CHAPTER IV
RESULTS AND DISCUSSION

In this work will focus on the commercial HZSM-5 catalysts which is widely used in the industry. Important parameters of catalyst, such as crystallinity, textural, and acid properties, are determined to be able to relate their catalytic activity to their properties. In the following Chapter, several techniques and the catalytic activity testing are used to describe their performance.

4.1 Catalyst Characterization

4.1.1 X-ray Fluorescence (XRF)

The chemical compositions of commercial HZSM-5 (SiO_2/Al_2O_3 molar ratios of 23, 80, 50 and 280) and modified HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 catalysts are determined by X-ray fluorescence (XRF) technique. The chemical composition, Si/Al molar ratio and theoretical acidity are summarized in Table 4.1. From the results, the theoretical acidity of catalysts determined based on the number of protons was attained according to its formula. The chemical

The chemical compositions of the chemical liquid deposition (CLD) treated catalysts were analyzed to decide the amount of deposited silica after CLD treatment. The result showed that the amount of SiO_2 with 1-cycle CLD treatment is increase in the amount of SiO_2 from the parent catalyst which imply that the silica deposition achieve on the external surface. Furthermore 2-cycle treatment shows the insignificant increase from 1-cycle treatment

In case of dealuminated catalyst (DeAl-HZ-5), the chemical compositions of the chemical liquid deposition (CLD) was employed to investigate the bulk Si/Al ratio. The SiO_2/Al_2O_3 molar ratio of dealuminated catalyst compared to the parent catalyst is increased from 285 to 289. It was proposed that some of framework aluminum(FAl) be able to eliminate the framework and leaving out its structure.

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

Catalysts	Chemical composition (wt %)			Si/Al molar ratio	SiO_2/Al_2O_3 molar ratio	Theoretical acidity (mmol/g)[a]
	SiO_2	Al_2O_3	Na_2O			
HZ-5(23)	92.61	7.29	0.10	10.78	21.56	1.545
HZ-5(50)	96.78	3.22	-	25.47	50.93	0.663
HZ-5(80)	98.01	1.99	-	41.88	83.75	0.397
HZ-5(280)	99.42	0.60	-	141.37	285.05	0.118
1-cycle CLD-(1.0)-HZ-5	99.41	0.58	-	144.67	289.35	0.1143
2-cycle CLD-(1.0)-HZ-5	99.47	0.53	-	158.23	316.94	0.1045
DeAl-HZ-5	99.41	0.58	-	144.92	289.85	0.1141

[a]Calculated values according to the information from International Zeolite Association(www.iza-online.org)

4.1.2 Surface Area Measurements

The textural properties obtained from the N_2 adsorption-desorption analyses of the parent catalyst (HZ-5(280)) and CLD treated HZSM-5 catalysts are presented in Table 4.2. It was found that the BET surface area, total pore volume, and micropore volume were decreased with increasing TEOS loading whereas a micropore volume-to-total pore volume (M/T) ratio was increased due to the narrowing or blocking of the pore opening of the zeolite (Cejka et al., 1996).

In case of dealuminated catalyst (DeAl-HZ-5), the dealuminated catalyst (DeAl-HZ-5) possessed lower all properties than the parent catalyst (HZ-5) due probably to the partial collapses of crystalline structure as aluminum atoms were extracted from the framework by the dealumination process (Muller et al., 2000).

Table 4.2 Textural properties of the parent and modified catalysts

Catalyst	Surface area (m^2/g)	Total pore volume(T) (cm^3/g)	Micropore volume(M)* (cm^3/g)	M/T ratio
HZ-5 (280)	432	0.275	0.177	0.64
1-cycle CLD (1.0)-HZ-5	412	0.251	0.171	0.68
1-cycle CLD (2.0)-HZ-5	344	0.208	0.144	0.69
2-cycle CLD (1.0)-HZ-5	364	0.216	0.155	0.72
3-cycle CLD (1.0)-HZ-5	350	0.196	0.151	0.77
DeAl-HZ-5	350	0.222	0.142	0.64

*Using t-plot method

4.1.3 X-ray Diffraction (XRD)

XRD patterns for the parent HZSM-5 and modified HZSM-5 are investigated any change in the crystalline structure of the samples as shown in Figure 4.1. A relative crystallinity for each sample was determined based on the sum of peak intensities between 22° and 25° in the XRD patterns (You and Park 2014). The scanning region of the diffraction angle 2θ was 5 to 40°, which covered most of the significant diffraction peak of the zeolite. It can be seen that the XRD patterns and relative crystallinity of the modified HZSM-5 via CLD treatment were nearly unchanged after being treated with TEOS. Although silica deposition occurred on the external or intra-crystalline surface of zeolite, the CLD treatment of TEOS did not influence on its framework structure.
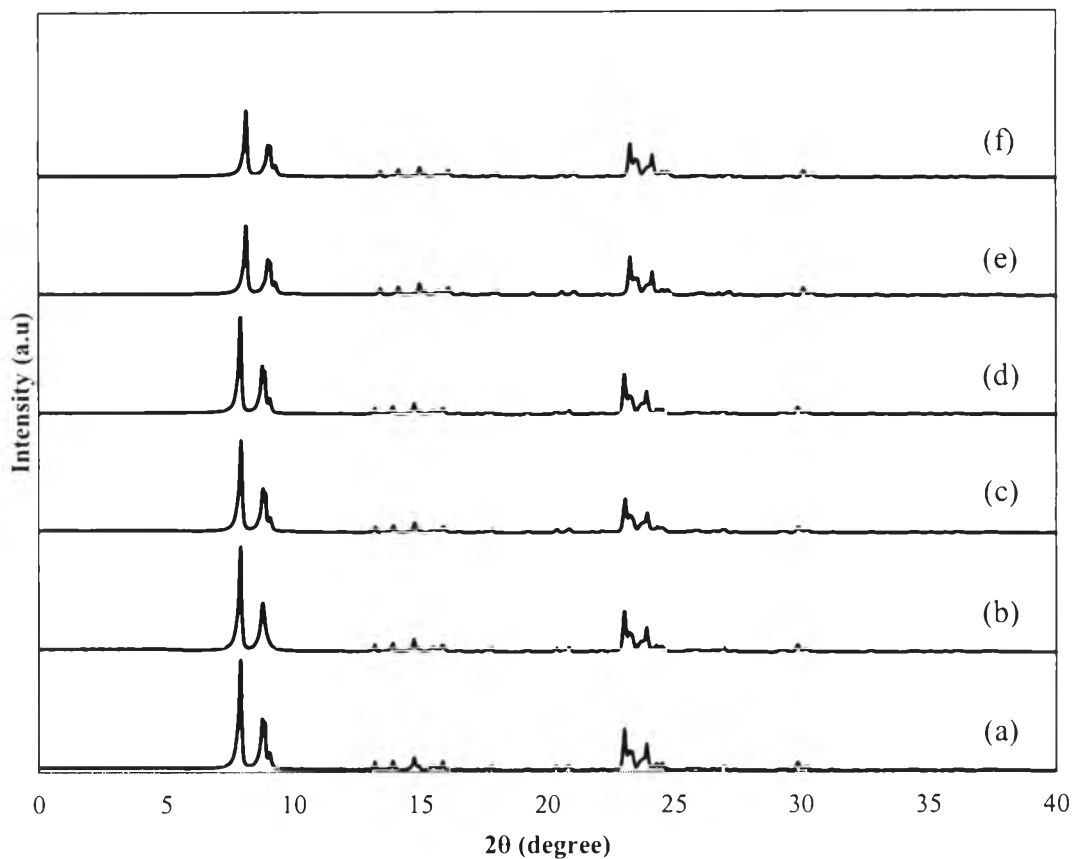
Figure 4.1 XRD patterns of (a) HZ-5(280) (b) 1-cycle CLD(0.5)-HZ-5, (c) 1-cycle CLD(1.0)-HZ-5, (d) 1-cycle CLD(1.5)-HZ-5, (e) 1-cycle CLD(2.0)-HZ-5, (f) DeAl-HZ-5 (280).

