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APPENDICES

Appendix A Experimental Data of Liquid Feed Calibration of GC 5890

1. Benzene

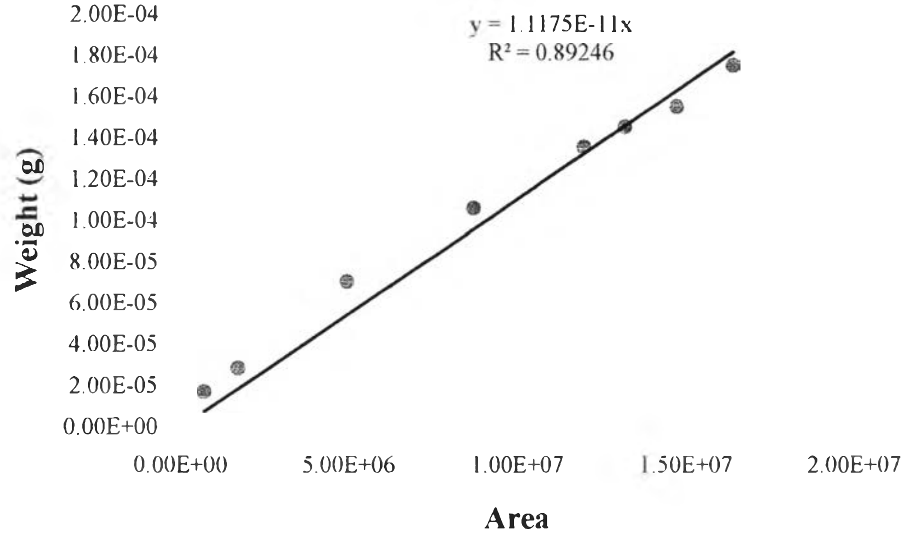

Figure A1 Calibration curve of benzene.

2. Ethanol

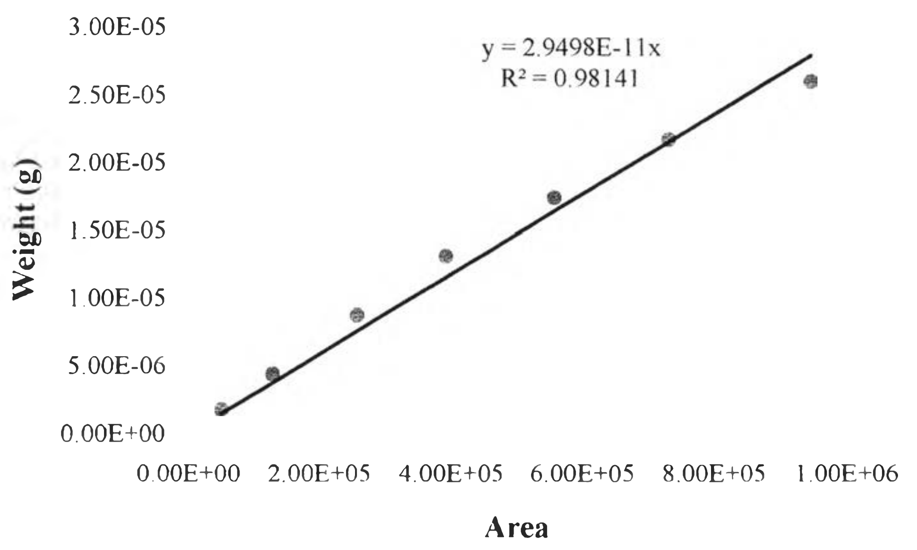

Figure A2 Calibration curve of ethanol.

Appendix B Experimental Data of Gas Flow Calibration of Sierra C100L Mass Flow Controller

