



CHAPTER II LITERATURE REVIEW

2.1 Catalytic Dehydration of Ethanol

Nowadays, with the increase in the oil prices, the shortage of natural resource, and also the heavy demand for ethylene and propylene, the catalytic dehydration of ethanol (or bio-ethanol from renewable resources) to ethylene and other hydrocarbons have received wide attention and have become interesting routes (Tsao *et al.*, 1979). The catalytic dehydration of ethanol or the bio-ethanol to ethylene (BETE) process is a simultaneous parallel endothermic set of reactions involving direct ethanol conversion (dehydration of ethanol into ethylene directly) and by the consecutive reactions (the dehydration of ethanol into diethyl ether and dehydration of diethyl ether into ethylene, respectively) as shown in Figure 2.1. Diethyl ether (DEE) is an intermediate which its formation is favored mainly between 150°C and 300°C, while ethylene formation is favored between 320°C and 500°C (Morschbacker, 2009). The conversion of ethanol is controlled by a single-site surface reaction, and depends on the diffusion of reagents and products inside the catalyst pellets. The ethanol conversion depends on the type of catalyst, its operational age, and the parameters of the operating process (reaction pressure, reaction temperature, space velocity, and ethanol concentration). These parameters are important factors for the purity of ethylene product and also the requirement of purification steps in order to produce polymer grade (high purity) ethylene.

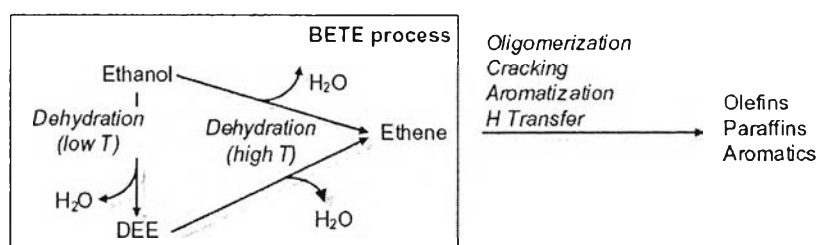


Figure 2.1 Transformation of ethanol into ethylene, olefins, and other hydrocarbons on acid catalysts (Gayubo *et al.*, 2010).

Typically, depending on these parameters, the ethanol conversion ranges from 95% to 99.5%, and the ethylene selectivity ranges from 95% to 99%. The main by-products from this reaction are composed of acetaldehyde and hydrogen. Other by-products formed by minor side reactions are acetic acid, ethyl acetate, acetone, methane, carbon dioxide, etc (Morschbacker, 2009). Apart from ethylene, other hydrocarbons involving olefins (propylene and butylenes), paraffins (ethane, propane, and butane) and aromatics (benzene, toluene and xylenes) can be produced via the catalytic dehydration of ethanol as well. These products strongly depend on the type of catalyst used and the operating parameters through different reactions including oligomerization, cracking, aromatization, and H transfer reaction as shown in Figure 2.1.

The catalytic dehydration of ethanol occurs in the vapor phase using fixed bed or fluidized bed reactors. For fixed bed reactors, the operation of the reactors can be isothermal or adiabatic. For the fluidized bed reactor, the operation of reactor usually is adiabatic. A generic process diagram of an ethanol-based ethylene plant is represented by Figure 2.2

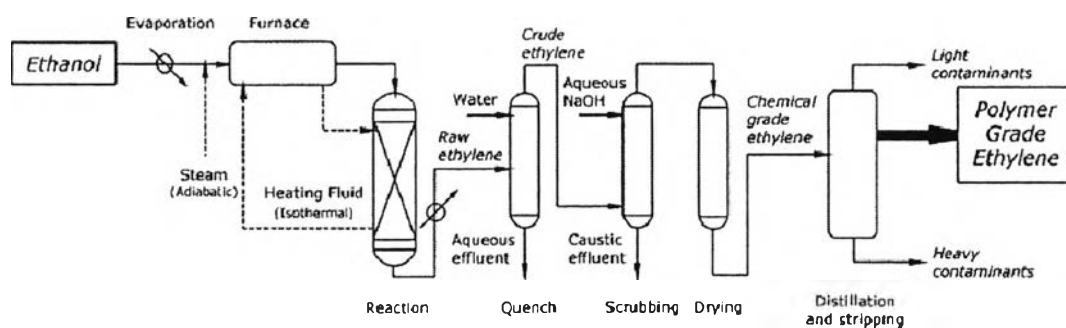


Figure 2.2 Representation of a generic process diagram of an ethanol-based ethylene plant (Morschbacker, 2009).

