

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

In this study, the as-received HZSM-5 catalysts with SiO₂/Al₂O₃ ratios of 23, 45 and 195 were designated as HZSM-5 (A), HZSM-5 (B), and HZSM-5 (C), respectively.

4.1.1 Catalyst composition

The chemical compositions of commercial HZSM-5 catalysts were analyzed by X-ray fluorescence (XRF) technique. The results are summarized in Tables 4.1. From this data, the Si/Al molar ratio was determined. It can be seen that the SiO₂/Al₂O₃ ratio calculated from XRF is higher than the value provided by suppliers. The HZSM-5 (A) and HZSM-5 (C) have high Al₂O₃ content because these catalysts contain the binder, Al₂O₃. HZSM-5 (A), HZSM-5 (B), and HZSM-5 (C) have Si/Al molar ratios of 77, 112, and 109, respectively. The Si/Al ratio decreases in the following order: HZSM-5 (B) > HZSM-5 (C) > HZSM-5 (A). From the results, the theoretical acidity of catalysts determined based on the number of protons was attained according to its formula.

Table 4.1 The chemical compositions of commercial HZSM-5 catalysts

Catalyst	Compound (wt%)					SiO ₂ / Al ₂ O ₃	Si/Al ^a	Theoretical acidity (mmol/g) ^b
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO			
HZSM-5 (A)	78.718	21.059	0.101	0.122	0.01	126	77	0.214
HZSM-5 (B)	98.937	0.93	0.0463	0.043	0.044	180	112	0.147
HZSM-5 (C)	77.189	22.559	0.102	0.057	0.093	198	109	0.151

^achemical formula is H_nAl_nSi_{96-n}O₁₉₂

^bcalculated values according to the information from International Zeolite Association (www.iza-online.org)

4.1.2 X-ray diffraction

Figure 4.1 presents the XRD patterns of the commercial HZSM-5 zeolites. It shows that the characteristic diffraction peaks corresponding to the patterns of ZSM-5 zeolite and do not contain any impurity phase. The high intensity peaks indicate that the catalysts have high crystallinity. The peak intensity in the low diffractive angle ($2\theta = 7-10^\circ$) increases with increasing Si/Al ratio. The higher crystallinity of the catalyst was obtained at high Si/Al due to the reduction of Al (Kumar *et al.*, 2000).

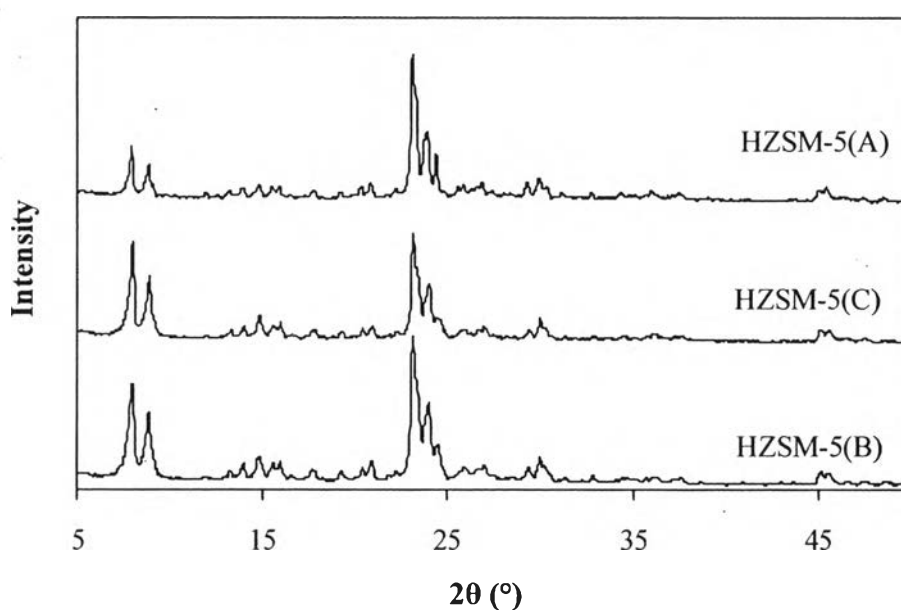


Figure 4.1 X-ray diffraction patterns of the investigated HZSM-5 catalysts.

4.1.3 Temperature programmed desorption of ammonia (NH₃-TPD)

Figure 4.2 shows the NH₃-TPD curves of the HZSM-5 catalysts with different Si/Al ratios. The low and high temperature peaks corresponding to ammonia desorption from weak acid sites and strong acid sites, respectively, can be observed for all the catalysts. The number of weak acid sites is higher than the number of strong acid sites for all the catalysts. It can be seen that the number of acid sites decreases as the Si/Al ratio increases. The low temperature peak ca. 125°C was shifted to a lower temperature ca. 115°C when the Si/Al is increased resulting in the decline in strength of weak acid sites. On the other hand, the strength of strong acid

sites is decreased as the Si/Al ratio is decreased. It is interesting to note that a moderate temperature peak between the low and high temperature peaks is observed for which those of HZSM-5 (A), HZSM-5 (B), and HZSM-5 (C) are ca. 230°C, 430°C and 305°C, respectively.

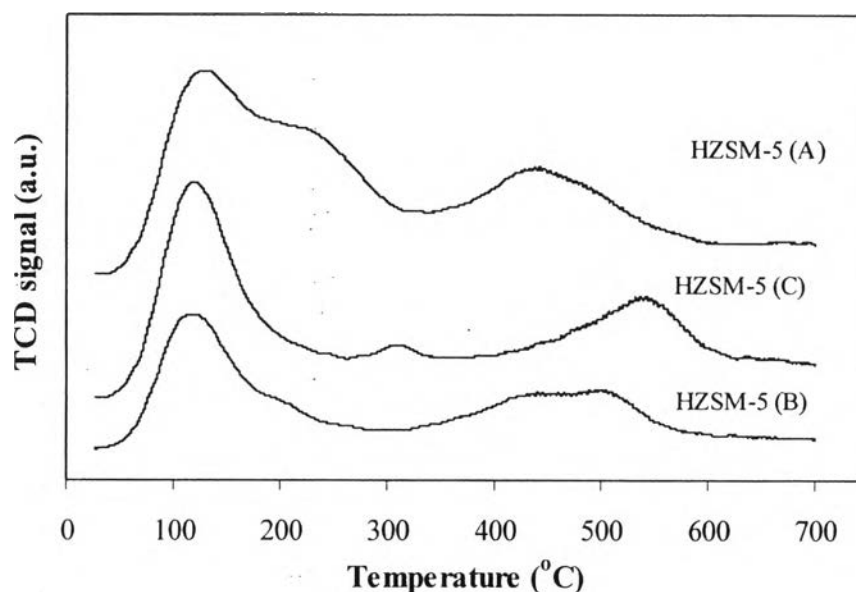


Figure 4.2 NH₃-TPD pattern of the investigated HZSM-5 catalysts.

