

## CHAPTER II

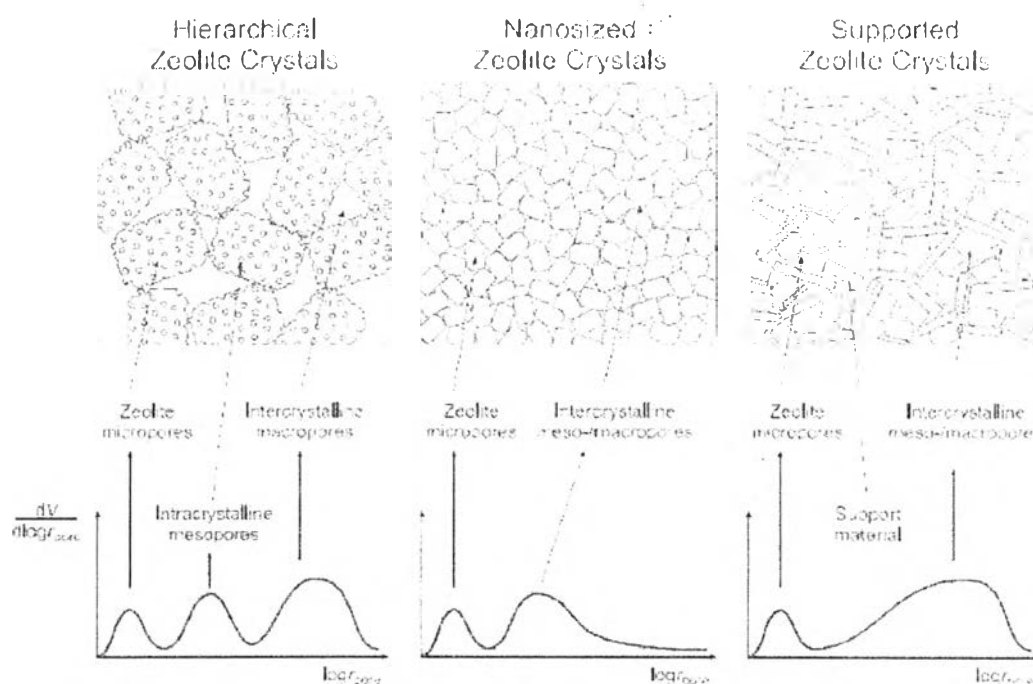
### THEORETICAL BACKGROUND AND LITERATURE REVIEW

Mesoporous zeolites can be divided into three categories; that are. (a) hierarchical zeolites, (b) nano-crystal sized zeolites, and (c) supported zeolites (Egeblad *et al.*, 2008) as shown in Figure 2.1. The hierarchical zeolites are the ones that have additional meso-porosity in each crystal, and also have intercrystalline pore, normally defined as macropore. The nano-crystal sized zeolites typically have crystal sizes below 100 nm. Either intracrystalline or intercrystalline systems can be found in the nano-crystal sized zeolites, defined as the micropore and mesopore system, respectively. The last category is supported zeolites, defined as those of which are supported or dispersed in the pore of another material. The mesopore systems therefore depend on the nature of the support material. Hierarchical mesoporous zeolite-synthesizing methods can be categorized as solid templating, supramolecular templating, indirect templating, and nontemplated methods. A solid material is employed to use in the solid templating method to grow a zeolite; then, it can be removed by combustion, dissolution, or sublimation. For the supramolecular templating method, a surfactant is employed to use as the mesopore template. For the indirect method, a nonzeolitic material is firstly formed, and then in the separation step, the mesoporous nonzeolitic material is transformed to a mesoporous zeolite. In addition, dealumination, desilication, and detitanation are defined as nontemplated methods (Taguchi and Schüth, 2005; Egeblad *et al.*, 2008).

#### **2.1 Micro-mesoporous Materials (Hierarchical Mesoporous Materials)**

Microporous materials such as SAPO-34 Beta, ZSM-5, Y and HMOR are the one of the most widely-used catalysts in many industries, especially in petrochemical industry. They have uniform pore size about 3-8 Å, and a uniform structure makes them have high catalytic activities but poor diffusivities for large molecules. On the other hand, mesoporous materials have high diffusivities for large molecules, but poor catalytic activities and hydrothermal stabilities, compared to the microporous materials. Therefore, micro-mesoporous materials are developed to

overcome the weaknesses of both microporous and mesoporous materials, which results in the improvement of catalytic activities, hydrothermal stabilities, and diffusivities for large molecules.