The catalytic dehydration process can be described by follows. First, the ethanol in storage tank is fed to the vaporizer. The vaporized ethanol is heated in the preheat zone in a furnace to reach the reaction temperature and sent to the reactor (usually involving four adiabatic reactors in series). The ethanol passes through the

catalyst, and is converted to ethylene through the catalytic dehydration process. Then, the ethylene and water vapor mixture leaves the bottom of the reactor and enters to the quench column tower. In this tower, the mixture is cooled, and the condensable polar substances are removed. After leaving the top of the quench column tower, the ethylene is passed through the caustic scrubbing tower in order to remove traces of carbon dioxide and through the desiccant dryer bed in order to produce chemical grade ethylene. The ethylene from the dryer is distilled in the ethylene column at low temperature and in order to remove heavy impurities, and is sent to a stripper in order to remove carbon monoxide. Finally, a polymer grade ethylene is obtained.

There are many reports on catalysts for the catalytic dehydration of ethanol to ethylene. This reaction was investigated over various solid acid catalysts such as zeolite and silica-alumina. The dehydration of ethanol into 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. The catalyst activity during the dehydration could be correlated with the number of strong Brønsted acid sites. Likewise, Arenamart *et al.* (2005) also studied the effect of using mordenite catalysts. They studied the effect of modifying the acidity of zeolites by dealumination, the effect of metal loading on dealuminated mordenite, and the effect of temperature. They concluded that dealuminated mordenite can improve catalytic activity because it had a higher surface area ($\text{Si/Al} = 26.90$) than the original sodium mordenite ($\text{Si/Al} = 5.66$). Metal-loaded dealuminated mordenite catalysts showed higher selectivity to ethylene than no-loaded dealuminated mordenite whereas Zn-loaded dealuminated mordenite had the highest selectivity to ethylene (96.6%) at temperature 350°C , a WHSV of 1.0 h^{-1} , and 1 h reaction time. Finally, for the effect of temperature, it was found that there was a change in product distribution, and the highest selectivity to ethylene was obtained at 350°C . The selectivity to ethylene was decreased when temperature was increased.

Other catalysts used in the catalytic dehydration of ethanol to ethylene were studied as well. Many researchers have investigated catalytic dehydration of ethanol over HZSM-5 zeolite. Costa *et al.* (1985), Talukda *et al.* (1997), and Takahara *et al.* (2005) studied the conversion of ethanol to hydrocarbons by the use of a ZSM-5

zeolite catalyst. The ethylene selectivity can reach up to 95% at a low temperature (300°C). However, Phillips *et al.* (1997) reported that H-ZSM-5 catalyst had poor hydrothermal stability and poor resistance to coke formation. There are many ways to improve catalysts activity and stability of H-ZSM-5. Zhang *et al.* (2008) and Ramesh *et al.* (2009) reported that phosphorus-modified H-ZSM-5 catalysts showed very high activity and stability in ethanol dehydration by selectively forming ethylene. The phosphorus-modified catalysts showed higher hydrothermal stability (up to 110 h) and resistance to coke formation as compared to unmodified H-ZSM-5. For the catalyst containing 3.4 wt% P (P/Al = 0.95), the main product was ethylene and the selectivity of ethylene was very high (99.4%) at the temperature range of 573 to 713 K. Moreover, the stability of H-ZSM-5 can be improved by modification with rare earth elements. Ouyang *et al.* (2009) reported that 3 wt% La modified H-ZSM-5 catalyst showed very high activity (conversion and selectivity more than 98%) and stability (more than 950 h) in ethanol dehydration for ethylene in a bioreactor (reaction temperature 260°C, LHSV 1.1 h⁻¹, and at 50% ethanol concentration). Both the fresh and regenerative catalysts showed much better stability and resistance to coke formation than the unmodified HZSM-5. With all of these modifications, the selectivity of ethylene was improved greatly. The stability of catalysts was also better because of the enhanced anti-coking ability.

