CHAPTER II
LITERATURE REVIEW

2.1 Dehydration of Methanol to Hydrocarbons

The methanol to hydrocarbons process has been studied by researchers since 1980s. Generally, methanol can be formed from coal or natural gas. Gasification of coal and steam reforming of natural gas produce synthesis gas (composed of CO and H_2), which can be converted to methanol. The methanol to hydrocarbons process is started from the dehydration of methanol into dimethyl ether and ethylene respectively, and then ethylene is converted by the various reactions.

Zeolites are used as a catalyst and a molecular sieve, which help to produce a specific product such as light olefins and aromatics. The light olefins are usually produced from methanol by using SAPO-34 (a silico-aluminophosphate of CHA topology) as a catalyst because SAPO-34 has small pore size (3.8 Å), which specifically selects small hydrocarbon molecules, like ethylene and propene, and limits the transfer of branched hydrocarbons and aromatics. The conversion of methanol to olefins on H-SAPO-34 catalyst was studied by Song *et al.* (2001). They investigated the effect of space velocity of methanol from 8 h^{-1} to 0.0008 h^{-1} with keeping the He flow constant and using constant reaction temperature at 400 °C. Thus, they found the increase of the ethylene selectivity when the space velocity was decreased. Temperature which was varied between 400 °C to 550 °C also affected to the ethylene selectivity, and the ethylene selectivity at 550 °C was higher than at other temperatures, but the rising temperature favored the coke deposition that involves with oligomerization, cyclization, hydrogen transfer, and alkylation (Moljord *et al.*, 1995; Chen *et al.*, 2000). Other researchers modified SAPO-34 by impregnation, ion-exchange or incorporation of metal for the improvement of catalytic performance and light olefin selectivity (Dubois *et al.*, 2003; Chen *et al.*, 2010; Salmasi *et al.*, 2011).

The production of heavy olefins, paraffins, or aromatics require large pore zeolites such as ZSM-5 (MFI), Beta (BEA), Mordenites (MOR), and Y (FAU) and suitable acidity. Park and Seo (2009) investigated the different pore structures of

CHA (8MR), LTA (8MR), MOR (8,12MR), MFI (10MR), BEA (12MBR), and FAU (12MR) zeolites. They found the highest light olefin yields were observed on CHA and LTA zeolites because of their selective small pore sizes. On the contrary, the high yield of C_5^+ and alkylaromatics were observed over MFI, BEA, and FAU zeolites as shown in Figure 2.1. The large cage zeolites, LTA and FAU, were able condense alkylbenzenes to polycyclic aromatic hydrocarbons (PAHs), which could cause the deactivation of the zeolite catalysts. The CHA zeolite had small cage whereas the MFI and BEA zeolite had sinusoidal pores, which resisted the condensation of PAHs in pores and reduced deactivation from coke. Although MOR zeolite had large pore sizes, but could produce light olefins because of the high acid strength, so it rapidly deactivate as well.

Nishi *et al.* (1998) also studied the selectivity of multi-branched-chain aliphatics over different pore structures of zeolites; H-ZSM-5 (HZ), H-Y (HY), and H-Modinite (HM). The results showed that HZ was more selective in C_{5+} (gasoline range) than the other zeolites in this research. Large-pore zeolites, like HM, had the higher selectivity of multi-branched-chain alkanes such as dimethylbutanes and trimethylpentanes (which was observed only on HM). On the other hand, HY has larger pore size than HM, which scarcely produced multi-branched-chain alkanes; therefore, the pore size of zeolites is not only the factor for multi-branched-chain alkanes formation but also the other factors such as acid density, acid strength, and pore structure.

In 1920's, ExxonMobil discovered Fischer-Tropsch (FT) process that converted coal into straight chain paraffinic hydrocarbons, which required the improvement on the production of high quality fuel. In 1970's, they developed Methanol-to-Gasoline (MTG) process that converts coal into synthesis gas and methanol as shown in Figure 2.2. Methanol was converted to liquid products with very low sulfur.

