CHAPTER I

INTRODUCTION

1. Motivation

Benzene, toluene, and xylenes are basic raw materials for other intermediates in many petrochemical industries (Wittcoff and Reuben, 1996). Benzene is the third most important organic chemical. Over half is used as ethylbenzene/styrene-driven. Styrene is a raw material for the production of polystyrene and styrene copolymer such as ABS and SAN. The second most important use is for cumene for the production of phenol and acetone. Moreover, it is basic chemical for the production of the two most important types of nylon. Benzene, via cyclohexane, can be converted to adipic acid, which is reacted with hexamethylenediamine to give nylon 66. Benzene can also be converted to caprolactam, the raw material for nylon 6. U.S. benzene sources and its demands in 1995 are shown in Figures 1 and 2, respectively.
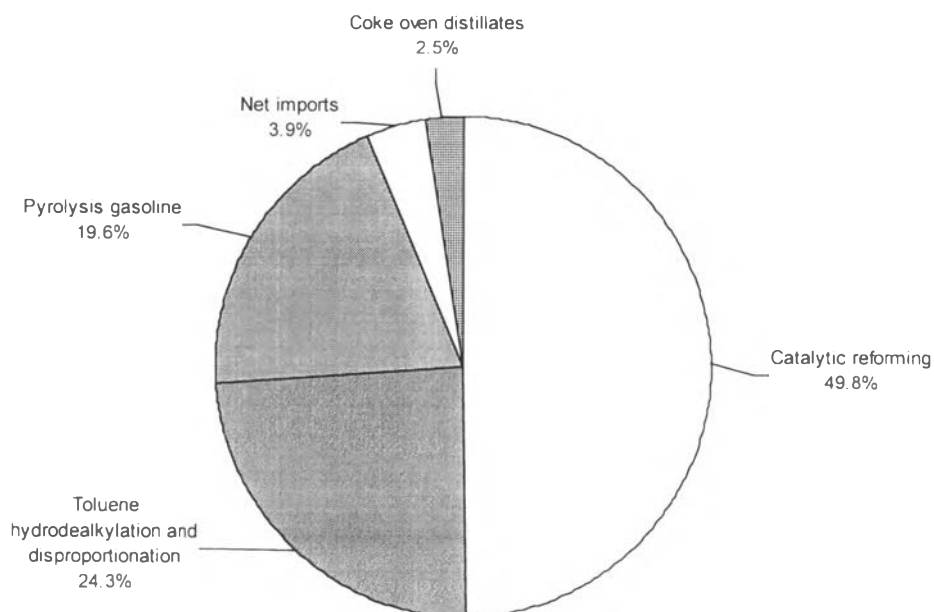

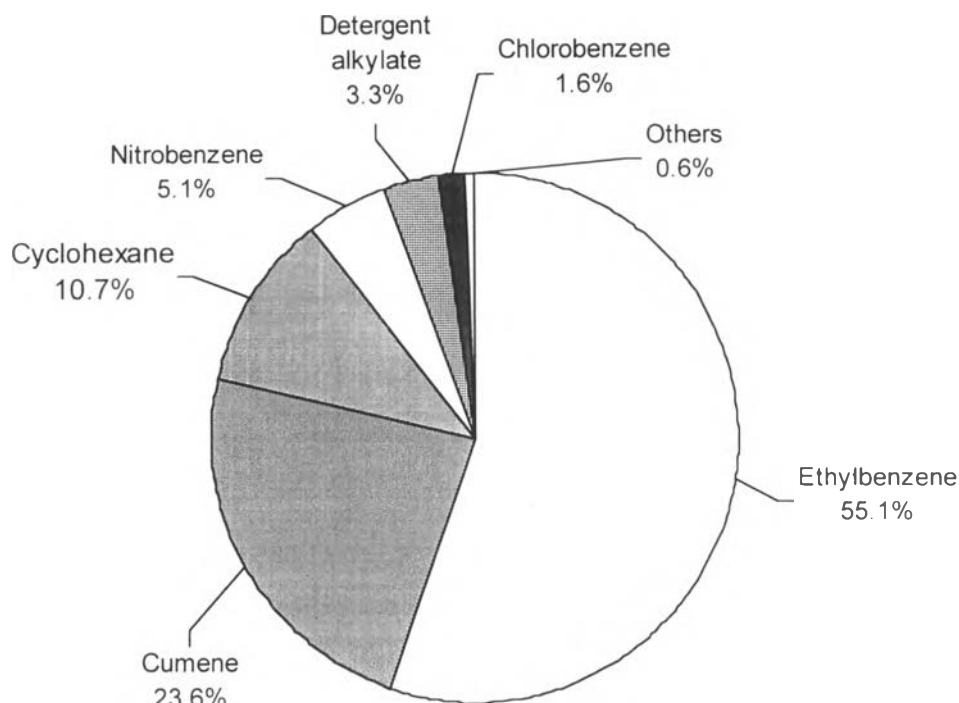**Figure 1** Sources of benzene in the United States in the early 1990s.

