# CHAPTER IV RESULTS AND DISCUSSION

In this work, since the commercial catalysts were mostly employed, the major principles were emphasized on the catalyst characterization and catalytic activity testing rather than the catalyst preparation method. The findings discovered from the experimentation are imparted in details in this Chapter IV.

# 4.1 Catalyst Characterization

To understand the property-reactivity relations of the catalysts utilized in this work pertaining to catalytic performance in p-ET selectivity and toluene conversion, a comprehensive characterization of the catalyst composition, surface area, pore volume, acidity as well as the amount of coke formation were determined by various techniques as described below.

# 4.1.1 X-ray fluorescence spectroscopy (XRF)

It is well known that composition of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> plays a role in the acidity of HZSM-5 catalysts, which affects the activity and selectivity of the catalyst. The improper acidity may lead to the formation of undesired reactions resulting in lower selectivity of the desired product. So, choosing the proper SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of HZSM-5 is necessary for obtaining the highest selectivity of the desired product. The chemical compositions of commercial HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of 23, 80, and 280) and synthesized HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 169 catalysts were analyzed by X-ray fluorescence (XRF) technique. The theoretical acidity was determined from the protons attained according to its formula. The chemical composition and theoretical acidity are shown in Table 4.1. The theoretical acidity was in the range of 0.131-1.393 mmol/g cat with varied SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of 23-280.

The compound compositions of unmodified HZSM-5 catalysts  $(SiO_2/Al_2O_3 \text{ molar ratio } 280)$  of and of CLD chemical liquid deposition (CLD) treated catalysts were analyzed to determine the amounts of deposited silica after chemical

liquid deposition (CLD) treatment at the external surface of HZSM-5. Table 4.2 illustrates the effects of TEOS amount and CLD treating cycle on the catalyst composition. The results showed that  $SiO_2$  was insignificantly increased after CLD treatment. This might be due to the limitation in detecting alumina at low concentrations by the XRF instrument employed.

 Table 4.1 The chemical composition of the HZSM-5 catalysts investigated

SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> molar	Chemical composition (mol %)		Theoretical acidity	
1410	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>		
23	95.63	4.37	1.393	
80	98.72	1.28	0.422	
169	99.41	0.59	0.196	
280	99.60	0.40	0.131	

 Table 4.2
 Effects of TEOS amount and CLD cycle on the HZSM-5 (280) catalyst

 composition

CLD treatment	Amount of TEOS	Compositio	on (mol%)
(cycle)	(ml/g of catalyst)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
-	-	99.60	0.40
1	0.2	99.62	0.38
1	0.6	99.61	0.39
1	1	99.63	0.37
1	2	99.61	0.39
2	1	99.63	0.37

# 4.1.2 Scanning Electron Microscope (SEM)

Figure 4.1 shows SEM images of the unmodified commercial ZSM-5 catalysts (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of 23, 80, and 280) and synthesized ZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of 169). The structures of commercial ZSM-5 catalysts were alike a spherical shape for the HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 280, and a rectangular shape for that with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 23, an oval shape for that of 80, and a spherical shape for that of 280. However, the structure of the synthesized ZSM-5 has a larger crystal size compared with the commercial ones which possess a similar size of less than 0.5 microns. The difference in structure of the commercial and synthesized ZSM-5 might be due to the different synthesize methods.



HZSM-5 23

HZSM-5 80





HZSM-5 280

Figure 4.1 SEM images of the unmodified HZSM-5

# 4.1.3 Surface Area Measurements

The textural properties of catalysts were determined by N<sub>2</sub> adsorptiondesorption method. The surface area, pore volume, as well as pore diameter of both the unmodified and CLD treated HZSM-5 catalysts are summarized in Table 4.3. The surface area of the unmodified commercial and synthesized HZSM-5 catalysts, which was observed to increase with increasing the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio, was in the range of ca 334-380 m<sup>2</sup>/g. Nevertheless, the synthesized catalyst possessed higher pore volume and micro pore volume than the commercial ones. This is because of the difference in preparation method. For the one-cycle CLD treated HZSM-5 (1 ml TEOS/g of catalyst) (HZSM-5 CLD1), the surface area and pore volume of modified HZSM-5 was lower than the unmodified catalyst, probably, due to the narrowing or blocking the pore opening of the zeolite (Cejka*et al*, 1996). The two-cycle CLD treatment (HZSM-5 CLD2) had lower surface area than HZSM-5 CLD1. This might be due to the more pore blocking or narrowing after the treatment.