In MTG reaction, methanol is converted to dimethyl ether (DME) by intermolecular dehydration reaction followed by the formation of light olefins (C_2-C_4). Later on, light olefins undergo further reactions to higher olefins. Finally, n-paraffins, iso-paraffins, and aromatics are formed as shown in Figures 2.3 and 2.4. HZSM-5 was used as a catalyst in MTG process, owing to the suitable pore size

(about 5.5 Å). The gasoline range is in the range of C_5-C_{10}. Jiménez-Cruz and Laredo (2004) reported the kinetic molecular diameters of linear and branched C_5-C_8, which were between 4.2 Å to 6.2 Å. Therefore, HZSM-5 is a very selective zeolite for gasoline production.
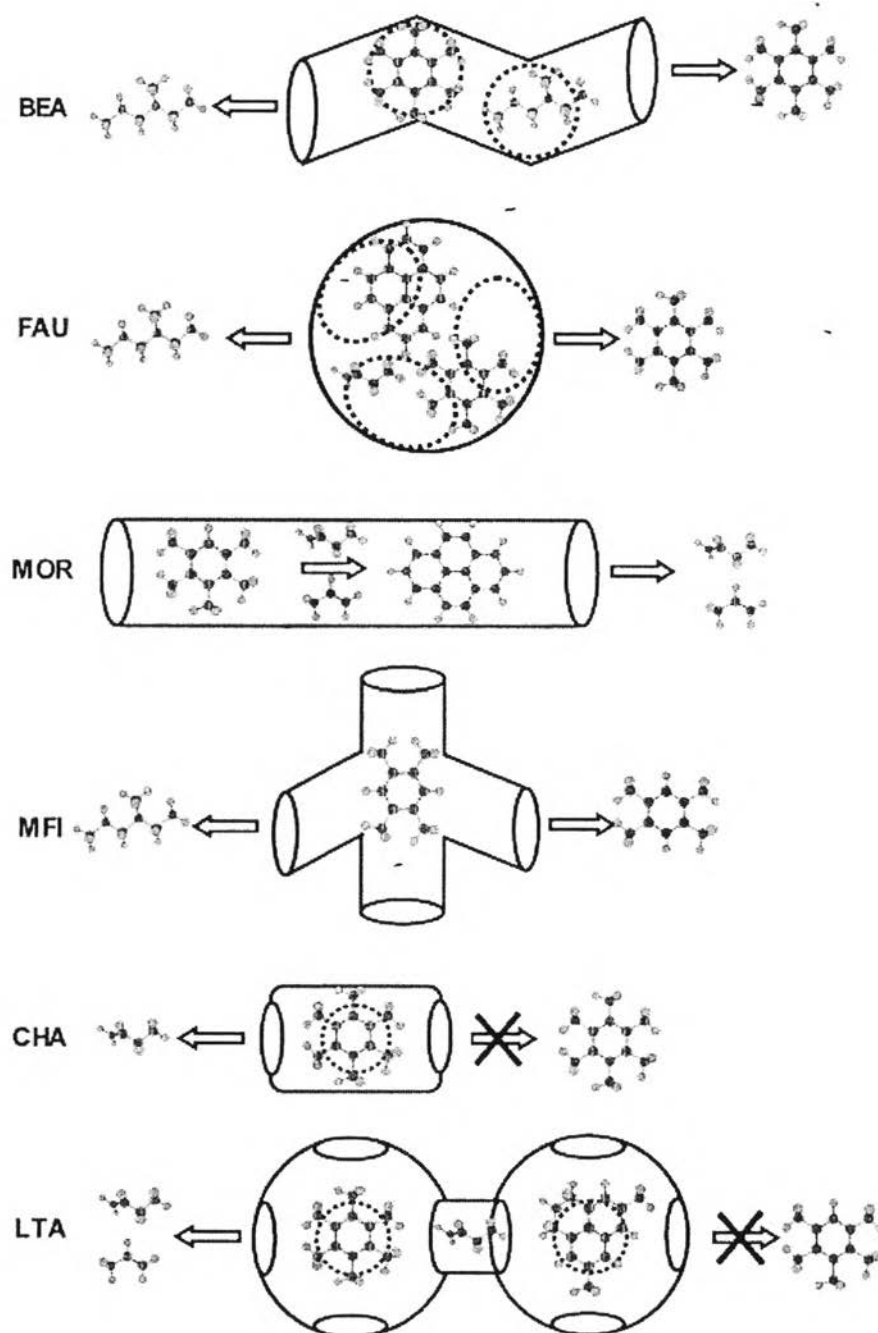

