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APPENDICES

Appendix A Another Catalyst Preparation

In this thesis work, another method for synthesized HZSM-5 zeolites was implemented from the work of Chareonpanich *et al.* (2003).

Methodology

Stir TPABr solution at 400 rpm then adjust pH of TPABr solution to 10.5 by HCl and NaOH. After that, drop silica and alumina source solution into TPABr solution. Stir the solution for haft an hour, the solution will be gel after stirring. Bring the gel into autoclave for hydrothermal at 150 – 240 °C for 18 – 72 h. The gel becomes powder after hydrothermal. Wash powder for reduce pH from 10.5 to 7 by deionized water. Dry the as-synthesized zeolite ZSM-5 at 120 °C for 4 h. Ion exchange procedure was carried out three times with 1 M NH_4NO_3 solution at 80 °C each for 4 h. Subsequently, the resultant catalyst was dried overnight at 120 °C, followed by calcination at 500 °C for 5 h to give H-form products (HZSM-5).

Results and Discussion

A1 Catalyst Characterization of Preparation I Catalyst

A1.1 X-ray Diffraction

The crystal structures were examined by X-ray diffraction. Figure A1 shows the XRD patterns of the ZSM-5 zeolite from zeolite structure databases and the synthesized ZSM-5 zeolite (SiO_2/Al_2O_3 = 185) was obtained at temperature 240 °C and crystallization time 18 h. It shows that the characteristic diffraction peaks corresponding to the patterns of ZSM-5 zeolite are observed. The diffractograms are composed of sharp peaks and a broad diffraction. The high intensity peaks indicate that the zeolite have high crystalline.

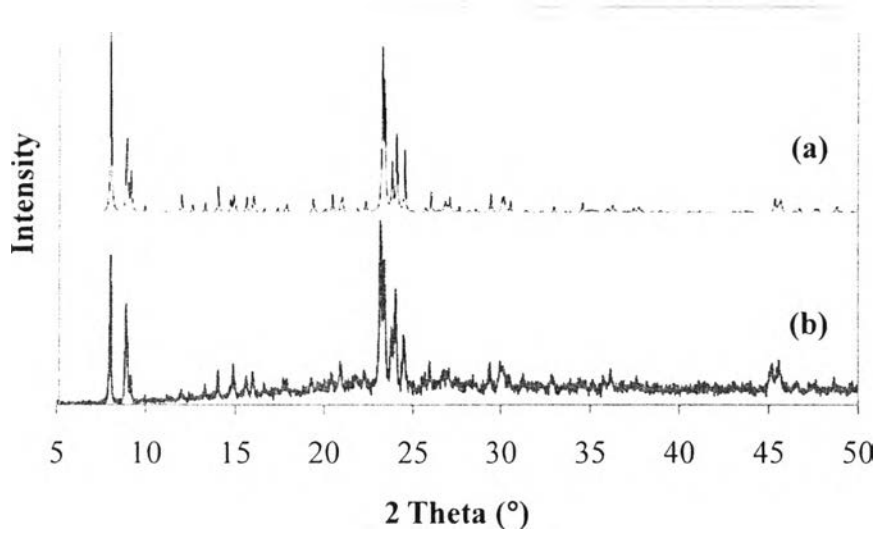


Figure A1 XRD patterns of the ZSM-5 zeolite. (a) ZSM-5 from zeolite structure databases, and (b) synthesized ZSM-5 (SiO_2/Al_2O_3 = 185) at 240 °C 18 h.

A1.2 FESEM

Figures A2 – A4 show SEM images for the prepared samples (Si/Al = 97.5) by using different temperatures and crystallization times of hydrothermal reaction as 150 °C (18 h, 24 h, 48h, 72 h), 180 °C (24 h, 48h, 72 h), and 240 °C (18 h). The ZSM-5 zeolites synthesized at different temperatures were achieved at a given crystallization time. The amorphous solid and crystalline phases were found at low crystallization time and low temperature. When crystallization time and temperature increased, the crystalline phase of the synthesized ZSM-5 zeolite will be increased.

