REFERENCES

Aboul-Gheit, A.K., Awadallah, A.E., El-Kossy, S.M., and Mahmoud, A.H. (2008) Effect of Pd or Ir on the catalytic performance of Mo/H-ZSM-5 during the non-oxidative conversion of natural gas to petrochemicals. Journal of Natural Gas Chemistry, 17, 337-343.

Adebajo, M.O. and Frost, R.L. (2005) Oxidative benzene methylation with methane over MCM-41 and zeolite catalysts: Effect of framework aluminum, SiO_2/Al_2O_3 ratio, and zeolite pore structure. Energy and Fuels, 19, 783-790.

Adebajo, M.O., Howe, R.F., and Long, M.A. (2001) Methylation of toluene with methane over ZSM-5 catalysts. Energy and Fuels, 15, 671-674.

Adebajo, M.O., Long, M.A., and Frost, R.L. (2004) Spectroscopic and XRD characterization of zeolite catalyst active for the oxidative methylation of benzene with methane. Spectrochimica Acta Part A, 60, 791-799.

Adebajo, M.O., Long, M.A., and Howe, R.F. (2000) Methane activation over zeolite catalysts: The methylation of benzene. Research on Chemical Intermediates, 26, 185-191.

Alvarez-Galvan, M.C., Mota, N., Ojeda, M., Rojas, S., Navarro, R.M., and Fierro, J.L.G. (2011) Direct methane conversion routes to chemicals and fuels. Catalysis Today, 171, 15– 23.

Baba, T. (2005) Conversion of methane over Ag^+-exchanged zeolite in the presence of ethane. Catalysis Surveys from Asia, 9, 147-154.

Baba, T. and Abe, Y. (2003) Metalcation-acidic proton bifunctional catalyst for methane activation: conversion of $^{13}CH_4$ in the presence of ethylene over metal cations-loaded H-ZSM-5. Applied Catalysis A: General, 250, 265-270.

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, 3919-3923.

Baba, T., Abe, Y., Nomoto, K., Inazu, K., Echizen, T., Ishikawa, A., and Murai, K. (2005) Catalytic transformation of methane over In-loaded ZSM-5 zeolite in the presence of ethene. Journal of Physical Chemistry B, 109, 4263-4268.

Chatterjee, M., Bhattcharya, D., Hayashi, H., Ebina, T., Onodera, Y., Nagase, T., Sivasanker, S., and Iwasaki, T. (1998) Hydrothermal synthesis and characterization of indium containing beta zeolite. Microporous and Mesoporous Materials, 20, 87-91.

Choudhary, V.R., Kinage, A.K., and Choudhary, T.V. (1997) Low-temperature nonoxidative activation of methane over H-galloaluminosilicate (MFI) Zeolite. Science, 275, 1286-1288.

Ding, B., Huang, S., and Wang, W. (2008) Methane activation over Ag-exchanged ZSM-5 zeolites: A theoretical study. Applied Surface Science, 254, 4944-4948.

Ernst, S. (2009) Advances in Nanoporous Materials. Oxford: Elsevier.

Halasz, J., Konya, Z., Fudala, A., Beres, A., and Kiricsi, I. (1996) Indium and gallium containing ZSM-5 zeolites: acidity and catalytic activity in propane transformation. Catalysis Today, 31, 293 – 304.

Halasz, J., Nyari, W., Meretei, E., Hannus, I., Nagy, J.B., and Kiricsi, I. (2003) Structural properties and catalytic activity in selective oxidation of In-containing ZSM-5 catalysts. Journal of Molecular Structure, 651–653, 315–322.

Han, S., Schmitt, K.D., and Chang, C.D. (2000) Why In^{3+} is not isomorphously substituted into zeolite ZSM-5: reaction of ZSM-5 with aqueous InF_3. Inorganica Chimica Acta, 304, 297–300.

Herman, R.G., Sun, Q., Shi, C., Klier, K., Wang, C.B., Hu, H., Wachs, I.E., and Bhasin, M.M. (1997) Development of active oxide catalysts for the direct oxidation of methane to formaldehyde. Catalysis Today, 37, 1-14.

He, S.J.X., Long, M.A., Attalla, M.I., and Wilson, M.A. (1992) Methylation of naphthalene by methane over substituted aluminophosphate molecular sieves. Energy and Fuels, 6, 498-502.

He, S.J.X., Long, M.A., Attalla, M.I., and Wilson, M.A. (1994) Methylation of naphthalene by methane-^{13}C over copper-exchanged silicoaluminophosphate. Energy and Fuels, 8, 286–287.

He, S.J.X., Long, M.A., Wilson, M.A., Gorbaty, M.L., and Maa, P.S. (1995) Methylation of Benzene by Methane-^{13}C over Zeolitic Catalysts at 400 °C. Energy and Fuels, 9, 616-619.

Kennedy, E.M., Lonyi, F., Ballinger, T.H., Rosynek, M.P., and Lunsford, J.H. (1994) Conversion of Benzene to Substituted Aromatic Products over Zeolite Catalysts at Elevated Pressures. Energy and Fuel, 8, 846-850.

KulprathipanjaS. (2010) Zeolites in industrial separation and catalysis. Weinheim: Wiley-VCH.

Lukyanov, D.B., and Vazhnova, T. (2009) Selective and stable benzene alkylation with methane into toluene over PtH-MFI bifunctional catalyst. Journal of Molecular Catalysis A: Chemical, 305, 95-99.

Luzgin, M.V., Gabrienko, A.A., Rogov, V.A., Toktarev, A.V., Parmon, V.N., and Stepanov, A.G. (2010) The "Alkyl" and "Carbenium" pathways of methane activation on Ga-modified zeolite BEA: ^{13}C solid-state NMR and GC-MS study of methane aromatization in the presence of higher alkane. Journal of Physical Chemistry, 114, 21555–21561.

Mavrodinova, V., and Popova, M. (2005) Selective *p*-xylene formation upon toluene disproportionation over MCM-22 and ZSM-5 zeolites modified with indium. Catalysis Communications, 6, 247–252.