**Figure 2.1** Categorization of mesoporous zeolites (Egeblad *et al.*, 2008).

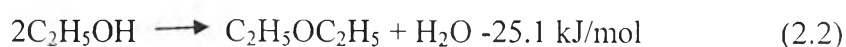
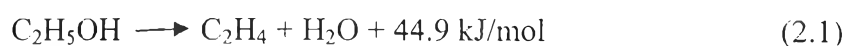
Liu *et al.* (2000, 2001) developed mesoporous aluminosilicates with hexagonal and wormhole structures, derived from Y (FAU), ZSM-5 (MFI) and Beta (BEA) zeolite seeds by using different templates. The hexagonal and wormhole mesostructures can be obtained from using cetyltrimethylammonium bromide (CTAB) and dodecylamine as a template, respectively (Liu and Pinnavaia, 2004). Three-dimensional framework structure and higher textual porosity can be obtained from the wormhole structure while the hexagonal structure exhibits a one-dimensional structure. A MSU-S mesoporous catalyst with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 55 was synthesized for methanol dehydration to dimethyl ether by using TPAOH as a structure directing agent and CTAB as a surfactant. The conversion was increased as the reaction temperature increased, and reached the equilibrium at 380 °C. The

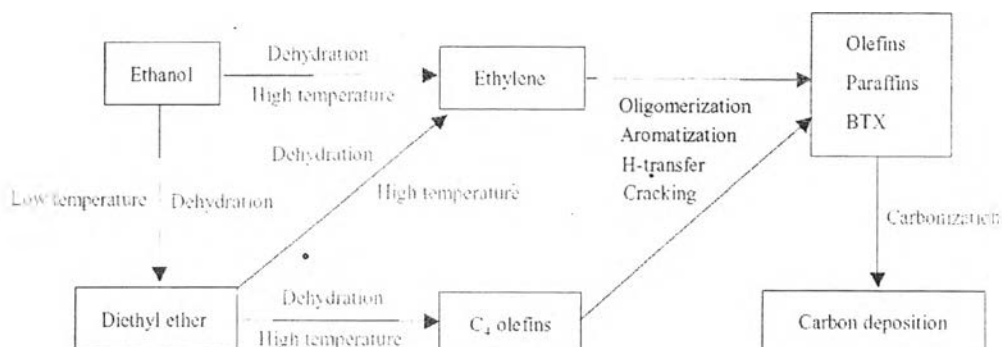
activity and selectivity of MSU-S were higher than those of Al-MCM-41 (Rashidi *et al.*, 2013).

MSU-S<sub>BEA</sub> with hexagonal and wormhole pore structures assembled from Beta zeolite seeds were compared with Al-MCM-41 and non-catalytic reaction in biomass pyrolysis. The MSU-S with hexagonal pore structure (MSU-S/H<sub>BEA</sub>) with a pore diameter of 3.0 nm was obtained from using a cetyltrimethylammonium chloride (CTAB) as a template, while the MSU-S with wormhole-like pore structure (MSU-S/W<sub>BEA</sub>) with a pore diameter of 3.6 nm was obtained from using a tallow tetramine as a template. The MSU-S exhibited the higher production of propylene in pyrolysis gas, aromatics, PAHs, and coke, than Al-MCM-41 (Triantafyllidis *et al.*, 2007).

## 2.2 Ethanol Dehydration to Hydrocarbons

At present, bio-ethanol becomes one of the alternative sources to replace the consumption of petroleum. Bio-ethanol can be produced by fermentation process by using sugarcane, sugar beet and starch crops. Bio-ethanol dehydration can be separated into two pathways. At a high reaction temperature, bio-ethanol can be converted to ethylene by intermolecular dehydration. However, at a low temperature, intramolecular dehydration is more favored to convert bio-ethanol to diethyl ether. Diethyl ether also can be converted to C<sub>4</sub> olefins and ethylene at a high temperature (Derouane *et al.*, 1978). Then, oligomerization, cracking, H-transfer or aromatization can be occurred, resulting in the formation of larger hydrocarbons as shown in Figure 2.2. The pathways of ethanol dehydration are shown in Equations 2.1 and 2.2 below (Chen *et al.*, 2010).





