



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Hydrogenolysis of Ethylbenzene

Firstly, hydrogenolysis of ethylbenzene (EB) was studied over the Pt/SiO₂ catalyst at 300°C, 100 psi, LHSV of 2 h⁻¹, and H₂/EB ratio of 6. It was found that the hydrogenolysis did not occur over the Pt/SiO₂ catalyst as no product was observed in the effluent liquid. It is indicated that the synthesized Pt/SiO₂ was not a promising catalyst for hydrogenolysis reaction. However, the literature revealed that catalysts containing molybdenum oxide (Covini *et al.*, 1965), nickel oxide (Van *et al.*, 1987), and nickel-molybdenum oxide (Jik *et al.*, 1987) were also sufficiently active for this purpose. Therefore, the Ni/Al₂O₃, Mo/Al₂O₃, and NiMo/Al₂O₃ catalysts were employed in order to study hydrogenolysis reaction under various conditions.

In order to discuss the reaction mechanisms, a detail reaction network should be constructed. To do this and find which products are primary, secondary, stable, or unstable, we need to consider the selectivity of products at different levels of conversion. The selectivities of different product from hydrogenolysis of ethylbenzene obtained over the commercial NiMo/Al₂O₃ catalyst versus ethylbenzene conversion are plotted in Figure 4.1. From the results obtained, it appeared that a series of parallel and consecutive reactions occurred when using ethylbenzene as a model feed. The results indicated that ethylbenzene underwent hydrogenolysis reaction yielding toluene and benzene. The selectivity into toluene decreased when the ethylbenzene conversion increased, whereas the selectivity into benzene increased. This behavior can be explained considering that toluene was a primary product from hydrogenolysis of ethylbenzene while benzene was a secondary one. On the basis of the results obtained, the reaction scheme for the ethylbenzene hydrogenolysis can be proposed as shown in Figure 4.2.

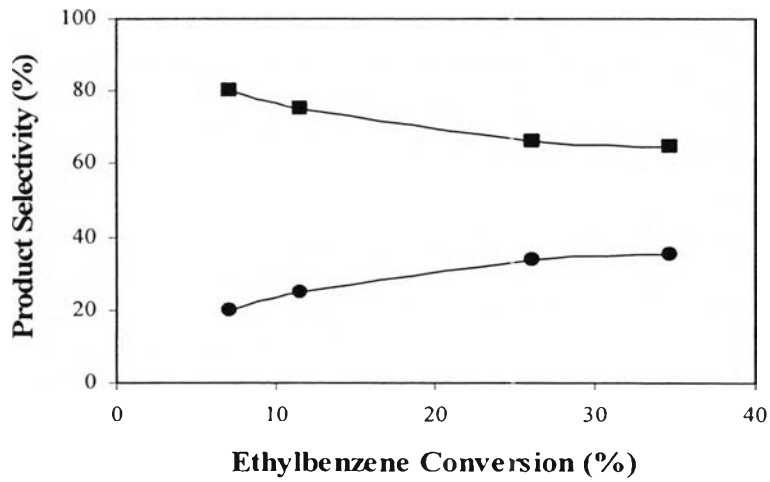


Figure 4.1 Selectivity of product from ethylbenzene hydrogenolysis: (■) toluene, and (●) benzene versus ethylbenzene conversion at 400°C, 50 psi, H₂/EB ratio = 4.

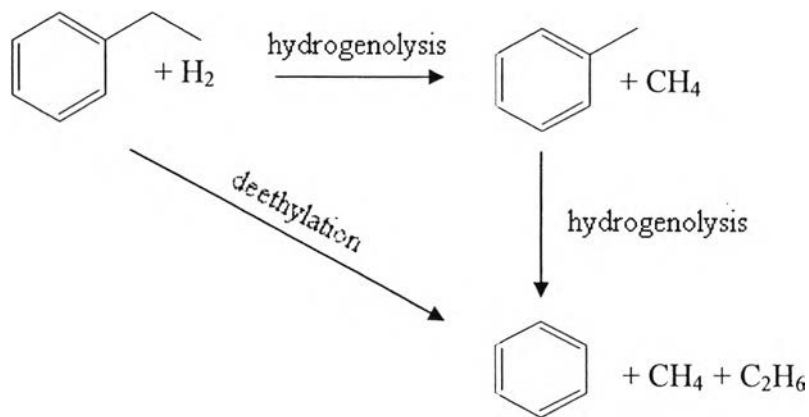


Figure 4.2 Proposed reaction pathways for ethylbenzene.

According to the analysis of gas products, methane was detected as a major composition with a small amount of ethane. This result demonstrated that some of benzene was directly produced from deethylation of ethylbenzene as shown in Figure 4.2.

