



CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Bioethanol

Bioethanol is a renewable product obtained by the direct conversion of biomass (corn, maize and wheat crops, waste straw, willow and popular trees, sawdust, reed canary grass, cord grasses, jerusalem artichoke, mysanthus, sorghum plants, sugar-cane, cassava, molasses, other grains, or even cornstalks, fruit and vegetable waste) or by glucose fermentation process. It has many attractive properties, for examples; it is a clear colorless liquid, its toxicity is low level, and it is a high octane substance. Thus, at the beginning, it was most popular used as the biofuel for petrol engines, which is an alternative fuel, to replace the fossil fuel. Moreover, it still has many advantages, which claimed as reasons to support its capability as the alternative energy, for examples:

- Bioethanol is a much cleaner fuel than petrol (gasoline) because it is a renewable fuel made from plants,
- It can be handled in a similar manner to petrol, and is often used as a low percentage blend to save on fuel costs – E10 is 10 % ethanol and 90 % petrol,
- It can help to reduce the greenhouse gas emission causing the global warming and make more environmentally friendly,
- The cost of production is low, and
- Less energy is consumed.

Therefore, a plenty of bioethanol utilization and development have been proposed. At present, high attention has been paid on the use of bioethanol as a feedstock for the production of light olefins and aromatic hydrocarbons. Light olefins and aromatic hydrocarbons are the important intermediate, and are highly valuable products in the petroleum and petrochemical industries, which can be produced by the steam cracking of naphtha in general. Nevertheless, the transformation of bioethanol to hydrocarbons is expected to be another route that provides high effectiveness and rewarding investment.

2.2 Transformation of Bioethanol to Hydrocarbons

The conversion of light alcohols such as methyl alcohol or ethyl alcohol to gasoline or hydrocarbon compounds has received wide attention in these days due to the global energy crisis and the heavy demand for hydrocarbons. Therefore, a number of researchers and engineers have tried to discover a novel process that can produce the hydrocarbon compounds like ethylene, propylene, other light olefins, and aromatic hydrocarbons from alcohols. In addition, currently the ideas related to energy conservation and environmental issues are greatly interested and realized; thus, not only can one develop a novel hydrocarbon producing process, but also the process must not have a negative influence on the environment, and it should have low energy consumption, simple equipment, and an easy control.

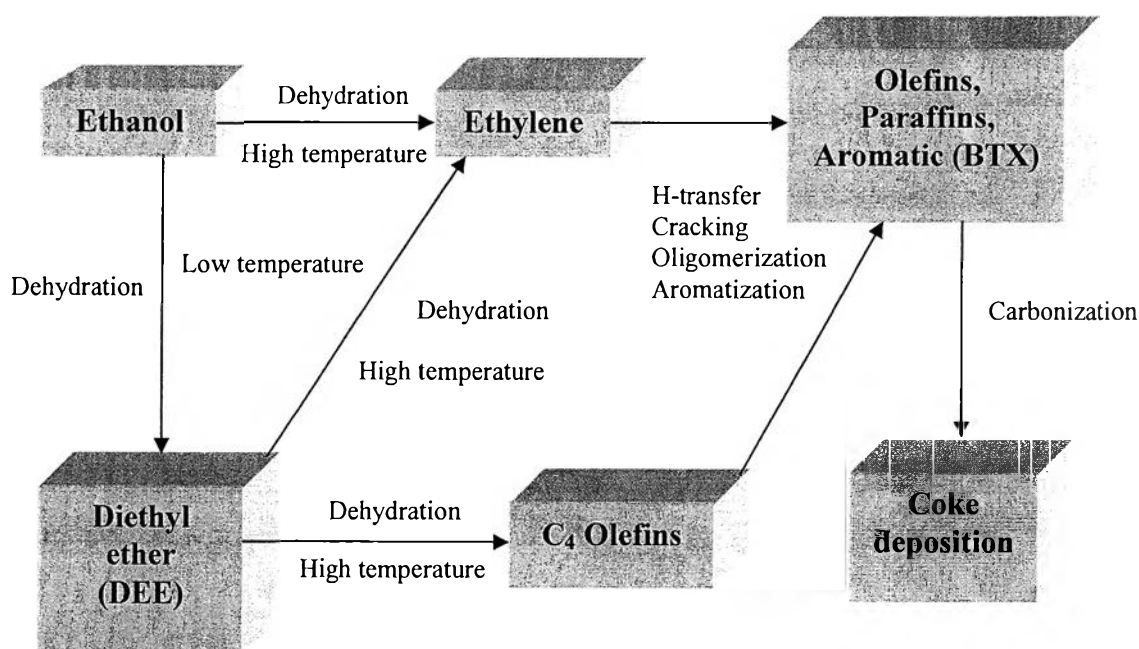
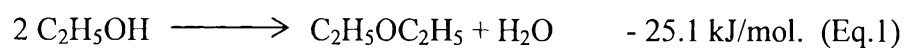


