REFERENCES

Aboul-Gheit, A.K., Aboul-Enein, A.A., Awadallah, A.E., Ghoneim, S.A., and Emam, E.A. (2010). Para-Xylene Maximization. Part VIII: Promotion of H-ZSM-5 Zeolite by Pt and HF Doping for Use as Catalysts in Toluene Alkylation with Methanol. Chinese Journal of Catalysis 31(9–10), 1209-1216.

Aboul-Gheit, A.K. and Awadallah, A.E. (2014) Non-oxidative conversion of natural gas to aromatics (GTA), ethylene (GTE), and hydrogen using Mo loaded on HZSM-5 and hydro-fluorinated HZSM-5 catalysts. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 36(5), 489-500.

Aboul-Gheit, A.K., Awadallah, A.E., Aboul-Enein, A.A., and Mahmoud, A.-L.H. (2011) Molybdenum substitution by copper or zinc in H-ZSM-5 zeolite for catalyzing the direct conversion of natural gas to petrochemicals under non-oxidative conditions. Fuel 90(10), 3040-3046.

Aboul-Gheit, A.K., El-Masry, M.S., and Awadallah, A.E. (2012) Oxygen free conversion of natural gas to useful hydrocarbons and hydrogen over monometallic Mo and bimetallic Mo–Fe, Mo–Co or Mo–Ni/HZSM-5 catalysts prepared by mechanical mixing. Fuel Processing Technology 102, 24-29.

Baba, T. and Sawada, H. (2002). Conversion of methane into higher hydrocarbons in the presence of ethylene over H-ZSM-5 loaded with silver cations. Physical Chemistry Chemical Physics 4(15), 3919-3923.

Bhat, Y.S., Das, J., Rao, K.V., and Halgeri, A.B. (1996). Inactivation of External Surface of ZSM-5: Zeolite Morphology, Crystal Size, and Catalytic Activity. Journal of Catalysis 159(2), 368-374.

Chen, L., Lin, L., Xu, Z., Li, X., and Zhang, T. (1995) Dehydro-oligomerization of methane to ethylene and aromatics over molybdenum/HZSM-5 catalyst. Journal of Catalysis 157(1), 190-200.

Choudhary, T.V., Aksoylu, E., and Goodman, D.W. (2003) Nonoxidative activation of methane. Catalysis Reviews 45(1), 151-203.

Feng, X., Jiang, G., Zhao, Z., Wang, L., Li, X., Duan, A., Liu, J., Xu, C., and Gao, J. (2010). Highly effective F-modified HZSM-5 catalysts for the cracking of naphtha to produce light olefins. Energy & Fuels 24(8), 4111-4115.

Georgiev, D., Bogdanov, B., Angelova, K., Markovska, I., and Hristov, Y. (2009, June 4-5) Synthetic zeolites- structure, classification, current trens in zeolite synthesis review. Inteernational Science Conferemce, Stara Zagora, Bulgaria (7), 1-5.

Guczi, L., Sarma, K., and Borkó, L. (1996) Non-oxidative methane coupling over Co-Pt/NaY bimetallic catalysts. Catalysis Letters 39(1-2), 43-47.

Guczi, L., van Santen, R.A., and Sarma, K. (1996). Low-temperature coupling of methane. Catalysis Reviews 38(2), 249-296.

Joesten, M.D., Hogg, J.L., and Castellion, M.E. (2007) The World of Chemistry: Essentials. Belmont: Thomson Brooks/Cole.

Khurana, J.M. and Vij, K. (2013) Nickel Nanoparticles as semiheterogeneous catalyst for one-pot, three-component synthesis of 2-amino-4 H-pyrans and pyran annulated heterocyclic moieties. Synthetic Communications 43(17), 2294-2304.

Lei, X.-g., Jockusch, S., Francesca Ottaviani, M., and Turro, N.J. (2003) In situ EPR investigation of the addition of persistent benzyl radicals to acrylates on ZSM-5 zeolites. Direct spectroscopic detection of the initial steps in a supramolecular photopolymerization. Photochemical & Photobiological Sciences 2(11), 1095-1100.

Lyons W.C. and Plisga G.J. (2011) Standard Handbook of Petroleum and Natural Gas Engineering. Burlington: Elsevier Science.