4.1.1 Effect of Reaction Temperature

The effect of reaction temperature on toluene selectivity and ethylbenzene conversion was studied at the temperature ranging from 400 to 500°C and the catalytic results are given in Figure 4.3.

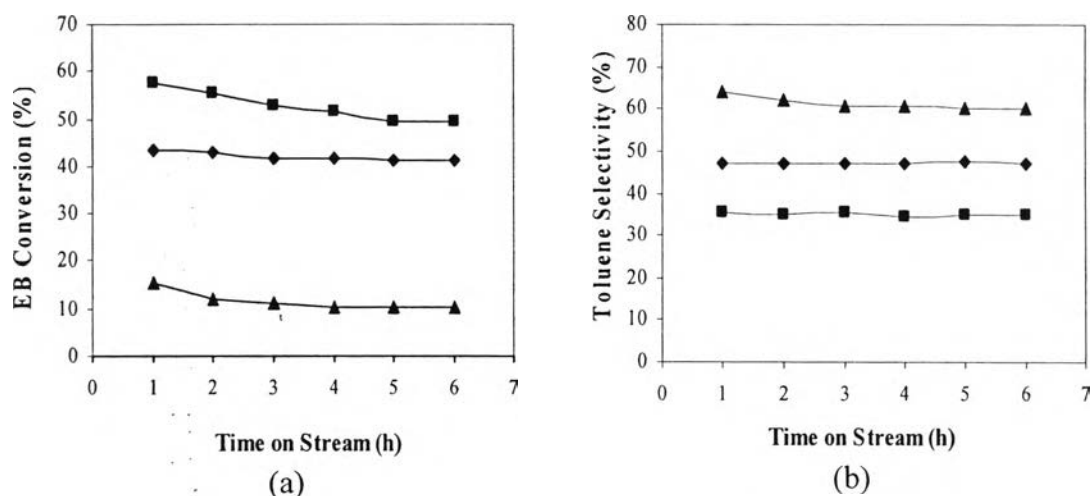


Figure 4.3 Catalytic activity of NiMo/Al₂O₃ catalyst for (a) ethylbenzene conversion, and (b) toluene selectivity at 50 psi, H₂/EB ratio = 4, LHSV = 2 h⁻¹, and temperature: (▲) 400°C, (◆) 450°C, and (■) 500°C.

As shown in Figure 4.3, it can be seen that when the reaction temperature increased from 400 to 500°C, the toluene selectivity decreased. This observation is in good agreement with the previous work (Van *et al.*, 1987). They proposed that the rate of the first hydrodemethylation increased less with temperature than the rate of the second one. It can be easily explained that at higher temperature secondary hydrogenolysis was favorable; ethylbenzene giving toluene, which in turn was hydrodemethylated into benzene. Despite the selectivity of toluene was relatively low at high temperature, the conversion of ethylbenzene showed inversely result; a high conversion shown in Figure 4.3(a). In order to achieve both high toluene selectivity and ethylbenzene conversion, the optimum liquid hourly space velocity (LHSV) must be elucidated.

4.1.2 Effect of LHSV

The effect of LHSV was investigated in the range of 2 to 4 h⁻¹ by changing the feed flowrate. The selectivity of toluene versus time on stream at 500, 450, and 400°C are presented in Figures 4.4, 4.5, and 4.6, respectively.