Figure 2.1 Several reaction pathways of ethanol transformation to hydrocarbons (Inaba *et al.*, 2005).

Bioethanol is proposed to be one of effective products that have many applications. It can be used as a feedstock for hydrocarbon production. However, several hydrocarbons are formulated under different conditions and reactions. For examples, the acidity of catalysts influences on the formation of ethylene which

greatly occurs over a weak acid catalyst. Moderate and strong acidity are suitable for other light olefins (e.g., propylene, butylene) formation and aromatics production, respectively. Moreover, reaction temperature is another factor that plays an important role on ethanol conversion and products distribution. Ethanol dehydration can be taken place by two competitive routes as shown in Figure 2.1 At the beginning, ethanol is converted to ethylene and/or diethyl-ether (DEE). Namely, at a low temperature (below 300°C), diethyl-ether (DEE) is produced in a significant quantity by intermolecular dehydration, which is an exothermic reaction taking place between two ethanol molecules as shown in Eq.1. On the other hand, at a high temperature (above 300°C), the formation of ethylene by the intramolecular dehydration of ethanol or some of diethyl-ether (DEE), which is an endothermic reaction, is favored as presented in Eq.2 (Ouyang *et al.*, 2009). Moreover, most previous related studies revealed that at a higher temperature, the production of ethylene was greater (Brathos *et al.*, 2006). However, at the same time, diethyl-ether (DEE) can be continuously converted to some of C₄ olefins as well as to ethylene by dehydration. Furthermore, ethanol dehydrogenation to acetaldehyde can also occur as a side reaction at a higher temperature (Chen *et al.*, 2007). Next, ethylene and C₄ olefins, formed by dehydration, can be converted via oligomerization, aromatization, H-transfer, or cracking to heavier hydrocarbons (olefins, paraffins, and BTX), which may be further transformed to deposited carbon by excess reactions.



2.2.1 Conversion of Ethanol to Ethylene

The catalytic dehydration of ethanol is not a conventional route for ethylene production, but this process is very attractive since it requires a lower reaction temperature than some conventional processes which transform the non-renewable fossil resources. In other words, the advantage of process using lower temperature is less total energy consumption. Furthermore, it also offers higher ethylene yield. According to the reaction pathways of ethanol transformation to

Temperature, space time, and water content in the ethanol feed were investigated in their work. Their results showed that the dehydration of ethanol to ethylene was complete above 300°C at the low values of space time. The water content in the feed and, in the reaction medium had a great effect on deactivation and on the product selectivity. Deactivation by coke was considerably attenuated as the water content in the reaction medium increased, and that also decreased the yield of hydrocarbons. On the other hand, the yield of gaseous olefins, particularly ethene, was increased. However, in order to avoid the irreversible deactivation of catalysts by the dealumination of the zeolite, the reaction temperature must be limited at 450°C. Below 400°C, the catalyst was stable under reaction-regeneration cycles.

Typically, the dehydration of ethanol into ethylene is catalyzed by various solid acid catalysts. The γ -alumina (γ -Al₂O₃) was the early catalyst employed to catalyze this reaction, but it required a higher reaction temperature (450°C) and offered lower yield (80 %) than a zeolite catalyst. Several zeolites have been widely studied because of their particular structures. If the morphology of zeolites is different, their acid density and acid strength may be different. These properties are crucial factors affecting to the catalytic activity and selectivity. Comparison of four catalysts; γ -Al₂O₃, H-ZSM-5 (Si/Al = 25), silicoaluminophosphate (SAPO-34), and Ni-substituted SAPO-34 (NiAPSO-34), was studied by Zhang *et al.*, (2008). Their results revealed that the catalytic activity of catalysts, ethanol conversion, and selectivity to ethylene decreased in the order: H-ZSM-5 > NiAPSO-34 > SAPO-34 > γ -Al₂O₃. Moreover, the stability of catalysts was investigated. It was found that the stability of NiAPSO-34 and SAPO-34 was better than that of the other two catalysts.