Mihalyi, R.M. and Beyer, H.K. (2001) Direct evidence for the incorporation of univalent indium into high-silica zeolite, H-ZSM-5, by thermal auto-reductive solid-state ion exchange. Chemical Communications, 21, 2242-2243.

Mihalyi, R.M., Beyer, H.K., Mavrodinova, V., Minchev, Ch, and Neinska, Y. (1998) Study of the reductive solid-state ion exchange of indium into an NH_4-beta zeolite. Microporous and Mesoporous Materials, 24, 143–151.

Mihalyi, R.M., Schay, Z., and Szegedi A. (2009) Preparation of In,H-ZSM-5 for DeNOx reactions by solid-state ion exchange. Catalysis Today, 143, 253–260.

Miro, E.E., Gutierrez, L., Lopez, J.M.R., and Requejo, F.G. (1999) Perturbed angular correlation characterization of indium species on In/H-ZSM5 catalysts. Journal of Catalysis, 188, 375–384.

Ogura, M., Ohsaki, T., and Kikuchi, E. (1998) The effect of zeolite structures on the creation of InO^+ active sites for NO_xreduction with methane. Microporous and Mesoporous Materials, 21, 533-540.

Olah, G.A. (1987) Electrophilic methane conversion. Accounts of Chemical Research, 20, 422-428.

Raul, F.L. (2003) Handbook of Zeolite Science and Technology. New York: Marcel Dekker.

Schutze, F.W., Berndt, H., Richter, M., Lucke, B., Schmidt, C., Sowade, T. and Grunert, W. (2001) 10-O-01 - Investigation of indium loaded zeolites and additionally promoted catalysts for the selective catalytic reduction of NOx by methane. Studies in Surface Science and Catalysis, 135, 1517–1524.

Solt, H., Lonyi, F., Mihalyi, R.M., Valyon, J., Gutierrez, L.B., and Miro, E.E. (2008) A mechanistic study of the solid-state reactions of H-mordenite with indium(0) and indium(III)oxide. Journal of Physical Chemistry, 112, 19423-19430.

Srisayan, T. (2012) Indium-Containing ZSM-5 Catalyst for Methylation of Benzene: Effect of Treatment and Co-feed. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.

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, 35-41.

Weckhuysen, B.M., Wang, D., Rosynek, M.P., and Lunsford, J.H. (1998) Conversion of methane to benzene over transition metal ion ZSM-5 zeolites catalytic characterization I. Catalytic characterization. Journal of Catalysis, 175, 338–346.

Yoon, K.J. and Tung, H.L. (1997) Oxidative coupling of methane over sodium-chloride-promoted zirconia supported on sodium-preimpregnated silica. Applied Catalysis, 159, 59-74.

Zamaro, J.M., Miro, E., Boix, A.V., Martinez-Hernandez, A., and Fuentes, G. (2010) In–zeolites prepared by oxidative solid state ion exchange (OSSIE): Surface species and structural characterization. Microporous and Mesoporous Materials, 129, 74-81.

Zhou, L.P., Li, X.W., Li, W., Tao, K.Y., and Li, H.X. (2000) Oxidative methylation of toluene with methane over basic zeolite catalysts promoted with alkali metal bromides and alkali metal oxides. Chinese Chemical Letters, 11, 827-830.

APPENDICES

Appendix A Calculation of Catalysts Composition

The catalysts composition is calculated based on the SiO_2/Al_2O_3 ratio of HZSM-5 equal to 23, 30, 50, 80 and 280.

The formula of HZSM-5 with SiO_2/Al_2O_3 ratio 23 is represented by $AlSi_{11.5}O_{25}H$.

The formula of HZSM-5 with SiO_2/Al_2O_3 ratio 30 is represented by $AlSi_{15}O_{32}H$.

The formula of HZSM-5 with SiO_2/Al_2O_3 ratio 50 is represented by $AlSi_{25}O_{52}H$.

The formula of HZSM-5 with SiO_2/Al_2O_3 ratio 80 is represented by $AlSi_{40}O_{82}H$.

The formula of HZSM-5 with SiO_2/Al_2O_3 ratio 280 is represented by $AlSi_{140}O_{282}H$.

Example of the weight of loaded In_2O_3 is represented by

$$m = \frac{5 \times 277.6 \times n}{750}$$

Where n = required In/Al ratio

m = weight of In_2O_3 required

The formula weight of HZSM-5 with SiO_2/Al_2O_3 ratio 23 is 750 g/mol.

The molecular weight of In_2O_3 is 277.6 g/mol.

The catalysts was prepared base on 5 g of HZSM-5.

The prepared catalysts were using the composition as shown in Table A1.

Table A1 The ingredients of prepared catalysts

SiO_2/Al_2O_3 ratio	In/Al ratios	HZSM-5 (g)	In_2O_3 (g)	Loading (wt. %)
23	0.1	5.00	0.0925	1.8
	0.3	5.00	0.2776	5.2
	0.5	5.00	0.4627	8.5
	1.0	5.00	0.9255	15.6
30	0.1	5.00	0.0723	1.4
	0.3	5.00	0.2169	4.1
	0.5	5.00	0.3615	6.7
	1.0	5.00	0.7230	12.6
50	0.1	5.00	0.0445	0.9
	0.3	5.00	0.1335	2.6
	0.5	5.00	0.2225	4.3
	1.0	5.00	0.4449	8.2
80	0.1	5.00	0.0282	0.6
	0.3	5.00	0.0846	1.7
	0.5	5.00	0.1411	2.7
	1.0	5.00	0.2822	5.3
280	0.1	5.00	0.0082	0.2
	0.3	5.00	0.0246	0.5
	0.5	5.00	0.0410	0.8
	1.0	5.00	0.0820	1.6

Appendix B Calibration Data and Feed Flow Adjustment

The calibration curve and regression equation of raw materials and some products is shown below. The response factors used for calculate the products amount that derived from the slope of calibration curve is also shown.

