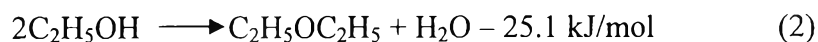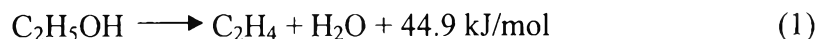# CHAPTER II
LITERATURE REVIEW

2.1 Catalytic Dehydration of Ethanol to Light Olefins

In the manufacturing of light olefins for petrochemicals, both ethylene and propylene are produced as monomers for polymerization. The integration of refining with petrochemicals leads to the optimization of all the processes involved, and the development of processes with an adjustable ratio of ethylene and propylene production have been becoming possible. The conventional method in petrochemical industry was studied by Wang *et al.* (2002). They reported that there were two process used for the production of light olefins via catalytic cracking, which differed from one another on how heavy or light hydrocarbons were employed as feedstock. When heavy hydrocarbons were used, they underwent primary cracking to form light naphtha olefins followed by secondary cracking to produce light olefins. Light-hydrocarbon feedstocks as the by-products from refining and petrochemical plants, such as C_4 and C_5 fractions were another feedstock suitable for further cracking into ethylene and propylene. The development of a new process for the catalytic dehydration from ethanol to light olefins from non-petroleum sources has become a higher priority worldwide than the traditional routes because of some advantages, such as the reduction of CO_2 emission, low production cost, and energy consumption (Takahara *et al.*, 2005).

One of the best non-petroleum or alternative processes for the production of ethanol is the fermentation of biomass to ethanol because biomass is an abundant and carbon-neutral renewable resource. The obtained bio-ethanol can be further converted valuable hydrocarbons via the catalytic dehydration that could take place toward two pathways. One is the intra-molecular dehydration of ethanol to ethylene and propylene, and another is the inter-molecular dehydration of ethanol to diethyl ether. At low temperatures, diethyl ether is produced in significant quantities, while at high temperatures ethylene and propylene were the dominant products (Zhang *et al.*, 2008). Two reactions can simultaneously occur in parallel during the catalytic dehydration of ethanol:

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O + 44.9 \text{ kJ/mol} \qquad (1)$$

$$2C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O - 25.1 \text{ kJ/mol} \qquad (2)$$

The basic products of the commercial ethanol dehydration are ethylene, which is one of the major feedstock for the petrochemical industry used in the production of polyethylene, ethylene oxide, ethylene dichloride, etc (Ouyang et al., 2009), and propylene, which is the basic raw chemical for producing polypropylene, propylene oxide, acrylic acid, acrylonitrile, and so forth (Takahashi et al., 2012).

With the reasons mentioned above, the catalytic dehydration of ethanol was not a conventional method to produce ethylene and propylene, but this procedure was an attractive alternative technology compared with the traditional routes. The simple process of catalytic dehydration can be described briefly (Morschbacker, 2009). First of all, the ethanol in storage tank is fed to the vaporizer. The vaporized ethanol is heated in a furnace to reach the reaction temperature, and is next passed through a dehydration reactor. Then, the ethanol is converted to ethylene and propylene over a catalyst, and enters to cool down in a quenching unit. After leaving the top of the quenching tower, the ethylene and propylene are passed through a scrubbing tower, a desiccant dryer column, and a distillation unit, respectively. The ethylene and propylene from the desiccant dryer column are then refined in the distillation unit at a low temperature, and have their heavy contaminants removed, to obtain ethylene and propylene.

There were many reports on catalytic dehydration of ethanol to ethylene and propylene. This reaction was investigated over various solid acid catalysts. Arenamnart et al. (2005) studied the effects of modifying the acidity of zeolites by de-alumination, temperature, and metal loading on de-aluminated mordenite. They concluded that the dealuminated mordenite catalyst can improve the catalytic activity because it had a higher surface area than the original mordenite. Metal-loaded dealuminated mordenite catalysts gave a higher selectivity to ethylene than un-loaded dealuminated one. Zn-loaded dealuminated mordenite had the highest selectivity to ethylene (96.6%) at 350 °C, and 1 hour time-on stream. Finally, the selectivity to ethylene decreased when temperature was increased. Moreover, the dehydration of ethanol to ethylene over various solid catalysts was studied by

Takahara *et al.* (2005). They found that H-mordenites were the most active for the dehydration process, and the catalytic activity during the dehydration could be correlated with the number of strong Bronsted acid sites. Toshihide (2008) studied the catalytic production of propylene from ethylene using zeolite catalysts. The result showed that the ethylene was converted to propylene over SAPO-34 at 450 °C with the yield of 52.2% and selectivity of 73.3% at the ethylene conversion of 71.2%.

