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APPENDICES

Appendix A Experimental Data of Catalytic Activity Test for Ethylation of Toluene with Ethanol over synthesized HZSM-5 Catalyst

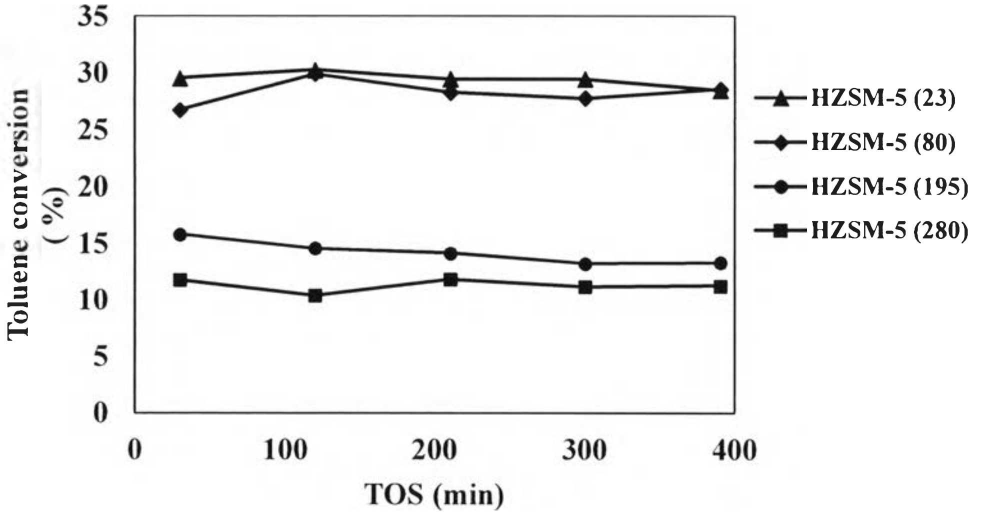


Figure A1 Toluene conversion as a function of TOS over various SiO_2/Al_2O_3 molar ratios of HZSM-5; reaction temperature 350 °C, toluene to ethanol molar ratio of 3, WHSV = 20 h^{-1}.

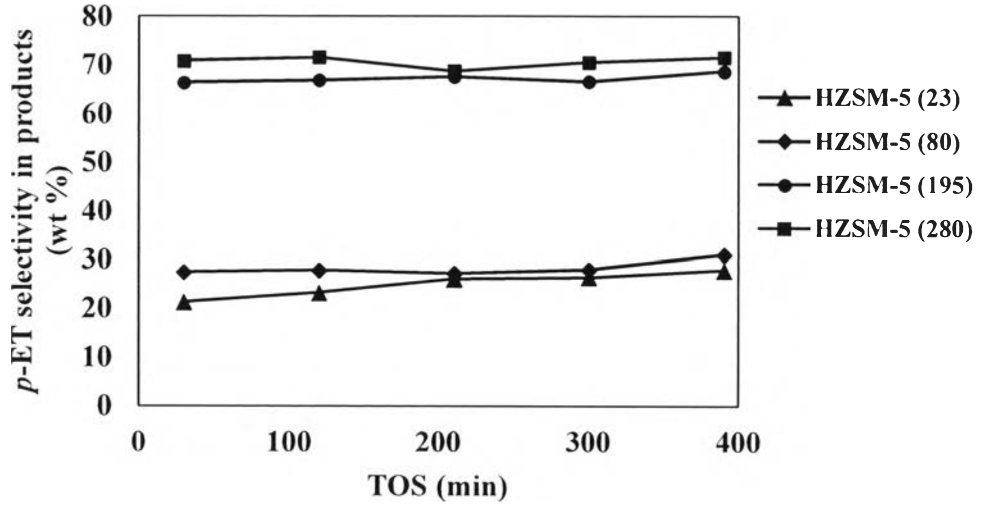


Figure A2 *p*-ET selectivity in products as a function of TOS over various SiO_2/Al_2O_3 molar ratios of HZSM-5; reaction temperature 350 °C, toluene to ethanol molar ratio of 3, WHSV = 20 h^{-1}.