4.1.4 Surface area measurements

The surface characteristics of the HZSM-5 catalysts determined by N₂ adsorption-desorption method are shown in Table 4.2. As for HZSM-5 with different Si/Al ratios, the BET surface area and total pore volume seem to be increased with increasing Si/Al ratio. According to Kumar *et al.* (2000), the increase in mesopore area and volume could be resulted from the reduction of framework Al atoms that cause the creation of mesopores. There was no change in pore diameter of the catalysts with different Si/Al ratios.

Table 4.2 Surface characteristics of the investigated HZSM-5 catalysts

Catalyst	BET surface area (m ² /g)	Micropore area ^a (m ² /g)	Total pore volume ^b (cm ³ /g)	Micropore volume ^a (cm ³ /g)	Pore diameter ^c (Å)
HZSM-5 (A)	310	176	0.307	0.093	3.67
HZSM-5 (B)	368	174	0.606	0.092	3.67
HZSM-5 (C)	300	122	0.528	0.063	3.67

^a Determined by t-method

^b Determined at P/P₀ = 0.99

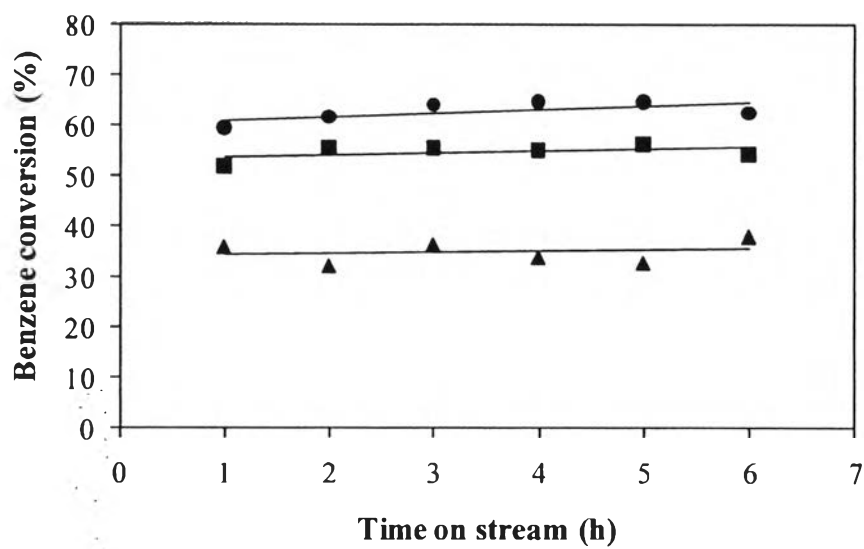
^c Determined by HK method

4.2 Catalytic Activity Testing

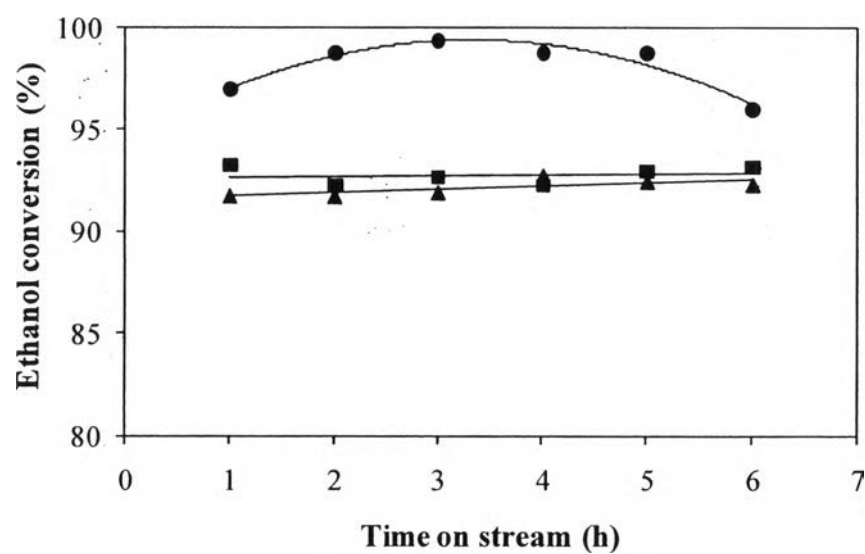
The catalytic activity of the catalysts was tested in a fixed-bed continuous down-flow reactor. The various parameters including SiO₂/Al₂O₃ ratio (23 to 195), reaction temperature (300 °C to 500 °C), weight hourly space velocity (5 h⁻¹ to 20 h⁻¹), and benzene-to-ethanol ratio (1 to 4) were investigated.

4.2.1 The effect of SiO₂/Al₂O₃ ratio

Figure 4.3 shows the effect of different SiO₂/Al₂O₃ ratios on the alkylation of benzene with ethanol for commercial HZSM-5 catalysts. The HZSM-5 (A) catalyst showed the highest benzene and ethanol conversions. According to their acid properties as shown in Table 4.1 and Figure 4.2, HZSM-5 (A) possesses the lowest Si/Al ratio and the highest acidity. It shows that the acidity of the catalyst plays an important role in the alkylation of benzene with ethanol. The conversion of benzene was high with the high catalyst acidity because strong acid sites were required for the activation of carbocations (Li *et al.*, 2009).



(a)



(b)

Figure 4.3 Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio: (●) HZSM-5 (A), (■) HZSM-5 (B) and (▲) HZSM-5 (C) on (a) benzene conversion, and (b) ethanol conversion at temperature 300°C , $B/E = 1$, $\text{WHSV} = 8 \text{ h}^{-1}$.

Since the conversion of ethanol for a given catalyst was higher than benzene conversion, therefore, the reaction of ethanol transformation into other hydrocarbons would occur simultaneously over this catalyst. According to the work by Moser *et al.* (1989), it was indicated that a low Si/Al catalyst transformed ethanol mainly on strong acidic sites based on AlOH groups.

