



## REFERENCES

- Adebajo, M.O., and Frost, R.L. (2005). Oxidative Benzene Methylation with methane over MCM-41 and Zeolite Catalysts: Effect of Framework Aluminum,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  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 Howe, R.F. (2000). Methane activation over zeolite catalysts: The methylation of benzene. Res. Chem. Intermed., 26(2), 185-191.
- Baba, T. (2005). Conversion of methane over  $\text{Ag}^+$ -exchanged zeolite in the presence of ethane. Catalysis Surveys from Asia, 9(3), 147-154.
- Baba, T., and Abe, Y. (2003). Metal cation-acidic proton bifunctional catalyst for methane activation: conversion of  $^{13}\text{CH}_4$  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. Phys. Chem. Chem. Phys., 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. J. Phys. Chem. B, 109(9), 4263-4268.
- Baba, T., Iwase, Y., Inazu, K., Masih, D., and Matsumoto, A. (2007). Catalytic properties of silver-exchanged zeolites for propene production by conversion of methane in the presence of ethane. Microporous and Mesoporous Materials, 101, 142–147.
- Chatterjee, M., Bhattacharya, 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.
- Ertl, G. (2008). Handbook of heterogeneous catalysis. Weinheim: Wiley-VCH Verlag.
- Gesser, H.D., and Hunter, N.R. (1998). A review of C-1 conversion chemistry. Catalysis Today, 42, 183-189.
- Hackworth, J.H., Koch, R.W., and Rezaian, A.J. (1995). Economic Evaluation and Market Analysis for Natural Gas Utilization - Topical Report. Washington DC: K&M Engineering and Consulting Corporation.
- 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  $\text{In}^{3+}$  is not isomorphously substituted into zeolite ZSM-5: reaction of ZSM-5 with aqueous  $\text{InF}_3$ . Inorganica Chimica Acta, 304, 297–300.
- He, S.J.X., Long, M.A., Attalla, M.I., and Wilson, M.A. (1994). Methylation of naphthalene by methane-carbon-13 over copper-exchanged silicoaluminophosphate. Energy Fuels, 8 (1), 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- $^{13}\text{C}$  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.

- Kosslick, H., Tuan, V.A., Walther, G., Storec, W. (1993). Study on the Isomorphous Substitution of Silicon by Indium in the MFI Framework. Crystal Research and Technology, 28(8), 1109–1114.
- Lunsford, J.H. (2000). Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century. Catalysis Today, 63, 165–174.
- 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: <sup>13</sup>C Solid-State NMR and GC-MS Study of Methane Aromatization in the Presence of Higher Alkane. J. Phys. Chem., 114(49), 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.
- Mcketta, J.J. (1993). Chemical Processing Handbook. New York: Marcel Dekker.
- 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<sub>4</sub>-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 DeNO<sub>x</sub> 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.
- Naccache, C.M., Meriaudeau, P., Sapaly, G., Tjep, L.V., and Taarit, Y.B. (2002). Assessment of the Low-Temperature Nonoxidative Activation of Methane over H-Galloaluminosilicate (MFI) Zeolite: A C-13 Labelling Investigation. Journal of Catalysis, 205, 217-220.

- Ogura, M., Ohsaki, T., and Kikuchi, E. (1998). The effect of zeolite structures on the creation of  $\text{InO}^+$  active sites for  $\text{NO}_x$  reduction with methane. Microporous and Mesoporous Materials, 21, 533-540.
- Olah, G.A. (1987). Electrophilic methane conversion, Acc.Chem.Res., 20, 422-428.
- Price, G.L. (2006). Catalyst Preparation: Science and Engineering. In Regalbuto, J (Eds.), Solid-State Ion-Exchange (pp. 283-295). New York: CRC Press.
- Schmidt, C., Sowade, T., Loffler, E., Birkner, A. and Grunert, W. (2002), Preparation and Structure of In-ZSM-5 Catalysts for the Selective Reduction of NO by Hydrocarbons. J. Phys. Chem., 106, 4085-4097.
- Schutze, F.W.; Berndt, H.; Richter, M.; Lucke, B.; Schmidt, C.; Sowade, T. and Grunert, W. (2001). Investigation of indium loaded zeolites and additionally promoted catalysts for the selective catalytic reduction of  $\text{NO}_x$  by methane. Studies in Surface Science and Catalysis, 135(Zeolites and Mesoporous Materials at the Dawn of the 21st Century), 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. J. Phys. Chem., 112, 19423-19430.
- Sowade, T., Schmidt, C., Schutze, F.-W., Berndt, H. and Grunert, W. (2003). Relations between structure and catalytic activity of Ce-In-ZSM-5 catalysts for the selective reduction of NO by methane I. The In-ZSM-5 system. Journal of Catalysis, 214, 100-112.
- 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.

## APPENDICES

### Appendix A Calculation of Catalysts Composition

The catalysts composition is calculated base on the Si/Al ratio of HZSM-5 equal to 20.

The formula of HZSM-5 with Si/Al ratio 20 is represented by  $\text{AlSi}_{20}\text{O}_{42}\text{H}$ .

The formula weight of HZSM-5 is 1260 g/mol.

The molecular weight of  $\text{InCl}_3$  is 221 g/mol.