Table A1 Product selectivity of the liquid sample testing over HZSM-5 with various SiO_2/Al_2O_3 molar ratio at 350 °C, toluene to ethanol molar ratio of 3, WHSV = 20 h^{-1}, TOS 390 min

SiO_2/Al_2O_3 molar ratio	Liquid product selectivity (wt %)						
	o-ET	*p*-ET	*m*-ET	Xylenes	EB	Benzene	Others*
23	2.47	27.77	61.53	1.48	1.17	0.35	5.23
80	4.22	30.98	61.67	0.45	0.4	0.09	2.19
195	0.09	68.72	27.54	0.58	0.45	0.25	2.36
280	0.11	71.6	27.07	0.25	0.13	0.06	0.79

* For instance; ethylene, trimethylbenzene, and heavy aromatics

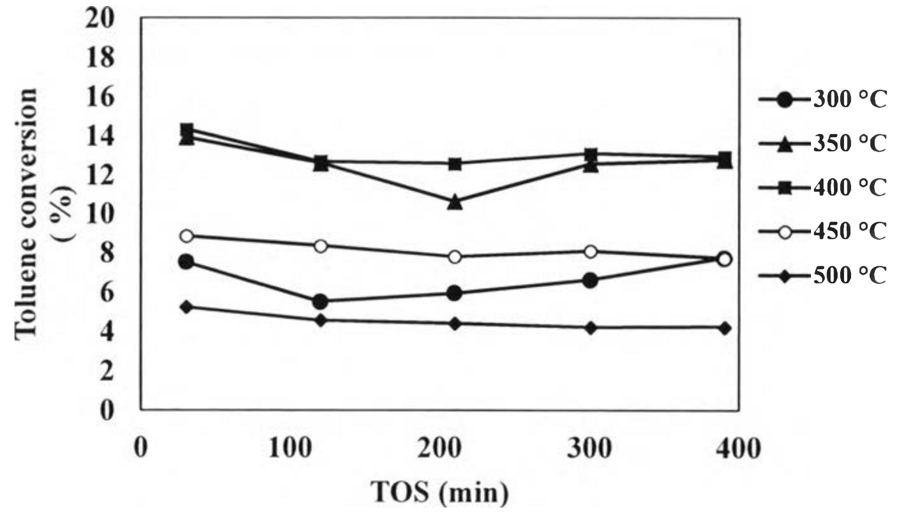


Figure A3 Toluene conversion as a function of TOS in over HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 at various reaction temperature; toluene to ethanol molar ratio of 3, WHSV = 20 h^{-1}.

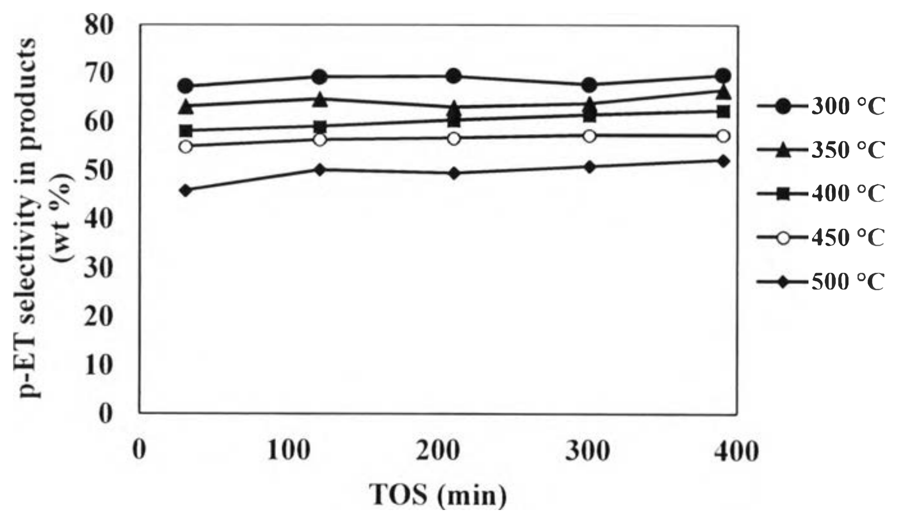


Figure A4 *p*-ET in products as a function of TOS over HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 at various reaction temperature; toluene to ethanol molar ratio of 3, WHSV = 20 h^{-1}.

