CHAPTER I
INTRODUCTION

Depleting oil resources, increasing oil price and environmental concerns have driven much effort to develop green technologies based on renewable sources. One of the promising alternatives is bio-mass which can be biochemically converted to bio-ethnaol via fermentation process (Ramesh *et al.*, 2010). Bio-ethanol is widely used as a fuel for transportation. Currently, bio-ethanol used as a feedstock for catalytic dehydration to obtain aromatic compounds or light compounds such as ethylene, propylene and p-xylene has been received much attention.

Many acid solid catalysts have been studied for the dehydration of ethanol. Earlier, γ-Al_2O_3 has been studied in this reaction as well as modified γ-Al_2O_3. Chen *et al.* (2007) studied on catalytic ethanol dehydration over TiO_2/ γ-Al_2O_3. They found that loaded TiO_2 showed high selectivity of ethylene. However, the operating temperature was still over 500 C° in order to achieve good ethanol conversion. Later on, HZSM-5 was found to be highly active as a highly-shape selective solid acid catalyst for dehydration of ethanol because of well-defined zeolite structure (Phillips and Datta, 1997). Its framework Si/Al ratio plays an important role on determining product distribution. In addition, HZSM-5 catalysts with metal oxides such as Co (Van Niekerk *et al.*, 1996), P (Lu and Liu, 2011) and La (Ouyang *et al.*, 2009) have been studied in order to improve product selectivity and activity. SAPO-34 has been employed as solid acid catalyst for ethanol conversion to light olefins and for cracking of C4 (Zhou *et al.*, 2008). The pore opening of this material allows only small molecules such as primary alcohols, linear paraffins, and olefins to diffuse through the pores. As a consequence, the large hydrocarbons or aromatic diffusion is restricted, leading to high yield and selectivity of lower olefins. Other silicoaluminophosphate molecular sieve such as SAPO-17, SAPO-18, SAPO-35 and SAPO-44 gave good selectivity to light olefins (Dubois *et al.*, 2003). Incorporation of an oxide into SAPO-34 could strongly influence on catalyst behavior in ethanol dehydration. Zhang *et al.* (2008) studied the catalytic dehydration of ethanol over SAPO-34 and Ni modified SAPO-34. Modified SAPO-34 possessed more weak acid sites than SAPO-34 because nickel generated new acid sites. Other transition metals have been used to modify SAPO-34. Chen *et al.* (2010) investigated on the effect of Mn and Zn over SAPO catalyst. Mn^{+2} and Zn^{+2} made the ethylene selectivity higher than the parent SAPO-34 because of smaller pore and higher acid density. Wei *et al.* (2008) investigated the synthesis, characterization, and catalytic performance of Me-SAPO-34 (Me=Co, Mn, Fe) for chloromethane transformation to light olefins. Metal oxides had strong influence on catalytic activity. Recently, Wongwanichsin (2013) studied the dehydration of bio-ethanol to light olefins over SAPO-34 modified with Ga_2O_3, GeO_2, SnO_2 and Sb_2O_3. Tin oxide and antimony oxide were able to increase the acidity of SAPO-34. Sb_2O_3/SAPO-34 gave a high concentration of ethane while SnO_2/SAPO-34 gave a high yield of propylene and cooking gas. Pasomsub (2013) also studied the catalytic activity of HZSM-5 modified with P_2O_5, Sb_2O_5 and Bi_2O_5. Oxides doped on a zeolite could lead to differences in product distribution because of different acid strength. Moreover, it was found that Sb_2O_5 could enhance the formation of aromatics like p-xylene and heavier aromatics because Sb_2O_5 doped on HZSM-5 had higher acid strength than the unmodified HZSM-5. The modified one could protonate hydrocarbon molecule to form cabenium ions. These ions then could react with small molecules to form larger molecules.

The catalytic activity can be substantially changed by the addition of oxides. Both tin and antimony oxides are acidic which could enhance the acid strength of catalysts. Tin oxide and antimony oxides are dual stable valences which their strength increases with the amount of oxygen substitution on the central atom. In this work, the difference on oxidation state of metal oxides doped on SAPO-34 zeolite will be studied in order to observe the effect on product distribution prepared by solid-solid interaction. Furthermore, the reduction of tin and antimony oxides on SAPO-34 will be carried on to obtain the metallic tin- and antimony-doped SAPO-34. The incorporation of tin and antimony are also investigated for the catalytic dehydration of ethanol.