By comparing the XRD patterns of the parent HZSM-5 (HZ-5) and dealuminated HZSM-5 (DeAl-HZ-5) catalysts, they are similar except that the DeAl-HZ-5 exhibited a relatively lower intensity implying that the crystal structure of the catalysts typically remained unchanged whereas there were probably more defect sites present in the DeAl-HZ-5 as indicated by the relatively decreased crystallinity of ca. 74% as presented in Table 4.3. The observed phenomenon was also corresponded to its decrease in micropore volume which in turn resulted in decreasing its surface area significantly.

Table 4.3 Relative crystallinity of the parent HZSM-5 and modified HZSM-5

Catalyst	Relative crystallinity(%)
HZ-5(280)	100
1-cycle CLD(0.5)-HZ-5	97.47
1-cycle CLD(1.0)-HZ-5	86.01
1-cycle CLD(1.5)-HZ-5	89.30
1-cycle CLD(2.0)-HZ-5	86.08
2-cycle CLD(1.0)-HZ-5	86.31
DeAl-HZ-5	74.36

4.1.4 Scanning Electron Microscopy (SEM)

Figure 4.2 shows SEM images of the parent HZMS-5 (HZ-5) and CLD treated catalysts with varying amount of TEOS and cycle of treatment. It can be seen that the structures of the commercial and the modified HZSM-5 via CLD treatment were close to be spherical in shape and had a crystal size of approximately 2 μm. However, the crystalline particles were aggregated with increasing both the TEOS loading and the cycle of treatment which could be ascribed to the silica network formed by deposition on the external or intra-crystalline surface of zeolite. At a given concentration of TEOS, double concentration can cause the crystalline particles to aggregate more than double cycles of treatment as observed in Figures 4.2(e) and 4.2(f), respectively.
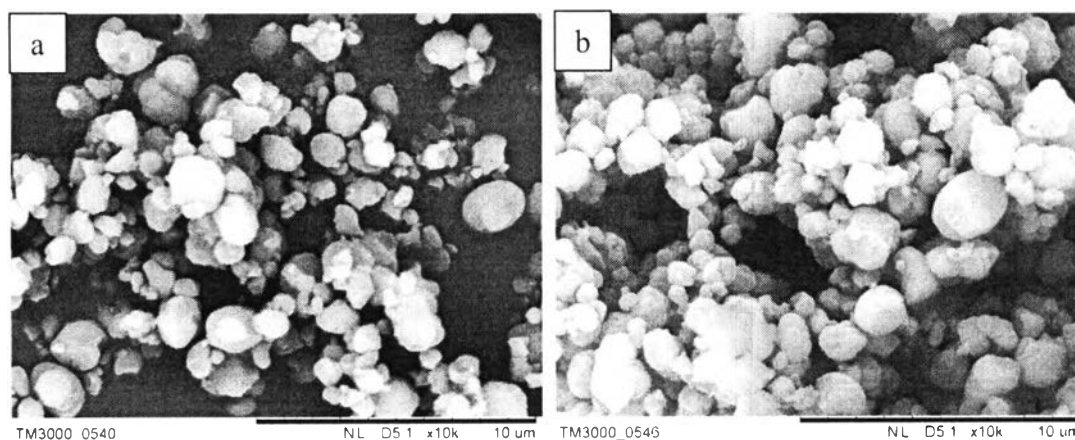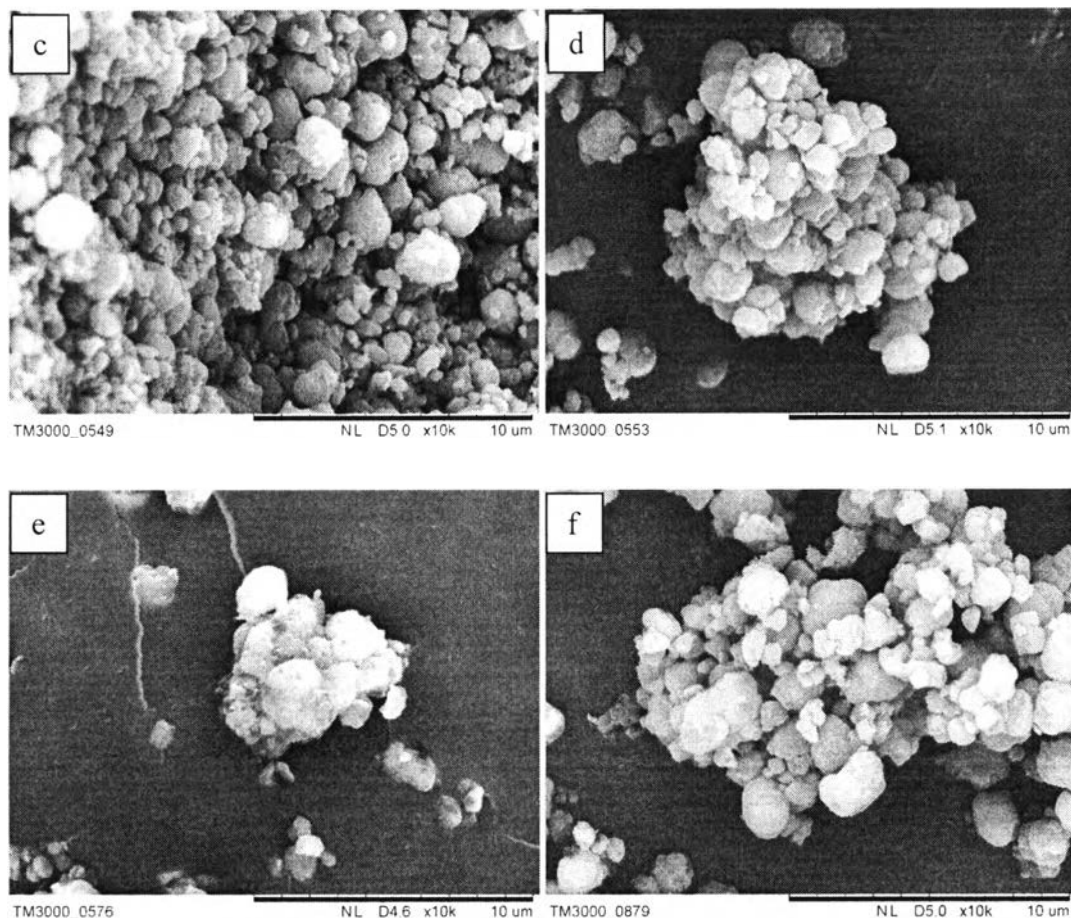
Figure 4.2 SEM images of the parent and modfied HZSM-5 catalysts (a) HZ-5(280) (b) 1-cycle CLD(0.5)-HZ-5, (c) 1-cycle CLD(1.0)-HZ-5,(d) 1-cycle CLD(1.5)-HZ-5, (e) 1-cycle CLD(2.0)-HZ-5, (f) 2-cycle CLD(1.0)-HZ-5.