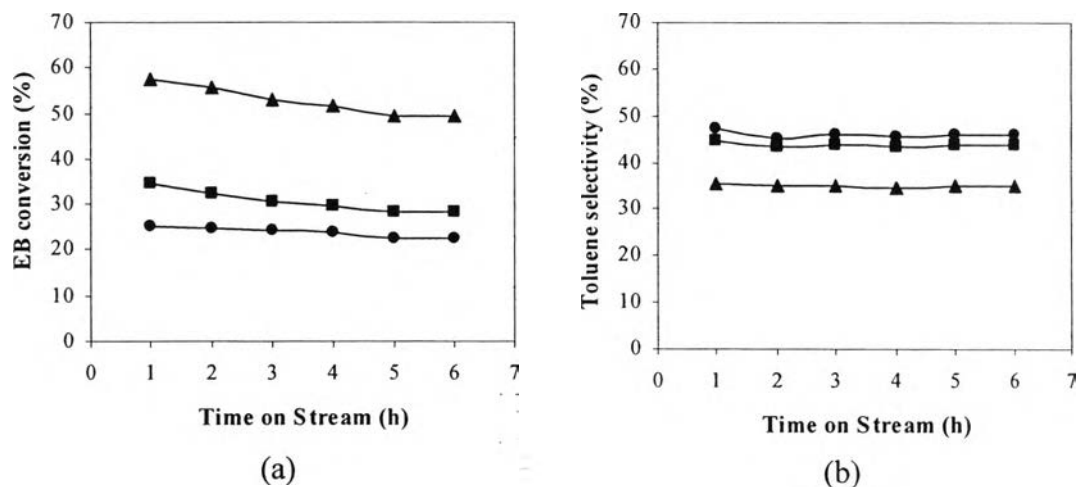


Figure 4.4 Catalytic activity of NiMo/Al₂O₃ catalyst for (a) ethylbenzene conversion, and (b) toluene selectivity at 500°C, 50 psi, H₂/EB ratio = 4, and LHSV: (▲) 2 h⁻¹, (■) 3 h⁻¹, and (●) 4 h⁻¹.

The analysis indicated that the higher LHSV the higher toluene selectivity; however, at higher LHSV ethylbenzene conversion was low. This phenomenon could be explained by that at a given temperature, as the LHSV was decreased, the contact time between ethylbenzene and catalyst was increased. This longer contact time allowed the sequential hydrogenolysis. This observation is in good agreement with Van work (1987) that at 500°C, by varying LHSV, the selectivity of toluene cannot be enhanced to be higher than benzene selectivity (Table 4.1). This result was also observed at the temperature of 450°C. Moreover, at 400°C; further increasing of LHSV to 4 h⁻¹ did not result in a noticeable change in toluene selectivity (Figure 4.5(b)) whereas the significant decreased in ethylbenzene conversion was observed (Figure 4.5(a)). In those cases, it is clear that the hydrogenolysis of ethylbenzene to toluene was not favorable at the temperature above 400°C.

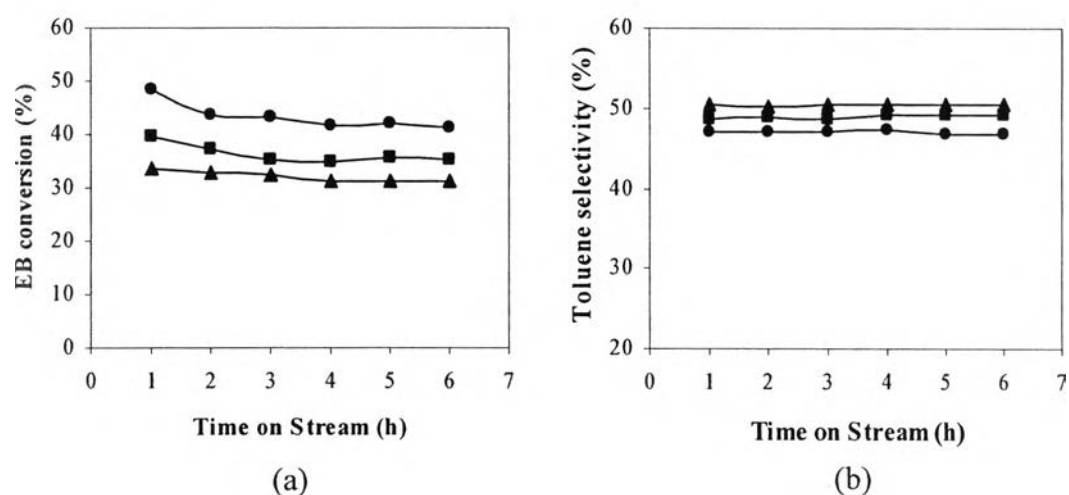


Figure 4.5 Catalytic activity of NiMo/Al₂O₃ catalyst for (a) ethylbenzene conversion, and (b) toluene selectivity at 450°C, 50 psi, H₂/EB ratio = 4, and LHSV: (▲) 2 h⁻¹, (■) 3 h⁻¹, and (●) 4 h⁻¹.