**Figure 2.2** Reaction pathways of ethanol to hydrocarbons (Inaba *et al.*, 2006).

### 2.2.1 Microporous Catalysts for Ethanol Dehydration

In 2005, Takahara *et al.* used H-mordenites with Si/Al = 20 and 90, HZSM-5 with Si/Al = 25 and 90, H-Beta with Si/Al = 25, H-Y with Si/Al = 5.5, and silica-alumina with Si/Al = 9.2 on the dehydration of ethanol to ethylene over solid acid catalysts. The reaction took place in a fixed-bed flow reactor under atmospheric pressure. The result indicated that catalytic activity decreased as follows : HM20 > HM90 > ZSM-5(25) > HB25 > ZSM-5(90) > HY5.5 > SA. Then, the amount of carbonaceous deposited on HM20 and HM90 were measured. As a result, the deposition on HM20 was 6 mg-C/g-cat, whereas it was only a trace on HM90. Moreover, in 2006, Inaba *et al.* studied ethanol conversion to aromatics hydrocarbons by using H-Beta (Si/Al<sub>2</sub> = 27), HZSM-5 (Si/Al<sub>2</sub> = 29, 190), USY (Si/Al<sub>2</sub> = 6.3) and HMOR (Si/Al<sub>2</sub> = 18.3) with impregnated metals, Mg, Cr, Fe, Co, Ni, Cu, Ga, Ru, Rh, Pd, Ag, Re, Ir, Pt and Au, on the zeolites. Catalytic activity was measured by using a fixed bed reactor at 400 °C. The 52.88 % highest selectivity of BTX can be obtained from HZSM-5 (Si/Al<sub>2</sub> = 29) with 92.24 % ethanol conversion. On the other hand, other zeolites; H-Beta (Si/Al<sub>2</sub> = 27), HZSM-5 (Si/Al<sub>2</sub> = 190), USY (Si/Al<sub>2</sub> = 6.3) and HMOR (Si/Al<sub>2</sub> = 18.3) showed the high ethanol conversion with ethylene selectivity of 86.50 %, 97.58 %, 96.21 % and 95.77 %, respectively as shown in Table 2.1

**Table 2.1** Ethanol conversion, ethylene, C<sub>3+</sub> olefins, paraffins, and BTX selectivity (Inaba *et al.*, 2006)

Catalyst	Ethanol Conversion (%)	Selectivity (%)				
		Diethyl Ether	Ethylene	C <sub>3+</sub> olefins	Paraffins	BTX
H-Beta(27)	94.77	1.66	86.50	3.18	3.14	3.95
HZSM-5 (29)	92.24	5.79	10.48	15.62	13.22	52.88
HZSM-5(190)	96.41	0.33	97.58	1.72	0.03	0.00
USY (6.3)	93.70	0.42	96.21	0.42	1.23	0.00
HMOR(18.3)	79.83	0.00	95.77	1.04	2.57	0.00

$\gamma$ -Al<sub>2</sub>O<sub>3</sub>, HZSM-5 (Si/Al<sub>2</sub> = 25), SAPO-34 and NiAPSO-34 were also studied on dehydration of ethanol to ethylene. SAPO-34 and NiAPSO-34 were synthesized by hydrothermal method while  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and HZSM-5 (Si/Al<sub>2</sub> = 25) were commercial catalysts. The ethanol conversion and ethylene selectivity were measured at different temperatures. 97.3 % of ethanol conversion of HZSM-5 was the highest at 325 °C due to its strong acidity while the other zeolites;  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SAPO-34 and NiAPSO-34 exhibited ethanol conversion of 90.1 % at 475 °C, 93.5 % and 96.5 % at 375 °C, respectively. The stability of these four catalysts was also investigated. SAPO-34 and NiAPSO-34 showed 86.0 % and 92.3 % ethylene yield, respectively, which still unchanged at 100 h time-on-stream while HZSM-5 and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> deactivated at 60 h and 80 h, respectively (Zhang *et al.*, 2008). In addition, the mechanistic insights on ethanol transformation to hydrocarbons was also studied using HZSM-5 (Si/Al = 16) under 30 bar at 350 °C. Ethanol was completely converted to ethylene, C<sub>3+</sub> hydrocarbons, diethyl ether, and water. In this work, C<sub>3+</sub> hydrocarbons were divided into three fractions, which were C<sub>3</sub>-C<sub>4</sub>, C<sub>5</sub>-C<sub>11</sub>, and C<sub>12+</sub>. C<sub>5</sub>-C<sub>11</sub> was the main fraction, while C<sub>3</sub>-C<sub>4</sub> was 1.2 times lower than the fraction of C<sub>5</sub>-C<sub>11</sub>, and C<sub>12+</sub> are traces. Among paraffins, propane, butanes, and pentanes were the main products, while among olefins, butenes were the main products. Carbon contents were measured by using IR spectroscopy. 89 % of microporosity was lost

after 25 h time-on-stream, but the catalyst still had high production of C<sub>3+</sub> hydrocarbons (Madeira *et al.*, 2010).