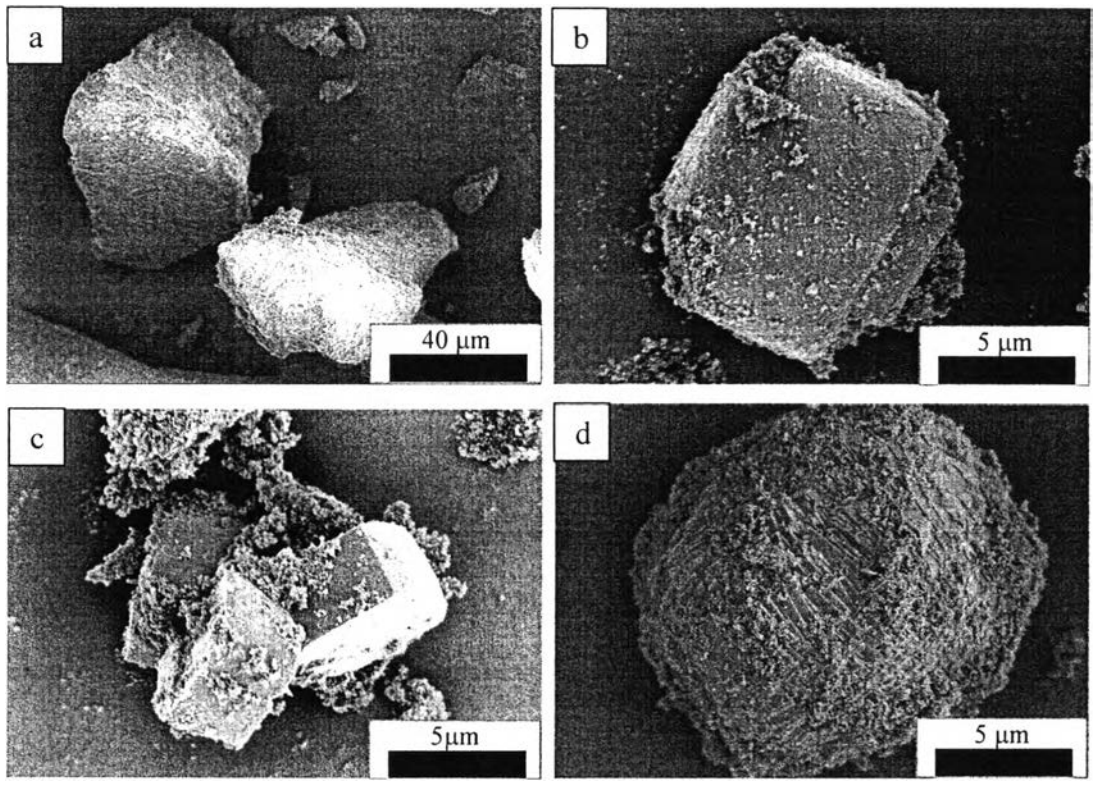


Figure A2 SEM images of the synthesized ZSM-5 zeolites obtained from temparature at 150 °C (a)18 h, (b) 24 h, (c) 48 h, and (d) 72 h.

