CHAPTER II
BACKGROUND AND LITERATURE REVIEW

Bio-ethanol is an environmentally friendly fuel, which has many attractive properties, such as clear colorless liquid, low toxicity, high octane substance, low production cost, low greenhouse gas and CO_2 emission, etc. In addition, it can be converted into more valuable hydrocarbon compounds, like paraffins, olefins, and aromatic hydrocarbons (e.g., benzene (B), toluene (T), and xylenes (X)).

2.1 Transformation of bio-ethanol to hydrocarbons

Hydrocarbons, like paraffins, olefins, and BTX aromatics, have been attracted in the petrochemical industries since they can be used as fuels and chemical substances. Normally, these hydrocarbons are mainly derived from the steam cracking of petroleum or natural gas feedstocks that have limited quantities. Because of, the high operating and production costs, the limitation of petroleum resources, and the shortage of natural resources, the catalytic transformation of bio-ethanol to hydrocarbons is the new alternative way that has become high competitive route and, therefore, has been drawing high attention (Guangwen et al., 2007).

The development of an effective catalyst is the important fundamental step in the catalytic transformation of bio-ethanol to more valuable hydrocarbons. However, the natures of catalyst have a significant effect on the reactant conversion and product distribution. So, the catalyst properties and reaction conditions have to be controlled to achieve the desired hydrocarbons. Zeolites are the effective catalysts which have been paid high attention for the catalytic transformation of bio-ethanol to hydrocarbons. They are porous or crystalline materials that have unique properties, such as a small size of pores, high porosity, high overall acidity, high intrinsic acidity (acid strength), and high heat of adsorption. The pore sizes and pore structures of zeolites make them suitable in shape selective reactions, and their acid strength are also suitable for bio-ethanol dehydration reaction. In addition, zeolites have been reportedly used to catalyze aromatic alkylation reactions in which they are effective for alkylation of aromatics to produce xylenes (Yashima et al., 1970; Kaeding et al.,

1981). Zeolites can be divided into many types depending on the size of their pore opening as shown in Table 2.1

Table 2.1 Structural characteristics of zeolites (Perego *et al.*, 2009)

Zeolites	IZA* code	Channel dimensionality	Channel type	Pore dimensions (nm)
Beta	BEA	3D	12	0.66 x 0.67
			12	0.56 x 0.56
AlPO$_4$-5,	AFI	1D	12	0.73 x 0.73
SSZ-33	CON	3D	12	0.59 x 0.70
			10	0.45 x 0.51
			12	0.64 x 0.70
L	LTL	1D	12	0.71 x 0.71
Mordenite	MOR	1D	12	0.70 x 0.65
Y, X	FAU	3D	12	0.74 x 0.74
ZSM-5	MFI	3D	10	0.53 x 0.56
			10	0.51 x 0.55
ZSM-11	MEL	3D	10	0.53 x 0.54

IZA* = International Zeolite Association

Bio-ethanol conversion for the production of hydrocarbons (e.g., paraffins, olefins, and BTX aromatics) has several pathways depending on reactions and conditions (e.g., temperature) as shown in Figure 2.1. Ethylene can be produced by the intramolecular dehydration of ethanol under fairly high reaction temperatures (~350 °C). In contrast, diethyl ether can be produced by the intermolecular dehydration between two ethanol molecules under low reaction temperatures (~200 °C). Diethyl ether can be continuously converted by dehydration to ethylene and C$_4$ olefins (Derouane *et al.*, 1978) when the temperature increases. Then, ethylene and C$_4$ olefins can be converted to heavier hydrocarbons (e.g., paraffins, olefins and BTX aromatics) by more complex reactions, such as oligomerization, aromatization, H-

