CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst Characterization

In this study, the synthesized HZSM-5 catalyst with SiO_2/Al_2O_3 ratio of 200 by hydrothermal process which was aged at room temperature for 24 h and at 140 °C for crystallization 72 h was designated as HZSM-5. The catalysts modified by CLD treatment were designated as CLD(x)-HZ5, where x represents the desired amount of TEOS. For dealuminated catalysts with varying times of 6 and 8 h, the catalysts were designated as DeAl(6)-HZ5, and DeAl(8)-HZ5, respectively. Furthermore, the catalysts with combined treatments of CLD and DeAl for silyation-dealumination sequence and dealumination-silylation sequence were designated as DeAl-CLD-HZ5 and CLD-DeAl-HZ5, respectively.

The catalysts prepared were characterized by various techniques, i.e. XRD, XRF, SEM, BET, TPD, and TPO. The catalytic activity testing for methylation of toluene with methanol over those catalysts was investigated. The results are presented and discussed in this chapter.

4.1.1 X-ray Diffraction (XRD)

The XRD powder patterns of the synthesized and modified HZSM-5 catalysts are shown in Figure 4.1. The scanning region of diffraction angle 2θ was between 5 and 35°. The MFI structure in HZSM-5 zeolite can be substantiated by the intensity peaks at 2θ 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 crystal structure of modified HZSM-5 catalysts is unchanged after the CLD treatment. This is because the silica deposition occurred on the external or intra-crystalline surface of zeolite, uninfluencing its framework structure (Zhao *et al.*, 2010).

However, the dealuminated HZSM-5 catalyst was not the cause of drastic change in the zeolite structure, although there was some decrease in the crystallinity of HZSM-5 after acid treatment. It is noticed that the peak intensity at

2θ being 23.08° of dealuminated catalysts slightly decreased from that of parent catalyst due to some part of the framework structure collapse (Yan *et al.*, 2003). Moreover, HZSM-5 samples practically did not change according to their low dealumination rate as compared to other catalysts (González *et al.*, 2011) and the acid treated samples exhibited the presence of extra-framework aluminum (EFAl) and the occurrence of Al framework dealumination due to acid treatment, and that may be the reason for a slight decrease in the intensity of XRD peaks (Viswanadham *et al.*, 2006). Therefore, modified by combined silylation and dealumination were decreased because effect from dealumination.
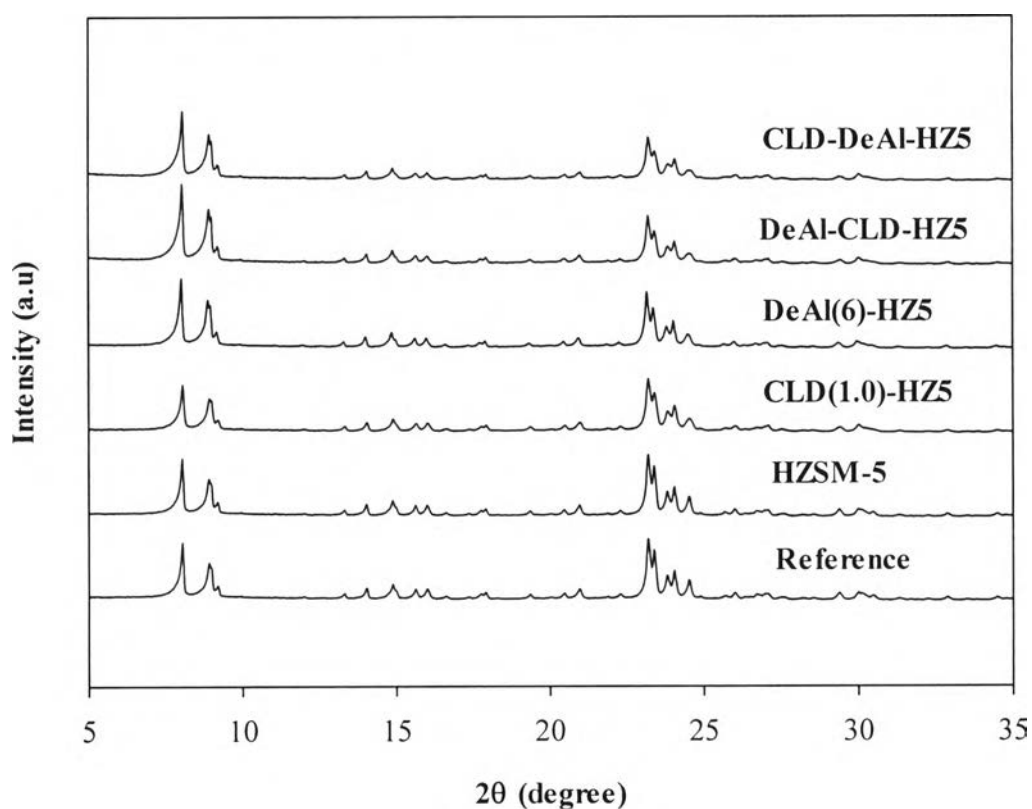

Figure 4.1 XRD powder patterns of the synthesized catalysts (A) HZSM-5, (B) CLD(1.0)-HZ5, (C) DeAl(6)-HZ5, (D) CLD-DeAl-HZ5, (E) DeAl-CLD-HZ5.

4.1.2 Catalyst Composition

It is well known that a composition of SiO_2 and Al_2O_3 plays a role in the acidity of HZSM-5 catalyst, hence its activity and selectivity. The chemical compositions of the as-synthesized and modified HZSM-5 catalysts were analyzed by X-ray fluorescence (XRF) technique as shown in Table 4.1. The parent HZSM-5 catalyst possesses a SiO_2/Al_2O_3 molar ratio of 214 which was slightly deviated from the desired value. The SiO_2/Al_2O_3 molar ratios of modified catalysts are in the range of 224-269. For the silylated HZSM-5 modified by CLD method, its SiO_2/Al_2O_3 molar ratios are considerably increased from 231 to 269 as an increase in TEOS amount. This is because the acid sites on external surface were covered by SiO_2 resulted from treated TEOS.

In case of dealuminated HZSM-5, its SiO_2/Al_2O_3 molar ratios are higher than the parent catalyst. The SiO_2/Al_2O_3 molar ratio was increased from 224 to 235 with increasing time of dealumination from 6 to 8 h, respectively. This is because oxalic acid could leach out some of the framework aluminum species (FAl) to become the extra-framework aluminums species (EFAl) or to leave the pore structure. Furthermore, the SiO_2/Al_2O_3 molar ratios of combination of CLD and DeAl are much higher than the parent catalyst due to the synergetic effects of TEOS and oxalic acid.