Figure 2.1 Molecular sieve of different zeolites (Park *et al.*, 2009).
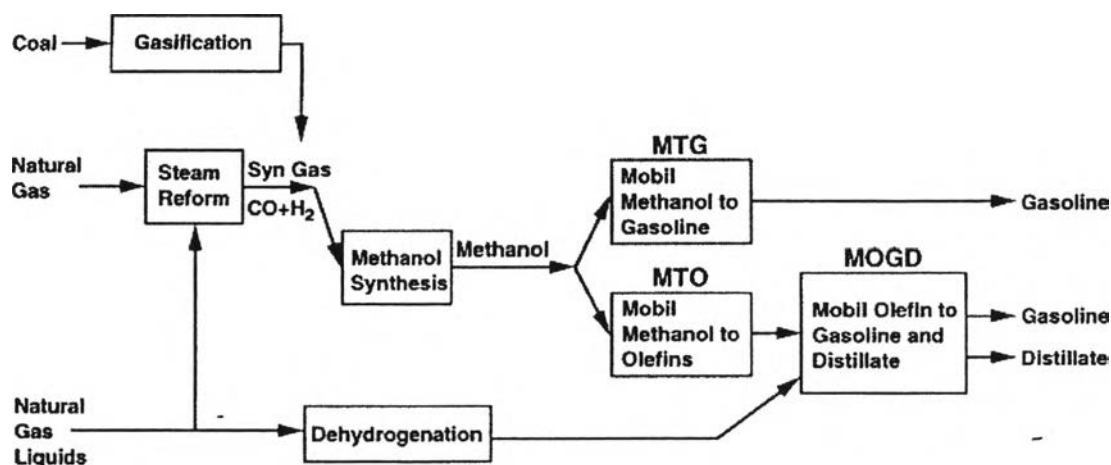
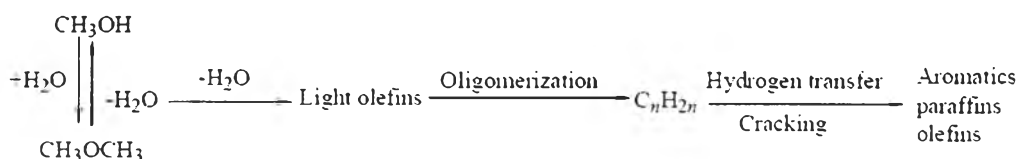**Figure 2.2** Methanol to gasoline and methanol to olefin technology (Stöcker, 1999).

Figure 2.3 The methanol to hydrocrabons pathway (Wei *et al.*, 2012).

2.2 Dehydration of Ethanol to Hydrocarbons

Previous topic discussed the methanol to hydrocarbons process that is applied to produce gasoline; however, methanol is prepared by coal or natural gas, which is not good for neither the environment nor the sustainable feedstock. Nowadays, people concern more about the environment and insufficient crude oil than before, so an alternative energy is biomass for producing ethanol, such as sugar canes, corns, sugar beets, potato, household wastes, and wood wastes. Glucose is fermented with yeast in the absence of oxygen; then, it produces the ethanol (bio-ethanol) as shown in the equation below (Tret'yakov *et al.*, 2010).
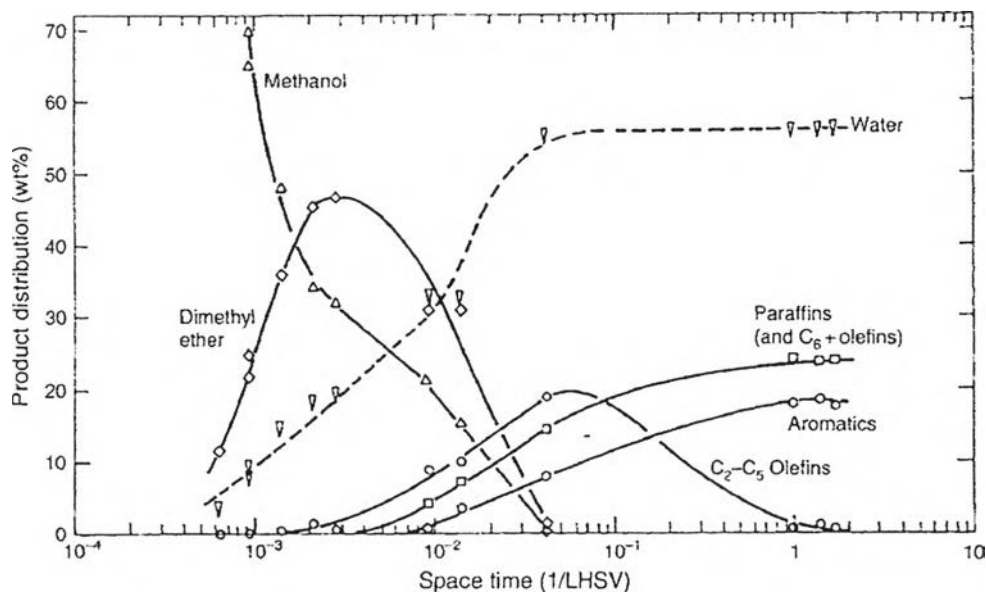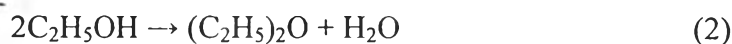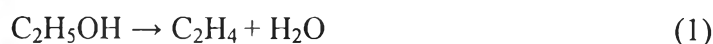
$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

Figure 2.4 Products from methanol vs. space time (Rigutto *et al.*, 2007).