transfer, and cracking, which are simultaneously occurred at a high temperature of ~500 °C. However, the heavier hydrocarbons may be further transformed to deposited carbon by excess reactions.
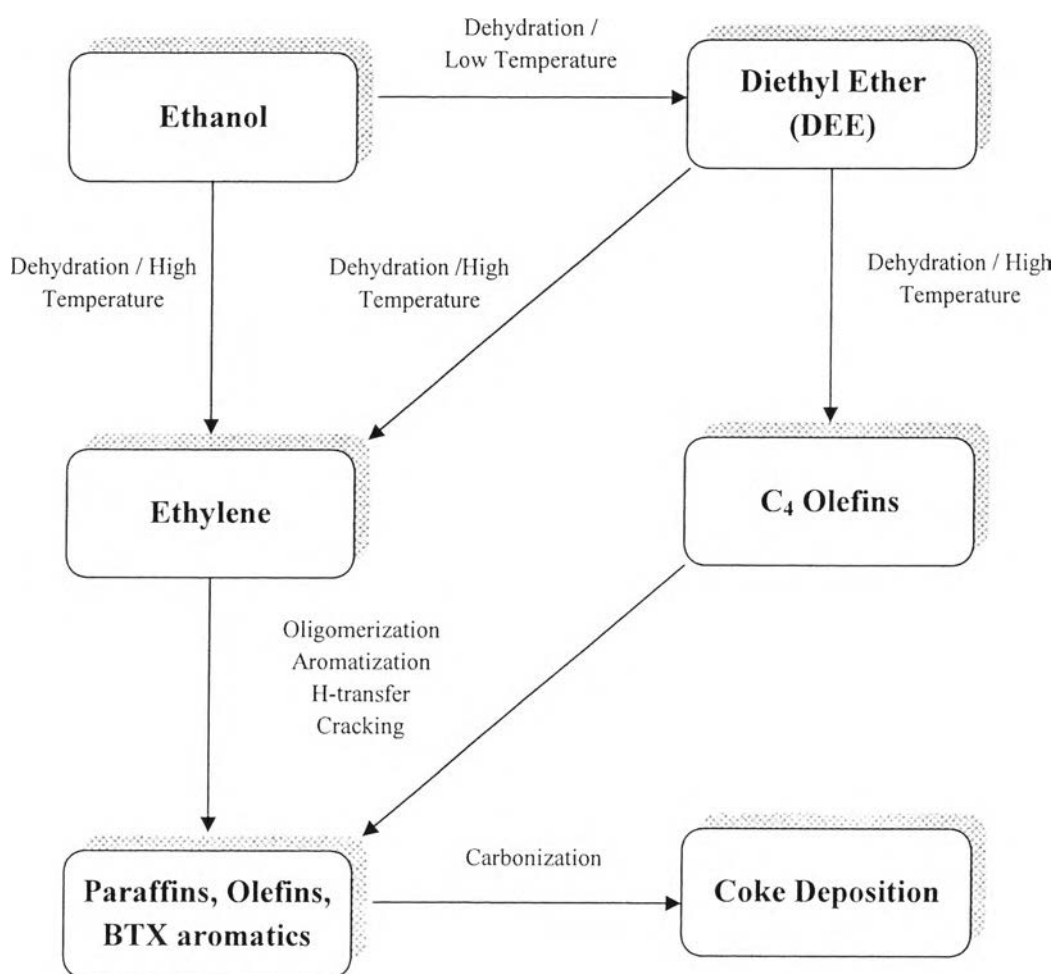

Figure 2.1 Several reaction pathways of ethanol dehydration to hydrocarbons (Inaba *et al.*, 2005).

Aromatic hydrocarbons, like benzene, toluene, and xylenes, are high commercial valuable products which can be derived from the catalytic transformation of bio-ethanol. They are important starting materials for the production of a wide variety of petrochemicals, such as monomers for polyamides, polyesters, resin, dye, synthesis fibers, detergents, and pharmaceutical products (Franck *et al.*, 1988). Benzene, toluene, and xylenes (BTX) are the three basic

materials that are used for the production of intermediates of several aromatic derivatives; most of which are produced by means of acid catalyzed reactions including alkylation, transalkylation, isomerization, and disproportionation.

The major product in the liquid hydrocarbons derived from the catalytic transformation of bio-ethanol is toluene (Saewong *et al.*, 2012), which is a low-value product and has low market demand in relative to that of other aromatics (e.g., benzene and xylenes). Therefore, the conversion of surplus toluene to more valuable aromatics, especially xylenes, is one of the interesting routes for the enhancement of process value.