However, Takahara *et al.*, (2005) also studied the dehydration of ethanol to ethylene over various solid acid catalysts, and compared the performance of selected catalysts among H-mordenites (HM20 and HM90), H-ZSM5 zeolites (HZSM5-25 and HZSM5-90), H-beta-zeolite (HB25), H-Y zeolite (HY5.5), and silica–alumina (SA9.2). The obtained results showed that the catalyst activity decreased in the following order: HM20 > HM90 > HZSM5-25 > HB25 > HZSM5-90 > HY5.5 > SA9.2, whereas the other result demonstrated that the H-mordenites were more active than the other solid acid catalysts tested.

Unfortunately, the original mordenite zeolite has rapid deactivation, indicating it is not effective as an industrial catalyst. Therefore, in order to enhance the potential of the mordenite zeolite, it needs to be modified in a way. A way of modifying the mordenite zeolite can be done by a careful removal of aluminum atoms from its framework. The results of Sawa *et al.*, (1989) and Aramendia *et al.*, (2002) confirmed that the obtained dealuminated mordenite really had slow deactivation, and gave high selectivity to lower olefins. Another feasible way is cation exchange (Canizares *et al.*, 1998). Apart from the two methods mentioned, the modification of mordenite zeolite with various metal promoters can also reduce the rate of catalyst deactivation as well as enhance the activity and selectivity to ethylene of a catalyst. In 2006, Arenamart and Trakarnpruk studied the aqueous ethanol conversion to ethylene over dealuminated mordenite (DM) and a series of DM/metal catalysts prepared by impregnation (IMP) and solid-state ion exchange (SSIE). Several metals such as Zn, Mn, Co, Rh, Ni, Fe and Ag were incorporated onto the dealuminated mordenite to prepare DM/single and mixed metal catalysts. The results revealed that all DM/metal catalysts showed high selectivity to ethylene and higher than dealuminated mordenite (DM). The catalysts prepared by impregnation method gave higher yields of ethylene than that from solid state ion exchange method. The DM/Zn and DM/Zn-Ag catalysts prepared by impregnation method were concluded to be the best catalyst for ethanol conversion to ethylene.

Moreover, Kojima *et al.*, (1981) discovered the fact that an alumina catalyst having high purity (less amount of alkali metal, sulfur, iron, and silicon component) can display high activity and high selectivity of the ethylene formation; derived from ethanol. Further, the adding of some amount of metal phosphate to that alumina can also improve the stability of own catalyst apart from the increase of activity and ethylene selectivity. The range of 0.1 to 1.0 wt% of metal phosphate is the appropriated percent loading; in particular, the alumina adding 0.5 wt% of magnesium hydrophosphate was revealed that the conversion of ethanol (96 mol %) and the yielding of ethylene (94 mol %) were increased. Also, it is observed that the life of catalyst was improved as compared to the common alumina catalyst.

2.2.2 Conversion of Olefins to Aromatics

In the industries of aromatic hydrocarbons manufacturing, BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) are the most commercially valuable aromatics, which also can be used as octane boosters for motor gasolines. Currently, the basic commercial processes for aromatic hydrocarbons production are solid-fuel (coal and shale oil) process, pyrolysis, and catalytic reforming (Ni *et al.*, 2010) of which the feedstock is derived from petroleum. Nevertheless, in the effort to develop a new process for aromatic hydrocarbons production to replace the processes using the derived petroleum as a feedstock, the alternative routes such as the catalytic aromatization of light alcohols (particularly methanol (methanol-to-gasoline process, MTO), olefins, and paraffins) have attracted great attention.

