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 90 that was aged at room temperature for 24 h in hydrothermal process at temperature 180 °C for 72 h was designated as HZ5A. The synthesized HZSM-5 catalysts with SiO_2/Al_2O_3 ratio of 185 were aged at room temperature for 30 min in hydrothermal process at temperature 150 °C for 24 h, at temperature 150 °C for 72 h, at temperature 180 °C for 24 h, and at temperature 180 °C for 72 h were designated as HZ5B1, HZ5B2, HZ5B3, and HZ5B4. The synthesized HZSM-5 catalyst with SiO_2/Al_2O_3 ratio of 185 was aged at room temperature for 12 h in hydrothermal process at temperature 180 °C for 72 h was designated as HZ5B5, as shown in Table 4.1.

Table 4.1 Parameters utilized for hydrothermal synthesis conditions

Catalyst	Expected SiO_2/Al_2O_3 ratio	Aging time (h)	Temperature (°C)	Crystallization time (h)
HZ5A	90	24	180	72
HZ5B1	185	0.5	150	24
HZ5B2	185	0.5	150	72
HZ5B3	185	0.5	180	24
HZ5B4	185	0.5	180	72
HZ5B5	185	12	180	72

4.1.1 Catalyst Composition

The chemical compositions of the synthesized HZSM-5 catalysts were analyzed by X-ray fluorescence (XRF) technique. The results are summarized in Table 4.2. From the data, the Si/Al molar ratio and its theoretical acidity were determined for each catalyst prepared. The calculated SiO_2/Al_2O_3 ratios of the samples were 91 for HZ5A, 181 for HZ5B3, 181 for HZ5B4, and 187 for HZ5B5. It was observed that effects of crystallization time and temperature on the synthesis of HZSM-5 catalysts were insignificant in the studied ranges. From the results, the theoretical acidity of catalysts determined based on the number of protons was attained according to its formula.

Table 4.2 The chemical compositions of the synthesized HZSM-5 catalysts

Catalyst	**Concentration (mol%)**			**Si/Al**[a]	**SiO_2/Al_2O_3**	**Theoretical acidity (mmol/g)**[b]
	Si	**Al**	**Na**			
HZ5A	97.835	2.139	0.026	45.73	91	0.354
HZ5B3	94.956	1.044	0.05	90.93	182	0.181
HZ5B4	98.861	1.091	0.048	90.59	181	0.182
HZ5B5	98.905	1.054	0.041	93.84	188	0.176

[a] Chemical formula is $H_nAl_nSi_{96-n}O_{192}$

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

4.1.2 X-ray Diffraction

The XRD patterns of synthesized HZSM-5 catalysts were examined by X-ray diffraction. Figure 4.1 shows the XRD patterns of the synthesized HZSM-5 catalysts under different hydrothermal conditions. It shows that the characteristic diffraction peaks corresponding to the patterns of HZSM-5 zeolite were observed. The high intensity peaks indicate that the synthesized zeolites have relatively high crystallinity.

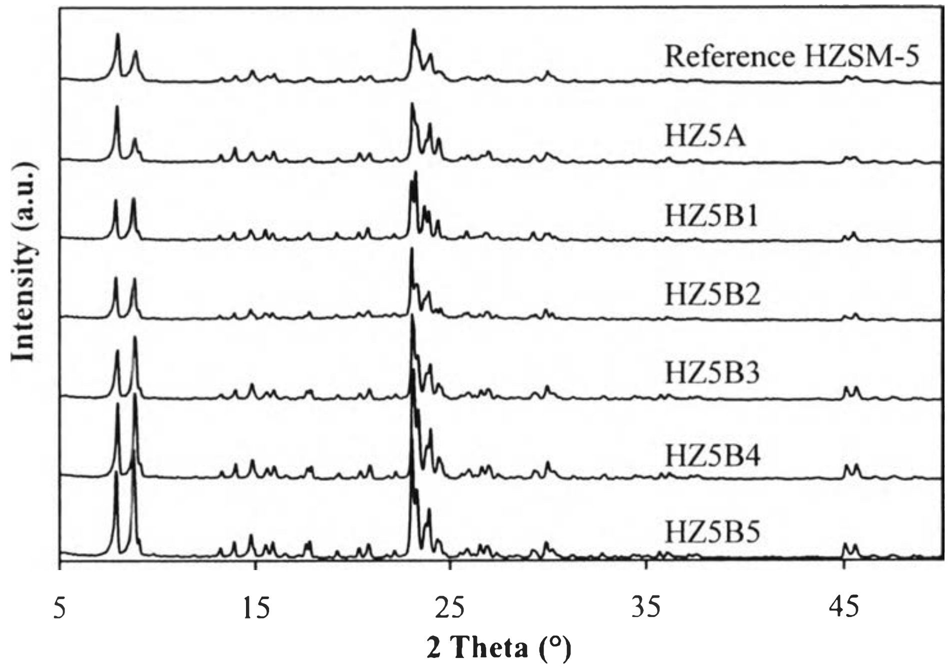


Figure 4.1 XRD patterns of the synthesized HZSM-5 catalysts.

The peak intensity at 23° (2θ) increased with increasing crystallization time and temperature in hydrothermal process. HZ5B5 possessed the highest peak intensity because it was synthesized at longer aging time, longer crystallization time, and higher temperature than the others. It was observed that the synthesized HZSM-5 catalysts had different degrees of crystallinity. The HZSM-5 synthesized at 150 °C had crystallinity lower than that synthesized at 180 °C. The crystallinity of HZSM-5 synthesized for 24 h was lower than that HZSM-5 synthesized for 72 h. The relative crystallinity of the synthesized HZSM-5 is shown in Table 4.3.

Table 4.3 Relative crystallinity of the synthesized HZSM-5 catalysts

Catalyst	Relative crystallinity (%)
HZ5A	50.96
HZ5B1	51.34
HZ5B2	61.35
HZ5B3	71.68
HZ5B4	86.13
HZ5B5	100.00

4.1.3 FESEM

Figure 4.2 shows SEM images of synthesized HZSM-5 catalysts with varying SiO_2/Al_2O_3 ratios and hydrothermal conditions. HZ5A crystals were near-spherical in shape and had a crystal size approximately 5 μm. HZ5B1, HZ5B2, HZ5B3, HZ5B4, and HZ5B5 crystals were of hexagonal cylindrical shape and approximately 2.5 to 3.75 μm in size. The crystal sizes of HZ5B1, HZ5B2, and HZ5B3 were similar although their crystallization time and temperature were different. However the plausible agglomeration of crystal particles was observed as increases in crystallization time and temperature. By comparing between HZ5B1 and HZ5B2 as well as between HZ5B3 and HZ5B4, the crystalline phases observed were in good agreement with Kumar *et al.* (2002) in which a small crystallite size was attained at a shorter crystallization time while a large one was attained at a longer crystallization time.