Many researchers had investigated the catalytic dehydration of ethanol to light olefins over zeolite catalysts, especially over HZSM-5 zeolite. Takahara *et al.* (2005) and Tret'yakov *et al.* (2010) presented that the ethylene selectivity could reach up to 95% at 300 °C. Since HZSM-5 catalyst had poor hydrothermal stability and poor resistance to coke formation, as reported by Phillips *et al.* (1997), there were many methods that had been employed to improve HZSM-5 catalysts activity and stability. For example, Gayubo *et al.* (2010) studied the hydrothermal stability of HZSM-5 catalysts. The catalysts were doped with Ni by using impregnation method, and were used for the transformation of bio-ethanol into hydrocarbons. It was reported that the impregnation of the HZSM-5 zeolite with Ni was a simple and reproducible technique. That was an effective way for preparing catalysts with high hydrothermal stability. The HZSM-5 catalyst doped with Ni had less BET surface area and micro-porous volume. The increase in the zeolite Ni content played important roles in decreasing the total acidity from 135 kJ(mol of $NH_3)^{-1}$ to 125 kJ(mol of NH3)$^{-1}$ for the catalyst with 1 wt.% of Ni and in attenuating acid strength. The doping of the zeolite with Ni had been proven to be effective in attenuating irreversible deactivation by the de-alumination of the HZSM-5 catalyst. The operating conditions to avoid irreversible deactivation of the catalyst were limited to a temperature of 400 °C and the feed containing 75 wt.% H_2O. This operation had been proven feasible, and had high selectivity of propylene. Ouyang *et al.* (2009) investigated the catalytic dehydration conversion of bio-ethanol to ethylene using HZSM-5 modified with 3 wt.% rare earth metal (La). The La-modified HZSM-5 catalysts were prepared by impregnating the HZSM-5 zeolite with an aqueous solution of lanthanum nitrate. They concluded that the 3wt.% of La modification over HZSM-5 catalyst showed very high activity and stability in ethanol dehydration

to ethylene in a bioreactor at the reaction temperature of 260 °C, LHSV 1.1 h^{-1}, and 50% ethanol concentration. Both the fresh and regenerative catalysts showed much better stability and resistance to coke formation than the unmodified HZSM-5 catalyst. NH$_3$-TPD results showed a decrease in the total surface acidity and acid strength distribution after doping La. The possible reason was that the partial de-alumination after doping La caused the decrease of acidity.

In addition, the modified catalytic dehydration of ethanol to propylene was rarely established when compared with the catalytic dehydration of ethanol to ethylene. Takahashi *et al.* (2012) investigated the effects of adding phosphorus on the conversion of ethanol to propylene over a ZSM-5 zeolite catalyst. The phosphorus modification on ZSM-5 (P-ZSM-5) catalysts were accomplished by using an impregnation method. The result showed that the activity of the catalyst was enhanced by the addition of phosphorus, and they suggested that the addition of phosphorus suppressed the oligomerization of propylene by decreasing the acidity of the active sites of the zeolite. Furthermore, the addition of phosphorus greatly enhanced the hydrothermal stability of the zeolite and substantially improved the catalyst during ethanol conversion. Song *et al.* (2010) investigated the phosphorus modification on HZSM-5 catalyst for the conversion of ethanol to propylene. The phosphorus modification on HZSM-5 samples was also done by using an impregnation method. They reported that the selectivity of propylene formation depended on the phosphorus content in the zeolites. The highest propylene yield of 32% was achieved over the HZSM-5 with Si/Al$_2$ molar ratios of 80, modified with phosphorus at a P/Al molar ratio of 0.5, and at the reaction temperature of 550 °C. Thus, propylene selectivity and catalytic stability were greatly improved by the modification of HZSM-5 catalyst with phosphorus. Because of the enhancement of propylene selectivity, the reduction of strong acid sites and coke deposition content was attributed to the increasing phosphorus.