Table 4.1 Chemical properties of the as-synthesized and modified HZSM-5 catalysts

Catalyst	Chemical Composition (wt%)			SiO_2/Al_2O_3 Molar Ratio
	Si	Al	Na	
HZSM-5	98.981	0.890	0.128	214
CLD(0.5)-HZ5	99.116	0.826	0.058	231
CLD(1.0)-HZ5	99.200	0.750	0.050	254
CLD(1.5)-HZ5	99.263	0.737	0.010	259
CLD(2.0)-HZ5	99.236	0.709	0.055	269
DeAl(6)-HZ5	99.087	0.851	0.061	224
DeAl(8)-HZ5	99.133	0.810	0.058	235
DeAl-CLD-HZ5	99.212	0.733	0.056	260
CLD-DeAl-HZ5	99.184	0.747	0.069	255

4.1.3 Scanning Electron Microscopy (SEM)

Morphological properties and particle sizes of catalyst investigated by SME are shown in Figure 4.2. The morphology of the synthesized HZSM-5 catalyst appears as irregular hexagonal prisms with rectangular insertion. The particle sizes are in the dimensions of LxWxH ranging from 11.5x5.0x4.2 to 13.6x6.5x6.4 in microns. According to SEM analysis, no significant changes in the particle size and morphology after silylation and dealumination of HZSM-5 could be observed.
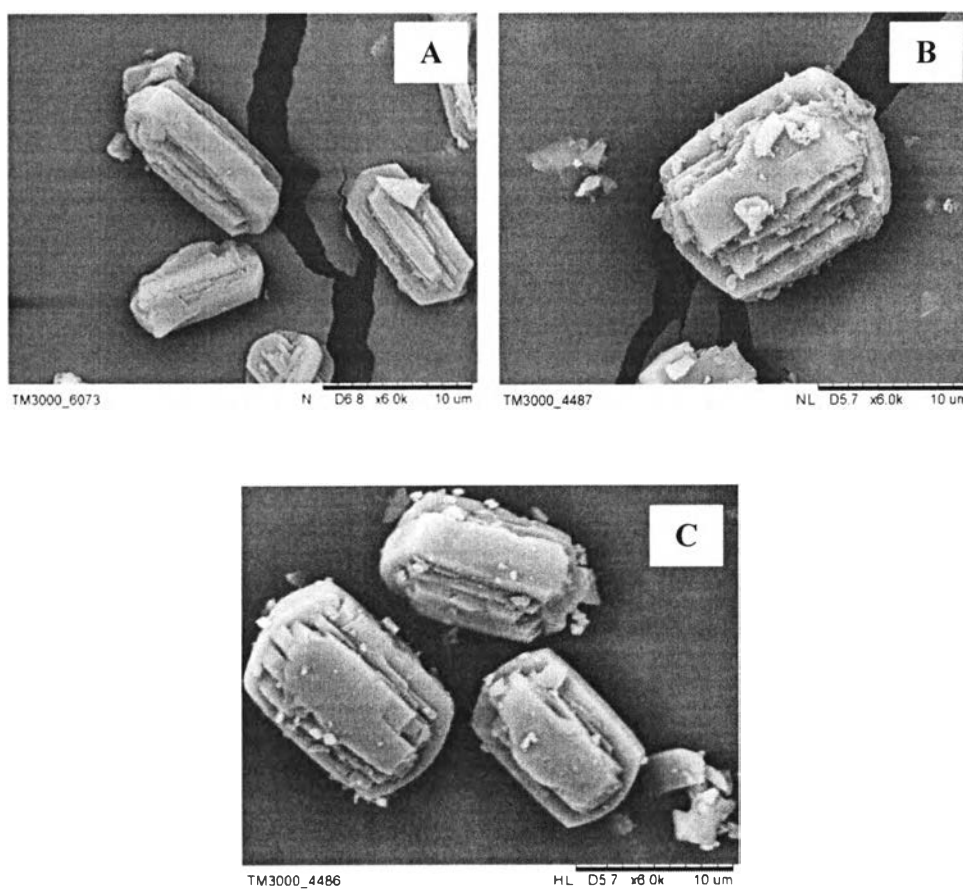

Figure 4.2 SEM images of (A) the as-synthesized HZSM-5, (B) silylation HZSM-5, and (C) dealumination HZSM-5 catalysts.

4.1.4 Determination of Textural Properties

The textural properties of all catalysts were determined by N_2 adsorption and desorption method. The surface area, pore volume, and total pore volume of both synthesized and modified catalysts are summarized in Table 4.2. The parent catalyst possesses BET surface area, total pore volume, micropore volume of 373 m^2/g, 0.291 cm^3/g, and 0.110 cm^3/g, respectively. The CLD treated catalysts show much lower surface area but less micropore volume and total pore volume than the parent catalyst. Moreover, these properties were decreased with increasing TEOS loading which generated inert SiO_2 layers on external surface resulting in the narrowed pore mouth of zeolite (Cejka et al., 1996).

The acid treated HZSM-5 catalysts (dealuminated ones) present lower surface area but higher total pore volume than parent HZSM-5. This can be ascribed to the loss of aluminum in the HZSM-5 structure, which resulted in higher mesoporosity. When dealumination time increasing, the BET surface area and micropore volume of DeAl(6)-HZ5 are higher than that of DeAl(8)-HZ5 due probably to the loss of crystallinity after treatment (González et al., 2011). On the other hand, the total pore volume of DeAl(6)-HZ5 is less than DeAl(8)-HZ5 because DeAl(8)-HZ5 can leach out some of the framework Al species (FAl) more than DeAl(6)-HZ5 and FAl become to the extra-framework Al species (EFAl), thus increasing the mesopores.

By comparison of treatment sequences of the combined silylation and dealumination, the CLD-DeAl-HZ5 has higher textural properties than the DeAl-CLD-HZ5 due to the fact that the leaching of framework Al species (FAl) from its structure to form the extra-framework aluminum species (EFAl) and the creation of mesopores could prevail by dealumination.

Table 4.2 Textural properties of the parent and modified HZSM-5 catalysts

Catalyst	BET Surface Area (m^2/g)	Micropore Volume^a (M) (cm^3/g)	Total Pore Volume (T) (cm^3/g)	M/T Ratio
HZSM-5	373	0.110	0.291	0.378
CLD(0.5)-HZ5	288	0.106	0.271	0.391
CLD(1.0)-HZ5	287	0.100	0.260	0.385
CLD(1.5)-HZ5	280	0.099	0.257	0.385
CLD(2.0)-HZ5	269	0.092	0.253	0.364
DeAl(6)-HZ5	319	0.116	0.314	0.369
DeAl(8)-HZ5	313	0.112	0.342	0.327
DeAl-CLD-HZ5	261	0.096	0.194	0.495
CLD-DeAl-HZ5	285	0.115	0.252	0.456

^{a}Determined by t-plot method

4.1.5 Acidity Determination

The acidity plays an important role in catalytic activity and selectivity of HZSM-5. IPA-TPD and NH$_3$-TPD experiments were carried out to determine the Brønsted acid sites and total acidity, respectively. IPA-TPD and NH$_3$-TPD results are shown in Table 4.3. The ratios of Brønsted to Lewis acid sites (B/L) and Brønsted to total acidity (B/Ta) are also presented in Table 4.3. Such ratios would be useful for the investigation of activity-chemical (acidity) property relation which will be further discussed.