4.1.5 TPD of Isopropylamine (IPA-TPD) and Ammonia (NH$_3$-TPD)

In order to understand the effects of the different modification methods on the acidity property of the HZSM-5 zeolite catalysts, IPA-TPD and NH$_3$-TPD technique are used to investigate the Brønsted acid sites and Total acidity which is an important fartor affecting to activitity and selectivity of the reaction. From Table 4.4 presents the acidity measured for the catalysts investigated in terms of Brønsted acid sites, Lewis acid sites, and total acidity. The treatment by TEOS on the parent HZSM-5 resulted in decreasing Lewis acid sites significantly, thus total acidity. However, the Lewis ones were insignificantly invariant whereas the

Brønsted ones were declined as an increase in TEOS loading. It could be implied that the external acid sites of the parent HZSM-5 were deactivated by silica deposition.

Table 4.4 Determination of acidity types for the parent and CLD treated HZSM-5 catalysts

Catalyst	Brønsted acid site (μmol/g)	Lewis acid site (μmol/g)	Total acidity (μmol/g)
HZ-5(280)	52.0	66.0	118.0
CLD(0.5)-HZ-5	50.3	21.3	71.6
CLD(1.0)-HZ-5	46.4	19.6	66.0
CLD(1.5)-HZ-5	39.9	20.1	60.0
CLD(2.0)-HZ-5	35.7	23.0	58.7

In Table 4.5, an increase in Lewis acid site at the same time a decrease in Brønsted acid site were observed for the dealuminated catalyst (DeAl-HZ-5) when compared to the parent one yielding its Brønsted acid site-to-Lewis acid site (B/L) ratio to decline by ca. 100%. It is postulated that by dealumination of the parent HZSM-5 (HZ-5) with oxalic acid the aluminum atoms in framework at external surface were extracted to form extra framework aluminum (EFAl) species with partial leaving its crystals.

Table 4.5 Determination of acidity types for the parent and dealuminated HZSM-5 catalysts

Catalyst	Brønsted acid site (B) (μmol/g)	Lewis acid site (L) (μmol/g)	Total acidity (μmol/g)	B/L ratio
HZ-5(280)	52.0	66.0	118.0	0.79
DeAl-HZ-5	28.9	76.1	105.0	0.38

4.1.6 ^{27}Al-MAS/NMR spectra

To obtain further information on the chemical environment of the aluminum atoms in the zeolite, ^{27}Al-MAS/NMR spectra were measured and are shown in Figure 4.3. Framework Aluminum species (FAl) are tetrahedrally coordinated (Al^{IV}), and the corresponding signal has a chemical shift of 50 to75 ppm. Since there were Al atoms originating from octahedrally coordinated (Al^{VI}) connected to the extra-framework aluminum (EFAl), a peak at a chemical shift of -5 to 10 ppm was observed in the 27Al-MAS/NMR spectra. Besides, a somewhat broader, less intense resonance around 25-50 ppm was also observed, indicating the presence of Al^{V} atoms as well as distorted tetrahedrally coordinated Al atoms in the EFAl species (Xu *et al.*, 2007). . FAl and EFAl species are represent to Brønsted acid site and Lewis acid site respectively, which were estimated on the basis of the integrated intensity of the Al^{IV}, Al^{VI} and Al^{V} peak in the 27Al-MAS/NMR spectra which show in Table 4.6.

As the result, the parent catalyst show a strong peak around 55 -70 ppm and a very weak peak at 0 ppm which assigned to octahedrally coordinated or EFAl species that were formed during the calcination. After CLD treatment, the ^{27}Al-MAS/NMR spectra show the decrease of peak area at chemical shift 50 to 70 ppm and increase of EFAl species with similarly in total peak area compared to the parent catalyst. Because of EFAl species which formed during the calcination (Fan *et al.*, 2007) still remain in the zeolite structure. Corresponding to its acidity the Lewis acid site are significant decreased after CLD treatment whereas the EFAl species are increased this might be the silica deposition could bury the EFAL species.