	Surface	Total pore	Micropore	Pore
Catalyst	area	volume	volume*	diameter**
	(m <sup>2</sup> /g)	(cc/g)	(cc/g)	(Å)
HZSM-5 (23)	334	0.266	0.143	6.14
HZSM-5 (80)	341	0.274	0.145	6.14
HZSM-5 (169)	371	0.291	0.140	6.14
HZSM-5 (280)	380	0.256	0.153	6.14
HZSM-5 CLD1	367	0.232	0.151	6.14
HZSM-5 CLD2	321	0.212	0.131	6.14

 Table 4.3 Textural properties of the HZSM-5 catalysts studied

\*Using t-plot method

\*\*Using NLDFT method

#### 4.1.4 TPD of Isopropylamine (IPA-TPD)

The acidity of HZSM-5 zeolites is an important factor affecting the activity and selectivity of the reaction. The suitable acidity depends on the nature of the reactions. For ethylation of toluene with ethanol, too much acidity leads to the higher probability of undesired reaction such as isomerization of p-ET to m-ET because the isomerization occurs much easier than alkylation. Since the IPA-TPD technique is widely used to investigate the Brönsted acid sites which are also active for the undesired reactions such as disproportionation of toluene, the catalysts investigated were subjected to the determination of Brönsted acid sites. Figure 4.2 shows IPA-TPD profiles of the HZSM-5 catalysts studied. Based on the area beneath a profile, Brönsted acid sites for individual catalysts were quantitatively increased with a decrease in SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio. This can be explained that when a Si<sup>4+</sup> cation was replaced by an Al<sup>3+</sup> cation, an additional positive charge is required to neutralize the net charge, hence, a higher Al<sub>2</sub>O<sub>3</sub> content required more positive charges for balancing its neutral charge. Although, a high content of proton (H<sup>+</sup>) as the cation can result in a strong acidic material, the acid strength and proton activity coefficients are increased with decreasing aluminum content (Saidina and Anggoro, 2002).



Figure 4.2 IPA-TPD profiles of the HZSM-5 catalysts studied.

# 4.1.5 X-ray Diffraction (XRD)

Figure 4.3 shows the XRD patterns of unmodified HZSM-5 and twocycle CLD treated HZSM-5. The scanning region of the diffraction angle 20 was 5 to 40°, which covered most of the significant diffraction peak of the zeolite. The MFI structure in HZSM-5 zeolite can be substantiated by the intensity peaks at 20 of 7.94, 8.88, 13.96, 14.78, 20.90, 23.08, 23.24, 23.40, 23.96, 24.58, and 25.84° in XRD patterns. The high intensity of peaks in the XRD patterns indicated that the zeolite samples have high crystallinity. The similar XRD patterns of HZSM-5 before and after silylation implied that the crystal structure of the catalysts remained unchanged after the silylation because the inert silica only deposited on the external surfaces of zeolite and did not influence ZSM-5 framework structure.



**Figure 4.3** XRD patterns of (a) unmodified HZSM-5 (280) (b) two-cycle CLD treatment(1 ml/g cat. of TEOS).

#### 4.2 Catalytic Activity Testing

To study the selective formation of *p*-ethyltoluene (*p*-ET) in the ethylation of toluene with ethanol using HZSM-5 catalysts. The effects of  $SiO_2/Al_2O_3$  molar ratios and reaction conditions on *p*-ET selectivity were studied over unmodified HZSM-5 zeolites. After that, the suitable  $SiO_2/Al_2O_3$  molar ratio of HZSM-5 was modified via CLD using TEOS as a deposition agent.

