.
- Inoue, M., Kominami, H., and Inui, T. Thermal Decomposition of alkoxides in an inert organic solvent : nevel method for the synthesis of homogeneous mullite precursor. J. Am. Ceram. Soc. 75 (1996): 2597-98.
- Inoue, M., Kominami, H., and Inui, T. Thermal Reaction of Aluminum Alkoxide in Glycol. J. Am. Ceram. Soc. 73 (1990): 1100-1102.
- Inoue, M., Kominami, H., and Inui, T. Thermal Reaction of Aluminum Alkoxide in Various Glycols and the Layer Structure of Their Products. J. Chem. Soc. Dalton Trans. (1991): 3331-3336.
- Inoue, M., Kominami, H., and Inui, T. Thermal Transformation of χ - alumina Formed by Thermal Decomposition of Aluminum Alkoxide in organic Media. J. Am.Ceram. Soc. 75 (1992): 2597-98.
- Inoue, M., Kondo, Y., and Inui, T. Ethylene Glycol Derivative of Boehmite. Inorg. Chem 27 (1988): 215-221.
- Inoue, M., Otsu, H., Kominami, H., and Inui, T. Synthesis of Thermally Stable, Porous Silica-Modified Alumina Via Formation of a Precursor in an Organic Solvent. Ind. Eng. Chem. Res. 35 (1996): 295-306.
- Jacobs, G., Das, T.K., Zhang, Y., Li, J., Racoillet, G., and Davis, B.H. Fischer-Tropsch synthesis: Support, loading, and promoter effects on the reducibility of cobalt catalysts. Appl. Catal. A 233 (2002): 263-281.
- Jager, B., and Espinoza, R. Advances in low temperature Fischer-Tropsch synthesis. Catal. Today 23 (1995): 17-28.
- Jayaram, V., and Levi, C.G. The Structure of δ -Alumina Evolved from the Melt and the γ - δ Transformation. Acta Metall. 37 (1989): 569-78.
- John, C.S., Alma, V.C.M., and Hays, G.R. Characterization of Transition Alumina by

- Solid-State Magic Angle Spinning Aluminum NMR. Appl. Catal. A (1983): 6341-46.
- Johnson, B.G., Bartholomew, C.H., and Goodman, D.W. The role of surface structure and dispersion in CO hydrogenation on cobalt. J. Catal. 128 (1991): 231-247.
- Jongsomjit, B., Panpranot, J., and Goodwin, J.G., Jr. Effect of zirconia-modified alumina on the properties of Co/g-Al₂O₃ catalysts. J. Catal. 215 (2003): 66-77.
- Jongsomjit, B., Sakdamnusun, C., and Praserthdam, P. Dependence of crystalline phases in titania on catalytic properties during CO hydrogenation of Co/TiO₂ catalysts. Mat. Chem. and Phys. 89 (2005): 395-401.
- Jongsomjit, B., Wongsalee, T., and Praserthdam, P. Catalytic behaviors of mixed TiO₂-SiO₂-supported cobalt Fischer-Tropsch catalysts for carbon monoxide hydrogenation. Mat. Chem. and Phys. 97 (2006): 343-350.
- Jongsomjit, B., Wongsalee, T., and Praserthdam, P. Characteristics and catalytic properties of Co/TiO₂ for various rutile:anatase ratios. Catal. Commun. 6 (2005): 705-710.
- Jongsomjit, B., Wongsalee, T., and Praserthdam, P. Study of cobalt dispersion on titania consisting various rutile:anatase ratios. Mater. Chem. Phys. 92 (2005): 572-577.
- Kaplan, W.D., Kenway, P.R., and Brandon, D.G. Polymorphic Basal Twin Boundaries and Anisotropic Growth in α -Al₂O₃. Acta Metall. Mater. 43 (1995): 35-48.
- Kittel, C. Introduction to Solid State Physics. 2nd ed. New York: John Wiley & Sons, 1956.
- Kohn, A., Katz, G., and Broder, J.D. Characterization of β -Ga₂O₃ and its Alumina Isomorph, θ -Al₂O₃. Am. Mineral. 42 (1957): 398-407.
- Kraum, M., and Baerns, M. Fischer-Tropsch synthesis: the influence of various cobalt compounds applied in the preparation of supported cobalt catalysts on their performance. Appl. Catal. A 186 (1999): 189-200.
- Kronberg, M. L. Plastic Deformation of Single Crystals of Sapphire-Basal Slip and Twinning. Acta Metall. 5 (1957): 507-24.
- Kusama, H., Okabe, K., Sayama, K., and Arakawa, H. Ethanol synthesis by catalytic hydrogenation of CO₂ over Rh---Fe/SiO₂ catalysts. Energy 22 (1997): 343-348.
- Levin, I., and Brandon, D. Metastable Alumina Polymorph: Crystal Structures and Transition Sequences. J. Am. Ceram. Soc. 81 (1998): 61.

- Li, S., Krishnamoorthy, S., Li, A., Meitzner, G.D., and Iglesia, E. Promoted Iron-Based Catalysts for the Fischer–Tropsch Synthesis: Design, Synthesis, Site Densities, and Catalytic Properties. *J. Catal.* 206 (2002): 202-217.
- Li, S., Li, A., Krishnamoorthy, S., and Iglesia, E. Effects of Zn, Cu, and K promoters on the structure and on the reduction, carburization, and catalytic behavior of iron-based Fischer-Tropsch synthesis catalysts. *Catal. Lett.* 77 (2001): 197-205.
- Li, T., Yang, Y., Zhang, C., An, X., Wan, H., Tao, Z., Xiang, H., Li, Y., Yi, F., and Xu, B. Effect of manganese on an iron-based Fischer–Tropsch synthesis catalyst prepared from ferrous sulfate. *Fuel* 86 (2007): 921-928.
- Li, X.H., Asami, K., Luo, M.F., Michiki, K., Tsubaki, N., and Fujimoto, K. Direct synthesis of middle iso-paraffins from synthesis gas. *Catal. Today* 84 (2003):59-65.
- Lippens, B. D. and J. H. De. Boer. Study of phase transformations during calcination of aluminum hydroxides by selected area electron diffraction. *Acta crystallogr.* 17 (1964): 1312.
- Liu, P., and Skogsmo, J. Space-Group Determination and Structure Model for κ -Al₂O₃ by Convergent-Beam Electron Diffraction (CBED). *Acta Crystallogr., Sect. B: Struct. Sci.* 47 (1991): 425-33.
- Luo, M., O'Brien, R., and Davis, B.H. Effect of palladium on iron Fischer-Tropsch synthesis catalysts. *Catal. Lett.* 98 (2004): 17-22.
- Martinez, A., Lopez, C., Marquez, F., and Diaz, 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.
- Martinez, A., Lopez, C., Marquez, F., and Duaz, 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.
- Mekasuwandumrong, O., Kominami, H., Praserttham, P., and Inoue, M. Synthesis of thermally stable χ -alumina by thermal decomposition of aluminum isopropoxide in toluene. *J. Am. Ceram. Soc.* 87 (2004a): 1543-1549.
- Mekasuwandumrong, O., Praserttham, P., Inoue, M., Pavarajarn, V., and Tanakulrungsank,W. Phase transformation behavior of nanocrystalline χ -alumina powder obtained by thermal decomposition of AIP in inert organic solvent. *J. mater. Sci.* 39 (2004b): 2417-2421.
- Mekasuwandumrong, O., Silveston, P.L., Praserttham, P., Inoue, M., Pavarajarn, V.,

- and Tanakulrungsank, W. Synthesis of thermally stable micro spherical χ -alumina by thermal decomposition of alumina isopropoxide in mineral oil. Inor. Chem. Comm. 6 (2003): 930-934.
- Mills, G.A. Catalysts for Fuels from Syngas. IEA Coal Research. London, 1988, p. 34.
- Misra, C. Industrial Alumina Chemicals. Washington: ACS Monograph, 1986.
- O'Brien, R.J., and Davis, B.H. Impact of copper on an alkali promoted iron Fischer-Tropsch catalyst. Catal. Lett. 94 (2004): 1-6.
- O'Brien, R.J., Xu, L., Spicer, R.L., Bao, S., Milburn, D.R., and Davis, B.H. Activity and selectivity of precipitated iron Fischer-Tropsch catalysts. Catal. Today 36 (1997): 325-334.
- Othmer, K. Encyclopedia of chemical technology. Vol. 6. 4 th ed. New York: A Wiley-Interscience Publication, John Wiley&Son, 1991.
- Pajonk, G., and Teichner, S. Aerogels. Berlin: Springer, 1986.
- Panpranot, J., Goodwin, J.G., Jr., and Sayari, A. Synthesis and characteristics of MCM-41 supported CoRu catalysts. Catal. Today 77 (2002): 269-284.
- Pauling, L. General Chemistry. 3rd ed. New York: Dover, 1988.
- Perego, C., and Villa, P.L. The catalytic process from laboratory to the industrial plant. In: D. SanFilippo (Ed.), Proceedings of the 3rd Seminar on Catalysis. Rimini, Italy, June 1994, Italian Chemical Society.
- Peri, J.B. Infrared and gravimetric study of the surface hydration of γ -alumina. J. Phys. Chem. 69 (1965): 211-219.
- Pirouz, P., Lawlor, B.F., Geipel, T., Bilde-Sorensen, J.B., Heuer, A.H., and Lagerlof, K.P.D. On Basal Slip and Basal Twinning in Sapphire ($(\alpha\text{-Al}_2\text{O}_3)$ -II. A New Model of Basal Twinning. Acta Metall. Mater. 44 (1996): 2153-64.
- Praserthdam, P., Inoue, M., Mekasuwandumrong, O., Tanakulrungsank, W., and Phatanasri, S. Effect of organic solvents on the thermal stability of porous silica-modified alumina powders prepared via one pot solvothermal synthesis. Inorg. Chem. Commu. 3 (2000): 671-676.
- Ragaini, V., Carli, R., Bianchi, C.L., Lorenzetti, D., Predieri, G., and Moggi, P. Fischer-Tropsch synthesis on alumina-supported ruthenium catalysts II. Influence of morphological factors. Appl. Catal. A 139 (1996): 31-42.
- Rao, V.U.S., Stiegel, G.J., Cinquegrane, G.J., and Srivastava, R.D. Iron-based catalysts for slurry-phase Fischer-Tropsch process: Technology review.

- Fuel Process. Technol. 30 (1992): 83-107.
- Reuel, R.C., and Bartholomew, C.H. The stoichiometries of H₂ and CO adsorption on cobalt: effects of support and preparation. J. Catal. 85 (1984): 63-77.
- Riva, R., Miessner, H., and Piero, G.D. Metal-support interaction in Co/SiO₂ and Co/TiO₂. Appl. Catal. A 196 (2000): 111-123.
- Rothaemel, M., Hanssen, K.F., Blekkan, E.A., Schanke, D., and Holmen, A.
The effect of water on cobalt Fischer-Tropsch catalysts studied by steady-state isotopic transient kinetic analysis (SSITKA). Catal. Today 38 (1997): 79-84.
- Sarikaya, Y., Sevinc, I., and Akinc, M. The effect of calcinations temperature on some of the adsorptive properties of fine alumina powders obtained by emulsion evaporation technique. Powder Technol. 116 (2001): 109-114.
- Scott, W.B., and Matijevic, E. J. Colloid Interf. Sci. 66 (1978): 447.
- Sevinc, I., Sarikaya, Y., and Akinc, M. Ceram. Int. 1 (1991): 17.
- Shirasuka, K., Yanagida, H., and Yamaguchi, G. The Preparation of η- Alumina and Its Structure. Yogyo Kyokai-shi 84 (1976): 610-13.
- Steynberg, A., and Dry, M. Fischer-Tropsch Technology. Amsterdam, Netherlands: Elsevier, 2004. p.3.
- Steynberg, A.P., Dry, M.E., Davis, B.H., and Breman, B.B. Fischer-Tropsch Technology Study, Surface Science and Catalysis. 152 (2004) 64.
- Storch, Golumbic, and Anderson, The Fischer-Tropsch and related synthesis. New York: John Wiley & Sons.
- Storch, H., Golumbic, N., and Anderson, R.B. Fischer-Tropsch and Related Synthesis. New York: Wiley, 1951.
- Stumpf, H.C., Russell, A.S., Newsome, J.W., and Tucker, C.M. Thermal Transformations of Aluminas and Alumina Hydrates. Ind. Eng. Chem. 42 (1950): 1398-403.
- Tsubaki, N., Sun, S., and Fujimoto, K. Different Functions of the Noble Metals Added to Cobalt Catalysts for Fischer-Tropsch Synthesis. J. Catal. 199 (2001): 236-246.
- Van der laan, G.P., and Beenackers, A.A.C.M. Kinetics and Selectivity of the Fischer-Tropsch Synthesis: A Literature Review. Catal. Rev.-Sci. Eng. 41 (3&4) (1999): 255-318.
- Wan, H.J., Wu, B.S., Zhang, C.H., Xiang, H.W., Li, Y.W., Xu, B.F., and Yi, F.
Comparative study of iron-based Fischer-Tropsch synthesis catalyst promoted with potassium or sodium. Catal. Commu., Articles in press.