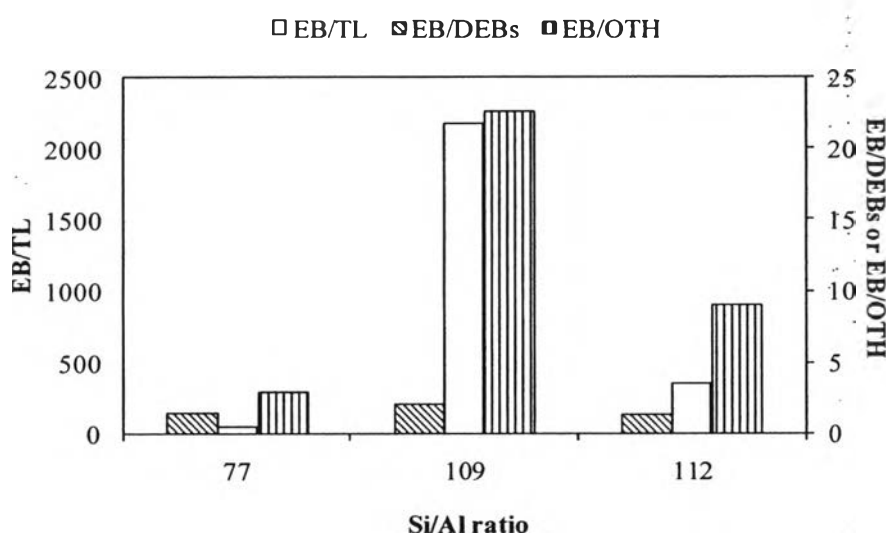
Table 4.3 shows the products selectivity of HZSM-5 catalysts with different Si/Al ratios. The liquid products excluding small amount of H₂O identified by GC-MS were ethylbenzene (EB), toluene, para-diethylbenzene (p-DEB), ortho-diethylbenzene (o-DEB), meta-diethylbenzene (m-DEB), and other substituted benzenes such as xylenes, ethyl toluene, propyl benzene, indane, and naphthalene. As shown in Table 4.3, EB was obtained with relatively high selectivity for all the catalysts due to its free diffusion without steric hindrance through the pores of HZSM-5. The selectivity to EB increases with increasing SiO₂/Al₂O₃ ratio. Figure 4.4 shows the ratio of products selectivity with different Si/Al ratios at 6 h on stream. It is observed from Table 4.3 that HZSM-5 (C) provides the high selectivity to EB and the low selectivity to other products. It can indicate that the secondary alkylation of EB with ethanol to produce other products would require the strong acid sites. Side reactions, further alkylation of EB and EB cracking, could be detrimental by the weak acidity of the catalyst. Among the products of DEB isomers, p-DEB shows the highest selectivity. The low selectivity to o-DEB might be due to the steric hindrance to diffusion (Li *et al.*, 2009). Park *et al.* (2003) reported that the para-isomer of DEB was formed as the primary product and this was subsequently isomerized into ortho- and meta-isomers on the surface acid sites of the catalyst. Toluene was obtained by the EB cracking. The selectivity to toluene decreases with increasing Si/Al ratio due to suppression of the EB cracking reaction.

Table 4.3 Effect of Si/Al ratio of HZSM-5 on the products selectivity ^a.

Catalyst	Si/Al ratio	Conversion (%)		Selectivity (%)					
		Benzene	Ethanol	EB	Toluene	p-DEB	m-DEB	o-DEB	Others ^b
HZSM-5 (A)	77	62.40	95.95	47.75	1.10	21.02	12.50	1.05	16.58
HZSM-5 (B)	112	54.22	93.15	53.69	0.15	25.15	14.39	0.67	5.96
HZSM-5 (C)	109	38.21	92.26	65.25	0.03	22.85	8.86	0.11	2.89

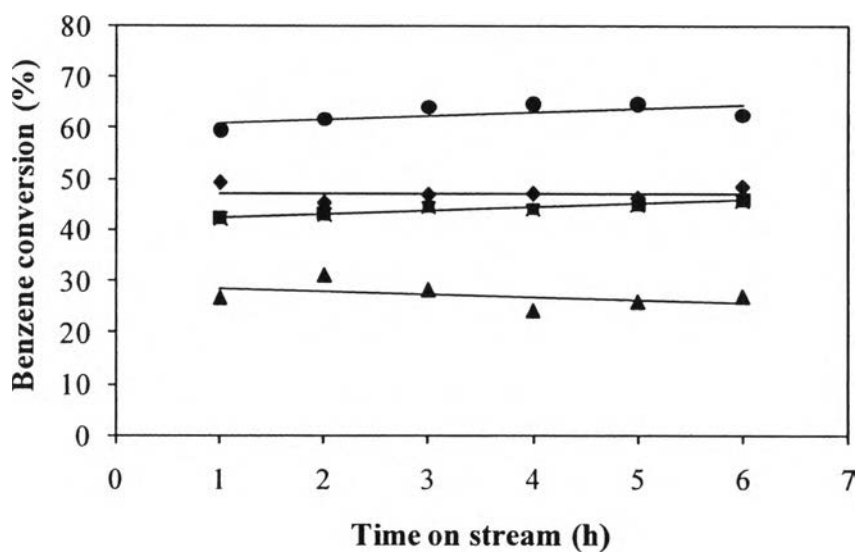
^a Reaction conditions: T = 300 °C, B/E = 1, WHSV = 8 h⁻¹, time on stream = 6 h.

^b For example, xylenes, ethyl toluene, propyl benzene, indane, and naphthalene.

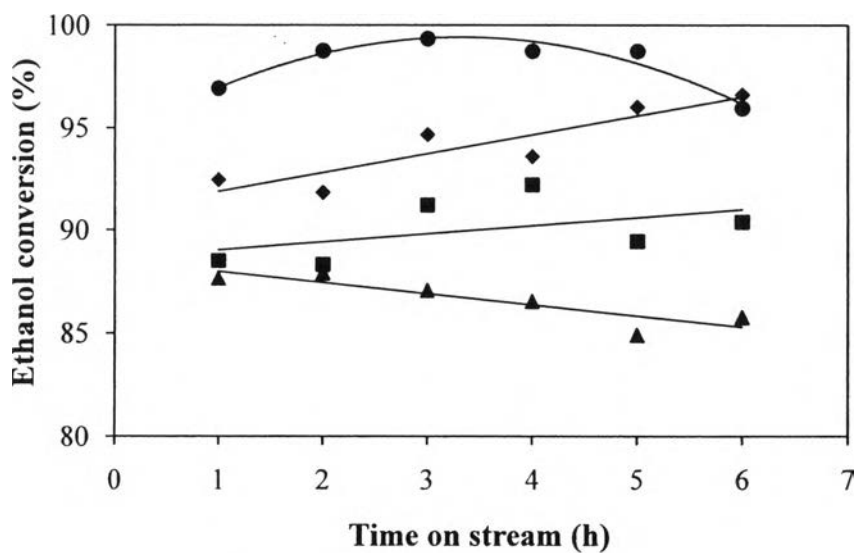
**Figure 4.4** Effect of Si/Al ratio on the products selectivity ratio at T = 300°C, B/E = 1, WHSV = 8 h⁻¹ and time on stream = 6 h.

4.2.2 The effect of temperature

The alkylation of benzene with ethanol was carried out at 300, 350, 400 and 500 °C over HZSM-5 (A) at WHSV of 8 h⁻¹ and B/E ratio of 1. The effect of temperature on the conversion of benzene is shown in Figure 4.5. It shows that the conversion of benzene decreases as the temperature increases. The benzene conversion was increased as a decrease in temperature due to its exothermic reaction. However, as the temperature is increased, the conversion of ethanol is slightly decreased.