In case of dealuminated catalyst, It can be seen that the peak area at chemical shift 50 to 75 ppm which represented FAl species is decreased from 3000 to 2300 due to the extraction of aluminum atom from its framework and almost leaching out from the zeolite structure as see in the decreasing of peak area at chemical shift -5-10 and 20-35 ppm.
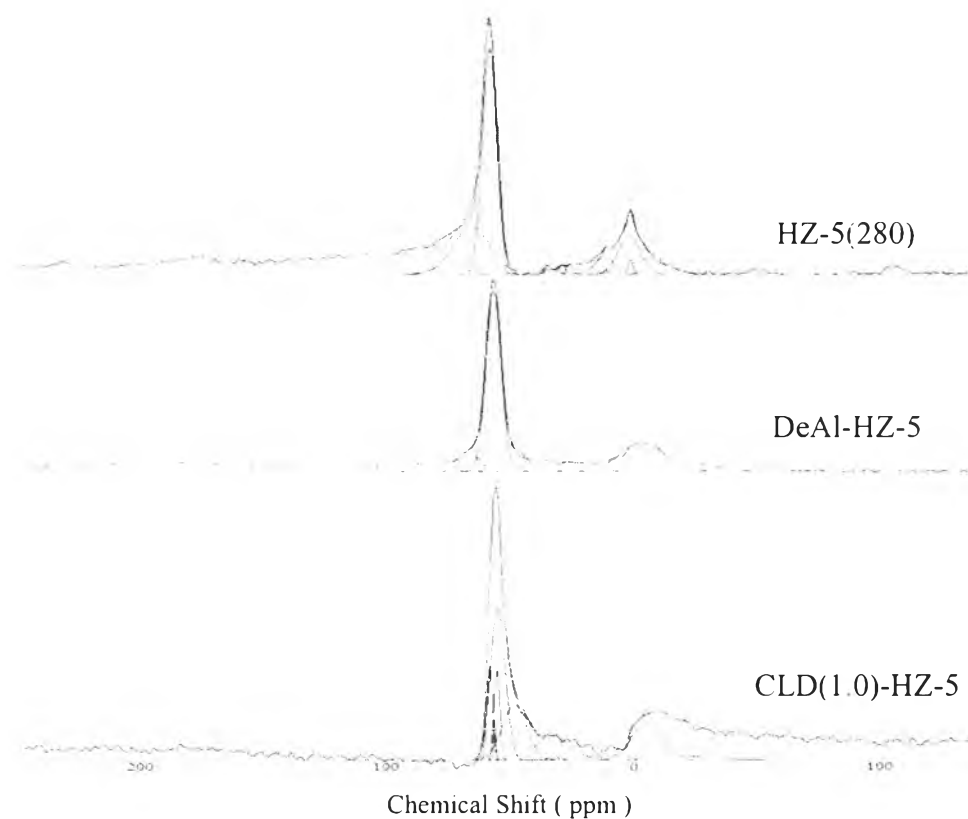
Chemical Shift (ppm)

Figure 4.3 ^{27}Al-MAS/NMR spectra of parent and modified HZSM-5 catalysts

Table 4.6 Aluminum coordinated formation of parent and modified catalysts

HZ-5 (280)		Area	Sum of Area	% Area	FAl/EFAl ratio
FAI	Peak at 50-70 ppm	3026.72		73.24	
EFAI	Peak at -5-10 ppm	1001.27	4132.37	26.76	2.74
	Peak at 20-35 ppm	104.38			
DeAl-HZ-5		Area	% Area	% Area	FAl/EFAl ratio
FAI	Peak at 50-70 ppm	2282.82		71.49	
EFAI	Peak at -5-10 ppm	705.28	3193.113	28.51	2.50
	Peak at 20-35 ppm	205.02			
CLD(1.0)-HZ-5		Area	Sum of Area	% Area	FAl/EFAl ratio
FAI	Peak at 50-70 ppm	2688.72		63.66	
EFAI	Peak at -5-10 ppm	1053.84	4223.35	36.64	1.75
	Peak at 20-35 ppm	480.80			

4.2 Catalytic Activity Testing

To enhance *p*-xylene selectivity in toluene alkylation with methanol using HZSM-5 catalysts. The effects of SiO_2/Al_2O_3 molar ratios on *p*-xylene selectivity are studied over parent HZSM-5 zeolites at toluene to methanol ratio of 4 , weight hourly space velocity of 24 h^{-1}, and temperature of 400 °C.

The most active commercial HZSM-5 zeolite was modified by silylation via chemical liquid deposition (CLD) with tetraethyl orthosilicate (TEOS) in range of 0.5-2.0 $ml.g^{-1}$, CLD cycle number in range of 1-3 cycle, or dealumination with oxalic acid.

4.2.1 Effect of SiO_2/Al_2O_3 Molar Ratio

A total of four HZSM-5 zeolites (SiO_2/Al_2O_3 = 23, 50, 80, 280) were used, respectively, for the toluene alkylation with methanol. Figure 4.3 shows the effect of different SiO_2/Al_2O_3 molar ratios on conversion of feedstock and *p*-xylene selectivity in liquid products. The *p*-xylene selectivity trends to increase with increasing SiO_2/Al_2O_3 ratio, there is a significant increase in p-xylene selectivity on HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280. HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 exhibits the highest *p*-xylene selectivity in liquid products of 66.83 wt%, on the other hand, toluene and methanol conversions trend to increase with decreasing SiO_2/Al_2O_3 molar ratios corresponding to the amount of strong acid sites which can lead to higher probability for the undesired reactions such as toluene disproportionation to xylenes and benzene (Zhu *et al.*, 2006) , isomerization of *p*-xylene to *m*-xylene which occurred much easier than alkylation (Liu *et al.*, 2010). The product distribution from Table 4.3 implied that a lower SiO_2/Al_2O_3 molar ratio of HZSM-5 produced more undesired products in such a reaction.
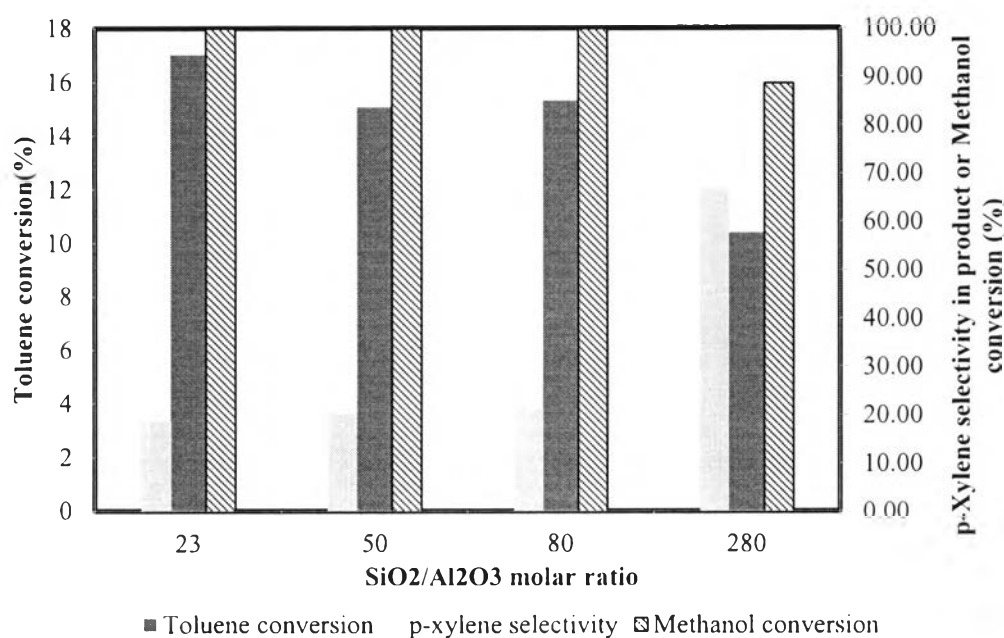
Figure 4.4 Effect of SiO_2/Al_2O_3 molar ratio on toluene conversion, methanol conversin and p-xylene selectivity in products over HZSM-5; reaction temperature 400 °C, toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min.

