REFERENCES

Aboul-Gheit, A.K., Hanafy, S.A., Aboul-Enein, A.A. and Ghoneim, S.A. (2011) Para-xylene maximization: Part IX—Activation of toluene methylation catalysts with palladium. Journal of the Taiwan Institute of Chemical Engineers, 42(5), 860-867.

Bearns, D.M., Castleman, A.W., Schäfer, F.P., and Toennies, J.P. (2004) Basic Principles in Applied Catalysis. Berlin:Springer-Verlag.

Basaldella, E.I., and Tara, J.C. (1995) Synthesis of LSX zeolite in the Na/K system. Influence of the Na/K ratio. Zeolites, 11, p.243-248.

Bekkum, V. H., Flanigen, E.M., Jacobs, P.A., and Jansen, J.C. 1991 Introduction to Zeolite Science and Practice, Amsterdam: Elsevier.

Breck, D.W. (1974) Zeolite Molecular Sieves: Structure, Chemistry and Use. London: John Wiley and Sons.

Cejka, J., filková, N., Wichterlová, B., Eder-Mirth, G. and Lercher, J.A. (1996) Decisive role of transport rate of products for zeolite para-selectivity: Effect of coke deposition and external surface silylation on activity and selectivity of HZSM-5 in alkylation of toluene. Zeolites, 17(3), 265-271.

Chen, N.Y.,Kaeding, and W.W. Dwyer, F.G. (1979) *P*ara-directed aromatic reactions over shape –selective molecular sieve zeolite catalysts. Journal of American Chemical Society, 101 (20-22), 6783-6784.

Csicsery, S.M., (1986) Pure apply. Chemistry. 58, 841-858.

Daley, R.F., (2005) Chapter 18 Aromatic Substitution Reactions. Organic Chemistry <http://ebookscard.org/students/pdf/chemistry/18aromatic%20substitutions.pdf)>

Degnan Jr, T.F. (2003) The implications of the fundamentals of shape selectivity for the development of catalysts for the petroleum and petrochemical industries. Journal of Catalysis, 216(1–2), 32-46.

De Lucas, A., Canizares, P., Durán, A. and Carrero, A. (1997) Dealumination of HZSM-5 zeolites: Effect of steaming on acidity and aromatization activity. Applied Catalysis A: General 154(1–2), 221-240.

Guisnet, M., and Magnou, P. (2010) Organic chemistry of coke formation. Applied Catalysis A: General, 212, 83-96.

Kulprathipanja, S. (2010) Zeolite in Industrial Seperation and Catalysis. Weinheim: WILEY-VGH Verlag GmbH & Co.KGaA.

Li, S., Zheng, A., Su, Y., Zhang, H., Chen, L., Yang, J., Ye, C., and Deng, F. (2007) Brønsted/Lewis Acid Synergy in Dealuminated HY Zeolite: A Combined Solid-State NMR and Theoretical Calculation Study J.AM. CHEM.. SOC, 129, 11161-11171.

Liu, B., Yu, Z., Meng, Y., Cui, L., and Zhu, Z. (2010) Preparation and characterization of shape-selective ZSM-5 catalyst for para-methyl ethylbenzene production with toluene and ethylene. Studies in Surface Science and Catalysis, 175, 271-274

Matar, S., Mirbach, M.J., and Tayim, H.A. (1989) Catalysis in Petrochemical Process. Netherlands: Kuwer Academic Publishers.

Mihályi, R.M., Kollár, M., Király, P., Karoly, Z. and Mavrodinova, V. (2012) Effect of extra-framework Al formed by successive steaming and acid leaching of zeolite MCM-22 on its structure and catalytic performance. Applied Catalysis A: General, 417–418(0), 76-86.

Norman, S.R., and Coxon J.M. (1993) Principles of Organic Synthesis. U.K.: Blackie Academic & Professional.

Stocker, M. (2005) Gas phase catalysis by zeolites. Microporous and Mesoporous Materials. Microporous and Mesoporous Materials, 82, 257–292.

Teng, H., Wang, J., Ren, X. and Chen, D. (2011) Disproportionation of Toluene by Modified ZSM-5 Zeolite Catalysts with High Shape-selectivity Prepared Using Chemical Liquid Deposition with Tetraethyl Orthosilicate. Chinese Journal of Chemical Engineering, 19(2), 292-298.

Wade, L.G. (2009) Chapter 17 Reactions of Aromatic Compounds. Organic Chemistry, 6.

Weitkamp, J., and Puppe, L. (1999) Catalysis and Zeolites-Fundamentals and Applications. Berlin : Springer verlag.