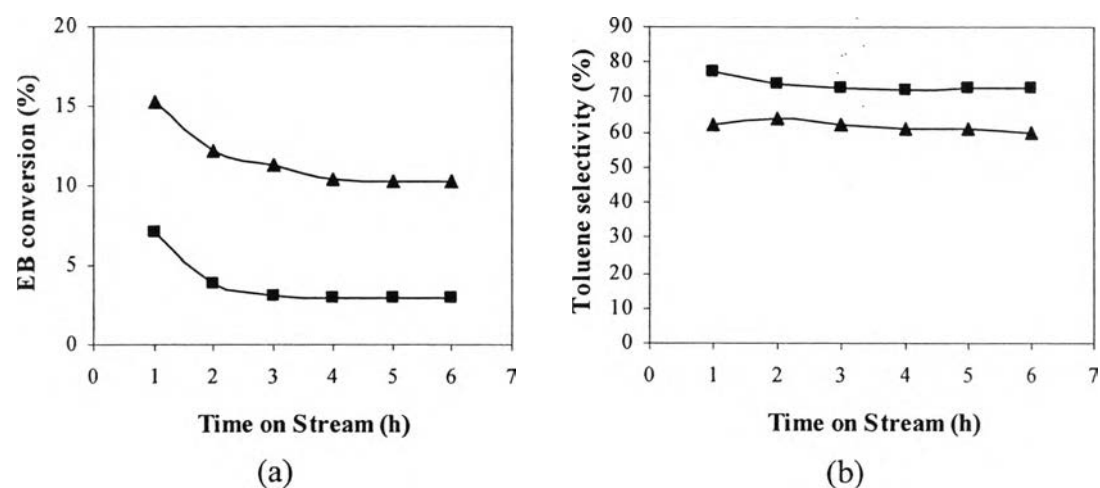


Figure 4.6 Catalytic activity of NiMo/Al₂O₃ catalyst for (a) ethylbenzene conversion, and (b) toluene selectivity at 400°C, 50 psi, H₂/EB = 4, and LHSV: (▲) 2 h⁻¹, and (■) 3 h⁻¹.

The results at temperature of 400°C, as well as the results at 450 and 500°C, tended to show that the selectivity of toluene increased as LHSV increased. However, at LHSV of 3 h⁻¹, the selectivity of toluene was high (Figure 4.6(b)) in contrast to the ethylbenzene conversion, a very low conversion around 3% (Figure

4.6(a)). Therefore, it is not economical to test at elevated LSHV because the ethylbenzene conversion would be lower than 3%.

From the above results, it is clear that at the temperature of 450 and 500°C, the rising of LHSV did not enhance toluene selectivity to be higher than benzene. Therefore, at 400°C and LHSV of 2 h⁻¹ were selected for further studies.

Table 4.1 Product distribution at 5 h TOS of different conditions

Temperature (°C)	LHSV (h ⁻¹)	Conversion (%)	Product distribution (%)	
			Benzene	Toluene
400	2	10.3	39.2	60.8
	3	3.0	27.6	72.4
450	2	41.8	53.2	46.8
	3	35.4	50.9	49.1
	4	31.1	49.7	50.3
500	2	49.3	65.0	35.0
	3	28.2	56.2	43.8
	4	22.6	54.0	46.0

4.1.3 Effect of H₂ to Feed Ratio

The effect of H₂ to feed ratio at 400°C is shown in Figure 4.7. The results showed that when a H₂ to feed ratio increased, the toluene selectivity increased while the ethylbenzene conversion slightly decreased. Van *et al.* (1987) suggested that alkylbenzenes were preferentially adsorbed perpendicularly to the metals surface by fixation of the terminal carbon of the alkyl chain. The presence of hydrogen may favor the formation of such species by competitive adsorption of H₂ and of alkylbenzenes on metallic sites. The hydrocarbon molecules were forced to occupy a minimum metallic surface and the σ - adsorption was favored by comparison with the π - adsorption. Such a behavior also underlines that multiple hydrogenolysis was not liable to occur easily. Therefore, the selectivity of toluene was enhanced by the increasing of H₂/EB ratio as shown in Figure 4.7. However, the further increasing of

H_2/EB ratio from 8 to 10 resulted in slightly increased in toluene selectivity meanwhile ethylbenzene conversion was lower as well, thus hydrogenolysis of ethylbenzene at a H_2/EB ratio of 10 was not economically feasible.