Table A2 Product selectivity of the liquid sample testing over HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 at various reaction temperature, toluene to ethanol molar ratio of 3, WHSV = 10 h^{-1}, TOS 390 min

Reaction temperature (°C)	Liquid product selectivity (wt %)						
	o-ET	*p*-ET	*m*-ET	Xylenes	EB	Benzene	Others*
300	0.21	69.69	26.1	0.4	0.16	0.04	3.4
350	0.1	66.58	31.95	0.24	0.13	0.02	0.98
400	0.16	62.46	35.72	0.35	0.19	0.07	1.05
450	0.26	57.33	38.33	1.25	0.35	0.29	2.19
500	0.26	52.19	36.08	3.94	0.89	2.86	3.77

* For instance; ethylene, trimethylbenzene, and heavy aromatics

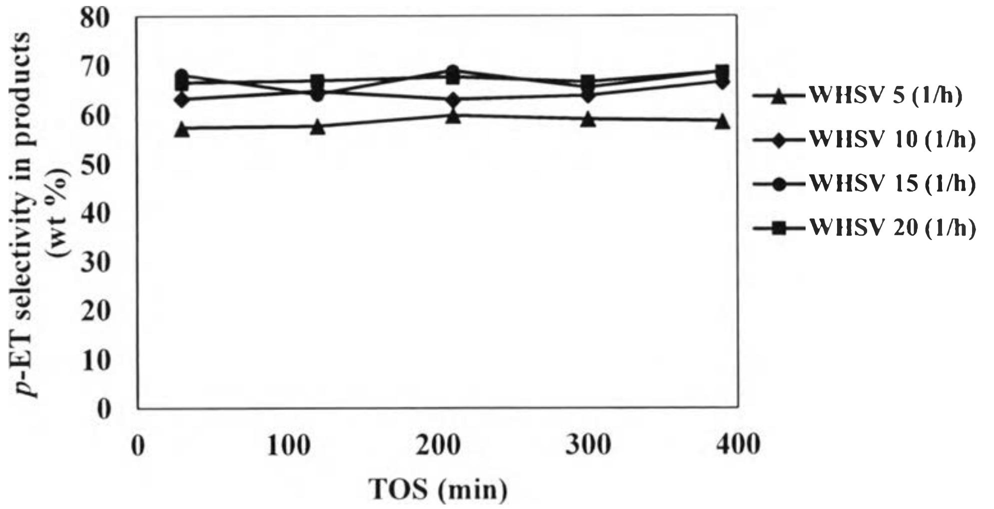


Figure A5 *p*-ET in products as a function of TOS over HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 at various WHSV; reaction temperature 350 °C, toluene to ethanol molar ratio of 3.