In order to increase yield of xylenes, possible catalytic processes such as xylenes isomerization, transalkylation, and disproportionation of toluene can be applied. Especially, the catalytic transformation of toluene by any mean to enhance xylene formation is an interesting route. Two main processes that can be used to transform surplus toluene into xylenes are disproportionation and transalkylation, which are acid catalyzed reactions as shown in Figure 2.2.
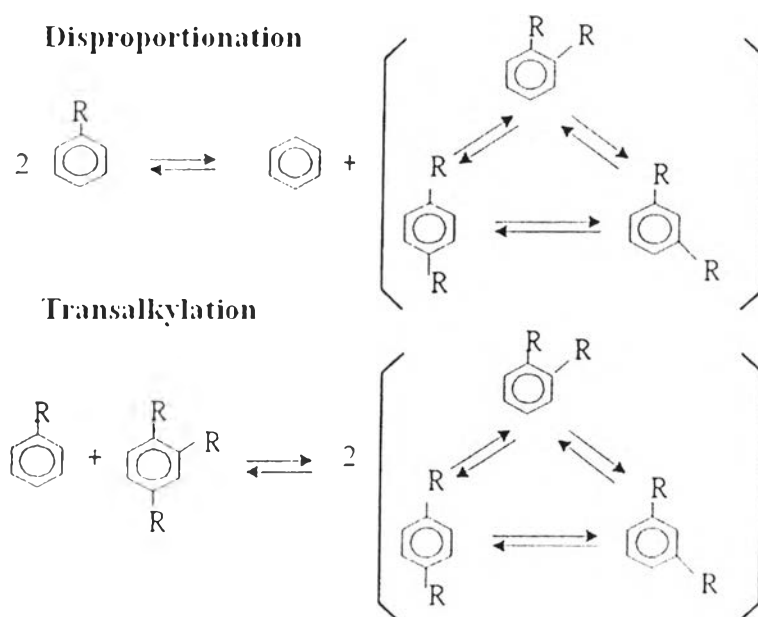
Figure 2.2 Disproportionation and transalkylation of toluene over zeolite catalysts (Tseng *et al.*, 1998).

Toluene disproportionation is one of the major practical processes for catalytic transformation of low valuable toluene into highly-valuable xylenes. For this process, two moles of toluene are converted to one mole of benzene and xylenes each as shown in Figure 2.2. Besides toluene disproportionation, xylenes disproportionation can be simultaneously occurred, resulting in the formation of trimethylbenzenes (TMBs). Both toluene and TMBs are low-cost feedstocks for mixed xylenes production through transalkylation as shown in Figure 2.2.

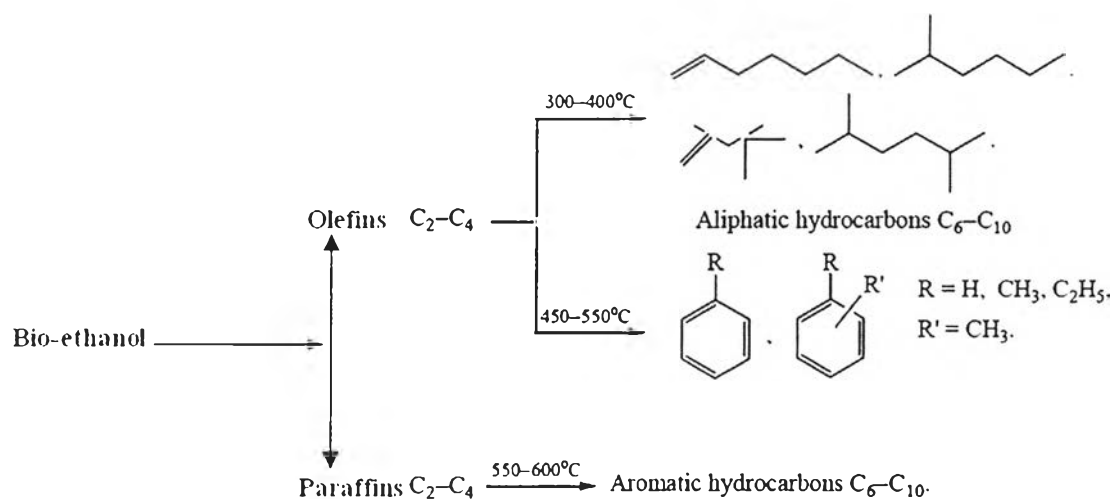## 2.2 Catalysts for transformation of Bio-ethanol