## 4.2.1 Effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Molar Ratio

To investigate the suitable SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of HZSM-5, various ratios of HZSM-5 catalysts were studied under a given reaction condition. Figure 4.4 shows the effect of various SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios on conversion of toluene and *p*-ET selectivity in liquid products. The highest *p*-ET selectivity was attained at 71.60 wt % on the HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 280. *p*-ET selectivity increased with an increase in SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio, but the toluene conversion was decreased. These can be ascribed that HZSM-5 with low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios which have more strong acid sites can lead to higher probability for the undesired reactions such as toluene disproportionation to xylenes and benzene. Moreover the more acid sites can lead to the higher isomerization of *p*-ET to *m*-ET which occurred much easier than alkylation (Liu *et al.*, 2010). The product selectivity from Table 4.4 reveals that the more undesired products formed as a lower SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of HZSM-5.



Figure 4.4 Effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio on ( $\blacksquare$ ) *p*-ET selectivity in products and ( $\blacksquare$ ) toluene conversion over HZSM-5; reaction temperature 350 °C, toluene to ethanol molar ratio of 3, WHSV = 20 h<sup>-1</sup>, and TOS = 390 min.

**Table 4.4** Effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio on the liquid product selectivity; reaction temperature 350 °C, toluene to ethanol molar ratio of 3, WHSV = 20 h<sup>-1</sup>, and TOS = 390 min

SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>		Liquid product selectivity (wt %)					
molar ratio	<i>p</i> -ET	<i>m</i> -ET	o-ET	Xylenes	Benzene	Others*	
23	27.77	61.53	2.47	1.48	0.35	6.40	
80	30.98	61.67	4.22	0.45	0.09	2.59	
195	68.72	27.54	0.09	0.58	0.25	2.82	
280	71.60	27.07	0.11	0.25	0.06	0.91	

\* For instance; ethylene, ethylbenzene, trimethylbenzene, and heavy aromatics

Figure 4.5 shows the effect of TOS on *p*-ET selectivity in products over various  $SiO_2/Al_2O_3$  molar ratios of HZSM-5. *p*-ET was slightly increases with an increase in TOS due to the coke formation at the external surface of HZSM-5. The portion of coke at the external caused the decreased external surface activity resulting in lowering the isomerization of *p*-ET to *m*-ET which mainly occurred at the external surface (Cejka *et al.*, 1996). Figure 4.6 shows the effects of TOS on toluene conversion, toluene conversion slightly decrease with an increase in TOS for HZSM-5 due to the decrease in active sites from deposited coke.



Figure 4.5 *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<sup>-1</sup>.

The amounts of deposited coke and TPO profiles are shown in Table 4.5 and Figure 4.7, respectively. The amounts of deposited coke were decreased and tended to form soft coke instead of hard coke as  $SiO_2/Al_2O_3$  molar ratio of HZSM-5 was increased. From all the catalysts studied, The HZSM-5 with  $SiO_2/Al_2O_3$  molar ratio of 280 was observed to be most suitable in terms of selectivity to *p*-ET as well as low coke formation, but low toluene conversion.



Figure 4.6 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<sup>-1</sup>.



Figure 4.7 TPO profiles of the HZSM-5 catalysts studied.

