CHAPTER I
INTRODUCTION

Social awareness in CO_2 emission alleviation and the economic motivation for the replacement of non-renewable energy sources have been promoted to increase the interest in biomass as raw materials for producing alternative fuels. Bio-ethanol is one of the main biomass-derived products which can be converted into hydrocarbon compounds (e.g., paraffins, olefins, benzene (B), toluene (T), and xylenes (X)). These hydrocarbons can be widely used as fuels and raw materials for petrochemical industries.

BTX aromatic hydrocarbons are the high commercial-value products, which are important raw materials in basic organic synthesis. They have been used for manufacturing plastics, resins, synthetic fibers, dyes, pharmaceutical products, and intermediates for detergents. From previous research, the ratio of B:T:X obtainable from the catalytic transformation of bio-ethanol was 25:50.2:24.8 (Saewong *et al.*, 2012). This is in contrast to the ratio from the global market demand of B:T:X that was roughly 47:20:33 for the year 2005 (Zukaskas, 2005). As a result of demand and supply, the price of toluene is relatively low as compared to that of the other aromatics. The conversion of toluene into more valuable aromatics is one of the interesting points for economic motivation. A discrepancy between production and market demand was also found in most xylene isomers, among which para-xylene apparently has the greatest market demand.

The current market for para-xylene is outstandingly directed towards the production of a variety of fibers, films, and resins. Para-xylene is an important precursor in the synthesis of dimethyl terephthalate and tetraphthalic acid, which are used in the production of industrial plastics such as polyethylene terephthalate (PET). Normally, para-xylene is formed by xylenes isomerization, toluene transalkylation, and toluene disproportionation. In the recent years, new zeolite catalysts for these processes have been introduced with the aim to improve the overall selectivity of the processes and to comply with the requirements of environmental legislation.

The catalytic transformation of bio-ethanol is one of interesting processes to convert low valuable raw materials, like low-molecular weight alcohol, to more

valuable products, like BTX. The chemical reactions involved in this process can be very complicated if dehydration, oligomerization, cracking, cyclization, hydrogen-transfer, and aromatization are simultaneously occurred. These chemical reactions are catalyzed by acidic catalysts whose properties (e.g., shape selectivity and acidic properties) play important roles on the selectivity of olefins and BTX. HZSM-5 zeolite having medium pore size is one of the attractive acidic catalysts for the catalytic transformation of bio-ethanol to BTX (Megumu *et al.*, 2005) due to its high shape selectivity and moderate acid strength, which are suitable for the production of BTX. Although HZSM-5 has excellent oligomerization properties, it has poor dehydrogenation, cyclization, and aromatization properties, and hence the zeolite requires an increase in acid properties, especially acid strength, by modification with various acidic oxides. For example, Ga_2O_3 (Saha and Sivasanker, 1992; Saewong *et al.*, 2012.) doped on HZSM-5 can increase the yield of liquid hydrocarbons and life time of Ga_2O_3-catalysts as compared with HZSM-5 alone. So, in this research Ga_2O_3 and other acidic oxides of P, Sb, and Bi were used to increase acid properties, especially acid strength, of HZSM-5 for the enhancement of aromatics production. Moreover, the oxides can also diminish the pore size of HZSM-5, and then cause more restricted diffusion of the large products (o- and m-xylene) in relative to the diffusion of p-xylene.

The aim of this research was to investigate the catalytic transformation of bio-ethanol to liquid hydrocarbons using the two consecutive layers of 2.0 wt % Ga_2O_3-doped on HZSM-5 and a zeolite based on various pore sizes; namely, H-X, H-Y, and H-Beta zeolites. Moreover, modified HZSM-5 catalysts doped with various acidic oxides of P, Sb, and Bi at various loading amounts (1.0 wt %, 2.0 wt %, 3.0 wt %, and 4.0 wt %) were also studied for the catalytic transformation of bio-ethanol to liquid hydrocarbons. These catalysts were investigated under the following aspects: catalyst formulation, acidic oxides size, and zeolite pore size.