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

The weight of loaded  $\text{InCl}_3$  is represented by

$$m = \frac{5 \times 221 \times n}{1260}$$

Where  $n$  = required In/Al ratio

$m$  = weight of  $\text{InCl}_3$  required

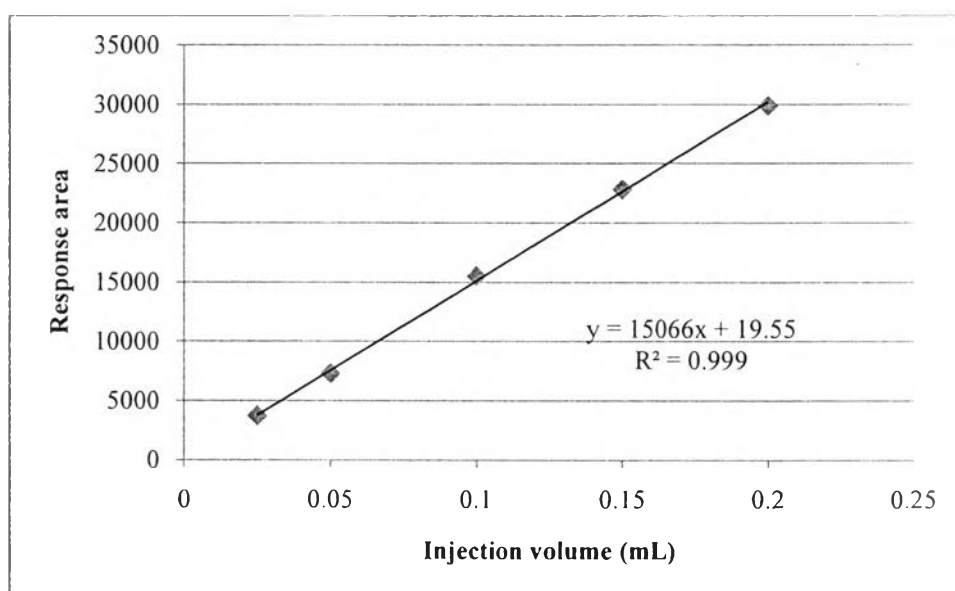
The prepared catalysts was using the composition as shown in Table A1.

**Table A1** The ingredients of prepared catalysts

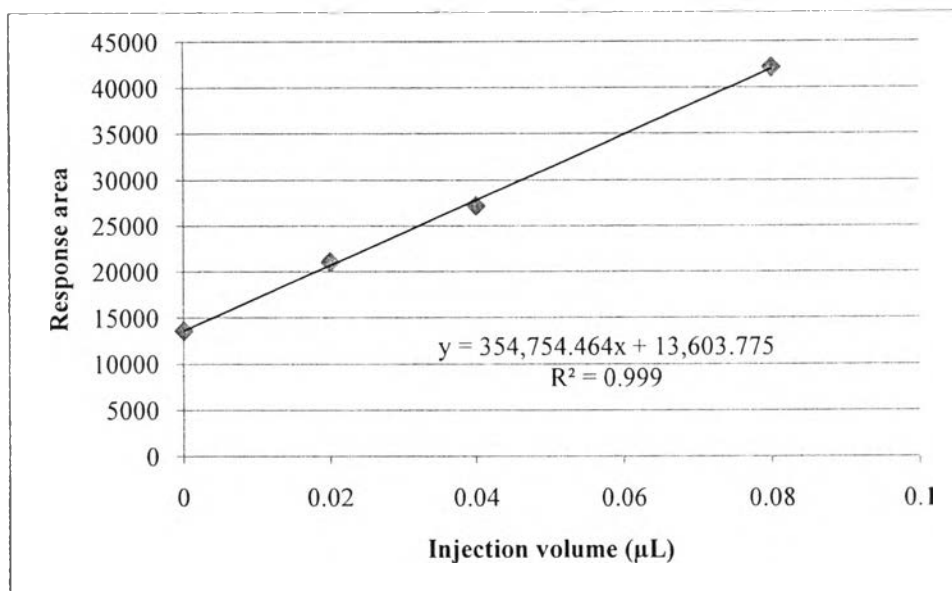
In/Al ratios	HZSM-5 (g)	$\text{InCl}_3$ (g)	Loading (wt. %)
0.1	5.00	0.0877	1.7
0.3	5.00	0.2631	5.0
0.5	5.00	0.4385	8.1
1.0	5.00	0.8770	14.9

## Appendix B Calibration Data and Feed Flow Adjustment

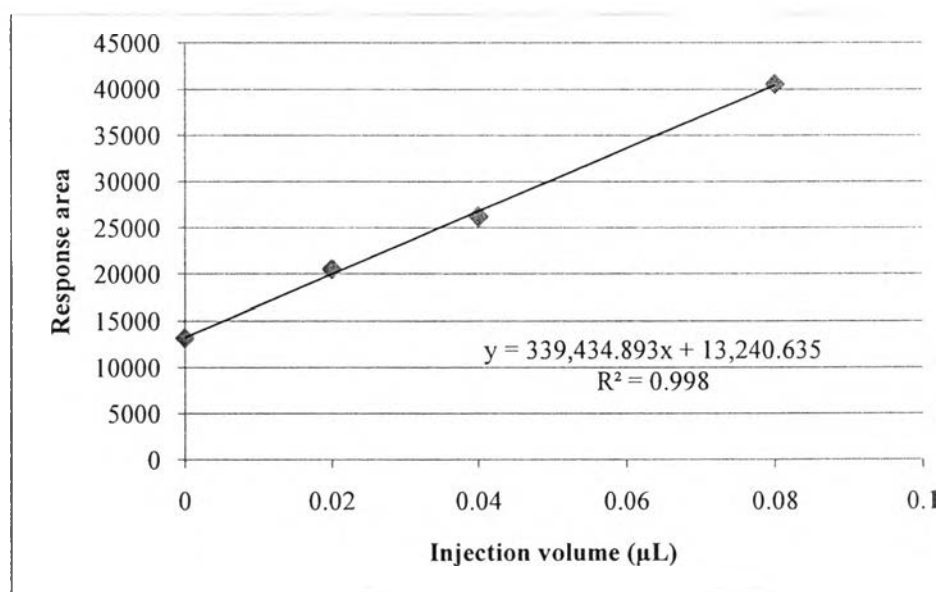
The calibration curve and regression equation of raw materials and some products is shown below. The response factors used for calculate the products amount that derived from the slope of calibration curve is also shown.



