

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

In this study, the synthesized HZSM-5 catalysts with initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of ca. 195, 260, and 280 obtained at 140 °C for crystallization 3 and 7 days are designated as HZ5-195(3), HZ5-195(7), HZ5-260(3), HZ5-260(7), HZ5-280(3), and HZ5-280(7) respectively. However, the HZ5-260(3) and HZ5-280(3) catalysts were not successfully obtained. This is because a longer period of crystallization time is required for the synthesis of high $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios.

This section discusses the initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios by using HZ5-195(7), HZ5-260(7), and HZ5-280(7) and the synthesis time by using HZ5-195(3) HZ5-195(7) and on the properties of those catalysts and performance for ethylation of benzene with ethanol to ethylbenzene (EB) of those catalyst.

4.1.1 X-ray Diffraction

The XRD patterns of the synthesized HZSM-5 catalysts with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios are given in Figure 1. It is evident that all the synthesized HZSM-5 catalysts have a typical MFI structure in which 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 high intensity of peaks in the XRD pattern is implied that the synthesized HZSM-5 catalysts have high crystallinity (Li *et al.*, 2009).

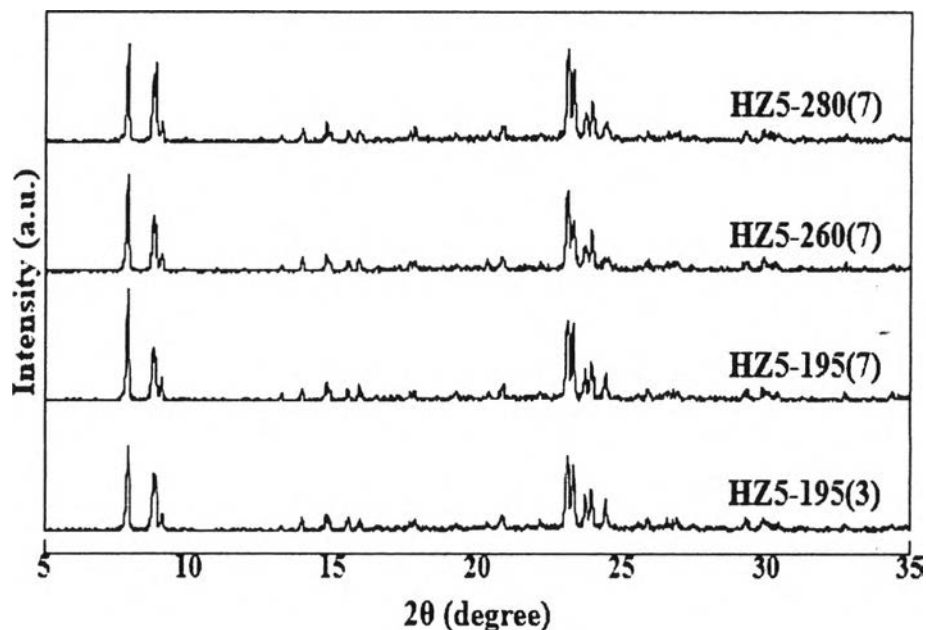


Figure 4.1 X-ray diffraction patterns of the synthesized HZSM-5 catalysts.

Table 4.1 Relative crystallinity of the synthesized HZSM-5 catalysts

Catalyst	Relative crystallinity (%)
HZ5-195(3)	80.18
HZ5-195(7)	84.33
HZ5-260(7)	86.18
HZ5-280(7)	100.00

The peak intensity in the high diffractive angle ($2\theta = 23.08^\circ$) increased with increasing synthesized time and $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios. HZ5-280(7) showed the highest peak intensity peak because of long period of synthesized time and high $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios. As shown in Table 4.1, it was noticed that the synthesized HZSM-5 catalysts contained different crystallinity. The crystallinity of HZSM-5 synthesized with initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 280 was higher than those of HZSM-5 synthesized with initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 260 and 195. Besides, the crystallinity of HZSM-5 synthesized for 7 days was higher than that of HZSM-5 synthesized for 3 days.

4.1.2 Catalyst Composition

The chemical compositions of synthesized HZSM-5 catalysts were

obtained by XRF technique. The results are summarized in Table 4.2. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in the samples were lower than those in the precursor gels due to the Al content of the products is normally observed to be slightly lower than that of the starting gel when TPA⁺ is used as the template agent. (Ali et al., 2003) The attained $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios are ranging from 157 to 195. It was found at a given crystallization time and the initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio played a role in obtaining the desired $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (195). However, at a given initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio, a longer crystallization time resulted in increasing the theoretical acidity. This is due to the lower content of Al atoms in the framework of such samples.