Table 4.3 The quantitative values of acidity for the parent and modified HZSM-5 catalysts

Catalyst	Bronsted Acid Site^a (B) (mmol/g)	Lewis Acid Site (L) (mmol/g)	Total Acidity^b (Ta) (mmol/g)	B/L Ratio	B/Ta Ratio
HZSM-5	0.134	0.046	0.181	2.913	0.740
CLD(0.5)-HZ5	0.095	0.042	0.137	2.262	0.693
CLD(1.0)-HZ5	0.084	0.043	0.127	1.953	0.661
CLD(1.5)-HZ5	0.073	0.046	0.119	1.587	0.613
CLD(2.0)-HZ5	0.066	0.046	0.112	1.438	0.589

Table 4.3(cont') The quantitative values of acidity for the parent and modified HZSM-5 catalysts

Catalyst	Bronsted Acid Site[a] (B) (mmol/g)	Lewis Acid Site (L) (mmol/g)	Total Acidity[b] (Ta) (mmol/g)	B/L Ratio	B/Ta Ratio
DeAl(6)-HZ5	0.080	0.060	0.140	1.333	0.571
DeAl(8)-HZ5	0.074	0.068	0.142	1.088	0.521
DeAl-CLD-HZ5	0.091	0.034	0.125	2.676	0.728
CLD-DeAl-HZ5	0.073	0.067	0.140	1.089	0.521

[a]Determined by IPA-TPD, [b]Determined by NH_3-TPD

As can be seen from table, the total acidity of all the modified HZSM-5 catalysts is less than that of parent HZSM-5. The CLD method provides similar amounts of Lewis acid sites to that of parent one while the Brønsted acid sites decrease from 0.095 mmol/g to 0.066 mmol/g with increasing TEOS loading. This is because the coverage of silica on ZSM-5 surface results in the elimination of the external Brønsted acid sites and silanol hydroxyls. Moreover, SiO_2 blocks the pore opening of zeolite which could be limits diffusion of products and reduces its acidic amount of zeolite but does not change its acidic strength (Zhu *et al.*, 2007).

The dealuminated catalysts have lower Brønsted acid sites but higher Lewis acid sites than the parent catalyst. The longer dealumination time resulted in lower Brønsted acid sites or higher Lewis acid sites. These results clearly confirmed that delaumination of HZSM-5 with oxalic acid is a preferred treatment for the removal framework Al species (FAl) as Brønsted acid sites, consequently, the increase in extra-framework Al species (EFAl) as Lewis acid sites. As a result the tendency of B/L ratio was decreased as an increase in dealumination time. The CLD-DeAl-HZ5 and DeAl-CLD-HZ5 have Brønsted acid sites and total acidity lower than the parent HZSM-5. For Lewis acid site, CLD-DeAl-HZ5 provides higher than the parent one because of generate extra-framework aluminum species.

4.2 Catalytic Activity Testing

In principle, the acid strength and acid type are the key properties of zeolite, which play a crucible role in the activity and selectivity of zeolite. Catalytic activity with methylation under various parameters including weight hourly space velocity (WHSV) of 24 and 40 h^{-1}, toluene-to-methanol (T/M) molar ratio of 4:1 and 8:1, and reaction temperature 400 °C were investigated for the selected catalysts.

The synthesized HZSM-5 catalyst with SiO_2/Al_2O_3 molar ratio of 214 was tested at reaction temperature 400 °C, WHSV 24 h^{-1}, and T/M molar ratio of 4:1. The results showed that p-xylene selectivity 71.67 %, m-xylene 13.02 %, o-xylene 4.73 % and toluene conversion 7.35 % and methanol conversion 93.92 % and the product distribution is shown in Table 4.4.

Table 4.4 Product distribution of parent HZSM-5 catalyst (Reaction conditions: 400 °C, T/M molar ratio of 4:1, WHSV 24 h^{-1}, and TOS 375 min)

Catalyst	Product Distribution (wt%)							
	p-xylene	m-xylene	o-xylene	BZ	TMBs[a]	EB	Ethyl methyl benzene	C9+
HZSM-5	71.67	13.02	4.73	0.07	3.77	0.20	3.22	2.45

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

4.2.1 Effect of Silylation

The parent HZSM-5 was modified via CLD using TEOS to deactivate the external acid sites. Figure 4.3 shows the catalytic activity at time on stream (TOS) of 375 min vs. TEOS amount used for the modification of HZSM-5 catalysts. The conversion of toluene for silylated HZSM-5 is almost linearly declined from ca. 10 to ca. 8 % with increasing TEOS amount from 0 to 2.0 ml/g cat. The decrease in conversion is probably caused by the hindrance of TEOS in the pores of silylated HZSM-5. The slightly increased selectivity to p-xylene with increasing TEOS contents from 0 to 1 ml/g cat can be observed. This was attributed to SiO_2 from TEOS deposited on the acidic sites of the external surface, which effectively

inhibited *p*-xylene from isomerization, thus, improving the selectivity. However, the pore opening was slightly reduced due to the deposition of TEOS near pore mouths. This severely restrained the diffusion and desorption of other aromatic hydrocarbon by-products formed in the pores and led to coke deposition and catalyst deactivation in a relatively short time on stream (Zhao *et al.*, 2010). Therefore, *p*-xylene selectivity reaches a maximum of ca. 75.62 % with TEOS amount used of 1 ml/g of catalyst. However, the excess of TEOS loading beyond 1.0 ml/g cat might be due to the formation of an uneven silica layer which blocks the pore opening, thus low shape-selectivity (Hui *et al.*, 2011). This effect can be obviously pronounced when considering a product distribution.
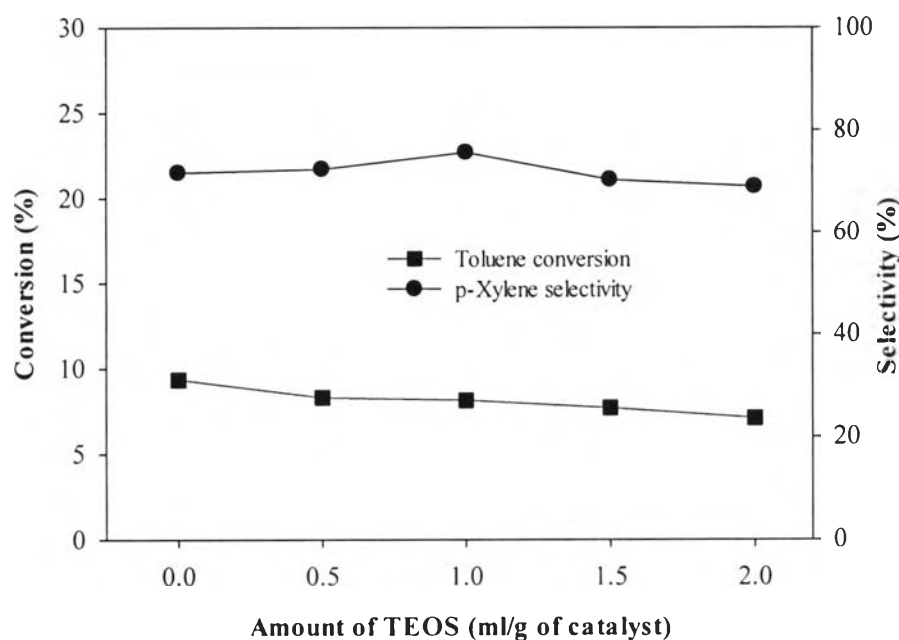

Figure 4.3 Effect of TEOS loading on catalytic activity of modified HZSM-5 catalysts (Reaction conditions: 400 °C, T/M malar ratio of 4:1, WHSV 24 h^{-1}, and TOS 375 min).

