CHAPTER I
INTRODUCTION

Nowadays, porous materials have been widely studied in the catalysis applications. Porous materials can be divided into three classes, which are microporous (<2 nm), mesoporous (2-50 nm) and macroporous (>50 nm) (Egeblad *et al.*, 2008). One of the best known microporous materials is zeolites, which have good catalytic activities and hydrothermal stabilities (Taguchi and Schüth, 2005). The most important problem of microporous zeolites is intracrystalline diffusion limitation. The diffusion in the pore is slower than a reaction, so large molecules cannot pass through the pore, which affects on catalytic performances. To overcome this problem, the mesoporous materials such as MCM-41, SBA-15 and MSU-S have been investigated (Mostafa *et al.*, 2013). Hierarchical mesoporous catalysts can be defined as the catalysts that have two types of pore system in the structure such as micropore and mesopore system. A MSU-S (Michigan State University-S) is one of the mesoporous catalysts, which can be synthesized by using CTAB as a pore directing agent. Due to its large pore diameter with uniform hexagonal pore structure (Liu *et al.*, 2001), large molecules can be formed in a reaction, and pass through the pore.

The world's population is growing up every day, so the energy consumption becomes one of the most critical issues now. Liquid hydrocarbon fuels such as gasoline, kerosene, and gas oil are high value products in transportations. Normally, they can be produced from crude oil distillation, but the world is running out of petroleum. Bio-ethanol becomes the one of the alternative sources that can be used instead of petroleum. Bio-ethanol can be produced by fermentation process by using sugarcane, sugar beet, and starch crops as feedstocks (Takahashi *et al.*, 2012). Many researchers have investigated the production of hydrocarbons by using bio-ethanol. Ethylene can be produced by dehydration of ethanol on solid acid catalysts such as H-mordenites, H-ZSM-5, H-Beta, H-Y, silica-alumina (Takahara *et al.*, 2005) and SAPO-34 (Zhang *et al.*, 2008). C_2-C_4 light olefins can be obtained by using Ce-modified nanocrystalline HZSM-5 (Bi *et al.*, 2010). High conversion of BTX can be obtained from loading of Ga and noble metals on HZSM-5 support (Inaba *et al.*, 2006). Acidity and porosity of nano-crystalline HZSM-5 can affect on the conversion of ethanol to gasoline-range hydrocarbons (Viswanadham *et al.*, 2012).

Sujeerakulkai (2014) studied the bio-ethanol dehydration by using MSU-S from beta-seed (MSU-S_{BEA}). The MSU-S_{BEA} exhibited high amounts of gas and oil production. The main product in gas was ethylene, and the main products in oils were C_9 aromatics, C_{10+} aromatics, and p-xylene. The petroleum fractions in oil were mostly gasoline and kerosene. In general, the stability of a hierarchical mesoporous catalyst is higher than a microporous catalyst. Ramasamy *et al.* (2014) compared the stability of a hierarchical HZSM-5 with a commercial HZSM-5 at the same Si/Al ratio on ethanol dehydration to hydrocarbons. At a low Si/Al ratio (40), the life time of the hierarchical HZSM-5 was 2 times longer than that of commercial HZSM-5, and the coke formation was 1.6 times higher. At a high Si/Al ratio (140), the hierarchical HZSM-5 had life time 5 times longer than conventional HZSM-5, and deposited 2.1 times higher amount of coke.

Two consecutive layers of different catalysts have been investigated by Pasomsub (2013) in order to convert bio-ethanol to liquid hydrocarbons. 2.0 %wt Ga_2O_3-doped on HZSM-5 was placed in the first layer whereas H-X, H-Y, or H-Beta was placed in the second layer. The result showed that the products from the first layer were mostly m-xylene and toluene. Then, the amount of heavy aromatic hydrocarbons (C_9 and C_{10+} aromatics) increased in the opposite direction of the amount of light aromatic hydrocarbons (benzene, toluene, and m-xylene), which reduced in the presence of the second layer.

The aim of this research was to enhance the production of liquid hydrocarbon products such as gasoline, kerosene, and gas oil by using two consecutive layers. A commercial H-Beta with a Si/Al_2 ratio of 37 or HZSM-5 with a Si/Al_2 ratio of 30 was placed in the first layer to produce oil. Then, more oil was expectedly produced in the hierarchical mesoporous MSU-S with BEA-seed or MFI-seed, which have a large pore diameter for large molecules of oil, such as gasoline, kerosene, and gas oil, to be formed. The stability of catalysts was studied in the second scope. The stability of hierarchical mesoporous MSU-S with BEA-seed and MFI-seed was compared with that of H-Beta and HZSM-5 throughout a long period of time-on-stream.