Weisz, P.B., (1980) Pure apply. Chemistry. 52, 2091-2103.

Xu, B., Bordiga, S., Prins, R. and Bokhoven, J. (2007) Effect of framework Si/Al ratio and extra-framework aluminum on the catalytic activity of Y zeolite. Applied Catalysis A: General 333, 245-253.

Zhao, Y., Wu, H., Tan, W., Zhang, M., Liu, M., Song, C., Wang. X. and Guo, X. (2010) Effect of metal modification of HZSM-5 on catalyst stability in the shape-selective methylation of toluene. Catalysis Today, 156(1–2), 69-73.

Zhu, Z., Chen, Q., Xie, Z., Yang, W. and Li, C. (2006) The roles of acidity and structure of zeolite for catalyzing toluene alkylation with methanol to xylene. Microporous and Mesoporous Materials, 88(1–3), 16-21.

Zheng, S., Heydenrych, H.R., Röger, H.P., Jentys, A. and Lercher, J.A. (2003) On the Enhanced Selectivity of HZSM-5 Modified by Chemical Liquid Deposition. Topics in Catalysis, 22(1-2), 101-106.

APPENDICES

Appendix A Calculation of Si/Al Ratio and Theoretical Acidity

From the chemical composition determined by XRF method, the Si/Al ratio is calculated as follows:

The general formula of ZSM-5 is $Na_nAl_nSi_{96-n}O_{192}$

In the case of commercial HZSM-5 SiO_2/Al_2O_3 = 280,

From XRF

SiO_2	=	99.4210 wt%	Al_2O_3	=	0.5967 wt%
Si	=	1.6545 mol	Al	=	0.0117 mol
Si/ Al=		141.3657			

From $Al_nSi_{96-n}O_{192}$,

Si/ Al = 141.3657 = (96-n)/n

	n	=	0.6743
So,	Si	=	95.3257
	Al	=	0.6743

From the chemical composition determined by XRF method, the theoretical acidity of zeolite is calculated as follows:

The general formula of HZSM-5 is $H_nAl_nSi_{96-n}O_{192}$

In the case of HZSM-5 (280) with,

Si = 95.3257

Al = 0.6743

From the above, the general formula of HZSM-5 is $H_{0.6743}\ Al_{0.6743}SiO_{192}$. The weight of unit cell of HZSM-5 (U) is

U = 0.6743 (1)+ 0.6743 (26.98)+ 95.3257 (28.09)+192(16.00)

U = 5768.0892 g

The theoretical acidity ($[H^+]$) of HZSM-5 (280) is

$[H^+]$ = 0.6743/5768.0892

$[H^+]$ = 0.1169 mmol/g

Appendix B Experimental Data of Catalytic Activity Test for Toluene Alkylation with Methanol using Modified HZSM-5

Table B1 Toluene and methanol conversion for various SiO_2/Al_2O_3 molar ratio; reaction temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

Catalysts	component	Conversion (%)						
		15 min	75 min	135 min	195 min	255 min	315 min	375 min
HZ-5 (23)	Toluene conversion (%)	16.12	15.59	14.34	16.45	18.53	14.64	17.02
	Methanol conversion (%)	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HZ-5 (50)	Toluene conversion (%)	14.46	15.24	15.65	15.00	15.37	15.06	15.07
	Methanol conversion (%)	99.70	99.87	99.90	99.89	99.72	99.92	99.92
HZ-5 (80)	Toluene conversion (%)	14.44	16.73	15.70	16.18	16.35	14.83	15.31
	Methanol conversion (%)	99.63	100.00	100.00	99.92	100.00	99.92	99.93
HZ-5 (280)	Toluene conversion (%)	10.33	10.00	10.72	9.59	10.31	10.52	10.38
	Methanol conversion (%)	93.81	91.45	87.19	88.71	86.50	83.64	88.64

Table B2 Product selectivity for various SiO_2/Al_2O_3 molar ratio; reaction temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