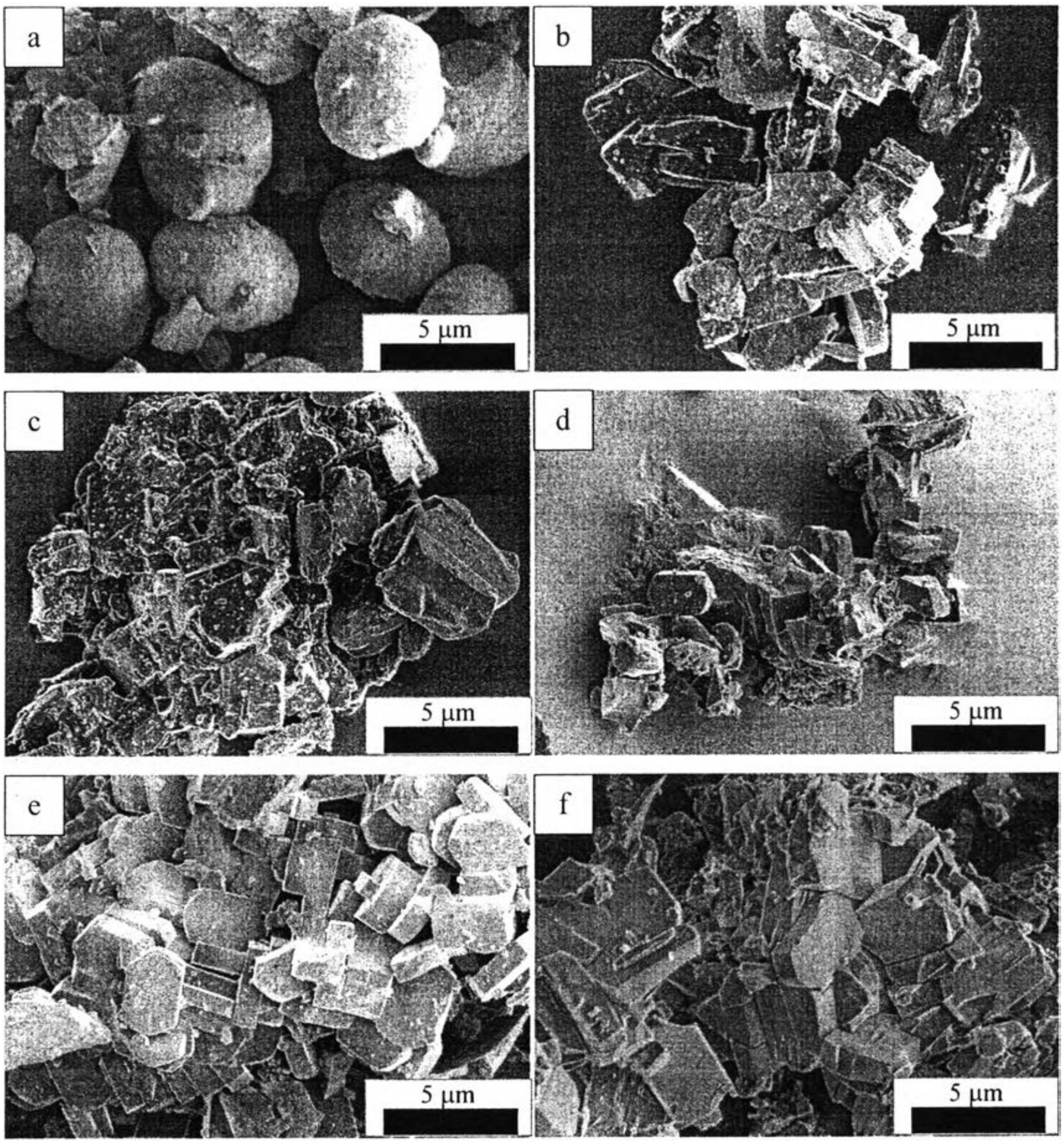


Figure 4.2 SEM images of the synthesized HZSM-5 catalysts (a) HZ5A, (b) HZ5B1, (c) HZ5B2, (d) HZ5B3, (e) HZ5B4, and (f) HZ5B5.

4.1.4 BET Surface Area Measurements

The N_2 adsorption-desorption isotherms of all the synthesized catalysts exhibited an IUPAC type I pattern, indicating the existence of micropores (microporous size less than 2 nm diameter) in their assembled frameworks (Rouquerol *et al.*, 1999). Table 4.4 shows the properties from the N_2 adsorption-desorption analysis of synthesized HZSM-5 catalysts. It was found that the BET surface area and micropore volume of the synthesized HZSM-5 catalysts were increased from 313.1 to 374.0 m^2/g, and 0.1312 to 0.1781 cm^3/g, respectively, with increasing time and temperature in hydrothermal synthesis.

Table 4.4 N_2 adsorption-desorption results of the synthesized HZSM-5 catalysts

Catalyst	S_{BET} (m^{2}g^{-1})	**Micropore volume**[a] (cm^{3}g^{-1})	**Total pore volume**[a] (cm^{3}g^{-1})
HZ5A	373.4	0.1685	0.2004
HZ5B1	313.1	0.1312	0.3630
HZ5B2	360.1	0.1690	0.1960
HZ5B3	364.8	0.1730	0.1758
HZ5B4	368.6	0.1741	0.1769
HZ5B5	374.0	0.1781	0.1788

[a] Determined by NLDFT method

4.1.5 TPD of Isopropylamine

Figure 4.3 shows the evolution profiles of the m/e = 41 signal obtained from the TPD of adsorbed isopropylamine on the synthesized HZSM-5 catalysts. Isopropylamine decomposes on Brönsted sites by the Hoffman elimination reaction producing propylene and ammonia. Therefore, quantifying the evolution of propylene as a function of temperature, allows for a reliable determination of the density of strong Brönsted sites, appearing at around 306 °C (Jongpatiwut *et al.*, 2004). However, the density of strong Brönsted acid sites is much higher on the zeolite synthesized at high temperature and long crystallization time. Table 4.5 presents the relative acidity of the synthesized catalysts determined from the areas of m/e = 41 evolution. It was noticed that the relative acidity of HZSM-5 synthesized at 150 °C was lower than that synthesized at 180 °C at a given crystallization time. In addition, the relative acidity of HZSM-5 synthesized for 24 h was lower than that synthesized for 72 h at a given crystallization temperature.

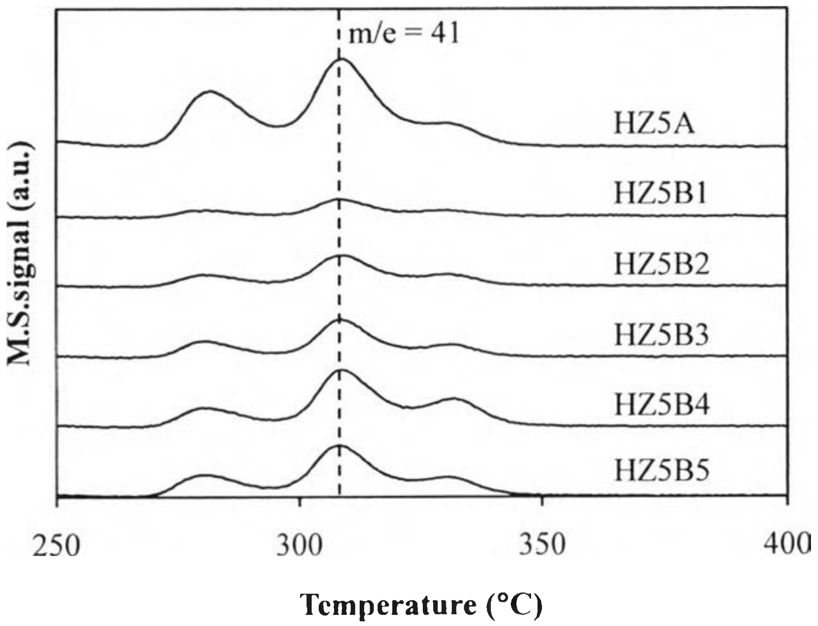


Figure 4.3 Evolution of m/e = 41 during TPD of isopropylamine on the synthesized HZSM-5 catalysts.

