

CHAPTER I

INTRODUCTION

1.1 Background

At present, the plastic waste management becomes a major concern. There are many researches on this matter and each involved different kinds of techniques. A thermal degradation of polymers at high temperature about 500-800°C can degrade large polymers into their reusable monomers. However, this technique has its drawback because of high cost of energy. In addition, formation of a variety of products is not so selective that it results in many products other than the monomer. By replacing the conventional thermal degradation, the catalytic degradation¹ has been introduced to overcome the problems.

Zeolites²⁻³ are widely used as catalysts for the catalytic degradation process because of their high stability, strong acidity, high selectivity and large surface areas in several hundreds square meters per gram. Acidity of zeolites is resulted from bridging hydroxyl group between aluminum and silicon atoms. Although the existence of Brønsted acid and Lewis acid sites are both found, it is known that a Brønsted acid site is the main active site in a hydrocarbon-cracking process. All zeolites, for examples, ZSM-5, zeolite Beta and mordenite exhibit strong acid sites when the balancing cation is a proton. Mordenite²⁻⁴ is one type of zeolites with straight pore with two sizes of pore-openings, 12-oxygen and 8-oxygen rings. Mordenite is very thermally stable up to 1000°C. The high stability of mordenite structure allows a modification to the mordenite catalyst with different Si/Al molar ratios by dealumination without collapse of the structure.

There are many reports about polymer cracking by different types of zeolites. It was found that the corresponding monomer is usually a major product; otherwise, isomerization and other competitive reactions that can take place at the same condition may result in other type of products. Moreover, the final product depends on type of the catalyst. Different zeolites display different structures and, as a result, different properties. Acid strength of zeolites depends on Si/Al ratios in catalyst as well. Activities of most of catalysts were compared without controlling variable parameters. For example, the influence of pore size of catalysts on their activities was studied using the catalysts having different structures and Si/Al ratios that result in significant error in catalytic activity. Therefore, in this study, a single type of the called mordenite catalyst was utilized to avoid the effect of catalyst structure and pore size. Dealuminated mordenite with various Si/Al ratios were prepared. The effects of temperature and Si/Al ratio in catalyst on the activity of mordenite in cracking of polyethylene and polypropylene have been studied.

1.2 Objectives

- To determine a precise method for preparing dealuminated mordenite with required Si/Al ratios.
- To find the optimal condition for catalytic cracking of polyethylene and polypropylene over mordenite with various Si/Al ratios.

1.3 Related Literature

There are several types of zeolites that are the most important catalysts for catalytic degradation of polymers. Those zeolite catalysts⁴⁻⁸ are, for example, ZSM-5, zeolite Beta and mordenite. There are many factors influencing the product distributions and catalytic activities of such zeolites in degradation of polymers. It cannot be pointed out that which factor is predominant owing to all of them play important roles to similar extent. Those factors are pore structure, acidity, crystal and particle size, and surface area of the zeolite catalysts as well as reaction temperature.

The temperature effect is supported by studies of the cracking reaction of high-density polyethylene (HDPE) over zeolites at various temperature.⁹⁻¹² At the temperature ranging from 290 to 430°C, the cracking reaction over ZSM-5⁹ at the temperature 430°C took place at the highest conversion of 91-94%. Gas products increased when the reaction temperature was increased. In contrast, it was found that conversion (92%) of HDPE over the USY-type zeolite¹⁰ at 356°C had higher value than conversions at 297 and 256°C (75% and 54%), respectively. With increasing temperature, the yields of liquid fraction obtained from the case of USY-type zeolite increased from 26 to 33 and 46%, respectively. Operation of the cracking reaction of *n*-hexane over zeolite HMCM-22 at low temperature can avoid the side reaction such as isomerization of *n*-hexane.¹¹ Catalytic cracking at low temperature usually requires longer period to complete the reaction. For example, cracking of polyethylene over SAPO-37 catalyst¹³ at the temperature of 450°C, 90% conversion was obtained within 100 min while the cracking reaction over the same catalyst at the temperature of 400°C gave only 70% conversion in a long period of 1,400 min. These results indicated that temperature has a strong effect on the catalyst activity and the product yield. Furthermore, the rate of increasing temperature affected the occurring of products. The rate of reaction depends on the heating rate of the catalyst and polymer, *i.e.* products was rapidly formed when the temperature was increased in a fast heating rate.^{9, 13}

The product distribution depends on not only the temperature but also the structure of catalysts. Different structures results in different pore sizes, acidity and activities of the catalysts. For example, polystyrene cracking at the temperature of 550°C by thermal cracking¹⁴ without catalyst gave the major product as the styrene monomer. When mordenite was used as the catalyst, toluene and styrene were products. ZSM-5 and sulfur-promoted zirconium (S-ZR) catalysts gave benzene, aromatics of C₁₀⁺ and styrene as products while an equilibrium conventional FCC catalyst (E-CAT) provided formation of styrene and ethylbenzene. Polystyrene cracking over ZSM-5 and MCM-41 catalyst indicated small pore of catalyst affected small products.¹⁵ In addition, considering catalytic cracking of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) over MCM-41, ZSM-5

and $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts¹⁶ at the temperature of 400°C, the highest value of conversion was obtained over the ZSM-5 type zeolite. In contrast, the conversion obtained over $\text{SiO}_2\text{-Al}_2\text{O}_3$ was poor. It is obvious that strong acidity of ZSM-5 that is a zeolite while others are not, is accounted for its high activity over other types of catalysts. Among these catalysts, the small channels of ZSM-5 resulted in formation of $\text{C}_3\text{-C}_8$ hydrocarbons while large pores of MCM-41 catalyst resulted in $\text{C}_3\text{-C}_{10}$ products. Moreover, the degradation of HDPE at the temperature of 360°C over various zeolites showed that the highest selectivity to liquid product was obtained over the large pore zeolite USY while the poor selectivity was obtained over the medium pore ZSM-5. Sakata *et al.*¹⁷⁻¹⁸ also reported that for degradation of polypropylene at the same temperature of 380°C, the major products were $\text{C}_5\text{-C}_{10}$ hydrocarbons when using large pore FSM (folded sheet material) as catalyst but $\text{C}_7\text{-C}_{10}$ hydrocarbons when using relatively small pore ZSM-5 as catalyst. The primary cracking step occurs on external surface of the catalysts and the secondary cracking step takes place in the channels of ZSM-5.¹⁹⁻²⁰ Relatively small pore size of the zeolite limits to some extent of the oligomerization of olefin products.²¹