Many types of zeolites have been developed with the aim to control selectivity during the transformation of bio-ethanol to liquid hydrocarbons. For examples, Megumu *et al.* (2005) studied the transformation of ethanol to hydrocarbons over several zeolite catalysts. This work showed the effect of different types of zeolite supports; USY (Si/Al_2 = 6.3), H-Mordenite (Si/Al_2 = 183), H-Beta (Si/Al_2 = 27), HZSM-5 (Si/Al_2 = 190), and HZSM-5 (Si/Al_2 = 29), on product selectivity. The catalytic activity was measured using a fixed-bed reactor at reaction temperature 400 °C. They found that HZSM-5 (Si/Al_2 = 29) showed a high conversion of ethanol with the BTX selectivity of 54.0 %, while some other zeolites; H-Beta (Si/Al_2 = 27), H-Mordenite (Si/Al_2 = 183), USY (Si/Al_2 = 6.3), and HZSM-5 (Si/Al_2 = 190) showed a high conversion of ethanol to ethylene at the selectivity of 87.9 %, 96.4 %, 97.9 % and 97.9 %, respectively as shown in Table 2.2. They also found that the acidity of the zeolite catalysts is important to BTX selectivity; however, the presence of a large number of acidity does not always lead to high BTX selectivity. Moreover, the results showed that the formation of BTX is greatly occurred when the HZSM-5 zeolites with low Si/Al_2 ratio are used and operated under a high temperature condition.

Dergachev and Lapidus (2008) and Tret *et al.* (2010) found that the strong Brönsted acid sites of HZSM-5 are important for product selectivity. Hence, the moderate acidity of zeolite is important for the formation of BTX, but not for ethylene. Figure 2.3 shows the products that can be formed from bio-ethanol, on HZSM-5. Bio-ethanol can be converted to light hydrocarbons, C_2–C_4 olefins and

paraffins, which C_2–C_4 olefins are transformed to larger aliphatic hydrocarbons (C_6–C_{10}) at a low temperature (300-400 °C) and transformed to aromatic hydrocarbons at a high temperature (450-550 °C). Moreover, C_2–C_4 paraffins can also be transformed to C_6-C_{10} aromatic hydrocarbons at a temperature about 550-600 °C. Gayubo *et al.* (2010) studied the transformation of bio-ethanol to hydrocarbons on HZSM-5 zeolite catalysts treated with NaOH. They found that the moderate acid strength and shape selectivity of HZSM-5 zeolite were suitable for the catalytic transformation of bio-ethanol to liquid hydrocarbons. Similarly, Ferreira *et al.* (2009) studied the effect of various types of zeolites; HZSM-5, H-Y, and H-Beta, on liquid hydrocarbons selectivity. The catalytic activity was measured using a fixed-bed reactor under operating conditions, 350 °C and 30 bars, which can enhance liquid hydrocarbons formation. They found that HZSM-5 showed the highest activity, and the deactivation of HZSM-5 was lower than that of H-Y, and H-Beta zeolites because the micropore size of HZSM-5 is smaller and its hydrogen transfer capacity is lower, which resists coke formation.

Table 2.2 Catalytic activity of zeolite catalysts (Megumu *et al.*, 2005)

Catalysts	Ethanol Conversion	Ethylene	C_{3+} olefins and paraffins	BTX	Selectivity (%)	
					BTX	Ethylene
H-Beta ($Si/Al_2 = 27$)	94.77	86.50	7.98	3.95	4.01	87.9
HZSM-5 ($Si/Al_2 = 29$)	92.24	10.48	34.63	52.88	54.0	10.7
HZSM-5 ($Si/Al_2 = 190$)	96.41	97.58	2.08	0.00	0.00	97.9
USY ($Si/Al_2 = 6.3$)	93.70	96.21	2.07	0.00	0.00	97.9
H-Mordenite ($Si/Al_2 = 183$)	79.83	95.77	3.61	0.00	0.00	96.4

Figure 2.3 Transformation of bio-ethanol to hydrocarbons on HZSM-5 (Dergachev *et al.*, 2008).