Table 4.5 Relative acidity of the synthesized HZSM-5 catalysts

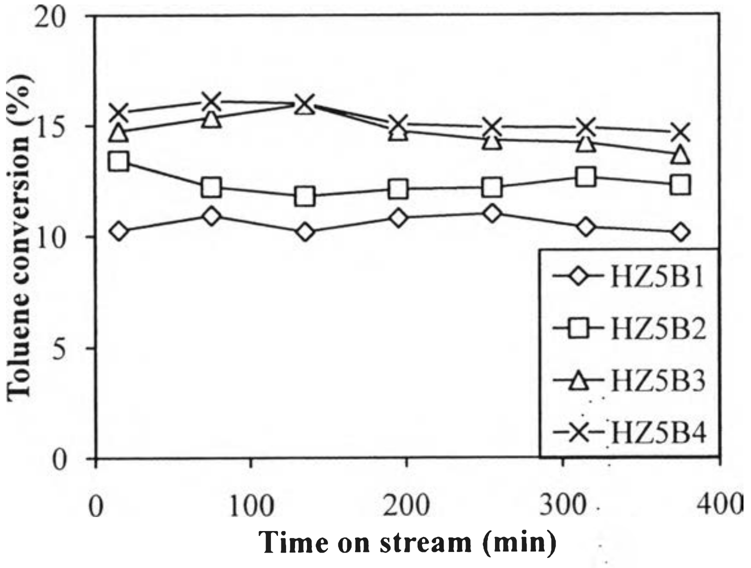
Catalyst	Relative acidity (%)
HZ5A	100.00
HZ5B1	20.15
HZ5B2	35.70
HZ5B3	37.62
HZ5B4	64.50
HZ5B5	57.93

4.2 Catalytic Activity Testing

Based on the characterization results, four HZSM-5 catalysts prepared in different hydrothermal conditions, namely HZ5B1 (150 °C/ 24 h), HZ5B2 (150 °C/ 72 h), HZ5B3 (180 °C/ 24 h) and HZ5B4 (180 °C for 72 h) were selected for their performance tests. Catalytic activity tests of methylation of toluene with methanol under various parameters including weight hourly space velocity (12 h^{-1} to 40 h^{-1}), toluene-to-methanol molar ratio (1:1 to 4:1), and reaction temperature (300 °C to 500 °C) were investigated for the selected catalysts. Moreover, the effect of SiO_2/Al_2O_3 ratio was also studied using HZ5A catalyst.

4.2.1 Effect of Hydrothermal Conditions for Synthesized HZSM-5 Catalysts

Figures 4.4 and 4.5 show the effect of hydrothermal conditions for synthesized HZSM-5 catalysts on the alkylation of toluene with methanol at reaction conditions: temperature = 400 °C, WHSV = 24 h^{-1}, and T/M = 4:1. The HZ5B4 catalyst gave the highest selectivity to *p*-xylene and *p*-xylene yield. This might be due to its highest micropore volume causing the diffusion limitations of *m*-, *o*-xylenes and heavy aromatic hydrocarbons. The conversion of toluene and methanol increased when using HZ5B4 as a catalyst because of its acidity that was the highest than the others.



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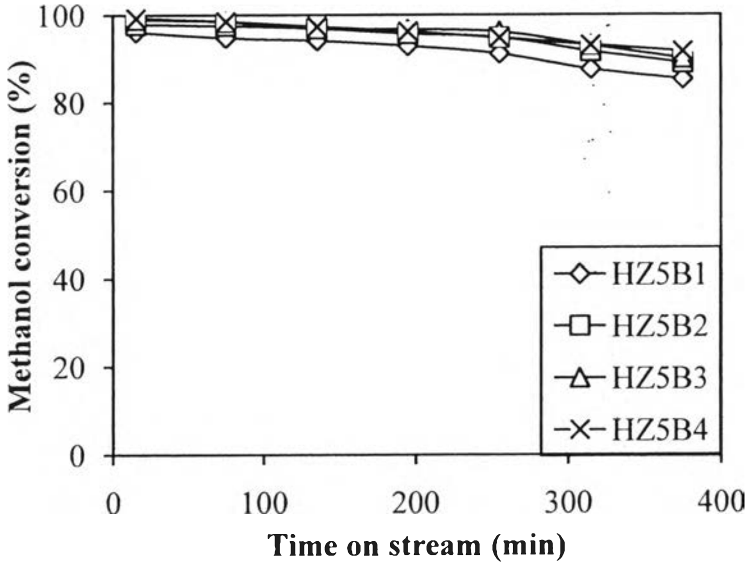


(b)

Figure 4.4 Conversion of (a) toluene and (b) methanol as a function of time on stream of HZSM-5 synthesized in different hydrothermal conditions (Reaction conditions: Temperature = 400 °C, WHSV = 24 h^{-1}, and T/M = 4:1).

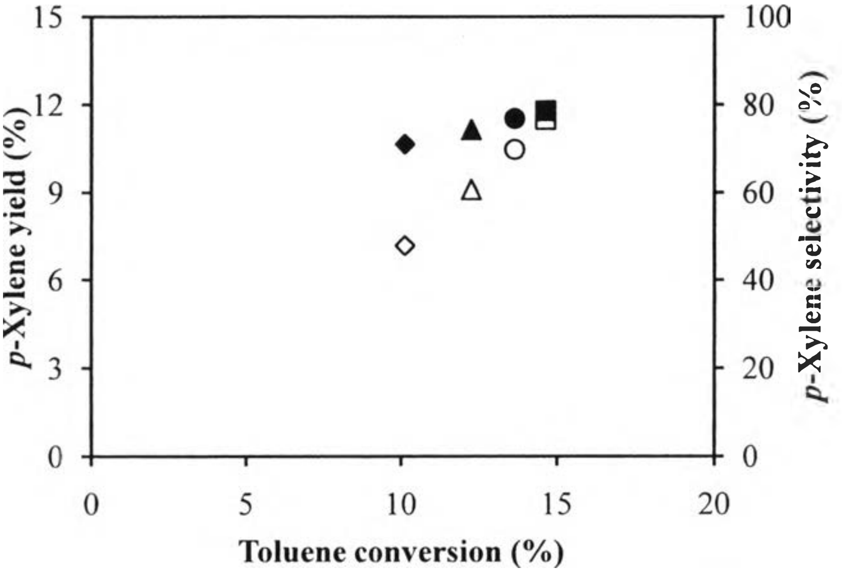


Figure 4.5 Plot of *p*-xylene yield and *p*-xylene selectivity versus toluene conversion over (◇,◆) HZ5B1, (△,▲) HZ5B2, (○,●) HZ5B3, and (□,■) HZ5B4 at temperature = 400 °C, WHSV = 24 h^{-1}, T/M = 4:1. Open symbol: *p*-xylene yield, filled symbol: *p*-xylene selectivity.

