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APPENDICES

Appendix A Sample Calculation of Si/Al Ratio and Determination of 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 $Na_nAl_nSi_{96-n}O_{192}$

If a complete ion-exchange is achieved and the formular of HZSM-5 is

Si = 98.98 wt% Al = 0.89 wt%

$Si = \frac{98.98}{28.08} = 3.524$ mol $Al = \frac{0.89}{26.98} = 0.032$ mol

Si/Al = 106.83

$SiO_2/Al_2O_3 = 213.67$

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

Si/Al = (96-n)/n = 106.83

107.83n = 96

n = 0.899 mol

So, Si = 95.10145

Al = 0.899

In the case of HZSM-5 $H_nAl_nSi_{96-n}O_{192}$

Therefore $H_{0.899}Al_{0.899}Si_{95.101}O_{192}$ is attained for the synthesized one.

From the above, the weight of unit cell of HZSM-5(U) can be determined as

U = 0.899(1) + 0.899(26.98) + 95.101(28.09) + 192(16.00)

U = 5768.065 g

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

$[H^+] = 0.899/5768$

$[H^+] = 0.15577$ mmol/g

Appendix B Experimental Data of Catalytic Activity Test for Toluene Alkylation with Methanol using Modified HZSM-5

Table B1 Toluene conversion, methanol conversion, and *p*-xylene selectivity of parent modified by chemical liquid deposition (CLD) varying amount of TEOS (Reaction conditions: 400 °C toluene to methanol molar ratio of 4:1, WHSV 24 h^{-1})

Catalyst	TOS (min)	Conversion (%)		*p*-Xylene selectivity (wt%)
		Toluene	Methanol	
HZSM-5	15	7.76	97.57	70.22
	75	7.58	97.82	71.34
	135	7.33	91.96	76.02
	195	7.63	92.72	74.00
	255	7.29	91.91	75.58
	315	7.77	99.55	72.70
	375	7.35	93.92	71.60
CLD(0.5)-HZ5	15	8.90	89.20	71.13
	75	9.40	85.10	74.30
	135	10.70	83.70	74.57
	195	7.90	89.70	74.83
	255	6.30	89.40	74.27
	315	6.30	88.50	74.81
	375	8.30	85.80	72.37
CLD(1.0)-HZ5	15	9.50	96.88	78.15
	75	8.93	95.85	80.16
	135	9.37	94.67	81.01
	195	8.86	97.82	79.87
	255	7.09	90.74	78.99
	315	6.00	98.05	78.24
	375	8.14	93.61	75.62

Table B1 (cont') Toluene conversion, methanol conversion, and *p*-xylene selectivity of parent modified by chemical liquid deposition (CLD) varying amount of TEOS (Reaction conditions: 400 °C toluene to methanol molar ratio of 4:1, WHSV 24 h^{-1})

Catalyst	TOS (min)	Conversion (%)		*p*-Xylene selectivity (wt%)
		Toluene	Methanol	
CLD(1.5)-HZ5	15	8.90	91.60	66.30
	75	7.20	94.80	71.14
	135	7.00	90.10	74.61
	195	7.50	80.80	73.27
	255	6.90	69.40	72.20
	315	6.40	60.50	73.79
	375	7.70	60.50	70.28
CLD(2.0)-HZ5	15	9.30	75.20	68.99
	75	9.20	72.00	68.67
	135	8.00	63.10	68.45
	195	9.20	72.00	68.71
	255	8.00	63.10	68.49
	315	5.40	63.70	69.57
	375	5.10	65.80	68.93

Table B2 Toluene conversion, methanol conversion, and *p*-xylene selectivity of modified by combined dealumination sequence chemical liquid deposition (Reaction conditions: 400 °C toluene to methanol molar ratio of 4:1, WHSV 24 h^{-1})

Catalyst	TOS (min)	Conversion (%)		p-Xylene selectivity (wt%)
		Toluene	Methanol	
CLD-DeAl-HZ5	15	10.09	96.59	69.12
	75	8.80	97.49	69.90
	135	8.17	97.02	67.96
	195	10.15	98.44	65.94
	255	10.45	98.38	62.29
	315	10.32	98.34	64.80
	375	8.26	95.94	67.30

Table B3 Toluene conversion, methanol conversion, and *p*-xylene selectivity of modified by chemical liquid deposition using 1 ml TEOS/g catalyst (Reaction conditons: 400 °C toluene to methanol molar ratio of 4:1, WHSV 24 and 40 h^{-1})

Catalyst	WHSV (h^{-1})	TOS (min)	Conversion (%)		*p*-Xylene selectivity (wt%)
			Toluene	Methanol	
CLD(1.0)-HZ5	24	15	9.50	96.88	78.15
		75	8.93	95.85	80.16
		135	9.37	94.67	81.01
		195	8.86	97.82	79.87
		255	7.09	90.74	78.99
		315	6.00	99.05	78.24
		375	6.14	93.61	75.62
	40	15	7.90	97.20	73.76
		75	7.50	94.38	73.46
		135	8.10	95.72	73.38
		195	7.30	95.22	72.91
		255	6.00	95.90	73.58
		315	7.69	96.60	73.49
		375	5.20	94.86	72.58

Table B4 Toluene conversion, methanol conversion, and *p*-xylene selectivity of modified by chemical liquid deposition using 1 ml TEOS/g catalyst (Reaction conditions: 400 °C toluene to methanol molar ratio of 8:1, WHSV 24 to 40 h^{-1})