To improve the catalytic activity in the transformation of ethanol to aromatic hydrocarbons, the acid strength of a zeolite has to be increased by the addition of other acidic catalysts. However, the addition of acidic catalysts can lead to an excess amount of required acid strength, and can easily cause the coke formation. So, the modification of metals and metal oxides on an acidic zeolite has been investigated. Tret *et al.* (2010) studied the catalytic transformation of bio-ethanol to hydrocarbons over several metals supported on HZSM-5 (Si/Al$_2$ = 25) Zeolite. The metals, Cu, Fe, Zn, Pd, Al, Co, Mn, La, Ce, Ni, and Cr, were loaded on HZSM-5 (Si/Al$_2$ = 25) by ion exchange, and the catalytic activity was measured at reaction temperature 450 °C. They found that the addition of Cr and Ni increased the yield of aromatic hydrocarbons to 34.10 % and 42.50 % by weight, respectively, while the addition of Cu, Fe, Zn, Pd, and Al increased the yield of C$_2$ olefins to 52.40 %, 36.30 %, 35.30 %, 34.90 %, and 32.40 % by weight, respectively. Moreover, the addition of Co, Mn, La, and Ce can increase the yield of C$_3$- C$_4$ olefins to 29.24 %, 30.45 %, 24.91 %, and 25.80 % by weight, respectively as shown in Table 2.3.

Table 2.3 Yield of hydrocarbons, wt %, on HZSM-5 (Si/Al_2 = 25) ion-exchanged with various metals (Tret *et al.*, 2010)

Metal Ions	Yield, wt %				
	C_2 olefins	C_3- C_4 olefins	Paraffin	C_{5+}	Aromatics
Cu	52.40	21.19	6.11	7.60	12.70
Fe	36.30	27.35	10.85	10.60	14.90
Zn	35.30	25.54	11.06	9.00	19.10
Pd	34.90	26.28	12.42	10.50	15.90
Al	32.40	21.21	19.89	8.40	18.10
Co	28.30	29.24	12.46	11.10	18.90
Mn	25.30	30.45	14.55	13.00	16.70
La	22.10	24.91	19.99	10.40	22.60
Ce	20.50	25.80	19.50	12.30	21.90
Ni	14.70	16.48	19.22	7.10	42.50
Cr	13.00	18.48	28.02	6.40	34.10

Megumu *et al.* (2005) studied the transformation of ethanol to hydrocarbons over several metals supported on HZSM-5 (Si/Al_2 = 29) zeolite. The metals, Mg, Cr, Fe, Co, Ni, Cu, Ga, Ru, Rh, Pd, Ag, Re, Ir, Pt, and Au, were impregnated on the HZSM-5 support, and the catalytic activity was measured at reaction temperature 400 °C in a fixed bed reactor. The results showed that Ga, Pd, Ir, Au, Ru, and Rh loaded on HZSM-5 can increase the conversion of ethanol with the BTX selectivity of 73.6 %, 61.0 %, 57.4 %, 56.8 %, 55.5 %, and 55.5 %, respectively as shown in Table 2.4. On the other hand, Fe and Au also appeared to be effective for the formation of C_{3+} olefins and paraffins, which may be precursors of aromatics.

Table 2.4 Catalytic activity of HZSM-5 (Si/Al$_2$ = 29) zeolite catalyst impregnated with various metals (Megumu *et al.*, 2005)

Catalysts	Ethanol Conversion	Ethylene	C$_{3+}$ olefin and paraffin	BTX	Selectivity (%)	
					BTX	Ethylene
HZSM-5	92.24	10.48	34.63	52.88	54.0	10.7
Mg/HZSM-5	36.90	92.49	6.83	0.00	0.00	93.1
Cr/HZSM-5	93.85	23.81	32.24	41.59	42.6	24.4
Fe/HZSM-5	96.96	11.15	37.70	51.15	51.2	11.2
Co/HZSM-5	94.82	76.16	12.64	10.20	10.3	76.9
Ni/HZSM-5	95.56	30.05	29.85	38.75	39.3	30.5
Cu/HZSM-5	90.06	91.89	0.92	4.53	4.70	94.4
Ga/HZSM-5	93.39	4.78	21.63	73.58	73.6	4.78
Ru/HZSM-5	91.48	12.20	32.19	55.35	55.5	12.2
Rh/HZSM-5	94.04	13.04	31.22	55.16	55.5	13.1
Pd/HZSM-5	92.89	10.38	28.52	60.83	61.0	10.4
Ag/HZSM-5	97.09	38.66	27.62	32.68	33.0	39.1
Re/HZSM-5	98.58	56.04	15.70	23.30	24.5	59.0
Ir/HZSM-5	91.50	11.49	31.10	57.36	57.4	11.5
Pt/HZSM-5	98.45	33.60	14.98	50.74	51.1	33.8
Au/HZSM-5	92.88	6.59	36.57	56.84	56.8	6.59