In addition, the catalytic dehydration of ethanol into light olefins (both ethylene and propylene) was also been studied. There are few reports on increasing in propylene yield in the catalytic dehydration of ethanol. Murata *et al.* (2007) studied the effects of surface modification of H-ZSM-5 catalysts with W and La. They reported that the selectivity for ethylene and propylene was much lower than those for aromatics such as benzene, toluene and xylenes (BTX) over H-ZSM-5 catalyst without modification. The addition of W and La was found to reduce aromatization and olefin dehydrogenation, and the selectivity for propylene and ethylene was improved whereas the selectivity for BTX was decreased. They also reported that the selectivity for propylene formation depended on the percentage of Brønsted acid sites on the catalyst surface. The propylene selectivity increased with higher temperatures up to 723K and then decreased at 773K. Moreover, they also proposed the simplified generic mechanism of conversion of ethylene to propylene as

shown in Figure 2.3. Briefly, the dehydration of ethanol forms ethylene, which trimerizes to give hexene, followed by β -fission to produce propylene.

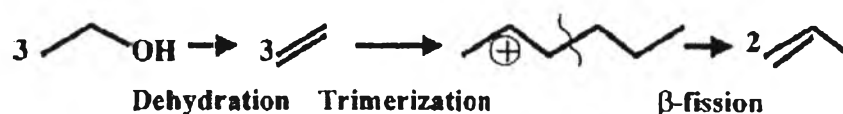


Figure 2.3 Postulated mechanism of the ethylene conversion to propylene (Murata *et al.*, 2007).

Other modification methods had also been established. Gayubo *et al.* (2010) studied the selective production of olefins from bio-ethanol on H-ZSM-5 zeolite catalysts modified with alkaline treatment. They treated H-ZSM-5 zeolite with 0.2M NaOH solution in order to modify the porous structure of the zeolite by increasing its mesoporosity and moderating the acid strength. After treatment, the selectivity of C₂-C₄ olefins was increased whereas the operating temperature of 300-400°C showed high yield and selectivity of propylene and butylenes. They also concluded that bio-ethanol conversion and product distribution depended on the operating conditions (temperature and space time).

Inaba *et al.* (2009) studied the effect of Fe-loading H-ZSM-5 and reaction temperature on the production of olefins from ethanol. They found that at 1 wt% Fe loading and a high temperature (450°C), the selectivity of C₃ olefins was improved. Song *et al.* (2010) also studied the modification method for increasing in propylene yield. In their work, phosphorus-modified ZSM-5 zeolites were used to transform ethanol to propylene. The selectivity of propylene formation depended on the phosphorus content in the zeolites. They reported that H-ZSM-5 (Si/Al₂ = 80) modified with phosphorus at P/Al molar ratio of 0.5 showed the highest propylene yield (32%), and the modification of the zeolite with phosphorous also improved the catalytic stability. Likewise, Inaba *et al.* (2011) also studied the production of C₃₊olefins (especially propylene) from ethanol using Fe and/or P-modified H-ZSM-5 zeolite catalysts. They reported that the co-modification of Fe and P could improve

the selectivity of C₃+olefins and propylene (23-35%), while modification with Fe or P alone did not improve the selectivity so much. Moreover, the addition of Fe and P can improve catalytic stability when both pure and aqueous ethanol were used as raw materials.

Recently, Furumoto *et al.* (2011) found another way for improving propylene yield. They used ZSM-5 zeolites modified with Al, Ga (having different acid strength) in order to study the effect of acidity for the conversion of ethanol to propylene. They reported that HZSM-5(Ga) and HZSM-5(Al) showed high propylene yields. The selective production of propylene from ethanol strongly depended on the SiO₂/M₂O₃ ratio and the W/F value. Also, phosphorous-modified HZSM-5(Ga) showed a good catalytic activity and stability. It confirmed that phosphorous modification is effective for improving the catalytic activity. In addition, the modification of H-ZSM-5 by varying Si/Al₂ ratio can improve propylene selectivity. Song *et al.* (2009) studied the catalytic performance of H-ZSM-5 (Si/Al₂ = 30, 80, and 280) and ZSM-5 (Si/Al₂ = 80) modified with various metals. They reported that H-ZSM-5 (Si/Al₂ = 80) provided high propylene yield because a moderate surface acidity favored propylene production. Furthermore, the catalytic activity and stability of the zeolite was improved by the modification of zirconium. Zr-modified ZSM-5(80) gave the highest yield (32%) of propylene at 773K. The surface acidity and the presence of metal ions played important roles on the production of propylene. Although H-ZSM-5 has excellent catalytic performance for dehydration of ethanol into ethylene and propylene due to the strong acidity, it also provides a wide range of products, especially aromatics, that could not be avoided at high ethanol conversion and high temperatures. Since major targets are light olefins, the formation of aromatic compounds is not preferable in this work.

