



## CHAPTER I INTRODUCTION

Light olefins such as ethylene and propylene are important intermediates which are widely used in the petrochemical industry. Ethylene is a gaseous organic compound used to produce many products, especially polymers such as high-density polyethylene, low-density polyethylene, linear low-density polyethylene and other chemicals such as ethylene dichloride and ethylene oxide. Propylene is an important feedstock used to produce many products also such as polypropylene and propylene oxide.

Several processes and feedstocks can be used to produce olefins, which also yield different output products and by products. Currently, there are three main industrial methods for the production of olefins including the steam cracking of hydrocarbons, fluid catalytic cracking in oil refineries, and paraffin dehydrogenation. Moreover, the oxidative coupling of methane, the oxidative dehydrogenation of paraffin and methanol to olefins (MTO) process (Froment *et al.*, 1992) are non-commercial processes that can be used to produce olefins as well. In recent years, with the increase in the oil prices, the shortage of natural resource, and also the growing demand for ethylene and propylene, the development of a new process for the production of light olefins from renewable resources has received wide attention. Ethylene can be produced from ethanol or bio-ethanol; that is a renewable resource, via catalytic dehydration process (Tsao *et al.*, 1979). Apart from that, other hydrocarbons, especially gasoline and aromatics, can be also produced via the catalytic dehydration process of ethanol. Bio-ethanol is seen as a good alternative because the source crops can be grown renewably and in most climates around the world (Seungdo *et al.*, 2003). Thus, the production of ethylene from bio-ethanol is an interesting route.

There are many reports on the production of ethylene from ethanol using various catalysts such as alumina, silica-alumina and zeolites. The conversion of ethanol over zeolite catalysts (Goto *et al.*, 2010) has been proposed by the following pathways: (1) the dehydration of ethanol into ethylene, (2) the oligomerization of ethylene into higher olefins, and (3) the cracking and/or aromatization of higher

olefins. However, there are few reports on the direct production of propylene from ethanol. Recently, the productions of propylene from ethanol by using H-ZSM-5 and ZSM-5 modified with various metals have been studied (Song *et al.*, 2009). The use of H-ZSM-5 with Si/Al<sub>2</sub> of 80 gave high propylene yield, and the use of Zr-modified ZSM-5 gave the highest propylene yield of 32% at 500°C. The production of propylene strongly depends on the surface acidity and metal modification. Moreover, H-ZSM-5 with Si/Al<sub>2</sub> of 280 modified with La (Inoue *et al.*, 2010), H-ZSM-5 with Si/Al<sub>2</sub> of 80 modified with phosphorus (Song *et al.*, 2010), and H-ZSM-5 modified with alkaline earth metals (Goto *et al.*, 2010) had been studied as well. Although H-ZSM-5 has excellent catalytic performance for both MTO process and the dehydration of ethanol into propylene due to the strong acidity, it also provides a wide range of products, especially aromatics and paraffins, that could not be avoided at high methanol or ethanol conversion and also at high temperatures.

In order to improve the selectivity to light olefins, a catalyst based on silicoaluminophosphate zeolite (SAPO-34) was widely used in the MTO process (Stöcker, 1999). There are many reports on the use of SAPO-34 for conversion methanol into olefins. Because of its narrow pores (about 4.4 Å) and mild acidity, SAPO-34 was a favorable catalyst in terms of activity and selectivity to light olefins (Wilson *et al.*, 1999). Recently, there were few reports on the use of SAPO-34 and modified SAPO-34 for the catalytic dehydration of ethanol to ethylene (Zhang *et al.*, 2008 and Chen *et al.*, 2010). The selectivity to ethylene was maximal (about 90%) at the temperature of 350°C and decreased with increasing temperature, but the selectivity to propylene had not been reported yet. Apart from that, ethylene and ethanol can be converted into propylene using the SAPO-34 catalyst (Oikawa *et al.*, 2006). However, the effect of reaction conditions was not clearly reported. In this study, the influence of parameters (the temperature, the space velocity and the reaction time) of using SAPO-34 as a catalyst for ethanol dehydration into olefins was investigated in terms of activity and selectivity with respect to light olefins. Moreover, the modification of commercial process and the economic evaluation of using this catalyst for light olefins production were studied as well.