Table 4.6 presents the effect of hydrothermal conditions for synthesized HZSM-5 catalysts on products selectivity. HZ5B4 gave the highest selectivity to *p*-xylene and the least selectivity to TMBs.

Table 4.6 Effect of hydrothermal conditions for synthesized HZSM-5 catalysts on the products selectivity[a]

Catalyst	Conversion (%)		Selectivity (%)			
	Toluene	Methanol	*p*-Xylene	*m*-Xylene	*o*-Xylene	TMBs[b]
HZ5B1	10.12	85.30	71.04	11.26	8.40	9.30
HZ5B2	12.25	89.00	74.27	10.34	6.13	9.26
HZ5B3	13.64	90.06	76.85	10.16	5.98	7.01
HZ5B4	14.64	91.66	78.61	9.97	5.60	5.81

[a] Reaction conditions: T = 400 °C, WHSV = 24 h^{-1}, T/M= 4:1, TOS = 375 min.

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

According to the estimations of methanol conversion to aromatics from self-aromatization and to alkyl group by methylation (see Appendix C), Table 4.7 shows the estimated fractions of methanol converted to aromatics ring and alkyl group from self-aromatization and by methylation, respectively, for the synthesized catalysts at reaction condition: temperature = 400 °C, WHSV = 24 h^{-1}, and T/M = 4:1.

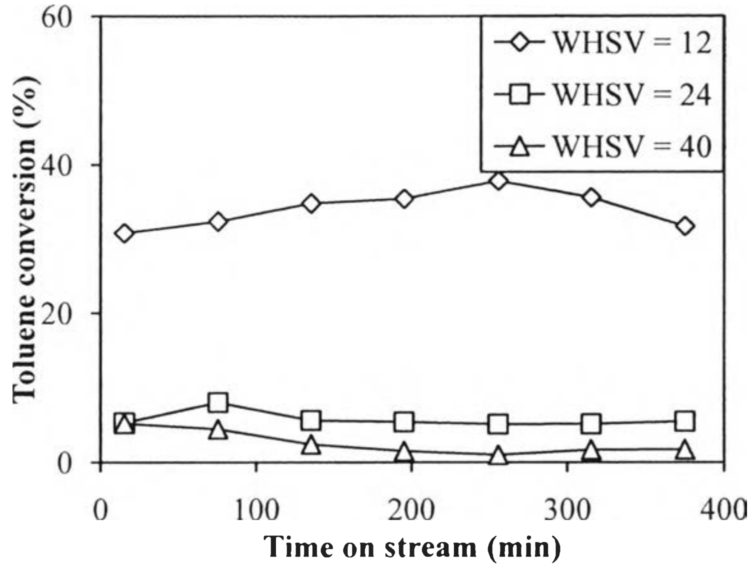
In overall, the self-aromatization was dominated and accounted for about 80% for all the catalysts at particular reaction conditions indicated. However, HZ5B4 seemed to yield the highest methanol conversion by methylation (the least self aromatization) resulting in the most toluene conversion as compared to the others (Table 4.6).

Table 4.7 The estimated fractions of methanol converted to aromatics ring and alkyl group from self-aromatization and by methylation for the synthesized catalysts

Catalyst	Methanol to aromatics ring (%) (self-aromatization)	Methanol to alkyl group (%) (methylation)
HZ5B1	82.1	17.9
HZ5B2	81.0	19.0
HZ5B3	80.4	19.6
HZ5B4	78.5	21.5

4.2.2 Effect of WHSV

The effect of WHSV on toluene conversion, methanol conversion and products selectivity was studied over the HZ5B4 using a feed T/M ratio of 1:1 at 400 °C. The conversion results are presented in Figure 4.6 by which the toluene and methanol conversions decreased with an increase in WHSV from 12 to 40 h^{-1}. This is because a decrease in contact time postponed the opportunity of the reaction steps to occur resulting in decreasing both conversions. The selectivity to *p*-xylene seemed to be the highest at a WHSV 24 h^{-1} as shown in Figure 4.7.



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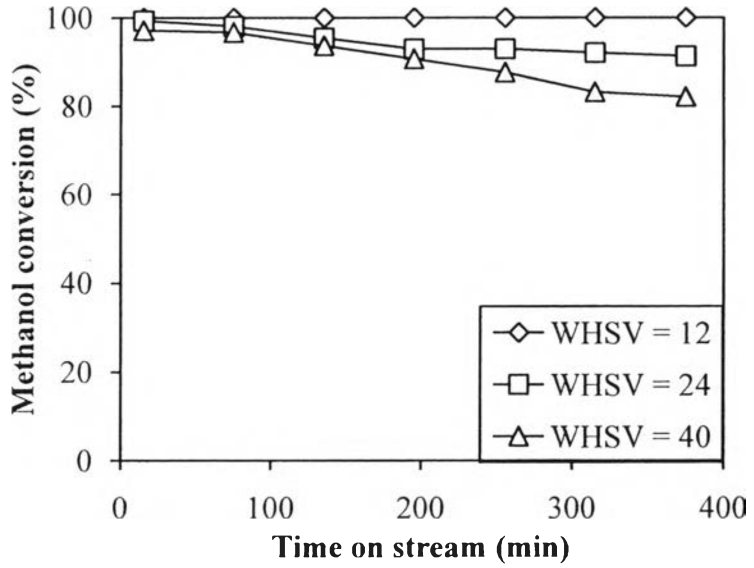


(b)

Figure 4.6 Conversion of (a) toluene and (b) methanol as a function of time on stream over HZ5B4 in different WHSV (Reaction conditions: Temperature = 400 °C, and T/M = 1:1).

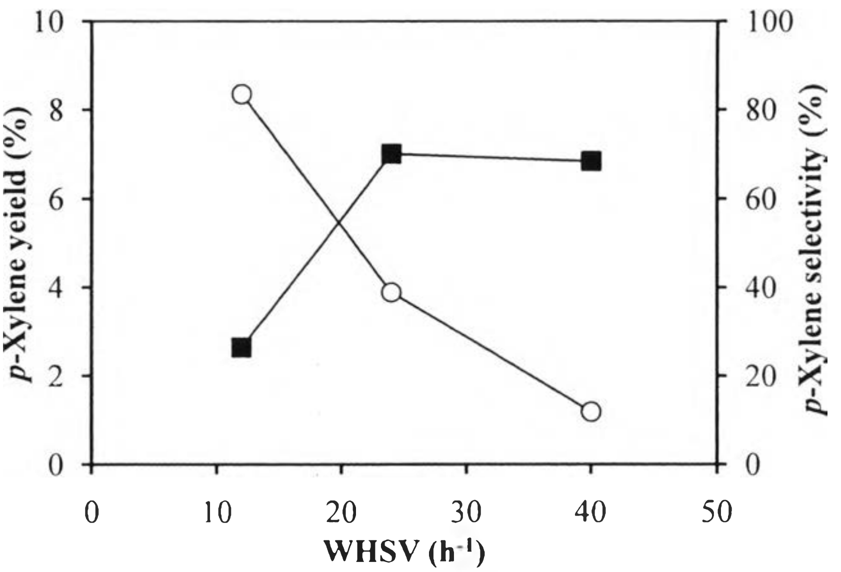


Figure 4.7 Plot of *p*-xylene yield and *p*-xylene selectivity versus WHSV over HZ5B4 at temperature = 400 °C and T/M = 1:1. Open symbol: *p*-xylene yield, filled symbol: *p*-xylene selectivity.

