

CHAPTER I

INTRODUCTION

p-Xylene is more important than other xylene isomers which including *o*-, *m*-xylene because it is an important precursor to terephthalic acid and dimethyl terephthalate which both are key components of polyethylene terephthalate (PET) production (Alabi *et al.*, 2012). Currently, *p*-xylene is produced by methylation of toluene and toluene disproportionation. Methylation of toluene with methanol could be an even more attractive process than disproportionation of toluene because methylation can be operated at lower temperatures than disproportionation. Moreover, methanol can be synthesized from the widely available and abundant natural gas especially by the emergence of new extraction technologies, e.g., fracking, to recover natural gas from unconventional sources. On the other hand, the toluene disproportionation produces large quantities of benzene and relatively high cost of product isolation and purification.

By reacting toluene and methanol over a zeolite catalyst, water and xylenes are formed with the following thermodynamic equilibrium composition of xylene isomers; 23.55 % *p*-xylene, 52.42 % *m*-xylene, and 24.03 % *o*-xylene at 400 °C (Ashraf, 2013). Also, *o*-, and *m*-xylene do not have much industrial demand and isomerization is needed to convert them to *p*-xylene. Various zeolite catalysts are employed. HZSM-5 has attracted more attention as *p*-selective alkylation catalyst, due to its unique pore size comparable to the molecular dimension of *p*-xylene. In order to improve the selectivity to *p*-xylene, the acidity and pore structure of zeolite need to be modified properly.

In earlier studies, various methods of modification of the zeolite were proposed by a number of researchers. Zheng and co-workers (2003) observed that chemical liquid deposition (CLD) and chemical vapor deposition (CVD) with inert silica methods can also improve *p*-selectivity from eliminating external acid sites and decreasing the pore sites. A successful decrease of pore sites of zeolites will result in the prevention for diffusion of aromatic molecules with relatively larger diameters. The CLD modification with tetraethyl orthosilicate (TEOS) significantly increased

the selectivity to *p*-xylene in the disproportionation of toluene as the diameter of TEOS is larger than the micropore openings of HZSM-5 zeolites. For creation of enhanced Brønsted acid sites which are both important factors in determining the activity and selectivity in the alkylation of toluene with methanol on zeolite catalysts, You and co-workers (2014) reported that zeolite can be dealuminated by various methods including steaming and pretreatment with chemicals such as HCl, oxalic acid, SiCl₄, and ammonium hexafluorosilicate. It is well-known that dealumination modifies its acidic property, it was also reported that only extra-framework Al species (EFAl) could be extracted in dealuminated ZSM-5 zeolite prepared through a treatment in aqueous acidic solution because of the narrow channel size of ZSM-5 zeolite. Moreover, Mihályi and co-worker (2012) studied the effect of dealumination by using citric or oxalic acid. They found that oxalic anion is better than citric anion because oxalic anion is smaller and easier entering into the zeolite channels. Therefore, the modified sequences with CLD and DeAl could be of interest for obtaining a higher *p*-xylene selectivity.

The purpose of this study was to synthesize HZSM-5 catalyst with SiO₂/Al₂O₃ ratio of 200 under hydrothermal conditions and to modify via i) chemical liquid deposition (CLD) ii) dealumination by acid treatment, and iii) dealumination with acid followed by CLD treatment or vice versa. The catalytic activity testing was carried out at various reaction conditions for the methylation of toluene with methanol.