Comparison of product distributions for the catalysts obtained before and after CLD treatment is shown in Table 4.5. The *p*-xylene selectivity with TEOS

amount of 0 to 1 ml/g cat is increased from 71.76 to 75.62 %, but *m*-xylene and *o*-xylene are decreased from 13.02 to 8.79 % and from 4.73 to 3.99 %, respectively, due to the reduction of external acid sites. As TEOS amounts exceeding 1.0 ml/g cat, all xylene isomer selectivities are decreased. In addition, benzene (BZ) and ethyl benzene (EB) are substantially increased since the blockage of pore opening would restrain xylenes to diffuse out yet allow for the secondary reactions to take place in the pores.

Table 4.5 Effect of CLD treatment on the product distribution (Reaction conditions: 400 °C, T/M molar ratio of 4:1, WHSV 24 h^{-1}, and TOS 375 min)

Catalyst	Product Distribution (wt%)							
	p-xylene	*m*-xylene	*o*-xylene	BZ	TMBs[a]	EB	Ethyl methyl benzene	C9[+]
HZSM-5	71.67	13.02	4.73	0.07	3.77	0.20	3.22	2.45
CLD(0.5)-HZ5	72.37	11.74	4.02	0.08	3.59	0.20	3.08	2.43
CLD(1.0)-HZ5	75.62	8.79	3.99	1.08	3.69	0.21	3.41	2.44
CLD(1.5)-HZ5	70.28	8.68	3.06	5.02	2.08	5.07	3.04	2.50
CLD(2.0)-HZ5	68.93	6.54	2.63	7.90	2.78	6.35	2.78	1.50

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

4.2.2 Effect of Dealumination

Since the size of oxalic acid (0.29x0.54 nm) makes its diffusion into large zeolite pores possible, it can therefore effectively remove aluminum species from the lattice by forming a complex of an aluminum ion surrounded by one oxalate ion and water ligands (Srivastava *et al.*, 2009). Figure 4.4 depicts catalytic activity of the HZSM-5 catalysts modified by dealumination with oxalic acid with the T/M molar ratio 4:1, and WHSV 24 h^{-1} at 400 °C. As can be seen, the toluene conversion for 6 h dealuminated catalyst (DeAl(6)-HZ5) is wavery between 6 and 12 % whereas that of the 8 h one (DeAl(8)-HZ5) is almost unchanged at ca. 8 %. However, a slight increase in toluene was attained for DeAl(6)-HZ5. This might be attributed to a shift from Brønsted acid sites to Lewis acid sites responsible for another reaction of

toluene rather than methylation. In addition, the p-xylene selectivity of DeAl(6)-HZ5 (70.96 %) yields higher than the DeAl(8)-HZ5 (66.31 %). As 8 h, the removal of framework Al species (FAl) was higher than 6 h, consequently results in higher amount of extra-framework Al species (EFAl) acting as Lewis acid sites as shown in Table 4.3. The longer the contact time between HZSM-5 and oxalic acid, the higher Al^{3+} ions would be leached out of the pore channels thus increasing the Si/Al ratio. It was also reported that Al^{3+} ions interact with Brønsted acid sites resulting in an enhanced acidity (Silaghi, 2014).

Product distribution is displayed in Table 4.6. The p-xylene selectivity is decreased, while other products are increased within 8 h of dealumination. At 8 h, the removal of framework Al species (FAl) was higher than 6 h, results in an increasing formation mesopores (Table 4.2). Therefore, m-, and o-xylene can diffuse out of the pore more than p-xylene, thus low p-xylene selectivity.

Table 4.6 Effect of dealumination treatment on the product distribution (Reaction conditions: 400 °C, T/M molar ratio of 4:1, WHSV 24 h^{-1}, and TOS 375 min)

Catalyst	Product Distribution (wt%)							
	p-xylene	m-xylene	o-xylene	BZ	TMBs[a]	EB	Ethyl methyl benzene	$C9^+$
HZSM-5	71.67	13.02	4.73	0.07	3.77	0.20	3.22	2.45
DeAl(6)-HZ5	70.96	12.28	4.35	2.10	2.53	0.22	3.74	3.05
DeAl(8)-HZ5	66.31	16.08	5.58	1.21	2.67	0.27	3.81	3.13

[a]TMBs = 1,2,3 Trimethylbenzene and 1,2,4 Trimethylbenzene.
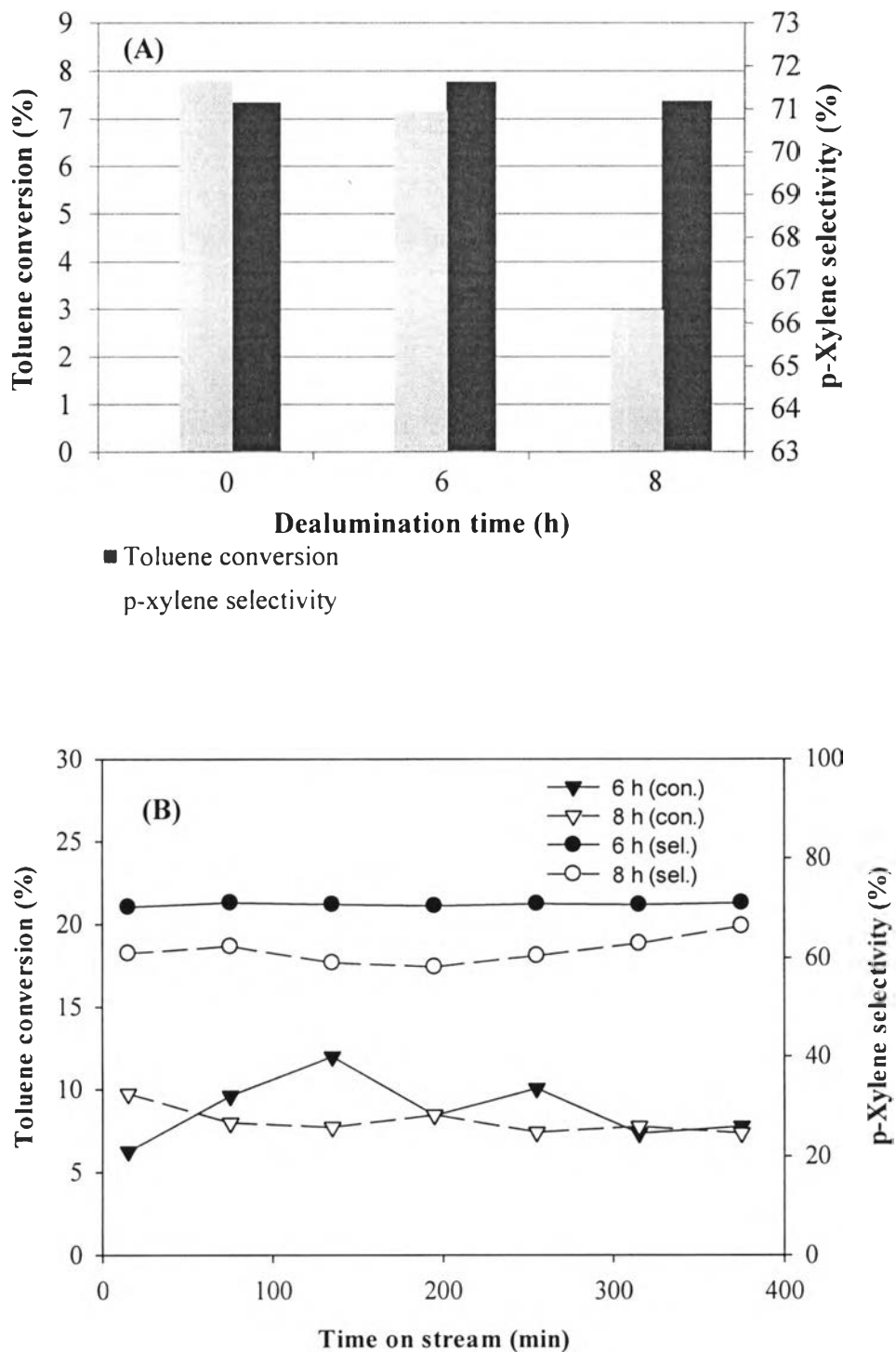
Figure 4.4 Effect of dealumination treatment on catalytic activity of the modified HZSM-5 catalysts (A) dealumination time and (B) time dependence (Reaction conditions: 400 °C, T/M malar ratio 4:1, WHSV 24 h⁻¹).