Table 4.8 presents the effect of WHSV on products selectivity. As can be seen, the selectivity to *p*-xylene increased as WHSV increased to 24 h^{-1} but decreased when WHSV increased to 40 h^{-1}. Therefore, the WHSV of 24 h^{-1} was used in further studied.

It should be noticed that at a WHSV of 12 h^{-1}, the presences of benzene, ethylene, and ethylbenzene were observed indicating that the occurrence of secondary reactions and cracking would be favorable at a low WHSV.

Table 4.8 Effect of WHSV on the products selectivity over HZ5B4[a]

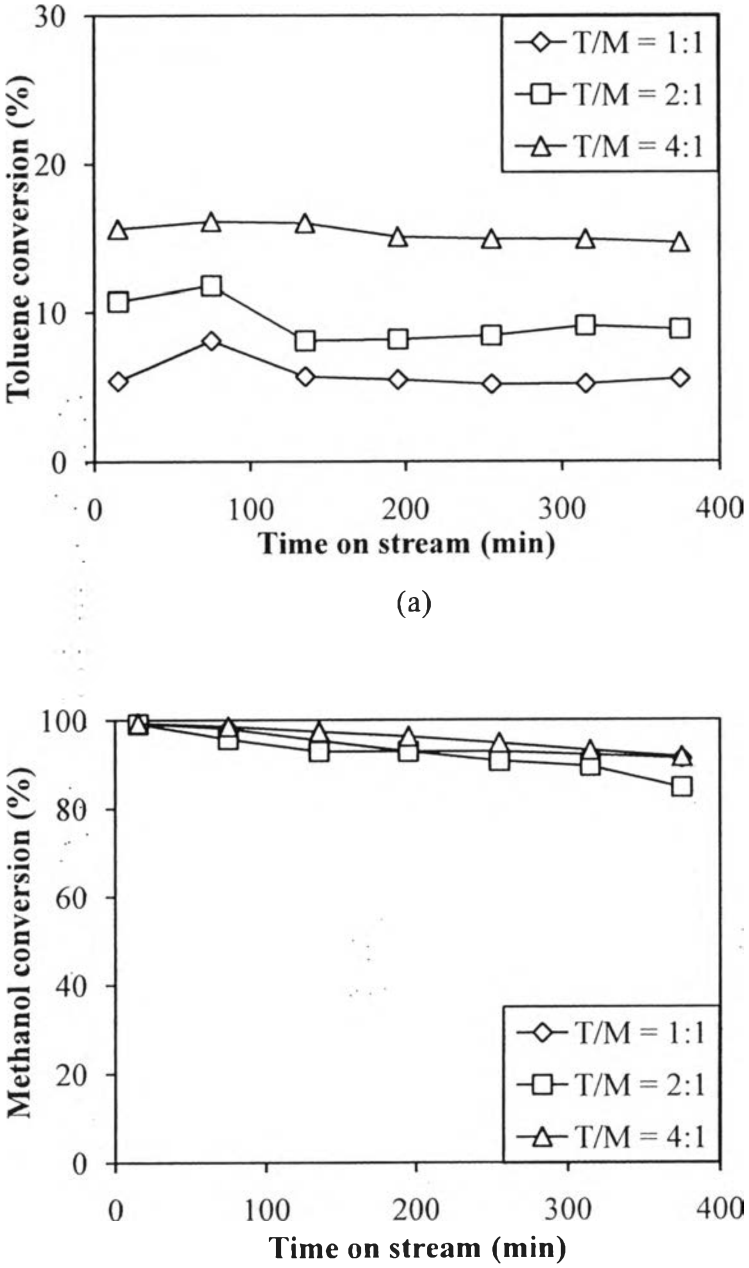
WHSV	Products Selectivity (%)						
(h^{-1})	BZ	Ethylene	EB	*p*-Xylene	*m*-Xylene	*o*-Xylene	TMBs[b]
12	1.36	0.11	0.44	28.78	38.25	14.39	16.67
24	-	-	-	70.16	11.96	7.83	10.05
40	-	-	-	68.45	12.55	9.59	9.41

[a] Reaction conditions: T = 400 °C, T/M= 1:1, TOS = 375 min.

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

4.2.3 Effect of T/M Ratio

The effect of T/M ratio was studied by varying the toluene-to-methanol (T/M) feed molar ratios from 1:1 to 4:1 over HZ5B4 at 400 °C and WHSV 24 h^{-1}. The conversions of toluene and methanol as a function of time on stream are given in Figure 4.8. The conversion of toluene was increases with increasing toluene concentration. According to Figure 4.9, this indicates that as the toluene concentration was increased, the selectivity to *p*-xylene was slightly increased because the reaction typically requires 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).



(a)

(b)

Figure 4.8 Conversion of (a) toluene and (b) methanol as a function of time on stream over HZ5B4 in different toluene-to-methanol (T/M) molar ratio (Reaction conditions: Temperature = 400 °C, and WHSV = 24 h^{-1}).

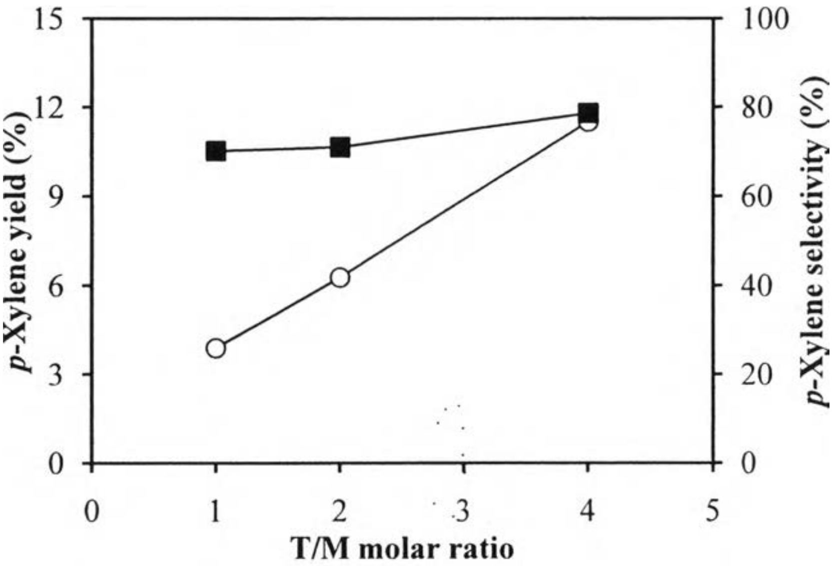


Figure 4.9 Plot of *p*-xylene yield and *p*-xylene selectivity versus T/M molar ratio over HZ5B4 at temperature = 400 °C and WHSV = 24 h^{-1}. Open symbol: *p*-xylene yield, filled symbol: *p*-xylene selectivity.

Table 4.9 presents the effect of T/M feed ratio on the products selectivity. The selectivity to *p*-xylene was increased (whereas the selectivity to the other products was decreased) with increasing T/M feed ratio resulting from high degree of dilution. In other words, as a toluene concentration increases, a selectivity to *p*-xylene increases.