- Wilson, S J. Phase Transformations and Development of Microstructure in Boehmite-Derived Transition Aluminas. Proc. Br. Ceram. Soc. 28 (1979): 281-94.
- Wilson, S. J. Phase transformations and development of microstructure in-derived transition aluminas. Proc. Br. Ceram. Soc. 28 (1979): 281-94.
- Xiong, H., Zhang, Y., Liew, K., and Li, J. Catalytic performance of zirconium-modified Co/Al₂O₃ for Fischer–Tropsch synthesis. J. of Molecular Catal. A: Chemical 231 (2005): 145-151.
- Xu, J., Bartholomew, C.H. Temperature-programmed hydrogenation (TPH) and in situ moëssbauer spectroscopy studies of carbonaceous species on silica-supported iron fischer-tropsch catalysts. J. Phys. Chem. B 109 (2005): 2392-2403.
- Young, R.S. COBALT: Its Chemistry, Metallurgy, and Uses. New York: Reinhpld Publishing Corporation, 1960.
- Zhang, C.H., Wan, H.J., Yang, Y., Xiang, H.W., and Li, Y.W. Study on the iron–silica interaction of a co-precipitated Fe/SiO₂ Fischer–Tropsch synthesis catalyst. Catal. Commun. 7 (2006): 733-738.
- Zhang, C.H., Yang, Y., Teng, B.T., Li, T.Z., Zheng, H.Y., Xiang, H.W., and Li, Y.W. Study of an iron-manganese Fischer-Tropsch synthesis catalyst promoted with copper. J. Catal. 237 (2006): 405-415.
- Zhang, J., Chen, J., Ren, J., Li, Y., and Sun, Y. Support effect of Co/Al₂O₃ catalysts for Fischer–Tropsch synthesis. Fuel 82 (2003): 581-586.
- Zhang, Y., Wei, D., Hammache, S., and Goodwin, J.G., Jr. Effect of water vapor on the reduction of Ru-promoted Co/Al₂O₃. J. Catal. 188 (1999): 281-290.
- Zhou, R.S., and Snyder, R.L. Structures and Transformation Mechanisms of the η , γ and θ Transition Aluminas. Acta Crystallogr., Sect. B: Struct. Sci. 47 (1991): 617-30.
- Zyl, V. Iron-based copper-containing catalyst. U.S. patent (2004), p.1
CODEN: WO 2004/047986 A1.

APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Calculation for the preparation of cobalt loading catalyst

Preparation of Co/Al₂O₃ with different Co loadings (5, 10, 15, and 20 wt%) by the incipient wetness impregnation method are shown as follows:

Reagent: - Cobalt (II) nitrate hexahydrate (Co(NO₃)₂ · 6H₂O)
 Molecular weight = 290.93 g/mol
 - Support: - Solvothermal synthesized-alumina support

Calculation:

5% Co/Al₂O₃

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:

Cobalt = 5 g
 Alumina = 100-5 = 95 g

For 2 g of alumina

Cobalt required = $2 \times (5/95)$ = 0.11 g

Cobalt 0.11 g was prepared from Co(NO₃)₂ · 6H₂O and molecular weight of Co is 58.93

$$\begin{aligned} \text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O required} &= \frac{\text{MW of Co(NO}_3)_2 \cdot 6\text{H}_2\text{O} \times \text{cobalt required}}{\text{MW of Co}} \\ &= (290.93/58.93) \times 0.11 = 0.54 \text{ g} \end{aligned}$$

Since the pore volume of the alumina support is 2.0 ml/g, 1.8 ml/g, 1.6 ml/g, and 1.3 ml/g for alumina support prepared with AIP 10 g, 15 g, 25 g, and 35 g, respectively. Thus, the total volume of impregnation solution which must be used is 4 ml for alumina support prepared with AIP 10 g, 3.6 ml for alumina support prepared with AIP 15 g, 3.2 ml for alumina support prepared with AIP 25 g, and 2.6 ml for alumina support prepared with AIP 35 g by the requirement of incipient wetness

impregnation method, the de-ionized water is added until equal pore volume for dissolve Cobalt (II) nitrate hexahydrate.

The others cobalt loading (10, 15, and 20 wt%) are calculated in the same method with calculation for 5% Co/Al₂O₃.

Calculation for the preparation of iron loading catalyst (Based catalyst)

Preparation of 1%Cu/20%Fe/Al₂O₃ by the sequential incipient wetness impregnation method is shown as follows:

- Reagent:**
- Iron (III) nitrate nonahydrate (Fe(NO₃)₃ · 9H₂O)
Molecular weight = 403.99 g/mol
 - Copper (II) nitrate trihydrate (Cu(NO₃)₂ · 3H₂O)
Molecular weight = 241.60 g/mol
 - Support: - Commercial γ-alumina support

Calculation:

1%Cu/20%Fe/Al₂O₃

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:

$$\begin{aligned} \text{Iron} &= 20 \text{ g} \\ \text{Copper} &= 1 \text{ g} \\ \text{Alumina} &= 100-20-1 = 79 \text{ g} \end{aligned}$$

For 5 g of alumina

$$\text{Iron required} = 5 \times (20/79) = 1.27 \text{ g}$$

Iron 1.27 g was prepared from Fe(NO₃)₃ · 9H₂O and molecular weight of Fe is 55.847

$$\begin{aligned} \text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O required} &= \frac{\text{MW of Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O} \times \text{iron required}}{\text{MW of Fe}} \\ &= (403.99/55.847) \times 1.27 = 9.19 \text{ g} \end{aligned}$$

$$\text{Copper required} = 5 \times (1/79) = 0.063 \text{ g}$$

Copper 0.063 g was prepared from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and molecular weight of Cu is 63.546

$$\begin{aligned} \text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \text{ required} &= \frac{\text{MW of Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \times \text{iron required}}{\text{MW of Cu}} \\ &= (241.60/63.546) \times 0.063 = 0.24 \text{ g} \end{aligned}$$

Since the pore volume of the alumina support is 1.0 ml/g for commercial γ -alumina support. Thus, the total volume of impregnation solution which must be used is 5 ml for commercial γ -alumina support by the requirement of incipient wetness impregnation method, the de-ionized water is added until equal pore volume for dissolve Iron (III) nitrate nonahydrate and Copper (II) nitrate trihydrate.

Calculation for the preparation of Cu-modified alumina iron loading catalyst

Preparation of Cu-modified alumina having 10 wt% of Cu by the incipient wetness impregnation method is shown as follows:

Reagent: - Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$)
Molecular weight = 241.60 g/mol
- Support: - Commercial γ -alumina support

Calculation:

10% Cu/ Al_2O_3

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:

$$\begin{aligned} \text{Copper} &= 10 \text{ g} \\ \text{Alumina} &= 100-10 = 90 \text{ g} \end{aligned}$$

For 5 g of alumina

$$\text{Copper required} = 5 \times (10/90) = 0.55 \text{ g}$$

Copper 0.55 g was prepared from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and molecular weight of Cu is 63.546

$$\begin{aligned} \text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O required} &= \frac{\text{MW of Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O} \times \text{copper required}}{\text{MW of Cu}} \\ &= (241.60/63.546) \times 0.55 = 2.09 \text{ g} \end{aligned}$$

Since the pore volume of the alumina support is 1.0 ml/g for commercial γ -alumina support. Thus, the total volume of impregnation solution which must be used is 5 ml for commercial γ -alumina support by the requirement of incipient wetness impregnation method, the de-ionized water is added until equal pore volume for dissolve Copper (II) nitrate trihydrate.

Preparation of Cu-modified alumina iron loading catalysts by the incipient wetness impregnation method is shown as follows:

- *1%Cu-promoted 20%Fe/10%Cu/Al₂O₃*

Reagent:

- Iron (III) nitrate nonahydrate (Fe(NO₃)₃ · 9H₂O)
Molecular weight = 403.99 g/mol
- Copper (II) nitrate trihydrate (Cu(NO₃)₂ · 3H₂O)
Molecular weight = 241.60 g/mol
- Support: - 10% Cu/Al₂O₃

Calculation:

1%Cu/20%Fe/10%Cu/Al₂O₃

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:

Iron	=	20 g	
Copper	=	1 g	
10%Cu/Al ₂ O ₃	=	100-20-1	= 79 g

For 5 g of 10%Cu/Al₂O₃

Iron required = $5 \times (20/79) = 1.27 \text{ g}$

Iron 1.27 g was prepared from Fe(NO₃)₃ · 9H₂O and molecular weight of Fe is 55.847

$$\begin{aligned} \text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O required} &= \frac{\text{MW of Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O} \times \text{iron required}}{\text{MW of Fe}} \\ &= (403.99/55.847) \times 1.27 = 9.19 \text{ g} \end{aligned}$$

$$\text{Copper required} = 5 \times (1/79) = 0.063 \text{ g}$$

Copper 0.063 g was prepared from $\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and molecular weight of Cu is 63.546

$$\begin{aligned} \text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O required} &= \frac{\text{MW of Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O} \times \text{iron required}}{\text{MW of Cu}} \\ &= (241.60/63.546) \times 0.063 = 0.24 \text{ g} \end{aligned}$$

The de-ionized water is added until equal pore volume of 10%Cu/Al₂O₃ for dissolve Iron (III) nitrate nonahydrate and Copper (II) nitrate trihydrate.

- 20%Fe/10%Cu/Al₂O₃ (without 1%Cu-promoted)

Reagent: - Iron (III) nitrate nonahydrate ($\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$)
Molecular weight = 403.99 g/mol
- Support: - 10% Cu/Al₂O₃

Calculation:

20%Fe/10%Cu/Al₂O₃

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:

$$\begin{aligned} \text{Iron} &= 20 \text{ g} \\ 10\% \text{Cu/Al}_2\text{O}_3 &= 100 - 20 = 80 \text{ g} \end{aligned}$$

For 5 g of 10%Cu/Al₂O₃

$$\text{Iron required} = 5 \times (20/80) = 1.25 \text{ g}$$

Iron 1.25 g was prepared from $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and molecular weight of Fe is 55.847

$$\begin{aligned}\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O required} &= \frac{\text{MW of Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O} \times \text{iron required}}{\text{MW of Fe}} \\ &= (403.99/55.847) \times 1.25 = 9.04 \text{ g}\end{aligned}$$

The de-ionized water is added until equal pore volume of 10%Cu/Al₂O₃ for dissolve Iron (III) nitrate nonahydrate.