It is well known that the H-ZSM-5 zeolite is one of effective catalysts for ethanol conversion to hydrocarbon compounds. Aromatic hydrocarbons are products obtained from bioethanol conversion using several zeolite catalysts. Inaba *et al.*, (2005) studied the conversion of ethanol to hydrocarbons over several zeolite catalysts and several metals supported on zeolites. Zeolite supports, such as H-Beta, H-ZSM-5, USY, and H-mordenite were used whereas several metals such as Mg, Cr, Fe, Co, Ni, Cu, Ga, Ru, Rh, Pd, Ag, Re, Ir, Pt, and Au were impregnated on the supports. It was reported that, in the case of using zeolites alone, H-ZSM-5 zeolite with a low Si/Al ratio showed high activity in the conversion of ethanol to BTX, while the other zeolites exclusively formed ethylene. In the case of modification of zeolite supports (particularly H-ZSM-5) by metal loading, the catalytic activity of catalysts increased. The presence of noble metals, particularly Rh, Pd, and Re, and some non-noble metals such as Ga, favored the BTX formation. On the other hand, the other metals, such as Cr, Fe, and Ni appeared to be effective for the formation of C₃₊ olefins and paraffins, which may be precursors of aromatics. Furthermore, it was discovered that there was only the Au-loaded HZSM-5 catalyst showed a slightly higher BTX selectivity and a slightly lower amount of carbon deposition than H-ZSM-5 alone. Moreover, Makarfi *et al.*, (2009) investigated the effect of structural units, Si/Al ratio on the activity and selectivity of synthetic H-ZSM-5 zeolite catalyst. They found that the higher the degree of H-ZSM-5 crystallization, the higher selectivity of liquid hydrocarbons was obtained.

In the petrochemical industries or petroleum refining, there are several commercial processes for the conversion of light hydrocarbons to aromatics such as Cyclar, Z-former, Aromax, and LNA. In 1998, Nagamori and Kawase developed the commercial process called Alpha process, which was applicable to upgrade olefins fractions from an ethylene plant to BTX and octane gasoline based materials, but the major objective in their research was to improve the lifetime of catalysts by hydrothermal treatment in the Alpha process. They used Zn-doped H-ZSM-5 zeolite as the catalyst. The results revealed that the hydrothermal treatment of Zn/H-ZSM-5 greatly reduced the acidic sites of external surface and strong acidic sites in the micropore of zeolite, which were the causes of coke deposition and deactivation. Namely, they found that hydrothermal treatment would inhibit the deactivation of the catalyst and increase the zinc stabilization simultaneously. Similarly, Saha and Sivasanker (1992) found that the influence of incorporating Zn in ZSM-5 increased its lifetime considerably apart from increasing the yield of the liquid products. Furthermore, the Zn/ZSM-5 catalyst produced more aromatics and less olefins than ZSM-5 itself.

Furthermore, many articles focused on the catalytic reaction of ethylene to aromatic hydrocarbons. A few early studies have been reported on the aromatization of ethylene over pure H-ZSM-5 and modified H-ZSM-5, such as Cu-loaded BZSM-5 (Mat *et al.*, 2006), Zn-, Re-, Mo₂C-, and Ga-loaded H-ZSM-5 (Lukyanov *et al.*, 1994; Qiu *et al.*, 1998; Brathos *et al.*, 2006). These studies showed the incorporation of metals such as gallium, zinc, or platinum resulted in a significantly increased aromatization activity.

Many researches were reported that the Ga-modified ZSM-5 catalyst was better catalyst for the catalytic conversion of ethylene to aromatics than the parent (H-ZSM-5) zeolite. For example, the results of Qiu *et al.*, (1998) revealed that the impregnation of gallium can improve the catalytic behavior of H-ZSM-5 for ethylene conversion and aromatics selectivity. The obtained results are expressed in Table 1, showing the obviously different performance of catalysts between the case of absent Ga promoting and the case of Ga-containing H-ZSM-5. It was apparent from the data that very small amounts of gallium were sufficient to cause a marked enhancement in the activity and selectivity behaviors of H-ZSM-5. Furthermore, they

discussed the role of the gallium promoter that it can be used to catalyze the dehydrogenation of the various acid-catalyzed oligomerization and cyclization intermediates.

Table 2.1 Ethylene conversion and product selectivity over Ga-containing H-ZSM-5 (Qiu *et al.*, 1998)

Ga (wt%)	C ₂ H ₄ conv. (%)	Selectivity								Aromatics select. (%)	Aromatics yield (%)
		Non- aromatics			Aromatics						
		C ₂	C ₃	C ₄₊	Bz	Tol	C ₈	C ₉	Naph		
0	40	12	58	10	6	9	0	0	0	15	6
0.1	65	8	20	0	32	28	10	0	0	69	45
0.5	91	4	5	0	38	31	7	1	3	79	72
2	92	4	3	0	35	31	7	4	6	82	75
5	93	2	4	0	34	31	8	4	4	81	75
10	92	8	4	0	34	31	7	5	3	80	74

1.0 g of catalyst; reaction temp = 520°C; CH₄ = 100 ml/min, C₂H₄ = 3 ml/min (τ = 1.4 s); data taken after 70 min on stream.