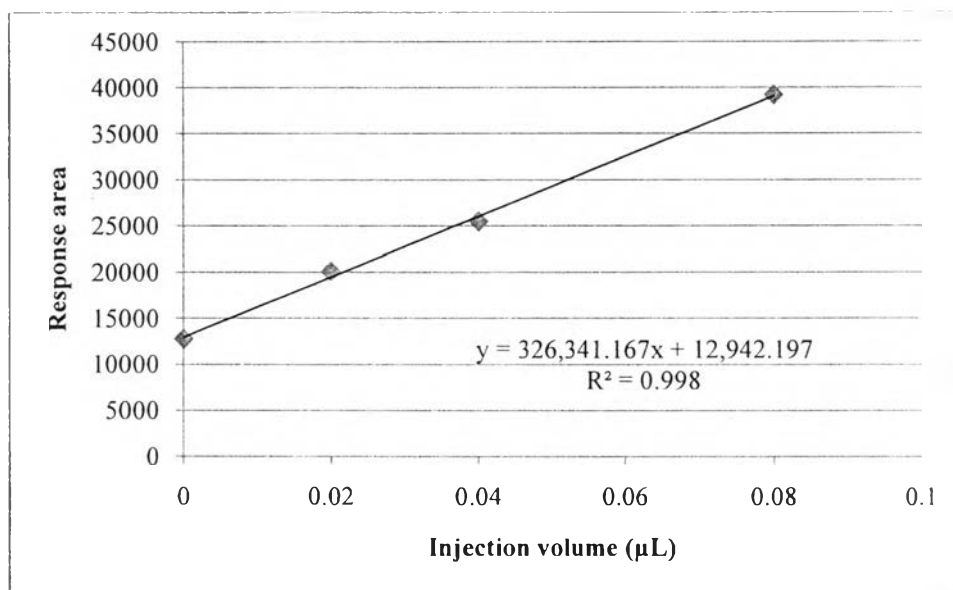
**Figure B1** Response area from GC FID as a function of injection volume of methane.



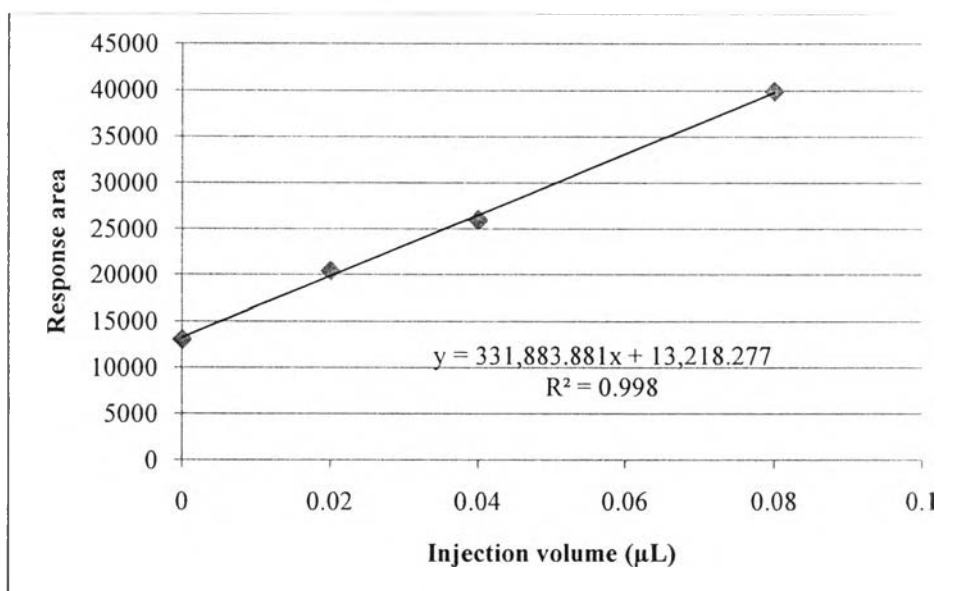
**Figure B2** Response area from GC FID as a function of injection volume of benzene.