Table 4.2 Chemical compositions and theoretical acidity of synthesized HZSM-5 catalysts

Catalyst	Compound (wt%)		$\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio)	Si/Al ^a	Theoretical acidity (mmol/g) ^b
	SiO_2	Al_2O_3			
HZ5-195(3)	99.004	0.996	169	84	0.1951
HZ5-195(7)	98.927	1.073	157	78	0.2100
HZ5-260(7)	99.058	0.942	179	89	0.1845
HZ5-280(7)	99.138	0.862	195	98	0.1688

^achemical formula is $\text{H}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192}$

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

4.1.3 Scanning Electron Microscopy (SEM)

Morphological properties and crystal sizes of the product samples were investigated by SEM. The results are presented in Figure 4.2 and Table 4.3. Figure 4.2 shows the SEM images of HZSM-5; HZ5-195(3), HZ5-195(7), HZ5-260(7), and HZ5-280(7) catalysts. It can be found that the HZSM-5 synthesized by NaOH is consistent with the character of micro scale crystal.

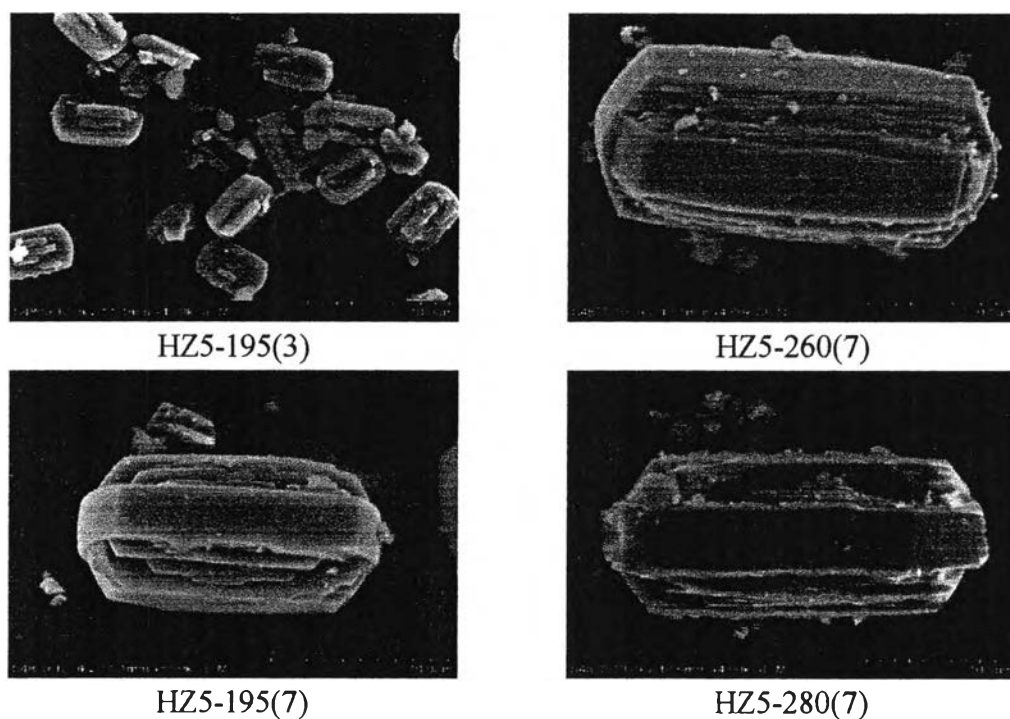


Figure 4.2 SEM images of the synthesized HZSM-5 catalysts.