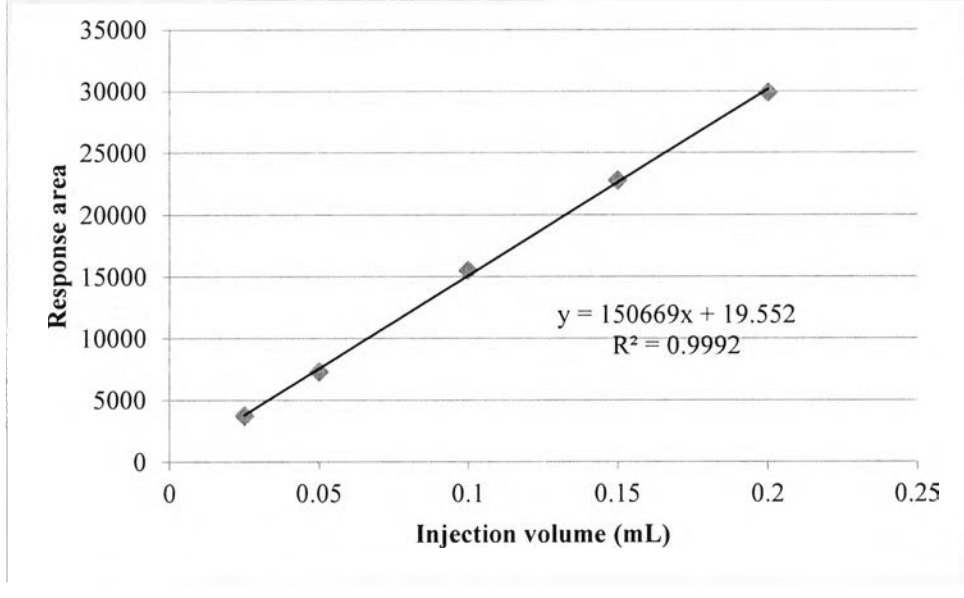

Figure B1 Response area from GC FID as a function of injection volume of methane.

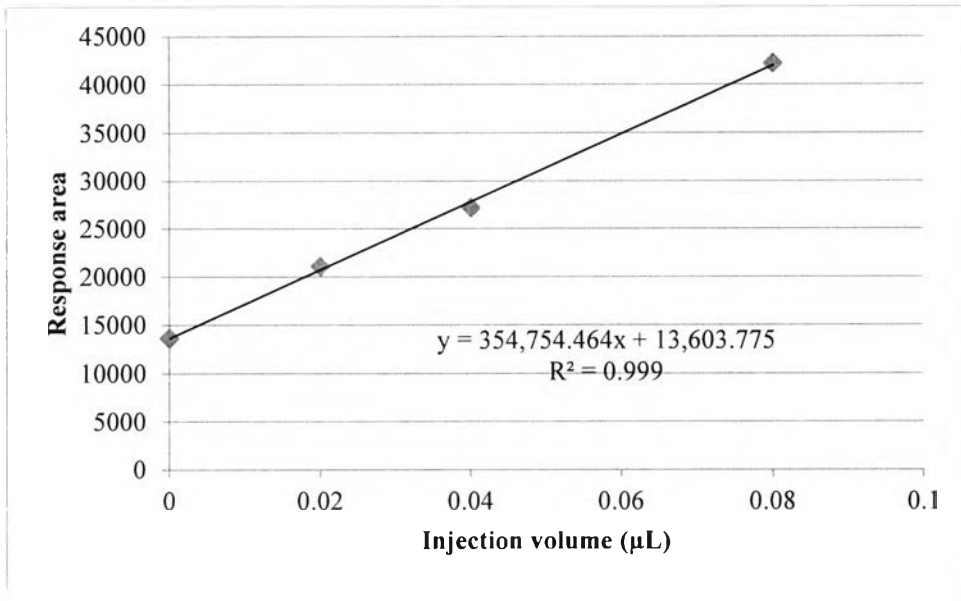

Figure B2 Response area from GC FID as a function of injection volume of benzene.

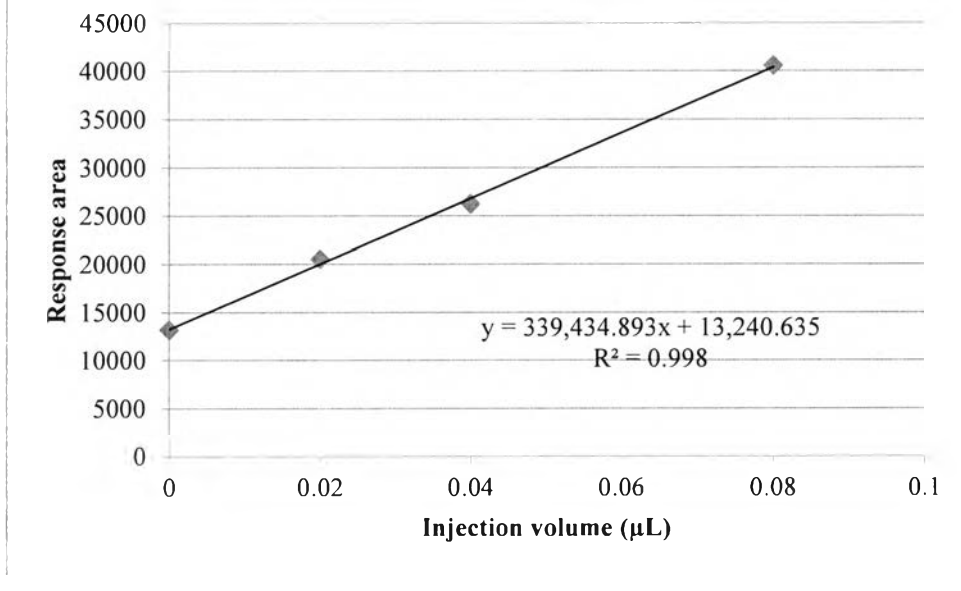

Figure B3 Response area from GC FID as a function of injection volume of toluene.