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

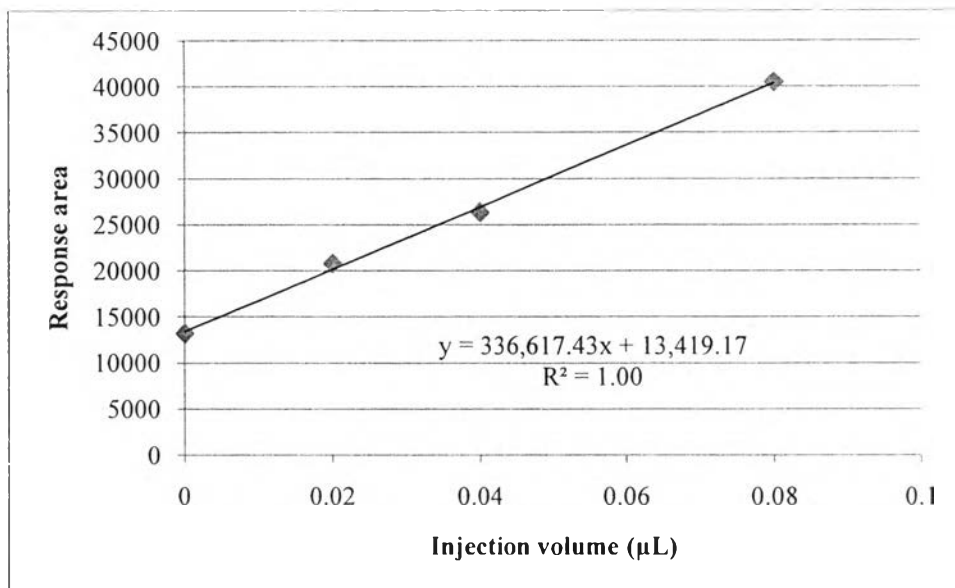


**Figure B4** Response area from GC FID as a function of injection volume of *p*-xylene.



**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
<i>p</i> -Xylene	326341167	0.86	379466473	106	40223446165
<i>m</i> -Xylene	331883881	0.86	385911490	106	40906617891
<i>o</i> -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)
WHSV (h <sup>-1</sup> )	M/B feed ratio	Methane	Oxygen	
1.8	45	21.0	9.0	0.940
6.6	19	15.0	15.0	0.250
	45	21.0	9.0	
	105	25.5	4.5	
13.2	45	21.0	9.0	0.125

### 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 N<sub>2</sub> treatment at 350 °C and N<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 300 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	31792	6233.2	4.6	0	0	0.19836	0.00013	0.065	100	0
40	31932	6239.6	6.9	0	0	0.19863	0.00019	0.097	100	0
70	31825	6262.3	6.8	0	0	0.19935	0.00019	0.095	100	0
100	31763	6225.6	6.5	0	0	0.19817	0.00018	0.091	100	0
130	31774	6178.1	6.6	0	0	0.19666	0.00018	0.093	100	0
160	31561	6120.1	6.6	0	0	0.19482	0.00018	0.094	100	0

**Table C2** The results of the reaction with N<sub>2</sub> treatment at 350 °C and N<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	32995	6515.8	76.1	0	0	0.20934	0.00212	1.013	100	0
40	33037	6486.9	51.9	0	0	0.20775	0.00145	0.696	100	0
70	33018	6656.5	39.8	0	0	0.21280	0.00111	0.521	100	0
100	32904	6566.4	31.7	0	0	0.20971	0.00088	0.421	100	0
130	32919	6566.6	28.4	0	0	0.20962	0.00079	0.377	100	0
160	33017	6643.6	26.1	0	0	0.21201	0.00073	0.343	100	0

**Table C3** The results of the reaction with N<sub>2</sub> treatment at 350 °C and N<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 400 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	31875	5641.4	186.9	4.23	3.17	0.18480	0.00539	2.917	96.604	3.396
40	31893	5855.6	74	0	0.89	0.18831	0.00208	1.107	98.938	1.062
70	31960	5881.7	46	0	0	0.18833	0.00128	0.680	100	0
100	31606	5894.5	32.7	0	0	0.18837	0.00091	0.484	100	0
130	31729	5958.5	22.9	0	0	0.19013	0.00064	0.336	100	0
160	31837	5974.4	12.3	0	0	0.19034	0.00034	0.180	100	0

**Table C4** The results of the reaction with O<sub>2</sub> treatment at 350 °C and N<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	32711	6672.9	51.1	0	0	0.21364	0.00142	0.666	100	0
40	32825	6668.7	42.1	0	0	0.21325	0.00117	0.550	100	0
70	32660	6741.6	37.9	0	0	0.21546	0.00106	0.490	100	0
100	32600	6627.3	34.1	0	0	0.21171	0.00095	0.449	100	0
130	32571	6719.1	31.6	0	0	0.21456	0.00088	0.410	100	0
160	32780	6735.2	29.6	0	0	0.21502	0.00082	0.384	100	0

**Table C5** The results of the reaction with H<sub>2</sub> treatment at 350 °C and N<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	33058	6282.5	13.5	0	0	0.20017	0.00038	<b>0.188</b>	<b>100</b>	0
40	32940	6249.7	12.4	0	0	0.19910	0.00035	<b>0.174</b>	<b>100</b>	0
70	32888	6420.4	8.9	0	0	0.20443	0.00025	<b>0.121</b>	<b>100</b>	0
100	32662	6417.7	6.7	0	0	0.20429	0.00019	<b>0.091</b>	<b>100</b>	0
130	32898	6457	5.8	0	0	0.20551	0.00016	<b>0.079</b>	<b>100</b>	0
160	32884	6420.1	4.6	0	0	0.20430	0.00013	<b>0.063</b>	<b>100</b>	0