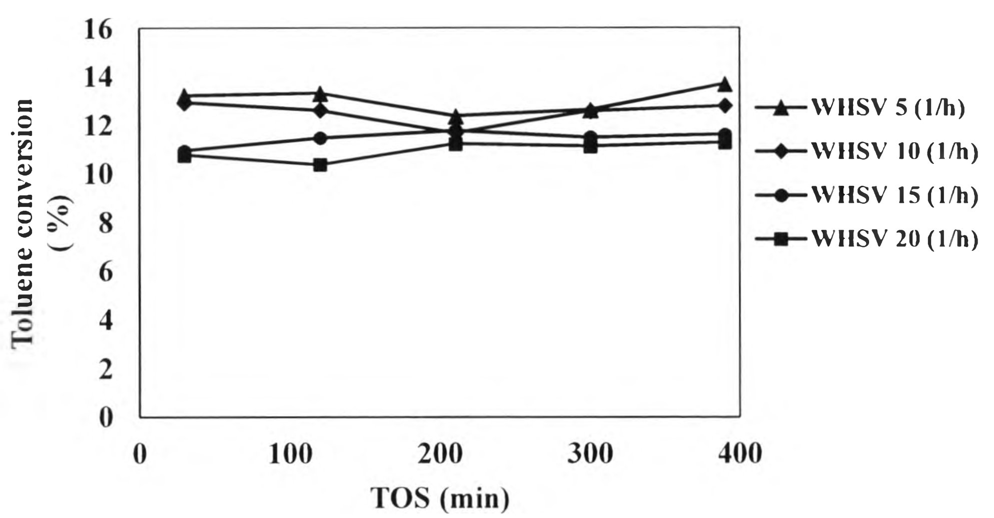


Figure A6 Toluene conversion as a function of TOS over HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 at various WHSV; reaction temperature 350 °C, toluene to ethanol molar ratio of 3.

Table A3 Product selectivity of the liquid sample testing over HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 at various WHSV, 350 °C , toluene to ethanol molar ratio of 3, TOS 390 min

WHSV (h^{-1})	Liquid product selectivity (wt %)						
	o-ET	*p*-ET	*m*-ET	Xylenes	EB	Benzene	Others*
5	0.2	58.57	39.65	0.27	0.18	0.12	1.01
10	0.1	66.58	31.95	0.24	0.13	0.02	0.98
15	0.12	68.66	29.65	0.25	0.21	0.06	1.05
20	0.11	71.6	27.07	0.25	0.13	0.06	0.79

* For instance; ethylene, trimethylbenzene, and heavy aromatics

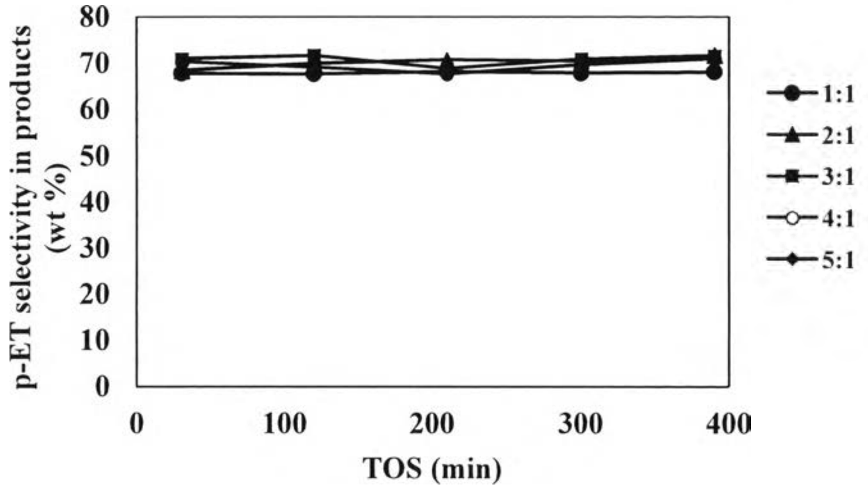


Figure A7 *p*-ET in products as a function of TOS over HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 at various toluene to ethanol molar ratios; reaction temperature 350 °C, WHSV 20 h^{-1}.