(a)



(b)

Figure 4.5 Effect of temperature: (●) 300°C, (◆) 350°C, (■) 400°C and (▲) 500°C on (a) benzene conversion, and (b) ethanol conversion for HZSM-5 (A), B/E = 1, WHSV = 8 h⁻¹.

Table 4.4 Effect of temperature on the products selectivity over HZSM-5 (A)^a

Temperature (°C)	Conversion (%)		Selectivity (%)					
	Benzene	Ethanol	EB	Toluene	p-DEB	m-DEB	o-DEB	Others ^b
300	62.40	95.95	47.75	1.10	21.02	12.50	1.05	16.58
350	48.32	96.62	46.47	10.20	8.07	4.37	1.07	29.82
400	45.79	90.39	45.52	14.54	3.87	1.92	0.64	33.51
500	26.81	85.77	19.42	29.32	0.69	0.40	0.10	50.07

^a Reaction conditions: B/E = 1, WHSV = 8 h⁻¹, time on stream = 6 h.

^b For example, xylene, ethyl toluene, propyl benzene, indane, and naphthalene.

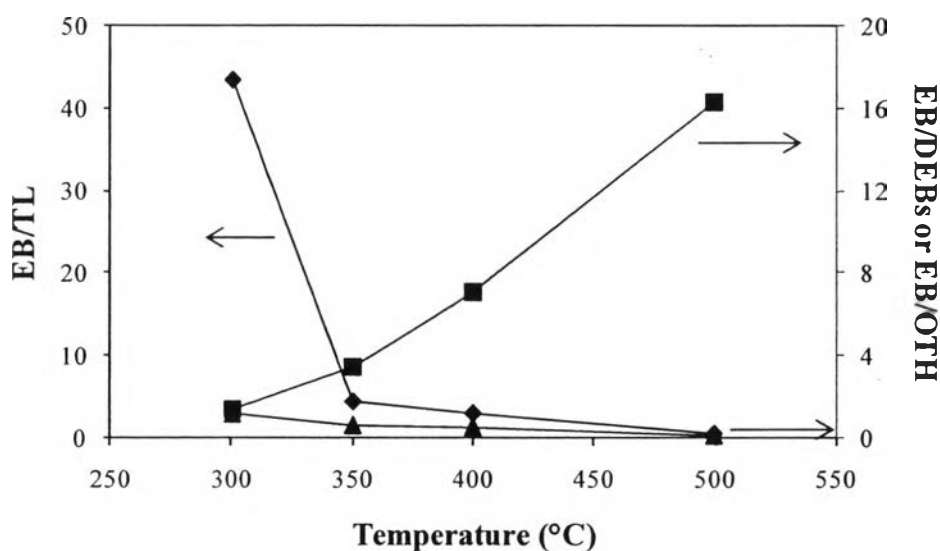


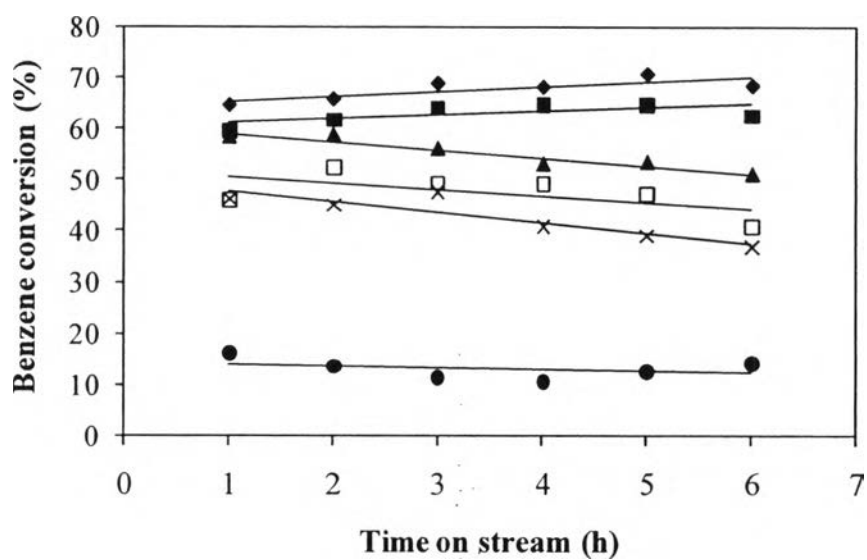
Figure 4.6 Effect of temperature on (♦) EB/TL, (■) EB/DEB and (▲) EB/OTH ratio at HZSM-5 (A), B/E = 1, WHSV = 8 h⁻¹, and time on stream = 6 h.

Table 4.4 shows the products selectivity at different temperatures over HZSM-5 (A). It can be observed that the EB selectivity slightly declined with increasing temperature from 300 °C to 400 °C in which the highest selectivity to EB is 47.75 % at 300 °C. When temperature was increased to 500 °C, the EB selectivity was dropped significantly to 19.42%. The selectivity to DEBs decreased with increasing temperature. Among the DEB isomers, the selectivity to p-DEB is the highest because the electrophilic reactions occur predominantly at the para position and free from steric hindrance (Nandhini *et al.*, 2006). As shown in Figure 4.6, the ratio of EB/DEBs is increased whereas the ratios of EB/OTH and EB/TL are decreased as the temperature is increased. According to Li *et al.* (2009), a higher temperature was favorable for the further alkylation and cracking reactions resulting in a higher selectivity to other products. The toluene selectivity significantly increases with increasing temperature indicating that the high temperature is favorable in the EB cracking reaction.

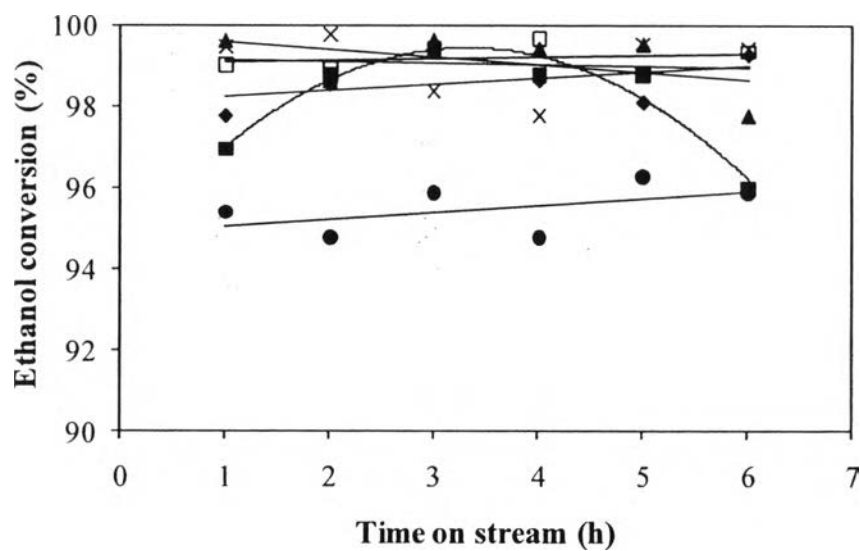
However, it was found that no reaction at the temperature lower than 300 °C. Therefore, the optimal temperature for the reaction of benzene alkylation with ethanol is 300 °C.