APPENDIX B

CALCULATION OF BET SURFACE AREA BY THE SINGLE POINT METHOD

From Brunauer-Emmett-Teller (BET) equation:

$$\frac{X}{V(1-X)} = \frac{1}{V_m C} + \frac{(C-1)X}{V_m C} \quad (\text{B.1})$$

Where: X = relative partial pressure of N_2 , P/P_0

P_0 = saturated vapor pressure of N_2 (or adsorbed gas) at the experimental temperature

P = equilibrium vapor pressure of N_2

V = volume of gas adsorbed at a pressure P ; ml at the NTP/ g of sample

V_m = volume of gas adsorbed at monolayer, ml. at the NTP / g of sample

C = constant

Assume $C \rightarrow \infty$, then

$$\frac{X}{V(1-X)} = \frac{X}{V_m} \quad (\text{B.2})$$

$$V_m = V (1-P/P_0)$$

From the gas law,

$$\frac{P_b V}{273} = \frac{P_t V}{T} \quad (\text{B.3})$$

Where: V = constant volume

P_b = pressure at 0°C

P_t = pressure at $t^\circ\text{C}$

$T = 273.15 + t$, K

$$P_1 = 1 \text{ atm} \quad \text{and thus,} \quad P_b = (273.15 / T)$$

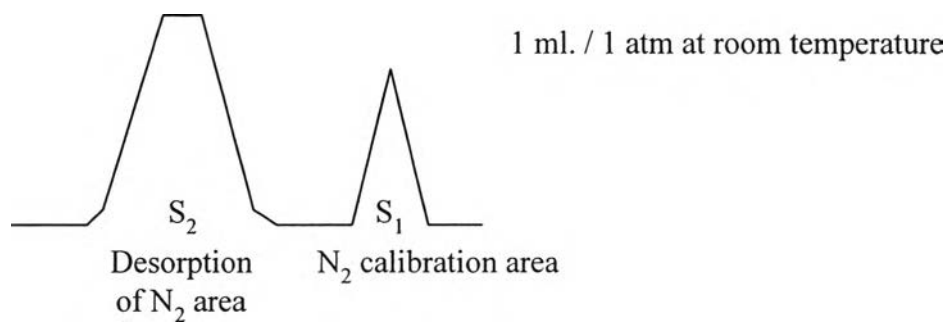
Partial pressure of Nitrogen:

$$\begin{aligned} P &= \frac{[\text{Flow of (He+N}_2\text{)} - \text{Flow of He}]}{\text{Flow of (He+N}_2\text{)}} & \text{(B.4)} \\ &= 0.3 \text{ atm} \end{aligned}$$

N₂ saturated vapor pressure, P_o = 1.1 atm

$$p = P / P_o = P / 1.1 = 0.3/1.1 = 0.2727$$

How to measure V



$$V = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \text{ ml. / g of catalyst} \quad \text{(B.5)}$$

Where, S₁ = Nitrogen 1 ml/1 atm of room temperature area

S₂ = Desorption of nitrogen area

W = Weight of the sample (g)

T = Room temperature (K)

Therefore,

$$\begin{aligned} V_m &= \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times (1-p) \\ V_m &= \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 0.7273 & \text{(B.6)} \end{aligned}$$

Surface area of catalyst:

$$S = \frac{N\sigma V_m}{M}$$

Where, N = Avogadro number = 6.02×10^{23}

σ = area occupied by one molecule of adsorbed nitrogen = 16.2×10^{-20}

M = volume of one mole nitrogen = $22410 \text{ cm}^3/\text{mol}$

Then,

$$S = 4.352 V_m$$

$$S = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 0.7273 \times 4.352$$

$$S = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 3.1582 \quad (\text{B.7})$$



APPENDIX C

CALCULATION FOR TOTAL H₂ CHEMISORPTION AND DISPERSION

Calculation of the total H₂ chemisorption and metal dispersion of the catalyst, a stoichiometry of H/Co = 1, measured by H₂ chemisorption is as follows:

Let the weight of catalyst used	=	W	g
Integral area of H ₂ peak after adsorption	=	A	unit
Integral area of 45 μl of standard H ₂ peak	=	B	unit
Amounts of H ₂ adsorbed on catalyst	=	B-A	unit
Concentration of Co (by AAS)	=	C	% wt
Volume of H ₂ adsorbed on catalyst	=	45×[(B-A)/B]	μl
Volume of 1 mole of H ₂ at 100°C	=	28.038	μl
Mole of H ₂ adsorbed on catalyst	=	[(B-A)/B]×[45/28.038]	μmole
Total hydrogen chemisorption	=	[(B-A)/B]×[45/28.038]×[1/W]	μmole /g of catalyst
	=	N	μmole /g of catalyst
Molecular weight of cobalt	=	58.93	
Metal dispersion (%)	=	$\frac{2 \times H_2 \text{ tot/g of catalyst} \times 100}{\text{No } \mu\text{mole Co}_{\text{tot}}/\text{g of catalyst}}$	
	=	$\frac{2 \times N \times 100}{\text{No } \mu\text{mole Co}_{\text{tot}}}$	
	=	$\frac{2 \times N \times 58.93 \times 100}{C \times 10^6}$	
	=	$\frac{1.179 \times N}{C}$	

APPENDIX D

CALCULATION FOR TOTAL CO CHEMISORPTION

Calculation of the total CO chemisorption of the catalyst, a stoichiometry of CO/Fe = 1, measured by CO chemisorption is as follows:

Let the weight of catalyst used	=	W	g
Integral area of CO peak after adsorption	=	A	unit
Integral area of 50 μ l of standard H ₂ peak	=	B	unit
Amounts of CO adsorbed on catalyst	=	B-A	unit
Concentration of Fe (by AAS)	=	C	% wt
Volume of CO adsorbed on catalyst	=	$50 \times [(B-A)/B]$	μ l
Volume of 1 mole of CO at 50°C	=	24.86	μ l
Mole of CO adsorbed on catalyst	=	$[(B-A)/B] \times [50/24.86]$	μ mole
Total CO chemisorption	=	$[(B-A)/B] \times [50/24.86] \times [1/W]$	μ mole /g of catalyst
	=	N	μ mole /g of catalyst

APPENDIX E

CALIBRATION CURVES

CO hydrogenation reaction

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 C₂-C₄ 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 chromatograms of catalyst sample are shown in Figure E.1.

The VZ10 column are used with a gas chromatography equipped with a flame ionization detector, Shimadzu modal 14B, to analyze the concentration of products including of methane, ethane, ethylene, propane, propylene and butane. The chromatograms of catalyst sample are shown in Figure E.2. Conditions uses in both GC are illustrated in Table E.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.

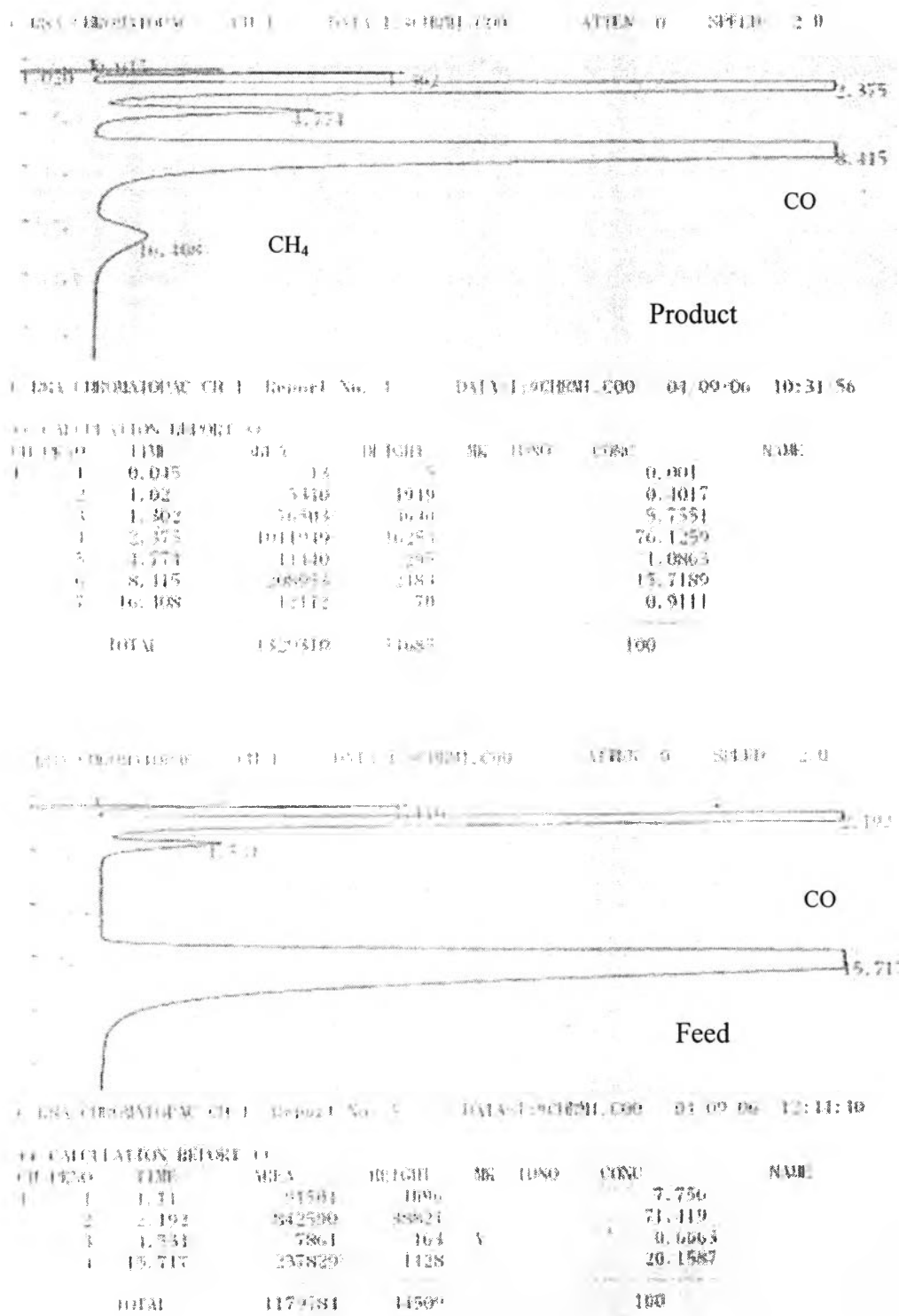


Figure E.1 The chromatograms of catalyst sample from thermal conductivity detector, gas chromatography Shimadzu model 8A (Molecular sieve 5A column).

