

CHAPTER I

INTRODUCTION

Nowadays, the main chemical compounds such as aromatics are one of the basic raw materials in the organic chemicals and polymer industry. Benzene (B), toluene (T) and xylenes (X), which are known collectively as BTX, are the most widely used aromatic hydrocarbons. The basic commercial processes for aromatic hydrocarbons production are solid-fuel (coal and shale oil) process, pyrolysis and catalytic reforming using crude oil, of which the feedstock is derived from crude oil. In the effort to develop new process for aromatic hydrocarbons production to replace crude oil.

Production of aromatics from renewable biomass resources could provide sustainable alternatives to fossil-based processes. Within this trend, the search for suitable biomass resources is primarily importance for the achievement of a promising process. So far, biomass-derived ethanol, glycerol, n-butyl alcohol/acetone and a mixture of C₂-C₅ alcohol have been reported (Yu *et al.*, 2012) as feedstocks in the production of aromatics. HZSM-5 is well known for its activity for conversion of alcohol and other oxygenates into aromatic hydrocarbons (Ni *et al.*, 2010). There are many processes related to this work such as methanol to gasoline (MTG), methanol to olefin (MTO) and ethanol to gasoline (ETG). In order the develop a new process for aromatic hydrocarbon production replace crude oil, catalytic aromatization of glycerol has a great attention and potential.

Catalyst modified by alkali-treatment has attracted extensive attention as an innovative post-treatment method and is regarded as a promising approach for the preparation of porous materials. Generally, alkali-treatment involves alkali-dissolution and alkali-modification, depending on the solution concentration used. The solution concentration required for alkali-dissolution is usually higher than that for alkali modification. The two alkali-treatments, dissolution and modification, have different purposes in zeolite preparation. Alkali modification utilizes low concentrations of the solution to treat zeolite samples with the aim of selectively removing silicon species and preserving the micropores. Improved catalytic performance and enhanced active site accessibility.

p-Xylene is the aromatic used as a raw material for terephthalate and polyester. The selective formation of *p*-xylene in the disproportionation of toluene and aromatization of n-alkane has been studied over acidic zeolites, especially ZSM-5 because its pore size is suitable for separating *p*-xylene from a mixture of xylene isomers. The concentration of xylene isomers are typically close to the thermodynamic equilibrium with 24% *o*-xylene, 53% *m*-xylene and 23% *p*-xylene over unmodified ZSM-5 zeolite due to the quick isomerization of *p*-xylene to *o*-xylene and *m*-xylene on the external acid sites. Therefore, the external surface modification of the ZSM-5 zeolite is required to enhance the *p*-xylene selectivity. The deposition of an inert silica layer (which has molecular size larger than the pore mouth of ZSM-5) onto the external surface of the zeolite crystals, can be achieved by chemical vapor deposition (CVD) and chemical liquid deposition (CLD) methods. In contrast, CLD is more easily transferred to industrial scale. After CLD treatment, *p*-xylene selectivity is enhanced due to the elimination of external acid sites (Teng *et al.*, 2011).

The objective of this work is to investigate the effect of alcohols feedstocks on the production of aromatic hydrocarbons over modified HZSM-5 by alkali and to study the reaction pathways for these reactions. The optimization of *p*-xylene selectivity over ZSM-5 catalyst by alkali treatment and silylation was investigated in this work.