CHAPTER I

INTRODUCTION

1.1 Background

The world demand in energy has increased dramatically in the past century and grows even stronger in the future. The non-renewable resources such as coal, natural gas, and crude oil, etc. are the most demanded resource while there is less crude oil available. Lubricant oil is a downstream product of crude oil. It becomes essential resources due to their energy necessary in normal life. Lubricant oil business is worldwide, profitable and complex. More than 60 percent of wastes which generated from oils come from used lubricant oils [1]. Incineration is a traditional way for disposing used lubricant oil to generate heat. This method produces toxic gaseous compounds and only shifts a solid waste problem to air pollution. In recent years, pyrolysis is studied as a method to reuse waste oil by removing its pollutants and cracking it into useful compounds such as fuels and chemicals. Thermal and catalytic degradations are the most promising cost-effective process for solving the environmental problem, e.g., plastic waste disposal. The products derived from thermal degradation show a wide range of carbon numbers. That requires further process for upgrading its quality [2]. In contrast, catalytic degradation allows the reaction to be performed at lower temperature. The product distribution can be controlled by a right selection of catalyst type. A number of acid porous solids, such as amorphous silica–alumina, zeolites, and ordered mesoporous materials have been used as catalysts. For example, ordered mesoporous materials such as Al-MCM-41 and Al-HMS, yield hydrocarbons within gasoline and gas oil fractions. ZSM-5 and zeolite beta produce light products, mainly gaseous and aromatic hydrocarbons [3]. However, the low acidity of mesoporous catalyst and the restriction of large molecules to access micropores catalyst are disadvantages for catalysis.

In recent years, several authors have reported a new class of porous materials combining the properties of both zeolites and ordered mesoporous aluminosilicates [4, 5]. These catalysts promote the cracking activity and produced more hydrocarbons with higher market value. Some literatures are discussed as follows;

R. A. Garcia *et al.* [3] reported the catalytic cracking of HDPE over hybrid ZSM-5/MCM-41 and compared with Al-MCM-41 and HZSM-5 at 380°C for 2 hours. The hybrid catalyst showed higher conversion of polyolefins than both Al-MCM-41 and HZSM-5. The product distributions obtained from HDPE cracking over the hybrid materials were similar to that over HZSM-5 zeolite. It mainly contained light hydrocarbons. Moreover, the products presented a high content of C_3–C_5 olefins, which was an interesting result regarding its possible use as raw chemicals.

J. Aguado *et al.* [6] investigated catalytic degradations of PP, LDPE, and HDPE over different samples of zeolite beta. Zeolite beta synthesized by the fluoride method had low activity for cracking of polyolefins. It was related to its large crystal size (12 μm) and poor aluminium incorporation. In contrast, zeolite beta synthesized from amorphous xerogels consisted of small crystallites ($\leq$ 200 nm). Polyolefins degraded with high conversion (40-60%) and good selectivity towards C_5-C_{12} hydrocarbons (60-70%), while heavier products were hardly obtained (< 6%). The incorporation of titanium into the BEA structure enhanced the catalytic activity, as denoted by the highest conversion per Al atom obtained with the Ti-Al-beta sample compared to Al-beta.

R. Nakao *et al.* [7] studied activity of homemade BEA zeolite prepared by a hydrothermal synthesis method (BEA(HTS)) in catalytic cracking of hydrocarbons compared with commercial BEA zeolites. The results showed that homemade BEA had more Brønsted acid sites than commercial BEA zeolites, and exhibited much higher activity in catalytic cracking of hydrocarbons, especially *n*-heptane. The initial activity of BEA(HTS) was about three times as high as that of HZSM-5. In addition, BEA (HTS) gave high *n*-heptane conversion even after the regeneration treatment.

S. Chaianansutcharit *et al.* [8] studied degradations of PP and PE over pure hexagonal mesoporous silica and aluminum-containing hexagonal mesoporous silica catalysts in a fixed bed catalytic reactor at 380 and 430°C, respectively. The liquid products were widely distributed in hydrocarbons with boiling point ranges of 36–405°C. By adding a small amount of aluminum to the hexagonal mesoporous material, aluminium-containing hexagonal mesoporous silica exhibited good performance in cracking heavy molecular weight hydrocarbons into light hydrocarbons. High liquid yields and less coke deposits were obtained in liquid-phase-contact reaction with increasing aluminum content. The liquid products were mainly composed of C_5–C_{10} hydrocarbons with boiling points of 36–174°C, and propene, butene, and butane were main components in gaseous products.

Ooi *et al.* [9] compared the cracking reaction of used palm oil catalyzed by zeolite beta/MCM-41 composite catalysts prepared by different methods; a direct method and a physical mixing. In the direct method, the composite was synthesized using hexadecyl-trimethylammonium chloride (C_{16}TMACl) and tetraethyl ammonium hydroxide (TEAOH) as templates and was crystallized at 140°C and 100°C, respectively. The test activities were performed at 450°C for 1 h. The composite prepared by physical mixing between zeolite beta and MCM-41 exhibited high conversion of used palm oil to products compared with those synthesized from the direct method. This result was inconsistent with other works. It might be explained by the amorphous structure of composite materials synthesized by the direct method. However, the selectivity of products was also enriched in C_2-C_5 olefins and C_6-C_{12} hydrocarbons.

The catalytic cracking of used lubricant oil and polyethylene in the mole ratio of 60 to: 40) over the microporous Fe/activated carbon catalyst operated at 430°C for 75 minutes was reported [10]. The product yields were 75.65% in liquid, 17.37% in gas phase, and 6.98% in residues. However, a few works has been reported on cracking lubricant oil using mesoporous materials. Hexagonal mesoporous Al- HMS with the -mole ratio of Si/Al of 200 was previously reported to be an effective catalyst for degradation of PP and PE into liquid products [8]. Thus, Al-HMS is chosen to be studied as a catalyst for cracking motor lubricant oil into valuable hydrocarbon products.

This research was aimed to demonstrate the direct synthesis of composite zeolite beta/Al-HMS and catalytic cracking of lubricant oil, grease and polypropylene. The reaction parameters such as time and temperature are studied and compared with pure zeolite beta and Al-HMS.

Objectives

1. To prepare Al-HMS and zeolite beta catalysts.
2. To synthesize zeolite beta/Al-HMS composite by direct a method.
3. To characterize all prepared catalysts.
4. To investigate the efficiency of zeolite beta/Al-HMS composite catalysts for cracking of lubricant oil, grease, and polypropylene.