Table 4.3 Crystal sizes of the synthesized HZSM-5 catalysts

Catalyst	Dimension (WxLxH, micron)
HZ5-195(3)	3.85 x 5.13 x 1.54
HZ5-195(7)	8.57 x 17.14 x 1.92
HZ5-260(7)	11.28 x 27.18 x 2.86
HZ5-280(7)	11.8 x 27.69 x 3.08

It can be found that the morphology of zeolite sample was alike irregular hexagonal prisms with rectangular insertion with crystal sizes of 3.85–11.8 μm in length, about 5.13–27.69 μm in width, and a narrow range of 1.54–3.08 μm in height. From Table 4.3 the crystal sizes were formed in order with the synthesis time. Generally, short crystallization time could provide smaller crystal size according to the study of Khatamin *et al.*(2009). Moreover, the crystal size depended on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio used. (Shirazi et al, 2008) It is interesting to note that the higher the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio, the larger the size of crystal is. As a result, the crystal size of the synthesized HZSM-5 was decreased in the following order: HZ5-280(7) > HZ5-260(7) > HZ5-195(7) > HZ5-195(3).

4.1.3 Surface Area Measurements

N₂ adsorption and desorption isotherm was also carried out by using a Quantachrome/Autosorb-1MP. The textural properties of the synthesized HZSM-5 catalysts determined by BET and t method a installed in this instrument. The isotherm shown in Figure 4.3 is corresponded to adsorption isotherm Type I with hysteresis loop, which is an evidence that synthesized HZSM-5 catalyst possesses a micropore structure.

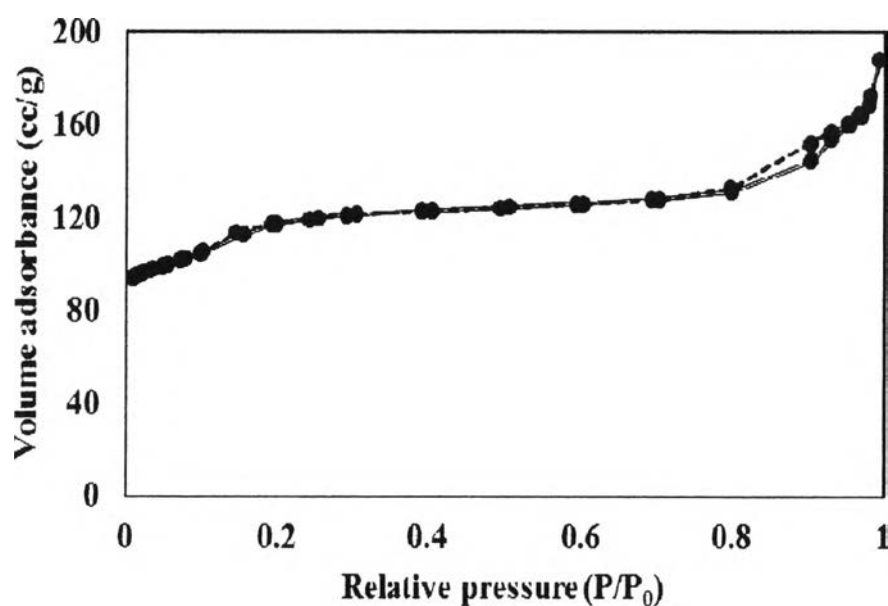


Figure 4.3 N₂ adsorption-desorption isotherm of the synthesized HZSM-5 catalyst.

Table 4.4 Textural properties of the synthesized HZSM-5 catalysts

Catalyst	BET Surface Area (m ² /g)	Micropore Volume (M) ^a (cm ³ /g)	Total Pore Volume (T) (cm ³ /g)	M/T ratio	Pore diameter (Å) ^b
HZ5-195(3)	371	0.140	0.291	0.481	6.14
HZ5-195(7)	325	0.136	0.240	0.567	6.14
HZ5-260 (7)	321	0.134	0.238	0.563	6.14
HZ5-280(7)	325	0.133	0.242	0.550	6.14

^aDetermined by t-plot method

^bDetermined by NLDFT method

Table 4.4 present the BET surface areas ranging from 321 to 371 m^2/g . The micropore to total pore volume (M/T) ratio was increased with the initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar 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. The M/T ratio was introduced as a parameter to be related to the catalyst activity. There was no change in pore diameter of the catalysts with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio.

4.2 Catalytic Activity Testing

The catalytic activity of the catalysts was carried out in a fixed-bed continuous down-flow reactor under the reaction conditions as follows: temperature (400 °C to 500 °C), weight hourly space velocity (15 and 20 h^{-1}), and benzene-to-ethanol ratio (2 to 6). The results of catalytic performance of alkylation of benzene with ethanol were carefully investigated.