**Table C6** The results of the reaction with H<sub>2</sub> treatment at 350 °C followed by O<sub>2</sub> treatment at 350 °C and N<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	33111	6543.7	95.6	0	9.7	0.21101	0.00290	<b>1.376</b>	<b>91.697</b>	8.303
40	33133	6801.1	20.6	0	0	0.21687	0.00057	<b>0.265</b>	<b>100</b>	0
70	33120	6750.6	11.2	0	0	0.21500	0.00031	<b>0.145</b>	<b>100</b>	0
100	33241	6800.7	7.7	0	0	0.21649	0.00021	<b>0.099</b>	<b>100</b>	0
130	33006	6688.8	5.9	0	0	0.21288	0.00016	<b>0.077</b>	<b>100</b>	0
160	33023	6702.5	5	0	0	0.21330	0.00014	<b>0.065</b>	<b>100</b>	0

**Table C7** The results of the reaction with N<sub>2</sub> treatment at 450 °C and N<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	33007	6630.9	46.4	0	0	0.21217	0.00129	0.609	100	0
40	33239	6716.9	37	0	0	0.21464	0.00103	0.480	100	0
70	33090	6790.9	33.2	0	0	0.21689	0.00092	0.426	100	0
100	32970	6812.8	30.1	0	0	0.21750	0.00084	0.386	100	0
130	32987	6701	28	0	0	0.21389	0.00078	0.365	100	0
160	32906	6574.5	25.7	0	0	0.20980	0.00072	0.341	100	0

**Table C8** The results of the reaction with O<sub>2</sub> treatment at 450 °C and N<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	33044	6710.5	68	0	0	0.21530	0.00189	0.880	100	0
40	33118	6633.4	50.7	0	0	0.21237	0.00141	0.665	100	0
70	33052	6634.8	41.1	0	0	0.21215	0.00115	0.540	100	0
100	33083	6688.9	35.5	0	0	0.21371	0.00099	0.463	100	0
130	32975	6644.9	31.3	0	0	0.21220	0.00087	0.411	100	0
160	32961	6695.4	28.6	0	0	0.21373	0.00080	0.373	100	0

**Table C9** The results of the reaction with H<sub>2</sub> treatment at 450 °C and N<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	33248	6542.5	14.9	0	0	0.20848	0.00042	0.199	100	0
40	33319	6649.8	6	0	0	0.21165	0.00017	0.079	100	0
70	33139	6550.6	4.4	0	0	0.20845	0.00012	0.059	100	0
100	33079	6558.4	3.7	0	0	0.20868	0.00010	0.049	100	0
130	33001	6513.3	3.2	0	0	0.20723	0.00009	0.043	100	0
160	30002	6499.8	3	0	0	0.20679	0.00008	0.040	100	0

**Table C10** The results of the reaction with H<sub>2</sub> treatment at 450 °C followed by O<sub>2</sub> treatment at 350 °C and N<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	33164	6567.8	85.3	0	12.7	0.21156	0.00269	1.273	88.272	11.73
40	33191	6592.2	23.7	0	3.6	0.21040	0.00075	0.356	88.063	11.94
70	33016	6638.2	12.8	0	0	0.21147	0.00036	0.169	100	0
100	32934	6685.6	8.6	0	0	0.21286	0.00024	0.113	100	0
130	33182	6727.2	6.7	0	0	0.21413	0.00019	0.087	100	0
160	33004	6785.7	5.4	0	0	0.21595	0.00015	0.070	100	0

**Table C11** The results of the reaction with N<sub>2</sub> treatment at 350 °C and 100% O<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	33118	6095	17.1	0	34.1	0.19516	0.00132	<b>0.679</b>	<b>35.977</b>	64.02
40	32879	5824	59.7	0	21.7	0.18742	0.00220	<b>1.175</b>	<b>75.525</b>	24.48
70	33019	6072.2	67	0	12.1	0.19528	0.00217	<b>1.110</b>	<b>86.111</b>	13.89
100	32973	6146.5	65.4	0	10.5	0.19756	0.00208	<b>1.054</b>	<b>87.468</b>	12.53
130	32740	6227.4	60.3	0	8.63	0.19994	0.00189	<b>0.948</b>	<b>88.675</b>	11.33
160	32581	6306.8	55.1	0	6.7	0.20227	0.00170	<b>0.841</b>	<b>90.211</b>	9.789

**Table C12** The results of the reaction with O<sub>2</sub> treatment at 350 °C and 100% O<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	32827	6316.4	34.7	0	32	0.20264	0.00176	<b>0.870</b>	<b>54.857</b>	45.14
40	33026	6287.1	56.5	0	27.4	0.20220	0.00226	<b>1.115</b>	<b>69.795</b>	30.21
70	32798	6242.5	50.7	0	18.7	0.20040	0.00188	<b>0.937</b>	<b>75.227</b>	24.77
100	32780	6354.2	44.6	0	11.9	0.20362	0.00154	<b>0.755</b>	<b>80.795</b>	19.21
130	32773	6351	42.3	0	8.4	0.20336	0.00139	<b>0.682</b>	<b>84.947</b>	15.05
160	32731	6553.8	40.9	0	8.3	0.20977	0.00135	<b>0.642</b>	<b>84.667</b>	15.33