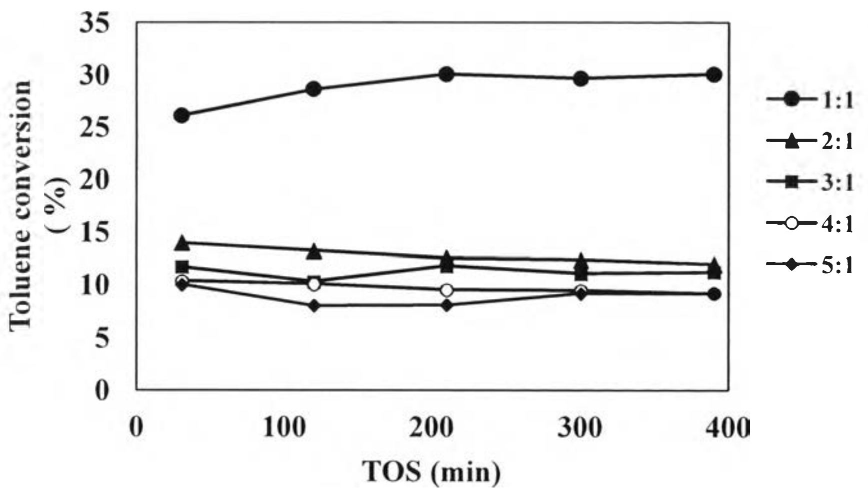


Figure A8 Toluene conversion as a function of TOS over HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 at various toluene to ethanol molar ratios; reaction temperature 350 °C, WHSV 20 h^{-1}.

Table A4 Product selectivity of the liquid sample testing over HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 at various toluene to ethanol molar ratios, 350 °C, WHSV = 20 h^{-1}, TOS 390 min

Toluene to ethanol molar ratio	Liquid product selectivity (wt %)						
	o-ET	*p*-ET	*m*-ET	Xylenes	EB	Benzene	Others*
1	0.1	68.04	28.75	0.77	0.28	0.05	2.01
2	0.14	71.73	25.82	0.39	0.16	0	1.77
3	0.11	71.6	27.07	0.25	0.13	0.06	0.79
4	0.1	70.98	27.77	0.31	0.15	0.04	0.64
5	0.16	72.36	26.17	0.28	0.17	0.16	0.7

* For instance; ethylene, trimethylbenzene, and heavy aromatics

Table A5 Catalytic activity testing over CLD treated HZSM-5 (SiO_2/Al_2O_3 molar ratio of 280) at 350 °C, at toluene to ethanol molar ratio of 3, WHSV = 20 h^{-1}, 60-80 mesh

Catalyst		Toluene conversion (%)				
CLD treatment (cycle)	Amount of TEOS (ml/g of catalyst)	30 min	120 min	210 min	300 min	390 min
-	-	14.69	14.28	14.29	13.36	13.15
1	0.2	12.71	12.13	12.43	13.05	13.06
1	0.6	12.67	12.11	12.55	12.46	12.76
1	1	12.45	12.58	11.57	11.64	12.57
1	2	12.99	12.18	12.29	12.24	11.90
2	1	9.53	10.43	9.76	10.35	9.86

Table A6 Product selectivity of the liquid sample testing over CLD treated HZSM-5 (SiO_2/Al_2O_3 molar ratio of 280) at 350 °C, at toluene to ethanol molar ratio of 3, WHSV = 20 h^{-1}, TOS 390 min, 60-80 mesh

Catalyst		Liquid product selectivity (wt %)						
CLD treatment (cycle)	Amount of TEOS (ml/g of catalyst)	*o*-ET	*p*-ET	*m*-ET	Xylenes	EB	Benzene	Others*
-	-	0.18	69.67	28.05	0.4	0.22	0.04	1.44
1	0.2	0.05	79.36	19.14	0.3	0.17	0.05	0.94
1	0.6	0.04	82.45	15.94	0.31	0.19	0.04	1.03
1	1	0.03	85.13	13.33	0.32	0.17	0.04	0.98
1	2	0.02	80.08	17.75	0.45	0.22	0.04	1.43
2	1	0.01	89.05	8.98	0.37	0.16	0.02	1.42

* For instance; ethylene, trimethylbenzene, and heavy aromatics

Table A7 Catalytic activity testing of *o*-xylene isomerization over unmodified and CLD treated HZSM-5 (SiO_2/Al_2O_3 molar ratio of 280) at 350 °C, at toluene to ethanol molar ratio of 3, WHSV = 20 h^{-1}, 60-80 mesh

Compound	Composition (wt%)
o-Xylene	97.75
p-Xylene	0.41
m-Xylene	0.02
Others	1.82