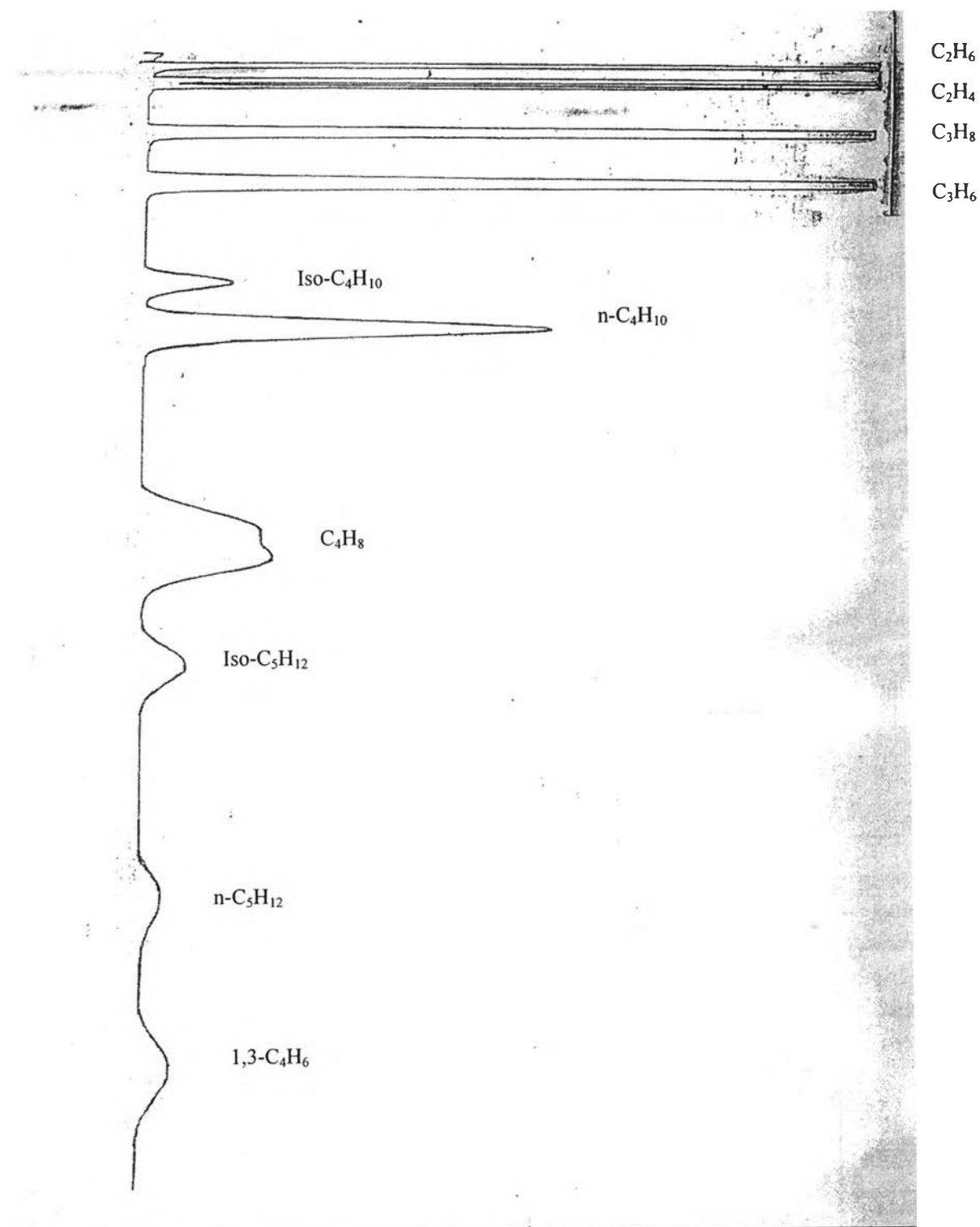


Figure E.2 The chromatograms of catalyst sample from flame ionization detector, gas chromatography Shimadzu modal 14B (VZ10 column).

Table E.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

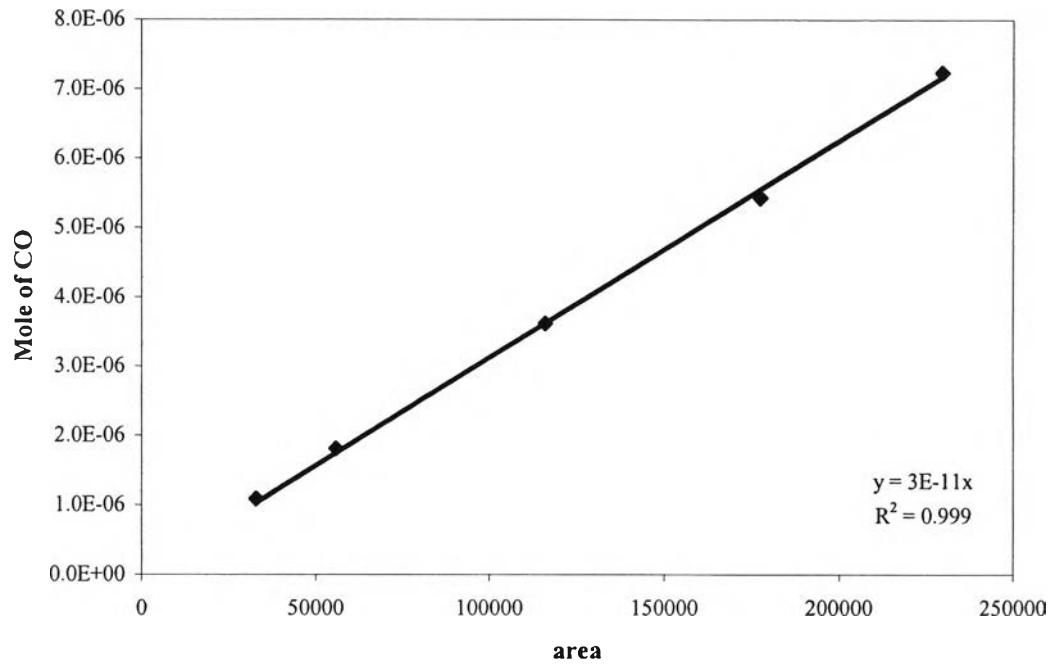


Figure E.3 The calibration curve of CO.

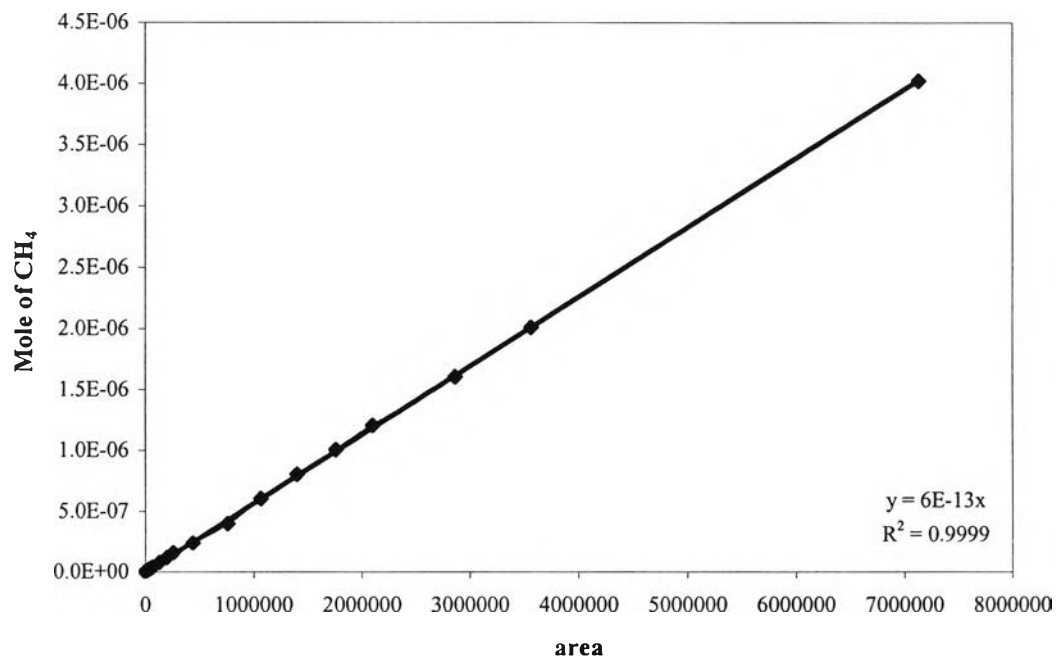


Figure E.4 The calibration curve of methane.

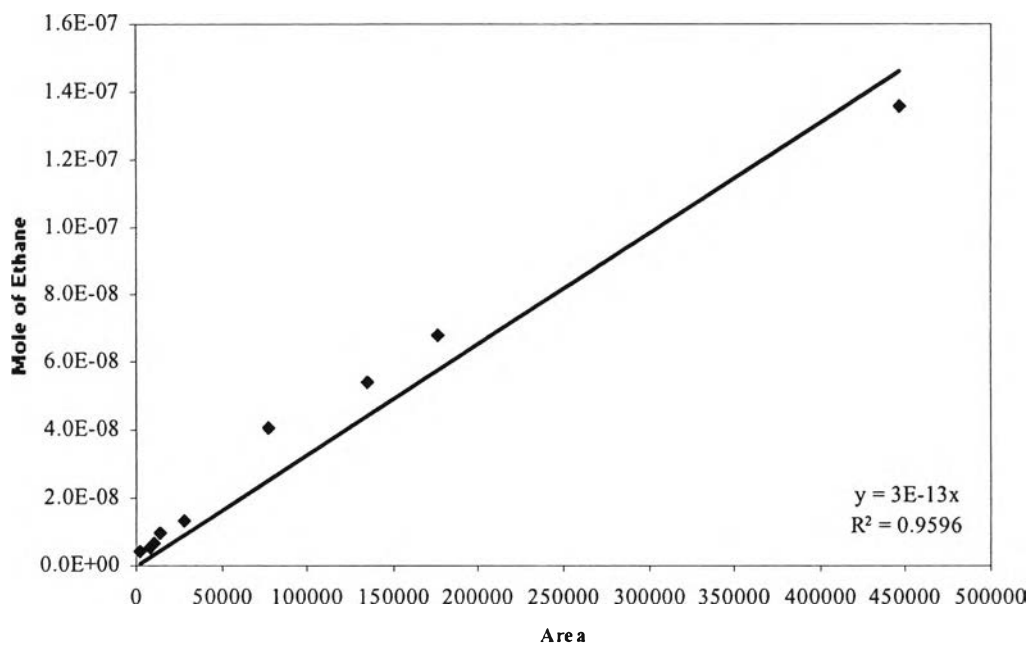


Figure E.5 The calibration curve of ethane.

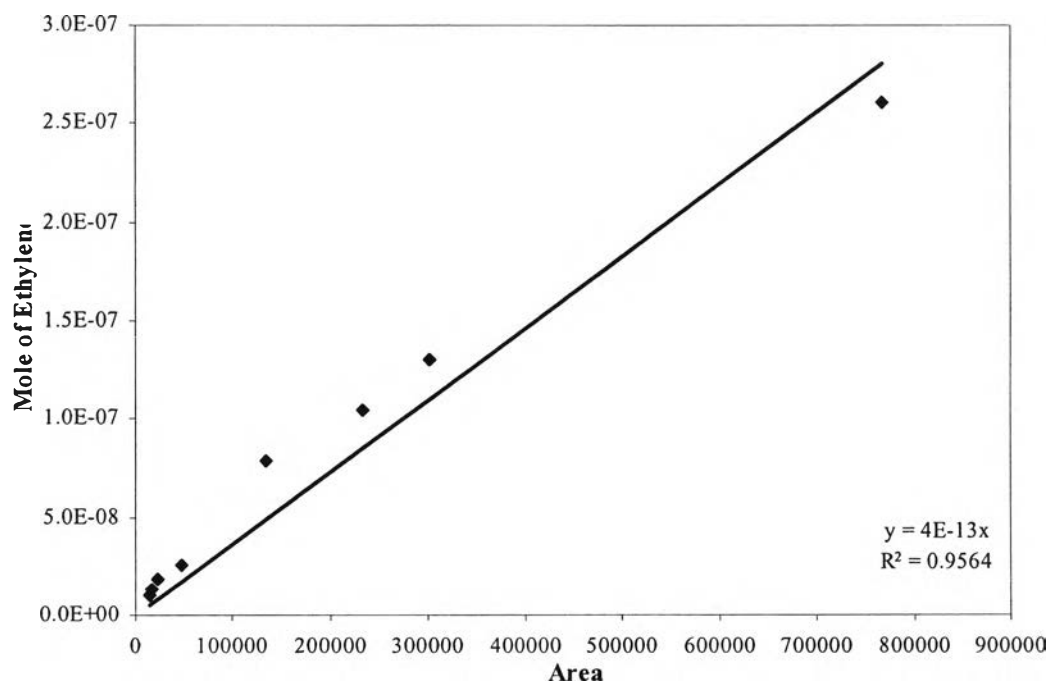


Figure E.6 The calibration curve of ethylene.