4.2.3 Effect of Combination of Silylation and Dealumination

Figure 4.5 illustrates the effects of modified by combination of CLD and DeAl with the T/M feed ratio 4:1, and WHSV 24 h^{-1} at temperature 400 °C. The modification sequence of SiO_2 deposition and dealumination has a significant influence on the p-xylene selectivity of catalysts. The catalyst subjected to the silylation-dealumination sequence (DeAl-CLD-HZ5) exhibited remarkably increased p-xylene selectivity as compared to the one subjected to the dealumination-silylation sequence (CLD-DeAl-HZ5). Since the deposition of SiO_2 attained from TEOS on the acidic sites of external surface as well as the narrowed pore mounts of channels could diminish the accessibility of oxalic acid towards the FAl located in both the inside and outside channels, hence, the availability of Bronsted acid sites was remained appreciable. On the other hand, CLD-DeAl-HZ5 showed lesser selectivity because the framework Al species (FAl) had more contact with oxalic acid, resulting in decrease of active sites as a consequence of the formation of more extra-framework species (EFAl) content. These results were supported by the increase of Lewis acid site in Table 4.3.

It could be speculate that the different modification sequences have different effects on narrowing the pore openings, which induces different diffusion resistance for o-xylene and m-xylene isomers, and hence exhibits different p-selectivity (Tan *et al.*, 2014).

Interestingly, the results scrutinization revealed that the DeAl-CLD-HZ5 catalyst can maintain its toluene conversion whereas the CLD-DeAl-HZ5 catalyst shows its slight decline in the course of reaction.
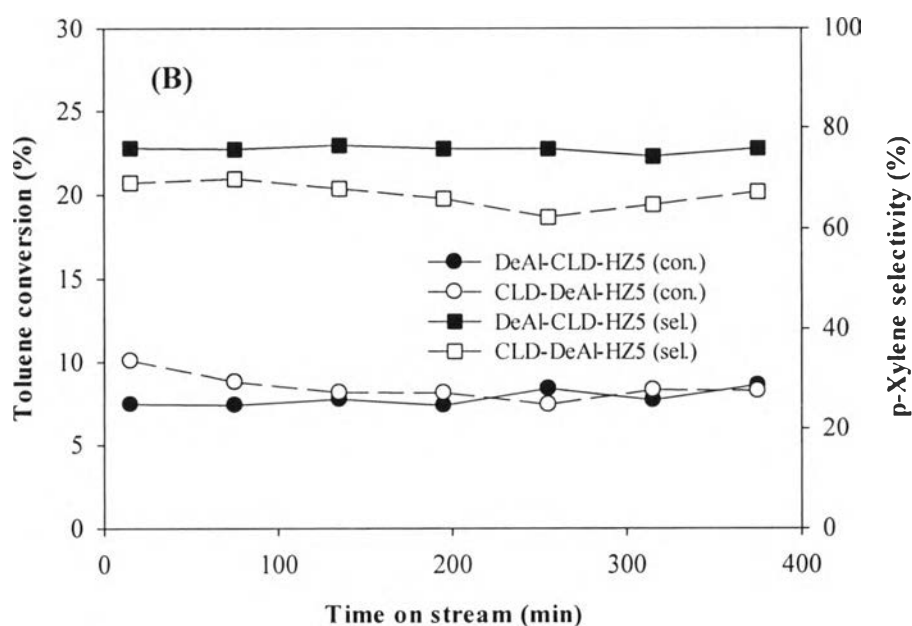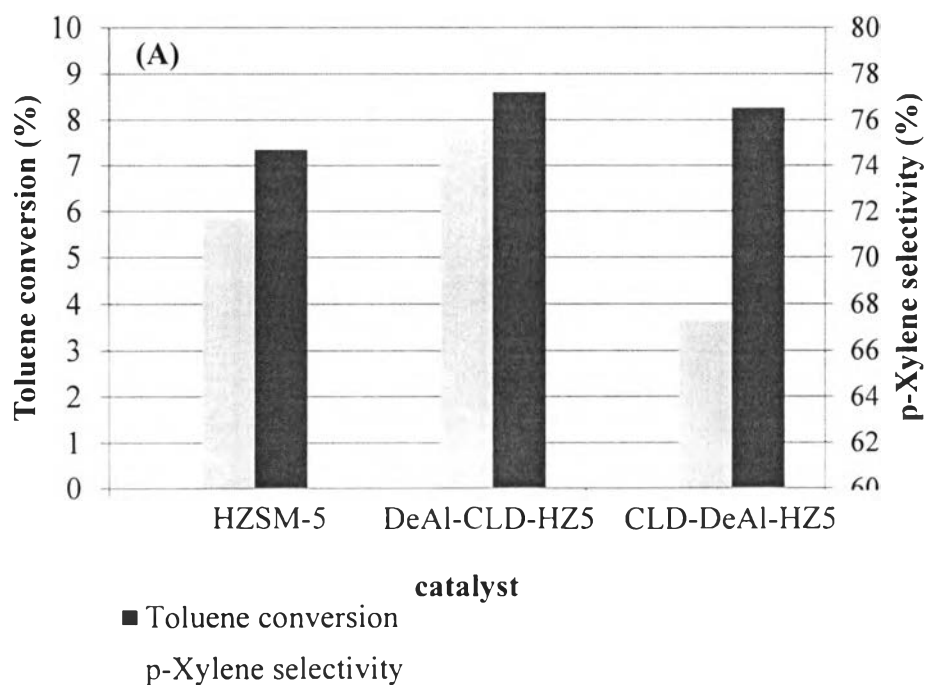
Figure 4.5 Effect of the combination of CLD and DeAl treatment on catalytic activity of the modified catalysts (A) modification sequence and (B) time dependence (Reaction conditions: 400 °C, T:M molar ratio 4:1, WHSV 24 h^{-1}).

Table 4.7 Effect of combined CLD and DeAl treatment on the product distribution over DeAl-CLD-HZ5 and CLD-DeAl-HZ5 catalysts (Reaction conditions: 400 °C, WHSV 24 h⁻¹, T/M molar ratio 4:1, and TOS 375 min)

Catalyst	Product Distribution (wt%)							
	p-xylene	*m*-xylene	*o*-xylene	BZ	TMBs[a]	EB	Ethyl methyl benzene	C9⁺
HZSM-5	71.67	13.02	4.73	0.07	3.77	0.20	3.22	2.45
DeAl-CLD-HZ5	75.72	12.59	3.93	2.10	1.64	0.22	2.50	0.89
CLD-DeAl-HZ5	67.29	14.09	4.45	0.25	3.54	0.30	8.19	1.07

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

Table 4.7 shows the effect of different modification sequences on the liquid product distribution. The *p*-xylene selectivity of DeAl-CLD-HZ5 (75.72%) is higher than CLD-DeAl-HZ5 (67.29%), while the *m*-, *o*-xylene and other products are lower than CLD-DeAl-HZ5. This is possibly SiO_2 reduces the pore mount of DeAl-CLD-HZ5 zeolite results in suitable for diffusion of *p*-xylene. However, CLD-DeAl-HZ5 occurs the mesopores leading to the bulkier products can easily diffuse out from the pore opening.