**Table C13** The results of the reaction with H<sub>2</sub> treatment at 350 °C and 100% O<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	32974.8	4847.5	200.1	1.7	62.8	0.16134	0.00718	<b>4.449</b>	77.661	22.339
40	33044.2	5527.6	138.3	0	19	0.18012	0.00433	<b>2.401</b>	89.079	10.921
70	32967.8	5798.2	97.7	0	8.4	0.18733	0.00293	<b>1.564</b>	92.874	7.126
100	32851.7	5967.5	70.7	0	5.9	0.19190	0.00212	<b>1.103</b>	93.069	6.931
130	32972.3	6009.9	52.7	0	3.4	0.19268	0.00155	<b>0.806</b>	94.556	5.444
160	33125.1	6057.3	40.5	0	2.7	0.19383	0.00120	<b>0.617</b>	94.385	5.615

**Table C14** The results of the reaction with H<sub>2</sub> treatment at 350 °C and 2% O<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	33247	6351.6	85.5	1.05	5.39	0.20454	0.00254	<b>1.243</b>	93.71	6.29
40	33153	6492.5	70.9	0	5.03	0.20858	0.00210	<b>1.007</b>	94.046	5.954
70	33089	6466.6	62.8	0	5.46	0.20754	0.00189	<b>0.908</b>	92.8	7.200
100	33024	6489.3	47.6	0	5.2	0.20783	0.00146	<b>0.700</b>	91.117	8.883
130	33228	6512.3	42.8	0	5.3	0.20843	0.00132	<b>0.635</b>	90.049	9.951
160	33211	6555.8	40.5	0	5.3	0.20975	0.00126	<b>0.601</b>	89.543	10.46

**Table C15** The results of the reaction with H<sub>2</sub> treatment at 350 °C and 21% O<sub>2</sub> carrier using In/Al ratio 0.5, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	33511	5919.5	126.7	0.9	46.7	0.19297	0.00471	2.442	74.892	25.11
40	33372	6062.3	118.3	0	36.7	0.19700	0.00421	2.136	78.318	21.68
70	33504	6115	106.6	0	22.5	0.19800	0.00353	1.782	84.15	15.85
100	33375	6189.1	91	0	15.6	0.19975	0.00292	1.463	86.732	13.27
130	33533	6261.7	76.6	0	12.2	0.20157	0.00244	1.209	87.556	12.44
160	33292	6208.1	64.4	0	9.6	0.19947	0.00203	1.019	88.259	11.74

**Table C16** The results of the reaction with H<sub>2</sub> treatment at 350 °C and 100% O<sub>2</sub> carrier using In/Al ratio 0.1, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion (%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	33373	5312.6	48.3	0	53.1	0.17162	0.00267	1.553	50.478	49.52
40	33357	5719.5	33.4	0	26.7	0.18349	0.00159	0.869	58.365	41.64
70	33183	5964.6	23.1	0	13.6	0.19067	0.00098	0.515	65.557	34.44
100	33252	6165.1	20.1	0	8.6	0.19684	0.00077	0.393	72.369	27.63
130	33388	6228.1	17.5	0	6.2	0.19871	0.00064	0.323	75.979	24.02
160	33237	6266.6	13.6	0	4.6	0.19979	0.00049	0.247	76.815	23.19

**Table C17** The results of the reaction with H<sub>2</sub> treatment at 350 °C and 100% O<sub>2</sub> carrier using In/Al ratio 0.3, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	25476	4052.7	69.1	0	66.4	0.13246	0.00358	<b>2.700</b>	<b>53.836</b>	46.16
40	25608	4411.8	52.2	0	33.6	0.14260	0.00229	<b>1.606</b>	<b>63.516</b>	36.48
70	25523	4623.6	38	0	10.8	0.14837	0.00133	<b>0.895</b>	<b>79.769</b>	20.23
100	25402	4525.1	27.1	0	6.6	0.14483	0.00092	<b>0.635</b>	<b>82.147</b>	17.85
130	25099	4557.9	19	0	4.2	0.14559	0.00063	<b>0.435</b>	<b>83.524</b>	16.48
160	25373	4632.9	13.8	0	2.6	0.14779	0.00045	<b>0.304</b>	<b>85.607</b>	14.39

**Table C18** The results of the reaction with H<sub>2</sub> treatment at 350 °C and 100% O<sub>2</sub> carrier using In/Al ratio 1.0, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	33345	5353.6	399.3	11.6	27.1	0.18234	0.01208	<b>6.628</b>	<b>92.053</b>	7.947
40	33386	5860.8	225.9	3.3	17.4	0.19320	0.00681	<b>3.524</b>	<b>92.441</b>	7.559
70	33343	5980.1	163.4	1.8	12	0.19508	0.00490	<b>2.509</b>	<b>92.992</b>	7.008
100	33177	6114	123.5	1.1	8.1	0.19811	0.00367	<b>1.852</b>	<b>93.767</b>	6.233
130	33468	6108.5	100.1	0.78	6.8	0.19724	0.00298	<b>1.509</b>	<b>93.67</b>	6.330
160	33129	6194.1	84	0	6.3	0.19948	0.00250	<b>1.252</b>	<b>93.727</b>	6.273

**Table C19** The results of the reaction with H<sub>2</sub> treatment at 350 °C and 100% O<sub>2</sub> carrier using In/Al ratio 1.0, WHSV 1.8 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	32526	3455.5	262.3	8.3	117	0.12031	0.01041	8.655	70.177	29.82
40	32828	4253	137.4	0	135	0.14245	0.00719	5.050	53.209	46.79
70	32935	4793.8	135.2	0	96.9	0.15863	0.00618	3.893	60.991	39.01
100	32812	5313.5	131.5	0	54.8	0.17401	0.00503	2.888	72.893	27.11
130	32868	5710.4	112.5	0	9.4	0.18497	0.00337	1.821	93.061	6.939
160	32582	5867.4	89.8	0	6.1	0.18925	0.00265	1.402	94.285	5.715