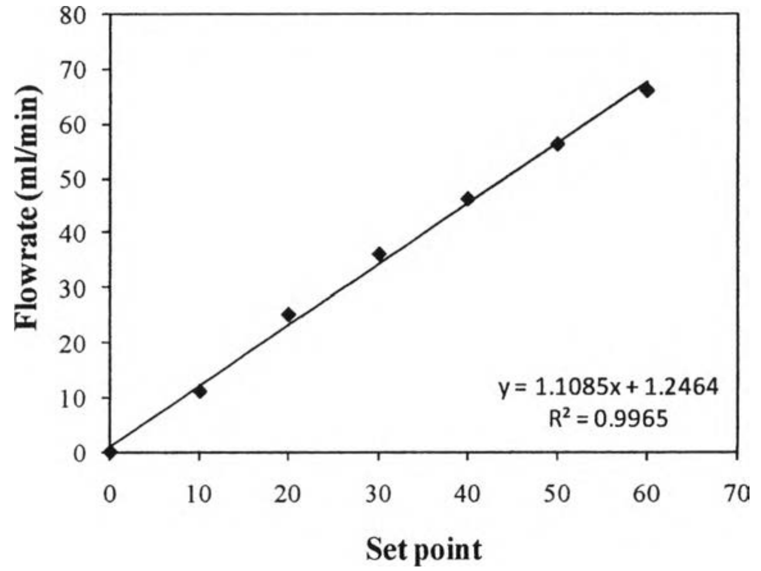

Figure B1 Calibration curve of nitrogen.

Appendix C Experimental Data of Liquid Feed Flow Calibration of Gilson 307 Pump

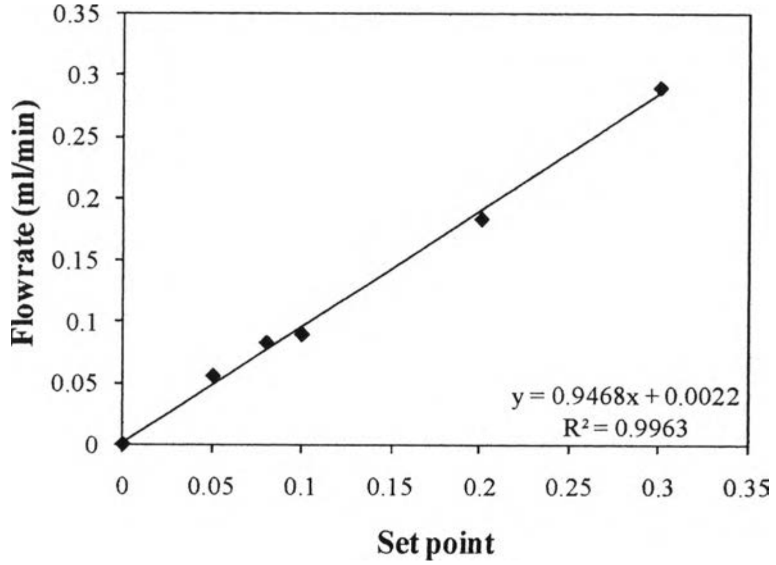

Figure C1 Calibration curve of liquid feed.

Appendix D Calculation of Si/Al Ratio and Theoretical Acidity

From the chemical composition determined by XRF method, the SiO_2/Al_2O_3 ratio is calculated as follows:

In the case of HZ5-195(3),

SiO_2 = 98.682 wt% Al_2O_3 = 1.075 wt%

SiO_2 = 1.647568 mol Al_2O_3 = 0.009876 mol

SiO_2/Al_2O_3= 166.8204

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 HZ5-195(3) with,

Si = 46.278 wt% Al = 10.5273 wt%

Si = 1.64775 mol Al = 0.01954 mol

Si/Al = 84.3143

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

Si/ Al= 84.3143= (96-n)/n

85.3143n = 96

n = 1.12525

So, Si = 94.87475

Al = 1.12525

From the above, the general formula of HZSM-5 is $H_{1.12525}Al_{1.12525}Si_{94.87475}O_{192}$. The weight of unit cell of HZSM-5 (U) is

U = 1.12525(1) + 1.12525(26.98) + 94.87475(28.09) + 192(16.00)

U = 5768.5162 g

The theoretical acidity ($[H^+]$) of HZSM-5 (B1) is

$[H^+]$ = 1.12525/5768.5162

$[H^+]$ = 0.19507 mmol/g

Appendix E The Other Catalyst Preparation

In this work, the other method for synthesizing ZSM-5 zeolites was adopted from the work of Rugwong and coworkers (Rugwong*et al.*, 2012) The detailed produre is described below.

This technique used NaOH as a mineralizing agent. HZSM-5 samples were synthesized from hydrogel solutions via hydrothermal synthesis with the following molar composition

$195SiO_2{:}Al_2O_3{:}20TPABr{:}\ xH2O$

where x = 3900, 4875, 5850, and 7800.

First, Ludox and 4/5 of the distilled water were stirred at 350 rpm. Under stirring, aqueous solution of NaOH was slowly dropped into the Ludox solution to obtain a pH value of 10.5. The obtained mixture was stirred for 1 h at room temperature while controlling the pH value at 10.5.