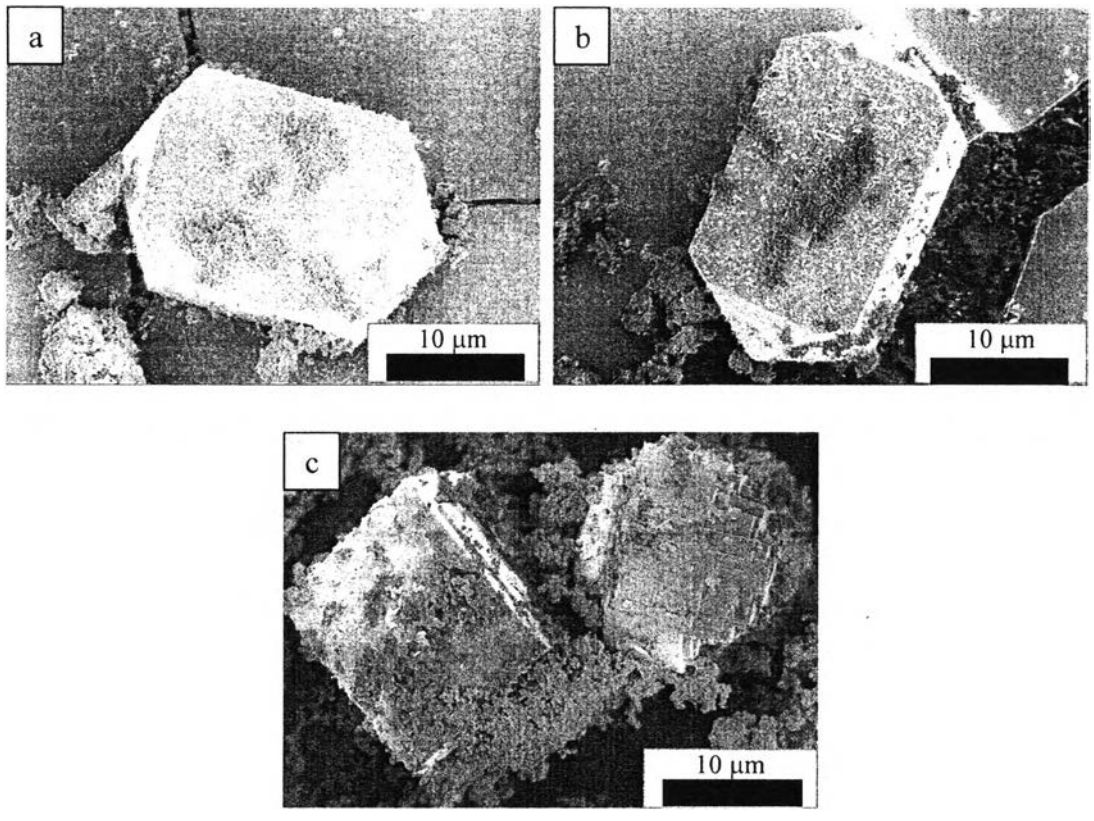


Figure A3 SEM images of the synthesized ZSM-5 zeolites obtained from temparature at 180 °C (a) 24 h, (b) 48 h, and (c) 72 h.

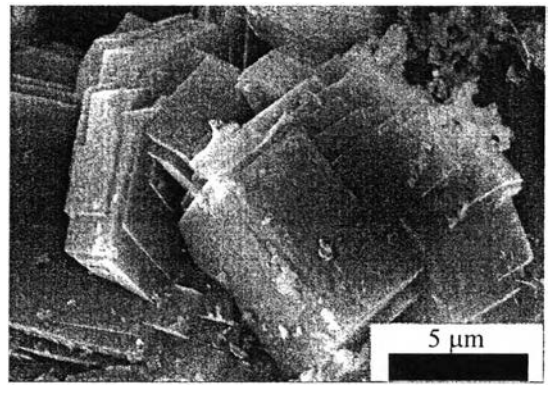


Figure A4 SEM image of the synthesized ZSM-5 zeolites obtained from temparature at 240 °C 18 h.

A1.3 N_2 Adsorption-Desorption

The surface characteristics of the synthesized ZSM-5 zeolites determined by N_2 adsorption-desorption method. Table A1 shows the properties from the N_2 adsorption-desorption analysis of synthesized ZSM-5 zeolite (SiO_2/Al_2O_3 = 185) from preparation I catalyst. The synthesized ZSM-5 zeolites obtained at temperature 150 °C and crystallization time 24 h and 48 h. The surface area of the synthesized ZSM-5 zeolites at 150 °C, 24 h and 150 °C, 48 h are 129.62, and 156.68 m^2/g respectively. It was found that the surface area was increased, when increased time in hydrothermal reaction.

A1 N_2 adsorption-desorption results of the synthesized ZSM-5 zeolites from preparation I catalyst

Samples[a]	S_{BET} (m^2g^{-1})	Micropore volume[b] (cm^3g^{-1})	Total pore volume[b] (cm^3g^{-1})
ZSM-5 (150 °C, 24 h)	129.62	0.0526	0.506
ZSM-5 (150 °C, 48 h)	156.68	0.0643	0.788

[a] SiO_2/Al_2O_3 molar ratio = 185

[b] Determined by NLDFT method

Appendix B 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 HZ5A

Si = 97.39 % wt Al = 2.06 %wt

Si = 3.468 mol Al = 0.076 mol

Si = 97.824 %mol Al = 2.151%mol

Si/Al = 45.49

SiO_2/Al_2O_3 = 90.07

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

Si/Al = (96 - n)/n = 45.49

45.49n = 96 - n

46.49n = 96

n = 2.07

So, Si = 93.93

Al = 2.07

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 HZ5A with,

Si = 93.93

Al = 2.07

From the above, the general formula of HZSM-5 is $H_{2.07}Al_{2.07}Si_{93.93}O_{192}$. The weight of unit cell of HZSM-5 (U) is

U = 2.07(1) + 2.07(26.98) + 93.93(28.09) + 192(15.99)

U = 5766.49 g

The theoretical acidity ($[H^+]$) of HZSM-5 (45) is

$[H^+]$ = 2.07/5766.49

$[H^+]$ = 0.358 mmol/g

However, the chemical compositions of the synthesized catalysts obtained by XRF technique was observed some remained of Na.