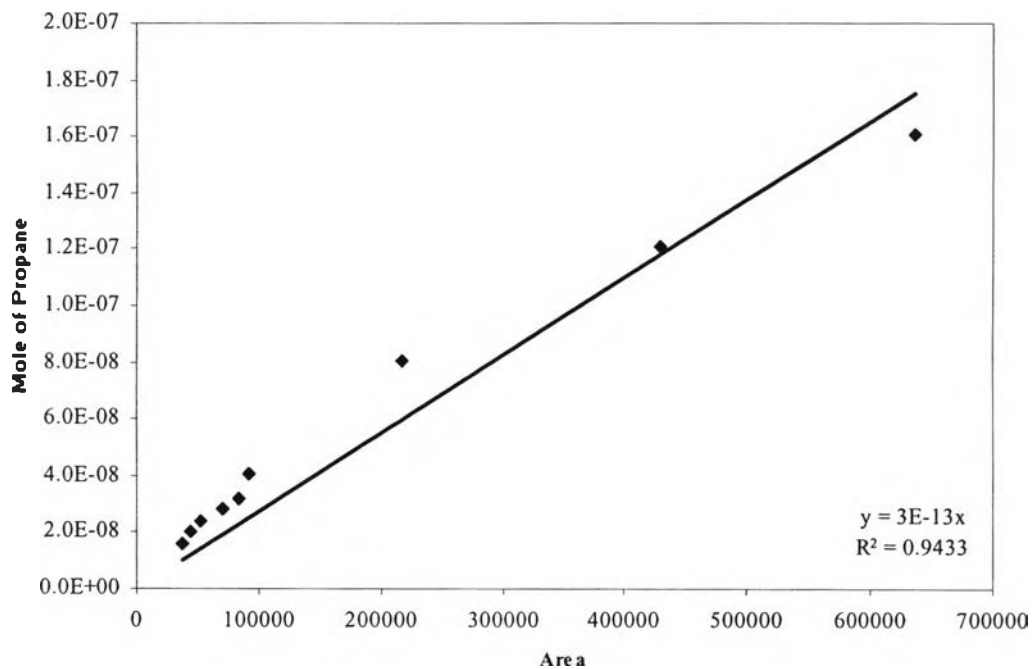


Figure E.7 The calibration curve of propane.

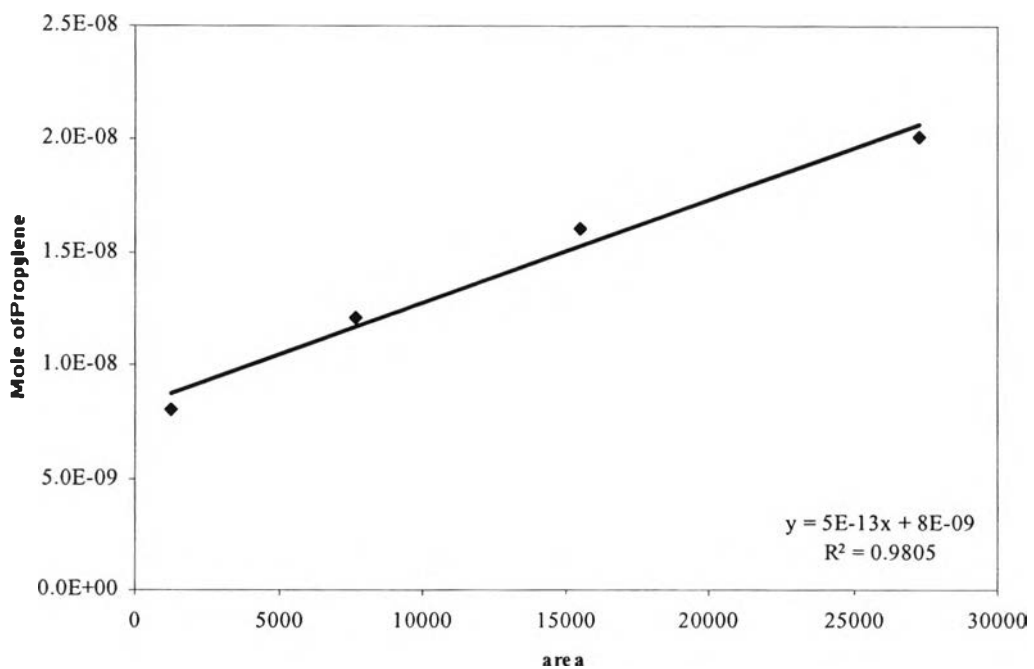


Figure E.8 The Calibration curve of propylene.

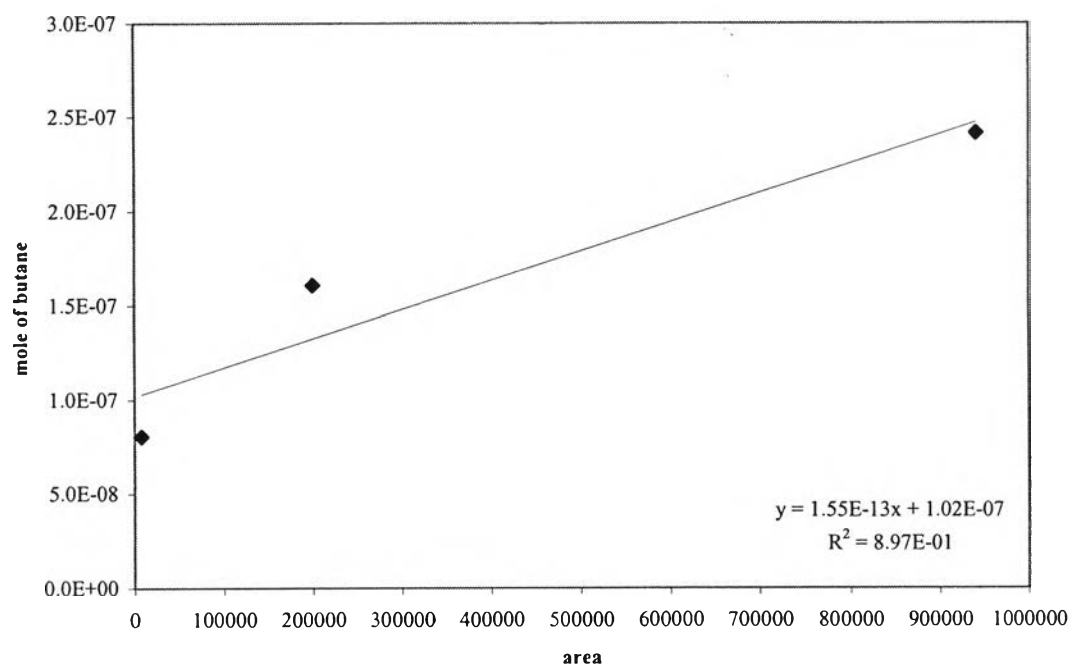


Figure E.9 The calibration curve of butane.

Fischer-Tropsch Synthesis reaction

This appendix showed the calibration curves for calculation of composition of reactant and products in FTS reaction. The reactant is CO. The products are hydrocarbons of C₁-C₇⁺ (such as methane, ethane, ethylene, propane, propylene, butane, butene, pentane, pentene, hexane, hexene, heptane, and heptene) and CO₂.

Analysis of CO and CO₂ were performed in a Carbosphere 80/100 6' x 1/8" x 0.085" SS packed column using a thermal conductivity detector. Analysis of hydrocarbon was carried out in a AT-Q 30m x 0.53 mm Heliflex capillary column using a flame ionization detector.

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.

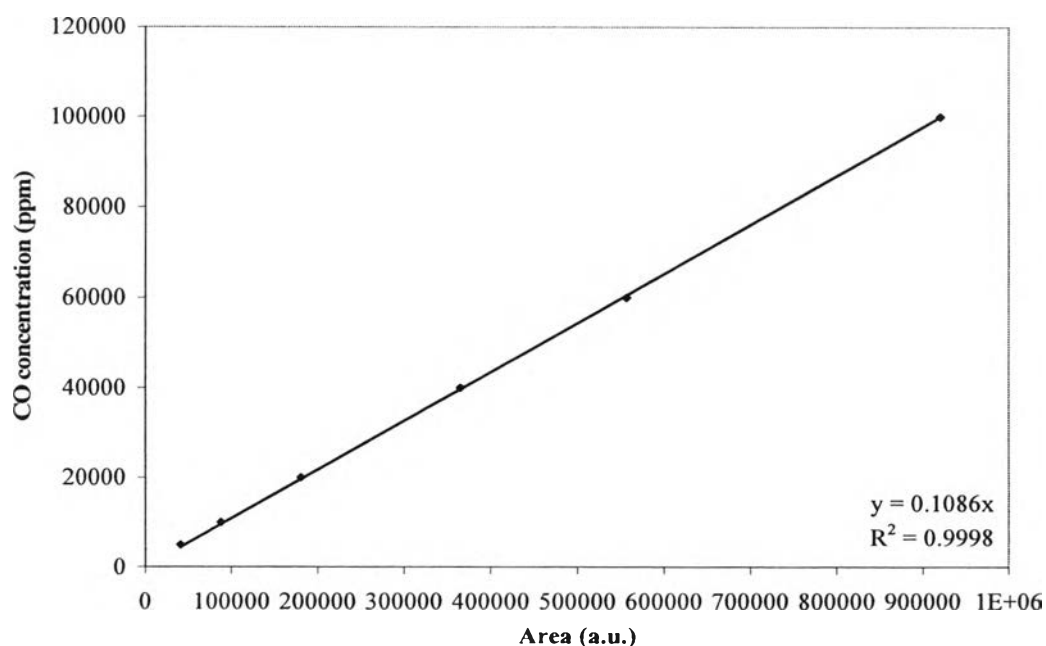


Figure E.10 The calibration curve of CO.

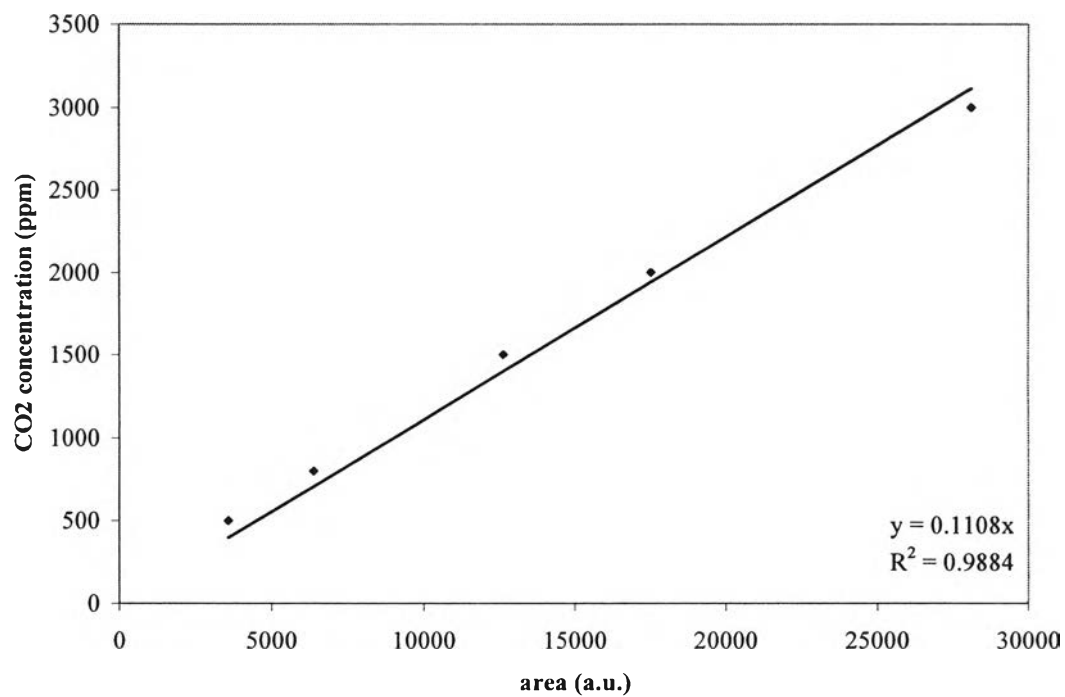


Figure E.11 The calibration curve of CO₂.