**Table C20** The results of the reaction with H<sub>2</sub> treatment at 350 °C and 100% O<sub>2</sub> carrier using In/Al ratio 1.0, WHSV 13.2 h<sup>-1</sup> and methane to benzene feed ratio 45 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	33364	5954.4	235.2	5.3	17	0.19647	0.00711	3.617	92.199	7.801
40	33239	6213.1	125.3	1.8	17.4	0.20156	0.00397	1.969	87.971	12.03
70	33355	6343.5	92.7	1	5.9	0.20449	0.00275	1.347	93.771	6.229
100	32952	6330.9	73.7	0	4.7	0.20351	0.00217	1.066	94.616	5.384
130	33233	6344	61.1	0	4	0.20356	0.00180	0.885	94.48	5.520
160	33202	6383.4	51.7	0	3	0.20452	0.00151	0.741	95.077	4.923

**Table C21** The results of the reaction with H<sub>2</sub> treatment at 350 °C and 100% O<sub>2</sub> carrier using In/Al ratio 1.0, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 19 at reaction temperature 350 °C

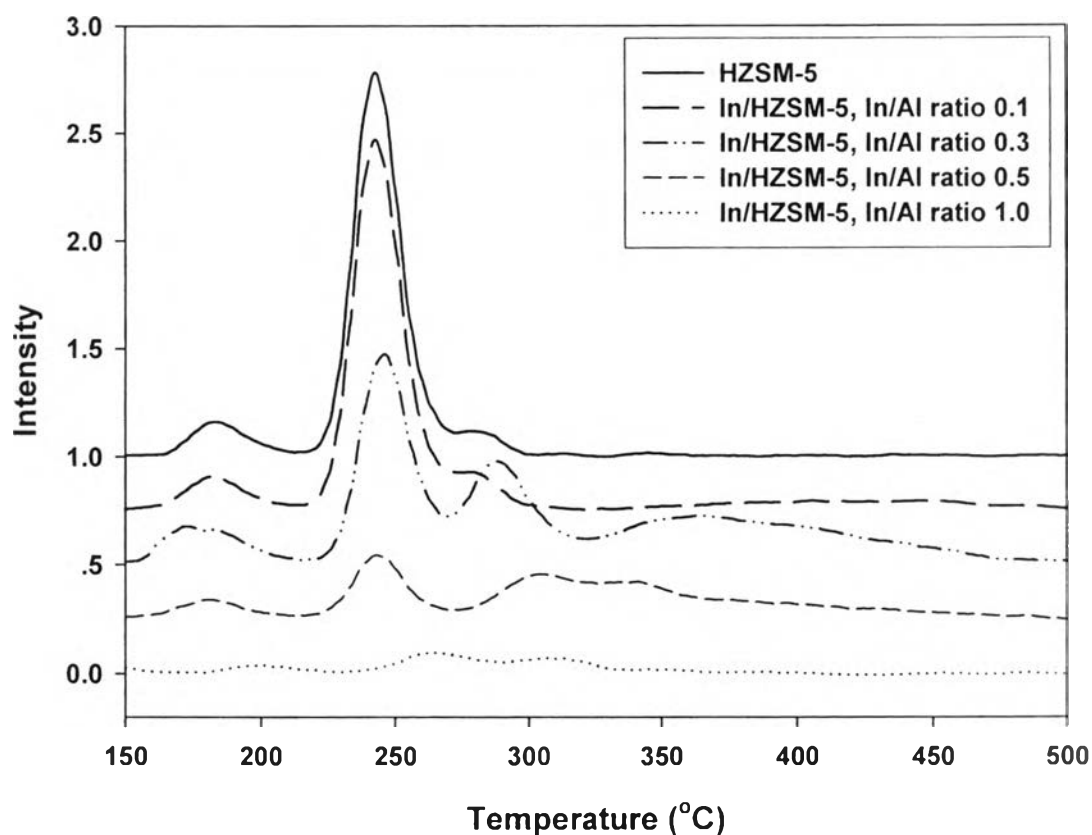
Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	27071	10922	402.7	4.4	55.1	0.36003	0.01270	<b>3.527</b>	<b>88.351</b>	11.65
40	27174	11762	178.1	1.1	37.2	0.37996	0.00591	<b>1.557</b>	<b>83.892</b>	16.11
70	27218	12021	121.1	0	20.1	0.38617	0.00387	<b>1.003</b>	<b>87.077</b>	12.92
100	27110	12121	92.5	0	15.6	0.38846	0.00297	<b>0.763</b>	<b>86.897</b>	13.10
130	27107	12214	74.7	0	13.9	0.39086	0.00243	<b>0.621</b>	<b>85.76</b>	14.24
160	27173	12303	62.1	0	11.5	0.39327	0.00202	<b>0.513</b>	<b>85.818</b>	14.18

**Table C22** The results of the reaction with H<sub>2</sub> treatment at 350 °C and 100% O<sub>2</sub> carrier using In/Al ratio 1.0, WHSV 6.6 h<sup>-1</sup> and methane to benzene feed ratio 105 at reaction temperature 350 °C