2.2 Production of Propylene using SAPO-34 Catalyst

Silicoaluminophosphate (SAPO-34) is one of the zeolite type catalysts, which had been synthesized by Union Carbide Corporation (UCC) in 1982. SAPO-34 has the chabazite-like structure which is shown in Figure 2.4. The structure

consists of doubled six-membered rings (D6R) forming one cavity per unit cell. The dimensions of these roughly elliptical cavities are approximately 6.7×10 angstrom. The cavities are interconnected to six others by a 4.4×3.1 angstrom elliptical eight-ring opening (Froment *et al.*, 1992 and Saeed *et al.*, 2003).

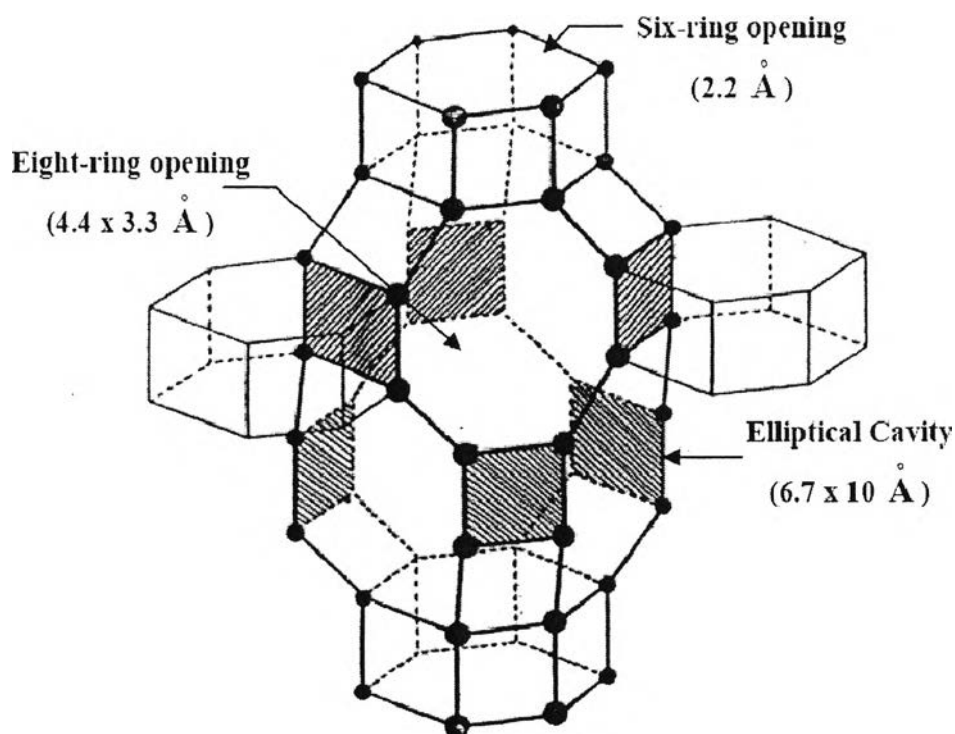


Figure 2.4 Schematic of pore structure of SAPO-34 (Saeed *et al.*, 2003).

For the acidity of SAPO-34, Wu *et al.* (2001) tested a sample of SAPO-34 using FTIR. The presence of the 3610 cm^{-1} Al-OH groups was believed to be responsible for the high activity of these catalysts for the conversion of methanol into light olefins. Whereas the acidity of the ZSM-5 zeolite decreased as the Si/Al ratio increased, SAPO-34 showed higher acidity with increasing Si/Al ratio. This can be explained that a SAPO crystal is obtained by silicon substitution into an aluminophosphate framework. The predominant mechanism appears to be silicon substitution by phosphorus, which leads to a SAPO crystal having a framework with

a net negative charge that can be referred to Brønsted acid sites (Lok *et al.*, 1984 and Saeed *et al.*, 2003).

SAPO-34 is widely used in the MTO process (Stöcker, 1999 and Wilson *et al.*, 1999) as well. There are many reports on the use of SAPO-34 for conversion methanol into olefins. The use of small pore zeolites and in particular SAPO-34 restricts the diffusion of heavy and branched hydrocarbons, and allows the selective formation of the light olefins due to the cage structure and the intermediate acidity of SAPO-34. Wu *et al.* (2004) and Abramova (2009) studied the synthesis of light olefins (both ethylene and propylene) from methanol on a SAPO-34 catalyst. They reported that the SAPO-34 catalyst was shown to be highly effective in the selectivity of ethylene and propylene formation. The total yield of C₂-C₃ olefins at 350-450°C was about 80%, and methanol conversion was up to 99%. The high efficiency of the SAPO-34 catalyst was the result of the microporous structure of zeolite and the high content of acid centers of medium strength. Although the catalyst was deactivated by coking, the catalyst activity was completely restored after regeneration with air at 550°C while the crystal structure and the acid properties did not change.