Ma, S., Guo, X., Zhao, L., Scott, S., and Bao, X. (2013) Recent progress in methane dehydroaromatization: from laboratory curiosities to promising technology. Journal of Energy Chemistry 22(1), 1-20.

Miao, S., Wang, Y., Ma, D., Zhu, Q., Zhou, S., Su, L., Tan, D., and Bao, X. (2004) Effect of Ag+ cations on nonoxidative activation of methane to C2-hydrocarbons. Journal of Physical Chemistry B 108(46), 17866-17871.

Moya, S.F., Martins, R.L., and Schmal, M. (2011) Monodispersed and nanostructrured Ni/SiO2 catalyst and its activity for non oxidative methane activation. Applied Catalysis A: General 396(1-2), 159-169.

Ngobeni, W.M. (2007) The nonoxidative conversion of light alkanes over metal-loaded H-ZSM-5 zeolite catalysts. Ph.D Dissertation, Faculty of Science, University of the Witwatersrand. Johannesburg, South Africa.

Rahimi, N. and Karimzadeh, R. (2011) Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review. Applied Catalysis A: General 398(1-2), 1-17.

Sarkar, B., Tiwari, R., Singha, R.K., Suman, S., Ghosh, S., Acharyya, S.S., Mantri, K., Konathala, L.N.S., Pendem, C., and Bal, R. (2012) Reforming of methane with CO2 over Ni nanoparticle supported on mesoporous ZSM-5. Catalysis Today 198(1), 209-214.

Sivasankar, B. (2008) Engineering Chemistry. New Delhi: McGraw-Hill Education.

Stoker, H.S. (2010) General, Organic, and Biological Chemistry.5th ed. Australia: Brooks/Cole Cengage Learning.

Thompson, C. and Nathanail, P. (2009) Chemical Analysis of Contaminated Land: Wiley.

Vitale, G., Molero, H., Hernandez, E., Aquino, S., Birss, V., and Pereira-Almao, P. (2013) One-pot preparation and characterization of bifunctional Ni-containing ZSM-5 catalysts. Applied Catalysis A: General 452, 75-87.

Vosmerikov, A.V., Zaykovskii, V.I., Korobitsyna, L.L., Kodenev, E.G., Kozlov, V.V., and Echevskii, G.V. (2006) Catalysts for non-oxidative methane conversion. Studies in Surface Science and Catalysis. 162: 913-920.

Wang, L., Tao, L., Xie, M., Xu, G., Huang, J., and Xu, Y. (1993) Dehydrogenation and aromatization of methane under non-oxidizing conditions. Catalysis Letters 21(1-2), 35-41.

Xu, Y. (2003) Direct conversion of methane under nonoxidative conditions. Journal of Catalysis 216(1-2), 386-395.

Yagita, H., Ogata, A., Obuchi, A., Mizuno, K., Maeda, T., and Fujimoto, K. (1996) Catalytic dehydrogenative coupling of methane on active carbon: effect of metal supported on active carbon. Catalysis Today 29(1-4), 433-436.

Yoshimura, Y., Kijima, N., Hayakawa, T., Murata, K., Suzuki, K., Mizukami, F., Matano, K., Konishi, T., Oikawa, T., Saito, M., Shiojima, T., Shiozawa, K., Wakui, K., Sawada, G., Sato, K., Matsuo, S., and Yamaoka, N. (2001) Catalytic cracking of naphtha to light olefins. Catalysis Surveys from Japan 4(2), 157-167.

Zhou, D., Zuo, S., and Xing, S. (2012) Methane dehydrogenation and coupling to ethylene over a Mo/HZSM-5 catalyst: A density functional theory study. The Journal of Physical Chemistry C 116(6), 4060-4070.