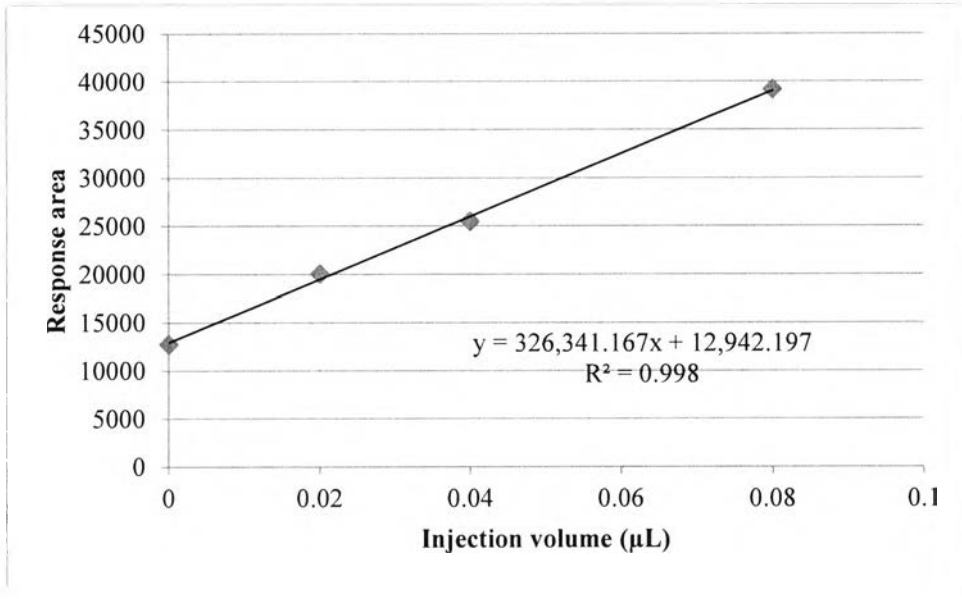

Figure B4 Response area from GC FID as a function of injection volume of *p*-xylene.

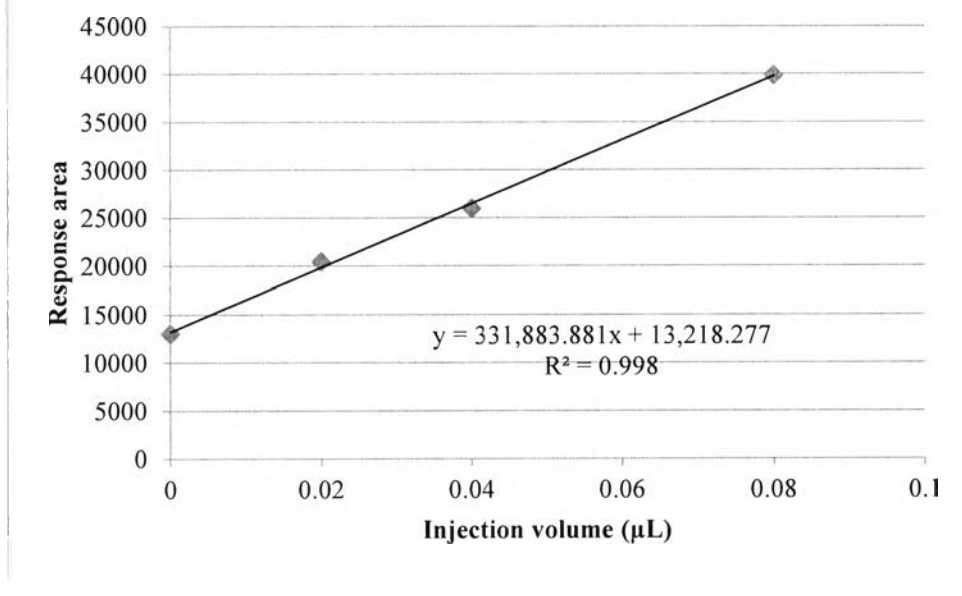

Figure B5 Response area from GC FID as a function of injection volume of *m*-xylene.

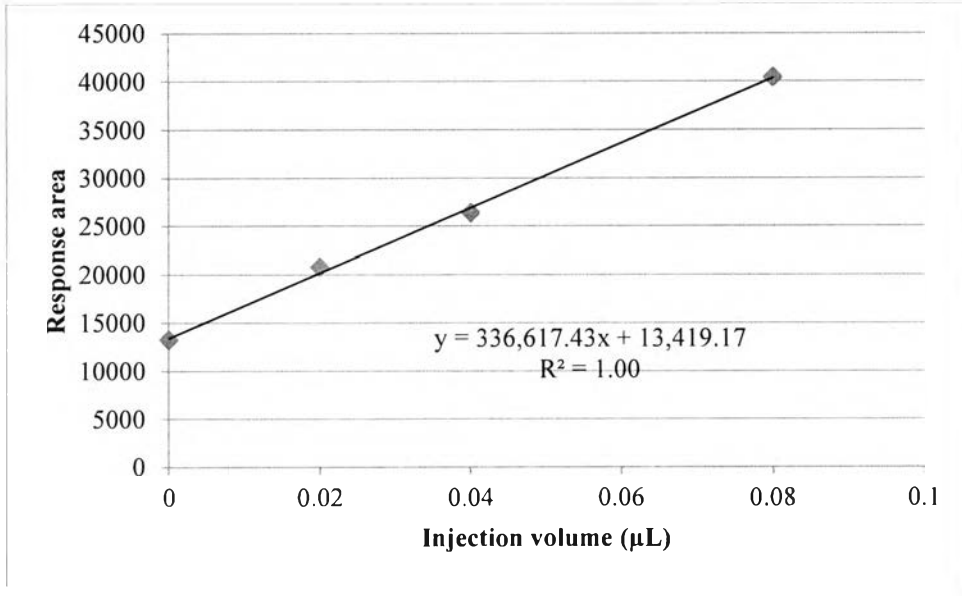

Figure B6 Response area from GC FID as a function of injection volume of *o*-xylene.