In the case of HZ5A,

Na = 0.021 %wt

Na = 0.00091 mol

Na = 0.026 %mol

So, H = 2.07 – 0.026 = 2.044

From the above, the general formula of HZSM-5 is $H_{2.044}Al_{2.044}Si_{93.93}O_{192}$. The weight of unit cell of HZSM-5 (U) is

U = 2.044(1) + 2.044(26.98) + 93.93(28.09) + 192(15.99)

U = 5765.77 g

The theoretical acidity ($[H^+]$) of HZSM-5 (45) is

$[H^+]$ = 2.044/5765.77

$[H^+]$ = 0.354 mmol/g

Appendix C Experimental Data of Catalytic Activity Test for methylation of Toluene with Methanol over Synthesized HZSM-5 Catalyst

Table C1 Catalytic activity testing over synthesized HZSM-5 with different hydrothermal condition for synthesized HZSM-5 catalysts at temperature 400 °C, WHSV = 24 h^{-1}, and T/M = 4:1

Component	Catalyst	Conversion (%)						
		15 min	75 min	135 min	195 min	255 min	315 min	375 min
Toluene	HZ5B1	10.26	10.93	10.20	10.80	11.00	10.37	10.12
	HZ5B2	13.41	12.22	11.79	12.11	11.17	12.62	12.25
	HZ5B3	14.75	15.36	15.97	14.74	14.33	14.18	13.64
	HZ5B4	15.62	16.12	16.00	15.05	14.91	14.88	14.64
Methanol	HZ5B1	96.07	94.77	94.13	92.94	91.16	87.60	85.30
	HZ5B2	97.84	97.49	96.93	95.72	94.82	91.65	89.00
	HZ5B3	98.94	98.45	96.84	96.72	96.15	93.04	90.06
	HZ5B4	99.28	98.57	97.39	96.28	94.81	93.12	91.66

Table C2 Catalytic activity testing over HZ5B4 with different WHSV at temperature 400 °C and T/M = 1:1

Component	WHSV (h^{-1})	Conversion (%)						
		15 min	**75 min**	**135 min**	**195 min**	**255 min**	**315 min**	**375 min**
Toluene	12	30.73	32.29	34.73	35.38	37.82	35.54	31.66
	24	5.40	8.10	5.69	5.46	5.16	5.19	5.55
	40	5.25	4.51	2.45	1.53	1.01	1.69	1.73
Methanol	12	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	24	99.29	98.04	95.41	92.92	92.95	92.10	91.31
	40	97.14	96.64	93.70	90.65	87.68	83.20	82.10

Table C3 Catalytic activity testing over HZ5B4 with different T/M ratio at temperature 400 °C, and WHSV = 24 h^{-1}

Component	T/M ratio	Conversion (%)						
		15 min	**75 min**	**135 min**	**195 min**	**255 min**	**315 min**	**375 min**
Toluene	1:1	5.40	8.10	5.69	5.46	5.16	5.19	5.55
	2:1	10.74	11.80	8.09	8.19	8.43	9.09	8.84
	4:1	15.62	16.12	16.00	15.05	14.91	14.88	14.64
Methanol	1:1	99.29	98.04	95.41	92.92	92.95	92.10	91.31
	2:1	99.14	95.73	92.94	92.91	90.78	89.54	89.73
	4:1	99.28	98.57	97.39	96.28	94.81	93.12	91.66

Table C4 Catalytic activity testing over HZ5B4 with different temperature at WHSV = 24 h^{-1}, and T/M = 4:1

Component	Temperature (°C)	Conversion (%)						
		15 min	**75 min**	**135 min**	**195 min**	**255 min**	**315 min**	**375 min**
Toluene	300	9.75	9.40	9.03	9.32	9.15	9.14	9.00
	400	15.62	16.12	16.00	15.05	14.91	14.88	14.64
	500	15.58	15.77	15.44	14.59	14.80	14.81	14.41
Methanol	300	93.60	91.90	90.30	86.49	90.06	88.18	86.62
	400	99.28	98.57	97.39	96.28	94.81	93.12	91.66
	500	99.61	98.71	97.17	93.64	92.88	94.24	94.71

Table C5 Catalytic activity testing over synthesized HZSM-5 with different aging time in hydrothermal reaction for synthesized HZSM-5 catalysts at temperature 400 °C, WHSV = 24 h^{-1}, and T/M = 1:1

Component	Catalyst	Conversion (%)						
		15 min	75 min	135 min	195 min	255 min	315 min	375 min
Toluene	HZ5B4	5.40	8.10	5.69	5.46	5.16	5.19	5.55
	HZ5B5	5.43	5.26	4.49	3.88	4.00	2.93	1.61
Methanol	HZ5B4	99.29	98.04	95.41	92.92	92.95	92.10	91.31
	HZ5B5	99.00	99.40	96.63	95.83	93.68	94.01	92.76

Table C6 Catalytic activity testing over HZ5A and HZ5B4 at temperature 400 °C, WHSV = 24 h^{-1}, and T/M = 4:1