Therefore, an alternative feedstock for hydrocarbons production is bio-ethanol, which was used in many research studies. Reactions of the ethanol to hydrocarbons resemble in the methanol to hydrocarbons. Kagyrmanova *et al.* (2011) studied the kinetic model of bio-ethanol dehydration over alumina-based catalysts. They did the experiments at atmospheric pressure and temperatures in the range of 350-450 °C. The major products were ethylene, diethyl ether, and butylene, and the main reactions were purposed as shown in the equations below

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad (1)$$

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \qquad (2)$$

$$(C_2H_5)_2O \rightarrow 2C_2H_4 + H_2O \qquad (3)$$

$$2C_2H_4 \rightarrow C_4H_8 \qquad (4)$$

Ethanol is converted to ethylene through parallel pathways that consist of direct ethanol conversion (Equation (1)) and via having diethyl ether as an intermediate (Equation (2) and (3)).

Cheng *et al.* (2012) used many solid acid catalysts that included zeolites (H-ZSM-5, H-mordenite, H-Y, and H-beta) and silica-alumina. The process was run at

the interval temperatures of 180 to 300 °C under atmospheric pressure. H- mordenite (SiO_2/Al_2O_3 = 20) was the most active catalyst, and gave the high ethylene yield from experiment results, but it was less stable than H-modenite at SiO_2/Al_2O_3 ratio of 90.

H-FAU and H-BEA produced ethylene as a main product from ethanol dehydration at 350 °C and 30 bar of pressure, while H-ZSM-5 mainly produced C_{3+} (especially C_5-C_{11}) with the higher stability than the other zeolites. C_{3+} hydrocarbons were composed of paraffins, olefins, naphtenes, and aromatics. Ethylene is converted to heavy hydrocarbon products followed by oligomers, dienes, and naphthenes respectively, and then the final products were aromatics and paraffins (Madeira *et al.*, 2009)

Therefore, ethanol can be converted to heavy hydrocarbons in the range of gasoline as shown in Figure 2.5, analogous to the methanol to gasoline (MTG) process. Xiao *et al.* (2006) used methanol and ethanol in their work. The reactions occurred in two pathways; the first was dehydration-methanolation to generate branched aliphatics, and the second was polycondensation to produce linear aliphatics and aromatics. As a result, ethanol was converted to a 30-40 % of liquid hydrocarbons, which contained 80 % of C_5-C_6 hydrocarbons by using H-ZSM-5 zeolite at 300-400 °C.
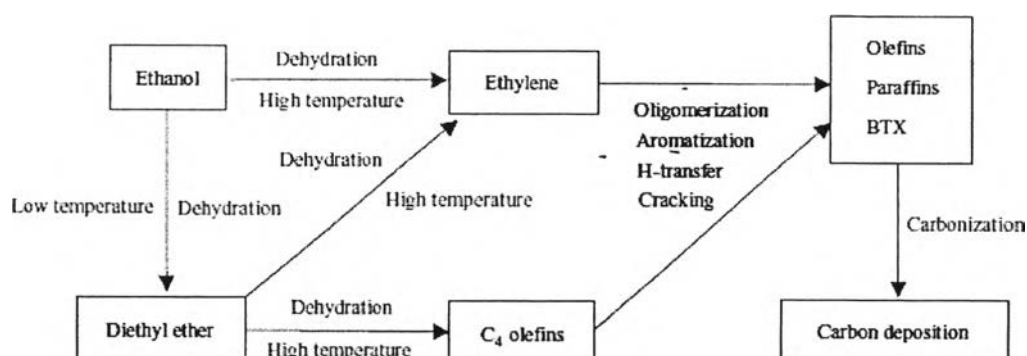

Figure 2.5 Reaction pathway of ethanol dehydration to hydrocarbons (Inaba *et al.*, 2006).