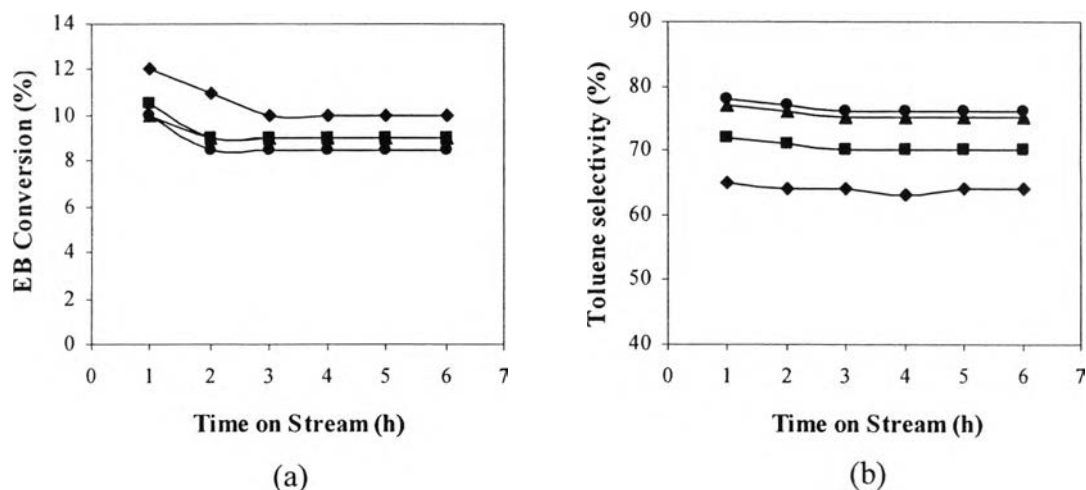


Figure 4.7 Catalytic activity of NiMo/Al₂O₃ catalyst for (a) ethylbenzene conversion, and (b) toluene selectivity at 400°C, 50 psi, LHSV = 2 h⁻¹, and H₂/EB ratio: (◆) 4, (■) 6, (▲) 8, and (●) 10.

From the obtained results, it is important to note that hydrogenolysis of ethylbenzene to toluene was principally determined by reaction temperature, LHSV, and H₂/feed ratio. The condition that provides the highest toluene selectivity is at 400°C, 50 psi, LHSV of 2 h⁻¹, and H₂/feed ratio of 8. Consequently, the hydrogenolysis of *para*-methylethylbenzene was studied at this condition.

4.1.4 Effect of Catalyst

The hydrogenolysis of ethylbenzene was also studied on the synthesized Mo/Al₂O₃, Ni/Al₂O₃, and NiMo/Al₂O₃ catalysts. The comparison in catalytic activity among four different catalysts at 400°C, 50 psi, LHSV of 2 h⁻¹, and H₂/EB ratio of 8 is presented in Table 4.2.

Table 4.2 Product selectivity and ethylbenzene conversion at 5 h TOS of different catalysts

Catalyst	Composition of liquid product (%)		Composition of gas product (%)		Conversion (%)
	Benzene	Toluene	Methane	Ethane	
Ni/Al ₂ O ₃	49.1	50.9	98.7	1.3	68.9
Mo/Al ₂ O ₃	54.5	45.5	53.6	46.4	1.7
NiMo/Al ₂ O ₃	44.9	55.1	85.4	14.6	31.0
Commercial NiMo/Al ₂ O ₃	28.1	71.9	92.1	7.9	9.1

As seen in Table 4.2, both Ni/Al₂O₃ and Mo/Al₂O₃ catalysts exhibited high selectivity of undesired product (benzene). The significant amount of benzene resulted in noticeable drop in toluene selectivity. Therefore, it is important to remark that these two reference catalysts did not show the significant activity for hydrogenolysis of ethylbenzene to toluene. On Mo/Al₂O₃ catalyst, most of benzene was produced via deethylation of ethylbenzene. This was proven by gas product analysis; the amount of ethane in gas stream was quite high. It is clear that the deethylation of ethylbenzene to benzene was the favorable reaction over Mo/Al₂O₃ catalyst. According to the work of Covini *et al.* (1965) the hydrogenolysis of alkylbenzene to benzene and to the corresponding alkane depended on the acidity of the molybdena-aluminas. It was purposed that molybdenum-alumina had stronger acid sites than alumina, or that molybdenum-alumina could dissociate hydrogen heterolytically to form protons required for the formation of the sigma complexes as presented in Figure 4.8.

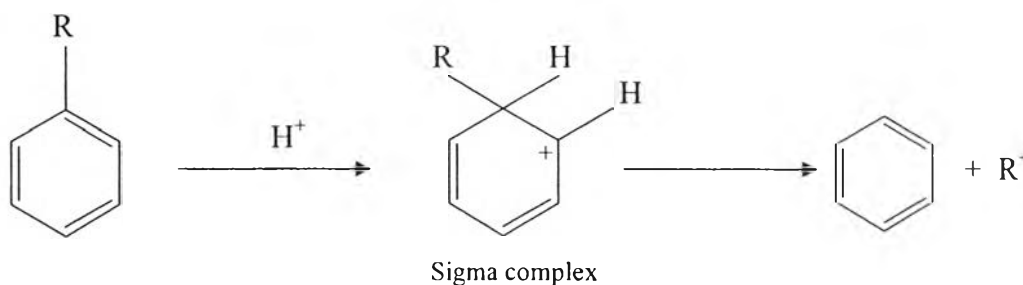


Figure 4.8 Dealkylation reaction occurs via carbonium ion (Covini *et al.*, 1965).

A sigma complex intermediate was produced by protonation of the aromatic ring and the complex was then decomposed to form benzene and alkyl carbonium ion. The alkyl carbonium ion loses a proton and be converted to an olefin which then reacts with hydrogen in the presence of the molybdenum-alumina catalyst. This phenomenon was not clearly seen on the Ni and NiMo based catalysts because their acidity was lower than that of Mo based catalyst (Table 4.3).