Barthos *et al.*, (2006) studied the decomposition and aromatization of ethanol on ZSM-5-based catalysts at 773-973 K in a continuous flow fixed bed reactor. Their study was divided into two parts. In the first part, the catalytic reaction of ethanol was investigated on pure and promoted ZSM-5 catalysts (Mo₂C, ZnO, Ga₂O₃ supported on ZSM-5), and the results were similar to the previous other studies in the same fashion. Namely, the deposition of various additives (Mo₂C, ZnO, Ga₂O₃) on ZSM-5 zeolite markedly promoted the formation of aromatics, converted from ethanol, and provided higher selectivity to aromatics than pure ZSM-5 zeolite. In the other part, it was the case of the study of ethylene conversion to aromatics. The experimental procedures were carried out at 773 K at the beginning, and after that, the temperature was raised to 873 K and finally at 973 K. The results obtained from the catalytic testing showed that the slow deactivation of

every catalyst occurred at 773 K, and proceeded with a much faster rate at 873-973 K. However, the highest conversion and selectivity to aromatics were measured on ZnO- and Ga₂O₃-promoted zeolite. On the latter sample, the deactivation rate of catalyst was also the lowest.

2.3 Aromatization of Ethylene over Hybrid Catalyst

In order to develop novel catalysts, a hybrid system of catalysts is a way that may be proposed. The hybrid catalysts are composite materials formed from a mechanical mixing of different catalysts. Bicomponents are mostly synthesized. However, there are some feasible ways that can also prepare the hybrid catalysts such as impregnation technique, ion exchange with metal ion salts, and chemical vapor deposition (CVD) technique, but they depend on the application of catalysts as well. Moreover, good novel hybrid catalysts should be able to synergize the catalytic performance. However, an individual component of hybrid catalyst can be modified.

For the aromatization of light olefins and paraffins, most hybrid catalysts were prepared by the mechanical mixing of H-ZSM-5 zeolite with a small amount of co-catalysts (ZnO precipitate or ZnO/Al₂O₃ co-precipitate). Le Van Mao *et al.*, (1997) mentioned that these hybrid catalysts can selectively convert a gaseous mixture of mainly ethylene and other light paraffins into BTX aromatics. Similarly, Dufresne and Le Van Mao (1994) studied the catalytic performance for the aromatization of pure and mixed olefinics and paraffinic feeds over the parent H-ZSM-5 zeolites, the chemically modified zeolites, and the hybrid catalysts. Their experimental results showed that the highest performance toward aromatics was obtained when the H-ZSM-5 zeolites were modified by zinc ions introduced by co-precipitation, and the oxide component was composed of a ZnO/Al₂O₃ co-precipitate.

From the literatures mentioned above, the transformation of bioethanol to aromatic hydrocarbons consists of two major reactions; namely, bioethanol is converted to ethylene and/or light olefins, and then the olefins are further converted to aromatics. Therefore, it is noticed that ethylene and/or the light olefins is an intermediate during the transformation. Moreover, the hybrid catalysts constituted of zinc oxide/aluminum oxide co-precipitate and an acidic catalyst, like H-ZSM-5 and

used in the aromatization of light olefins were studied because of their synergistic performance. The presence of a co-precipitate was presumed to raise the migration of hydrogen species attached on the acid sites of zeolite, and it results in more acid sites of zeolite for ethylene aromatization (Dufresne and Le Van Mao, 1994).

Thus, in this work, the two consecutive beds of catalysts were applied to enhance the bioethanol conversion to aromatics. The dehydration of bioethanol to olefins such as ethylene was expected to occur at Bed #1 of MgHPO_4 -doped activated alumina catalyst, and the aromatization of olefins to aromatics (particularly BTX) was expected to take place at Bed #2 of H-ZSM-5-based catalysts. The modified H-ZSM-5 zeolites (Zn- and Ga- supported H-ZSM-5) and hybrid catalysts (zinc oxide/aluminum oxide co-precipitate mixed with H-ZSM-5 zeolite) were used as catalysts in Bed #2. In addition, the economics of a proper process designed for bioethanol conversion to aromatics using a series of two consecutive catalytic beds was estimated.