Table A8 Composition in liquid products and *o*-xylene conversion in *o*-xylene isomerization

Catalyst	*o*-Xylene Conversion	Composition in liquid products (wt %)			
		o-Xylene	*p*-Xylene	*m*-Xylene	Others*
HZSM-5 (280)	9.37	88.38	3.46	3.92	4.24
HZSM-5 CLD1	4.99	92.76	2.68	1.49	3.06
HZSM-5 CLD2	3.83	93.92	2.43	1.49	2.16

* For instance; benzene, toluene and other aromatics

Reaction temperature 350 °C, WHSV = 20 h^{-1}, particle size 60-80 mesh, and TOS = 120 min.

Appendix B Other Catalyst Characterization

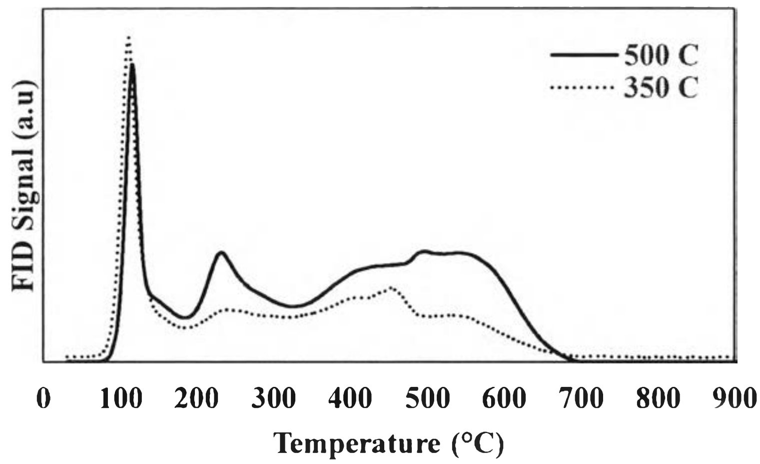


Figure B1 TPO profiles of spent HZSM-5 at 350 °C and 500 °C (SiO_2/Al_2O_3 molar ratio of 280, toluene to ethanol molar ratio of 3, WHSV = 10 h^{-1}, TOS 390 min).