Table 4.3 pH of catalyst slurry

Catalyst	pH of catalyst slurry
Ni/Al ₂ O ₃	7.08
Mo/Al ₂ O ₃	4.28
NiMo/Al ₂ O ₃	5.40
Commercial NiMo/Al ₂ O ₃	5.53

When Ni/Al₂O₃ was used as a catalyst for hydrogenolysis of ethylbenzene, a small amount of ethane was obtained (Table 4.2). This demonstrated that deethylation reaction was not the dominant pathway for benzene formation. Therefore, it is clear that benzene was produced from the secondary hydrogenolysis of ethylbenzene which is in good agreement with the work of Van *et al.* (1987). They suggested that the great selectivity of sequential hydrogenolysis of alkylbenzene was observed over nickel based catalyst. Another argument in not favor deethylation re-

action may be found in the acidity of catalyst. According to the concept discussed in part of Mo/Al₂O₃; deethylation reaction occurred by using acid sites of the catalyst. However, the latter reaction did not occur on Ni/Al₂O₃ because Ni/Al₂O₃ catalyst exhibited natural (Table 4.3). It can be concluded that the doping of Mo/Al₂O₃ by Ni can inhibit deethylation since the amount of ethane detected from NiMo/Al₂O₃ system was lower than in the case of unpromoted Mo/Al₂O₃ catalyst whereas the promoting Ni/Al₂O₃ by Mo seems to inhibit secondary hydrogenolysis reaction. These two cases resulted in increasing of toluene selectivity. Therefore, it is important to note that mono-metallic catalysts had lower activity in hydrogenolysis of ethylbenzene to toluene than bi-metallic catalyst. In the case of NiMo/Al₂O₃ catalysts, the synthesized one gave higher amount of ethane (Table 4.2). It indicated that the synthesized NiMo/Al₂O₃ favored deethylation reaction that induced a low selectivity of toluene. It may be due to the effect from the preparation. The agglomeration of the metal may be occur during the preparation step of synthesized NiMo and gave larger metal size which is suitable for deethylation reaction. Therefore, it can be seen that among four different catalysts, the commercial NiMo/Al₂O₃ catalyst gave the highest amount of toluene under the same conditions, thus NiMo/Al₂O₃ catalyst was selected to apply for the hydrogenolysis of *para*-methylethylbenzene.

By considering the results obtained from the Ni/Al₂O₃ catalyst (Table 4.2), the ethylbenzene conversion was quite high and the selectivity of toluene was somewhat low. It is of interest to vary an LHSV over the Ni/Al₂O₃ catalyst in order to increase the selectivity of toluene. The results are presented in Table 4.4.

Table 4.4 Product selectivity at different levels of LHSV

LHSV (h ⁻¹)	Selectivity (%)		Conversion (%)
	Benzene	Toluene	
2	49.1	50.9	68.9
6	41.1	58.9	40.9
10	32.1	67.9	24.6
14	29.2	70.8	16.7

The results showed that the increasing of LHSV can enhance the selectivity of toluene. At LHSV of 14 h^{-1} , the selectivity of products nearly equal to the results obtained from the hydrogenolysis of ethylbenzene over the commercial NiMo/Al₂O₃ catalyst but the ethylbenzene conversion was higher. Therefore, the hydrogenolysis of *p*-MEB was also studied over the synthesized Ni/Al₂O₃ at an LHSV of 14 h^{-1} .

4.2 Hydrogenolysis of *para*-Methylethylbenzene (*p*-MEB)

The hydrogenolysis of *p*-MEB was studied over the commercial NiMo/Al₂O₃ and the synthesized Ni/Al₂O₃ catalysts under the optimum conditions. The optimum condition for each catalyst is shown in Table 4.5.

Table 4.5 The optimum conditions of different catalysts

Catalyst	Commercial NiMo/Al ₂ O ₃	Synthesized Ni/Al ₂ O ₃
Temperature (°C)	400	400
Pressure (psi)	50	50
H ₂ /feed	8	8
LHSV (h ⁻¹)	2	14

The *p*-MEB conversion and the selectivity of product from the hydrogenolysis of *p*-MEB over the commercial NiMo/Al₂O₃ catalyst are shown in Figure 4.9(a) and (b), respectively. Figure 4.9(b) illustrated that *p*-MEB was hydrogenolyzed into *p*-xylene, toluene, and ethylbenzene, with the major product of *p*-xylene. In order to discuss the reaction mechanisms, the reaction pathways were proposed as shown in Figure 4.10.