**Table 4.5** The amount of coke formed on the unmodified HZSM-5 catalysts after 390 min on stream (Reaction condition: 350 °C, toluene to ethanol molar ratio of 3, WHSV =  $20 \text{ h}^{-1}$ )

Catalyst	Amount of carbon (wt.%)
HZSM-5 (23)	19.91
HZSM-5 (80)	7.85
HZSM-5 (280)	2.98

# 4.2.2 Effect of Reaction Temperature

To investigate the proper reaction temperature of the reaction, HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 280 was studied at various reaction temperatures under a given WHSV and toluene to ethanol molar ratio. Figure 4.8 illustrates that the toluene conversion reaches a maximum at 400 °C and is decreased with further increasing temperature. The decline in conversion of toluene at high temperatures was due to the dealkylation of products instead of undergoing alkylation. The low conversion at low temperature (300 °C) was probably due to the insufficient energy for the alkylation. As seen in Table 4.6 the p-ET selectivity was dropped and m-ET selectivity was increased with an increase in reaction temperature. This can be explained that when the reaction temperature was increased, isomerization activity was increased and yet the diffusivity difference between the *m*- and *p*-isomers was decreased resulting in the higher probability of *m*-ET formation by isomerization of *p*-ET. At high temperature (500 °C), benzene and xylenes selectivity were significantly increased resulting from the disproportionation of toluene, which was taken place at higher temperatures compared with the alkylation due to higher activation energies for the transfer of methyl groups at the transition state with two toluene molecules and acid sites (Voloshina et al., 2009). On the other hand, a too low reaction temperature can result in lowering the diffusion out from the pore of the products leading to the higher probability of undesired reactions. From all temperatures studied, the temperature of

 $350 \,^{\circ}\text{C}$  providing both high toluene conversion and high *p*-ET selectivity was selected for further studies.



**Figure 4.8** Effect of reaction temperature: on (**•**) *p*-ET selectivity in products, (**•**) ethanol conversion, and (**•**) toluene conversion over HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 280; Toluene to ethanol molar ratio = 3, WHSV = 10 h<sup>-1</sup>, and TOS = 390 min.

**Table 4.6** Effect of temperature on the liquid product selectivity over HZSM-5 with  $SiO_2/Al_2O_3$  molar ratio of 280, toluene to ethanol molar ratio = 3, WHSV = 10 h<sup>-1</sup>, and TOS = 390 min

Temperature		Liquid product selectivity (wt %)				
(°C)	р-ЕТ	<i>m</i> -ET	o-ET	Xylenes	Benzene	Others*
300	69.69	26.10	0.21	0.40	0.04	3.56
350	66.58	31.95	0.10	0.24	0.02	1.11
400	62.46	35.72	0.16	0.35	0.07	1.23
450	57.33	38.33	0.26	1.25	0.29	2.54
500	52.19	36.08	0.26	3.94	2.86	4.66

\* For instance; ethylene, ethylbenzene, trimethylbenzene, and heavy aromatics



Figure 4.9 Toluene conversion as a function of TOS over HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 280 at reaction temperature 350 °C and 500 °C; toluene to ethanol molar ratio of 3, WHSV = 20 h<sup>-1</sup>.

**Table 4.7** The amounts of formed coke on the unmodified HZSM-5 catalyst at 350 °C and 500 °C after 390 min on stream (Toluene to ethanol molar ratio of 3, WHSV = 20  $h^{-1}$ )

Reaction temperature (°C)	Amount of carbon
	(wt.%)
350	2.98
500	4.02

Figure 4.9 shows toluene conversion of HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 280 at different reaction temperature of 350 °C and 500 °C. The changes in toluene conversion were insignificantly observed for both temperatures. This can be implied that the coke formation had a little influence on the toluene conversion. On the other hand, toluene conversion at 350 °C was observed to be higher than that at 500 °C due to the dealkylation of ethyltoluene at high temperature (Parikh *et al.*, 1992). Table 4.7 presents the amount of deposited coke at reaction temperatures of 350 °C and 500 °C. The amount of deposited coke was increased with an increase in reaction temperature. This due to the increased decomposition activity of products at higher

temperature. This is because the decomposition (dealkylation and cracking) reactions are favorable at high temperature.