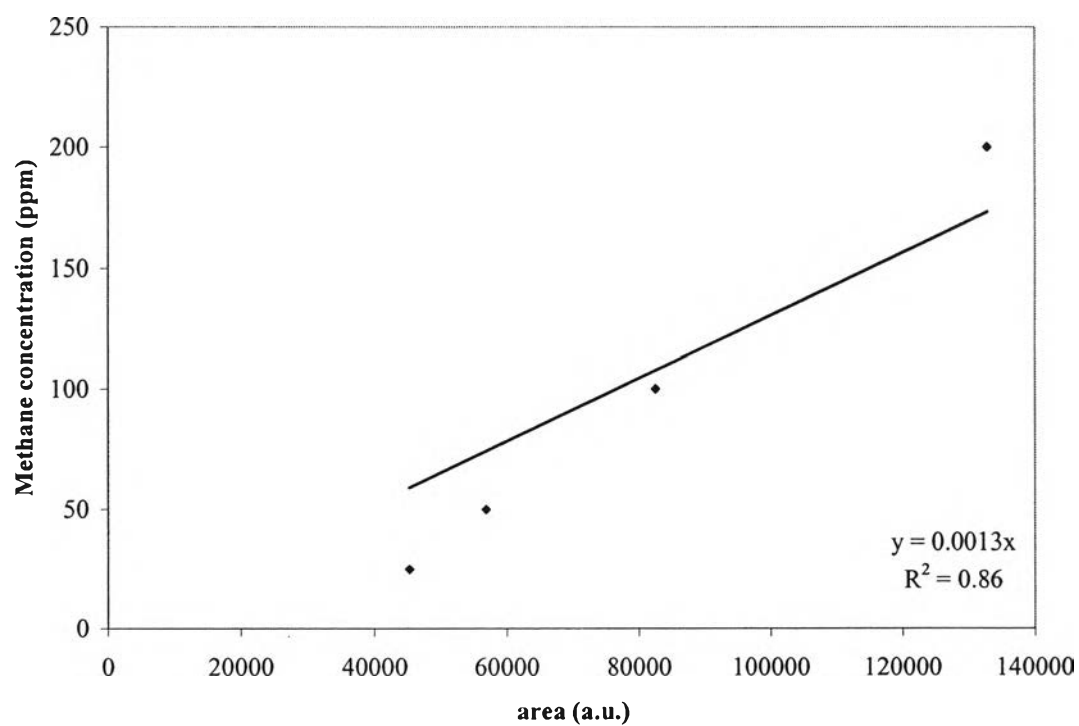


Figure E.12 The calibration curve of methane.

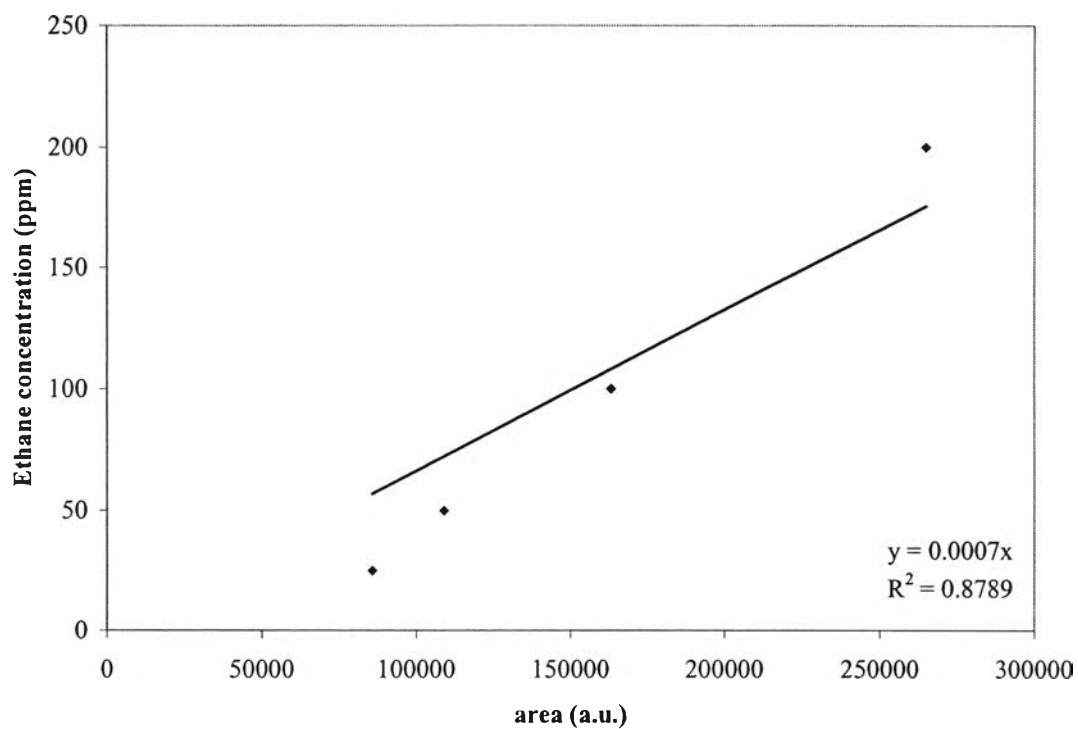


Figure E.13 The calibration curve of ethane.

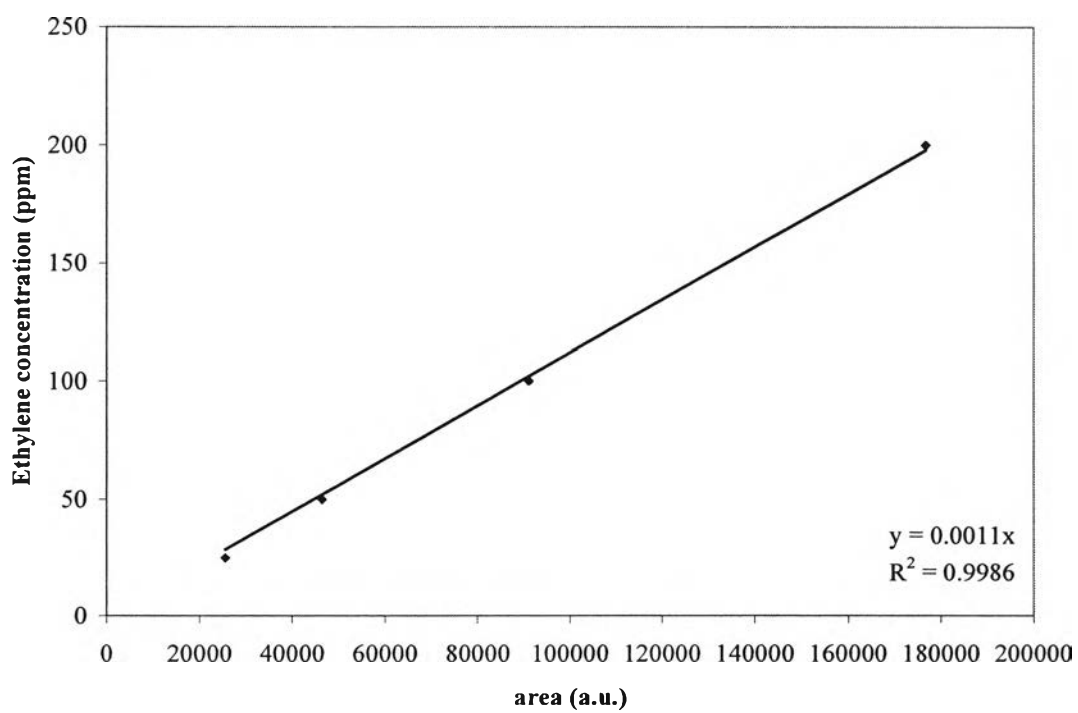


Figure E.14 The calibration curve of ethylene.

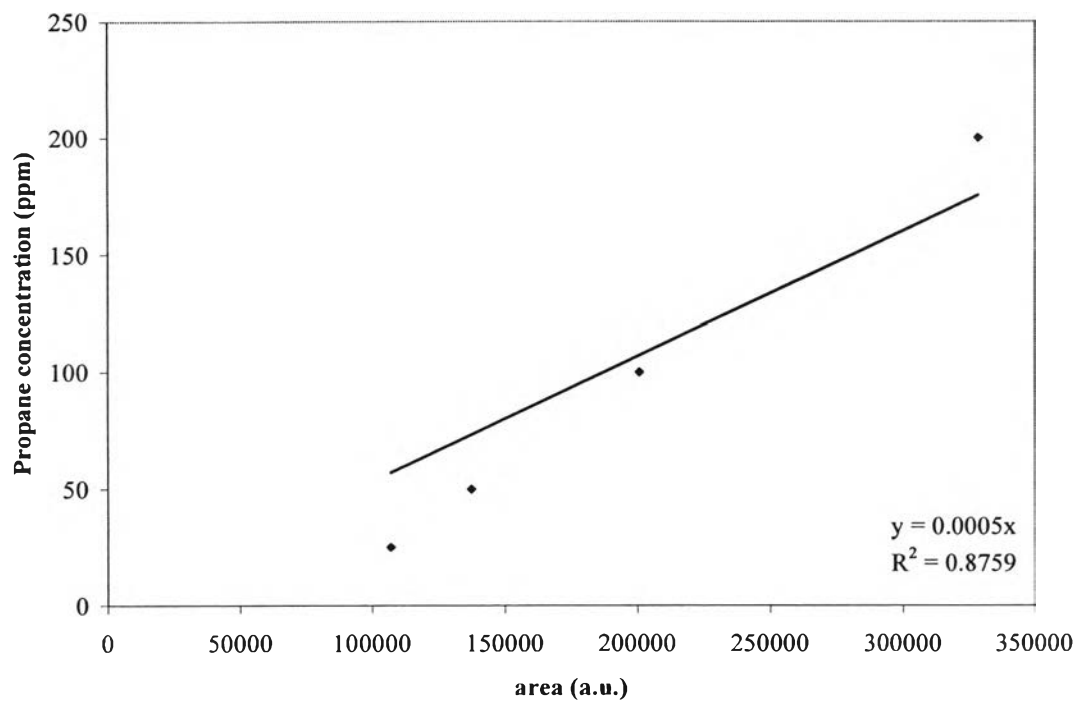


Figure E.15 The calibration curve of propane.

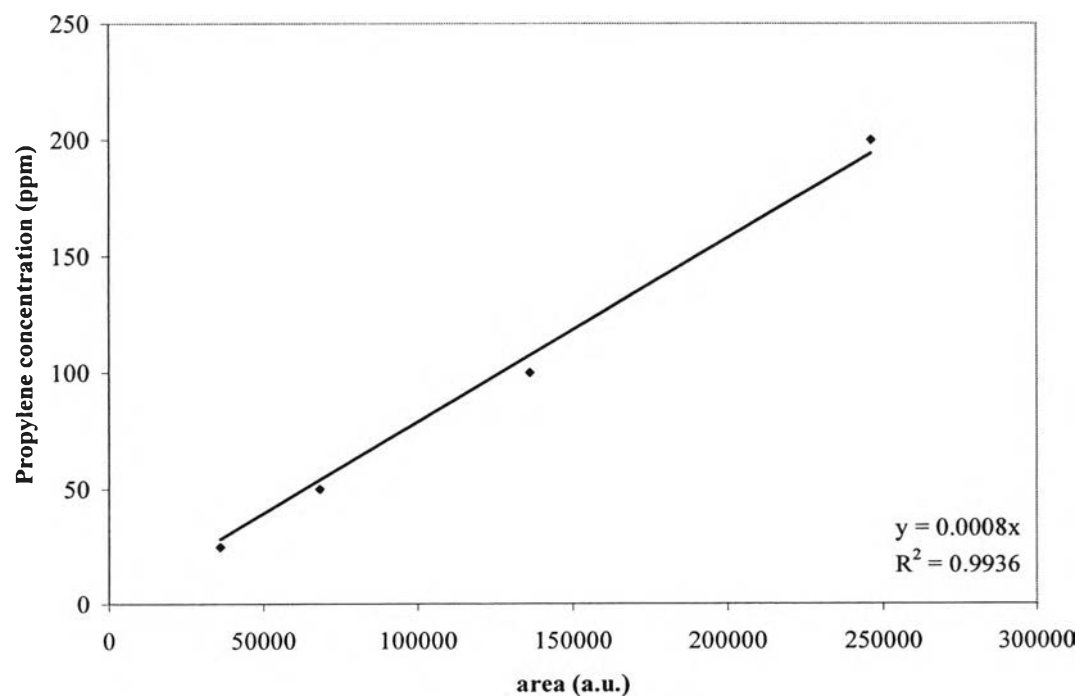


Figure E.16 The Calibration curve of propylene.