Figure 2 Major uses of benzene in the United States in the early 1990s.

Xylenes are also important raw material. There are 3 xylenes i.e. *ortho-*, *meta-*, and *para-* xylenes. Among them, *para*-xylene is the most important because it can be converted to purified terephthalic acid (PTA) for the production of polyester fibers. *m*-Xylene occurs in largest quantity, but it has only specialized uses. So, it is isomerized to more *p*-xylene. *o*-Xylene is used for three main products i.e. plasticizer, unsaturated polyesters and alkyds. Toluene is less valuable organic compound than benzene and xylenes. In 1996, about one fourth was utilized in hydrodealkylation for the production of benzene and disproportionation for the production of benzene and xylenes. Eleven percent was used as raw material for toluene diisocyanate (TDI).

Therefore, the production of the aromatics is vital process, particularly reforming process, which converts much lower price C6 to C8 paraffins to aromatics.

2. Historical Perspective

In 1939 the first catalytic reforming process using molybdenum oxide supported on alumina catalyst was jointly developed by Standard Oil of New Jersey (Exxon), Standard of Indiana (Amoco), and M.W. Kellogg Company. In 1949, UOP introduced the first process (Platforming™) using Pt/Alumina as a dual-function catalyst having both acidic and metallic sites. This process was further improved by Chevron in 1968 (Rase, 2000). The catalysts used were effective for improving the octane number of heavy naphtha (C8-C10). Beginning in the 1970s, the catalysts were introduced having one or more additional metallic components including rhenium, iridium, and tin. These bimetallic and multimetallic catalysts exhibit greatly improved stability (cycle length) and selectivity. Unfortunately, the catalyst were much less effective for improving the octane rating of light naphtha (C5-C8), due to their low selectivity to aromatics and their excessive irreversible hydrocracking over acid sites to light hydrocarbon.

In 1980, it was found that Pt supported on potassium form of L zeolite (Pt/KL) exhibited exceptionally high activity and selectivity for n-hexane aromatization (Bernard, 1980). Commercialization of the process soon followed, with Chevron researchers, announcing their Aromax reforming process. However, the drawback of this catalyst is its sensitivity to sulfur. Therefore, the development of this catalyst in order to withstand in the presence of sulfur became the main objective in this area. As mentioned previously, xylenes are also valuable when compare to n-alkanes feed. But, there are not much literature related to the aromatization of long chain alkanes, such as n-octane but these reactions would indeed have very important industrial application. The specific introductions are present in each chapter.

3. Scope of Work

In chapter II, the aim is to increase sulfur tolerance of Pt/KL by preparing the catalyst by vapor phase impregnation (VPI) and adding rare earth element (Ce and Yb). The activity and selectivity for *n*-hexane aromatization were tested under clean, sulfur-, and water-containing feeds. All the fresh catalysts as well as spent catalysts under various conditions were analyzed by a combination of techniques including FT-IR of adsorbed CO, hydrogen chemisorption, EXAFS/XANES, and temperature programmed oxidation (TPO).

In chapter III, the Pt/KL (VPI) catalyst was tested for its activity and selectivity for *n*-octane aromatization compared to Pt/KL (IWI) and Pt/SiO$_2$ catalysts. The product distributions were discussed. The cause of catalyst deactivation and regeneration were also investigated. Reaction temperature, weight hourly space velocity (WHSV), and reactant feed were varied to explain the reaction pathways. Again, all catalysts were characterized by several techniques including FT-IR of adsorbed CO, hydrogen chemisorption, TPO, and iso-butane sorption.

In chapter IV, 1%Pt was loaded on different large pore aluminosilicate zeolites including BEA, MAZ, and FAU. The activity and product distribution of Pt/K-BEA, Pt/K-MAZ, and Pt/K-FAU for *n*-octane aromatization were investigated compared to those of Pt/K-LTL and Pt/SiO$_2$ catalysts. The fresh (reduced) catalysts were analyzed by FT-IR of adsorbed CO, hydrogen chemisorption, TPD, and AAS. Moreover, the spent catalysts were analyzed by TPO.

Chapter V summarizes the preliminary study of *n*-octane aromatization over Pt-containing extra-large pore aluminophosphate zeolite i.e. VPI-5 (Pt/VPI-5). VPI-5 was synthesized and analyzed by XRD, SEM, BET, and TPD techniques. TPO was also utilized to study the coke formation during reactions.

In chapter VI, conclusions and recommendations are reported. Besides the experimental data illustrated in chapters II to V. There are more information and data, which are useful for future studies. The additional information and data were collected in Appendices. Appendix A summarizes detailed information of various zeolites used in this research. Appendix B shows the dual-function mechanism for catalytic reforming. Appendix C summarizes the data excluded in the previous chapters. Appendix D illustrates schematic diagrams of reaction testing, highly

sensitive temperature programmed oxidation and hydrogen chemisorption. This appendix also concludes images of DRIFTS cell, EXAFS cell, Teflon vessel with microwave oven. The electronic diagram of auto-sampling system invented is also included.