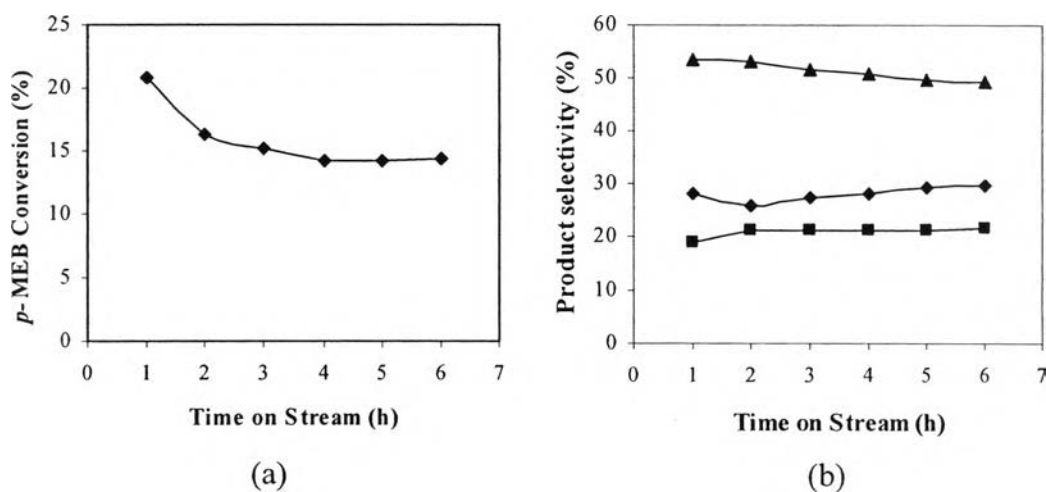


Figure 4.9 Catalytic activity of the commercial NiMo/Al₂O₃ catalyst for (a) *p*-MEB conversion, and (b) Product selectivity: (▲) *p*-xylene, (●) toluene, and (■) ethylbenzene at 400°C, 50 psi, LHSV = 2 h⁻¹, and H₂/*p*-MEB ratio = 8.

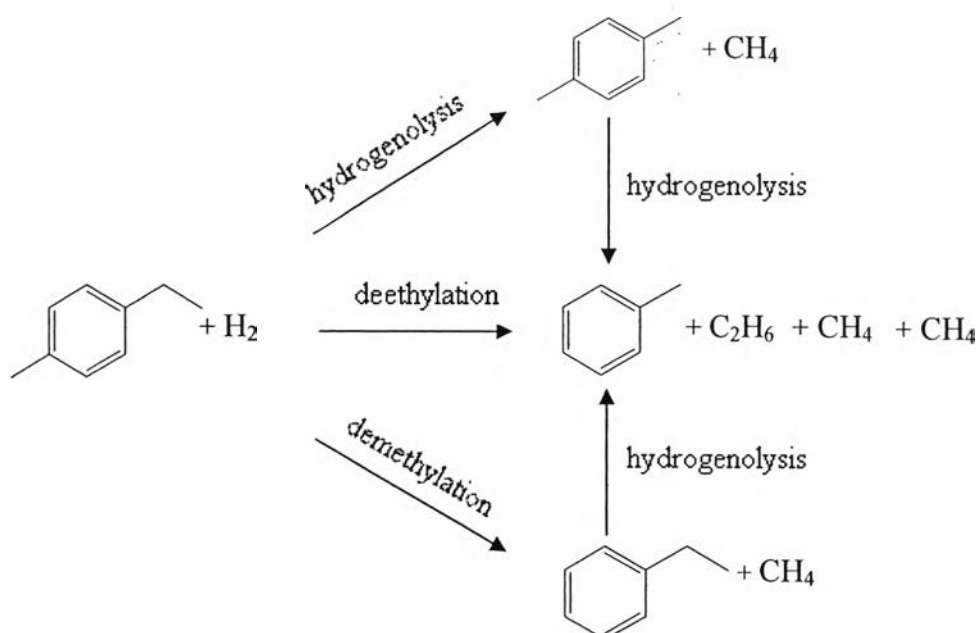


Figure 4.10 Proposed reaction pathways of *p*-MEB hydrogenolysis over the commercial NiMo/Al₂O₃ catalyst.

It was observed that *p*-MEB underwent the primary hydrogenolysis yielding *p*-xylene as a product while the secondary one yielding toluene. Toluene was also produced via deethylation of ethylbenzene. Ethylbenzene was observed in small amount, from dealkylation of methyl groups attached to the aromatic rings. However, the significant amount of *p*-xylene suggested that the primary hydrogenolysis of *p*-MEB was the most favorable reaction over the commercial NiMo/Al₂O₃ under this condition which is consistent with the hydrogenolysis of ethylbenzene.