4.2.3 The effect of WHSV

The effect of the WHSV on benzene conversion, ethanol conversion and product selectivity was studied over the HZSM-5 (A) using a feed B/E ratio of 1 at 300 °C. The results are presented in Figure 4.7. As an increase in WHSV, both benzene and ethanol conversions found a significant decline. The reaction between benzene and ethanol was reduced because of the decrease in contact time, resulting in decreasing both the benzene and ethanol conversion. The conversions of benzene were slightly decreased from 5 h⁻¹ to 14 h⁻¹ and significantly decreased at a WHSV of 20 h⁻¹.



(a)



(b)

Figure 4.7 Effect of WHSV: (\blacklozenge) 5, (\blacksquare) 8, (\blacktriangle) 10, (\square) 12, (\times) 14 and (\bullet) 20 h^{-1} on (a) benzene conversion, and (b) ethanol conversion for HZSM-5 (A), B/E = 1, T = 300 $^{\circ}\text{C}$.

Table 4.5 Effect of WHSV on the products selectivity over HZSM-5 (A)^a

WHSV (h ⁻¹)	Conversion (%)		Selectivity (%)					
	Benzene	Ethanol	EB	Toluene	p-DEB	m-DEB	o-DEB	Others ^b
5	68.25	99.23	43.83	1.31	23.34	14.12	1.06	16.33
8	62.40	95.95	47.75	1.10	21.02	12.50	1.05	16.58
10	50.82	97.76	53.13	1.29	18.92	11.74	0.85	14.06
12	40.45	99.32	54.61	0.84	18.61	10.85	0.78	14.32
14	36.59	99.40	58.29	0.77	17.10	9.97	0.72	13.16
20	14.08	95.85	69.20	0.50	13.78	8.94	0.92	6.68

^a Reaction conditions: T = 300°C, B/E = 1, time on stream = 6 h.

^b For example, xylene, ethyl toluene, propyl benzene, indane, and naphthalene.

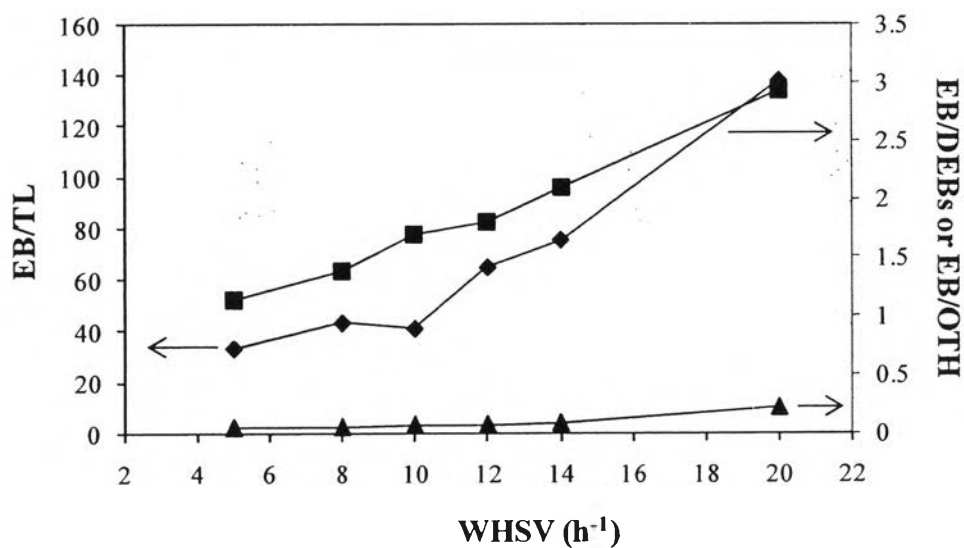
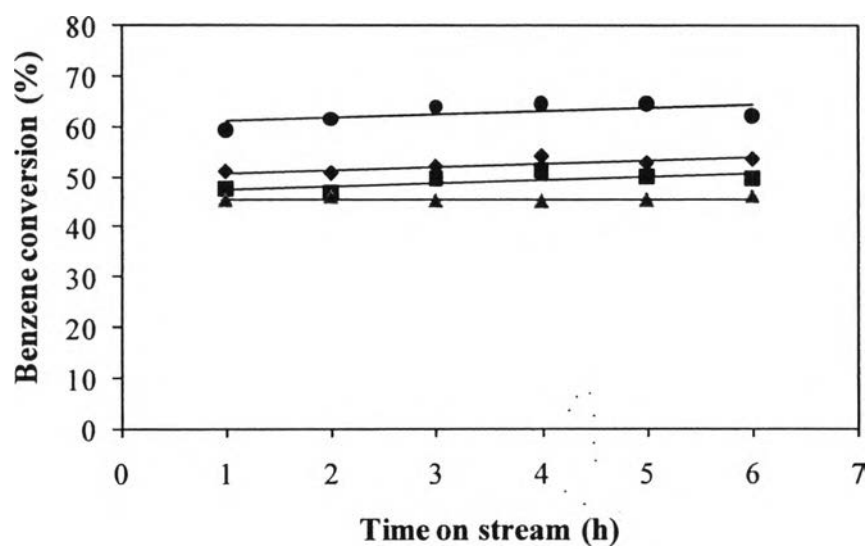


Figure 4.8 Effect of WHSV on (♦) EB/TL, (■) EB/DEB and (▲) EB/OTH ratio for HZSM-5 (A), B/E = 1, T = 300 °C, and time on stream = 6 h.