Viswanadham *et al.* (2012) investigated the acidity and the porosity of H-ZSM-5 zeolite in ethanol to gasoline (ETG) reaction. The two different Si/Al ratios of micro crystalline ZSM-5 (Z and ZA) were used to study the acidity effect. The effect of porosity were compared between the micro crystalline ZSM-5 (Z) and the nano crystalline ZSM-5 (NZ), which stacked in mesoporosity form. The temperature programmed desorption of NH_3 (NH_3-TPD) showed the acidity of three zeolites. Z and NZ zeolites have higher acidity than ZA because the acidity of zeolites was governed by the ratio of Si/Al in framework, but the crystal size did not affect the acidity. Thus, NZ and Z zeolites chiefly produced liquid hydrocarbons; on the contrary, ZA zeolite mainly produced the gas composition as shown in Table 2.1. The formation of C_{5+} paraffins and C_{6+} aromatics occured only over NZ and Z zeolites, which have high acidity. The gasoline was mainly composed of aromatics and iso-paraffins, but when the reaction temperature increased from 450 °C to 500 °C, iC_{10} was converted to aromatics (from aromatization reaction) and propene (from cracking reaction) for NZ and Z, respectively. Hence, NZ zeolite was the most active for the gasoline production because it had strong acidity and mesoporous stack.

2.3 Factors on The Zeolites Activity

Many catalysts, not only zeolite catalysts but also aluminium oxide and acid catalysts, have been used for dehydration reaction. However, zeolites are more suitable than others because of their shape selectivity for specific products.

Zeolites were found in 1940's, and aluminosilicate-type zeolties consist of SiO_4 and AlO_4^- tetrahedra in a 3-dimensional structure. The pore openings of zeolites are estimated based on the carbon number of ring; for examples, an 8-membered ring possesses small pore opening (~4.1 Å), 10-membered ring represents medium pore (~5.5 Å), and a 12-membered ring an opening of a large pore (~7.4 Å). The different pore sizes of zeolites were applied in many applications as shown in Table 2.2.

The zeolite activity was governed by some factors, such as Si/Al ratio (related to acid strength and acid density), the type and amount of metal in zeolite, catalyst topology, crystal size, and processing conditions (Niaei *et al.*, 2013).

Table 2.1 Gas and liquid compositions on various zeolite catalysts at two reaction temperatures (Viswanadham *et al.*, 2012)

Catalysts	NZ	Z	ZA	NZ	Z	ZA
Si/Al ratio	30	30	100	30	30	100
Temperature (°C)	450			500		
Gas analysis(wt%)	31.5	37.6	57.6	29.9	48.7	64.8
Liquid analysis(wt%)	68.5	62.4	42.4	70.1	51.3	35.2
- Paraffins	1.0	0.3	0.4	1.7	1.1	0.0
- i-Paraffins	**11.4**	**13.0**	**4.1**	**9.5**	**8.5**	**2.9**
- Aromatics	**38.6**	**38.7**	**35.3**	**50.6**	**36.3**	**31.8**
- Naphthenes	3.5	1.6	1.0	1.8	0.6	0.2
- n-Olefins	0.4	0.1	0.1	0.9	0.0	0.1
- Iso-olefins	11.7	7.7	1.0	5.2	4.1	0.1
- Di-olefins	0.1	0.0	-	0.1	0.0	-
- Naphtheno-olefins	1.1	0.2	0.4	0.1	0.2	0.0

Table2.2 Characteristics of zeolites (Chu and Chen, 1995; Reddy *et al.*, 1995; Zhang *et al.*, 2001)

	H-X	H-Y	H-MOR	H-Beta	H-ZSM-5
Si/Al ratio	3.5	7	9.5	13.5	20
Pore opening (Å)	7.4	7.4	6.5×7.0 / 2.6×5.7	6.6×6.7 (straight) / 5.6×5.6 (tortuous)	5.4×5.6 (straight) / 5.1×5.5 (zig-zag)
Membered rings	12	12	12 / 8	12 / 12	10 / 10
Channel structure	3-D interlinking	3-D interlinking	1-D interlinking	3-D interlinking	2-D Large intersection

The comparison of some zeolite, ZSM-5, ZSM-11, ZSM-12 and ZSM-34, showed the effect from those acidity and pore size. The amount and the strength of acid site increased in the order ZSM-12 < ZSM-11 < ZSM-5 < ZSM-34. Although, ZSM-34 had the highest acidity, it was the least active because of its accessibility to acid sites was lower than the others (Bessell, 1995).