Table 4.7 Product distribution for various SiO_2/Al_2O_3 molar ratio; reaction temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

SiO_2/Al_2O_3 molar ratio	Product distribution (wt %)						
	p-Xylene	m-Xylene	o-Xylene	BZ	TMBs[a]	EB	Other[b]
23	18.65	36.48	15.22	3.53	6.40	0.37	19.34
50	20.27	40.12	16.52	0.80	7.39	0.26	14.63
80	21.31	43.02	18.85	0.31	9.70	0.11	6.70
280	66.83	13.70	8.38	0.10	6.63	0.16	4.02

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

[b] Other = Ethylmethylbenzene, $C9^{+}$

From the previous work Jirapon Techajiranon investigated the synthesized HZSM-5 catalysts with SiO_2/Al_2O ratio of 90 and 180. The catalytic testing results are summarized in Table 4.7. The HZ5A catalysts with SiO_2/Al_2O ratio of 90 showed the higher both toluene and methanol conversion than the HZ5B4 catalyst with SiO_2/Al_2O ratio of 181, but give less selectivity to p-xylene. This result assured that the HZSM-5 catalyst with lower acidity (a higher SiO_2/Al_2O ratio) resulting in higher p-xylene selectivity.

Table 4.8 Comparison of synthesized catalysts (Techajiranon .*et al* 2012) with SiO_2/Al_2O ratio of 90 and 181 on conversion, and product distribution; reaction temperature of 400 °C, toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

SiO_2/Al_2O_3 molar ratio	Conversion (%)		Product distribution (wt %)			
	Toluene	Methanol	p-Xylene	m-Xylene	o-Xylene	TMBs[a]
HZ5A(90)	22.20	100	29.09	41.44	16.03	13.44
HZ5B4(181)	14.64	91.7	78.61	9.97	5.60	5.81

The parent catalysts were analyzed by TPO technique to observe the coke formation. Figure 4.6 illustrates the comparison of TPO profiles between the various SiO_2/Al_2O_3 molar ratio of parent catalysts. As can be seen. the TPO profiles tended to form soft coke instead of hard coke as SiO_2/Al_2O_3 molar ratio of HZSM-5 was increased. From Table 4.8, the amount of carbon deposition of parent catalyst were 7.01%, 5.10 and 3.87% for HZ-5(23), HZ-5(80) and HZ-5(280), respectively. The amount of carbon deposition was increased with decreasing SiO_2/Al_2O_3 molar ratio correspond to the number of acid sites which can lead to higher probability for the coke formation.
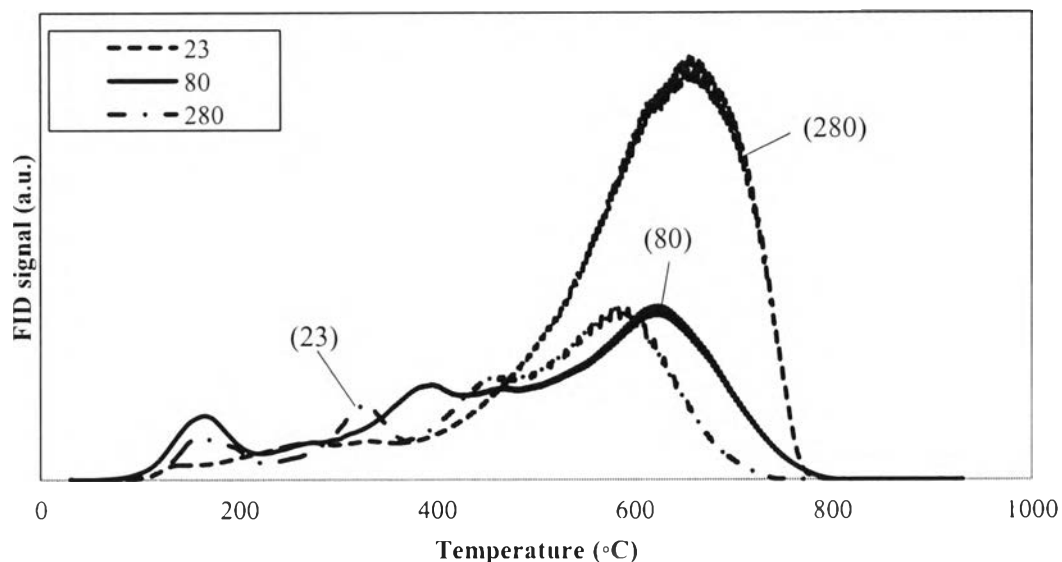
Figure 4.5 TPO profiles of parent HZSM-5 with various SiO_2/Al_2O_3 molar ratios of HZ-5(23), HZ-5(80), and HZ-5(280).

Table 4.9 The amount of carbon deposition on the parent HZSM-5 with various SiO_2/Al_2O_3 molar ratios after 375 min on stream

Catalysts	Amount of carbon deposition (wt.%)
HZ-5(23)	7.01
HZ-5(80)	5.10
HZ-5(280)	3.87

It is obvious that the HZSM-5 catalyst with SiO_2/Al_2O_3 molar ratio of 280 was observed to be most suitable in terms of selectivity to p-xylene and low coke formation.

4.2.2 Effect of TEOS Loading

The parent HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 was modified via CLD treatment with TEOS. The effect of the amount of TEOS on p-xylene selectivity and toluene conversion is shown in Figure 4.5. It can be seen that the *para*-xylene selectivity was reached its maximum whereas the toluene conversion