The conversion of ethanol to propylene over HZSM-5 type zeolite containing alkaline earth metal was studied by Daisuke *et al.,* (2010). They concluded that the propylene yield and the catalytic stability of this zeolite strongly depended on the metal/Al and SiO$_2$/Al$_2$O$_3$ ratios as well as on the reaction conditions.

Among the metal loaded-HZSM-5 zeolites, the Sr-HZSM-5 zeolite having a Sr/Al ratio of 0.1 and a SiO_2/Al_2O_3 ratio of 184 exhibited the highest propylene yield of 32% and a high catalytic stability at the reaction condition of 500 °C. The high performance of Sr-HZSM-5 zeolite was due not only to the control of acidity by the modification with Sr, but also by the other factors, probably by the physical blockage of the channel structure of HZSM-5 zeolite by Sr cations.

Moreover, Furumoto *et al.* (2011) studied the effect of HZSM-5 zeolite on the conversion of ethanol to propylene. HZSM-5(Ga) and HZSM-5(Al) with various SiO_2/M_2O_3 ratios were synthesized, and investigated for the catalytic performance on ethanol conversion to propylene. They concluded that HZSM-5(Ga) and HZSM-5(Al) showed high propylene yields, and the yield depended strongly on the SiO_2/M_2O_3 ratio and the W/F value. These results indicated that the acid strength was a crucial factor for the selective production of propylene. In addition, the hydrothermal stability of HZSM-5(Ga) was higher than HZSM-5(Al) catalyst. It was found that phosphorus modification on HZSM-5(Ga) zeolite improved the propylene yield relative to the unmodified zeolite. Also, phosphorus-modified HZSM-5(Ga) with a P/Ga ratio of 0.3 showed a good catalytic activity and stability because of the decreases in both gallium content in the zeolite framework and coke deposition.

2.2 Light Olefins Production by Using SAPO-34 Catalysts

In 1982, the molecular sieve SAPO-34 had been synthesized by the Union Carbide Laboratories (Zhang *et al.*, 2008). The small-pore molecular sieve SAPO-34 was recognized as an active catalyst to give a narrow range of product distribution with a high selectivity to ethylene and propylene in the ethanol conversion reaction (Wilson *et al.*, 1982). The framework structure of SAPO-34 belongs to the natural zeolite Chabazite (CHA), which is shown in Figure 1. The CHA structure consists of double six-membered ring (D6R) units that are linked together by tilted 4-membered rings. The pore structure is comprised of eight-membered rings with the 0.43×0.43 nm opening into the large ellipsoidal cavities of 0.67×1.0 nm (Saeed *et al.*, 2003). The effective dimension of the pores in Chabazite is varied and depends upon the

extent and type of ion-exchanged cations. Three different cationic sites had been determined from diffraction data for dehydrated crystals, as shown in Figure 1: **Site I** in the centre of the D6R, **Site II** at the centre of 6-ring, and **Site III** at the 8-ring pore window (Saxton *et al.*, 2010). A key feature in the nature of microporous zeolites is their shape-selectivity. Three types of shape selectivity were defined (Weisz, 1980) : a) reactant selectivity, b) product selectivity, and C) transition-state selectivity (Weitkamp, 2000). Of all SAPO catalysts known to date, SAPO-34 is so far the most widely studied and desirable catalyst for the ethanol to light olefins process. Other SAPOs such as SAPO-44, SAPO-47, and SAPO-56 had received much less attention. The technology for bio-ethanol production from biomass had been widely used and well established (Chen *et al.*, 1994). This process can therefore provide an indirect way of converting non-renewable resources to industrially-valuable light olefins and other value-added products.
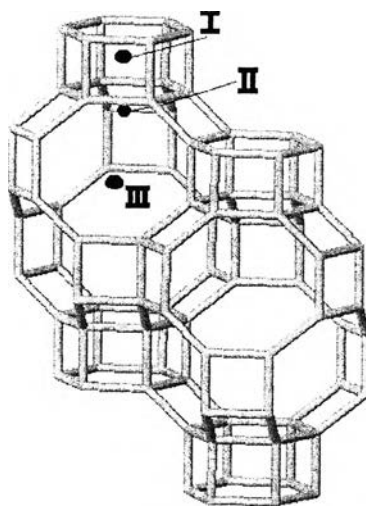

Figure 2.1 Schematic representation of the Chabazite (CHA) structure showing cation positions (Saxton *et al.*, 2010).

