CHAPTER I
INTRODUCTION

p-Xylene is the most important intermediate in xylene isomers which include *o*-, *m*- and *p*-xylene. It is mainly used for producing terephthalic acid which is a major component in the production of polyester fibers. Additionally, chemical additives, agricultural chemicals also require *p*-xylene as a feedstock. Currently, *p*-xylene is produced by disproportionation of toluene and *p*-xylene-oriented isomerization of mixed xylene isomers. However, these processes will produce a large quantity of benzene, hence, the cost of isolation and purification is relatively high. The catalytic methylation of toluene is, therefore, a very promising alternative method of producing *p*-xylene without any by-product. A variety of zeolites have been used for catalyzing this reaction such as acidic zeolite, HZSM-5 because of its suitable pore size for *p*-xylene diffusion. Unmodified HZSM-5 zeolite can be used as a catalyst but the selectivity to *p*-xylene is relatively low. This is because the acid sites on the external surface of the catalyst would cause an isomerization of *p*-xylene to o- and m-xylene resulting in decreasing the selectivity to *p*-xylene. It was suggested that the selectivity to *p*-xylene could be improved by the catalyst modification with various methods such as impregnation of metallic or nonmetallic compounds, coke deposition, dealumination, chemical liquid deposition (CLD), chemical vapor deposition (CVD), etc. Deposition of an inert silica layer onto the external surface of the HZSM-5 catalyst by CLD has been demonstrated to be effective for obtaining a high *p*-xylene selectivity due to the deactivated external acid sites (Cejka*et al.*, 1996). In addition, the acid properties and resultant catalytic activity of zeolite materials are known to be related to the degree of substitution of aluminum for silicon in the framework. As the dealumination with acid agent which have molecular diameters larger than zeolite pore openings, they could be used to selectivity remove the framework aluminum at the external surface of HZSM-5 catalyst

The purpose of this study was to attain and compare a higher selectivity to *p*-xylene over HZSM-5 catalysts by the deactivation of its external acid sites with

silylation or dealumination techniques. The selective formation of *p*-xylene in the methylation of toluene with methanol is studied. The effects of SiO_2/Al_2O_3 molar ratios and reaction conditions on *p*-xylene selectivity are studied over unmodified HZSM-5 zeolites. The most active commercial HZSM-5 zeolite is modified by silylation via chemical liquid deposition (CLD) with tetraethyl orthosilicate(TEOS) in range of 0.5-2.0 $ml.g^{-1}$, CLD cycle number in range of 1-3 cycle, or dealumination with oxalic acid.