The DeAl-CLD-HZ5 catalyst was chosen for further studies to improve its *p*-xylene selectivity by altering reaction conditions, i.e., WHSV and feed molar ratio.

4.2.4 Effect of Weight Hourly Space Velocity (WHSV)

To investigate the optimum WHSV of the reaction. Figure 4.6 presents the results of toluene conversion and *p*-xylene selectivity profiles by variation of WHSV over DeAl-CLD-HZ5 at 400 °C with the T/M molar ratio 4:1. It can be observed that toluene conversion is decreased with increasing WHSV from 24 to 40 h⁻¹. It is possibly because a contact time between the active sites of the catalyst surface and feed reactants decrease result in less opportunity of the reactants to be consumed for the reaction. *p*-Xylene selectivity is increased with an increase in

WHSV from 24 to 40 h^{-1}. Because the reduction of contact time would be beneficial for the isomerization reaction since the chances which a desired product would transform to any products could be minimized.
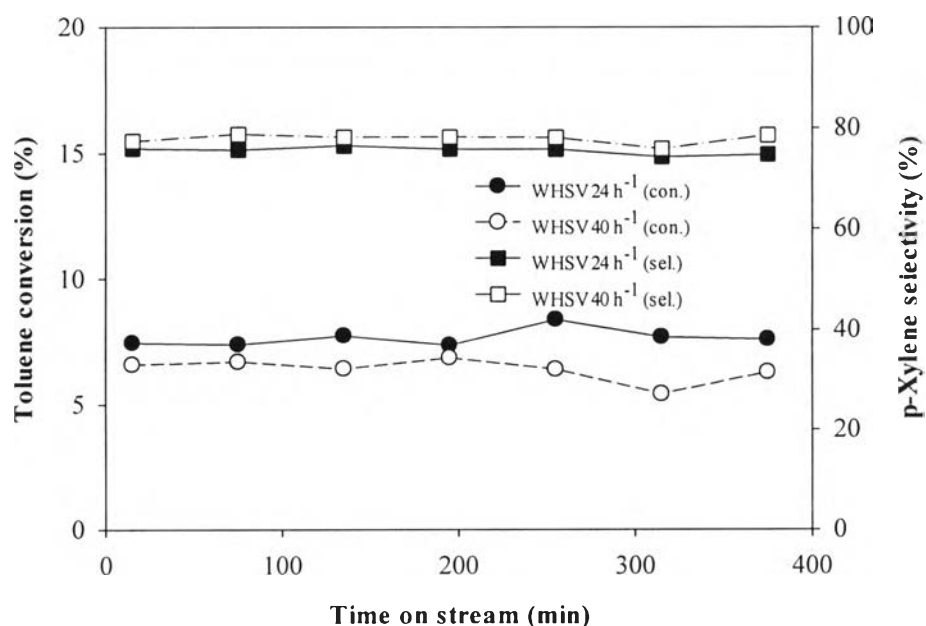

Figure 4.6 Effect of different WHSV over DeAl-CLD-HZ5 catalyst (Reaction conditions: 400 °C, T:M molar ratio 4:1).

Table 4.8 Effect of WHSV on the product distribution over DeAl-CLD-HZ5 catalyst (Reaction conditions: 400 °C, T/M molar ratio 4:1, and TOS 375 min)

WHSV (h^{-1})	Product Distribution (wt%)							
	p-xylene	m-xylene	o-xylene	BZ	TMBs[a]	EB	Ethyl methyl benzene	C9$^+$
24	75.72	12.59	3.93	2.10	1.64	0.22	2.50	0.89
40	78.60	10.20	2.50	2.31	1.21	0.33	2.20	1.69

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

Table 4.8 shows the liquid product distribution over DeAl-CLD-HZ5 catalyst by variation of WHSV. p-Xylene selectivity was increased with an increase in WHSV from 24 to 40 h^{-1}. At WHSV of 24 h^{-1}, long contact time, allow secondary reaction such as isomerization of the p-xylene to m- and o-xylene formation. On the contrary, at WHSV of 40 h^{-1}, a short contact time, m-, and o-xylene were decreased. In the experiment range, the maximum p-xylene selectivity reached 78.60% at WHSV of 40 h^{-1}. In order to acquire the highest selectivity of p-xylene selectivity of p-xylene, the WHSV of 40 h^{-1} was selected for further studies.

4.2.5 Effect of Toluene to Methanol (T/M) Molar Ratio

Figure 4.7 shows the p-xylene selectivity and toluene conversion profiles by variation of T/M molar ratio over DeAl-CLD-HZ5 at 400 °C, and WHSV 40 h^{-1}. As anticipated, toluene conversion is declined as an increase in T/M molar ratios. However, the p-xylene selectivity is insignificantly increased with respect to T/M molar ratios. This is because insufficient methanol to react with toluene and alkylation reaction typically requires for operating at toluene-to-methanol molar ratios greater than unity, and at a high degree of dilution under atmospheric pressure to improve methanol utilization (Kulprathipanja, 2010).

It was reported that nano-sized ZSM-5 catalysts were modified by SiO_2, P_2O_5 and MgO which operated at the reaction condition of toluene to methanol ratios of 8:1, at a reaction temperature of 460 °C showing excellent stability as well as p-xylene selectivity of 98% (Tan $et\ al.$, 2014).

Table 4.9 shows product distribution over DeAl-CLD-HZ5 variation T/M molar ratios. According to the product distribution, p-xylene selectivity is increased and slight larger amounts of m- and o-xylenes are also produced as T/M ratio increases from 4:1 to 8:1.
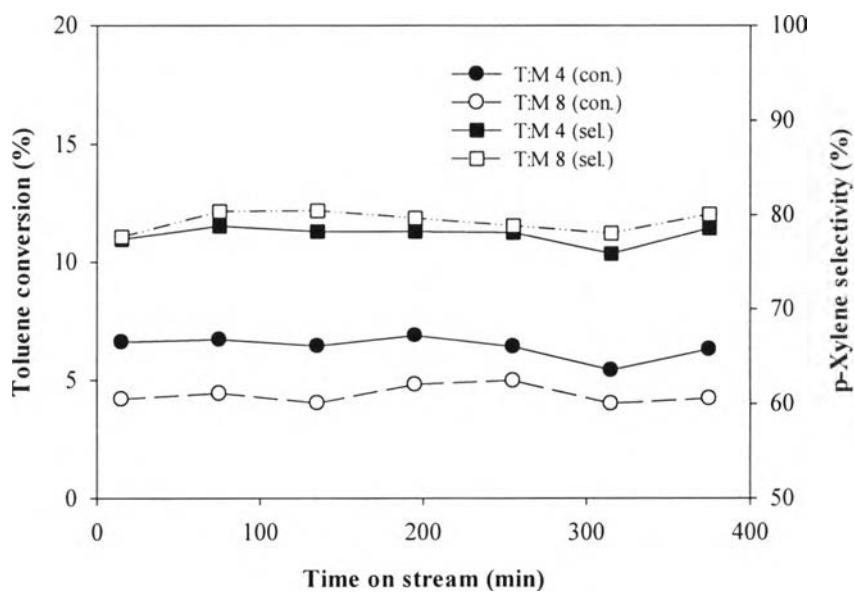
Figure 4.7 Effect of T/M molar ratio over DeAl-CLD-HZ5 catalyst (Reaction conditions: 400 °C, WHSV 40 h⁻¹).