## 4.2.3 Effect of Weight Hourly Space Velocity (WHSV)

To investigate the optimum WHSV of the reaction, HZSM-5 with  $SiO_2/Al_2O_3$  molar ratio of 280 was studied at various WHSV's under a given reaction temperature and toluene to ethanol molar ratio. The effect of WHSV on *p*-ET selectivity in the liquid product, and toluene conversion are depicted in Figure 4.10. The *p*-ET selectivity was increased, whereas the toluene conversion was decreased with an increase in WHSV. With a decrease in the WHSV, a longer contact time between the active sites of the catalyst surface and feed reactants can lead to the higher probability for the secondary reactions such as isomerization of the primary products to occur.



Figure 4.10 Effects of WHSV on ( $\blacksquare$ ) *p*-ET selectivity in products and ( $\blacksquare$ ) toluene conversion of HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 280; reaction temperature 350 °C, toluene to ethanol molar ratio of 3, and TOS = 390 min.

Table 4.8 shows the liquid product selectivity over HZSM-5 with  $SiO_2/Al_2O_3$  molar ratio of 280 at various WHSV's. *p*-ET selectivity was increased with an increase in WHSV, but *m*-ET. Less undesired product was observed as WHSV increased. So, isomerization activity seemed to be decreased as a WHSV was

increased. In the experiment range, the maximum *p*-ET selectivity was more than 70 wt % at WHSV of 20 h<sup>-1</sup>. To attain the highest selectivity of *p*-ET, the WHSV of 20 h<sup>-1</sup> was selected for further studies.

**Table 4.8** Effect of WHSV on the liquid product selectivity 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 = 3, and TOS = 390 min

WHSV		Liquid product selectivity (wt %)						
(h <sup>-1</sup> )	<i>p</i> -ET	m-ET	o-ET	Xylenes	Benzene	Others*		
5	58.57	39.65	0.20	0.27	0.12	1.19		
10	66.58	31.95	0.10	0.24	0.02	1.11		
15	68.66	29.65	0.12	0.25	0.06	1.27		
20	71.60	27.07	0.11	0.25	0.06	0.92		

\* For instance; ethylene, ethylbenzene, trimethylbenzene, and heavy aromatics

## 4.2.4 Effect of Toluene to Ethanol Molar Ratio

Figure 4.11 shows the effect of toluene to ethanol molar ratio on the catalytic performance. Toluene conversion was decreased with an increase in toluene to ethanol molar ratio, while ET and *p*-ET selectivities were increased and remained unchanged at toluene to ethanol molar ratio of more than 3. The decline in ET selectivity as the increased toluene to ethanol molar ratio was low because of the higher probability of ethanol to access the active sites, resulting in the formation of undesired products other than ET such as over-alkylated products and heavy aromatics (Yu and Tan, 2006). An excess of toluene might lead to the higher probability of toluene disproportionation, but this was not obviously observed, at least in the experimental range (toluene to ethanol molar ratio from 1 to 5). This might be due to the catalyst employed (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) was not suitable for the toluene disproportionation reaction, which prefers low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios HZSM-5 (Hui *et al.*, 2011). Toluene conversion was decreased with an increase in toluene to ethanol ratio because lesser ethanol could react with toluene.



**Figure 4.11** Effect of toluene to ethanol molar ratio on (**n**) ET selectivity in products. (**n**) *p*-ET selectivity in products, and (**n**) toluene conversion over HZSM-5 with  $SiO_2/Al_2O_3$  ratio of 280; reaction temperature 350 °C, WHSV = 20 h<sup>-1</sup>, and TOS = 390 min.

## 4.2.5 Effect of CLD treatment

The parent HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 280 was modified by silylation via CLD using TEOS to deactivate the external acid sites. The effects of TEOS and CLD cycle on *p*-ET selectivity and toluene conversion are shown in Table 4.9. *p*-ET selectivity reaches a maximum at TEOS of 1 ml/g of catalyst, and the conversion of toluene is decreased with an increase in TEOS amount. The two-cycle CLD treatment could improve *p*-ET selectivity, but lower the toluene conversion. These can be explained that a low amount of TEOS was not able to influence substantially the *p*-selectivity because of a low coverage of deposited silica. An excess of TEOS might cause the formation of an uneven silica layer, and thus resulted in a lower shape-selectivity, and multi-cycle depositions could improve the uniformity of the silica layer. (Hui *et al.*, 2011). Toluene conversion was decreased after modification due to the deactivation of external acid sites and narrowing or blocking the pore opening of the zeolite.