Time on stream (min)	FID area					Total aromatic (μmol)	Total aromatic product (μmol)	Benzene conversion(%)	selectivity (%)	
	Reactants		Products						Toluene	Other
	Methane	Benzene	Toluene	C8	C9+					
10	36833	2326.1	287.5	15.4	7.6	0.08255	0.00858	<b>10.392</b>	<b>93.361</b>	6.639
40	36931	2523.4	217.6	6.4	10.2	0.08673	0.00647	<b>7.466</b>	<b>93.626</b>	6.374
70	36674	2611.8	174.6	4	7	0.08820	0.00514	<b>5.825</b>	<b>94.677</b>	5.323
100	36835	2680.2	145.8	2.9	5.1	0.08950	0.00426	<b>4.761</b>	<b>95.332</b>	4.668
130	36828	2709	124.1	2.1	4.5	0.08977	0.00362	<b>4.034</b>	<b>95.469</b>	4.531
160	36583	2698.1	105.5	1.6	3.1	0.08886	0.00306	<b>3.439</b>	<b>96.177</b>	3.824

## Appendix D Raw Data of Catalysts Characterization

The temperature program desorption (TPD) characterization results is shown in Figure D1. The peak in the range of 150 to 200 °C represented to the weak Bronsted acid while the peak in the range of 220 to 300 °C represented to the strong Bronsted acid.



**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

Acid sites	HZSM-5		In/Al ratio 0.1		In/Al ratio 0.3		In/Al ratio 0.5		In/Al ratio 1.0	
	Temp (°C)	Area	Temp (°C)	Area	Temp (°C)	Area	Temp (°C)	Area	Temp (°C)	Area
	206.6	5.56	204.9	5.73	198.8	8.70	202.9	3.67	227.9	1.57
	284.4	42.65	284.6	42.56	288.9	29.27	285.6	8.66	314.9	3.69
	305.0	12.78	310.6	15.35	344.0	16.69	378.0	11.87	371.3	2.16
<b>Weak acid</b>		<b>5.56</b>		<b>5.73</b>		<b>8.70</b>		<b>3.67</b>		<b>1.57</b>
<b>Strong acid</b>		<b>55.43</b>		<b>57.91</b>		<b>45.96</b>		<b>20.53</b>		<b>5.85</b>
<b>Total acid</b>		<b>60.99</b>		<b>63.64</b>		<b>54.65</b>		<b>24.19</b>		<b>7.42</b>

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  $7.672 \times 10^6$

The weight of used catalysts is 0.0400 g.

The acidity of catalysts in  $\mu\text{mol/g}$  was calculated by

$$\text{Acidity } (\mu\text{mol/g}) = \frac{\text{Area}}{(7.672 \text{ area}/\mu\text{mol}) \times (0.0400 \text{ g})}$$

The acidity of the catalyst is already shown in Table 4.4.

The temperature program oxidation (TPO) characterization results are shown in Table D2.

The calibration factor was calculated by using CO<sub>2</sub> calibration.

The injection loop valve is 100 μL.

Mole of injected CO<sub>2</sub> calculated from ideal gas law.

$$n = \frac{(1 \text{ atm}) \times (100 \text{ } \mu\text{L})}{(0.0821 \text{ atm}\cdot\text{L}/\text{mol}\cdot\text{K}) \times (298 \text{ K})} = 4.087 \text{ } \mu\text{mol}$$

The calibration factor is represented by

$$\text{Calibration factor} = \frac{\text{CO}_2 \text{ area}}{4.087 \text{ } \mu\text{mol}}$$

The amount of carbon deposition determined by the area from TPO result divided by the calibration factor. Carbon deposition is calculated as the weight of carbon observed per weight of catalyst used.

**Table D2** Calculation of carbon deposition from TPO

Spent catalyst carrier gas	TPO result (area)	CO <sub>2</sub> calibration (area)	Calibration factor (area/μmol)	Carbon (μmol)	Carbon (mg)	Spent catalyst used (mg)	Carbon deposition (%)
N <sub>2</sub>	33059	16595	4060	8.142	0.0977	20.4	0.48
2% O <sub>2</sub>	215948	16671	4079	52.95	0.6353	21.6	2.94
21% O <sub>2</sub>	606698	14805	3622	167.5	2.010	20.2	9.95
100% O <sub>2</sub>	745863	13201	3230	230.9	2.771	21.5	12.89



## CURRICULUM VITAE

**Name:** Mr. Trisik Srisayan

**Date of Birth:** July 1, 1987

**Nationality:** Thai

**University Education:**

2006–2010 Bachelor Degree of Engineering in major of Petrochemicals and Polymeric Materials, Faculty of Engineering and Industrial Technology, Silpakorn University, Sanamchandra Palace Campus, Nakornprathom, Thailand

**Work Experience:**

2009 Position: Internship Student

Company name: The Siam Cement Group

**Proceedings:**

1. Srisayan, T.; Jermwongratanachai, T.; Kitiyanan, B. and Apphakvan, T. (2012, April 24) Indium-Containing ZSM-5 Catalyst for Methylation of Benzene: Effect of Treatment and Co-feed. Proceedings of 3<sup>rd</sup> Research Symposium on Petrochemical and Materials Technology and 18<sup>th</sup> PPC Symposium on Petroleum, Petrochemicals and Polymers, Bangkok, Thailand.