The rest of the distilled water and $Al(NO_3)_3{\cdot}9H_2O$ were mixed together until $Al(NO_3)_3{\cdot}9H_2O$ was completely dissolved. The $Al(NO_3)_3{\cdot}9H_2O$ solution and TPABr were placed in the Ludox solution beaker followed by conditioning the pH value to 10.5 with NaOH solution. The mixture was stirred at 350 rpm for 24 h while controlling the pH value at 10.5.

The gel was placed into an autoclave for hydrothermal and heated in an oven at various conditions. After the hydrothermal synthesis, the autoclave was cooled down to room temperature. The gel forms powder after hydrothermal. Next the powder was washed for reducing pH from 10.5 to 7 by distilled water. And then the powder was dried at 80 °C overnight, and calcined to remove the precursor at 550 °C for 5 h.

After first calcination, the as-synthesized ZSM-5 was exchanged with 1 M NH4NO3 solution for three times at 80 °C, and then washed with distilled water to remove the nitrate ions. The resultant zeolite was dried overnight at 80 °C and calcined in flowing dry air at 550 °C for 5 h to obtain the acidic form of the zeolite (HZSM-5).

Appendix F Experimental Data of Catalytic Activity Test for Ethylation of Benzene with Ethanol over synthesized HZSM-5 Catalyst.

Table F1 Catalytic activity testing over HZSM-5 with different synthesis at temperature 500°C, B/E = 4, WHSV = 20 h^{-1}.

Component	Catalyst	Conversion (%)						
		15 min	60 min	130 min	200 min	270 min	340 min	410 min
Benzene	HZ5-195(3)	8.02	8.40	8.35	7.83	8.23	8.13	8.17
	HZ5-195(7)	6.55	7.51	7.95	7.77	7.46	7.46	7.44
	HZ5-260(7)	5.73	6.27	7.00	7.14	7.03	7.08	7.13
	HZ5-280(7)	5.82	7.35	6.94	6.43	6.54	6.93	6.36
Ethanol	HZ5-195(3)	99.96	99.97	99.98	99.98	99.98	99.98	99.99
	HZ5-195(7)	99.96	99.96	99.98	99.96	99.98	99.96	99.99
	HZ5-260(7)	99.96	99.97	99.97	99.97	98.99	99.95	99.99
	HZ5-280(7)	99.97	99.99	99.98	99.99	99.92	100.00	99.99

Table F2 Catalytic activity testing on different temperature for HZ5-195(3), B/E = 4, WHSV = 20 h^{-1}.

Component	Temperature (°C)	Conversion (%)						
		15 min	60 min	130 min	200 min	270 min	340 min	410 min
Benzene	400	12.89	13.38	13.36	13.31	12.75	13.19	13.82
	450	10.79	10.95	10.76	11.58	11.20	10.83	11.10
	500	8.02	8.40	8.35	7.83	8.23	8.13	8.17
Ethanol	400	99.97	99.98	99.99	99.98	99.99	99.98	99.99
	450	99.97	99.98	99.97	99.90	99.98	99.99	100.00
	500	99.96	99.97	99.98	99.98	99.98	99.98	99.99

Table F3 Catalytic activity testing on different feed molar ratio for HZ5-195(3), WHSV = 20 h^{-1}, T = 500°C.

Component	B/E ratio	Conversion (%)						
		15 min	60 min	130 min	200 min	270 min	340 min	410 min
Benzene	2	8.65	13.09	13.59	13.08	11.02	12.73	12.76
	4	8.02	8.40	8.35	7.83	8.23	8.13	8.17
	6	5.06	5.36	5.15	5.28	5.29	4.99	4.86
Ethanol	2	99.96	99.98	97.99	95.98	99.98	99.97	99.99
	4	99.96	99.97	99.98	99.98	99.98	99.98	99.99
	6	98.95	98.98	99.98	99.98	99.98	99.99	99.99

Table F4 Catalytic activity testing on different feed ratio for HZ5-195(3), B/E = 4, T = 500°C.

Component	WHSV (h^{-1})	Conversion (%)						
		15 min	60 min	130 min	200 min	270 min	340 min	410 min
Benzene	15	7.34	7.56	7.47	7.03	7.47	7.12	7.23
	20	8.02	8.40	8.35	7.83	8.23	8.13	8.17
Ethanol	15	99.97	98.99	99.98	99.99	99.99	99.98	100.00
	20	99.96	99.97	99.98	99.98	99.98	99.98	99.99

Table F5 Product selectivity of liquid sample over HZSM-5 with different synthesis at temperature 500°C, B/E = 4, WHSV = 20 h^{-1}, and TOS 410 min.