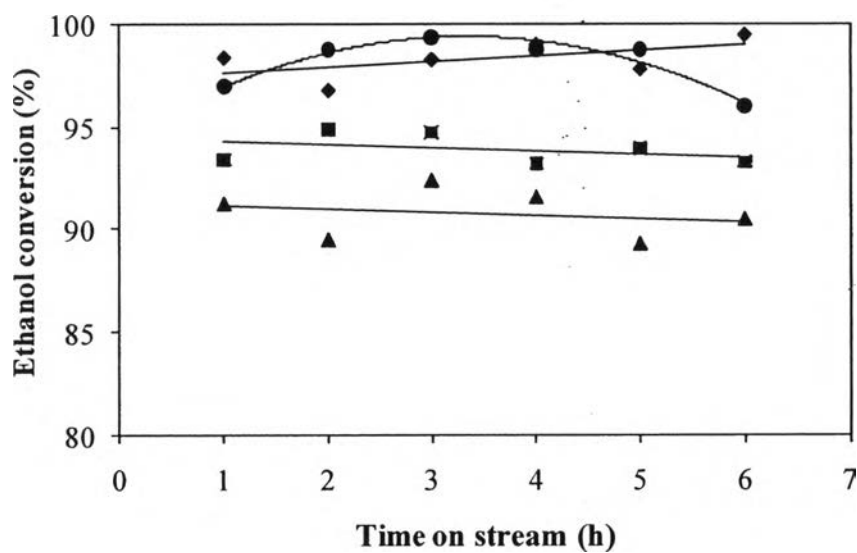
Table 4.5 presents the effect of WHSV on products selectivity. It shows that selectivity to EB increased as WHSV increased from 5 h^{-1} to 20 h^{-1} . According to Figure 4.8, the product selectivity ratios of EB/TL, EB/DEBs, and EB/OTH are increased when the WHSV is increased. With decreasing the contact time, subsequent alkylation and cracking reactions of EB seemed to be lessened (Li *et al.*, 2009). The selectivity to DEB isomers decreases slightly when the WHSV increase from 5 h^{-1} to 20 h^{-1} . As mentioned above, p-DEB was formed as primary product and then isomerized into m-DEB and o-DEB. The selectivity to toluene decreases with increasing WHSV because of the suppression of EB cracking reaction. The selectivity to other alkylated products is decreased as an increase in the contact time.

4.2.4 The effect of B/E feed ratio

The effect of B/E feed ratio was studied by varying the benzene to ethanol (B/E) feed molar ratios from 1 to 4 over HZSM-5 (A) at $300 \text{ }^\circ\text{C}$ and WHSV 8 h^{-1} . The conversions of benzene and ethanol as a function of time are shown in Figure 4.9. The benzene conversion was significantly declined as a B/E feed ratio was increased from 1 to 4. This is probably because the dilution of ethanol by benzene. The probability of benzene interacting with ethyl cations was reduced, and then the reduction of benzene conversion was obtained (Odedairo *et al.*, 2010). With an increase in feed ratio, the conversion of ethanol is decreased.



(a)



(b)

Figure 4.9 Effect B/E feed ratio: (●) 1, (◆) 2, (■) 3 and (▲) 4 on (a) benzene conversion, and (b) ethanol conversion for HZSM-5 (A), WHSV = 8 h⁻¹, T = 300 °C.

Table 4.6 Effect of B/E feed ratio on the products selectivity over HZSM-5 (A)^a

B/E feed ratio	Conversion (%)		Selectivity (%)					
	Benzene	Ethanol	EB	Toluene	p-DEB	m-DEB	o-DEB	Others ^b
1	62.40	95.95	47.75	1.10	21.02	12.50	1.05	16.58
2	53.51	99.51	60.46	2.31	15.80	9.16	0.62	11.65
3	49.87	93.25	65.93	1.67	14.75	7.21	0.50	9.94
4	46.07	90.46	72.69	1.51	11.41	5.28	0.76	8.35

^a Reaction conditions: T = 300 °C, WHSV = 8 h⁻¹, time on stream = 6 h.

^b For example, xylene, ethyl toluene, propyl benzene, indane, and naphthalene.

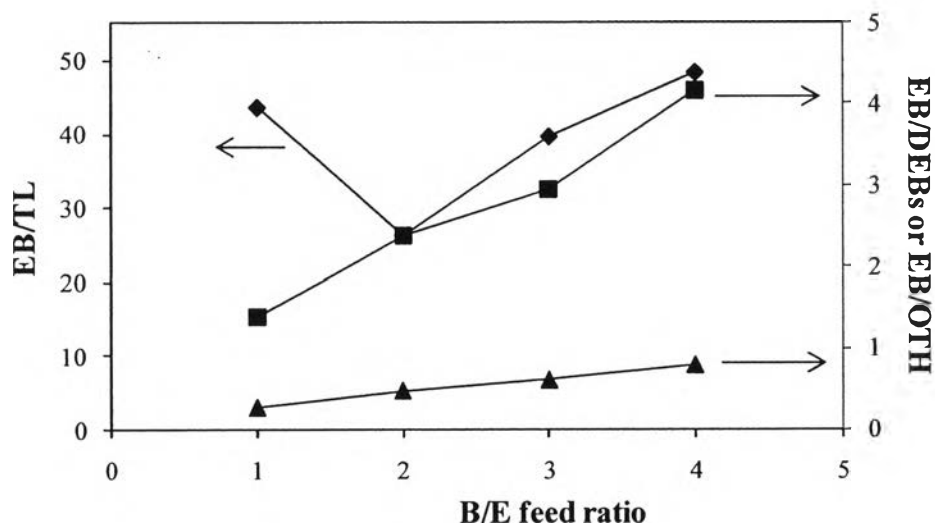


Figure 4.10 Effect of B/E feed ratio on (♦) EB/TL, (■) EB/DEB and (▲)EB/OTH ratio at HZSM-5 (A), WHSV = 8 h⁻¹, T = 300 °C, and time on stream = 6 h.

Table 4.6 presents the effect of B/E feed ratio on the products selectivity. The selectivity to EB was increased with increasing B/E feed ratio. However, the selectivity to DEB isomers and other products decreased simultaneously when the feed ratios increased. According to Figure 4.10 the significantly increase in EB/DEB and EB/OTH ratio as the increase in B/E. It also results from the dilution of ethanol. The high EB selectivity at higher benzene to ethanol ratios results from the suppression of further alkylation of EB by ethyl cations.

4.2.5 Ethanol Selectivity

It has been reported that HZSM-5 are active for ethanol conversion to hydrocarbons. As mention above, the ethanol conversion is higher than the benzene conversion indicating that the reaction of ethanol transformation into other hydrocarbons would occur simultaneously over HZSM-5 catalyst. The yield of varying amount of paraffin, olefin, and aromatic hydrocarbons is given from the reaction in the conversion of ethanol. The ethanol conversion into non-aromatic and aromatic with various effects is shown in Table 4.7 to Table 4.10. From Table 4.7, HZSM-5 (A) obtained the lowest ethanol aromatization to aromatic ring. With increasing temperature and feed B/E ratio, the ethanol aromatization is increased. The ethanol aromatization is decreased as the feed B/E is increased.

Table 4.7 Effect of Si/Al ratio of HZSM-5 on the ethanol conversion^a

Catalyst	Si/Al	Ethanol conversion (%)	Selectivity (%)	
			Non-aromatic	Aromatic
HZSM-5 (A)	77	95.95	67.07	32.93
HZSM-5 (C)	109	92.26	51.52	48.48
HZSM-5 (B)	112	93.15	61.47	38.53

^a Reaction conditions: T = 300 °C, B/E = 1, WHSV = 8 h⁻¹, time on stream = 6 h.