On other sides, propylene can be produced from ethylene via zeolite catalysts. Oikawa *et al.* (2006) concluded that the rate and selectivity of propylene formation in the conversion of ethylene strongly depended on Brønsted acid sites and the pore size of catalytic material. For the effect of pore size on the selectivity of propylene at 723K, using the silicoaluminophosphate molecular sieve, SAPO-34, showed very high selectivity for propylene (80%) while the selectivity for iso-butene was very low. The pore size of SAPO-34 is approximately equal to the kinetic diameter of propylene (about 4.4 angstrom) and smaller than the kinetic diameter of iso-butene (5.0 angstrom) or bigger hydrocarbons, while ethylene has a kinetic diameter of 3.9 angstrom; therefore SAPO-34 is selective for produce propylene from ethylene. Moreover, the acid strength is also an important factor determining the activity for propylene formation. The catalyst having higher acid strength than SAPO-34, e.g., H-[Al]-ZSM-5 can convert propylene to other higher hydrocarbons, such as C₅ hydrocarbons, whereas the catalysts having lower acid strength than SAPO-34, e.g., H-[B]-ZSM-5 and 5A (Ca-A) zeolite exhibit a lower rate of

propylene formation than SAPO-34. These results show that SAPO-34, with moderate acid strength, provides a high selectivity for propylene. The carbenium ion mechanism for the conversion of ethylene into propylene over solid acid catalysts were also proposed by Oikawa *et al.* (2006) as shown in Figure 2.5.

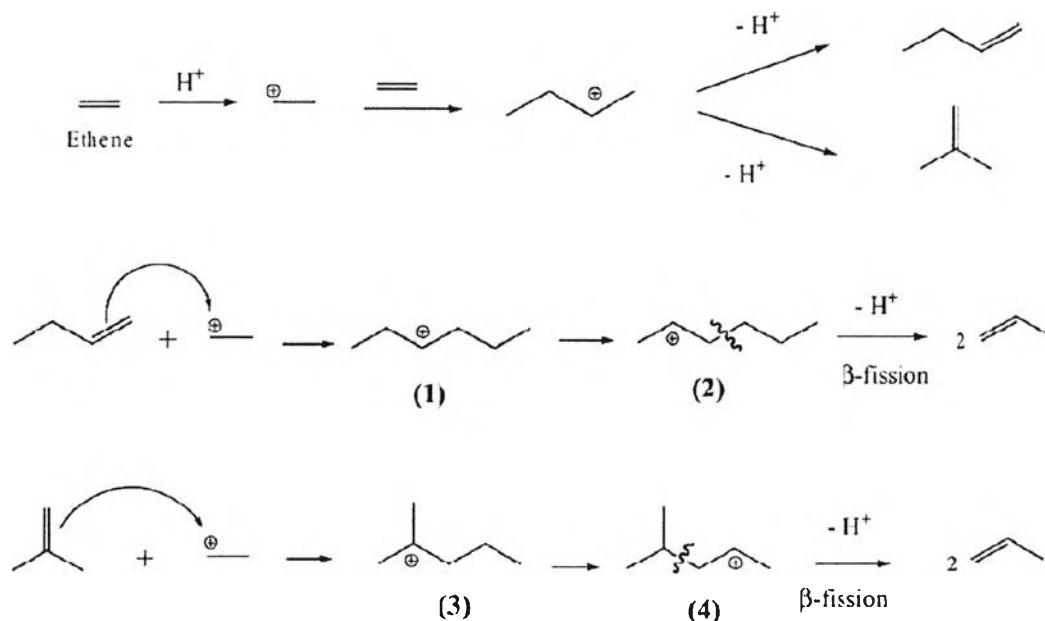


Figure 2.5 Reaction scheme for the conversion of ethylene into propylene over solid acid catalysts (Oikawa *et al.*, 2006).