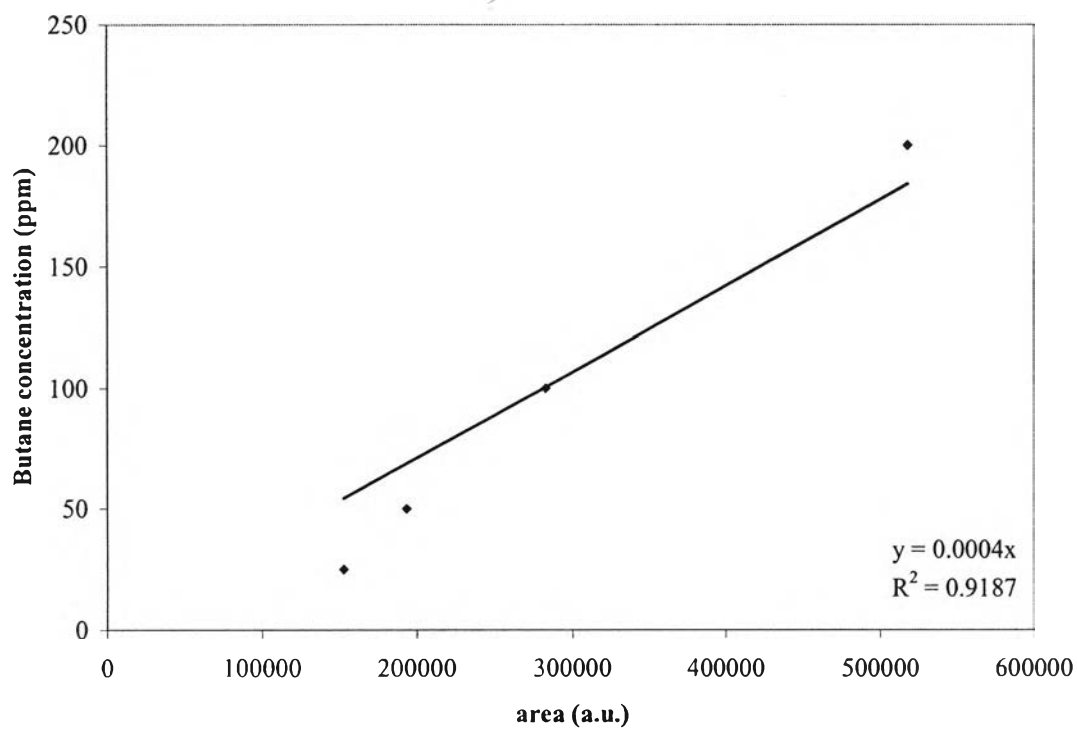


Figure E.17 The calibration curve of butane.

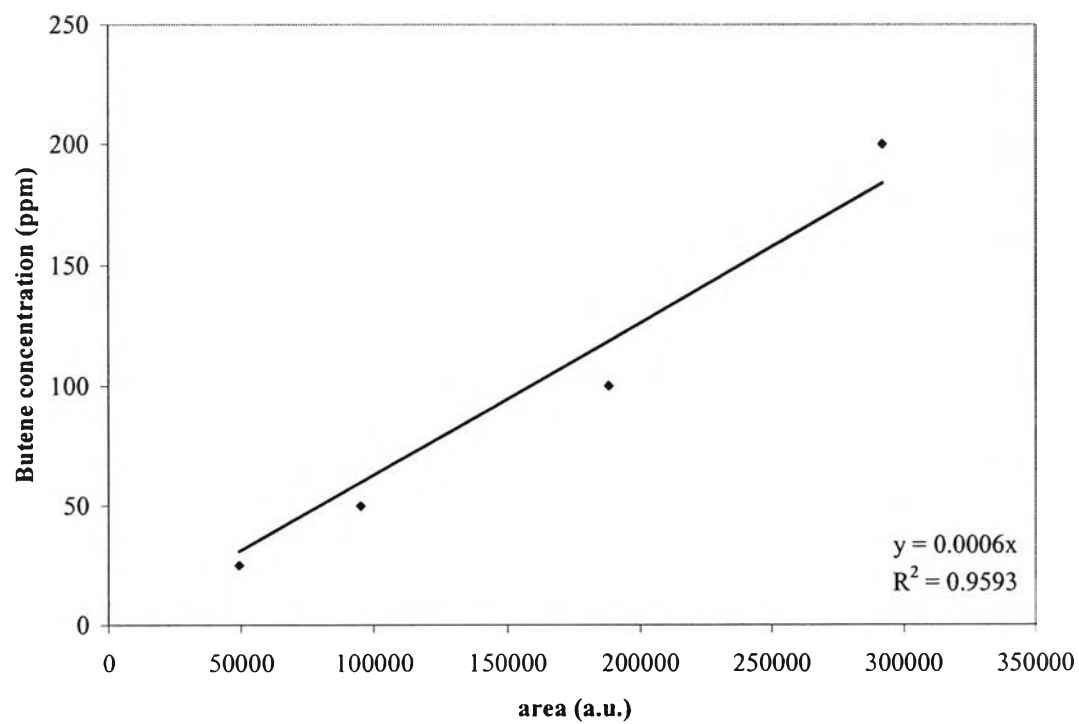


Figure E.18 The calibration curve of butene.

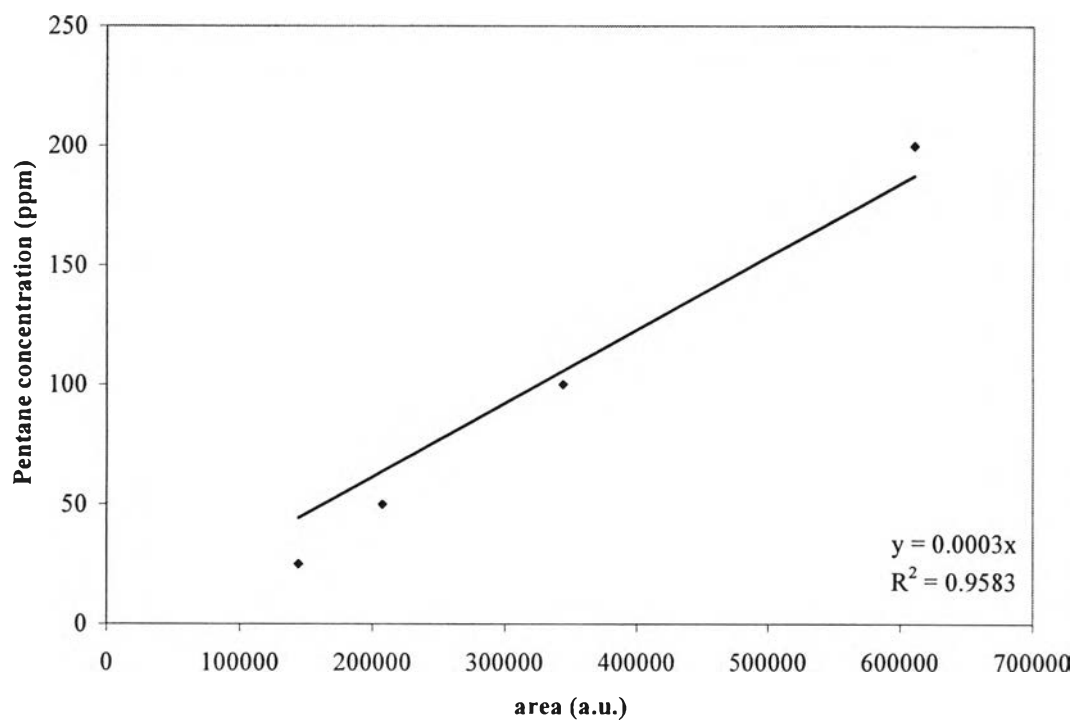


Figure E.19 The calibration curve of pentane.

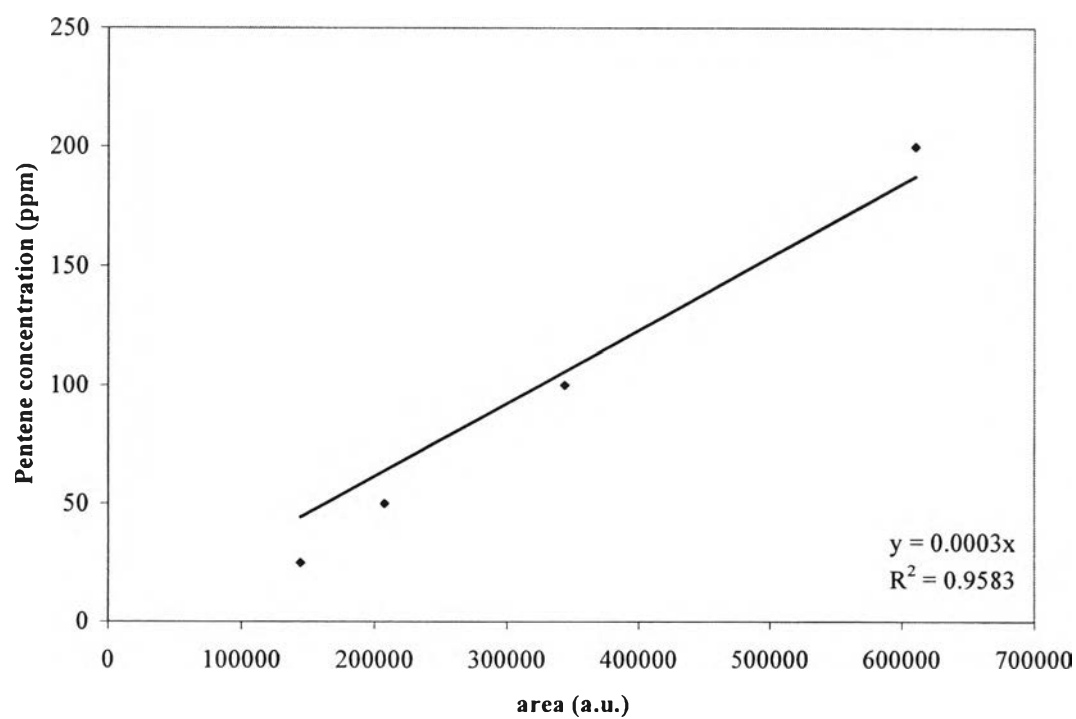


Figure E.20 The calibration curve of pentene.

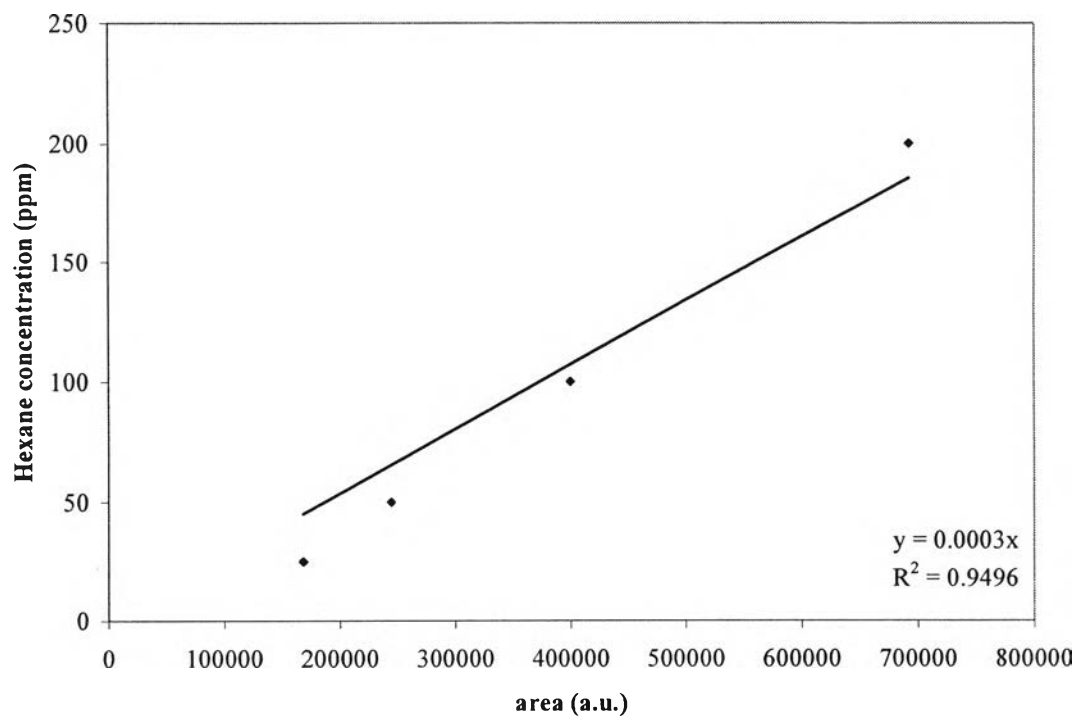


Figure E.21 The calibration curve of hexane.