Table 4.8 Effect of temperature on the ethanol conversion over HZSM-5 (A)^a

Temperature (°C)	Ethanol conversion (%)	Selectivity (%)	
		Non-aromatic	Aromatic
300	95.95	67.07	32.93
350	96.62	50.87	49.13
400	90.39	46.20	53.80
500	85.77	35.38	64.62

^a Reaction conditions: B/E = 1, WHSV = 8 h⁻¹, time on stream = 6 h.

Table 4.9 Effect of WHSV on the ethanol conversion over HZSM-5 (A)^a

WHSV (h ⁻¹)	Ethanol conversion (%)	Selectivity (%)	
		Non-aromatic	Aromatic
5	99.23	69.23	30.77
8	95.95	67.07	32.93
10	97.76	58.13	41.87
12	99.42	52.11	47.89
14	99.40	49.32	50.68
20	95.85	36.39	63.61

^a Reaction conditions: T = 300°C, B/E = 1, time on stream = 6 h.

Table 4.10 Effect of B/E feed ratio on the ethanol conversion over HZSM-5 (A)^a

B/E feed ratio	Ethanol conversion (%)	Selectivity (%)	
		Non-aromatic	Aromatic
1	95.95	67.07	32.93
2	99.51	83.29	16.71
3	93.25	90.06	9.94
4	90.46	95.13	4.87

^a Reaction conditions: T = 300 °C, WHSV = 8 h⁻¹, time on stream = 6 h.

4.2.6 The Coke Formation

The spent catalysts were analyzed by TG/DTA technique to observe the coke formation over the HZSM-5 catalysts at reaction conditions: $T = 300^{\circ}\text{C}$, WHSV 8 h^{-1} , feed B/E ratio of 2, and time on stream 6 h. As shown in Figures 4.11 and 4.12, the amount of coke deposit over the spent HZSM-5 (C) and HZSM-5 (B) are 4.7 wt% and 3.9 wt%, respectively. Sun *et al.* (2009) reported that the amount of carbon deposit over acidic zeolites was proportion to the acidity. The decrease of acidity suppresses the carbon deposit formation. This is agreement with the TG results. The HZSM-5 (B) showed the lowest acidity, therefore, this catalyst obtained the low amount of coke deposit.

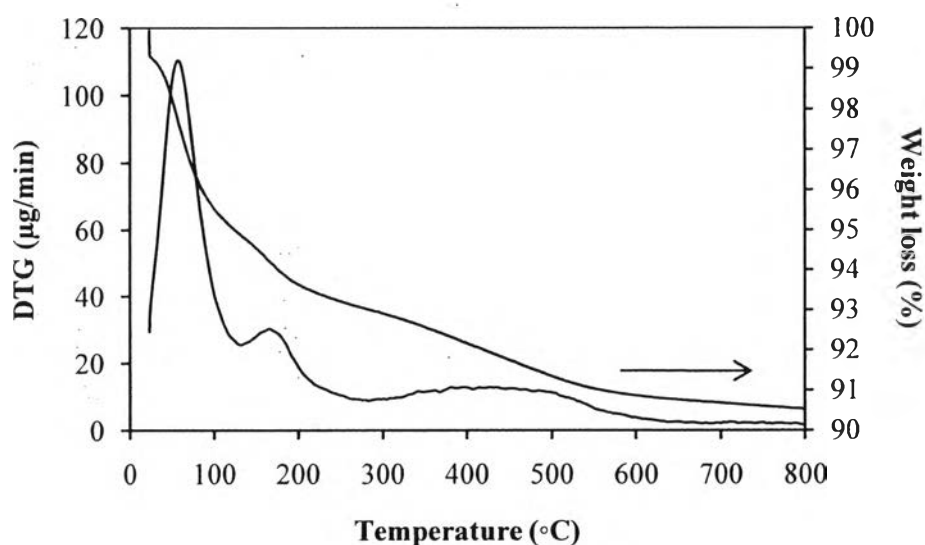


Figure 4.11 TG/DTG profile of the spent HZSM-5 (C) catalyst.

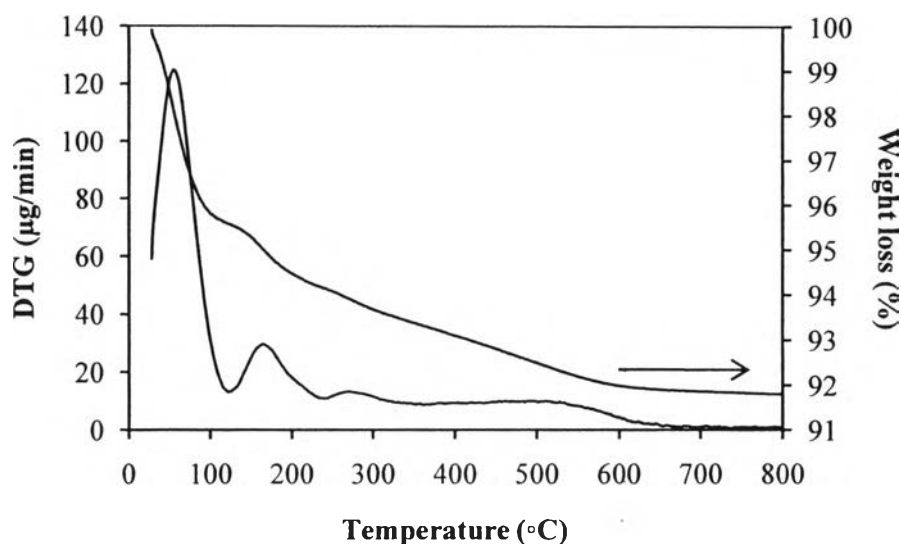


Figure 4.12 TG/DTG profile of the spent HZSM-5 (B) catalyst.

4.2.7 The Proposed Mechanism

The proposed mechanism for the alkylation of benzene with ethanol is shown in Figure 4.13. EB was formed as the primary product by primary alkylation of benzene with ethanol. The alkylation reaction occurs through electrophilic reaction via a carbocation intermediate. The rate determining step is the electrophilic attack by carbocation (Raimondo *et al.*, 1997). With further alkylation of EB, p-DEB was formed as the primary product and subsequently isomerized into m-DEB and o-DEB over HZSM-5 catalyst. DEBs can further alkylate to produce other aromatic hydrocarbons such as propyl benzene and ethyl toluene. Finally, the formation of polyaromatic hydrocarbons was obtained by cyclization over the catalyst surface.