Component	Catalyst	Conversion (%)						
		15 min	75 min	135 min	195 min	255 min	315 min	375 min
Toluene	HZ5A	22.32	25.02	20.43	19.99	22.75	22.25	22.20
	HZ5B4	15.62	16.12	16.00	15.05	14.91	14.88	14.64
Methanol	HZ5A	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	HZ5B4	99.28	98.57	97.39	96.28	94.81	93.12	91.66

Table C7 Catalytic activity testing over commercial HZSM-5 and synthesized HZSM-5 (HZ5A) at temperature 400 °C, WHSV = 24 h^{-1}, and T/M = 4:1

Component	Catalyst	Conversion (%)						
		15 min	**75 min**	**135 min**	**195 min**	**255 min**	**315 min**	**375 min**
Toluene	Commercial	25.61	25.38	25.11	25.72	22.24	23.49	25.32
	HZ5A	22.32	25.02	20.43	19.99	22.75	22.25	22.20
Methanol	Commercial	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	HZ5A	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table C8 The stability test of the alkylation of toluene with methanol over HZ5B4 at temperature 400 °C, WHSV = 24 h^{-1}, T/M = 4:1 and TOS = 50 h.

Time (min)	Conversion (%)		*p*-Xylene Selectivity (%)
	Toluene	Methanol	
15	99.24	15.79	84.33
75	97.99	16.82	84.15
195	97.21	15.03	81.87
255	95.30	15.39	79.99
315	95.35	13.42	77.86
435	92.82	13.09	75.70
495	92.09	12.64	74.56
735	88.38	11.1	70.88
855	87.76	12.66	70.27
975	85.21	12.56	67.64
1095	84.77	10.45	66.99
1215	86.35	10.28	66.25
1335	82.47	11.02	65.28
1695	86.01	9.4	63.94
1935	85.14	10.21	61.77
2175	85.64	9.55	61.78
2655	85.96	9.21	59.91
2895	84.19	9.05	59.12
3015	87.30	9.43	63.14

Table C9 The estimated fractions of methanol converted to aromatics ring and alkyl group from self-aromatization and by methylation for the synthesized catalysts at temperature 400 °C, WHSV = 24 h^{-1}, T/M= 4:1, TOS = 375 min

Catalyst	Methanol to aromatics ring (%) (self-aromatization)	Methanol to alkyl group (%) (methylation)
HZ5B1	82.1	17.9
HZ5B2	81.0	19.0
HZ5B3	80.4	19.6
HZ5B4	78.5	21.5

Table C10 The estimated fractions of methanol converted to aromatics ring and alkyl group from self-aromatization and by methylation for HZ5B4 with different WHSV at temperature 400 °C, T/M= 4:1, TOS = 375 min

WHSV (h^{-1})	Methanol to aromatics ring (%) (self-aromatization)	Methanol to alkyl group (%) (methylation)
12	88.0	12.0
24	86.3	13.7
40	86.6	13.4

Table C11 The estimated fractions of methanol converted to aromatics ring and alkyl group from self-aromatization and by methylation for HZ5B4 with different T/M at temperature 400 °C, WHSV = 24 h^{-1}, TOS = 375 min

T/M ratio	Methanol to aromatics ring (%) (self-aromatization)	Methanol to alkyl group (%) (methylation)
1:1	86.3	13.7
2:1	82.1	17.9
4:1	78.5	21.5

Table C12 The estimated fractions of methanol converted to aromatics ring and alkyl group from self-aromatization and by methylation for HZ5B4 with different temperature at WHSV = 24 h^{-1}, T/M = 4:1, TOS = 375 min

Temperature (°C)	Methanol to aromatics ring (%) (self-aromatization)	Methanol to alkyl group (%) (methylation)
300	85.7	14.3
400	78.5	21.5
500	82.9	17.1

Table C13 The estimated fractions of methanol converted to aromatics ring and alkyl group from self-aromatization and by methylation for the synthesized catalysts at temperature 400 °C, WHSV = 24 h^{-1}, T/M= 1:1, TOS = 375 min

Catalyst	Methanol to aromatics ring (%) (self-aromatization)	Methanol to alkyl group (%) (methylation)
HZ5B4	86.3	13.7
HZ5B5	85.6	14.4

Table C14 The estimated fractions of methanol converted to aromatics ring and alkyl group from self-aromatization and by methylation with different SiO_2/Al_2O_3 at temperature 400 °C, WHSV = 24 h^{-1}, T/M= 4:1, TOS = 375 min