Beta zeolite was compared with ZSM-5, ZSM-12, ZSM-11, and Y zeolites. The acid strength determined from NH_3-TPD reduced in the order of ZSM-5 = ZSM-12 > BEA > ZSM-11 > Y. The number of acid site was ranked in the order of Y > BEA > ZSM-5 = ZSM-12 ~ ZSM-11. Beta zeolite exhibited the highest methylation activity and resistant deactivation than those zeolites because beta zeolite had three-dimensional large pore structures without supercages (like in Y zeolite, which caused rapid deactivation) (Pu and Inui, 1996).

H-ZSM-5, H-L, H-Y, and H-Beta zeolites were compared in the alkylation of isobutane. Isobutane over H-Y and H-Beta zeolites was converted to the large amount of C_8-C_{16} hydrocarbons because 12-membered ring zeolite and three-dimensional pore structure of those zeolites enhanced a product diffusivity. On the other hand, the diffusivity in H-ZSM-5 and H-L were limited in the 10-membered ring and one-dimensional structure, respectively (Sekine *et al.*, 2012).

The aromatics from ethanol were not occurred over H-Silicalite (without aluminum), but ethanol was instead converted to aliphatic hydrocarbons, which indicated the necessity of strong acid site for the aromatization (Choudhary and Nayak, 1985).

The influence of SiO_2/Al_2O_3 ratio was investigated by Talukdar *et al.* (1997). The ZSM-5 with SiO_2/Al_2O_3 ratios of 40 and 206 was studied in the conversion of ethanol to hydrocarbons. The lower SiO_2/Al_2O_3, which had a higher amount of Bronsted acid sites, tended to convert light olefins to aromatic and paraffins. The other literatures reported the result in the same trend (Miyamoto *et al.*, 2000; Shirazi *et al.*, 2008)

The effect of acidity and pore geometry of Ga_2O_3/HZSM-48 for the dehydrogenation of propane were studied by Ren *et al.* (2012). The decreasing acidity was governed by the rising of Si/Al ratio because Al in the framework was

partially removed. So, the increasing Si/Al ratio decreased the propane conversion. On the other hand, the propene selectivity increased.

2.4 Metal Oxide Catalysts for Dehydration

The introduction of metal oxide, such as alkali metals, alkaline earths and transition metals, affected to the product distributions. Schulz and Bandermann (1993) added various metals into zeolites, and observed the effect of metals on the ethanol conversion. They found the improvement of aromatic hydrocarbons yield with using Cr and Ni.

Methanol to gasoline reaction was improved by adding metal oxides. Zaidi and Pant (2004) impregnated 7 wt% of ZnO or CuO into HZSM-5. Products was analyzed by using GC-TCD and GC-FID. The methanol conversion over CuO/ZSM-5 zeolite decreased more rapidly than over CuO/ZnO/ZSM-5 zeolite. CuO/ZnO/ZSM-5 zeolite was synergetic between the advantage of ZnO (reducing the coke) and CuO (increasing acidic sites).

Pure Ga_2O_3 was active for the dehydrogenation of propane. Also, the synergic effect was found on the mixture of Ga_2O_3 and HZSM-5, in which the aromatization on the catalyst mixture occurred in the following reactions. First, propane was converted to propene over gallium oxide; then, propene diffused into HZSM-5 pore and reacted with oligomerization and then cyclization. Finally, naphthenic compounds moved to gallium oxide, and changed to aromatics (Gnep *et al.*, 1989).

The other reports found the same trend on gallium oxide effect. The physical mixtures of group 13 oxides (Ga_2O_3, In_2O_3, Tl_2O_3 and Al_2O_3) and H-ZSM-5 catalysts (1:1 by weight) were used to enhance aromatics from methanol dehydration. Ga_2O_3/HZSM-5 enhanced the aromatic hydrocarbon (C_6 to C_9) yield up to 46%, especially C_8H_{10} and C_9H_{12}. However, In_2O_3/HZSM-5 and Tl_2O_3/HZSM-5 immediately deactivated. The amount of Ga_2O_3 loading affected to the methanol conversion and aromatic yield; hence, the optimum aromatic hydrocarbon yield was obtained at 50 wt% of Ga_2O_3 loading. Various Si/Al ratio of HZSM-5 (30, 50, and

80) gave a different aromatic yield; so the increasing Si/Al ratio induced to form more aromatics (Freeman *et al.*, 2002).