Catalyst	WHSV (h^{-1})	TOS (min)	Conversion (%)		*p*-Xylene selectivity (wt%)
			Toluene	Methanol	
CLD(1.0)-HZ5	24	15	2.60	98.14	73.79
		75	2.60	97.95	74.21
		135	3.30	97.52	74.60
		195	3.20	96.53	74.50
		255	3.50	97.55	72.28
		315	2.70	97.62	73.77
		375	3.30	98.12	74.05
	30	15	2.51	96.84	75.73
		75	2.36	97.58	75.68
		135	2.41	97.36	75.39
		195	2.57	97.52	75.28
		255	2.30	97.69	75.49
		315	2.64	97.83	75.38
		375	2.47	97.74	75.64
	40	15	2.03	90.00	77.26
		75	2.00	96.20	77.55
		135	2.00	91.60	77.72
		195	2.20	95.80	77.14
		255	2.50	94.80	77.29
		315	1.60	96.00	78.01
		375	1.90	97.80	77.21

Table B5 Toluene conversion, methanol conversion, and *p*-xylene selectivity of modified by chemical liquid deposition sequence dealumination (Reaction conditions: 400 °C toluene to methanol molar ratio of 4:1, WHSV 24 and 40 h^{-1})

Catalyst	WHSV (h^{-1})	TOS (min)	Conversion (%)		*p*-Xylene selectivity (wt%)
			Toluene	Methanol	
DeAl-CLD-HZ5	24	15	7.47	97.86	75.97
		75	7.41	98.92	75.72
		135	7.76	97.53	76.51
		195	7.38	99.70	75.82
		255	8.40	96.63	75.79
		315	7.71	97.67	74.30
		375	7.61	96.99	74.74
	40	15	6.60	93.80	77.43
		75	6.71	97.00	78.83
		135	6.43	98.70	78.23
		195	6.87	93.30	75.25
		255	6.41	93.70	78.15
		315	5.42	93.30	75.87
		375	6.29	94.80	78.60

Appendix C Effect of Toluene Disproportionation and Self-aromatization of Methanol on Synthesized HZSM-5 Catalyst

Disproportionation of toluene always produces benzene and xylenes. It can be seen from Table C1 that benzene significantly increased. The absence of ethylbenzene and ethyl methyl benzene in this reaction might be due to without methanol reactant to react with xylenes. This has a distinct advantage since that makes the separation of isomers easily and significantly decreases the cost of recovery of *p*- and *o*-xylene. Trimethylbenzene (TMBs) are formed by disproportionation of xylene formed and tetramethylbenzene are formed by disproportionation of trimethylbenzene thus formed (MA *et al.*, 2001). Toluene conversion of this reaction about 4.6 %.

Table C1 Product distribution of synthesized HZSM-5 catalyst on toluene disproportionation reaction (Reaction conditions: 400 °C, WHSV 24 h^{-1}, and TOS 375 min)

Catalyst	Product Distribution (%)							
	p-xylene	*m*-xylene	*o*-xylene	BZ	TMBs[a]	EB	Ethyl methyl benzene	$C9^+$
HZSM-5	22.06	29.67	10.72	34.27	1.93	0.00	0.00	1.22

[a]TMBs = 1,2,3 Trimethylbenzene and 1,2,4 Trimethylbenzene

Methanol aromatization is a complicated process that includes dehydration, polymerization, and cyclization. The product distribution for the self-aromatization of methanol reactions is shown in Table C2. Methanol conversion leads to a wide span of products including methane, ethylene, propylene, butenes, C_5 hydrocarbons, C_6^+ aliphatics, other light paraffins (C_{2-4}), and aromatics. Moreover, C_3 hydrocarbons were converted to toluene, xylenes and other products (Youming *et al.*, 2011). Methanol conversion is 98.1 %

Table C2 Product distribution of synthesized HZSM-5 catalyst on self-aromatization of methanol reaction (Reaction conditions: 400 C, WHSV 24 h^{-1}, and TOS 375 min)

Catalyst	Product Distribution (%)								
	Toluene	*p*-xylene	*m*-xylene	*o*-xylene	BZ	TMBs[a]	EB	Ethyl methyl benzene	$C9^{+}$
HZSM-5	24.57	21.03	14.36	14.00	18.52	1.93	3.25	0.42	1.22

[a]TMBs = 1,2,3 Trimethylbenzene and 1,2,4 Trimethylbenzene

Appendix D Summary of Product Distribution over various Catalysts (TOS 375 min, same condition)

Table D1 Product distribution of various catalysts (Reaction conditions: 400 °C, T/M molar ratio of 4:1, WHSV 24 h^{-1}, and TOS 375 min)

Component	Amount (wt %) obtained with								
	HZSM-5	CLD(0.5) -HZ5	CLD(1.0) -HZ5	CLD(1.5) -HZ5	CLD(2.0) -HZ5	DeAl(6) -HZ5	DeAl(8) -HZ5	DeAl-CLD -HZ5	CLD-DeAl -HZ5
p-Xylene	71.67	72.37	75.62	70.28	68.93	70.96	66.31	75.72	67.29
m-Xylene	13.02	11.74	8.79	8.68	6.54	12.28	16.08	12.59	14.09
o-Xylene	4.73	4.02	3.99	3.06	2.63	4.35	5.58	3.93	4.45
Benzene	0.07	0.08	1.08	5.02	7.90	2.10	1.21	2.10	0.25
TMBs[a]	3.77	3.59	3.69	2.08	2.78	2.53	2.67	1.64	3.54
EB	0.20	0.20	0.21	5.07	6.35	0.22	0.27	0.22	0.30
Ethyl methyl benzene	3.22	3.08	3.41	3.04	2.78	3.74	3.81	2.50	8.19
$C9^+$	2.45	2.43	2.44	2.50	1.50	3.05	3.13	0.89	1.07

aTMBs = 1,2,3 Trimethylbenzene and 1,2,4 Trimethylbenzene

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