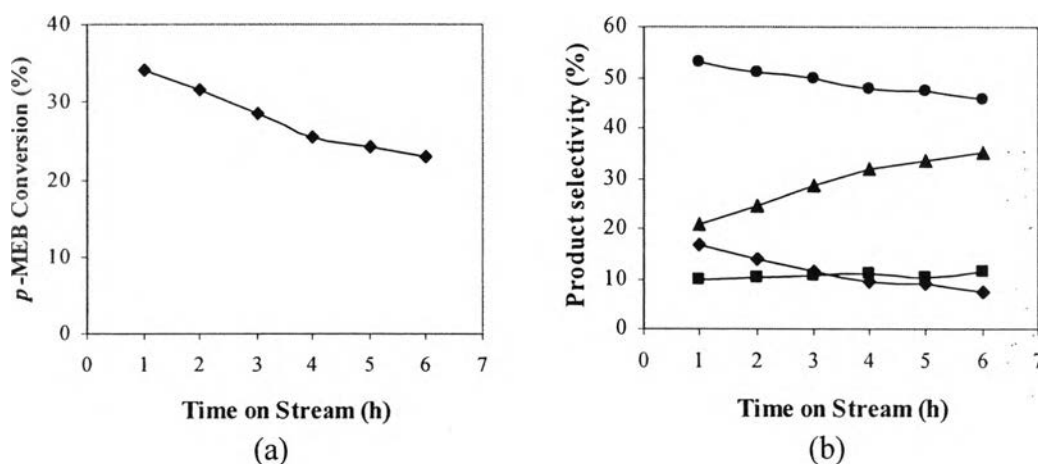


Figure 4.11 Catalytic activity of the synthesized Ni/Al₂O₃ catalyst for (a) *p*-MEB conversion, and (b) Product selectivity: (▲) *p*-xylene, (●) toluene, (■) ethylbenzene, and (◆) benzene at 400°C, 50 psi, LHSV = 14 h⁻¹, and H₂/*p*-MEB ratio = 8.

In contrast to the results obtained from the hydrogenolysis of *p*-MEB over the synthesized Ni/Al₂O₃ catalyst. Toluene was formed as the major product instead of *p*-xylene. Moreover, benzene was also detected as a product. It is indicated that not only primary and secondary hydrogenolysis, but tertiary hydrogenolysis was also observed. Based on the obtained results, the reaction mechanisms were proposed as shown in Figure 4.12.

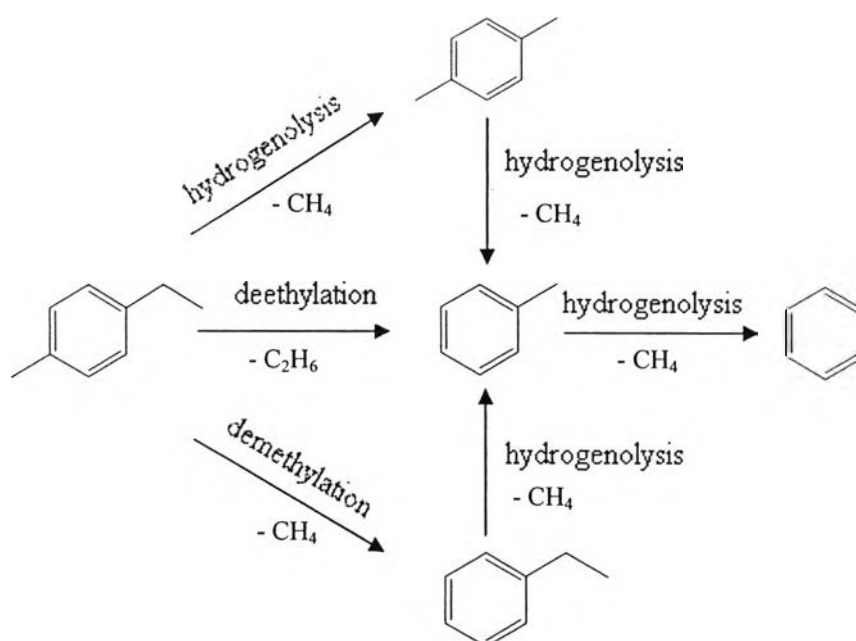


Figure 4.12 Proposed reaction pathways of *p*-MEB hydrogenolysis over the synthesized Ni/Al₂O₃ catalyst.

Based on the gas product analysis, the selectivity of methane was around 98% and the remaining was ethane. It is indicated that deethylation reaction was not the dominant pathway of toluene formation. Therefore, there would be two possible pathways for toluene formation; (1) stepwise hydrogenolysis of *p*-MEB to toluene and (2) the demethylation of *p*-MEB to ethylbenzene, which is hydrogenolyzed into toluene.