The effect of Phosphorus (P) doped on HZSM-5 (Si/Al = 12.5) catalyst for the conversion of ethanol to hydrocarbons was investigated (Jiangyin and Yancong., 2010). The catalytic activity was performed in a continuous-flow fixed-bed quartz tubular reactor at reaction temperature 450 °C. P-modified HZSM-5 (Si/Al = 12.5) catalysts were prepared by impregnation method with different phosphorus (P) loading of 0, 1.0 wt %, 2.0 wt %, 3.0 wt %, 4.0 wt %, and 5.0 wt %, respectively. They reported that ethanol conversion was almost 100 % in most cases, but the product selectivity of each catalyst was different. The catalytic activity was increased significantly when P species was added into HZSM-5 catalysts. P-modified HZSM-5 catalysts favored the formation of C$_1$- C$_4$ paraffins and aromatic hydrocarbons, but suppressed the formation of C$_3$- C$_4$ olefins. 3.0 % P-modified HZSM-5 catalyst showed an excellent activity in liquid hydrocarbons selectivity. Moreover, the result

also showed the main compositions of liquid hydrocarbons were aromatics, mostly xylenes and toluene. The fraction of xylenes in P-modified HZSM-5 was higher than that of HZSM-5 alone.

In addition, Barthos *et al.* (2006) investigated the effect of different metal oxides on HZSM-5 catalyst in the decomposition and aromatization of ethanol. Ga_2O_3, Mo_2O, and ZnO-modified HZSM-5 were prepared by impregnation method and operated in a continuous-flow fixed-bed reactor at 500 °C and 600 °C. They found that these catalysts markedly enhanced the conversion of ethanol, promoted the formation of aromatic hydrocarbons, and provided higher selectivity to benzene and toluene than pure HZSM-5 catalyst. Especially, Ga_2O_3-modified HZSM-5 exhibited the highest yield of aromatics, mostly toluene, and the aromatics yield increased with increasing temperature from 500 °C to 600 °C. Similarly, Saewong *et al.* (2012) studied the transformation of bio-ethanol to aromatic hydrocarbons using the dual-bed catalytic systems. $MgHPO_4/Al_2O_3$ was packed on the first bed, whereas the catalysts used in the second bed were pure HZSM-5, Ga_2O_3/HZSM-5, ZnO/HZSM-5, and ZnO-Al_2O_3 combined with HZSM-5 (Hybrid catalyst). These catalysts were prepared by impregnation method, and the catalytic activity was measured using a fixed-bed reactor under the reaction temperatures of 350 °C at the first bed and 500 °C at the second bed, and atmospheric pressure. They found that 0.5 wt % $MgHPO_4$-doped Al_2O_3 can practically maintain its activity (both on bio-ethanol conversion and ethylene selectivity) in a long period of time. Moreover, 2.0 wt % Ga_2O_3/HZSM-5 used in the second bed can convert ethylene to heavy hydrocarbons, and gave the highest oil yield with the highest mono-aromatic content, which mostly consisted of toluene. However, the results showed that all metal oxide-modified HZSM-5 catalysts gave higher aromatics yield than HZSM-5 alone. This is an evidence indicating that the dopants on the HZSM-5 catalyst can significantly improve the aromatic hydrocarbons production from bio-ethanol.

2.3 Catalysts for transformation of aromatics

In the past, liquid Friedel-Crafts (Belenki *et al.*, 1964) and HF-BF$_3$ catalyst (Lien *et al.*, 1953) were normally used for the transformation of aromatics, but these catalysts are highly corrosive, difficult to handle, and cannot be economically recovered. So, metal oxide catalysts, such as CoO-MoO$_3$ on aluminosilicate/alumina and noble metal or rare earth over alumina were developed and used (Well, 1991). Currently, zeolites; for examples, Beta, Mordenite, HZSM-5, Y, and other large-pore zeolites, are predominant (Haag *et al.*, 1987) because they are less corrosive and more economically competitive.

