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Catalytic Cracking of Polyolefins in the Molten Phase—Basic Study for the Process Development of Waste Plastics Liquefaction

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Abstract: The cracking of polyolefins, especially polyethylene in the molten state was effectively catalyzed by the powdery spent FCC (Fluid Catalytic Cracking) catalyst which was dispersed in it. The activation energy of the catalytic cracking of polyethylene was about 74 kJ/mol. The cracked product was naphtha and middle distillate as the major product and gaseous hydrocarbon (C_1-C_4) as the minor product while little heavy oil was produced. The chemical compositions of the product were: aromatic hydrocarbons, isoparaffins and branched olefins, whereas that of the non-catalyzed products were: n-olefins and n-paraffins with minor amount of dienes with increasing the process time. Additionally, the product pattern shifted from naphtha rich product to kerosene and gas-oil rich product. However, any catalytic product showed low fluid point (< -10 ^{o}C), while that of the non-catalyzed product was as high as 40 ^{o}C. Catalyst could process, more than 100 times by weight of polyethylene with fairly small amount (~ 30 wt%) of coke deposition. Spent catalyst gave higher hydrocarbons while fresh catalyst gave gaseous product as the major product. Other polyolefins such as polypropylene and polystyrene were tested on same catalyst to show that their reactivity is higher than that of polyethylene and gave the aliphatic products, alkyl benzenes and C_6-C_9 iso-paraffins as the major product. Product pattern of the cracked product suggested that the reaction proceeded via the primary reactions making paraffins and olefins which were followed by the isomerization, secondary cracking, aromatization and hydrogen transfer which based on the carbenium ion mechanism.

Key words: Polyolefin, spent FCC (Fluid Catalytic Cracking) catalyst, catalytic cracking, carbenium ion mechanism, superior stability.

1. Introduction

Plastic is one of the most valuable products for modern human life. They are used for every field in human life. Among them, the petroleum-derived plastics are widely used for the living materials such as film or bottle and structural materials such as cars or home electronics and have been used with huge quantity. For example, the amount of plastics consumed in Japan reaches about ten millions t/year [1]. Since most of them are non-biodegradable materials, the wasted plastic material remains on the earth for a long time, even they are used for the one-way purpose. For a long time, the waste plastics has been treated for the land-fill or burned off to reduce its material volume and recover heat. Recycling of waste plastics should be regarded from the stand point of new resource utilization and environmental protection.

Mechanical recycling of mixed plastics to make low grade plastic products and thermal recovery which generate electric power has been thought to be the new promising recycle method. However, the mechanical recycling such as bottle to bottle is not the final solution method of the waste plastics. Also, the land-fill method has generated new problems on the filling space or the pollution of underground water.

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The feedstock recycling to their raw material has shown to some success for a single material such as PET (Polyethylene Terephthalate) or PMMA (Polymethyl Methacrylate). However, the mixed plastics are quite hard for the feedstock recycling from the stand point of the technology as well as the product quality. For example, if the raw waste plastics contain organic chlorine such as PVC (Poly Vinyl Chloride), the product oil contains organic chlorine, which cause the generation of dioxin when it is burned.

The production of liquid material from plastics is also assumed to be the promising method of the waste plastic utilization. The method of the plastic liquefaction has been classified into two parts. One is the thermal cracking and another one is the catalytic cracking. Thermal (non-catalytic) cracking has been the major method for the liquefaction of waste plastics because of the simplicity of the process [2]. Reactions proceed following the free radical mechanism, to give complex mixture of products composed of paraffins, olefins, dienes, aromatics, et al. In the case of the free radical-based reaction, the skeletal isomerization is minor one compared to the dissociation reaction. In run to improve the quality of thermally-cracked products, the secondary catalytic reforming of the cracked product had been tried to make aromatic hydrocarbons [3-5]. It has been well known that the reactivity of polyolefins is different for each material and is shown to be in the order PS (Polystyrene) >> PP (Polypropylene) >> PE (Polyethylene) [3]. This marked difference in the reactivity of each polyolefins is based on their chemical structure and makes it hard to process the cracking of the mixed plastics, especially in the batch type operation.

Solid acid catalyst which is the common catalyst for the cracking of heavy fractions petroleum has been used for the cracking of waste plastics, which produce branched light hydrocarbons and aromatic hydrocarbons as the major product and large amount of coke [6, 7]. The catalytic cracking of hydrocarbons is conducted in the gas phase and carbenium ions are assumed to be the active intermediate of the reaction [5, 8, 9]. The reaction phase is the liquid-solid system, because the plastics never vaporize due to their extreme high molecular weight. However, since the reaction products vaporize at reaction temperature (> 380 ^{o}C), the catalytic system is the gas-liquid-solid system.