was decreased with increasing amount of TEOS. The TEOS employed in excess of 1 ml/g of catalyst resulted in decreasing in *para*-xylene selectivity. The highest *para*-xylene selectivity of ca. 81 % was achieved with the toluene conversion of ca. 8 % at 400 °C, WHSV of 24 h^{-1}, toluene-to-methanol molar ratio of 4:1, and TOS of 375 min. This might be because a layer of inert silica deposited onto the external surface of HZ-5 crystals deactivated the external acid sites which are active for the isomerization of *p*-xylene to the undesired products; however, the excess of TEOS might cause the formation of an uneven silica layer blocking the pore opening, and thus resulted in a lower shape-selectivity (Hui *et al.*, 2011).
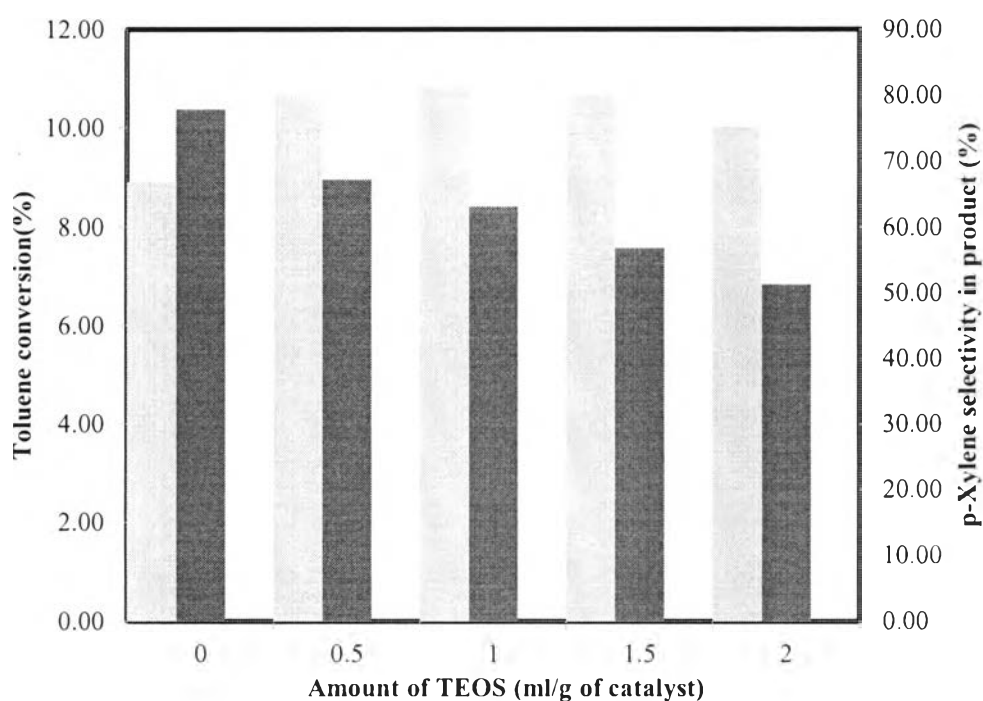

Figure 4.6 Effect of TEOS loading on (∎) toluene conversion and ( ) selectivity in products over HZ-5; reaction temperature 400 °C, toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min.

Comparison of product distributions for the catalysts obtained before and after CLD treatment is presented in Table 4.9. Evidently, the decline of external acid sites after CLD treatment influenced on increasing *p*-xylene selectivity because

the isomerization activity of p-xylene to m-xylene, o-xylene which typically formed at the external surface was decreased after CLD treatment.

Table 4.10 Product distribution for the parent and CLD treated HZSM-5 catalysts; reaction temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

| Catalyst | Product distribution (wt %) | | | | | | | | p-xylene selectivity in xylenes |
	p-Xylene	m-Xylene	o-Xylene	BZ	TMBs[a]	EB	Ethylmethyl benzene	C9+	
HZ-5(280)	66.83	13.70	8.38	0.10	6.63	0.16	2.15	1.87	75.17
CLD(0.5)-HZ-5	79.97	8.09	3.67	0.11	4.99	0.14	1.44	1.41	87.18
CLD(1.0)-HZ-5	81.39	6.45	3.00	0.16	3.34	0.18	3.24	2.10	89.59
CLD(1.5)-HZ-5	79.92	8.74	4.97	0.11	3.13	0.13	1.76	1.08	85.35
CLD(2.0)-HZ-5	75.21	8.80	4.38	0.20	2.14	0.26	6.59	2.26	75.82

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

4.2.3 Effect of CLD Treatment Cycle

The effect of CLD treatment cycle on toluene and methanol conversions, and product selectivity was study on CLD (1.0)-HZ-5 which exhibited the highest p- xylene selectivity compared to the other amount of TEOS loading on HZ-5 catalysts. From Figure 4.7 it could be seen that the para-xylene selectivity reached optimum with two-cycle of CLD treatment. The p-xylene selectivity increased with one-cycle of CLD treatment from 81.39 to 84.84. It was proposed that multi-cycle depositions not only increased the amount of silica deposited on HZSM-5 zeolite external surface but also improved the uniformity of the silica layer .On the other hand, the three-cycle treatment showed both decreased in feedstock conversion and p-xylene selectivity which compared to two-cycle treatment.
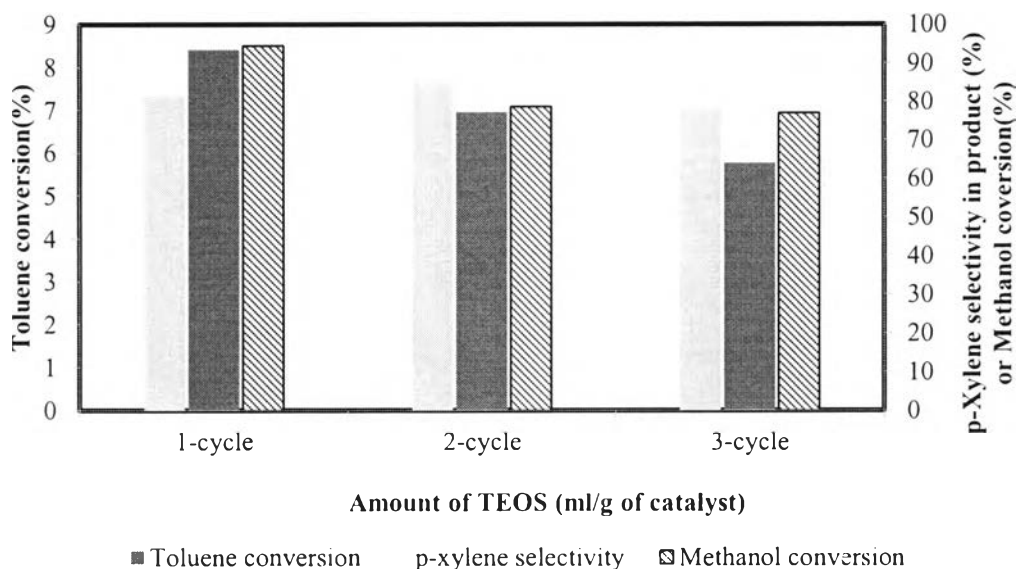
Figure 4.7 Effect of CLD treatment cycle on toluene conversion, Methanol conversion and selectivity in products over HZ-5; reaction temperature 400 °C, toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min.