Because of the size of toluene, there have been some research interests in the properties and activities of zeolites having medium- or large-pore size for toluene disproportionation reaction. For examples, Ikai *et al.* (1990) studied the disproportionation and transalkylation of toluene over HZSM-5 (Si/Al$_2$ = 35.8), and Beta (Si/Al$_2$ = 31.3) zeolites, for the aim to increase xylenes selectivity. The zeolite powder was pelletized, crushed and sieved to 12-20 mesh particles and the catalytic activity was measured in a continuous fixed-bed reactor system under the temperature range 300-450 °C. They found that the conversion of toluene increased with increasing reaction temperature and Beta (Si/Al$_2$ = 31.3) zeolite gave a less benzene to xylenes ratio, and a less light gases yield than HZSM-5 (Si/Al$_2$ = 35.8) zeolite did. The highest para- to meta-xylene ratio appeared over Beta (Si/Al$_2$ = 31.3) zeolite at 300 °C. Moreover, at reaction temperature above 350 °C, small amounts of trimethylbenzene can be formed from transalkylation of toluene and xylenes. Jagannath *et al.* (1993) studied the effect of different types of zeolites on disproportionation of toluene. Three zeolites used in this work were HZSM-5 (Si/Al$_2$ = 40), Mordenite (Si/Al$_2$ = 15) and Beta (Si/Al$_2$ = 30) zeolites. The zeolite powder was pelletized, crushed and sieved to 12-18 mesh particles and the reactions were conducted in a continuous fixed-bed reactor system under the temperature 400 °C. They found that Beta (Si/Al$_2$ = 30) zeolite gave the highest yield of xylenes among all zeolites. This is an evidence indicating that Beta (Si/Al$_2$ = 30) zeolite has high activity and selectivity for the disproportionation of toluene because of its high acidity and large-pore size that can sorb bulkier molecules, like toluene, xylenes, and

trimethylbenzenes. Moreover, Peng *et al.* (1998) investigated the selective formation of para-xylene via the disproportionation of toluene over various types of zeolites. HZSM-5 (Si/Al$_2$ = 15), Mordenite (Si/Al$_2$ = 11) and Beta (Si/Al$_2$ = 15) zeolites were tested using a continuous fixed-bed reactor under atmospheric pressure for their activity. They found that Beta (Si/Al$_2$ = 15) zeolite showed the highest para-xylene fraction in xylenes, followed by HZSM-5 (Si/Al$_2$ = 15) and Mordenite (Si/Al$_2$ = 11) with the para-xylene fraction of 25.5 %, 25.3 %, and 24.4 %, respectively.

Besides toluene disproportionation, toluene transalkylation is the competitive reaction which can be simultaneously occurred to transform aromatic hydrocarbons as shown in Figure 2.2. This process is normally catalyzed by large-pore zeolites such as Beta, Y, Mordenite, HZSM-12, and USY, which are zeolites that can also be used for toluene disproportionation. Catalytic activity and stability are main properties that should be considered. For examples, zeolites having large-pore sizes were investigated for activity and xylenes selectivity (Jiri *et al.*, 2004). These zeolites were Beta (Si/Al$_2$ = 12.5), Mordenite (Si/Al$_2$ = 10), L (Si/Al$_2$ = 3.1), and Y (Si/Al$_2$ = 2.7) zeolites. The catalytic activity was measured at reaction temperature of 400 °C with the weight hourly space velocity (WHSV) of 5 h^{-1}. They found that Y (Si/Al$_2$ = 2.7), Mordenite (Si/Al$_2$ = 10), Beta (Si/Al$_2$ = 12.5), and L (Si/Al$_2$ = 3.1) zeolites exhibited the xylene selectivity of 11.1 %, 10.7 %, 10.5 %, and 8.8 %, by volume, respectively. Moreover, the results also showed that Mordenite (Si/Al$_2$ = 10) and L (Si/Al$_2$ = 3.1) zeolite were deactivated much faster than Beta (Si/Al$_2$ = 12.5) and Y (Si/Al$_2$ = 2.7) zeolites. Andrea *et al.* (2010) investigated the catalytic activity of large-pore zeolites (Beta (Si/Al$_2$ = 12.5, 46.0, 75.0), Y (Si/Al$_2$ = 2.7) and Mordenite (Si/Al$_2$ = 10)) in transalkylation reaction. The catalytic activity was measured in a tubular continuous fixed-bed glass microreactor and was operated under temperature range of 300-450 °C with WHSV of 5 h^{-1}. The zeolite powder was pressed, crushed and sieved to obtain a fraction between 0.75 and 0.36 mm. They found that Beta (Si/Al$_2$ = 12.5) zeolite exhibited the highest toluene conversion and the xylene distribution of 36.9 wt % as well as higher stability with increasing time-on-stream (T-O-S). Its structure and pore dimensions appeared to be less affected by coke formation; therefore, it has higher stability, and less deactivation at