Catalysts	component	Selectivity (%)						
		15 min	75 min	135 min	195 min	255 min	315 min	375 min
HZ-5 (23)	*p*-xylene selectivity in products	19.32	22.31	20.29	19.71	20.53	22.09	18.65
	p-xylene selectivity in xylenes	0.26	0.27	0.28	0.28	0.29	0.30	0.29
HZ-5 (50)	*p*-xylene selectivity in products	20.50	22.22	21.85	20.73	20.78	21.50	20.27
	p-xylene selectivity in xylenes	0.26	0.28	0.27	0.27	0.27	0.27	0.26
HZ-5 (80)	*p*-xylene selectivity in products	21.10	21.80	21.31	21.70	21.68	21.77	21.31
	p-xylene selectivity in xylenes	0.26	0.26	0.26	0.26	0.26	0.26	0.26
HZ-5 (280)	*p*-xylene selectivity in products	67.11	67.29	63.95	67.09	68.31	68.22	66.83
	p-xylene selectivity in xylenes	75.19	75.38	74.14	75.32	75.77	75.98	75.17

Table B3 Toluene and methanol conversion for various amount of TEOS loading; reaction temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

Catalysts	component	Conversion (%)						
		15 min	75 min	135 min	195 min	255 min	315 min	375 min
HZ-5(280)	Toluene conversion (%)	10.33	10.00	10.72	9.59	10.31	10.52	10.38
	Methanol conversion (%)	93.81	91.45	87.19	88.71	86.50	83.64	88.64
1-cycle CLD(0.5)-HZ-5	Toluene conversion (%)	10.53	9.30	8.43	8.31	9.63	8.19	9.81
	Methanol conversion (%)	100.00	85.24	88.74	86.16	82.30	85.30	86.31
1-cycle CLD(1.0)-HZ-5	Toluene conversion (%)	9.26	8.68	8.73	8.18	8.42	8.26	8.41
	Methanol conversion (%)	96.66	92.78	92.95	93.58	92.20	94.47	94.51
1-cycle CLD(1.5)-HZ-5	Toluene conversion (%)	7.60	7.48	8.30	8.08	7.68	8.13	7.58
	Methanol conversion (%)	96.43	97.31	95.76	93.08	97.85	93.58	93.75
1-cycle CLD(2.0)-HZ-5	Toluene conversion (%)	7.95	6.93	8.51	8.18	9.30	7.03	6.84
	Methanol conversion (%)	99.59	99.43	99.23	98.66	99.32	99.18	98.46

Table B4 Product selectivity for various amount of TEOS loading; reaction temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

Catalysts	component	Selectivity (%)						
		15 min	75 min	135 min	195 min	255 min	315 min	375 min
HZ-5(280)	*p*-xylene selectivity in products	67.11	67.29	63.95	67.09	68.31	68.22	66.83
	p-xylene selectivity in xylenes	75.19	75.38	74.14	75.32	75.77	75.98	75.17
1-cycle CLD (0.5)-HZ-5	*p*-xylene selectivity in products	77.71	79.92	79.54	79.21	80.50	79.48	79.97
	p-xylene selectivity in xylenes	86.33	87.73	88.09	87.78	87.64	87.64	87.18
1-cycle CLD (1.0)-HZ-5	*p*-xylene selectivity in products	78.92	81.26	81.45	81.59	81.47	80.64	81.39
	p-xylene selectivity in xylenes	89.57	88.73	89.36	89.55	89.69	88.17	89.59
1-cycle CLD (1.5)-HZ-5	*p*-xylene selectivity in products	78.10	77.59	78.70	75.85	78.75	76.69	79.92
	p-xylene selectivity in xylenes	85.47	84.32	84.74	84.74	85.71	85.21	85.35
1-cycle CLD (2.0)-HZ-5	*p*-xylene selectivity in products	73.60	77.50	73.65	75.66	73.45	76.59	75.21
	p-xylene selectivity in xylenes	85.92	86.46	86.97	87.18	86.34	85.83	85.09

Table B5 Toluene and methanol conversion for various CLD treatment cycle; reaction temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

Catalysts	Component	Conversion (%)						
		15 min	75 min	135 min	195 min	255 min	315 min	375 min
1-cycle CLD(1.0)-HZ-5	Toluene conversion (%)	9.26	8.68	8.73	8.18	8.42	8.26	8.41
	Methanol conversion (%)	96.66	92.78	92.95	93.58	92.20	94.47	94.51
2-cycle CLD(1.0)-HZ-5	Toluene conversion (%)	7.10	6.61	7.01	6.57	5.82	6.63	6.95
	Methanol conversion (%)	85.96	82.94	79.88	76.01	69.16	69.30	78.71
3-cycle CLD(1.5)-HZ-5	Toluene conversion (%)	6.94	6.96	7.83	8.35	7.10	8.76	6.84
	Methanol conversion (%)	89.43	79.31	87.03	87.53	84.62	82.87	78.82

Table B6 Product selectivity for various CLD treatment cycle; reaction temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