Table 4.9 Effect of T/M ratio on the products selectivity over HZ5B4[a]

T/M	**Conversion (%)**		**Selectivity (%)**			
ratio	**Toluene**	**Methanol**	***p*-Xylene**	***m*-Xylene**	***o*-Xylene**	**TMBs[b]**
1:1	5.55	91.31	70.16	11.96	7.83	10.05
2:1	8.84	89.73	70.99	11.85	9.06	8.10
4:1	14.64	91.66	78.61	9.97	5.60	5.81

[a] Reaction conditions: T = 400 °C, WHSV = 24 h^{-1}, TOS = 375 min.

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

4.2.4 Effect of Reaction Temperature

The alkylation of toluene with methanol was carried out at 300, 400 and 500 °C over HZ5B4 with a WHSV of 24 h^{-1}, and a T/M ratio of 4:1. According to Figure 4.10, the conversion of toluene was increased as a temperature was increased due to its nature of endothermic reaction. According to Figure 4.11, for methylation of toluene and xylene isomerization on HZSM-5 catalyst, it was suggested that the high *p*-xylene selectivity obtained above 300 °C was because the rate of reaction was governed by a diffusion limitation at high temperature (Mirth *et al.*, 1993).

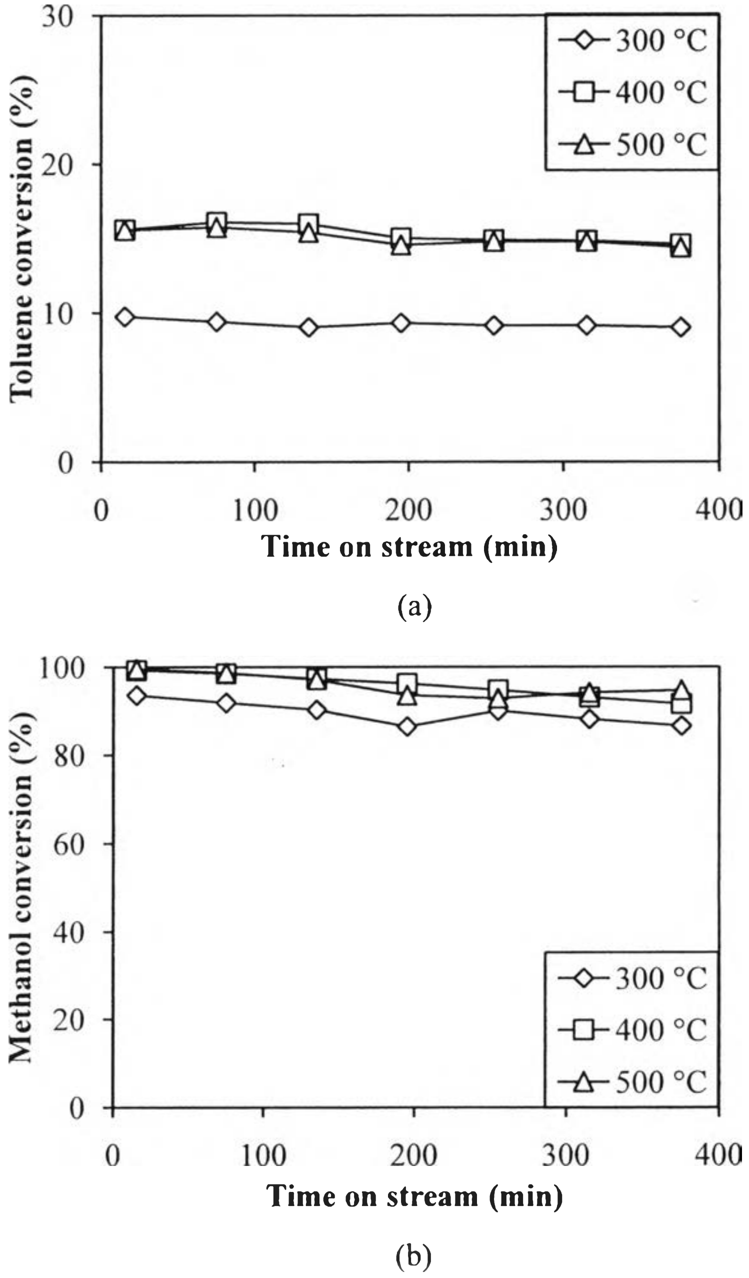


Figure 4.10 Conversion of (a) toluene and (b) methanol as a function of time on stream over HZ5B4 with different reaction temperature (Reaction conditions: WHSV = 24 h^{-1}, and T/M = 4:1).

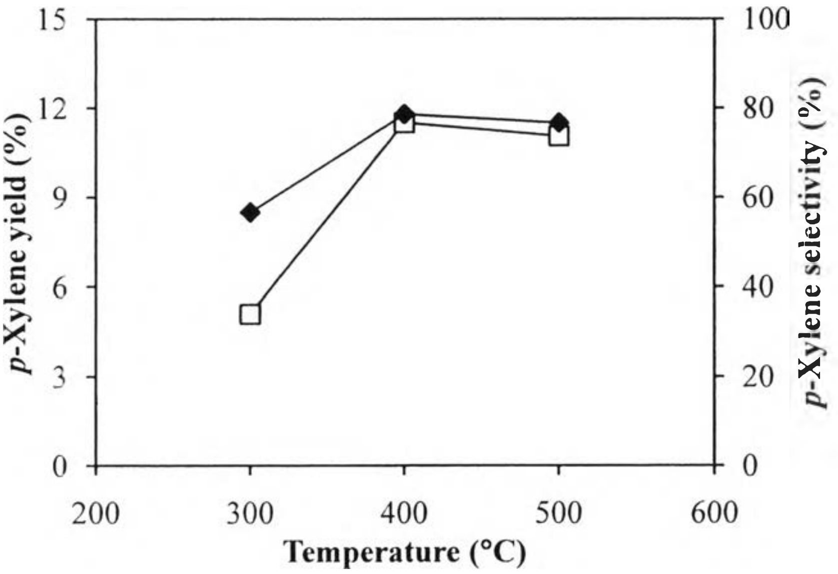


Figure 4.11 Plot of *p*-xylene yield and *p*-xylene selectivity versus temperature over HZ5B4 at WHSV =24 h^{-1}, and T/M = 4:1. Open symbol: *p*-xylene yield, filled symbol: *p*-xylene selectivity.

Table 4.10 shows the products selectivity at different temperatures over HZ5B4. It can be observed that the *p*-xylene selectivity increased with increasing temperature from 300 °C to 400 °C in which the highest selectivity to *p*-xylene was 78.61% at 400 °C. As a reaction temperature was increased to 500 °C, the *p*-xylene selectivity was slightly decreased but the other isomers (*m*- and *o*-) were slightly increased indicating that the influence of izomerization reactions. Since, it was found that no reactions was occurred at the temperature lower than 300 °C, therefore, the temperature of 400 °C was selected for the further studies.