Alkylation of benzene involving ethanol as an alkylating agent over the synthesized HZSM-5 catalysts yielded ethylbenzene as the primary product. The mixture of diethylbenzene isomers (meta, para, and ortho) came from the second alkylation of ethylbenzene. Small amounts of methanol, toluene, xylene isomers, resulting from ethanol decomposition and alkylation of benzene, and toluene, were also observed. Cumene, Propyl-benzene, ethyltoluene (meta, para, and ortho), 1,2,3-trimethylbenzene and butenylbenzene were formed only in small quantities.

4.2.1 Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ Molar Ratio

Figure 4.4 shows the effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio on the conversion of benzene and EB selectivity for the HZSM-5 synthesized. The HZ5-195(3) with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio ca.169 provided the highest values of both EB selectivity and benzene conversion. This is because HZ5-195(3) had the smallest crystal size compared with the others and the result was in agreement with that of Gao *et al.* (2010) in which a small crystal is beneficial for EB diffusion and increases high EB selectivity. When comparing at a similar crystal size, the benzene conversion was decreased as $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio was increased. This was also conformed

with that reported by Yuan *et al.* (2004).

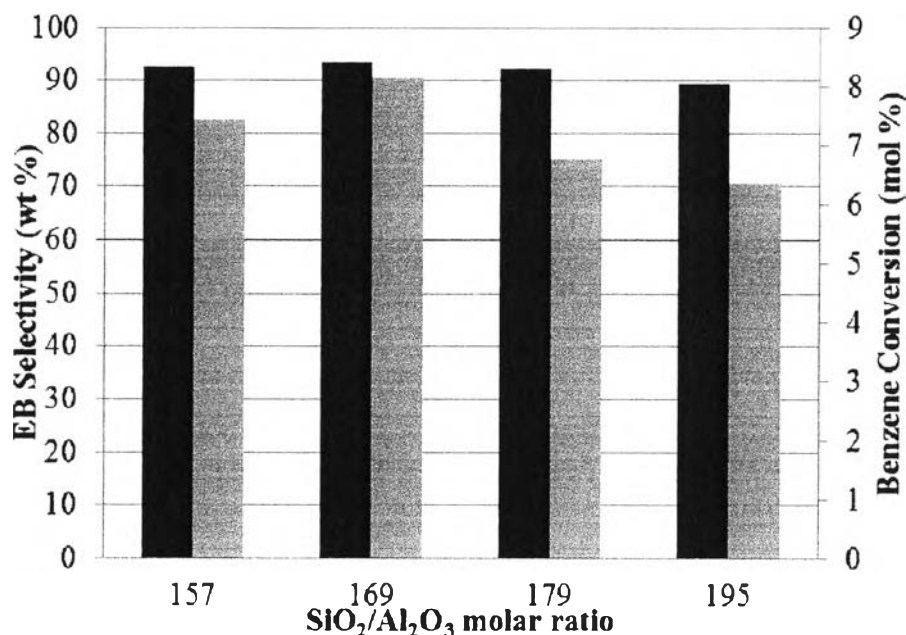


Figure 4.4 Effect of SiO₂/Al₂O₃ molar ratio on (■) EB selectivity and (▒) Benzene conversion over HZSM-5 at 500 °C, B/E = 4, WHSV = 20 h⁻¹, and TOS = 410 min.

4.2.2 Effect of Textural Properties and Acidity

Table 4.5 indicates that HZ5-280(3) was almost lowest M/T ratio indicating the dominance of mesopore volume. The plentiful micropores would allow EB to diffuse out of the pore more difficult than the other having the abundance of mesopores. Moreover, the dominance of mesopore volume is inescapably related to the contact time in which the increase in the contact time between the rest of EB in the pore and other carbenium ion can be a negative effect on the product quality in terms of EB selectivity. However, benzene conversion tended to increase with decreasing M/T ratio. It can be explained that the increase in micropore volume may allow any products and/or benzene to diffuse out of the pores difficultly, so the benzene remaining in the pore can have enough time to react with anything in the pore, resulting in high benzene conversion.

