CHAPTER I
INTRODUCTION

Xylenes are important raw materials as intermediates used in petrochemical industries. There are 3 isomers of xylene, viz. ortho-, meta- and para-xylenes. Para-xylene is the most valuable among the isomers since oxidation of this compound produces terephthalic acid, which is widely used in the production of polyester fibers, synthetic resins, vitamins, and other pharmaceuticals. U.S. xylene derivative demand is shown in Table 1.1. Besides xylenes, toluene is also obtained from crude oil distillation. Usually, it is used as a solvent due to relatively cheap price. One way to make higher value substance from toluene is to convert toluene to xylenes by disproportionation reaction.

Table 1.1 U.S. DMT/PTA demand (as PTA equivalent)

(Million Pounds)						Compound Growth Rate (%)
	1996	1997	1998	1999	2000	1996-2000
Polyester Fibers	3360	3309	3260	3211	3163	-1.5
PET Bottle Resin	1960	2137	2329	2536	2767	9.0
Net Exports	414	435	456	479	503	5.0
Other	1103	1200	1286	1362	1424	8.3
Domestic Demand	6838	7081	7322	7591	7857	3.6

Therefore, toluene disproportionation is an industrial process used for the production of benzene and xylenes. The reaction is carried out over various acid zeolites, such as mordenite, faujasite and ZSM-5 to yield products with distribution normally close to thermodynamic equilibrium (Kaeding, 1997). The uses of the ZSM-5 zeolite as a catalyst are especially interesting because the kinetic diameters of the aromatic hydrocarbons involved in the reaction are very close to the ZSM-5 pore size (Bhaskar and Do, 1990). However, toluene conversion and para-selectivity are

controlled by several parameters, such as, type of zeolite catalyst, temperature, crystal size, acidity (Bhat *et al.*, 1995), and modified metal (Uguina *et al.*, 1993,b), etc. The effect of these parameters has been studied by a large number of researchers using industrial zeolites.

The shape and product selectivity mechanisms are based on the difference in the diffusion rates of xylene isomers and the amount of external acid sites (Kunieda *et al.*, 1999). These non-selective acid sites of zeolite are the main cause of the decrease in the para-selectivity due to the occurrence of secondary isomerization of para-xylene primary product on the surface. Therefore, surface modification techniques become more important in increasing the selectivity of zeolite.

The enhancement of shape selectivity of ZSM-5 and FAU using bulky organic silicon compounds could be obtained by chemical vapor deposition (CVD) which is one of the important modification methods (Kim *et al.*, 1999). Although this technique changes neither the channel size nor acidity in pores by depositing silica at the external surface of zeolite, it narrows down the pore opening size due to inert silica coated on the external surface resulting in the reduction of product yields. Therefore, further studies on this technique to determine the optimal deposition condition, such as, the effect of deposition time (Roger *et al.*, 1998), number of cycle (Shaikh *et al.*, 1999) and deposition temperature (Manstein *et al.*, 2002) were performed.

In addition, another interesting zeolite modification technique nowadays is seeding technique (Li *et al.*, 2002). Two layers of zeolite product can be prepared using two-step crystallization procedure. The ZSM-5 seed will be coated with silicalite shell which has very low acidity to passivate the surface acidity of ZSM-5.

In this work, the disproportionation of toluene was studied on new synthetic route of ZSM-5 and faujasite zeolites using synthesized atranes (silatrane and alumatrane) as zeolite synthesis precursors and alkaline base as hydrolysis agent via sol-gel process followed by hydrothermal treatment (Phiriyawirut *et al.*, 2003). The effect of temperature, Si/Al ratio and pore diameter of zeolites were studied to determine the critical catalytic parameters in this reaction. Moreover, the effect of Si/Al ratio on the CVD modification of tetraethoxysilane (TEOS) and comparison between CVD and seeding technique were focused, as well.