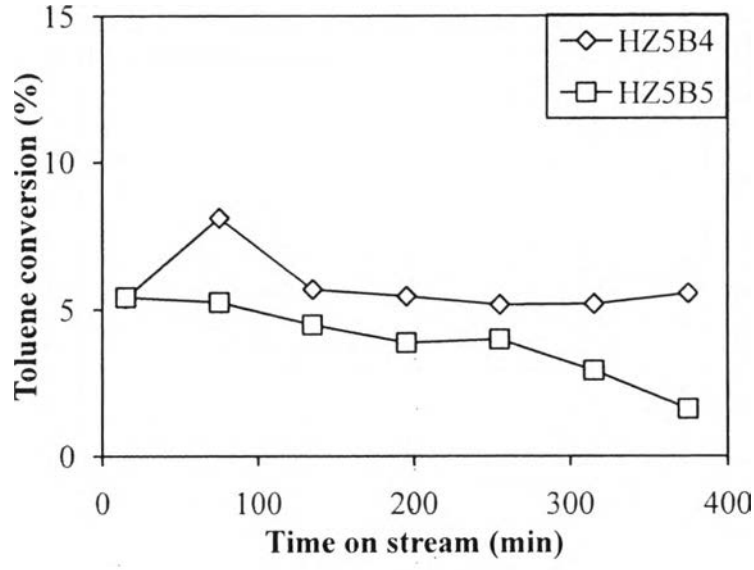
Catalyst	Methanol to aromatics ring (%) (self-aromatization)	Methanol to alkyl group (%) (methylation)
HZ5A	60.3	39.7
HZ5B4	78.5	21.5

Table C15 The estimated fractions of methanol converted to aromatics ring and alkyl group from self-aromatization and by methylation for commercial HZSM-5 and the synthesized HZSM-5 at temperature 400 °C, WHSV = 24 h^{-1}, T/M= 4:1, TOS = 375 min

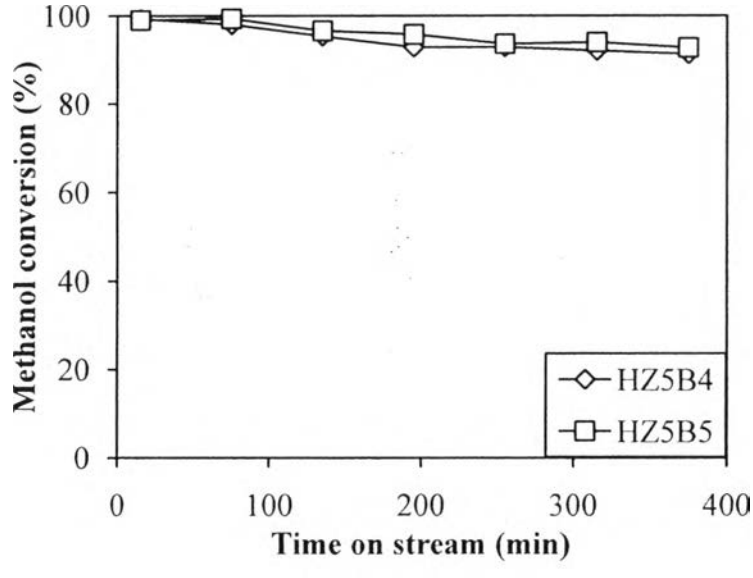
Catalyst	Methanol to aromatics ring (%) (self-aromatization)	Methanol to alkyl group (%) (methylation)
Commercial	58.6	41.4
HZ5A	60.3	39.7

Appendix D Effect of Aging Time in Hydrothermal Reaction for Synthesized HZSM-5 Catalysts

Figures D1, D2 and Table D1 show the effect of aging time in hydrothermal reaction for synthesized HZSM-5 catalysts on the alkylation of toluene with methanol. The synthesized HZ5B4 catalyst gave slightly higher selectivity to *p*-xylene than HZ5B5 catalyst. Therefore, aging time in hydrothermal reaction did not affect the selectivity to *p*-xylene.



(a)



(b)

Figure D1 Conversion of (a) toluene and (b) methanol as a function of time on stream of HZSM-5 synthesized with different aging times (Crystallization time = 72 h and temperature = 180 °C), (Reaction conditions: temperature = 400 °C, WHSV = 24 h^{-1}, and T/M = 1:1).

