CHAPTER I
INTRODUCTION

p-Ethyltoluene (*p*-ET) is an important precursor made for subsequent dehydrogenation and polymerization to poly(*p*-methylstyrene) (PPMS), a polymer which can replace polystyrene. PPMS has advantages over polystyrene such as higher glass transition temperature and lower density (Kaeding, 1983). *p*-ET production from ethylation of toluene with ethanol would provide advantages of utilizing toluene to replace benzene which is somewhat more value product in polystyrene production.

Traditional acid catalysts, used for alkylation known as Friedel-Craft catalysts (such as $AlCl_3$, HCl), have some disadvantages such as corrosive and environmental problems. When these catalysts are used, a large amount of non-desired isomers and products are formed with causing an adverse effect on the quality of the products. With advances in the synthesis, zeolites have made a new possibility to develop a new process for selective production (such as selective isomers) due to the shape selectivity and acid properties of zeolite. Many types of zeolite were studied for improving the selectivity of the desired products and ZSM-5 was founded as a suitable zeolite for *p*-selective alkylation of mono-aromatic products due to the suitable shape-selectivity of zeolites (Liu *et al.*, 2010).

Although ZSM-5 was founded as a suitable catalyst for *p*-ET production, modification of catalyst is necessary to obtain the highest p-isomer. The way to improve *p*-selectivity for *p*-ET was studied for many years, starting from reducing the pore size by impregnation of metal oxide to improve product selectivity (Bhandakar and Bhatia, 1994), reducing the strong acid sites to prevent side reaction such as isomerization of *p*-ET and disproportionation of toluene (Chen and Feng, 1992), deactivating of external acid site to prevent isomerization at the non-shape selective reaction at the external surface (Yu and Tan, 2006). Liu *et al.* (2010) reported that ZSM-5 with high SiO_2/Al_2O_3 ratios was found to be suitable for the selective alkylation of toluene with ethylene due to the lower acidity, but external surface modification is still necessary to prevent side reactions at the external surface. To eliminate to external acid sites, chemical liquid deposition (CLD) and

chemical vapor deposition (CVD) with inert silica have been demonstrated to be effective to eliminate external acid sites. As compared to CLD, CVD is more difficult to operate and apply for industrial scale production.

The purposes of this work are to study the effects of various SiO_2/Al_2O_3 molar ratios of HZSM-5 and reaction conditions (such as reaction temperature, WSHV, toluene to ethanol molar ratio) on *p*-ET selectivity, and to modify the suitable SiO_2/Al_2O_3 molar ratio of HZSM-5 via CLD using TEOS to study the effects on *p*-ET selectivity in ethylation of toluene with ethanol.