APPENDICES

Appendix A Calibration Curves for Methane and Gas Product

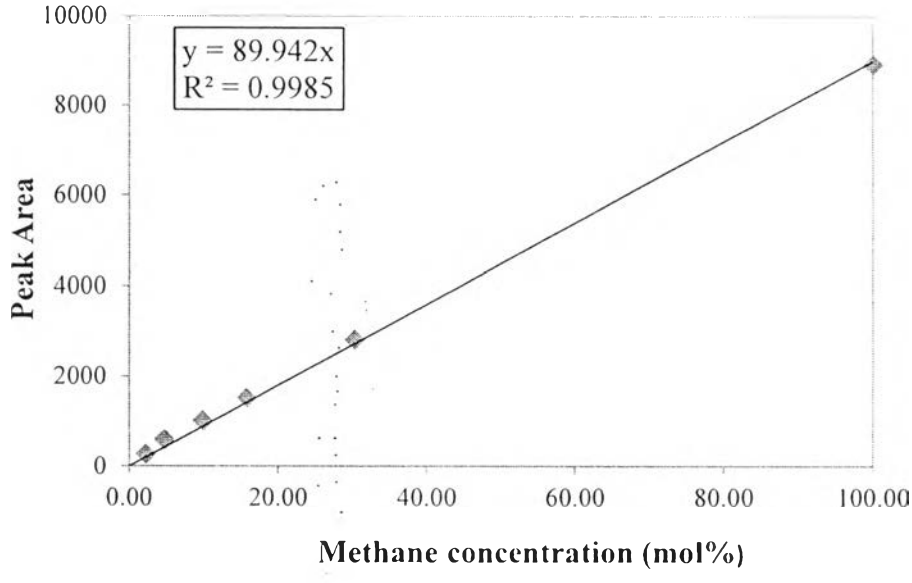

Figure A1 The relationship between methane concentration (CH_4) and peak area.

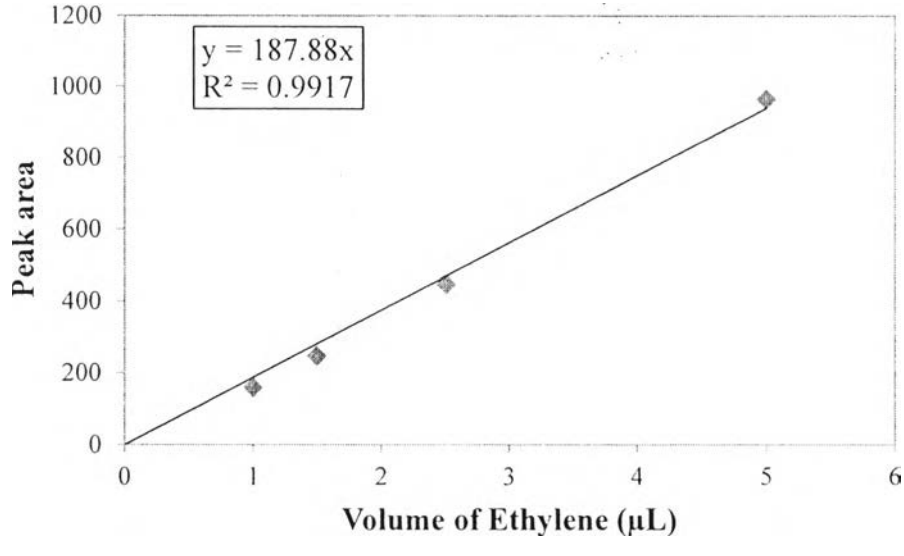

Figure A2 The relationship between volume of ethylene (C_2H_4) and peak area.

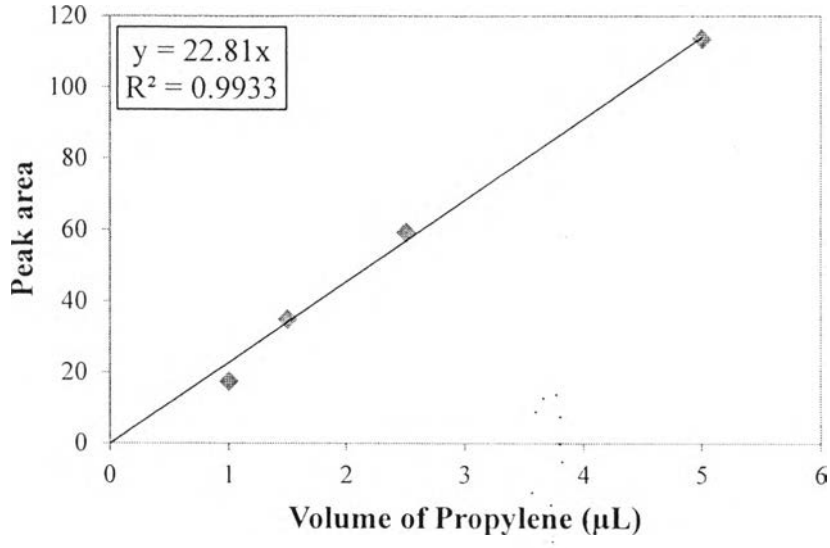

Figure A3 The relationship between volume of propylene (C_3H_6) and peak area.