Table 4.5 Catalytic performance for the synthesized HZSM-5 catalysts at 500°C, B/E = 4, WHSV = 20 h⁻¹, and TOS = 410 min

Catalyst	M/T ratio	Theoretical acidity (mmol/g)	Benzene conversion (%)	Selectivity (%)				
				EB	Toluene	Xylenes	DEBs	Others*
HZ5-195(3)	0.481	0.1951	8.17	93.41	2.29	1.66	0.26	2.39
HZ5-195(7)	0.567	0.2100	7.44	92.76	2.53	1.64	0.32	2.74
HZ5-260(7)	0.563	0.1845	7.13	92.21	3.01	1.63	0.30	2.84
HZ5-280(7)	0.550	0.1688	6.36	89.36	3.91	2.86	0.65	3.21

* For instance; ethylene, methanol, trimethylbenzene, ethyltoluene, and heavy aromatics

It is well known that acidity plays an important role in alkylation reactions. A strong acid site is beneficial for secondary reactions such as decomposition, isomerization, and polymerization (Zhu *et al.*, 2006). In the conventional alkylation of benzene with ethylene or ethanol the conversion of benzene was increased markedly with an increase in catalyst acidity because strong acid sites were required for the activation of carbocations. Alkyl carbonate has been found to easily decompose over acidic or basic materials because surface acidity plays an important role in its decomposition (Li *et al.*, 2009). Ethanol may undergo significant decomposition over the strongly acidic HZ5-195(7). Thus ethylation over HZ5-195(7) catalyst provided high contents of toluene, xylene and DEB compounds that caused the poor catalytic activity. Use of the HZ5-260(7) and HZ5-280(7) catalysts resulted in the slight decline in benzene conversion indicating that poor acidity was not suitable for the alkylation of benzene with ethanol either.

From above section which demonstrates that HZ5-195(3) was the best catalyst with small crystal size, low M/T ratio, and suitable surface acid properties as well as providing catalytic activity in terms of EB selectivity. Therefore, the HZ5-195(3) was brought to perform the ethylation of benzene with ethanol to optimize reaction conditions such as reaction temperature, B/E feed molar ratio, WHSV, and to determine its coke formation.

4.2.3 Effect of Reaction Temperature

The reaction temperatures were studied at 400, 450 and 500 °C over HZ5-195(3) catalyst, with the feed ratio 4:1 for B/E, WHSV = 20 h⁻¹, and TOS = 410 min. The plots of benzene conversion and EB selectivity versus temperature for HZ5-195(3) catalyst are shown in Figure 4.5. It shows that the highest EB selectivity is attained at 500°C in the investigated temperature range. From the results, it indicates that the optimum temperature providing the highest benzene conversion was 400 °C. According to Gao and co-workers (2010), the decrease in reaction temperature could provide the diffusing out from the pore more slowly affecting the resultant product such as EB which would be attacked by a free ethanol or carbenium ion of ethanol, producing DEBs. However, the increase in reaction temperature resulted in the increase in decomposition rate of products, as the decomposition led to the increases of benzene and bulkier molecules, which block the micropore channels of the catalyst and deactivated the catalyst. This was corresponding to the result at 500 °C in which the decomposition rate resulted in the lowest benzene conversion.

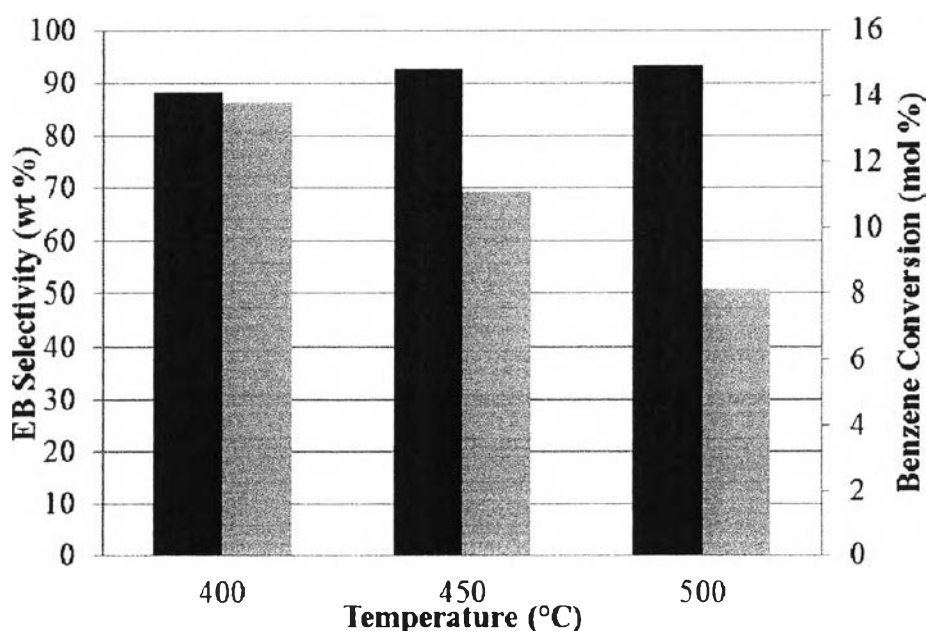


Figure 4.5 Effect of reaction temperature on (■) EB selectivity and (▒) Benzene conversion over HZ5-195(3) catalyst; B/E = 4, WHSV = 20 h⁻¹, and TOS = 410 min.