In the present study, which is the preliminary study for the process development of the liquefaction of waste plastics, the liquid phase catalytic cracking of polyolefins (PE, PP and PS) was conducted by using a kind of solid acid catalyst (spent catalyst of FCC (Fluid Catalytic Cracking) process of petroleum residues, FCC (U)) and virgin equilibrated FCC catalyst. The target of this study is to get the high quality hydrocarbon fuel or the chemical feedstock, under conditions by which the process is easily industrialized. The main reason of the utilization of FCC (U) is that their weak activity (low coking) and low cost.

2. Material and Methods

An agitated type of reaction apparatuses were used as shown in Fig. 1. Reactor was used a conventional autoclave reactor with the inner volume of 250 mL, where the catalyst powder (particle diameter ~ 50 μm) was dispersed in the molten plastic to catalyze its cracking. The plastics were cracked at 410 ^{o}C to 450 ^{o}C that were used 75 g with 5 g to 15 g spent FCC catalyst. The products flow out of the reactor as the vapor with 100 mL/min N_2 to be condensed to liquid oil by ice water condenser. After the products were condensed to liquid, the un-condensed products were deeply cooled at -80 ^{o}C to collect light oil (mainly C_3 and C_4 hydrocarbons). The effused and condensed products were taken out with a certain time internal and were measured for their volume and weight. The liquid product (cracked oil) was measured for the carbon number distribution with GC-FID (Gas Chromatograph-Flame Ionization Detector) (GC: Shimadzu GC-14B) and for the chemical structure with PONA (Paraffins, Olefins, Naphthenes, Aromatics) analysis system (GC: Shimadzu GC-17A).

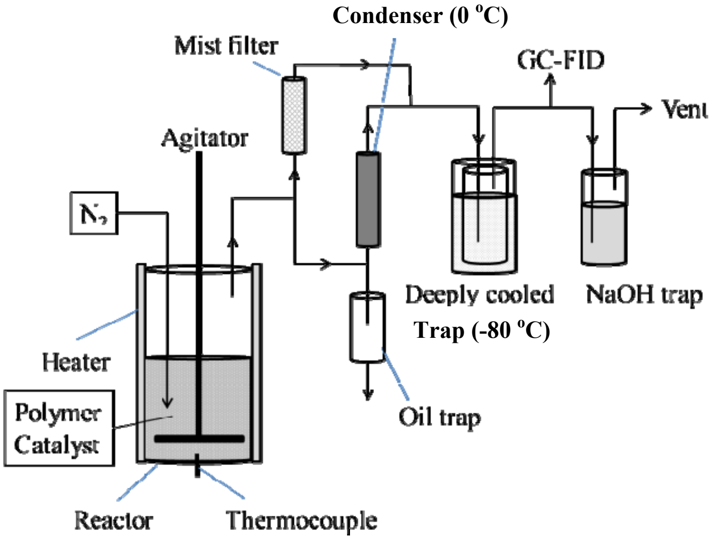

Fig. 1 **Reaction apparatus for the catalytic cracking.**

Table 1 **Chemical composition of FCC catalyst.**

Component	Composition [wt%]	
	FCC (N)	FCC (U)
Al_2O_3	22.1	15.4
SiO_2	77.1	44.8
SO_3	0.58	1.10
CaO	0.22	1.17
Other metal oxide (Ti, V, Mn, Fe, Ni, La and Ce)	-	33.85

The un-condensed products which come out of the deeply cooled trap were measured their volume and composition by GC-FID (Shimadzu GC-14B). The amount of deposited carbonaceous materials on the catalyst after reaction was measured by the TGA-DTA (Thermogravimeter-Differential Thermal Analyzer) method (ULBAC) under air condition.

The samples used for the reaction is the recovered polyethylene (high density (PE (H)) and low density (PE (L))) and polypropylene, which had been recovered from materials used for a certain purpose (not known). They are assumed to contain certain additives. Polystyrene was commercially available virgin pellet that was produced by Wako pure chemical industries.

Catalyst used was the commercially available equilibrated unused FCC catalyst and its spent one (FCC (U)). Their chemical compositions were analyzed by XRF (X-Ray Fluorescence) that are shown in Table 1. FCC catalyst has been used in a FCC plant for cracking residual oil in the oil refinery fractions. In general, the FCC catalyst is said that composed of zeolite, silica-alumina, activated alumina and clay. The USY (Ultra Stable Y-type zeolite) is used for this FCC catalyst. However, the actual component of FCC catalyst is not clear. Also, the spent FCC catalyst contained some types of heavy metal oxides (Table 1).