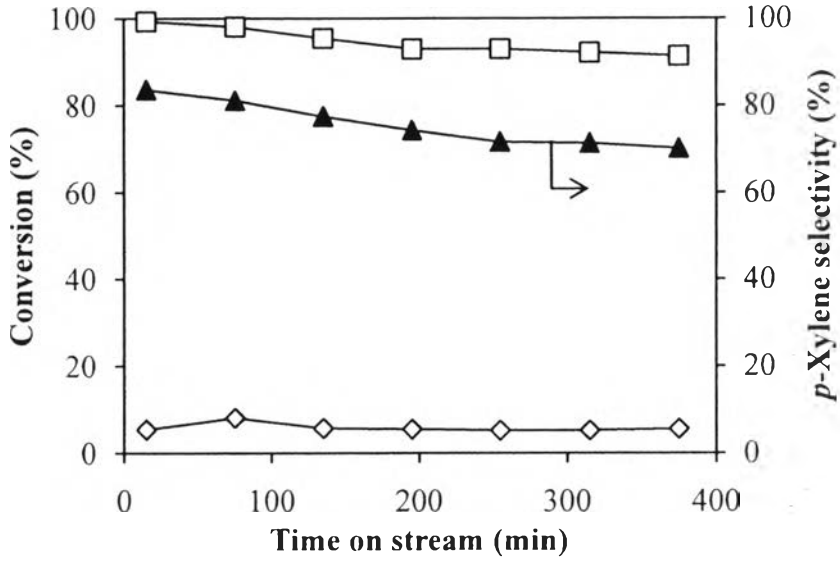


Figure D2 Conversion and *p*-xylene selectivity over HZ5B4 at temperature = 400 °C, WHSV = 24 h^{-1}, and T/M = 1:1. Open symbol: (◇) toluene conversion, and (□) methanol conversion, filled symbol: (▲) *p*-xylene selectivity.

Table D1 Effect of aging time in hydrothermal reaction for synthesized HZSM-5 catalysts on the products selectivity[a]

Catalyst	Conversion (%)		Selectivity (%)			
	Toluene	Methanol	*p*-Xylene	*m*-Xylene	*o*-Xylene	TMBs[b]
HZ5B4	5.55	91.31	70.16	11.96	7.83	10.05
HZ5B5	1.61	92.76	69.71	14.76	5.96	9.56

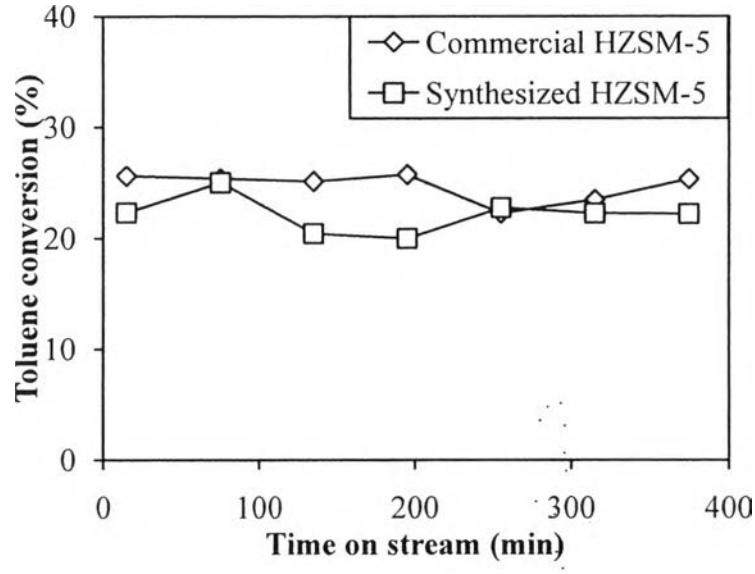
[a] Reaction conditions: T = 400 °C, WHSV = 24 h^{-1}, T/M= 1:1, TOS = 375 min.

[b] TMBs = 1,2,3 Trimethylbenzene and 1,2,4 Trimethylbenzene.

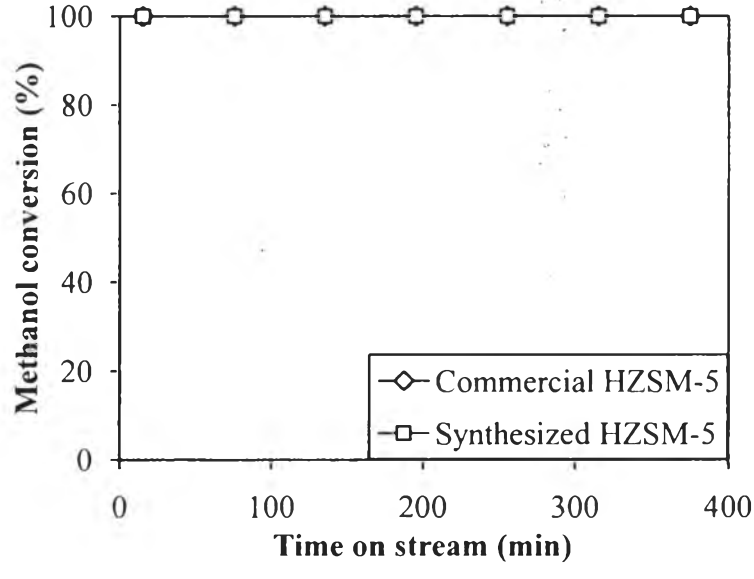
Appendix E Comparison of Catalytic Activity between a Commercial HZSM-5 and the Synthesized HZSM-5