Table 4.6 Effect of temperature on the products selectivity over HZ5-195(3) catalyst; B/E = 4, WHSV = 20 h⁻¹, and TOS = 410 min

Temperature (°C)	Selectivity (%)				
	EB	Toluene	Xylenes	DEBs	Other*
400	88.13	1.32	0.46	0.79	9.31
450	92.74	1.67	0.90	0.28	4.42
500	93.41	2.29	1.66	0.26	2.39

* For instance; ethylene, methanol, trimethylbenzene, ethyltoluene, and heavy aromatics

Table 4.6 shows the variation of the reaction products at different reaction temperature. Normally, at low reaction temperatures the polymerization reaction, exothermic reaction, was found to be a main reaction for which EB transform itself to be DEBs group. At high reaction temperatures the isomerization and/or cracking reaction, the endothermic reaction, was found to be a main reaction for which EB was cracked into toluene and xylenes. However, the reaction performed at 500 °C provided the highest selectivity to EB (93.41 %), which may be due to the moderate reaction temperature so as not to accommodate the secondary reaction.

Figure 4.6 represents the products selectivity at different temperature over HZ5-195(3). When the mass ratios of EB-to-Xylenes and EB-to-DEBs were compared at different temperatures, the highest EB-to-DEBs was obtained at 500 °C. This is because of the exothermic reaction of the alkylation of EB-to-DEBs.

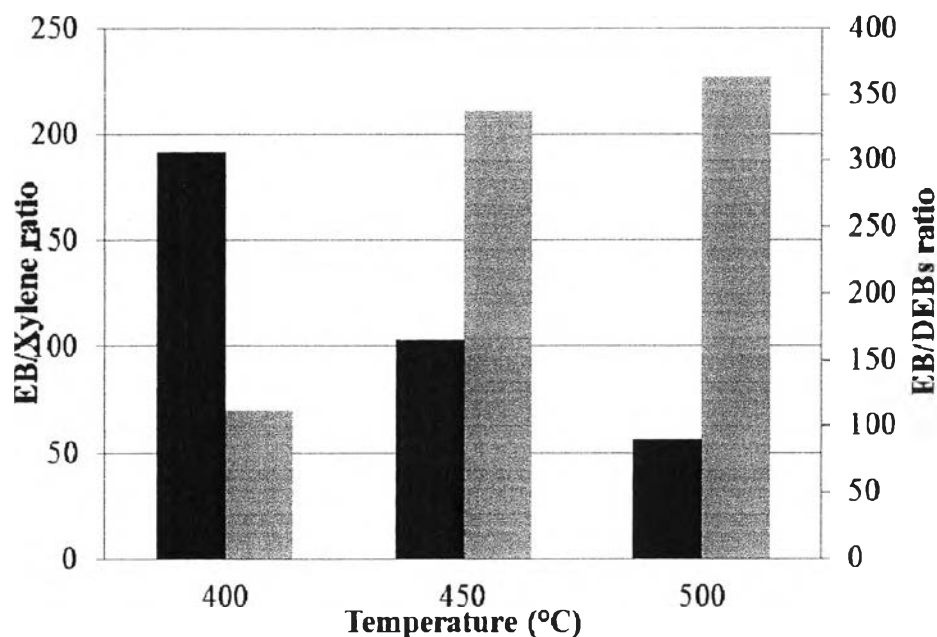


Figure 4.6 Effect of reaction temperature on (■) EB/Xylenes ratio and (▒) EB/DEBs ratio over HZ5-195(3) catalyst; B/E = 4, WHSV = 20 h⁻¹, and TOS = 410 min.