Table B1 The response factor calculated from calibration curve of each substances

Chemicals	Slope(Area/ml)	Density(g/ml)	(Area/g)	MW(g/mol)	Response factor (Area/mol)
Methane	150669	-	-	-	**3685027598**
Benzene	354754464	0.88	403130073	78	**31444145673**
Toluene	339434893	0.87	390155049	92	**35894264547**
p-xylene	326341167	0.86	379466473	106	**40223446165**
m-xylene	331883881	0.86	385911490	106	**40906617891**
o-xylene	336617430	0.88	382519807	106	**40547099523**

The value of response factors calculated from the calibration curve that shown in Table B1 is further used in the products quantification for each chemical. For the non-calibrated chemicals found during the analysis would use the response factor of *p*-xylene to represent and calculate amount of that chemicals.

In the case of feed adjustment, the feed flow controller and catalyst weight in various reaction conditions is shown in Table B2.

Table B2 Flow controller adjustment and catalyst weight in various reaction conditions

Reaction condition		**Flow controller adjustment (ml/min)**		**catalyst weight (g)**
M/B feed ratio	**WHSV (h^{-1})**	**Methane**	**Oxygen**	
23	2.8	5	5	0.16
70	2.8	5	5	0.20
	2.8	8	2	0.22
104	6.1	8	2	0.10
	12.3	8	2	0.05

Appendix C Raw Data of Reaction Results

The reaction results as a raw data of GC FID peak area and calculated data are shown below.

Table C1 The results of the reaction with O_2 treatment at 350 °C and N_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 0.5, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	8775.8	1003.2	0.13	0	0	0.03191	3.62E-06	**0.01**	**100**	0
40	8666.8	976.4	0	0	0	0.03105	0	**0.00**	**100**	0
70	8721.9	975.7	0	0	0	0.03103	0	**0.00**	**100**	0
100	8705.1	959.4	0	0	0	0.03051	0	**0.00**	**100**	0
130	8755.0	974.5	0	0	0	0.03099	0	**0.00**	**100**	0
160	8767.5	956.8	0	0	0	0.03043	0	**0.00**	**100**	0

Table C2 The results of the reaction with H_2 treatment at 700 °C and N_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 0.5, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	8864.9	973.5	1.10	0	0	0.03099	3.06E-05	**0.10**	**100**	0
40	8807	946.3	0.29	0	0	0.03010	8.08E-06	**0.03**	**100**	0
70	8777.6	954.6	0.15	0	0	0.03036	4.18E-06	**0.01**	**100**	0
100	8750.7	987.3	0.10	0	0	0.03140	2.79E-06	**0.01**	**100**	0
130	8796.2	959.9	0.09	0	0	0.03053	2.40E-06	**0.01**	**100**	0
160	8774.4	962.1	0.06	0	0	0.03060	1.62E-06	**0.01**	**100**	0

Table C3 The results of the reaction with H_2 treatment at 700 °C followed by O_2 treatment at 350 °C and N_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 0.5, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	8790.2	994.7	17.2	0	6.7	0.03228	0.00065	**2.00**	**74.21**	25.79
40	8730.4	999.1	5.6	0	0.8	0.03195	0.00018	**0.55**	**88.19**	11.81
70	8710.9	1000.4	3.1	0	0.1	0.03190	0.00009	**0.28**	**98.41**	1.59
100	8757.8	995.8	1.9	0	0.0	0.03172	0.00005	**0.17**	**100.00**	0.00
130	8688.4	957.7	1.5	0	0.0	0.03050	0.00004	**0.14**	**100.00**	0.00
160	8744.7	966.1	1	0	0.0	0.03075	0.00003	**0.09**	**100.00**	0.00

Table C4 The results of the reaction with H_2 treatment at 600 °C followed by O_2 treatment at 350 °C and N_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 0.5, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	8886.0	1028.2	15.7	0	8.10	0.03334	0.00064	**1.92**	**68.47**	31.53
40	8817.4	1047.7	5.0	0	0.80	0.03348	0.00016	**0.48**	**87.51**	12.49
70	8916.8	1055.5	3.0	0	0.06	0.03365	0.00009	**0.25**	**98.16**	1.84
100	8877.1	1059.5	2.0	0	0.00	0.03375	0.00006	**0.17**	**100.00**	0.00
130	8814.6	1035.5	1.3	0	0.00	0.03297	0.00004	**0.11**	**100.00**	0.00
160	8873.2	1054.0	1.0	0	0.00	0.03355	0.00003	**0.08**	**100.00**	0.00

Table C5 The results of the reaction with H_2 treatment at 800 °C followed by O_2 treatment at 350 °C and N_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 0.5, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	8966.8	920.9	13.3	0	6.40	0.02982	0.00053	**1.78**	**69.96**	30.04
40	8935.6	932.7	4.5	0	0.74	0.02981	0.00014	**0.48**	**87.25**	12.75
70	8857.9	917.6	2.6	0	0.12	0.02926	0.00008	**0.26**	**96.04**	3.96
100	8856.8	946.9	1.7	0	0.00	0.03016	0.00005	**0.16**	**100.00**	0.00
130	8941.7	942.8	1.2	0	0.00	0.03002	0.00003	**0.11**	**100.00**	0.00
160	8986.3	951.1	0.9	0	0.00	0.03027	0.00003	**0.08**	**100.00**	0.00

Table C6 The results of the reaction with H_2 treatment at 700 °C followed by O_2 treatment at 350 °C and N_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 0.5, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 300 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	8938.0	1014.3	12.8	0	4.40	0.03272	0.00047	**1.42**	**76.53**	23.47
40	8845.3	1014.6	5.0	0	0.76	0.03242	0.00016	**0.49**	**88.06**	11.94
70	8831.2	983.5	3.1	0	0.07	0.03137	0.00009	**0.28**	**98.02**	1.98
100	8841.8	1014.9	2.4	0	0.00	0.03234	0.00007	**0.21**	**100.00**	0.00
130	8766.8	1002.3	1.8	0	0.00	0.03193	0.00005	**0.16**	**100.00**	0.00
160	8832.8	1013.6	1.6	0	0.00	0.03228	0.00004	**0.14**	**100.00**	0.00