Table 4.10 Effect of temperature on the products selectivity over HZ5B4[a]

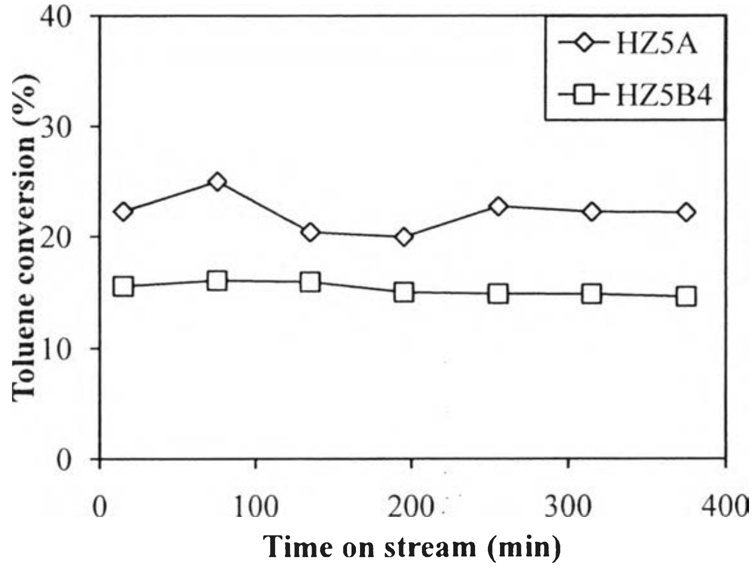
Temperature (°C)	**Conversion (%)**		**Selectivity (%)**			
	Toluene	**Methanol**	***p*-Xylene**	***m*-Xylene**	***o*-Xylene**	**TMBs[b]**
300	9.00	86.62	56.62	20.59	15.57	7.23
400	14.64	91.66	78.61	9.97	5.60	5.81
500	14.41	94.71	76.67	12.80	6.19	4.34

[a] Reaction conditions: WHSV = 24 h^{-1}, T/M = 4:1, TOS = 375 min.

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

4.2.5 Effect of SiO_2/Al_2O_3 Ratio

Figure 4.12 shows the effect of different SiO_2/Al_2O_3 ratios on the alkylation of toluene with methanol over the synthesized HZSM-5 catalysts. The HZ5A catalyst having a SiO_2/Al_2O_3 of 90 showed higher both toluene and methanol conversions than the HZ5B4 catalyst having a SiO_2/Al_2O_3 of 181. It was also observed that the HZ5A could convert the methanol to its completion, but give significantly less selectivity to *p*-xylene. According to the work by Moser et al. (1989), it was indicated that a low Si/Al catalyst transformed methanol mainly on strong acidic sites based on AlOH groups. Since the conversion of methanol for a given catalyst was higher than toluene conversion, therefore, the reaction of methanol transformation into other hydrocarbons would occur simultaneously over this catalyst. Figure 4.13 shows the catalytic activity of the toluene methylation over HZ5B4 that gave higher *para*-selectivity than HZ5A.



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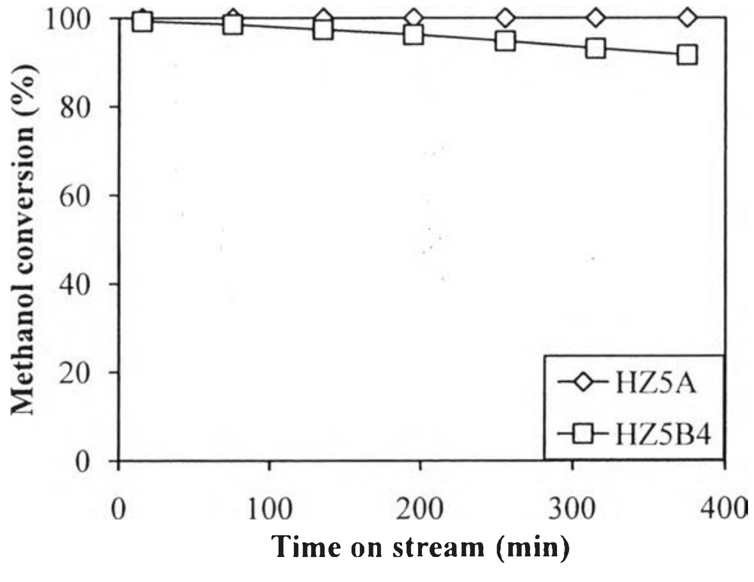

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Figure 4.12 Conversion of (a) toluene and (b) methanol as a function of time on stream over HZ5A and HZ5B4 (Reaction conditions: Temperature = 400 °C, WHSV = 24 h^{-1}, and T/M = 4:1).

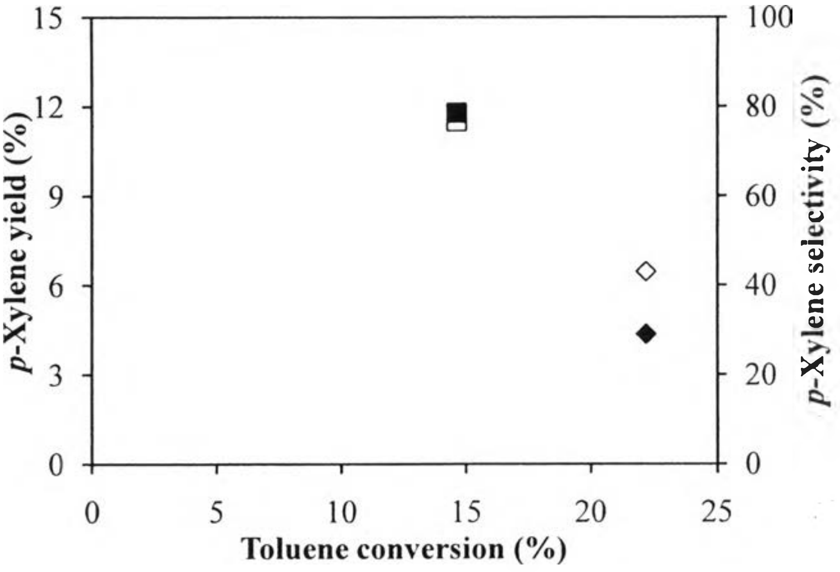

Figure 4.13 Plot of *p*-xylene yield and *p*-xylene selectivity versus toluene conversion over (◇,◆) HZ5A and (□,■) HZ5B4 at temperature = 400 °C, WHSV = 24 h^{-1}, and T/M = 4:1. Open symbol: *p*-xylene yield, filled symbol: *p*-xylene selectivity.

Table 4.11 shows the products selectivity of HZSM-5 catalysts with different SiO_2/Al_2O_3 ratios. When increasing SiO_2/Al_2O_3 ratio, the selectivity to *p*-xylene increased. The HZ5B4 provided higher selectivity to *p*-xylene and lower selectivity to the other products than the HZ5A. In addition to the viewpoint of the acidity of catalysts (zeolite), the contributions of methyl group of methanol to self-aromatization and methylation were also considered in this work. The estimations for such contributions on both catalysts are presented in Table 4.12. It is apparent that the fraction on methylation for HZ5A is about twice as high as compared to that of HZ5B4. This is a reason why the HZ5B4 yielded lower toluene conversion and selectivity to TMBs than the HZ5A.

Table 4.11 Effect of SiO_2/Al_2O_3 ratio of the synthesized HZSM-5 on the products selectivity [a]

Catalyst	Conversion (%)		Selectivity (%)			
	Toluene	Methanol	*p*-Xylene	*m*-Xylene	*o*-Xylene	TMBs[b]
HZ5A	22.20	100.00	29.09	41.44	16.03	13.44
HZ5B4	14.64	91.66	78.61	9.97	5.60	5.81

[a] Reaction conditions: T = 400 °C, WHSV = 24 h^{-1}, T/M = 4:1, TOS = 375 min.