4.2.4 Effect of B/E Feed Molar Ratio

The effect of feed molar ratio (benzene to ethanol) on benzene conversion and product selectivity was investigated over HZ5-195(3) catalyst. Effect of benzene to ethanol mole ratio in the feed mixture on benzene conversion was studied by varying the ratio from 2:1 to 6:1 at 500 °C, and WHSV 20 h⁻¹. Figure 4.7 presents the results of benzene and ethanol conversions as a function of B/E feed molar ratio. The conversion of benzene was significantly declined with increasing B/E feed ratio from 2:1 to 6:1. This is probably because the increment of B/E feed ratio seemed to add a large excess of aromatic reactant to the system which can interfere the opportunity of benzene interacting with ethyl cations, a large excess of aromatic reactant can block the rest of the active sites of the catalyst surface (Odedairo *et al.*, 2010), as a result a lower benzene conversion was obtained. However, the ethanol conversion was almost constant at 100% conversion at all B/E feed molar ratios.

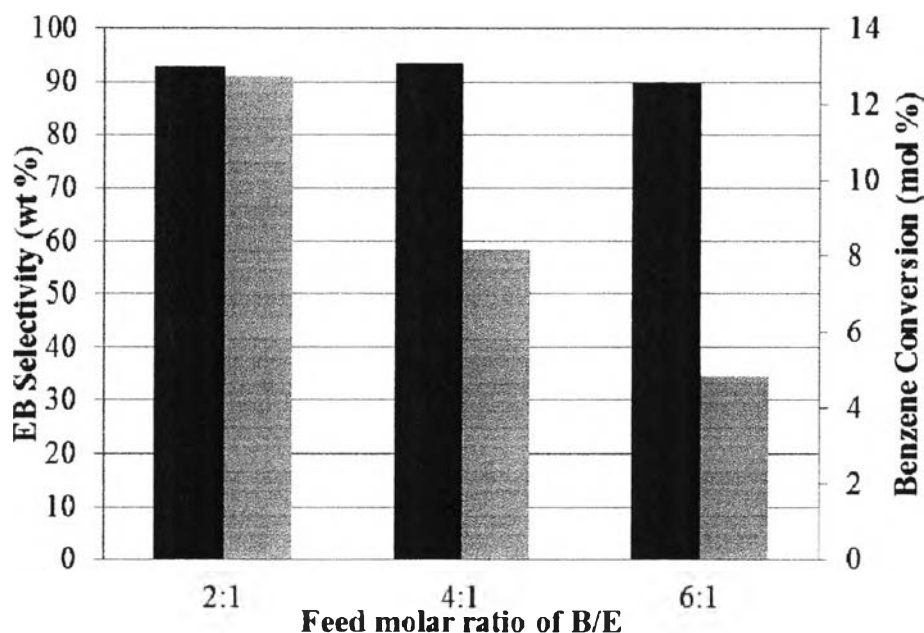


Figure 4.7 Effect of B/E feed ratio: on (■) EB selectivity, and (■) Benzene conversion for HZ5-195(3) catalyst; $T = 500\text{ }^{\circ}\text{C}$, $\text{WHSV} = 20\text{ h}^{-1}$, and $\text{TOS} = 410\text{ min}$.

Table 4.7 Effect of B/E feed molar ratio on the products selectivity over HZ5-195(3) catalyst; $T = 500\text{ }^{\circ}\text{C}$, $\text{WHSV} = 20\text{ h}^{-1}$, $\text{TOS} = 410\text{ min}$

B:E feed ratio	Selectivity (%)				
	EB	Toluene	Xylenes	DEBs	Other*
2:1	92.81	1.61	1.36	0.27	3.96
4:1	93.41	2.29	1.66	0.26	2.39
6:1	89.71	3.96	3.25	0.58	2.50

* For instance; ethylene, methanol, trimethylbenzene, ethyltoluene, and heavy aromatics

Table 4.7 shows the effect of B/E feed ratio to the products selectivity. The selectivity to EB was increased with increasing B/E feed ratio whereas the selectivity to DEB isomers was decreased. This might be also resulted from the dilution of ethanol. The results attainable were conformed to those obtained by Odedairo *et al.* (2010) with which the high EB selectivity at higher benzene to ethanol ratios was attributed to the suppression of further alkylation of EB by ethyl cations. However, the EB was selectivity decreased because of the overwhelmed

benzene in feed that caused the secondary reactions occurred. Therefore, the suitable B/E feed ratio was attained at 4:1 as for the highest EB selectivity.