Table 4.11 Product distribution for the different CLD treatment cycle over HZSM-5 catalysts with; reaction temperature 400 °C toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min

Catalyst	Product distribution (wt %)								p-xylene selectivity in xylenes
	p-Xylene	m-Xylene	o-Xylene	BZ	TMBs[a]	EB	Ethylmethyl benzene	C9+	
1-cycle	81.39	6.45	3.00	0.16	3.34	0.18	3.24	2.10	89.59
2-cycle	84.84	5.03	2.30	0.13	1.85	0.23	3.60	1.71	92.05
3-cycle	78.25	6.27	4.21	0.13	4.23	0.27	3.35	2.95	88.19

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

Figure 4.8 demonstrate the comparison of TPO profiles between the parent (HZ-5) and sililated catalysts with various CLD treatment cycle. The TPO profiles revealed that the 1-cycle treatment show oxidation of coke at higher temperature compared to the parent and further increase in cycle treatment with 2-

cycle show the same result as 1-cycle treatment. It was proposed that the product difficult to diffuse out of the catalysts pore due to blocking of the pore opening by formation of silica deposition from TEOS modification. Thus, there is probability of product to form hard coke formation inside zeolite pore

At low oxidation temperatures, ca. 300 °C the coke components are not poly aromatic. The retention of the "coke" molecules on the catalysts is generally due to their strong adsorption and to their low volatility which can form by undesired reaction from external acid site (Guisnet et $al.$, 2001). Thus the peak at 300 °C of silylated catalyst show no peak which can represent the deactivation of external acid site.
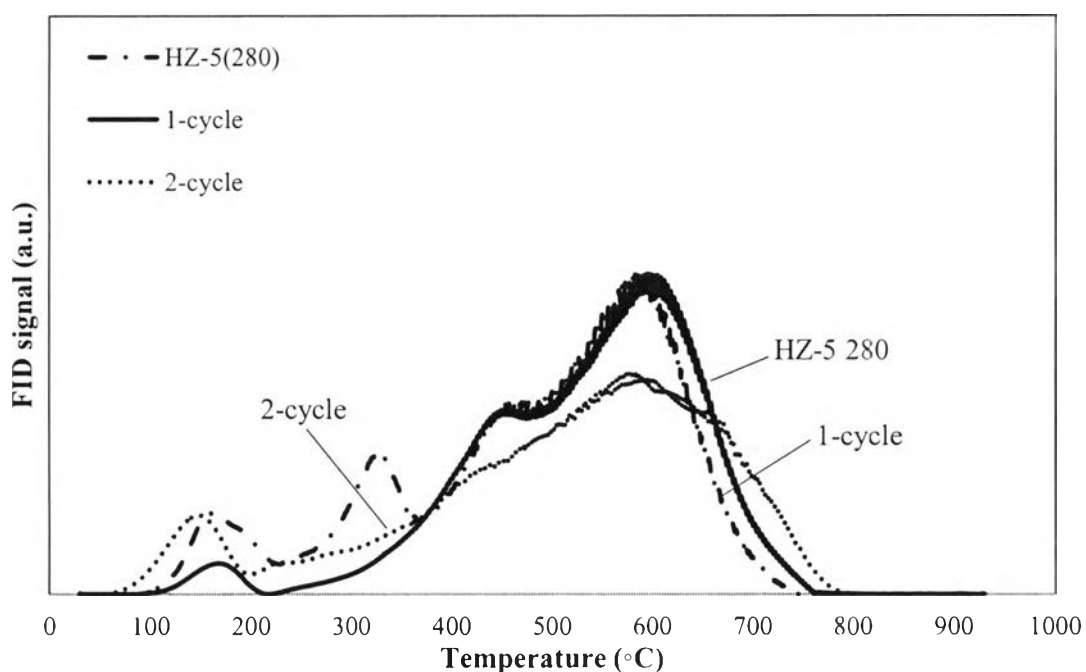

Figure 4.8 TPO profiles of parent HZSM-5 and silylated catalysts with various CLD-cycle treatment

Table 4.12 The amount of carbon deposition on the parent HZSM-5 catalysts and modified catalysts via CLD treatment after 375 min on stream

Catalysts	Amount of carbon deposition (wt.%)
HZ-5(280)	3.74
1-cycle	3.46
2-cycle	3.29
3-cycle	2.96

The amounts of carbon deposition on the parent and CLD treated HZSM-5 catalysts were showed in Table 4.12.The amount of coke deposition was decreased with increase of cycle treatment number due to deactivation of external acid site which amount of coke direct variation to the acidity of the catalyst.