3. Results and Discussion

3.1 Catalytic and Non-catalytic Cracking (Thermal Cracking) of Polyethylene

Fig. 2 shows the effusion diagram of the catalytic cracking of PE (H) with and without catalyst. It is clear from the date that the catalyzed system gave liquid product more rapidly and higher oil yield than the non-catalyzed system did, even the reaction temperature was lower by 420 °C for the catalyzed system. Also, the significant difference is that the catalyzed system gave no deposited carbonaceous material on the reactor wall whereas a fairly large amount of black solid material deposited on the reactor wall under non-catalyzed system. Another characteristic feature was that the fluid point of the

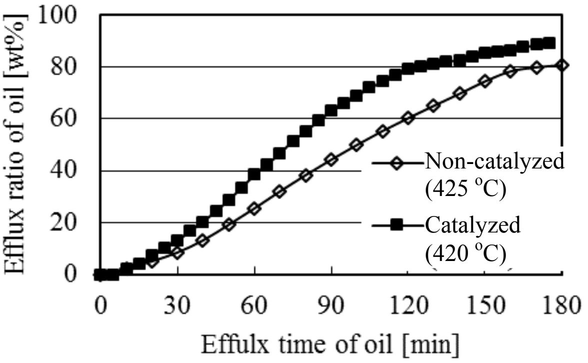

Fig. 2 Catalytic cracking of molten polyethylene (PE: 75 g; FCC (U): 10.0 g).

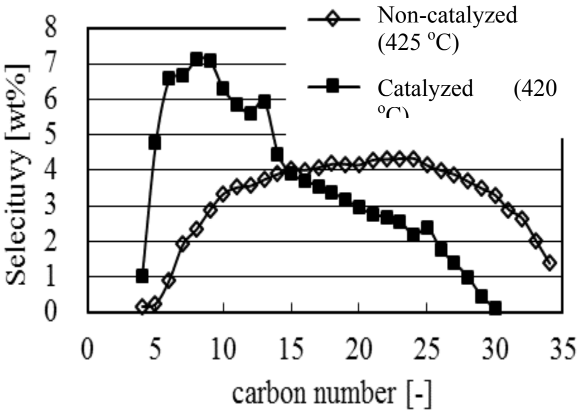

Fig. 3 Carbon number distribution of product oil (PE: 75 g; FCC (U): 10.0 g).

Table 2 Chemical structure of product (naphtha + middle distillate).

Product	Product composition [wt%]	
	Catalytic [a]	Non-catalytic [b]
n-Paraffin	11.0	55.4
i-Paraffin	22.5	2.1
Olefins	11.5	32.0
Aromatics	45.0	4.5
Not clear	10.0	6.0

* Reaction condition: PE (H) = 75 g; [a]T = 420 °C; catalyst = 10.0 g; [b]T = 425 °C; non-catalytic.

product oil was around 40 °C for the non-catalyzed system whereas that of the catalyzed system was below -20 °C.

Fig. 3 and Table 2 show the product distribution and the chemical composition of the product. It is obvious from the data shown in Fig. 3 that the carbon number of the products of the catalyzed system was distributed to the shorter carbon chain side compared to that of the non-catalyzed system.

3.2 Reactivity of Polyolefins

Figs. 4 and 5 show the reactivity of PE, PP and PS. In this experiment, the reaction operation was performed in the step-wise heating as shown in Fig. 4 because of the marked differences of each polymer. As can be seen in Fig. 4, PP and PS made liquid product at 350 °C or lower temperature, whereas PE (H) showed much lower reactivity giving liquid product at 420 °C for a long time. Products pattern displayed in Fig. 5 shows that PS gave C_8 (ethyl benzene), C_{17} and C_{18} (aromatic hydrocarbons), and PP gave mainly branched aliphatic hydrocarbons with different carbon number, whereas the product of PE cracking showed wide distribution, whose component was the mixture of aliphatic and aromatic hydrocarbons.

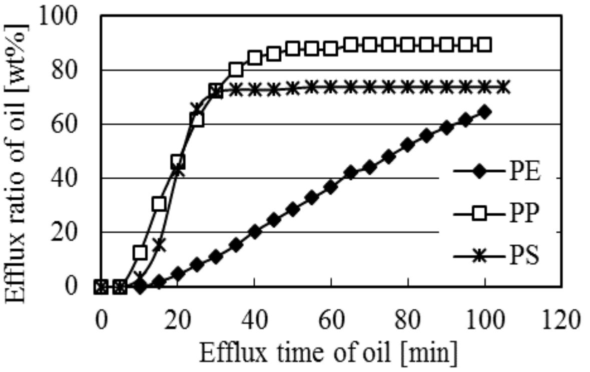

Fig. 4 Effusion diagram of polyolefin cracking over FCC catalyst (reaction temperature 420 °C; FCC (U): 10.0 g).