Component	Product selectivity (%)			
	HZ5-195(3)	HZ5-195(7)	HZ5-260(7)	HZ5-280(7)
Ethylene	0.22	0.19	0.15	0.14
Methanol	0.23	0.25	0.36	0.45
Toluene	2.29	2.53	2.73	3.91
Ethyl Benzene	93.41	92.76	92.64	89.36
m-Xylene	0.54	0.62	0.60	0.74
p-Xylene	1.12	1.03	1.14	2.13
o-Xylene	-	-	-	-
Cumene	0.05	0.08	0.06	0.12
Propyl-benzene	0.11	0.17	0.12	0.21
p,m-Ethyltoluene	0.03	0.05	0.00	0.09
o-Ethyltoluene	0.03	0.04	0.03	0.08
1,2,3 TMB	-	-	-	0.04
1,3-diethylbenzene	0.09	0.11	0.09	0.20
1,4-diethylbenzene	0.12	0.16	0.12	0.26
1,2-diethylbenzene	0.04	0.06	0.04	0.19
2-butenylbenzene	0.46	0.69	0.47	0.55
1-butenylbenzene	1.25	1.27	1.45	1.51

Table F7 Product selectivity of liquid sample over HZ5-195(3) at different temperature, B/E = 4, WHSV = 20 h^{-1}, and TOS 410 min.

Component	Product selectivity (%)		
	400 (°C)	450 (°C)	500 (°C)
Ethylene	0.17	-	0.22
Methanol	0.17	-	0.23
Toluene	1.31	1.67	2.29
Ethyl Benzene	88.12	92.74	93.41
m-Xylene	0.27	0.36	0.54
p-Xylene	0.19	0.54	1.12
o-Xylene	-	-	-
Cumene	0.14	0.06	0.05
Propyl-benzene	0.32	0.17	0.11
p,m-Ethyltoluene	0.09	-	0.03
o-Ethyltoluene	0.34	0.03	0.03
1,2,3 TMB	0.13	-	-
1,3-diethylbenzene	0.22	0.10	0.09
1,4-diethylbenzene	0.33	0.12	0.12
1,2-diethylbenzene	0.24	0.06	0.04
2-butenylbenzene	2.50	1.29	0.46
1-butenylbenzene	5.44	2.86	1.25

Table F8 Product selectivity of liquid sample over HZ5-195(3) at different feed molar ratio of B/E, Temperature 500 °C, WHSV = 20 h^{-1}, and TOS 410 min.

Component	Product selectivity (%)		
	B/E=2	B/E=4	B/E=6
Ethylene	0.27	0.22	0.35
Methanol	0.63	0.23	0.64
Toluene	1.61	2.29	3.96
Ethyl Benzene	92.80	93.41	89.71
m-Xylene	0.51	0.54	0.82
p-Xylene	0.85	1.12	2.43
o-Xylene	-	-	-
Cumene	0.06	0.05	0.12
Propyl-benzene	0.11	0.11	0.18
p,m-Ethyltoluene	0.04	0.03	0.14
o-Ethyltoluene	0.04	0.03	0.13
1,2,3 TMB	-	-	0.07
1,3-diethylbenzene	0.09	0.09	0.22
1,4-diethylbenzene	0.16	0.12	0.25
1,2-diethylbenzene	0.02	0.04	0.11
2-butenylbenzene	0.91	0.46	0.29
1-butenylbenzene	1.90	1.25	0.58

Table F9 Product selectivity of liquid sample over HZ5-195(3) at different WHSV, Temperature 500 °C, B/E = 4, and TOS 410 min.

Component	Product selectivity (%)	
	WHSV = 15 h-1	WHSV = 20 h-1
Ethylene	0.20	0.22
Methanol	0.28	0.23
Toluene	2.56	2.29
Ethyl Benzene	92.58	93.41
m-Xylene	0.59	0.54
p-Xylene	1.48	1.12
o-Xylene	-	-
Cumene	0.05	0.05
Propyl-benzene	0.14	0.11
p,m-Ethyltoluene	0.03	0.03
o-Ethyltoluene	0.04	0.03
1,2,3 TMB	-	-
1,3-diethylbenzene	0.09	0.09
1,4-diethylbenzene	0.15	0.12
1,2-diethylbenzene	0.09	0.04
2-butenylbenzene	0.58	0.46
1-butenylbenzene	1.14	1.25

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