4.2.4 Effect of Dealumination Treatment

The acid properties and resultant catalytic activity of zeolite materials are known to be related to the degree of substitution of aluminum for silicon in the framework. As the molecular diameter of oxalic acid is larger than zeolite pore openings, they could be used to selectivity remove the framework aluminum at the external surface of HZSM-5 catalyst. The parent HZSM-5 with SiO_2/Al_2O_3 molar ratio of 280 was modified by dealumination with oxalic acid. From Figure 4.9 and 4.10 illustrates the comparison of catalytic activity between the parent (HZ-5) and dealuminated (DeAl-HZ-5) catalysts. As can be seen, no distinguishable performance on selectivity to p-xylene in product could be observed for both of the catalysts. However, a slight increase in toluene was attained for the DeAl-HZ-5. This might be attributed to A shift from Bronsted acid sites to lewis acid sites responsible for another reaction of toluene rather than methylation. As can be seen in the product selectivity which p-selectivity slightly decreased from the parent to the other product.
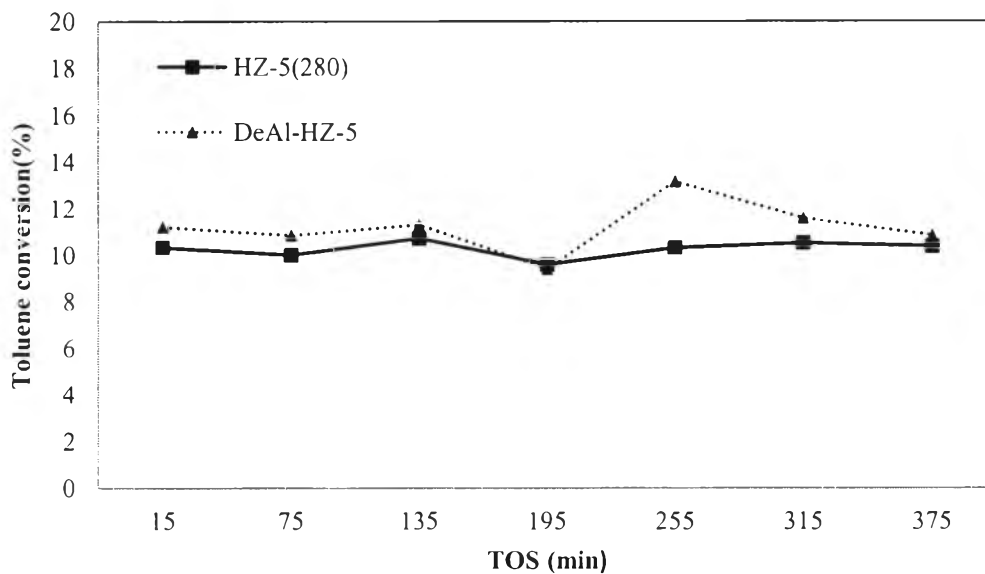
Figure 4.9 Effect of dealumination with oxalic acid on toluene conversion over the parent HZSM-5; reaction temperature 400 °C, toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min.
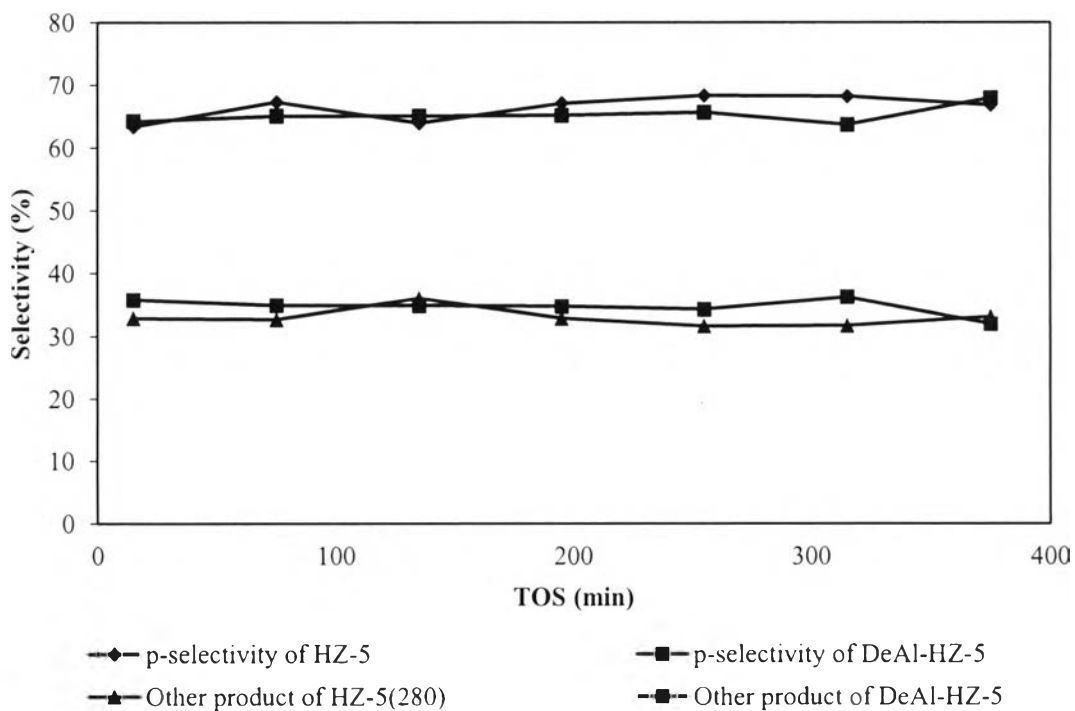

Figure 4.10 Effect of dealumination with oxalic acid on p-xylene selectivity and other product over the parent HZSM-5; reaction temperature 400 °C, toluene to methanol molar ratio of 4, WHSV = 24 h^{-1}, and TOS = 375 min.

Figure 4.11 demonstrate the comparison of TPO profiles between the parent (HZ-5) and dealuminated (DeAl-HZ-5) catalysts. As can be seen, the TPO profiles of dealuminated (DeAl-HZ-5) catalysts slight increase of hard coke formation It was proposed that the coordination of the EFAL species to the oxygen atom nearest to the framework aluminum results in the enhanced acid strength of zeolite due to the existence of the Brønsted/Lewis acid sites synergy (Li *et.al.*, 2007) but the amount of coke formation which show in Table 4.13 was remain the same as the parent one.

Table 4.13 The amount of carbon deposition on the parent HZSM-5 catalysts and dealuminated catalysts after 375 min on stream

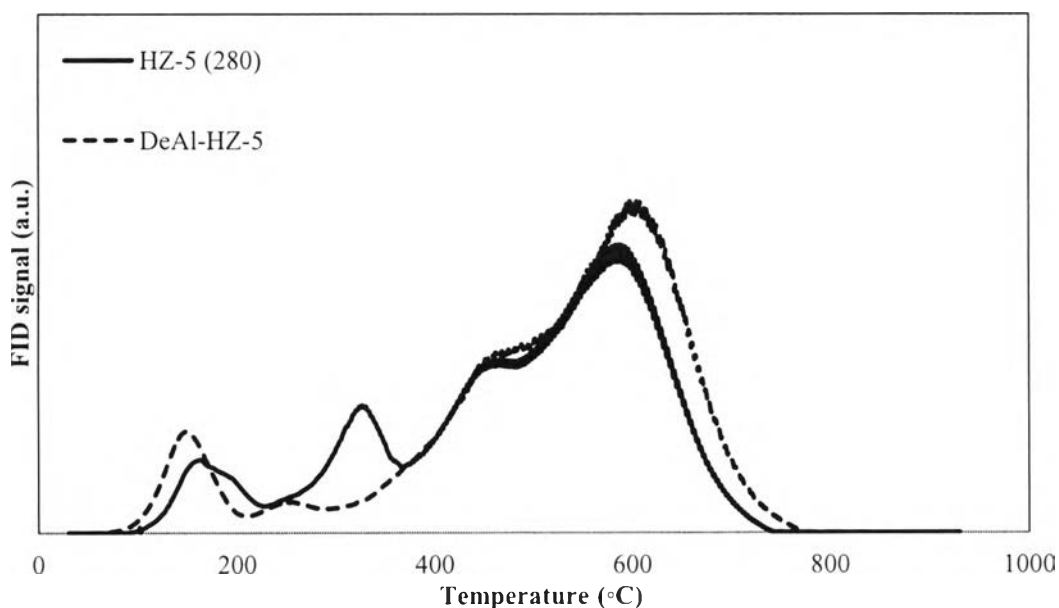| Catalysts	Amount of carbon deposition (wt %)
HZ-5 (280)	3.74
DeAl-HZ-5	3.71

Figure 4.11 TPO profiles of parent HZSM-5 and DeAl-HZ-5 catalyst.