For this proposed carbenium ion mechanism for the conversion of ethylene into propylene, the fission of a carbon-carbon bond at the β -position of the hexyl carbenium ion (**(2)**) and the 4-methyl-2-pentyl carbenium ion (**(4)**) is an important reaction in the selective production of propylene. It is expected that both the acid strength of Brønsted acid sites and the pore size of solid acid catalysts govern the formation of propylene in the conversion of ethylene. The other effects of using SAPO-34 including of particle size and mole fraction of Si were also reported (Baba *et al.*, 2008). In the case of SAPO-34 which has small particle sizes (smaller than 3 μm), the selectivity of propylene was about 80%. For SAPO-34 with particle sizes from 6-17 μm gave propylene selectivity about 75% whereas SAPO-34 with a 26 μm

particle size gave lower propylene selectivity (12.5%). The rate of propylene formation also varied with the variation in the particle size, and had a tendency to increase with decreasing particle size. The variation in the selectivity for propylene could have been caused by both the particle size and the different Si mole fractions which are related to the Brønsted acid sites. However, the effect of SAPO-34 particle size on the selectivity for propylene was stronger than the effect of the mole fraction of Si in the SAPO-34 lattice.

Recently, there are few reports on the use of SAPO-34 and modified SAPO-34 for the catalytic dehydration of ethanol to ethylene. Zhang *et al.*, (2008) studied the effect of temperature (275-375°C) and reaction time (100 h) on the conversion of ethanol and selectivity to ethylene over SAPO-34 and Ni-modified SAPO-34. They reported that an increase in temperature increased the selectivity to ethylene up to a certain temperature, after which it decreased. With SAPO-34 and Ni-modified SAPO-34, the selectivity to ethylene was maximal (94.3% and 98.3%, respectively) at 350°C (LHSV = 3 h⁻¹). For the stability of these catalysts, SAPO-34 and Ni-modified SAPO-34 exhibited effective catalytic activity and stability, and provided 86.0% and 92.3% yield of ethylene, respectively, which remained unchanged for 100 h of time on stream. In addition, Chen *et al.* (2010) studied the effect of metal modification (Mn-modified SAPO-34 and Zn-modified SAPO-34) and space velocity (WHSV 2-30 h⁻¹) on the conversion of ethanol and selectivity to ethylene. They reported that Mn-SAPO-34 exhibited the best conversion of ethanol and selectivity to ethylene (99.4% and 98.4%, respectively) at 340°C (WHSV = 2 h⁻¹). For the effect of space velocity, the ethanol conversion and the ethylene selectivity decreased with increasing space velocity. At the low mass space velocity, the ethanol may contact with catalysts completely in the reaction. With the molar hourly space velocity increasing, the residence time of ethanol became shorter, leading to a large number of un-reacted ethanol left in products. However, the selectivity to propylene at high reaction temperatures and low space velocity had not yet been reported.

From the literatures above, using SAPO-34 catalyst can convert not only ethanol into ethylene (Zhang *et al.*, 2008 and Chen *et al.*, 2010) but also ethylene into propylene (Oikawa *et al.*, 2006); thus, the direct conversion of ethanol into propylene is possible. Surprisingly, Oikawa *et al.*, 2006 also established that ethanol can be

converted into propylene using the SAPO-34 catalyst under 33.8kPa ethanol at 400°C, and ethanol was completely converted to light olefins with 51.0% propylene yield and 38.1% ethylene yield. However, the effect of reaction conditions was not clearly reported.

The objectives of this work were: (1) to study the effect of using SAPO-34 in the catalytic conversion of ethanol to light olefins at various operating conditions, (2) to modify and design a commercial plant for the production of light olefins, and then (3) to study the economic evaluation for using this catalyst in the ethanol-based light olefins plant.

The scope of this research covered the following:

Part 1. Catalyst Testing

- The reactor used in this reaction is an isothermal fixed-bed reactor.
- The ethanol concentration was fixed at 99.5%.
- The effect of temperature and LHSV were studied by varying temperatures between 350 °C and 500°C and LHSV between 0.2 h⁻¹ and 1.0 h⁻¹, as follows.

LHSV Temp	0.2 h ⁻¹	0.5 h ⁻¹	1.0 h ⁻¹
350 °C	(1)	(2)	(3)
400 °C	(4)	(5)	(6)
450 °C	(7)	(8)	(9)
500 °C	(10)	(11)	(12)

Part 2. Modification of a Process

- The process was modified from the existing plant, and uses the catalyst from Part 1.
- The separation plant for polymer grade olefins was focused.

Part 3. Economic Evaluation

- Economic evaluation was subjected to the catalyst and the process in Part 1 and Part 2, respectively.
- Net present value (NPV), internal rate of return (IRR), profitability index (PI), and payback period (PB) were the parameters used in economic evaluation.