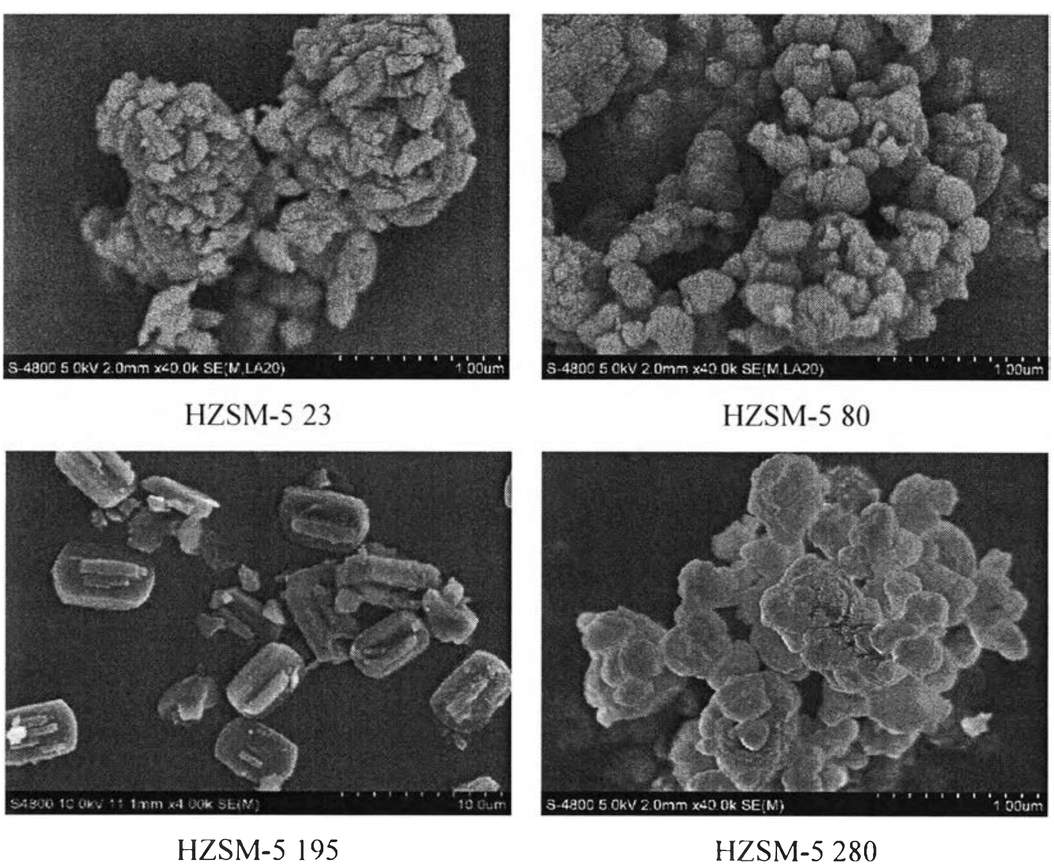
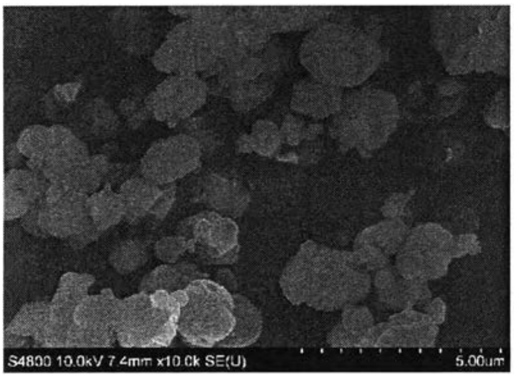
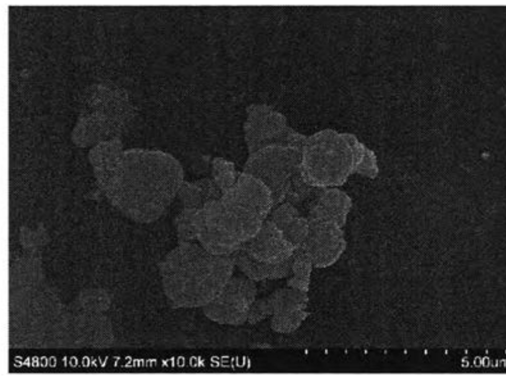


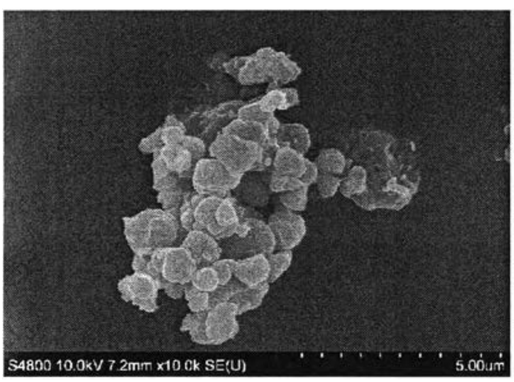
Figure B2 SEM images of the unmodified commercial and synthesized HZSM-5.



CLD-HZSM-5 (0.2 ml/g of catalyst)

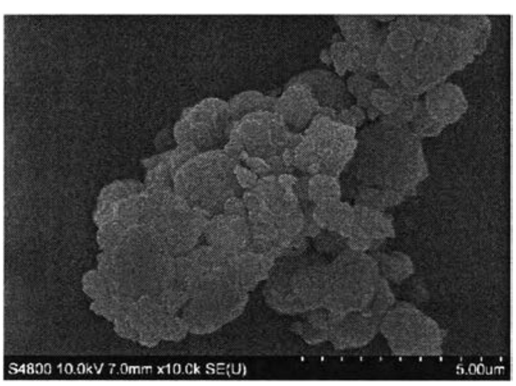


CLD-HZSM-5 (0.6 ml/g of catalyst)



CLD-HZSM-5 (1 ml/g of catalyst)

CLD-HZSM-5 (2 ml/g of catalyst)



2 cycle CLD-HZSM-5
(1 ml/g of catalyst)

Figure B3 SEM images of the various CLD treated HZSM-5.