The dehydration reaction on Ga, Sn, Ge, and Sb loading over SAPO-34 zeolite was studied by Wongwanichsin (2013). The acid strength of modified zeolites decreased in order : Sb_2O_3/SAPO-34 > Ga_2O_3/SAPO-34 > GeO_2/SAPO-34 > SnO_2/SAPO-34. Ethanol conversion was 93-97%, and the main product was gases for all SAPO-34 catalysts. However, zeolites with 5 wt% of Ga_2O_3 and Sb_2O_3 had significantly higher extracted oil yield than the others. Kerosene and gas oil yields were increased by using 5 wt% GeO_2/SAPO-34. Aromatics compounds were not observed on the unmodified SAPO-34, but SAPO-34 after modified with Ga and Ge significantly improved the aromatics yield, especially C_{10+} aromatics. So, acidic oxides enhanced the acid strength of catalysts, and led to propylene transformation to heavy hydrocarbons.

Liquid hydrocarbons were produced by using two consecutive layers of catalysts. The consecutive layers consisted of 2% Ga_2O_3/HZSM-5 as a first layer and one of these zeolites (H-X, H-Y, or H-Beta) as a second layer, and the reaction took place at 500°C. The Ga_2O_3 on the first layer affected to the product distribution. The oil yield from Ga_2O_3/HZSM-5 catalyst raised from 6.13% to 6.95%, and the major oil components were benzene, m-xylene, p-xylene, C_9 and C_{10}^+ aromatics with a low toluene amount. In addition, C_3 hydrocarbons can be converted to heavy hydrocarbons by promoting with Ga_2O_3. However, some hydrocarbons were cracked to methane and ethane. The amount of gas oil, light vacuum gas oil, and heavy vacuum gas oil were significantly increased when Ga_2O_3 was loaded into zeolites. In the second layer, those zeolites (H-X, H-Y, and H-Beta) promoted heavy aromatic hydrocarbons such as C_9 and C_{10}^+ aromatics, and enhanced p-xylene selectivity. Because of the high acid density of H-X or the high acid strength of H-Beta, the selectivity of C_9 and C_{10}^+ aromatics was enhanced by the disproportionation and transalkylation reactions (Pasomsub, 2013).

2.5 Micro/Mesoporous Composites (Hierarchical Mesoporous Zeolite)

Microporous zeolites, such as ZSM-5, Beta, Y, and SAPO-34, were generally used in the dehydration of ethanol or methanol because of their acidity, thermal stabilities, and specific pore sizes. However, the pore diameters of those zeolites were about 3-8 Å that limited the mass transfer of large hydrocarbons. Therefore, mesoporous zeolites were alternative zeolite for improving the diffusion rate of reactants and products, but it had low the catalytic activity and the hydrothermal stability when compared with microposous zeolites. Micro/mesoporous composites (hierarchical zeolites) were combined the advantage from both zeolites, which had the high acidity from microporous zeolites and the high diffusivity form mesoporous zeolites. Hierarchical zeolites can be synthesized via various templates, such as hard templates (carbon nanoparticles, carbon nanotubes, resins, or biological templates), soft templates (polymers and surfactants), and zeolites seed. Moreover, post treatment techniques (desilication and dealumination) can also make mesoporous zeolites.

H-Beta zeolite with a Si/Al ratio of 27 was treated by various concentrations of NaOH. The higher concentration of NaOH induced the mesoporosity of the beta zeolite. After treated with NaOH, the diameter of mesopore was approximately 3-12 nm, and the pore volume in the mesoporous region was enlarged significantly. However, the partial collapse of zeolite structure under a higher concentration of NaOH (>0.3M) in the post treatment step was observed from the transmission electron microscopy (TEM) measurement. Ruthenium was impregnated into H-meso-beta zeolite, and the catalyst was used to study in Fischer–Tropsch (FT) reaction. The Ru/H-meso-beta gave a higher selectivity of C_5-C_{11} hydrocarbons than the conventional zeolites and metal oxide, and it also increased the iso-paraffins to n-paraffins ratio (Cheng *et al.*, 2012).

The ZSM-5/MCM-48 composite (the Si/Al ratio of 80) was synthesized by using a cetyltrimethyl ammonium bromide (CTAB) as a template. When the zeolite composite performed in methanol to gasoline reaction, the methanol conversion reached up to about 99 % at 420 °C. The major product from the reaction consisted of aromatics and C_{5+} hydrocarbons. However, aromatics from ZSM-5/MCM-48 composite were reduced harshly when compared with those from ZSM-5 zeolite

because of the interconnection between microporous and mesoporous channel (Di *et al.*, 2012).