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

Table 4.12 The estimated fractions of methanol converted to aromatics ring and alkyl group from self-aromatization and by methylation for the synthesized catalysts

Catalyst	Methanol to aromatics ring (%) (self-aromatization)	Methanol to alkyl group (%) (methylation)
HZ5A	60.3	39.7
HZ5B4	78.5	21.5

4.2.6 The Catalyst Stability Test

The stability of the catalyst was carried out on the alkylation of toluene with methanol over HZ5B4 at temperature of 400 °C, a WHSV of 24 h^{-1}, and T/M of 4:1. The results are shown in Figure 4.14. It was found that at time on stream of 3015 min, the conversion of methanol is dropped from 99.24% to 87.30%. Moreover, the selectivity to *p*-xylene was decreased significantly from 84.33% to 63.14% at time on stream of 3015 min. This is because of catalyst deactivation due to the blockage of micropores by the carbon deposition.

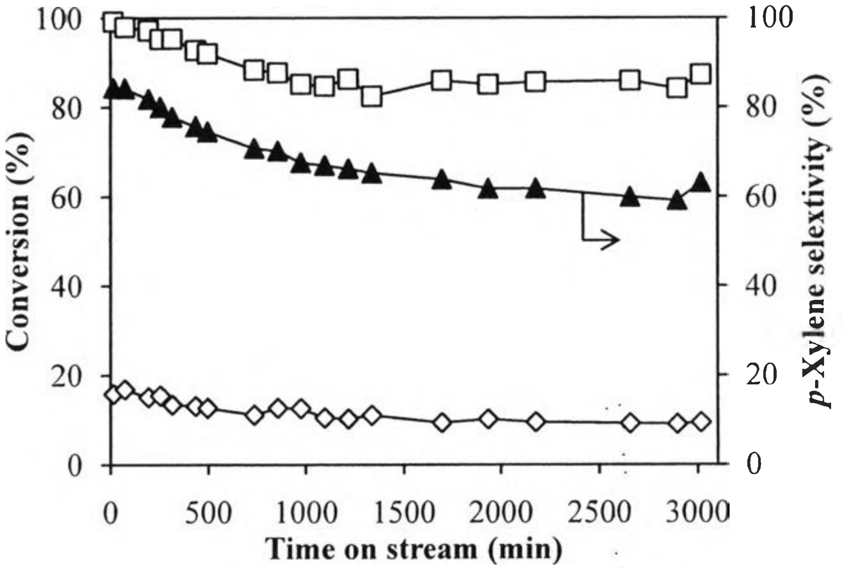

Figure 4.14 Conversion and *p*-xylene selectivity over HZ5B4 at temperature = 400 °C, WHSV = 24 h^{-1}, T/M = 4:1 and TOS = 3015 min. Open symbol: (◇) toluene conversion, and (□) methanol conversion, filled symbol: (▲) *p*-xylene selectivity.

4.2.7 Characterization of Carbon Deposition

The spent catalysts were analyzed by TPO technique to observe the coke formation. The spent HZ5B4 catalysts were characterized for the coke formation. As shown in Figure 4.15, the TPO profiles show two peaks in that the first one is at temperature about 400 °C and the second one is at 700 °C indicating at least two different types of carbon were formed at different locations in which the majority of carbon deposited was contributed to a high temperature carbon formation. 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 the polyaromatic molecules formed by hydrogen transfer reaction on acidic caetalysts (Guisnet *et al.*, 2001). Moreover, the amount of carbon formed under different operating conditions which were determined by TPO technique are shown in Table 4.13.

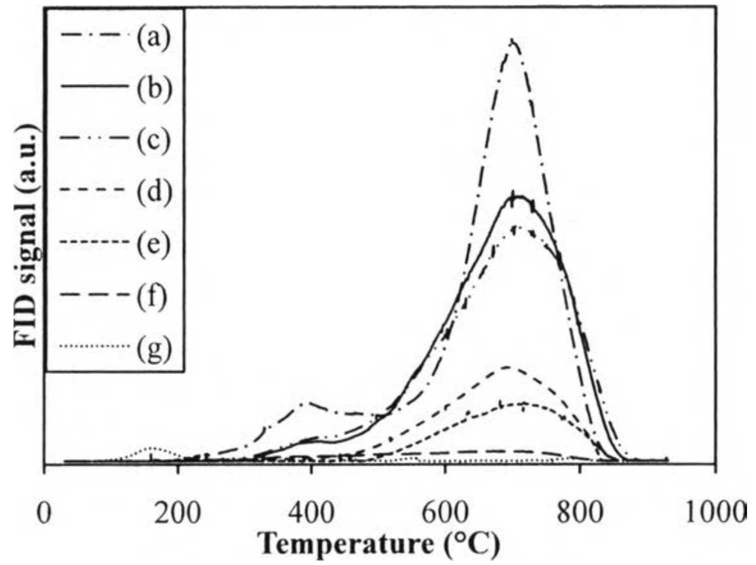

Figure 4.15 TPO profiles of spent HZ5B4 catalysts at various reaction conditions taken at TOS = 375 min: (a) Temp. = 400 °C, WHSV = 12 h^{-1}, and T/M = 1:1, (b) Temp. = 400 °C, WHSV = 40 h^{-1}, and T/M = 1:1, (c) Temp. = 400 °C, WHSV = 24 h^{-1}, and T/M = 1:1, (d) Temp. = 300 °C, WHSV = 24 h^{-1}, and T/M = 4:1, (e) Temp. = 500 °C, WHSV = 24 h^{-1}, and T/M = 4:1, (f) Temp. = 400 °C, WHSV = 24 h^{-1}, and T/M = 2:1, and (g) Temp. = 400 °C, WHSV = 24 h^{-1}, and T/M = 4:1.

From Table 4.13, the amount of carbon formation of spent HZ5B4 at the same temperature (400 °C) and T/M ratio (1:1) was 15.96%, 14.97% and 13.24% for reaction conditions (a), (b) and (c), respectively, in which the carbon formation seemed to be the least at a WHSV of 24 h^{-1}. At the same temperature (400 °C) and WHSV (24 h^{-1}), the amount of carbon formation of spent HZ5B4 was 13.24%, 0.69%, and 0.35% for reaction conditions (c), (f), and (g), respectively, it was found that the coke formation decreased with increasing T/M ratio. The amount of carbon formation of spent HZ5B4 at the same WHSV (24 h^{-1}) and T/M ratio (4:1) was 6.19%, 3.16% and 0.35% for reaction conditions (d), (e) and (g), respectively, in which the carbon formation seemed to be the least at temperature 400 °C.

It is apparent that the reaction condition (g) which yielded the least carbon formation also resulted in the best performance of the catalysts investigated in terms of conversion, selectivity to *p*-xylene, and catalyst deactivation by coke formation.

Table 4.13 Carbon formation on the spent HZ5B4 catalysts at each reaction condition

Reaction condition	**Carbon amount (wt%)**
a	15.96
b	14.67
c	13.24
d	6.19
e	3.16
f	0.69
g	0.35