The structure and chemical properties of the SAPO-34 catalyst as well as various process parameters influence the ethylene and propylene production. Many factors that perform major roles to activity and selectivity are pore size, shape, particle size, and catalyst acidity. However, reaction parameters such as temperature, space velocity, and feed composition also have significant effects on product

distribution. In general, weak acidity, reductions in contact time, and modification with suitable promoters can enhance the selectivity of light olefins (Dubois *et al.,* 2003). Wilson and Barger (1999) studied the characteristics of SAPO-34 such as shape selectivity, acid site density, and acid site strength. The result showed that SAPO-34 exhibited the best performance based on the selectivity to ethylene and propylene (light olefins), minimum paraffinic and aromatic by-products, and catalyst stability. The synthesis of ethylene and propylene from methanol over a microporous SAPO-34 catalyst was described by Abramova (2009). The SAPO-34 catalyst was shown to be highly effective in the selectivity of ethylene and propylene formation. The total yield of C_2-C_3 olefins at 350-450 °C was 77-84%, and methanol conversion was up to 96-99%. After regeneration with air at 550 °C, the catalyst activity and selectivity in methanol conversion were completely restored, while the crystal structure and the acid properties of zeolite and SAPO-34 catalyst were well preserved.

Recently, it has been found that using SAPO-34 catalyst could convert not only ethanol to ethylene but also ethylene into propylene as reported by Oikawa *et al.,* (2006). They concluded that the selectivity to propylene strongly depended on the pore size of catalyst. SAPO-34 catalyst exhibited the highest selectivity to propylene (80%), while the selectivity to 2-methyl propylene (isobutylene) was very low. The SAPO-34 pore size (0.45×0.45 nm) was approximately equal to the kinetic diameter of propylene (0.45 nm) and smaller than that of 2-methyl propylene (0.50 nm). In addition, the acid strength was also an important factor for the formation of propylene. For example, H-Al-ZSM-5, which had higher acid strength than SAPO-34 catalyst, can convert propylene to other hydrocarbons such as C_5 or higher hydrocarbons, while H-B-ZSM-5 with lower acid strength exhibited a lower rate of propylene formation than SAPO-34 catalyst. Moreover, Zhang *et al.* (2008) studied the activity and stability of Al_2O_3, HZSM-5 (Si/Al = 25), SAPO-34 and Ni-SAPO-34 as catalysts in the dehydration of ethanol to ethylene. They concluded that the conversion of ethanol and the selectivity to ethylene decreased in the order: H-ZSM-5>Ni-SAPO-34>SAPO-34>Al_2O_3. For the stability of catalysts, Ni-SAPO-34 and SAPO-34 were better than other two catalysts. When both activity and stability of the

four catalysts were taken into account, Ni-SAPO-34 was the suitable catalyst for the dehydration of ethanol to ethylene.

There were a few researcher groups that had studied on the modified SAPO-34 catalyst for the catalytic dehydration of ethanol to light olefins (both ethylene and propylene). Chen *et al.* (2010) studied the optimization of reaction conditions and the dehydration of ethanol to ethylene over SAPO-11, SAPO-34, impregnated SAPO-11 and SAPO-34 with Mn and Zn. They reported that the conversion of ethanol and selectivity of ethylene decreased in the following order: Mn-SAPO-34>Zn-SAPO-34>SAPO-11>Mn-SAPO-11>Zn-SAPO-11>SAPO-34. According to the NH_3-TPD profiles of samples, Mn^{2+}- or Zn^{2+}-modified SAPO-34 exhibited the higher desorption temperatures of both weak and strong acid sites than SAPO-34. Additionally, the weak acid sites existed the most in amount on Mn-SAPO-34, while the strong acid sites existed the most in amount on Zn-SAPO-34. The results indicated that the increases, especially in the weak acid sites and the total acid density (both weak and strong acid sites), were beneficial to the catalytic dehydration of ethanol to ethylene. The optimal reaction conditions were as follows: 5% loading amount of Mn^{2+} and Zn^{2+}, 2 h^{-1} WHSV, 10 h reaction time, a reaction temperature of 340 °C, and 20% ethanol concentration in the feed. In different parts of the substrate, the conversion of methanol to light olefins (especially propylene) had been mentioned. For instances, Niekerk *et al.* (1995), Kang (2000), Dubois *et al.* (2002) and Wei *et al.* (2007) investigated the influence of modifying SAPO-34 with Co, Fe, Mn, and Ni by using an impregnation method. As a result, the modification of SAPO-34 for methanol to light olefins brought about more stable catalytic activity, and improved ethylene and propylene production.