Figure E1 shows the conversion of toluene and methanol in the alkylation of toluene with methanol over commercial HZSM-5 catalyst with a SiO_2/Al_2O_3 = 90 and the synthesized HZSM-5 catalyst (HZ5A) at temperature 400 °C, WHSV of 24 h^{-1}, and T/M ratio of 4:1. The conversion of toluene was slightly decreased when using HZ5A as a catalyst and the conversion of methanol over both catalysts were invariant. According to Figure E2 and Table E1, HZ5A catalyst gave slightly higher selectivity to *p*-xylene than commercial HZSM-5 catalysts.

A commercial HZSM-5 catalyst (from Süd-Chemie) with a SiO_2/Al_2O_3 ratio of 90 was investigated for its catalytic activity to compare with that of the synthesized HZSM-5 catalyst with the same SiO_2/Al_2O_3 ratio (HZ5A).



(a)



(b)

Figure E1 Conversion of (a) toluene and (b) methanol as a function of time on stream over commercial HZSM-5 and synthesized HZSM-5 (HZ5A) (Reaction conditions: Temperature = 400 °C, WHSV = 24 h^{-1}, and T/M = 4:1).

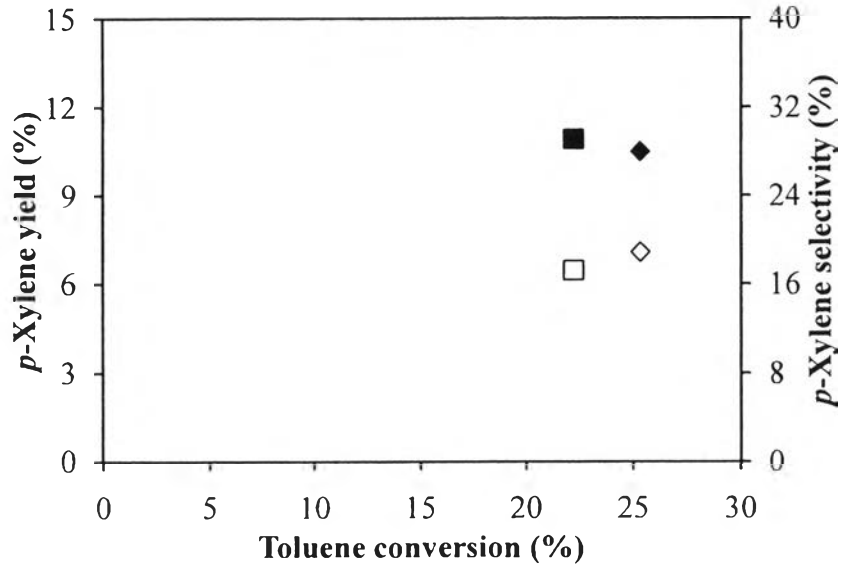


Figure E2 Plot of *p*-xylene yield and *p*-xylene selectivity versus toluene conversion over (◇,◆) commercial HZSM-5 catalyst and (□,■) synthesized HZSM-5 (HZ5A) catalyst at temperature = 400 °C, WHSV = 24 h^{-1}, and T/M = 4:1. Open symbol: *p*-xylene yield, filled symbol: *p*-xylene selectivity.

Table E1 Catalytic activity test of commercial HZSM-5 catalyst and synthesized HZSM-5 (HZ5A) catalyst on the products selectivity [a]

Catalyst	Conversion (%)		Selectivity (%)			
	Toluene	Methanol	*p*-Xylene	*m*-Xylene	*o*-Xylene	TMBs[b]
Commercial	25.32	100.00	27.94	40.14	18.82	13.09
HZ5A	22.20	100.00	29.09	41.44	16.03	13.44

[a] Reaction conditions: T = 400 °C, WHSV = 24 h^{-1}, T/M = 4:1, TOS = 375 min.

[b] TMBs = 1,2,3 Trimethylbenzene and 1,2,4 Trimethylbenzene.

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1. Techajiranon, J., Rirksomboon, T., and Jongpatiwut, S. (2011, April 26) Methylation of Toluene with Methanol Using Synthesized HZSM-5 Catalysts. Proceedings of The 2nd Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and The 17th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.