CHAPTER I
INTRODUCTION

With the world economy becoming more interconnected and dependent, finding new alternative resources of energy and industrial valuable products has become very critical to remain competitive in market demand. In recent years, one of the best alternatives has been biomass, which can be thermochemically or biochemically converted to combustible liquids or gases (Zhang *et al.,* 2010). Chenrubini (2010) reported that in 2006 the total world production of bio-ethanol, which was one of the most commonly-used biomass feedstock for biochemical conversion process, reached 51.3 billion liters. Up to now, there have been three main industrial processes to produce light olefins, including the fluid catalytic cracking in oil refinery, steam cracking of hydrocarbons, and paraffin dehydrogenation (Fatourehchi *et al.,* 2010). Light olefins (especially, ethylene and propylene) are primarily used for production of chemicals such as ethylene oxide, ethylene dichloride, polyethylene, polypropylene, propylene oxide, and so forth (Corma *et al.,* 2005). Therefore, the use of bio-ethanol as a feedstock for catalytic dehydration to produce light olefins has received attention.

Many solid acid catalysts have been employed for the dehydration of ethanol. Zhang *et al.* (2008) reported that the dehydration of ethanol with Al_2O_3 catalyst required a high reaction temperature (450 °C) and produced low ethylene yield. Recently, HZSM-5 zeolite was focused on the catalytic dehydration of ethanol to light olefins. Makarfi *et al.* (2009) studied the effect of the Si/Al ratio on the activity and selectivity of HZSM-5 catalyst for the conversion of ethanol to propylene. They found that the formation of propylene depended on the Si/Al ratio. In addition, many researchers have studied the modification of HZSM-5 catalysts with metals such as Fe (Inaba *et al.,* 2009), La (Inone *et al.,* 2010), and P (Takahashi *et al.,* 2012) to improve propylene selectivity. However, the strong acidity and acid sites in HZSM-5 would lead to the by-production of aromatics, so coking or deactivation easily occurred on the catalyst. In particular, the SilicoAluminoPhosphate (SAPO-34) has received high attention as it gave a narrow range of product distribution with a high selectivity to ethylene and propylene in the methanol to olefins (MTO) process (Dubois *et al.*, 2003). The framework structure of SAPO-34 is the natural zeolite chabazite (CHA). The effective pore openings (about 4.5 angstrom) of SAPO-34 could only adsorb straight chain molecules such as primary alcohols, linear paraffin, and olefins, but not branched isomers and aromatics (Wilson *et al.*, 1999). Due to the narrow pores, SAPO-34 having three dimensions and mild acidity was successfully applied in the MTO process. There are few reports on the catalytic dehydration of ethanol to ethylene and propylene by using SAPO-34. Chen *et al.* (2010) studied the dehydration reaction of bio-ethanol to ethylene over Mn-SAPO-34 and Zn-SAPO-34 catalysts. The highest yield of ethylene was up to 97.8% over Mn-SAPO-34 at the reaction temperature of 340 °C. Zhang *et al.* (2008) compared the activity and stability of Al_2O_3, HZSM-5 (Si/Al=25), SAPO-34, and Ni-SAPO-34 catalysts for ethanol conversion to ethylene. They reported that the activity and stability of Ni-SAPO-34 and SAPO-34 were better than other two catalysts. Moreover, Oikawa *et al.* (2006) investigated that ethylene could convert to propylene by using SAPO-34. They found that SAPO-34 catalyst exhibited the highest selectivity of propylene (80%).

It is well known that HZSM-5 and SAPO-34 are two of potential catalysts for the catalytic dehydration of ethanol to light olefins. Furthermore, it is necessary that HZSM-5 and SAPO-34 must have the moderate concentration and strength distribution of acid sites to produce the high yield of propylene, because the high concentration of acid sites and the strong acidity might lead to propylene transformation to aromatics and fast deactivation of the catalysts. However, an increase in acidity of SAPO-34 catalyst by mixing with oxides of Ga, Ge, Sn, and Sb and a decrease in acidity of HZSM-5 catalyst by using alkaline treatment with KOH solution have not been established for the catalytic dehydration of bio-ethanol to light olefins. Therefore, the effects of acidic oxides of Ga and Sn metals and acidic oxides of Ge and Sb semimetals doped on SAPO-34 catalyst for the catalytic dehydration of bio-ethanol to light olefins were investigated in the work. In addition, the catalytic performance of HZSM-5 catalysts treated with KOH solutions at various concentrations were studied as well.