From the literature reviews above, the catalytic dehydration of ethanol to propylene were not much more established than the dehydration of ethanol to ethylene. This was a reason why researchers turned their focus onto the development of SAPO-34 catalyst to enhance the production of propylene from ethanol. SAPO-34 catalyst is a new generation of crystalline microporous molecular sieves. It was discovered from the attempt on incorporating Si into the AluminoPhosphate ($AlPO_4$) molecular sieves. The porous structure of SAPO-34 catalyst is not the only factor

that must be taken into account to reach a high selectivity of ethylene and propylene, but also the mild acidity of SAPO-34 catalyst is a very interesting alternative to attain high selectivity for light olefins. Flanigan *et al.* (1986) and Derouane *et al.* (1988) reported that silicon atoms incorporated into the $AlPO_4$ structure resulted in creating Bronsted acidity, and this resulted SAPO-34 could be used as an acid catalyst. Chen *et al.* (1994) prepared and studied samples of SAPO-5, SAPO-17, SAPO-18, and SAPO-34 to understand their Bronsted acidity. Using DRIFT spectroscopy for analysis, the acid strength of the samples were in the following order: SAPO-5<SAPO-17<SAPO-18, and SAPO-34. For the dehydration of ethanol to light olefins, they found that smaller cages of SAPO-18 and SAPO-34 yielded higher activity and selectivity towards olefins than those of SAPO-5 and SAPO-17. However, among all samples, SAPO-5 exhibited the longest life time because the accumulation of coke was less favorable for its one-dimensional 12-ring channels.

Kang *et al.* (2000) studied the synthesis of GaAPSO-34 to improve the acidic property of SAPO-34 crystal for methanol to olefins. GaAPSO-34 catalysts with various Al/Ga ratios (Al/Ga = 40, 20, 10, 5, and 0) were successfully synthesized by rapid crystallization. From the characterization results, the crystal and the particle size decreased with an increase in the Ga content incorporated into SAPO-34 catalyst. The selectivity to ethylene increased with using the catalyst with Al/Ga = 20 compared with the pure SAPO-34 catalyst. However, with the decreases in acid sites and particle size due to the incorporation of higher Ga content in the catalyst, the selectivity to ethylene was not enhanced.

Nawaz *et al.* (2009) studied the catalytic performance of Sn-Pt/SAPO-34 with the assumption that weak acid sites could convert propyl cations to propylene. The Sn-Pt/SAPO-34 and Sn-Pt/HZSM-5 catalysts were prepared by sequential co-impregnation method to 1 wt.% of Sn and 0.5 wt.% of Pt loading on the two supports. The results showed that the SAPO-34 supported catalyst was much better than the HZSM-5 supported catalyst. IR and TPD analysis suggested that both Lewis and Bronsted acid sites existed on the SAPO-34 supported catalyst, and these were stable after metal impregnation. This suitable acidity selectively converted intermediates to propylene. Treesukol *et al.* (2005) and Barias (1995) described that the intensities of the corresponding bands associated with chemisorbed ammonia were decreased after

loading with Sn and Pt as compared to those of the original SAPO-34 catalyst. Two possible explanations on the enhancement of propylene selectivity were the location of Pt atoms on Bronsted acid sites; thus consuming some acid sites, and the Sn promoter was believed to reduce the Lewis acid sites on the catalyst.