higher reaction temperatures than Mordenite (Si/Al_2 = 10) and Y (Si/Al_2 = 2.7) zeolites. Moreover, Tseng *et al.* (2002) investigated transalkylation of toluene and heavy aromatics. Transalkylation of toluene and 1,3,5-trimethylbenzene (1,3,5-TMB) were conducted in a continuous-flow fixed-bed microreactor under the temperature of 673 K and WHSV = 5.5 h^{-1}. They found that HZSM-12 (Si/Al_2 = 120), Beta (Si/Al_2 = 12.5), Mordenite (Si/Al_2 = 22.9), and USY (Si/Al_2 = 14) exhibited the xylenes yield of 33.5 %, 31.5 %, 31.1 %, and 19.8 % by weight, respectively. Moreover, HZSM-12 (Si/Al_2 = 120), Beta (Si/Al_2 = 12.5), Mordenite (Si/Al_2 = 22.9), and USY (Si/Al_2 = 14) gave the xylenes to benzene ratio of 3.50 %, 4.94 %, 4.87 %, and 12.84 %, respectively.

In summary, among a large number of active promoters investigated with the aim of enhancing liquid hydrocarbons production in the catalytic dehydration of bio-ethanol, Ga and P elements gave the predominant activity and selectivity for aromatic hydrocarbons. The oxides form of Ga is an amphoteric compound that can act as both an acid and a base while P is an acidic element. In general, acidity, especially acid strength, is required for oligomerization, cyclization, and aromatization reactions. An element in a reduced form, like Ga, can enhance dehydrogenation reaction to achieve high aromatic yields (Megumu *et al.*, 2005) whereas an element in an oxides form, like Ga_2O_3, can enhance ethanol dehydration reaction to achieve high ethanol conversion (Barthos *et al.*, 2006). Besides ethanol dehydration, acidic oxides can also enhance dehydrocyclization reaction, which requires both acidic oxides and acid catalysts. Since an oxide alone does not catalyze the branching reaction, it requires an acidic function to initially generate carbenium ions which further undergo desired isomerization. Sometimes, some weak acidic sites alone is not sufficient to generate some carbenium ions because it is too weak to protonate ethanol, so some appropriate oxide promoters would be needed to catalyze the dehydration of ethanol to give olefins that are easily further protonated. The required oxides must not be too strongly or too weakly acidic. Since Ga_2O_3-doped HZSM-5 was known to be the best catalyst to convert ethanol to aromatics, but toluene was produced in a high quantity; therefore, in order to transform surplus toluene, one of some selected zeolites with various pore sizes was consecutively loaded, as the second layer, right after the Ga_2O_3-modified HZSM-5. So, in this

work, the two consecutive layers of Ga_2O_3-doped HZSM-5 and some medium- or large- pore size zeolites were studied, aiming to improve the selectivity of BTX. HZSM-5, H-Y, and H-Beta were the zeolites that potentially have high activity in the transformation of toluene. However, HZSM-5 has been studied for toluene disproportionation in many previous works and found not as good as H-Beta and H-Y zeolites; therefore, zeolite H-X, which has a pore size close to that of zeolite H-Y and has not been used for this purpose before, was used instead of HZSM-5. So, H-X, H-Y, and H-Beta zeolites were used as supports in the second layer to transform surplus toluene produced from the first layer of Ga_2O_3-modified HZSM-5, aiming to enhance aromatics production. Moreover, other acidic oxides of P, Sb, and Bi were also investigated to modify the acid properties of HZSM-5 for the enhancement of aromatics production. P, Sb, and Bi are elements in Group VA in the periodical table that gives an acidic property. Considering the fact that elements in the same group have similar properties but different sizes, so, this work investigated the effect of promoter size on bio-ethanol dehydration to liquid hydrocarbon over the HZSM-5 support. These reaction runs were performed in a continuous U-tube fixed-bed reactor at 500 °C under atmospheric pressure for 8 hours.