Xiao *et al.* (2006) developed a technique for synthesizing hierarchical mesoporous zeolites by using a mesoscale cationic polymer, polydiallydimethyl-ammonium chloride (PDADMAC), as a template. After that, Yin *et al.* (2013) followed the Xiao's technique to synthesize hierarchical mesoporous zeolite Beta. The hierarchical mesoporous zeolite Beta was used in the alkylation of benzene with isopropanol to cumene; and it was found to enhance the catalytic activity and selectivity because of a good molecular transfer.

The formation of hierarchical mesoporous zeolites was improved by zeolite seeds or protozeolitic particles. The hierarchical mesoporous zeolites from zeolite seeds had a good thermal stability and acidity. The various zeolite seeds, Y (FAU), ZSM-5 (MFI), and Beta (BEA) zeolites, were used to form an aluminosilicate mesostructure (MSU-S). A different pore structure was induced by various templates. For examples, hexagonal pore structure (MSU-S/H) with a pore size of 3.0 nm was formed by using cetyltrimethyl ammonium bromide (CTAB), and wormhole-like pore structure (MSU-S/W) with a pore size of 3.6 nm was formed by using tallow tetramine. The MSU-S/W with three-dimension had higher textural porosity than the MSU-S/H. However, both MSU-S catalysts exhibited higher hydrothermal stability and catalytic activity than conversional mesoporous aluminosilicates (Liu *et al.*, 2001; Liu and Pinnavaia, 2004; Xiao, 2004).

In summary, the heavy liquid hydrocarbons can be produced from bio-ethanol by using modified beta zeolite. The beta zeolite modified with Ga_2O_3 and GeO_2 improved the conversion of bio-ethanol to heavy hydrocarbons in the U-tube reactor at 450 °C for 8 hours.

Si/Al ratio also affects to the products such as aromatics that favor to occur at a low Si/Al ratio. Hence, this research aimed to use modified beta zeolite in the bio-ethanol dehydration process, and investigated the effect of Si/Al ratio of beta zeolite, which governs the amount of acid site and the acid strength of zeolites. Different Si/Al ratios (different amounts of acid site and the acid strength) of zeolite can affect to the product distribution and heavy liquid hydrocarbons yield. In the experiments,

three different Si/Al ratios of beta zeolite (Si/Al$_2$ ratio = 27, 37, and 300) were used in bio-ethanol dehydration.

Mesoporous structure can improve the diffusivity and the large hydrocarbons selectivity. Micro/mesoporous composites have both advantages from microporous and mesoporous zeolites; thus, heavy hydrocarbons may be increased by using micro/mesoporous composite. Two micro/mesoporous composites were then used in the research. MSU-S/H$_{BEA}$ with hexagonal pore structure was formed by using cetyltrimethyl ammonium bromide template (CTAB).

Table 2.3 Experimental design in the first scope

Si/Al$_2$ of Beta Zeolite	Without Loading	5 wt% of Ga	5 wt% of Ge
27	(1)	(4)	(7)
37	(2)	(5)	(8)
300	(3)	(6)	(9)

Table 2.4 Experimental design in the second scope

	Without Loading	5 wt% of Ga	5 wt% of Ge
MSU-S/H$_{BEA}$	(10)	(11)	(12)

The objectives of this research work were to study the effect of acid density and acid strength (various Si/Al ratios of Beta zeolite) on product distribution from the catalytic dehydration of bio-ethanol, and to compare the activity of MSU-S with different pore structures (hexagonal pore structure and wormhole-like pore structure) on the catalytic dehydration of bio-ethanol.

The scope of this research covered as follows. In the first scope, the dehydration of bio-ethanol was performed in a U-tube reactor using these conditions; 99.5% of bio-ethanol, LHSV 0.5 h^{-1}, reaction temperature at 450°C under

atmospheric pressure for 8 hours. In the second scope, 5 wt% of Ga or Ge was impregnated into all Si/Al_2 ratios of H-Beta zeolite (Si/Al_2 = 27, 40 and 300). 3 g of modified H-Beta zeolite was used in the bio-ethanol dehydration process. In the last scope, the hexagonal pore structure of MSU-S was synthesized by using cetyltrimethyl ammonium bromide template. Then, $MSU-S/H_{BEA}$ was impregnated by 5 wt% of Ga or Ge. 3 g of modified $MSU-S/H_{BEA}$ was used in the bio-ethanol dehydration process.