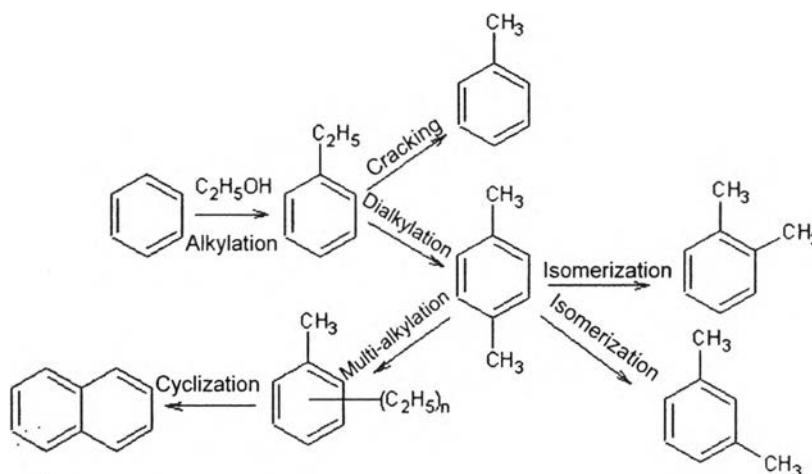


Figure 4.13 A proposed mechanism for the alkylation of benzene with ethanol over HZSM-5 catalyst.

4.2.8 The Stability Test

The stability of the HZSM-5 (A) catalyst was carried out on the alkylation of benzene with ethanol at a feed B/E of 2, 300 °C and WHSV 8 h⁻¹. The results are shown in Figure 4.14. It is found that when the time on stream is 34 h, the conversion of benzene and ethanol is dropped to from 47.89% to 22.67% and from 91.21% to 82.65%, respectively. Moreover, the selectivity to EB decreased significantly to 46.09% from 57.56% when time on stream is 34 h. The deactivation of the catalyst usually occurs as the micropore of catalysts is blocked by the coke deposited.

Because of the hydrophilicity of HZSM-5 zeolite from aluminum in zeolite framework groups and external surface silanol groups, it prefers to adsorb ethanol lead to the enrichment of ethanol on the surface of catalyst. Then ethanol can be convert to ethylene that can polymerize to form coke easily (Sun *et al.*, 2009).

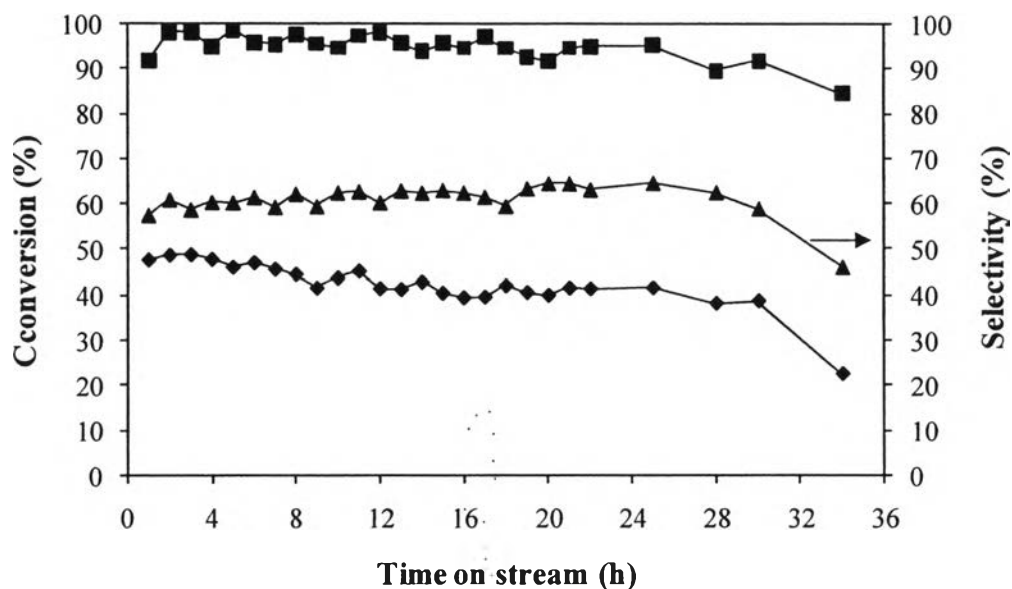


Figure 4.14 (◆) Benzene conversion, (■) ethanol conversion, and (▲) EB selectivity over HZSM-5 (A), $T = 300\text{ }^{\circ}\text{C}$, $\text{WHSV} = 8\text{ h}^{-1}$, and $\text{B/E} = 2$.

The temperature programmed oxidation (TPO) was performed to analyze coke formation on the spent catalyst. As shown in Figure 4.15, the TPO profiles show two peaks that the first one at temperature about $340\text{ }^{\circ}\text{C}$ and the second at $700\text{ }^{\circ}\text{C}$. According to Guisnet *et al.*, (2001), the oxidation of coke at low temperature could be the coke from the condensation and rearrangement of polyaromatic products. On the opposite, the oxidation of coke at high temperature could be polyaromatic molecules that formed by hydrogen transfer reaction on acidic catalysts. The amount of coke is 7.09 wt%.

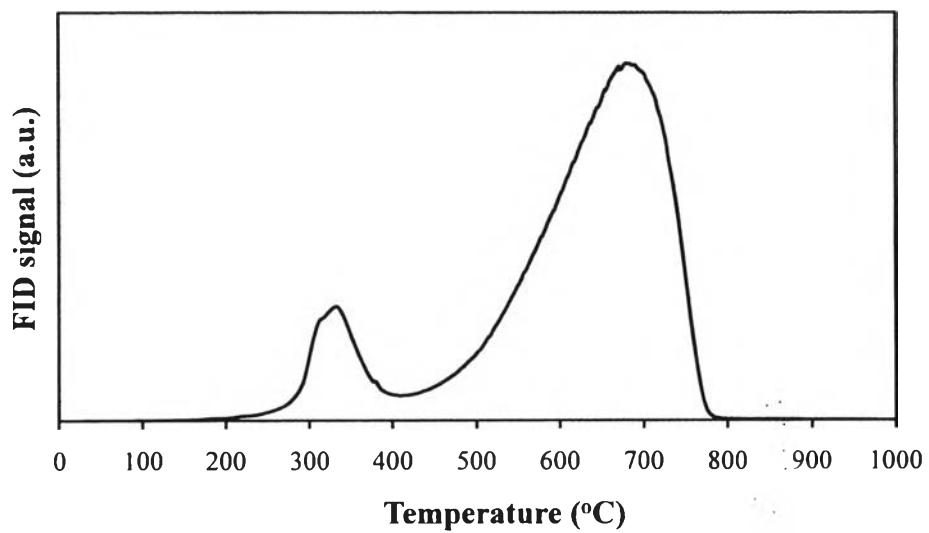


Figure 4.15 TPO profile of spent catalyst on alkylation of benzene with ethanol over HZSM-5 (A), $T = 300\text{ }^{\circ}\text{C}$, $\text{WHSV} = 8\text{ h}^{-1}$, feed B/E = 2, and TOS = 34 h.