Zhang *et al.* (2006) prepared Sb_2O_5/SiO_2 and Sb_2O_3/SiO_2 catalysts with Sb_2O_3 and Sb_2O_5 loading in the range of 1-20 wt.% by incipient wetness impregnation of silica with the solutions of $SbCl_5$ and $SbCl_3$, respectively. They concluded that SbO_x entities on either Sb_2O_5/SiO_2 or Sb_2O_3/SiO_2 catalysts were well dispersed on the silica surface. The SbO_x species on the Sb_2O_3/SiO_2 catalysts with Sb_2O_3 loading lower than 5 wt.% were mostly highly-dispersed Sb^{3+} oxidic entities. The aggregated SbO_x species would arise while Sb_2O_3 loading reached 5 wt.%. Highly-dispersed Sb^{3+} oxide entities were more active than highly-dispersed Sb^{5+} oxide entities in methane selective oxidation. Water *et al.* (2004) improved the catalytic activity of Ge-ZSM-5 catalyst for the dehydration of 2-propanol. The propylene yield in the 2-propanol dehydration reaction at 180 °C was as high as 98% for Ge-ZSM-5 and only 40% for the unmodified ZSM-5.

In this work, the mild acidity of supported SAPO-34 catalyst with good shape selectivity was experimentally studied in order to produce light olefins, especially propylene, from the catalytic dehydration of bio-ethanol. To date, however, no study on Ga, Ge, Sn, and Sb doped on SAPO-34 catalyst has been accomplished. Therefore, this research will focus on the performance of Ga, Ge, Sn, and Sb mixed with SAPO-34 catalyst by physical mixing, aiming to increase the light olefins yield for the catalytic dehydration of bio-ethanol. Due to the fact that Ga and Sn are acidic metals, and Ge and Sb are acidic semimetals, both groups metallic promoters would help to enhance the acidity of SAPO-34 support.

Furthermore, it is well known that HZSM-5 and SAPO-34 are good catalysts for ethanol dehydration to ethylene. In addition, both HZSM-5 and SAPO-34 have been found to exhibit the high catalytic reactivity for the direct conversion of ethylene to propylene. Oikawa *et al.* (2006) reported that SAPO-34 showed the highly selective conversion of ethylene to propylene due to the shape selectivity of the small pore SAPO-34 and the modest acid strength of acidic protons. Lin *et al.*

(2009) found that HZSM-5 exhibited the highest activity for the direct conversion of ethylene to propylene, and the conversion of ethylene increased with the degree of H^+ exchange in the HZSM-5 catalyst. Moreover, Duan et al. (2012) studied the conversion of ethanol to propylene over HZSM-5 (Si/Al$_2$=25, molar ratio)/SAPO-34 with different weight ratios prepared by hydrothermal synthesis and physical mixing. They concluded that hydrothermal synthesis of HZSM-5/SAPO-34 catalyst showed different morphology, acidity, and catalytic performance from HZSM-5/SAPO-34 catalyst prepared by physical mixing. The hydrothermal catalyst with the HZSM-5 /SAPO-34 weight ratio of 4 gave the highest propylene yield of 34.5%. The synergy between HZSM-5 with SAPO-34 might be one of the possible reasons for the high yield of propylene on the mixed HZSM-5/SAPO-34 catalyst. In addition, conversion of ethanol to propylene over HZSM-5 type zeolites containing alkaline earth metals (Mg, Ca, Sr, and Ba) were synthesized by Goto et al., (2010). They reported that the propylene yield and the catalytic stability of HZSM-5 were strongly dependent on metal/Al and SiO_2/Al_2O_3 ratio as well as on the reaction conditions. The results indicated that Sr-HZSM-5 catalyst had a SiO_2/Al_2O_3 ratio of 184 and Sr/Al ratio of 0.1 exhibiting the highest propylene yield of 32% with highly catalytic stability at the reaction condition of 500 °C and W/F value of 0.03 g cat/ml/min. The higher performance of Sr-HZSM-5 catalyst was not only due to the control of acidity from the modification with Sr but also from other factors as well, such as, the physical blocking of the channel structure of HZSM-5 catalyst by Sr cations at the intersection of straight channel.