Table C7 The results of the reaction with H_2 treatment at 700 °C followed by O_2 treatment at 350 °C and N_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 0.5, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 400 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	8944.2	988.3	13.7	0	14.30	0.03217	0.00074	**2.29**	**51.77**	48.23
40	8827.9	934.0	4.1	0	2.90	0.02989	0.00019	**0.62**	**61.30**	38.70
70	8876.4	994.0	2.3	0	0.79	0.03170	0.00008	**0.26**	**76.54**	23.46
100	8920.8	997.7	1.5	0	0.37	0.03178	0.00005	**0.16**	**81.96**	18.04
130	8874.2	1018.9	0.9	0	0.18	0.03243	0.00003	**0.09**	**84.71**	15.29
160	8842.7	1013.7	0.6	0	0.08	0.03226	0.00002	**0.06**	**88.56**	11.44

Table C8 The results of the reaction with H_2 treatment at 700 °C followed by O_2 treatment at 350 °C and N_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 0.5, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 450 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	8922.4	983.9	12.7	0	16.60	0.03206	0.00077	**2.39**	**46.16**	53.84
40	8890.8	1007.5	4.5	0	5.50	0.03230	0.00026	**0.81**	**47.83**	52.17
70	8835.9	1021.3	2.1	0	1.80	0.03258	0.00010	**0.32**	**56.66**	43.34
100	8899.3	1035.0	1.1	0	0.74	0.03296	0.00005	**0.15**	**62.49**	37.51
130	8866.6	1013.3	0.7	0	0.35	0.03225	0.00003	**0.08**	**68.39**	31.61
160	8809.0	1038.3	0.5	0	0.22	0.03304	0.00002	**0.06**	**72.97**	27.03

Table C9 The results of the reaction with H_2 treatment at 700 °C followed by O_2 treatment at 350 °C and N_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 0.5, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 500 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	8981.8	948.2	12.8	0	21.30	0.03104	0.00089	**2.85**	**40.24**	59.76
40	8999.5	986.0	4.0	0	5.90	0.03162	0.00026	**0.82**	**43.17**	56.83
70	8930.7	974.6	2.0	0	2.20	0.03111	0.00011	**0.35**	**50.46**	49.54
100	8875.3	1033.3	1.3	0	0.93	0.03292	0.00006	**0.18**	**61.04**	38.96
130	8964.9	969.3	0.8	0	0.44	0.03086	0.00003	**0.11**	**67.08**	32.92
160	8886.9	968.9	0.8	0	0.37	0.03084	0.00003	**0.10**	**70.67**	29.33

Table C10 The results of the reaction with H_2 treatment at 700 °C and O_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 0.5, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	8963.0	946.8	15.4	0	8.20	0.03074	0.00063	**2.06**	**67.79**	32.21
40	8891.3	943.2	12.2	0	5.70	0.03048	0.00048	**1.58**	**70.58**	29.42
70	8874.5	944.1	11.4	0	3.10	0.03042	0.00039	**1.30**	**80.47**	19.53
100	8871.1	933.2	10.6	0	1.90	0.03002	0.00034	**1.14**	**86.21**	13.79
130	8825.5	952.7	10.1	0	0.82	0.03060	0.00030	**0.99**	**93.24**	6.76
160	8866.1	927.5	9.5	0	0.64	0.02978	0.00028	**0.94**	**94.33**	5.67

Table C11 The results of the reaction with H_2 treatment at 700 °C and O_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 0.1, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	9000.1	871.6	3.3	0	2.49	0.02787	0.00015	**0.55**	**59.76**	40.24
40	8949.6	862.7	3.4	0	2.10	0.02758	0.00015	**0.53**	**64.47**	35.53
70	8850.2	860.9	3.0	0	1.40	0.02750	0.00012	**0.43**	**70.60**	29.40
100	8858.4	896.7	3.0	0	1.10	0.02863	0.00011	**0.39**	**75.35**	24.65
130	8880.3	873.5	2.7	0	0.65	0.02787	0.00009	**0.33**	**82.32**	17.68
160	8864.7	895.3	2.6	0	0.49	0.02856	0.00008	**0.30**	**85.60**	14.40

Table C12 The results of the reaction with H_2 treatment at 700 °C and O_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 0.3, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	8880.7	910.4	9.1	0	6.4	0.02937	0.00041	**1.41**	**61.44**	38.56
40	8911.6	938.2	9.9	0	5.4	0.03025	0.00041	**1.36**	**67.26**	32.74
70	8790.4	913.6	9.1	0	2.9	0.02938	0.00033	**1.11**	**77.86**	22.14
100	8822.4	927.0	8.5	0	2.2	0.02977	0.00029	**0.98**	**81.24**	18.76
130	8821.3	923.0	8.1	0	1.6	0.02962	0.00027	**0.90**	**85.01**	14.99
160	8825.7	911.0	7.9	0	1.3	0.02922	0.00025	**0.86**	**87.20**	12.80

Table C13 The results of the reaction with H_2 treatment at 700 °C and O_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 1.0, WHSV 2.8 h^{-1} and methane to benzene feed ratio 70 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	8943.9	778.7	14.5	0.09	0.44	0.02518	0.00042	**1.66**	**96.85**	2.62
40	8869.7	728.7	22.3	0.56	1.90	0.02386	0.00069	**2.88**	**90.35**	6.87
70	8791.0	723.4	19.0	0.25	1.60	0.02358	0.00058	**2.44**	**91.88**	6.90
100	8798.2	741.4	16.3	0	1.30	0.02406	0.00049	**2.02**	**93.36**	6.64
130	8875.6	738.5	13.4	0	0.90	0.02388	0.00040	**1.66**	**94.35**	5.65
160	8842.5	723.5	10.5	0	0.50	0.02331	0.00030	**1.31**	**95.92**	4.08