Furthermore, Duan *et al.* (2013) used the HZSM-5/SAPO-34 composite catalysts in the comparative studies of ethanol to propylene prepared by hydrothermal synthesis and physical mixing. This work used HZSM-5 with different Si/Al<sub>2</sub> in the ratio of 25, 38, and 200 and 1 and 4 % wt loading percentages of HZSM-5 in SAPO-34. The reaction conditions were 500 °C, 0.1MPa, 0.5 g catalysts, total flow rate = 80 ml/min with TOS = 3 h. The ethanol was completely converted to ethylene by SAPO-34, and then ethylene was converted to propylene by the HZSM-5. The propylene yield was ranked from high to low as follows: ZS(25)-MM-4, ZS(38)-MM-4, and ZS (25)-HS-4 as shown in Table 2.2. In the same year, Pasomsub (2013) studied the two consecutive layers of catalysts in order to convert bio-ethanol to liquid hydrocarbons. The first layer was filled by 2%wt Ga<sub>2</sub>O<sub>3</sub>/HZSM-5, and the second layer was filled by a zeolite with different pore sizes, which were H-X, H-Y, and H-Beta. It was found that both HZSM-5 and Ga<sub>2</sub>O<sub>3</sub>/HZSM-5 samples gave around 96.5 % ethanol conversion, which was not significantly different, but the presence of Ga<sub>2</sub>O<sub>3</sub> can increase the amount of oil from 6.13 % to 6.95 %. Mostly, the oil from Ga<sub>2</sub>O<sub>3</sub>/HZSM-5 consisted of benzene, m- and p-xylene, C<sub>9</sub> and C<sub>10+</sub> aromatics. Then, the products from the first layer passed into the second layer. The presence of H-X, H-Y, and H-Beta did not affect the oil and aromatics yields, but increased the selectivities of C<sub>9</sub> and C<sub>10+</sub> aromatics. The oil and aromatics yields were ranked as follows: 2GaHZ5 > 2GaHZ5:Y > 2GaHZ5:X > 2GaHZ5:β while C<sub>9</sub> and C<sub>10+</sub> aromatics selectivities were ranked as follows: 2GaHZ5:X > 2GaHZ5:Y > 2GaHZ5:β > 2GaHZ5 and 2GaHZ5:X > 2GaHZ5:β > 2GaHZ5:Y > 2GaHZ5. It was explained that C<sub>9</sub> and C<sub>10+</sub> aromatics can be formed by transalkylation and disproportionation of benzene, toluene, and m-xylene in the second layer because H-X, H-Y, and H-Beta had large pore diameter and moderate acidity.

**Table 2.2** Catalytic activities of catalysts for dehydration of ethanol (Duan *et al.*, 2013)

Catalysts	Yield (%wt)							
	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>5+</sub>
SAPO-34	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0
ZS (25)-MM-1	Trace	87.8	0.2	6.9	0.1	4.9	0.2	Trace
ZS (25)-MM-4	0.1	24.0	1.0	34.5	6.8	20.7	9.2	3.7
ZS (38)-MM-4	0.2	25.6	1.0	33.7	8.6	19.4	7.9	3.5
ZS (200)-MM-4	Trace	91.2	0.1	5.3	Trace	3.2	0.1	0.1
ZS (25)-HS-1	0.2	12.1	1.6	25.3	14.5	20.7	19.1	6.5
ZS (25)-HS-4	0.1	26.6	1.5	32.3	6.9	20.0	9.0	3.7
HZSM-5	0.9	10.4	4.3	16.4	35.5	8.0	21.6	2.9

ZS(m)-MM,HS-n ; ZS = HZSM-5, MM = physical mixing, HS = hydrothermal synthesis, m = Si/Al<sub>2</sub> ratio, n = % loading of HZSM-5