Moreover, insufficient information has been established about the base treatment of HZSM-5 catalyst. Ogura et al. (2001) studied the alkaline treatment technique by using 1-5 M NaOH solution for the modification of structural and acid catalytic properties of HZSM-5 catalyst. They found out that the selective removal of the siliceous species from HZSM-5 framework could occur without changing of the HZSM-5 structure. The dissolved siliceous species could be easily precipitated onto the surface of HZSM-5 crystals and formed a layer of amorphous silica. Zhao et al. (2011) investigated that the alkaline treatment of HZSM-5 catalyst with different SiO_2/Al_2O_3 ratios could produce light olefins. The HZSM-5 catalysts were treated in

0.2 M NaOH solution for 300 min at 90 °C. They reported that HZSM-5 catalyst with the SiO_2/Al_2O_3 ratio of 50 treated in NaOH 0.2 M presented a higher selectivity toward light olefins as compared to the untreated HZSM-5 catalyst. In addition, Gayubo et al. (2010) studied the selective production of olefins from bio-ethanol on HZSM-5 zeolite catalysts treated with NaOH solution. They reported that the treatment of the HZSM-5 catalyst with 0.2 M NaOH solution was effective for modifying the porous structure of the zeolite and moderating acid strength. A short treatment of 10 min could decrease the acid strength of the sites from 135 kJ (mol of $NH_3)^{-1}$ to 125 kJ (mol of $NH_3)^{-1}$, which was an effective for increasing the selectivity of propylene and for attenuating the deactivation by coke. Furthermore, it is necessary that HZSM-5 catalyst must have the proper concentration and strength distribution of acid sites for achieving a high yield of propylene. Too high concentration of acid sites and too strong acidity may lead to the transformation of propylene to aromatics and the fast deactivation of the catalyst. Therefore, in order to produce the high yield of propylene with good catalytic stability, it is necessary that HZSM-5 catalyst must have the moderate concentration and strength distribution of acid sites. However, the study on catalytic performance and the selectivity of light olefins by using KOH–treated HZSM-5 catalyst has not been employed. Potassium ion is expected to modulate the acidity of HZSM-5. Moreover, K ion is bigger than Na one; therefore, the exchange of K ion in the zeolite pore is believed to yield an appropriate pore size of HZSM-5 that may allow some species of olefins to be selectively produced. Thus, in this work, the catalytic performance of HZSM-5 catalyst treated with KOH solutions at various concentrations was investigated for dehydration of bio-ethanol to light olefins

In summary, the catalytic dehydration from ethanol to light olefins for this work can be proposed as follows. Firstly, some promoters (Ga, Sn, Ge, and Sb) were used to enhance the acidity of SAPO-34. Secondly, alkaline treatment using KOH solutions were employed to suppress the acidity of HZSM-5 as well as to modulate its pore size. Either way was expected to be a method to enhance the propylene yield from the catalytic dehydration of ethanol.

The objectives of this research were to study the effect of acidic oxides of Ga, Sn, Ge, and Sb doped on SAPO-34 catalyst for the catalytic dehydration of bio-ethanol to light olefins, especially propylene and investigate the catalytic performance of HZSM-5 treated with KOH solutions at various concentrations for the catalytic dehydration of bio-ethanol to light olefins.

The scope of this research covered the following:

Scope 1: Effect of oxides loading

Controlled parameters

- The reactor used in this research was an isothermal fixed-bed reactor.
- The amount of SAPO-34 catalyst was fixed at 3 g.
- The bio-ethanol concentration was fixed at 99.5% in the feed.
- The reaction temperature was fixed at 400 °C.
- The reaction time was fixed at 45 min.
- The LHSV was fixed at 0.5 h^{-1}.

Table 2.1 The number of experiments for the first scope

% Loading / Catalyst	GeO_2/ SAPO-34	Ga_2O_3/ SAPO-34	SnO/ SAPO-34	Sb_2O_3/ SAPO-34
3 %	(1)	(3)	(5)	(7)
5 %	(2)	(4)	(6)	(8)

Scope 2: Effect of HZSM-5 catalysts treated with KOH solutions

Controlled parameters

- The reactor used in this research was an isothermal fixed-bed reactor.
- The bio-ethanol concentration was fixed at 99.5%.
- The amount of HZSM-5 (SiO_2/Al_2O_3 = 40 molar ratio) catalyst was fixed at 3 g.
- The reaction temperature was fixed at 400 °C.
- The reaction time was fixed at 45 min.

- The LHSV was fixed at 0.5 h^{-1}.

Table 2.2 The number of experiments for the second scope

Catalyst Concentration (M)	0.1	0.5	0.9
HZSM-5	(9)	(10)	(11)