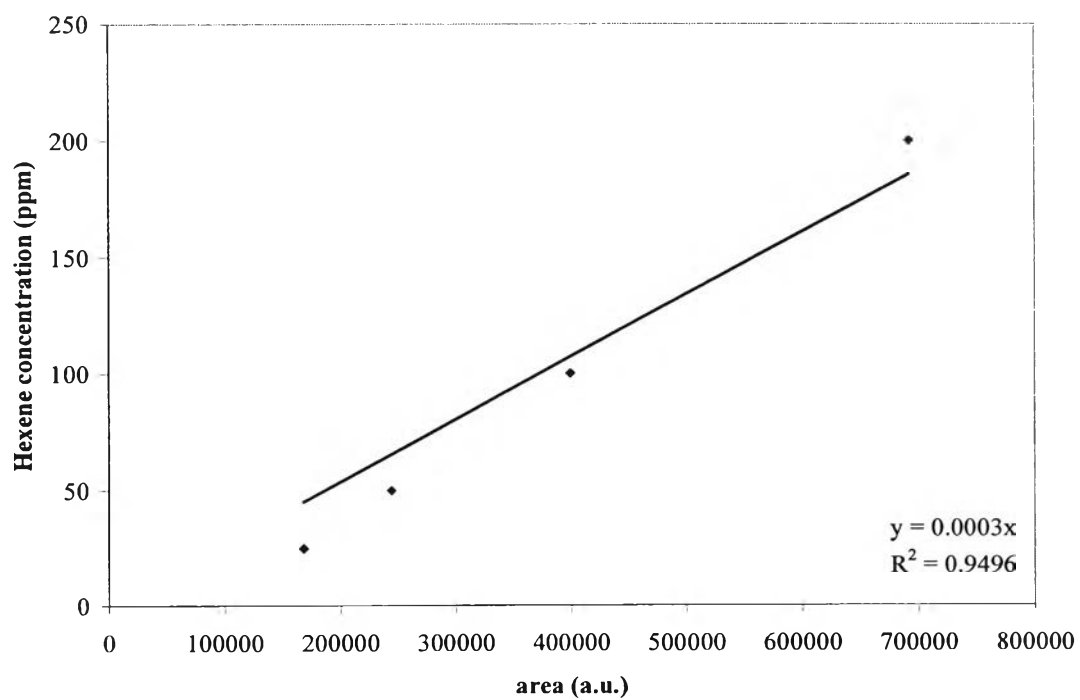


Figure E.22 The calibration curve of hexene.

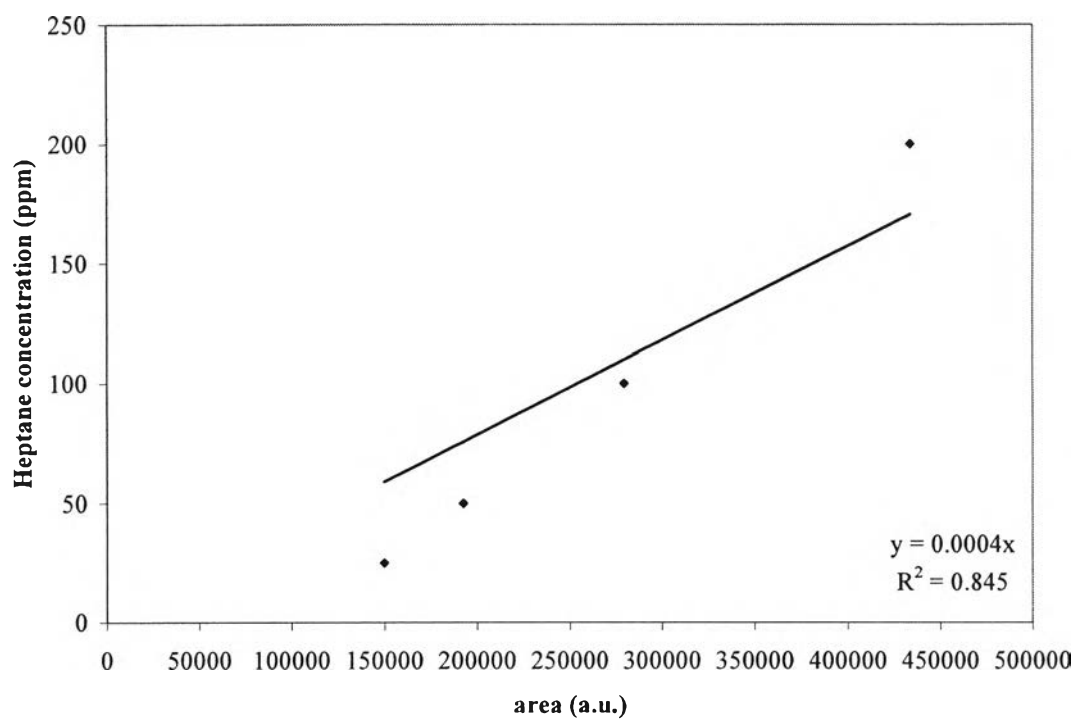


Figure E.23 The calibration curve of heptane.

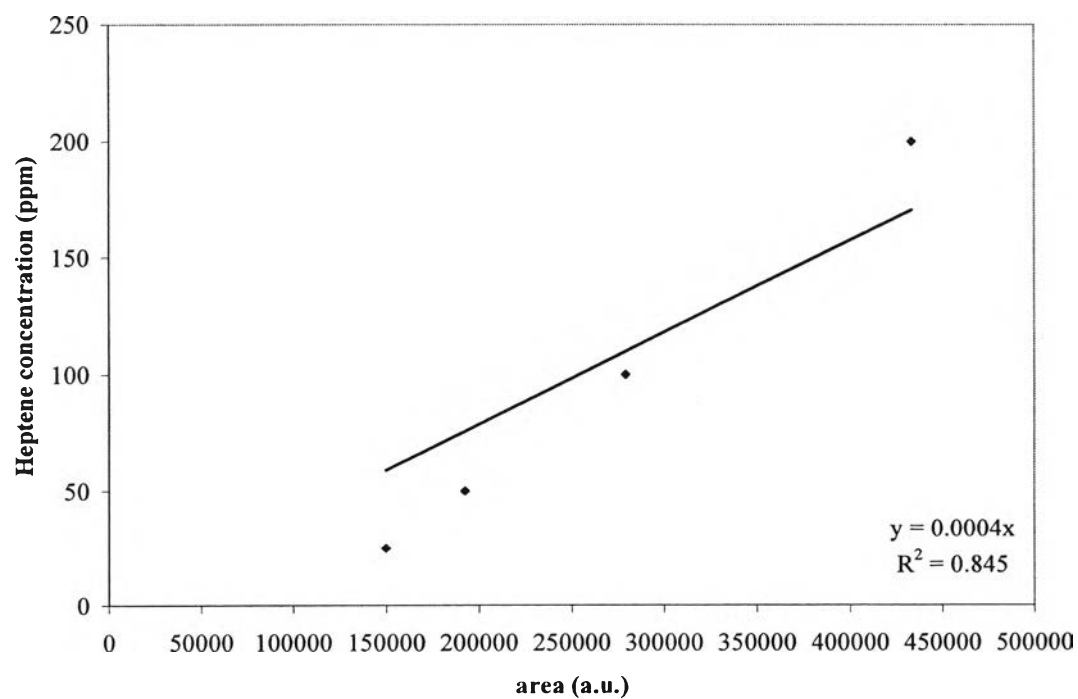


Figure E.24 The calibration curve of heptene.

APPENDIX F

CALCULATION OF CO CONVERSION, REACTION RATE, TOF, AND SELECTIVITY

The catalyst performance for the CO hydrogenation and FTS were evaluated in terms of activity for CO conversion, reaction rate, TOF, and selectivity.

CO conversion

Activity of the catalyst performed in term of carbon monoxide conversion and reaction rate. Carbon monoxide conversion is defined as moles of CO converted with respect to CO in feed:

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

where mole of CO can be measured employing the calibration curve of CO in Figure E.3 (for CO hydrogenation) and E.10 (for FTS reaction), Appendix E., i.e.,

For CO hydrogenation:

$$\text{mole of CO} = (\text{area of CO peak from integrator plot on GC-8A}) \times 3 \times 10^{-11} \quad (\text{ii})$$

Reaction rate

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

For example, the reaction rate from CO hydrogenation can be calculated as:

Let the weight of catalyst used	=	W	g
Flow rate of CO	=	8	cc/min
Reaction time	=	60	min

$$\begin{aligned}
 \text{Weight of CH}_2 &= 14 \text{ g} \\
 \text{Volume of 1 mole of gas at 1 atm} &= 22400 \text{ cc} \\
 \text{Reaction rate (g CH}_2\text{/g of catalyst/h)} &= \frac{[\% \text{ conversion of CO}/100] \times 60 \times 14 \times 8}{W \times 22400} \quad (\text{iii})
 \end{aligned}$$

TOF

TOF was calculated from reaction rate and H₂ chemisorption (Or CO chemisorption) that is as follows:

$$\text{TOF (s}^{-1}\text{)} = \frac{[\text{reaction rate}]}{[\text{H}_2 \text{ chemisorption}/2]} \quad (\text{in case of H}_2 \text{ chemisorption}) \quad (\text{iv})$$

$$= \frac{[\text{reaction rate}]}{[\text{CO chemisorption}]} \quad (\text{in case of CO chemisorption}) \quad (\text{v})$$

Selectivity

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

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

Where B is product, mole of B can be measured employing the calibration curve of products such as methane, ethane, ethylene, propane, propylene, butane, butene, pentane, pentene, hexane, hexene, heptane, and heptene in Figure E.4-E.9 (for CO hydrogenation) and E.12-E.24 (for FTS reaction), Appendix E., i.e.,

For CO hydrogenation:

$$\text{mole of CH}_4 = (\text{area of CH}_4 \text{ peak from integrator plot on GC-14B}) \times 6 \times 10^{-13} \quad (\text{vii})$$

APPENDIX G

LIST OF PUBLICATIONS

1. Kamonchanok Pansanga, Okorn Mekasuwandumrong, Joongjai Panpranot, and Piyasan Prasertthdam, "Synthesis of Nanocrystalline Alumina by Thermal Decomposition of Aluminum Isopropoxide in 1-Butanol and their Applications as Cobalt Catalyst Supports", *Kor. J. Chem. Eng.*, In Press, Corrected Proof.
2. Kamonchanok Pansanga, Joongjai Panpranot, Okorn Mekasuwandumrong, Chairit Satayaprasert, James G. Goodwin, Jr., and Piyasan Prasertthdam, "Effect of Mixed γ and χ Crystalline Phases in Nanocrystalline Al_2O_3 on the Dispersion of Cobalt on Al_2O_3 ", *Catal. Commun.*, Revised.
3. Kamonchanok Pansanga, Nattaporn Lohitharn, Andrew C. Y. Chien, Edgar Lotero, Joongjai Panpranot, James G. Goodwin, Jr., and Piyasan Prasertthdam, "Copper-Modified Alumina as a Support for Iron Fischer Tropsch Synthesis Catalysts", *Catal. Lett.*, Submitted.

VITAE

Miss Kamonchanok Pansanga was born on 23th March 1981, in Samutsongkhram, Thailand. She received her Bachelor degree of Engineering with Chemical Engineering from King Mongkut's Institute of Technology Ladkrabang, Thailand in March 2003. Since June 1, 2003, she has been studying for her Doctor degree of Engineering from the department of Chemical Engineering, Chulalongkorn University.