Catalysts	Component	Selectivity (%)						
		15 min	75 min	135 min	195 min	255 min	315 min	375 min
1-cycle CLD(1.0)-HZ-5	*p*-xylene selectivity in products	78.92	82.26	81.45	81.59	81.47	80.64	81.39
	p-xylene selectivity in xylenes	89.57	88.73	89.36	89.55	89.69	88.17	89.59
2-cycle CLD(1.0)-HZ-5	*p*-xylene selectivity in products	85.23	85.98	85.55	84.88	84.28	85.04	84.84
	p-xylene selectivity in xylenes	92.53	92.21	92.05	91.90	91.74	91.12	92.04
3-cycle CLD(1.5)-HZ-5	*p*-xylene selectivity in products	81.79	82.27	81.62	81.22	80.36	79.76	78.25
	p-xylene selectivity in xylenes	91.29	90.68	90.26	89.69	89.36	88.91	88.19

Table B7 Toluene and methanol conversion for parent and dealuminated catalysts; reaction temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

Catalysts	Component	Conversion (%)						
		15 min	75 min	135 min	195 min	255 min	315 min	375 min
HZ-5(280)	Toluene conversion (%)	10.33	10.00	10.72	9.59	10.31	10.52	10.38
	Methanol conversion (%)	93.81	91.45	87.19	88.71	86.50	83.64	88.64
DeAl-HZ-5	Toluene conversion (%)	11.21	10.85	11.30	9.40	13.16	11.58	10.85
	Methanol conversion (%)	95.26	94.75	93.93	94.96	92.26	91.44	94.63

Table B8 Product selectivity for parent and dealuminated catalysts; reaction temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

Catalysts	Component	Selectivity (%)						
		15 min	75 min	135 min	195 min	255 mm	315 min	375 min
HZ-5(280)	*p*-xylene selectivity in products	67.11	67.29	63.95	67.09	68.31	68.22	66.83
	p-xylene selectivity in xylenes	75.19	75.38	74.14	75.32	75.77	75.98	75.17
DeAl-HZ-5	*p*-xylene selectivity in products	64.23	65.07	65.10	65.21	65.67	63.74	67.97
	p-xylene selectivity in xylenes	73.23	73.77	73.62	74.30	73.92	73.75	75.82

Table B9 *p*-Xylene selectivity and other product selectivity for parent and dealuminated catalysts; reaction temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

Catalysts	Component	Selectivity (%)						
		15 min	75 min	135 min	195 min	255 min	315 min	375 min
HZ-5(280)	*p*-xylene selectivity (%)	67.11	67.29	63.95	67.09	68.31	68.22	66.83
	Other product selectivity (%)	32.89	32.71	36.05	32.91	31.69	31.78	33.17
DeAl-HZ-5	*p*-xylene selectivity (%)	64.23	65.07	65.10	65.21	65.67	63.74	67.97
	Other product selectivity (%)	35.77	34.93	34.90	34.79	34.33	36.26	32.03

Table B10 The estimation of methanol converted to aromatics ring and methanol to alkyl group from self-aromatization for parent and modified catalysts at temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}

Catalysts	Methanol to aromatic ring (%)		
	TOS(min)		
	15	75	135
HZ-5 (280)	41.55	42.99	41.89
CLD(1.0)-HZ-5	53.80	52.55	51.46
DeAl-HZ-5	43.11	42.97	44.24

Table B11 Toluene conversion of toluene disproportionation reaction over the parent HZSM-5 catalysts and modified catalysts at temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}

Catalysts	Toluene conversion (%)		
	TOS(min)		
	15	75	135
HZ-5 (280)	0	0	0
CLD(1.0)-HZ-5	0	0	0
DeAl-HZ-5	0	0	0

CURRICULUM VITAE

Name: Mr. Nut Tangphianphan

Date of Birth: January 15, 1989

Nationality: Thai

University Education:

2012–2013 Master of Science in Petroleum Technology, The Petroleum and Petrochemical College (PPC), Chulalongkorn University, Bangkok, Thailand.

2007–2010 Bachelor of Science Program in Industrial chemistry, King Mongkut's Institute of Technology Ladkrabang, Bangkok Thailand.

Working Experience:

2009-2010 Position: Student Trainee

Company name: TOA PAINT CO.,LTD.

Presentations:

Nut, T., Thirasak, R., and Siriporn, J. (2014, April 22) Toluene Alkylation with methanol using Modified HZSM-5 Catalysts. Poster present at The 5th Research Symposium on Petrochemical and Materials Technology and The 20th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.