Moreover, the product distribution depends on the cations that neutralizing the framework negative charge. Gas products from cracking of polyethylene over PZSM-5 was formed in less quantity than that obtained from HZSM-5.²² Replacement of protons by phosphorus cation resulted in the decrease of the proton quantity and that results in decreasing the number of Brønsted acid sites. Consequently, the cracking products are in the range of liquid products rather than the smaller gas products. It was found that replacement of protons in zeolite HZSM-5 by molybdenum cation resulted in less value of conversion²³ of *n*-hexane cracked. The values of conversion at the temperature of 315°C were 44.9 and 18.4% over HZSM-5 and Mo-HZSM-5 catalysts, respectively. It was reported that catalytic activity of the USY zeolite with various acidity on its external surface was directly proportional to the acidity on external surface but not the total acidity of the catalyst. The activity of the USY zeolite for polypropylene cracking decreased with decreasing its acidity on external surface from 9.7 to 7.7 and 6.5 μmol of pyridine adsorbed in one gram of catalyst.²⁴

Uemichi *et al.*²⁵ reported applied silica-alumina and HZSM-5 to catalytic cracking of polypropylene. The liquid yield obtained from polypropylene cracking over the mixed catalysts of silica-alumina and HZSM-5 (at the ratio of 9:1) is greater than that over only ZSM-5. With increasing the portion of ZSM-5 in the mixed catalyst, the liquid yield decreased while benzene fractions in liquid products increased.

The particle size of catalyst was found to have influence on the product distribution and reaction time.²⁶⁻²⁷ The degradation of a polymer on the catalyst with small particles was obtained in a rapid action, achieving high conversion and high liquid yield due to its large external surface area. A report of polyethylene wax degradation over the MFI-type zeolite²⁶ that had different particle sizes ranged from 0.2 to 4.0 μm showed that the catalyst with the particle size less than 1.0 μm made complete conversion of polyethylene wax. The MFI-type catalyst with the particle size of 4 μm provided the conversion of only 61%. Furthermore, the catalyst with small particle size gave the larger amount of liquid products within short reaction time. However, it was reported that activity of the catalyst was affected by its particle size less than by its acidity.²⁷

The catalytic activity depends on synthesis methods of the zeolites. The synthesis methods affected the crystal size of the zeolites. Aguado *et al.*²⁸ reported that zeolite Beta was prepared by two different methods, the so-called fluoride method and non-fluoride method. The fluoride method was a preparation of catalyst using a HF solution. The zeolite Beta obtained from the fluoride method exhibited lower activity in polymer cracking than that of the zeolite prepared by the non-fluoride method did. This was owing to the large 12- μm crystal size of the zeolite beta obtained from the fluoride method and that resulted in extremely low external surface area of 8 m^2/g only. In contrast, the non-fluoride method gave zeolite Beta with a smaller 0.1- μm crystal size and an external surface area of 93.5 m^2/g that was relatively much higher than that of the zeolite prepared by the fluoride method. The catalyst prepared by the fluoride method exhibited activity of 12.5%, 8.1% and 11.8% conversions for HDPE, LDPE and polypropylene and the catalyst prepared by the non-

fluoride method had activity of 40, 53 and 52% conversions of HDPE, LDPE and polypropylene, respectively. However, These two types of catalysts had much different Si/Al ratios of 85 and 39 that also certainly affected the cracking activities.

Loading level of catalyst^{11,29} was another important effect in catalytic reaction. For example, at the temperature of 520°C, the increase of loading level of ZSM-5 resulted in the increase of % conversions in the order of 32 > 16 > 4 > 0%, respectively.²⁹

From a recent study of the catalytic cracking of LDPE over Al-MCM-41 in a continuous screw-kiln reactor,³⁰ thermal degradation gave the hydrocarbon products having a wide range of carbon-atom number from C₅ to C₅₅, while Al-MCM-41 provided relatively narrow range of C₅-C₁₂ products as major products. Furthermore, the screw speeds were varied in the range of 3-15 rpm. The product output increased from 19.6 up to 41.2 g.h⁻¹ with screw speed. A trend to lower conversion was observed when the screw speed was increased. This was in agreement with shorter residence time. Turnover frequency was dropped off with decreasing the screw speed.

Deactivation behaviors of zeolites are closely related to coke formation³¹⁻³² on the catalysts because coke deposition lowered the number of active sites and the surface area of the catalyst. For the catalytic degradation of *n*-heptane over zeolites CIT-1, MCM-22, SSZ-24 and Beta at the temperature of 450°C,³² the highest conversion was received over zeolite CIT-1. The activities were decreased in the order of CIT-1 > MCM-22 > SSZ-24 > Beta. The highest level of deactivation was found on zeolite SSZ-24 not zeolite Beta because of coke deposited on the one directional large-pore zeolite SSZ-24 and caused pore blocking in the catalyst. The three dimensional large-pore zeolite Beta had capability to resist coke formation. The formation of coke diminished the catalytic cracking on those zeolites.