Appendix B Calibration Curves for Flow Meter

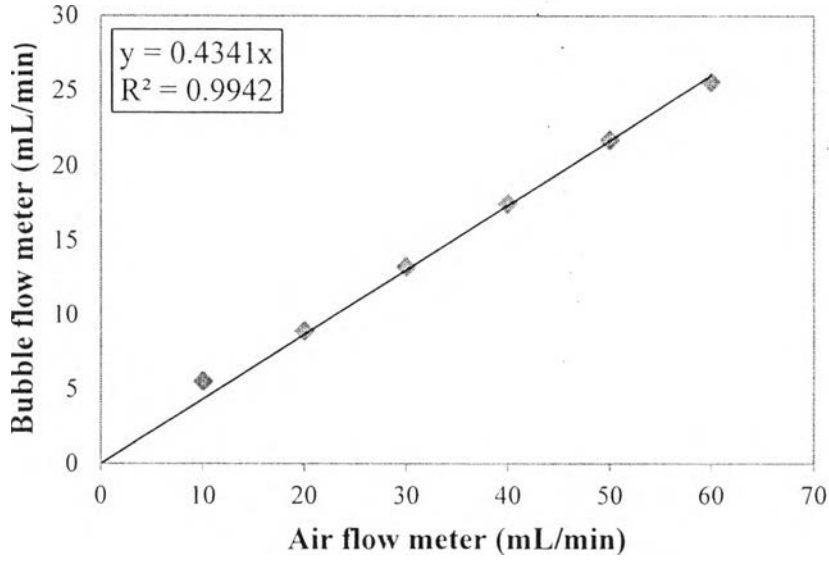

Figure B1 The relationship between bubble flow meter and methane air flow meter.

Appendix C Experimental Data of Catalytic Activity Tests for Methane Dehydrogenation and Coupling to Ethylene

Table C1 Catalytic activity test of HZSM-5 catalyst using 20% methane as a feed at reaction temperature 750 °C, with GHSV 1500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 conversion (mol%)	Ethylene selectivity (%)	Propylene selectivity (%)
15	12.38	0	0
30	20.17	0	0
60	15.00	0	0
90	13.59	0	0
120	11.49	0	0
150	8.56	0	0
180	9.00	0	0

Table C2 Catalytic activity test of 1%Ni/HZSM-5 catalyst using 20% methane as a feed at reaction temperature 750 °C, with GHSV 1500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 conversion (mol%)	Ethylene selectivity (%)	Propylene selectivity (%)
15	15.03	0	0
30	28.48	0	100.00
60	25.15	43.12	56.88
90	24.62	31.03	68.97
120	16.11	10.63	89.37
150	6.84	12.91	87.09
180	0	0	0

Table C3 Catalytic activity test of 3%Ni/HZSM-5 catalyst using 20% methane as a feed at reaction temperature 750 °C, with GHSV 1500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 conversion (mol%)	Ethylene selectivity (%)	Propylene selectivity (%)
15	16.10	0	0
30	29.29	0	100.00
60	29.83	0	100.00
90	24.07	0	100.00
120	14.72	0	100.00
150	3.48	0	0
180	0	0	0

Table C4 Catalytic activity test of 1%Ni/HZSM-5 catalyst using 20% methane as a feed at reaction temperature 800 °C, with GHSV 1500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 conversion (mol%)	Ethylene selectivity (%)	Propylene selectivity (%)
15	23.49	0	0
30	29.02	100.00	0
60	28.27	100.00	0
90	33.37	100.00	0
120	35.74	100.00	0
150	28.11	100.00	0
180	14.07	100.00	0

Table C5 Catalytic activity test of HZSM-5 (HF) catalyst using 20% methane as a feed at reaction temperature 750 °C, with GHSV 1500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 conversion (mol%)	Ethylene selectivity (%)	Propylene selectivity (%)
15	13.97	0	0
30	18.26	0	0
60	17.65	0	0
90	15.80	0	0
120	16.70	0	0
150	18.26	0	0
180	10.35	0	0