Table C14 The results of the reaction with H_2 treatment at 700 °C and O_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 1.0, WHSV 2.8 h^{-1} and methane to benzene feed ratio 23 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	6151.5	1840.8	34.7	0.48	3.7	0.05961	0.00107	**1.80**	**90.30**	8.59
40	6169.8	1829.8	27.2	0.21	3.6	0.05904	0.00085	**1.44**	**88.90**	10.50
70	6135.4	1840.4	24.1	0	3.5	0.05929	0.00076	**1.28**	**88.53**	11.47
100	6130.2	1781.3	21.5	0	3.4	0.05733	0.00068	**1.19**	**87.63**	12.37
130	6173.9	1797.8	19.5	0	3.1	0.05779	0.00062	**1.07**	**87.58**	12.42
160	6123.6	1810.4	17.6	0	3.0	0.05814	0.00056	**0.97**	**86.80**	13.20

Table C15 The results of the reaction with H_2 treatment at 700 °C and O_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 1.0, WHSV 2.8 h^{-1} and methane to benzene feed ratio 104 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	9426.8	572.6	12.9	0	0.54	0.01858	0.00037	**2.01**	**96.40**	3.60
40	9355.7	500.4	22.1	0.8	0.48	0.01656	0.00065	**3.91**	**95.11**	1.84
70	9435.9	504.8	20.4	0.48	0.40	0.01665	0.00060	**3.58**	**95.35**	1.67
100	9318.1	484.9	17.9	0.61	0.10	0.01594	0.00052	**3.27**	**95.60**	0.48
130	9434.7	513.8	16.4	0.19	0.25	0.01681	0.00047	**2.82**	**96.40**	1.31
160	9382.2	502.6	14.0	0	0.58	0.01639	0.00040	**2.47**	**96.43**	3.57

Table C16 The results of the reaction with H_2 treatment at 700 °C and O_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 1.0, WHSV 6.1 h^{-1} and methane to benzene feed ratio 104 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	9397.2	683.6	14.7	0.17	0.08	0.02216	0.00042	**1.88**	**98.52**	0.48
40	9369.4	669.8	12.7	0.08	0.50	0.02167	0.00037	**1.70**	**96.07**	3.38
70	9365.5	678.8	10.0	0	0.44	0.02188	0.00029	**1.32**	**96.22**	3.78
100	9355.3	627.6	7.8	0	0.34	0.02018	0.00023	**1.12**	**96.26**	3.74
130	9342.6	655.0	6.5	0	0.21	0.02102	0.00019	**0.89**	**97.20**	2.80
160	9336.8	645.5	5.1	0	0.11	0.02067	0.00014	**0.70**	**98.11**	1.89

Table C17 The results of the reaction with H_2 treatment at 700 °C and O_2 carrier using SiO_2/Al_2O_3 ratio 50, In/Al ratio 1.0, WHSV 12.3 h^{-1} and methane to benzene feed ratio 104 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	9434.3	788.7	6.4	0	0.15	0.02526	0.00018	**0.72**	**97.95**	2.05
40	9390.3	754.9	7.5	0	0.22	0.02422	0.00021	**0.89**	**97.45**	2.55
70	9426.5	743.6	6.6	0	0.19	0.02384	0.00019	**0.79**	**97.56**	2.44
100	9336.1	750.3	6.0	0	0.16	0.02403	0.00017	**0.71**	**97.68**	2.32
130	9349.6	785.4	5.3	0	0.14	0.02513	0.00015	**0.60**	**97.70**	2.30
160	9415.3	766.8	4.6	0	0.12	0.02452	0.00013	**0.53**	**97.73**	2.27

Table C18 The results of the reaction with H_2 treatment at 700 °C and O_2 carrier using SiO_2/Al_2O_3 ratio 23, In/Al ratio 1.0, WHSV 2.8 h^{-1} and methane to benzene feed ratio 104 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	9425.2	610.7	10.7	0	1.90	0.01977	0.00035	**1.75**	**86.32**	13.68
40	9406.3	595.4	6.5	0	1.15	0.01914	0.00021	**1.10**	**86.36**	13.64
70	9351.1	600.2	4.0	0	0.70	0.01922	0.00013	**0.67**	**86.49**	13.51
100	9354.3	623.9	2.3	0	0.40	0.01992	0.00007	**0.37**	**86.57**	13.43
130	9358.0	652.1	1.5	0	0.25	0.02079	0.00005	**0.23**	**87.05**	12.95
160	9335.0	654.7	1.0	0	0.16	0.02085	0.00003	**0.15**	**87.51**	12.49

Table C19 The results of the reaction with H_2 treatment at 700 °C and O_2 carrier using SiO_2/Al_2O_3 ratio 30, In/Al ratio 1.0, WHSV 2.8 h^{-1} and methane to benzene feed ratio 104 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	9407.1	520.5	14.6	0	2.20	0.01701	0.00046	**2.71**	**88.15**	11.85
40	9387.2	574.0	6.8	0	0.95	0.01847	0.00021	**1.15**	**88.92**	11.08
70	9343.3	575.9	5.3	0	0.79	0.01848	0.00017	**0.91**	**88.26**	11.74
100	9333.9	577.5	4.1	0	0.60	0.01850	0.00013	**0.70**	**88.45**	11.55
130	9260.0	579.8	2.6	0	0.35	0.01852	0.00008	**0.44**	**89.28**	10.72
160	9338.5	587.1	1.4	0	0.18	0.01871	0.00004	**0.23**	**89.71**	10.29

Table C20 The results of the reaction with H_2 treatment at 700 °C and O_2 carrier using SiO_2/Al_2O_3 ratio 80, In/Al ratio 1.0, WHSV 2.8 h^{-1} and methane to benzene feed ratio 104 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	9506.1	657.8	7.6	0	0.60	0.02115	0.00023	**1.07**	**93.42**	6.58
40	9520.4	621.4	9.6	0	0.46	0.02004	0.00028	**1.39**	**95.90**	4.10
70	9446.1	646.0	9.8	0	0.43	0.02083	0.00028	**1.36**	**96.23**	3.77
100	9478.2	631.1	9.4	0	0.21	0.02034	0.00027	**1.31**	**98.05**	1.95
130	9418.5	617.4	9.1	0	0.17	0.01989	0.00026	**1.30**	**98.36**	1.64
160	9386.9	616.7	9.1	0	0.08	0.01987	0.00026	**1.29**	**99.27**	0.73