Table 4.9 Effect of T/M feed molar ratio on the products selectivity over DeAl-CLD-HZ5 catalyst (Reaction conditions: 400 °C, WHSV 40 h⁻¹, and TOS 375 min)

T:M	Product Distribution (wt%)							
	p-xylene	m-xylene	o-xylene	BZ	TMBs[a]	EB	Ethyl methyl benzene	C9⁺
4:1	78.60	10.20	2.50	2.31	1.21	0.33	2.20	1.69
8:1	80.39	12.20	3.09	2.60	0.21	0.25	0.20	0.89

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

4.2.6 Consideration of Textural and Activity Characteristics Related to
       Catalytic Activity

The Brønsted to Lewis acid site ratio (B/L) are plotted in relation to
p-xylene selectivity and toluene conversion as illustrated in Figures 4.8 and 4.9,
respectively. These figures show that the p-xylene selectivity and toluene conversion
slightly increased as the B/L ratio increased. At the first region, B/L ratio was very
low because dealumination method can removes framework aluminum (FAl) and
forming extra-framework (EFAl) resulting in high the Lewis acid sites. Brønsted
acidity can affect the p-xylene selectivity and toluene conversion. After modification,
HZSM-5 can reduce Brønsted acid sites. Thus, toluene and methanol cannot be
converted to p-xylene and other products. Because toluene and methanol occur
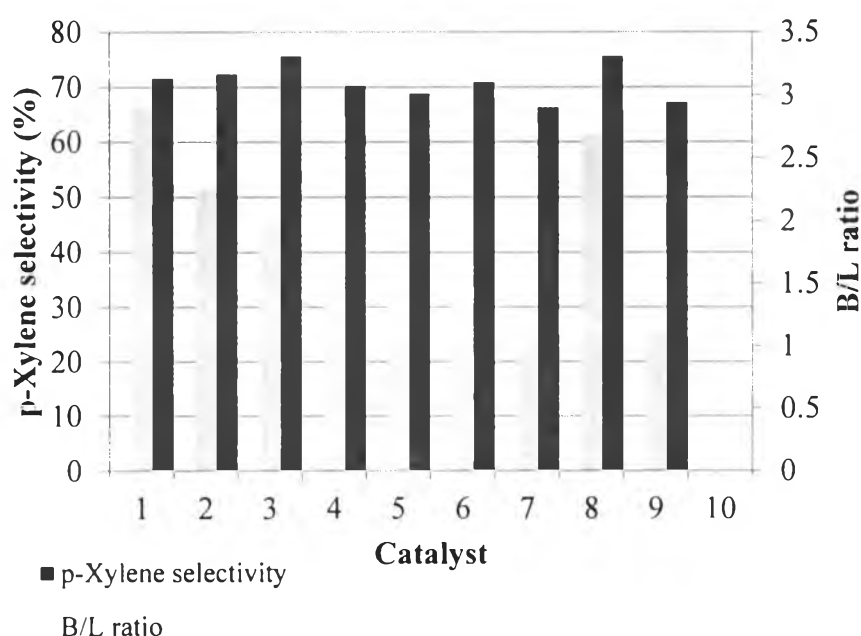reaction via Brønsted acid sites.

Figure 4.8 p-Xylene selectivity as a function of B/L ratio over (1) HZSM-5, (2)
CLD(0.5)-HZ5, (3) CLD(1.0)-HZ5, (4) CLD(1.5)-HZ5, (5) CLD(2.0)-HZ5, (6)
DeAl(6)-HZ5, (7) DeAl(8)-HZ5, (8) DeAl-CLD-HZ5, and (9) CLD-DeAl-HZ5
(Reaction conditions: 400 °C, T/M malar ratio of 4:1, WHSV 24 h^{-1}, and TOS 375
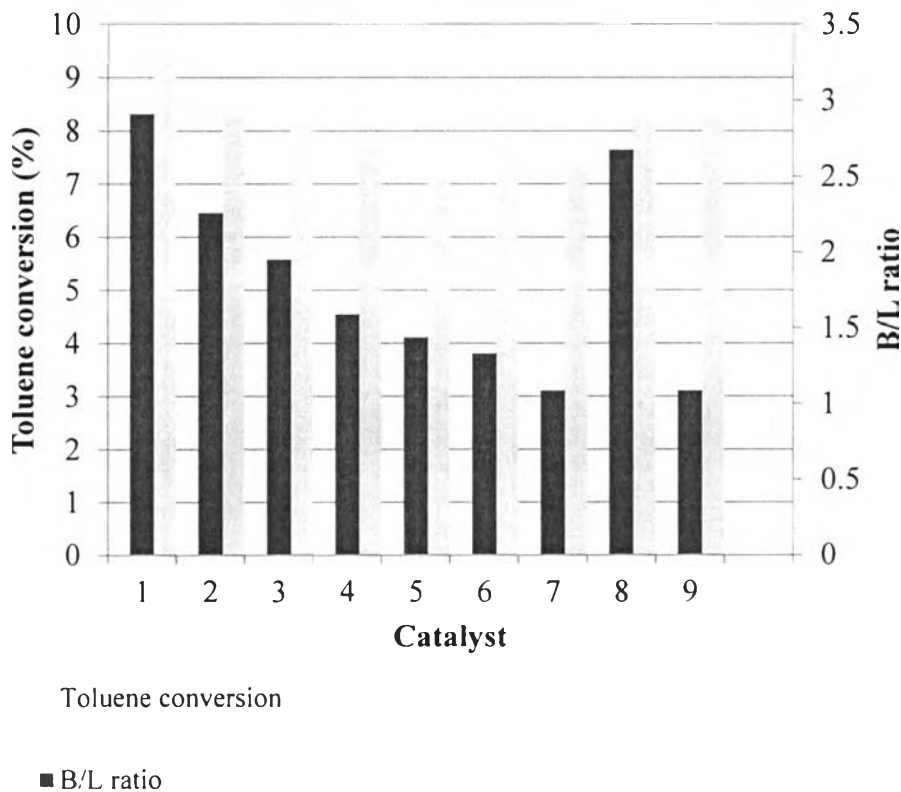min).

Toluene conversion

■ B/L ratio

Figure 4.9 Toluene conversion as a function of B/L ratio over(1) HZSM-5, (2) CLD(0.5)-HZ5, (3) CLD(1.0)-HZ5, (4) CLD(1.5)-HZ5, (5) CLD(2.0)-HZ5, (6) DeAl(6)-HZ5, (7) DeAl(8)-HZ5, (8) DeAl-CLD-HZ5, and (9) CLD-DeAl-HZ5 (Reaction conditions: 400 °C, T/M malar ratio of 4:1, WHSV 24 h^{-1}, and TOS 375 min).