Table C6 Catalytic activity test of 1%Ni/HZSM-5 (HF) catalyst using 20% methane as a feed at reaction temperature 750 °C, with GHSV 1500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 conversion (mol%)	Ethylene selectivity (%)	Propylene selectivity (%)
15	17.58	0	0
30	24.67	0	0
60	22.69	19.41	80.59
90	20.90	22.53	77.47
120	17.08	27.85	72.15
150	14.95	38.53	61.47
180	11.75	42.61	57.39

Table C7 Catalytic activity test of 3%Ni/HZSM-5 (HF) catalyst using 20% methane as a feed at reaction temperature 750 °C, with GHSV 1500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 conversion (mol%)	Ethylene selectivity (%)	Propylene selectivity (%)
15	15.70	0	0
30	28.77	0	100.00
60	26.33	0	100.00
90	28.41	0	100.00
120	27.45	0	100.00
150	27.73	0	100.00
180	13.59	0	0

Table C8 Catalytic activity test of 1%Ni/HZSM-5 catalyst using pure methane as a feed at reaction temperature 750 °C, with GHSV 1500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 conversion (mol%)	Ethylene selectivity (%)	Propylene selectivity (%)
15	17.23	0	0
30	8.04	0	0
60	9.83	0	0
90	10.02	0	0
120	1.93	0	0
150	1.76	0	0
180	1.76	0	0

Appendix D Calculation of Carbon Balanced of Methane

From the Methane conversion of HZSM-5 at 750°C, the carbon balanced of methane is calculated as follows:

C inlet

CH_4 inlet obtained from methane calibration curve

$= 1.84 \times 10^{-6}$ mol

C lost in reaction

At TOS 15 min, the CH_4 conversion = 12.38 mol%

Therefore, CH_4 lost in reaction $= (12.38 \times 1.84 \times 10^{-6})/100$

$= 2.28 \times 10^{-7}$ mol

The amount of C in CH_4 which is used in reaction

$= 2.28 \times 10^{-7}$ mol x 12 g/mol

$= 2.74 \times 10^{-6}$ g

For 15 min reaction, the amount of C $= 2.74 \times 10^{-6}$ g x15 min

$= 4.11 \times 10^{-5}$ g

For TOS 30, 60,90,120,150 and 180 min, The amount of C is shown as Table D1.

Table D1 The amount of C in methane reaction using HZSM-5

TOS (min)	CH_4 conversion (mol%)	The amount of C (g)
15	12.38	4.11×10^{-5}
30	20.17	6.69×10^{-5}
60	15.00	4.98×10^{-5}
90	13.59	4.51×10^{-5}
120	11.49	3.81×10^{-5}
150	8.56	2.84×10^{-5}
180	9.00	2.99×10^{-5}
	Total C	3.00×10^{-4}

So, Accumulation of C through course of reaction is 3.00×10^{-4} g

From coke formation obtained from TPO techniques, the amount of coke formation using HZSM-5 is 0.11 wt%

Therefore, the amount of C in 0.2 g HZSM-5= (0.11*0.2)/100

$= 2.20*10^{-4}$ g

According to the amount of C lost in reaction and C in spent HZSM-5, it shows that HZSM-5 can be only converted methane to coke.

CURRICULUM VITAE

Name: Ms. Suchada Kongbin

Date of Birth: Oct 4, 1989

Nationality: Thai

University Education:

2012–2014 Master of Science in Petrochemical Technology, The Petroleum and Petrochemical College (PPC), Chulalongkorn University, Bangkok, Thailand.

2008–2012 Bachelor of Science Program in Industrial Chemistry, Chiang Mai University, Chiang Mai, Thailand.

Working Experience:

2008-2009	Position:	Student Trainee, Department of Quality Assurance
	Company name:	Zeon Advanced Polymix Company Limited

Presentations:

1. **Suchada,** K.; and Rirksomboon. (2014, April 22) Methane Dehydrogenation and Coupling to Ethylene Using Ni/HZSM-5 Catalysts. Poster presented at The 5th Research Symposium on Petrochemical and Materials Technology and The 20th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.