### 2.2.2 Mesoporous Catalysts for Ethanol Dehydration

Mesoporous catalysts for ethanol dehydration also have been studied. A mesoporous HZSM-5 zeolite with secondary mesoporosity and structural microporosity was synthesized to convert ethanol to hydrocarbons in a fixed bed reactor at 360 °C, and 300 psig. The comparison between mesoporous HZSM-5 and conventional HZSM-5 with the same Si/Al ratio exhibited that the hierarchical HZSM-5 gave the higher catalytic activity and diffusion rate, which can increase life time of the catalysts by reducing coke formation. From TPO experiments, at a low Si/Al ratio (40), the life time of the nano-crystal sized HZSM-5 was 2 times longer than that of the conventional HZSM-5. Moreover, the nano-crystal sized HZSM-5 was 1.6 times higher coke formation than the conventional zeolite. At a high Si/Al ratio (140), the nano-crystal sized HZSM-5 had 5 times longer life time than the conventional HZSM-5 and 2.1 times higher amount of coke deposited (Ramasamy *et al.*, 2014). Other mesoporous catalysts were also investigated. Al-MCM-41 with

$\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 30 was synthesized for methanol dehydration by using TEOS as a silica source, and CTAB as a structure-directing agent. Various amounts of TPAOH, added as a co-surfactant, were represented as CTAB/TPAOH ratios. The result indicated that a high concentration of TPAOH can increase the particle size and total acidity. The conversion of methanol and selectivity of dimethyl ether are shown in Table 2.3

**Table 2.3** List of the synthesized MCM-41 samples (Naik *et al.*, 2010)

Catalyst code	Catalyst type	[CTAB/TPAOH]	Methanol Conversion, %	DME Selectivity, %
MC-1	Al-free MCM-41	-	6	100
MC-2	Al-MCM-41	$\infty$	45	98
MC-3	Al-MCM-41	0.75	72	98
MC-4	Al-MCM-41	0.20	73	97

In addition, ethanol dehydration to diethyl ether over copper and cerium phosphotungstate supported on MCM-41 was also investigated. Cu and Ce cations in MCM-41 were used to replace protons in  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . The supported catalysts were synthesized by a two-step impregnation method. Table 2.4 shows the amount of loading Cu (or Ce): P: W in the catalysts, conversion of ethanol and diethyl ether selectivity. Catalytic activity was measured at reaction temperature about 300 °C, and the CeHPW/MCM was higher than CuHPW/MCM. The 30 % loading of CeHPW on MCM (30 CeHPW/MCM) exhibited the highest ethanol conversion (88.3 %) with 85 % selectivity of diethyl ether due to its highest acidity (Trakarnpruk, 2013).



**Table 2.4** Conversion of ethanol and diethyl ether selectivity at various Cu and Ce loadings (Trakarnpruk, 2013)

Catalyst	Cu or Ce : P : W Molar Ratio	Ethanol Conversion (%)	Diethyl Ether Selectivity (%)
MCM	0	-	-
20 CuHPW/MCM	1.1:1.0:11.9	75.4	77.1
30 CuHPW/MCM	1.2:1.0:11.8	81.0	78.3
20 CeHPW/MCM	0.6:1.0:12.1	83.2	84.5
30 CeHPW/MCM	0.7:1.0:12.0	88.3	85.0

Moreover, the hierarchical mesoporous MSU-S assembled from BEA-seed has been studied in bio-ethanol dehydration process. Sujeerakulkai (2014) studied the catalytic activity of hexagonal MSU-S from beta-seed (MSU-S<sub>BEA</sub>) on bio-ethanol dehydration. The MSU-S<sub>BEA</sub> was synthesized by using CTAB as a hexagonal mesopore template. The reaction took place in a U-tube fixed bed reactor at 450°C under atmospheric pressure. The result exhibited that the pore diameter of the synthesized MSU-S<sub>BEA</sub> was 2.7 nm. From the catalytic activity, MSU-S<sub>BEA</sub> exhibited high gas and oil composition. The main product in gas was 93.6 %wt ethylene. The compositions of main products in oil were 28 %wt C<sub>9</sub> aromatics, 20.5 %wt C<sub>10+</sub> aromatics, and 18.5 %wt p-xylene. The petroleum fractions in oil were mostly gasoline and kerosene, whose contents were about 48.5 %wt and 47.2 %wt, respectively.