4.2.5 Effect of WHSV

Figure 4.8 presents the results of ethylbenzene selectivity, benzene conversion, and ethanol conversion against WHSV (weight hourly space velocity). The reaction was investigated over HZ5-195(3) catalyst at 500 °C with the B/E feed ratio 4:1, and varying WHSV with 15 and 20 h⁻¹. It can be observed that benzene conversion was significantly increased with increasing WHSV from 15 to 20 h⁻¹. This can be interpreted in lieu of the contact time. With a decrease in the WHSV, a longer contact time between the active sites of the catalyst surface and feed reactants can lead to higher probability for the secondary reactions to occur consuming more benzene. On the contrary, the increased EB selectivity with increasing WHSV can be attributed to the suppression of secondary reactions caused by reducing the contact time providing the diffusion of the product out from the reaction zone quickly, thus leading to high EB selectivity.

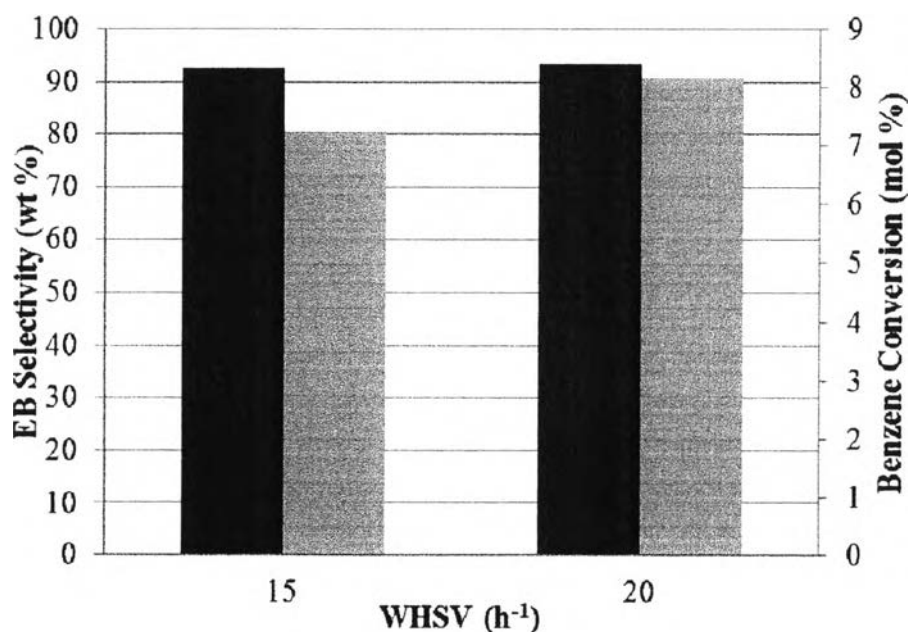


Figure 4.8 Effect of WHSV: on (■) EB selectivity, and (■) Benzene conversion for HZ5-195(3) catalyst, B/E = 4, T = 500 °C, and TOS = 410 min.

4.2.6 Coke Formation

The spent catalysts were analyzed by the temperature programmed oxidation (TPO) technique to observe the coke formation over the HZ5-195(3) catalyst at different B/E feed molar ratios along with specific reaction conditions: T = 500°C, WHSV = 20 h⁻¹, and TOS = 410 min.

Table 4.8 Coke formation of the spent HZ5-195(3) catalyst

B/E feed molar ratio	Benzene conversion (%)	Amount of carbon (wt%)
2:1	12.76	4.66
4:1	8.17	4.98
6:1	4.86	3.54
Pure benzene	0.49	3.23

As shown in Table 4.8, the amounts of coke deposition over the spent HZ5-195(3) catalyst at B/E ratios of 2 and 4 are 4.66 and 4.98 wt%, respectively. It can be observed that the increased amount of benzene in feed influenced the increment of coke formation corresponding to the observations by Duang-udom (2011) and Rugwong (2012). The coke formation would increase because benzene could be cracked easier at its higher amount. As a result, the conversion of benzene was decreased with the increased coke formation. On contrary, at B/E ratio of 6 the lower benzene conversion was observed with the less amount of coke formation. To investigate the effect of benzene on the coke formation, pure benzene was fed at the given reaction conditions. It is revealed that the moderate amount of coke with an insignificant benzene conversion was attained. This might be ascribed to the rapid decomposition of benzene resulting in the coke formation which in turn covered the active sites and/or blocking the pores for other reactions to proceed further.