Table 4.9 Effects of TEOS amount and CLD cycle on toluene conversion and p-ETselectivity in liquid products

CLD treatment	Amount of TEOS	Toluene conversion	<i>p</i> -ET selectivity in products
(cycle)	(ml/g of catalyst)	(%)	(wt %)
-	-	13.15	69.67
1	0.2	13.06	79.36
1	0.6	12.76	82.45
1	1	12.57	85.13
l	2	11.89	80.08
2	l	9.86	89.05

Reaction temperature 350 °C, toluene to ethanol molar ratio of 3, WHSV = 20  $h^{-1}$ , particle size 60-80 mesh, and TOS = 390 min.

The product selectivity in Table 4.10 reveals that p-ET selectivity was increased, but *m*-ET was dropped after the CLD treatment. This is because due to the reduction of external acid sites, was achieved resulting in the suppression of the isomerization activity of *p*-ET to *m*-ET. *o*-ET which typically formed at the external surface was observed to decrease after the modification.

**Table 4.10** Effect of CLD treatment on the liquid product selectivity; reaction temperature 350 °C toluene to ethanol molar ratio = 3, WHSV = 20 h<sup>-1</sup>, and TOS = 390 min

Catalyst	Liquid product selectivity (wt %)						
	р-ЕТ	<i>m</i> -ET	o-ET	Xylenes	Benzene	Others*	
HZSM-5 (280)	69.67	28.05	0.18	0.40	0.04	1.67	
HZSM-5 CLD1	85.13	13.33	0.03	0.32	0.04	1.15	
HZSM-5 CLD2	89.05	8.98	0.01	0.37	0.02	1.57	

\* For instance; benzene, toluene and other aromatics

**Table 4.11** The amount of coke formed on the parent and CLD treated HZSM-5 catalysts after 390 min on stream (Reaction temperature 350 °C Toluene to ethanol molar ratio of 3, WHSV =  $20 h^{-1}$ , particle size 60-80 mesh)

Catalyst	Amount of carbon (wt.%)
HZSM-5 (280)	7.08
HZSM-5 CLD1	6.03
HZSM-5 CLD2	5.98

The amounts of deposited coke on the parent and CLD treated HZSM-5 catalysts were showed in Table 4.11. The amounts of deposited coke on CLD treated HZSM-5 were lower than that of the parent one. This might be due to the decreased acid sites after the treatment, which lower the probability of the coke formation from the decomposition of hydrocarbon species.

## 4.2.6 o-Xylene isomerization

In order to investigate catalytic properties at external acid sites, o-xylene which has a kinematic diameter larger than the pore opening of HZSM-5, was selected for the isomerization at the external surface of HZSM-5. The composition in feed is showed in Table 4.12. The reaction was studied over unmodified HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 280, the one-cycle and two-cycle CLD treated HZSM-5 (280). The composition in products and conversion are shown in Table 4.13. The results reveal that the conversion of o-xylene was significantly decreased from 9.37 to 3.83 % after modification. Moreover, *m*-xylene formation typically formed by isomerization at the external surface was decreased after modification. This could be conformed to the deactivation of external acid sites after modification.

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

 Table 4.12
 Composition of o-xylene as a feed reactant

\* For instance; benzene, toluene and other aromatics

 Table 4.13 Composition in liquid products and o-xylene conversion in o-xylene

 isomerization

Catalyst	o-Xylene	<i>o</i> -Xylene Composition in liquid products (wt %)			
	Conversion (%)	o-Xylene	<i>p</i> -Xylene	<i>m</i> -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<sup>-1</sup>, particle size 60-80 mesh, and TOS = 120 min.