### 2.3 Governing Parameters on Catalytic Performances

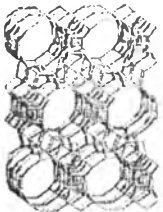
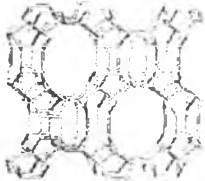

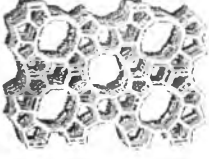
For bio-ethanol dehydration, firstly,  $\gamma$ -alumina was employed as a catalyst, but it required a high reaction temperature of about 450 °C, and gave a low ethylene yield (about 80 %). Later, zeolites were employed instead of  $\gamma$ -alumina because they required a lower temperature, and gave higher ethylene yield (Zhang *et al.*, 2008). Zeolites can be classified into many categories, depending on their properties as

shown in Table 2.5. Many parameters such as Si/Al ratio, reaction temperature, pore structure, pore size, acidity, and crystal size, even in synthesizing conditions, can affect to the catalytic performances.

The first parameter is Si/Al ratio, which can affect on the acid strength and acid density of zeolites. High acid strength can be acquired from a low Si/Al ratio. On the other hand, high acid density can be justified by a high Si/Al ratio. In 1997, Talukdar *et al.* studied the effects of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and reaction temperature on the conversion of ethanol to hydrocarbons. The HZSM-5 zeolites with two  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 40 and 206 were used in the reaction. The results showed that with increasing reaction temperature, the olefinic and aromatic fractions were increased. Gaseous  $\text{C}_{6+}$  and  $\text{C}_1\text{-C}_5$  paraffins can be produced at a low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, while light olefins ( $\text{C}_2\text{-C}_4$ ) can be produced at a high  $\text{SiO}_2/\text{Al}_2\text{O}_3$ . Not only bio-ethanol dehydration, but also methanol dehydration was also studied. Li *et al.* (2013) studied the effect of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of HZSM-5 in HZSM-5/MCM-41 composite on methanol dehydration to dimethyl ether. The hydrothermal technique was employed to prepare the micro-mesoporous composite molecular sieve, HZSM-5/MCM-41, with various  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 25, 38, 50, and 150. The hexagonal mesoporous structure was formed by CTAB. The HZSM-5/MCM-41 exhibited the higher BET surface area due to the hierarchical porosity. As a result, for methanol dehydration, HZSM-5 with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 150 exhibited 100 % DME selectivity, whereas HZSM-5/MCM-41 exhibited little lower DME selectivity than HZSM-5 because of lower total acidity. The DME selectivity of HZSM-5/MCM-41 was increased with increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio due to the decrease of strong acid site. Moreover, the Si/Al ratios of other zeolites such as H-Beta also had influences on catalytic performance. Sujeerakulkai and Jitkarnka (2014) studied the effect of Si/Al<sub>2</sub> ratios of H-Beta on bio-ethanol dehydration to heavy hydrocarbons. H-Beta with Si/Al<sub>2</sub> ratio of 27, 37, and 300 were used in this work. From the catalytic activity testing, H-Beta with Si/Al<sub>2</sub> ratio of 37 exhibited the highest amount of oil and the lowest amount of gas than those with Si/Al<sub>2</sub> ratio of 27 and 300. Ethylene was the main component in the gas stream in all ratios. The oil from H-Beta ratio of 37 consisted of 40 % BTEX, 38.8 % of  $\text{C}_9$  aromatics, and 24.8 % of  $\text{C}_{10+}$  aromatics. The result from H-Beta ratio of 37 showed the decreases of ethylene and benzene

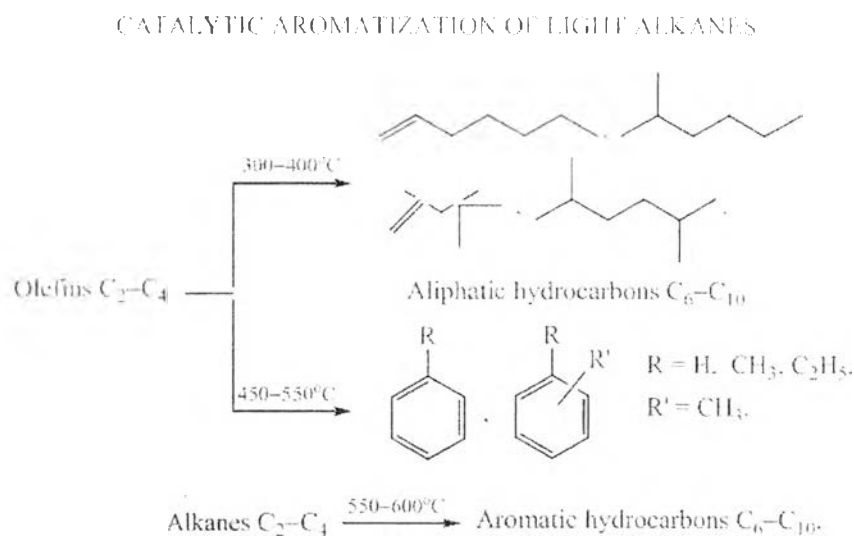
and the increases of C<sub>9</sub> and C<sub>10+</sub> aromatics, compared to those at the ratio of 27, and 300. This may be resulted from alkylation reaction on the catalyst that had moderate acidity.