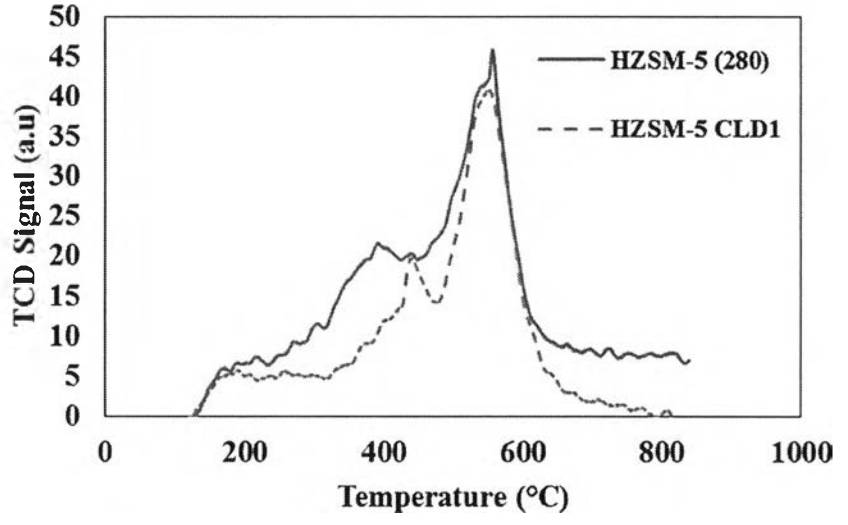


Figure B4 NH_3-TPD Profile of the catalyst studied.

Appendix C 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 $SiO_2/Al_2O_3 = 23$,

From XRF

SiO_2	=	92.81 wt%	Al_2O_3	=	7.19 wt%
Si	=	1.5447 mol	Al	=	0.1410 mol
Si/ Al	=	10.9524			

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

Si/ Al	=	10.9524	= (96-n)/n
11.9524n	=	96	
n	=	8.0319	
So, Si	=	87.9681	
Al	=	8.0319	

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 (B1) with,

Si = 87.9681

Al = 8.0319

From the above, the general formula of HZSM-5 is $H_{8.03186}Al_{8.03186}Si_{87.96814}O_{192}$. The weight of unit cell of HZSM-5 (U) is

U = 8.0318(1)+8.0318(26.98)+87.9681(28.09)+192(16.00)

U = 5767.7565 g

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

$[H^+]$ = 8.0319/5767.7565

$[H^+]$ = 1.393 mmol/g

Appendix D Calculation of the minimum ratio the bed length to the particle size

$$\frac{L_b}{d_p} > \frac{8n}{Pe_p}\ln(\frac{1}{1-x})$$

L_b= length of bed

d_p = diameter of particle

Pe = Peclet number

n = order of reaction

x = conversion of reaction

Taking Pe_p = 0.5 for the low Reynolds region of interest for laboratory–scale operation .

Taking d_p = 0.05 cm for the particle sieve at mesh 20-40

Assume n = 1

If x = 0.4

$$\frac{L_b}{0.05} > \frac{8}{0.5}\ln(\frac{1}{1-0.4})$$

$$L_b = 0.04 \text{ cm}$$

If x = 0.5

$$\frac{L_b}{0.05} > \frac{8}{0.5}\ln(\frac{1}{1-0.5})$$

$$L_b = 0.55 \text{ cm}$$

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Presentations:

Athawut, S., Thirasak, R. (2013, April 23) Ethylation of Toluene with Ethanol using Modified HZSM-5 Catalysts. Poster present at The 4th Research Symposium on Petrochemical and Materials Technology and The 19th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.