The Brønsted acid site to total acidity (B/Ta) ratio and micropore volume to total pore volume (M/T) ratio are plotted in relation to p-xylene selectivity as illustrated in Figures 4.10. *p*-Xylene selectivity decreases with increasing B/Ta ratio. The *p*-xylene selectivity increases with increasing of M/T ratio. The *p*-xylene selectivity shows the highest at T/M about 0.4, then increasing M/T ratio more than 0.4 results in significantly decline of *p*-xylene selectivity. The increasing of B/Ta ratio was affected by creation of mesopore volume which allow the bulky molecules can easily diffuse out of the pore. Therefore, the *p*-xylene selectivity is low.
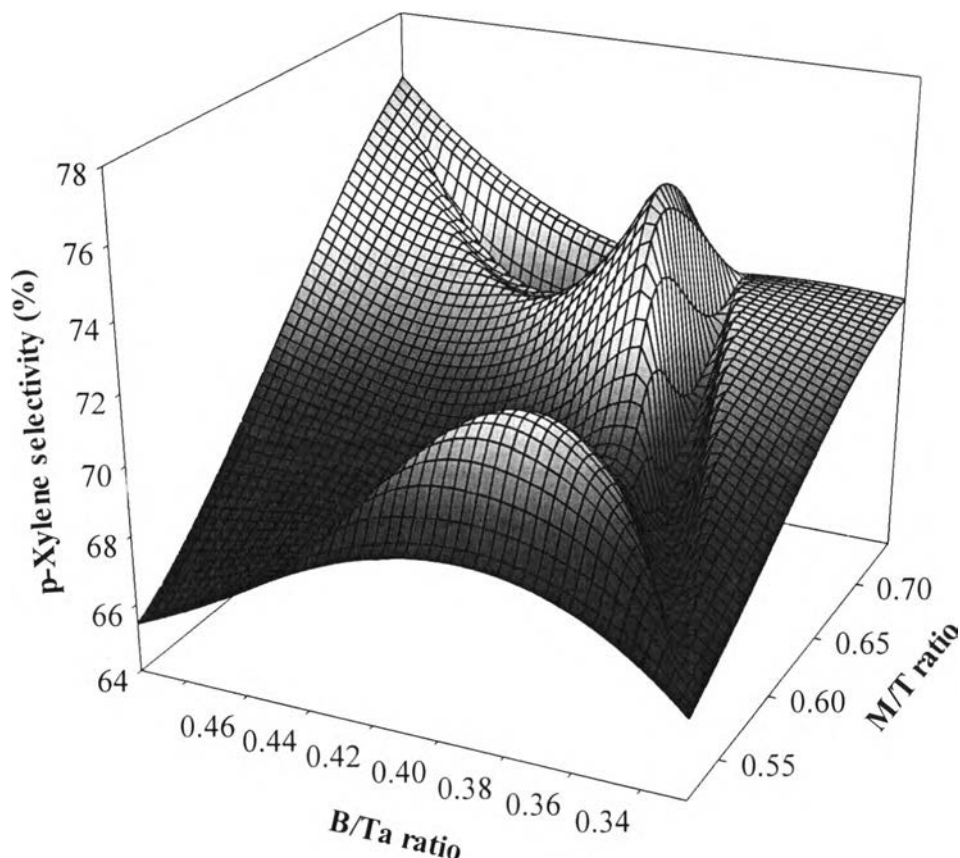
Figure 4.10 The plots of *p*-xylene selectivity vs. Brønsted acid site to total acidity (B/Ta) ratio and micropore volume to total pore volume (M/T) ratio (Reaction conditions: 400 °C, T/M molar ratio 4:1, WHSV 24 h^{-1}).

4.2.7 Characterization of Carbon Deposition

The spent catalysts were analyzed by TPO technique to observe the coke formation as shown in Figure 4.11 and Table 4.10. TPO profiles of catalysts show two peaks at 290 and 500 °C. These results indicate that the peak at 290 °C could correspond to soft coke and the peak at 500 °C could be associated to hard coke. Therefore, HZSM-5 preferred formation of soft coke higher than hard coke. The amount of carbon deposition on spent the parent and modified HZSM-5 catalysts at temperature 400 °C, T/M molar ratio 4:1, and WHSV 24 h^{-1}. The parent HZSM-5

catalyst is the highest coke formation due to coke is preferentially formed on strong acid sites (Table 4.3). The amounts of deposited coke on CLD treated HZSM-5 is lower than the parent one. This is because a decreased in external acid sites and SiO_2 pore blockage after the CLD treatment, which low the probability of the coke formation from the decomposition of hydrocarbon species. For modified varying time of dealumination. As can be seen, DeAl(8)-HZ5 shows coke formation lower than DeAl(6)-HZ5 due to a decrease in framework aluminium species (FAl) as well as in number of strong acid sites. DeAl-CLD-HZ5 catalyst provides the coke deposition lower than CLD-DeAl-HZ5. This is because DeAl-CLD-HZ5 passivation acid sites on the external surface where decompose the carbon more than CLD-DeAl-HZ5. From all the catalysts studied, The DeAl-CLD-HZ5 was observed to be most suitable in terms of selectivity to p-xylene as well as low coke formation.
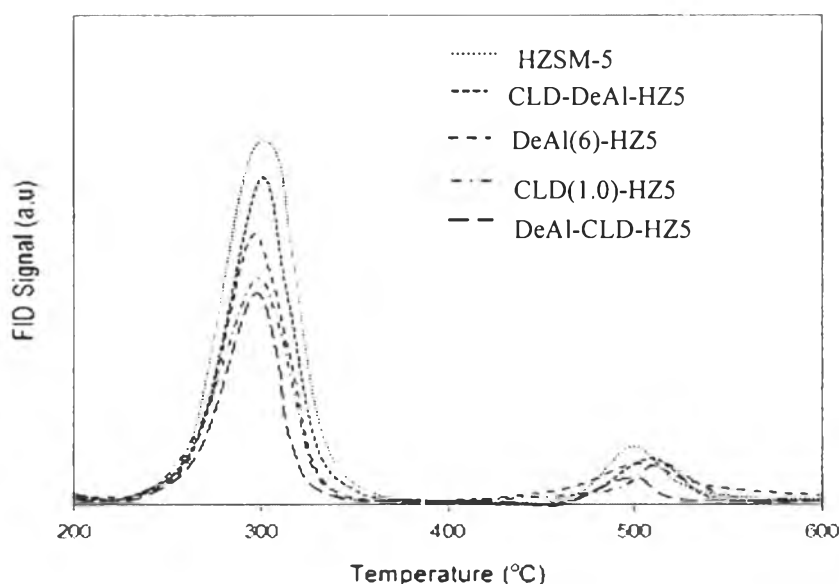
Figure 4.11 TPO profiles of the HZSM-5 catalysts after reaction at 400 °C.

Table 4.10 Carbon formation on the spent the parent and modified HZSM-5 catalysts

Catalyst	Amount of Carbon Deposition (wt %)
HZSM-5	4.32
CLD(0.5)-HZ5	3.95
CLD(1.0)-HZ5	3.46
CLD(1.5)-HZ5	3.42
CLD(2.0)-HZ5	3.28
DeAl(6)-HZ5	3.88
DeAl(8)-HZ5	3.01
DeAl-CLD-HZ5	2.65
CLD-DeAl-HZ5	3.97