**Table 2.5** Structural characteristics of zeolites (Perego *et al.*, 2009; Baerlocher and McCusker, 2002)

Zeolite	IZA Code	Channel Dimensionality	Type Channel	Pore Dimension (nm)	Structure
Beta	BEA	3D	12	0.66 x 0.67	
			12	0.56 x 0.56	
Mordenite	MOR	1D	12	0.70 x 0.65	
Y	FAU	3D	12	0.74 x 0.74	
ZSM-5	MFI	3D	10	0.53 x 0.56	
			10	0.51 x 0.55	

The second parameter is reaction temperature. Degachev and Lapidus (2009) studied the catalytic aromatization of light alkanes. They found that the reaction temperature can affect the products distribution. At higher temperatures

(450 °C – 500 °C), the conversion of olefins (C<sub>2</sub>-C<sub>4</sub>) to aromatic hydrocarbons was favored, whereas the conversion of alkanes (C<sub>2</sub>-C<sub>4</sub>) to aromatic hydrocarbons was favored at 550 °C – 600 °C. At lower temperatures (300 °C – 400 °C), the olefins were rather converted to aliphatic hydrocarbons (C<sub>6</sub>-C<sub>10</sub>) as shown in Figure.2.3.



**Figure 2.3** Scheme of transformations of C<sub>2</sub>-C<sub>4</sub> olefins and alkanes on pentasil (Degachev and Lapidus, 2009).

A highly-affecting parameter on zeolite performance is crystal size. Bi *et al.* (2010) compared the performance of nanoscale HZSM-5 zeolite on bio-ethanol to ethylene with that of microscale HZSM-5 by using a fixed bed reactor at 240 °C under atmospheric pressure. Nanoscale and microscale HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 26 and 25) with the crystal size of 50 – 100 nm and 1 – 3 μm, respectively, were used in this work. The result showed that the ethanol conversion and ethylene selectivity over nanoscale HZSM-5 was still constant during 630 h reaction time, while those of microscale decreased after 60 h reaction. Ethylene was the main product in the gas stream of both nanoscale and microscale HZSM-5. The diffusion path of nanoscale was much shorter than those of microscale because the crystal size of nanoscale was much smaller, which consequently affected the stability of the zeolites. The nanoscale HZSM-5 gave higher stability than microscale HZSM-5. Furthermore,

Rownaghi *et al.* (2011) studied uniform ZSM-5 crystal size on the yield of gasoline-range hydrocarbons. Nanocrystal and conventional ZSM-5 with the same Si/Al ratio were synthesized by following a single-templating procedure. Then, both ZSM-5 were used in methanol dehydration using a fixed bed reactor at 370 °C under atmospheric pressure. It was found that the nanocrystal ZSM-5 exhibited higher methanol conversion, and the selectivity of light olefins, paraffins, and aromatics as shown in Table 2.6 due to their lower diffusion limitations and higher concentration of strong acid sites.