Table C21 The results of the reaction with H_2 treatment at 700 °C and O_2 carrier using SiO_2/Al_2O_3 ratio 280, In/Al ratio 1.0, WHSV 2.8 h^{-1} and methane to benzene feed ratio 104 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	Selectivity (%)	
	Reactants		Products							
	Methane	Benzene	Toluene	C8	C9+				Toluene	Other
10	9599.3	573.5	0.14	0	0.60	0.01824	3.90E-06	**0.02**	**100.00**	0.00
40	9506.5	599.1	0.73	0	0.46	0.01907	2.03E-05	**0.11**	**100.00**	0.00
70	9360.1	611.5	0.92	0	0.43	0.01947	2.56E-05	**0.13**	**100.00**	0.00
100	9461.2	615.2	0.98	0	0.21	0.01959	2.73E-05	**0.14**	**100.00**	0.00
130	9444.6	603.4	0.88	0	0.17	0.01921	2.45E-05	**0.13**	**100.00**	0.00
160	9449.8	588.0	0.89	0	0.08	0.01872	2.48E-05	**0.13**	**100.00**	0.00

Appendix D Raw Data of Catalysts Characterization

The temperature program desorption (TPD) characterization results is shown in Figure D1.

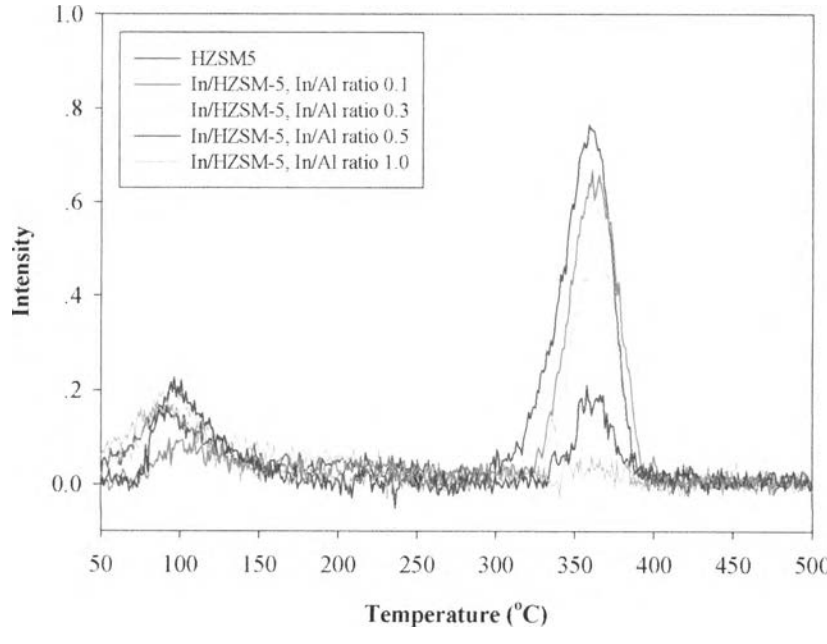

Figure D1 Temperature program desorption (TPD) profiles of catalyst with various In/Al ratios.

The desorption temperature and peak area, calculated from integration program (fityk) using Gaussian curve from obtained TPD profile, are shown in Table D1.

Table D1 Desorption temperature and peak area of HZSM-5 catalysts

Acid sites	Area				
	HZSM-5, SiO_2/Al_2O_3 23	**HZSM-5, SiO_2/Al_2O_3 30**	**HZSM-5, SiO_2/Al_2O_3 50**	**HZSM-5, SiO_2/Al_2O_3 80**	**HZSM-5, SiO_2/Al_2O_3 280**
Weak acid	1.4	2.8	2.3	3.1	0.4
Strong acid	41.2	37.2	31.6	23.9	7.7
Total acid	42.6	40.0	33.9	27.0	8.1

Table D2 Desorption temperature and peak area of HZSM-5 and In/HZSM-5 with SiO_2/Al_2O_3 50

Acid sites	Area	Area of In/HZSM-5, SiO_2/Al_2O_3 50			
	HZSM-5, SiO_2/Al_2O_3 50	**In/Al ratio 0.1**	**In/Al ratio 0.3**	**In/Al ratio 0.5**	**In/Al ratio 1.0**
Weak acid	2.3	2.5	3.1	1.3	0.7
Strong acid	31.6	34.5	28.6	15.3	5.3
Total acid	33.9	37	31.7	16.6	6

The calculation of acidity from TPD peak area used the calibration factor from propylene to calculate.

The area of propylene per mole from the calibration is equal to 7.672×10^6

The weight of used catalysts is 0.0500 g.

The acidity of catalysts in μmol/g was calculated by

$$\text{Acidity } (\mu\text{mol/g}) = \frac{\text{Area}}{(7.672 \text{ area}/\mu\text{mol}) \times (0.0500 \text{ g})}$$

The acidity of the catalyst is already shown in Table 4.5 and 4.6.

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Proceedings:

1. Niyomthong, N., Jermwongratanachai, T., Kitiyanan, B. and Apphakvan, T. (2013, April 10-11) Direct Methylation of Benzene by Methane using Indium-Containing ZSM-5 Catalysts: Effect of Reaction Temperature and Silica to Alumina Ratio. Poster presented at FineCat 2013 Symposium on heterogeneous catalysis for fine chemicals, Palermo, Italy.
2. Niyomthong, N., Jermwongratanachai, T., Kitiyanan, B. and Apphakvan, T. (2013, April 23) Indium-Containing ZSM-5 Catalyst for Methylation of Benzene: Effect of Silica/Alumina Ratios and Reaction Conditions. Proceedings of the 4th Research Symposium on Petrochemical and Materials Technology and the 19th PPC Symposium on Petroleum, Petrochemicals and Polymers, Bangkok, Thailand.