**Table 2.6** Methanol conversion and hydrocarbon distribution (Rownaghi *et al.*, 2011)

Catalyst	Conversion (%)	Hydrocarbon Distribution					
		Methanol	Ethylene	Propylene	Paraffins (C <sub>1</sub> -C <sub>4</sub> )	Aromatics (BTX)	Other HC
Nano-ZSM-5	100	0	6.6	13.8	33.6	34.2	11.7
Con-ZSM-5	50	43.6	9.6	-	15	18	9.6

Viswanadham *et al.* (2012) also studied the catalytic performance of nanocrystalline HZSM-5 in ethanol dehydration to gasoline. The HZSM-5 with various acidity and porosity were synthesized in this work. Two micro-crystalline HZSM-5 samples with different Si/Al ratios of 30 and 100, represented by Z and ZA, respectively, were compared to nano-crystalline (NZ) with Si/Al ratio of 30. The NZ gave about 70 % higher amount of liquid yields and 30 % lower amount of gas yield. The Z exhibited the same patterns of liquid and gas yield, but the trend was inverted with using ZA. The paraffins formation was ranked as follows: NZ < Z < ZA. The predominant product of all catalysts was propane. The NZ gave the highest olefins formation (about 30 %), followed by Z and ZA. The gasoline distribution was compared at two reaction temperatures (450 °C and 500 °C). At 450 °C, the NZ and Z

exhibited close gasoline yield, but ZA gave a lower gasoline yield. At 500 °C, the NZ exhibited the highest gasoline yield, followed by Z and ZA in the percentages of 74 %, 59 %, and 47 % as shown in Table 2.7. In summary, it is evident that the crystal size has many effects on the catalytic performances. A smaller crystal size gave a higher surface area that can result in higher mesoporosity, higher stability, and higher conversion than a bigger crystal size.

Acidity is also the one parameter that can affect the catalytic performances of zeolites. Furumoto *et al.* (2011) studied the effect of acidity of ZSM-5 zeolite on conversion of ethanol to propylene by protonation of ZSM-5 zeolite with Al, Ga, and Fe at different  $\text{SiO}_2/\text{M}_2\text{O}_3$  ratios of 200, 150, 100, 75, and 50. As a result, the HZSM-5(M) (M = Al, Ga, and Fe) exhibited 100 % conversion of ethanol at 500 °C, and the propylene yield strongly depended on  $\text{SiO}_2/\text{M}_2\text{O}_3$  ratio and W/F ratio. Both HZSM-5 (Ga) and HZSM-5 (Al) gave high propylene yield with the  $\text{SiO}_2/\text{M}_2\text{O}_3$  ratio of 70 and 74, respectively. The propylene yield of HZSM-5 (Al) dramatically decreased with increasing time-on-stream while HZSM-5 (Ga) showed a little decrease. Then, phosphorus-modified HZSM-5 (Ga) was also studied for its stability and catalytic activity, and it was found that at  $\text{P}/\text{Ga} = 0.3$ , the HZSM-5 (Ga) showed high catalytic stability due to the reduction of strong acid sites on HZSM-5.

**Table 2.7** Gas and gasoline compositions from various catalysts (Viswanadham *et al.*, 2012)

Temperature	450 °C			500 °C		
Catalysts	NZ	Z	ZA	NZ	Z	ZA
Gas Analysis						
Gas Composition	31.5	37.6	57.6	29.9	48.7	64.8
Liquid Analysis						
Liquid Composition	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	35.5	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
Others	1.9	1.0	0.1	0.4	0.7	0.1
RON	91.0	87.1	105.5	95.4	90.5	108.4

In conclusion, hydrocarbons from bio-ethanol dehydration can be produced using commercial microporous zeolites such as H-Beta or HZSM-5, but they have diffusion limitation for large molecules. To overcome the weakness of commercial microporous zeolites, mesoporous zeolites have been developed and employed. Although mesoporous zeolites have better diffusion limitation, they have low total acidity and low hydrothermal stability in general. Thus, hierarchical mesoporous zeolites have been developed to combine the advantages of both microporous and mesoporous zeolites, which result in a catalyst that have high acidity, high hydrothermal stability, and high diffusion limitation for large molecules.

In this work, two consecutive layers of catalysts were studied on the purpose of increasing the amount of heavy liquid hydrocarbon from bio-ethanol dehydration

process. The first layer was filled by a commercial microporous zeolite; that is, H-Beta or HZSM-5 with Si/Al<sub>2</sub> ratio of 37 and 30, in order to produce BTX and heavy hydrocarbon compounds. Then, hydrocarbons from the first layer were preferably oligomerized in the hierarchical mesoporous MSU-S, which have a bigger pore diameter, so that liquid hydrocarbons such as gasoline, kerosene, and gas oil can be further produced in a large amount. The hierarchical mesoporous MSU-S in the second layer was synthesized by using BEA-seed or MFI-seed and CTAB as a hexagonal pore template. The reaction took place in a U-tube fixed bed reactor at 450 °C for 8 hours.