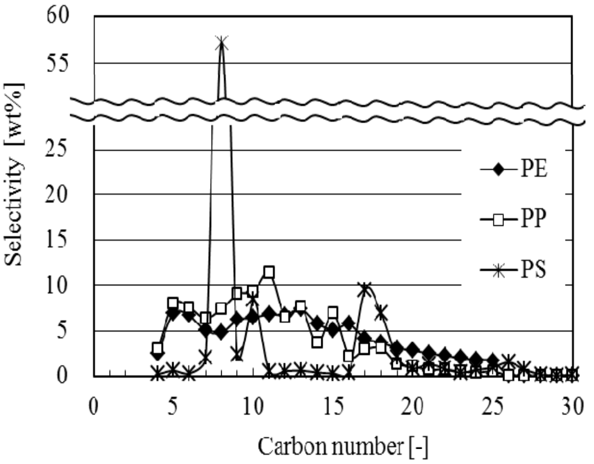

Fig. 5 Catalytic cracking of polyolefins on FCC (U) catalyst (reaction temperature: 420 °C; FCC(U): 10.0 g).

Table 3 Results of polyolefin cracking.

Catalyst	Polyolefin	Critical temperature [°C]		Product yield [wt%]		
		T_i[a]	T_{max}[b]	Oil	Gas	Coke
FCC (N)	PE (H)	300	390	88	3.1	1.2
FCC (U)	PE (H)	400	420	89	1.4	0.4
FCC (U)	PE (L)	380	410	78	2.2	1.5
FCC (U)	PP	390	400	95	2.0	0.8
FCC (U)	PS	350	380	89	0.1	6.1

*Raction condition: catalyst = 10.0 g; polymer = 75.0 g; heating rate (shown in Fig. 4); [a] initial temperature of oil effusion; [b] temperature of maximum reaction.

In Table 3, the results of a variety of polyolefin and catalyst are summarized. It is clear from the data in Table 3 that the reactivity of PP and PS is much higher than PE. They began to react at around 350 °C and finished at around 400-410 °C in the presence of spent catalyst FCC (U). On the other hand, PE started to be cracked at around 400 °C in the presence of FCC (U) catalyst, to reach the maximum level at 400-420 °C and finished at this temperature within 3 hours.

The reactivity of PE (L) was higher than that of PE (H), probably based on the difference in their chemical structure (side chain). The fresh FCC catalyst (FCC (N)) showed higher catalytic activity than FCC (U), naturally because it has higher density of active site of stronger acid. However, in this case, the FCC (N) gave lower oil yield and higher gas and coke yield (shown in Table 3). This result suggests catalytic activity of the FCC (N) is too strong for polyolefin cracking.

3.3 Effect of Reaction Conditions and Catalyst

Figs. 6 to 9 show the effusion diagrams with the different reaction temperature and catalyst amount. The data in Fig. 6 shows that the cracking rate of the PE (H) increased with increasing reaction temperature from 410 °C to 430 °C and that the oil yield at the end of reaction was higher for the higher reaction temperature as shown in Table 3. The data shown in Fig. 6 gave the apparent activation energy about 74 kJ/mol, which are by about 220 kJ/mol much lower than that of the non-catalyzed system [2]. These phenomena will be discussed in the later chapter. The product pattern was quite similar for 3 levels of reaction temperature, except the C_{25}^+ products of the reaction at 410 °C.

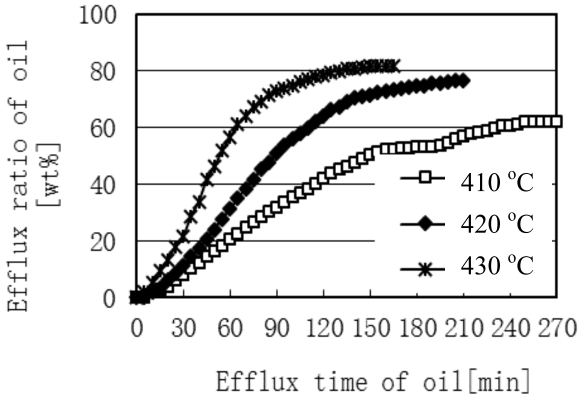

Fig. 6 Effect of reaction temperature on the PE cracking exclude light oil (PE (H): 75 g; FCC (U): 10.0 g).

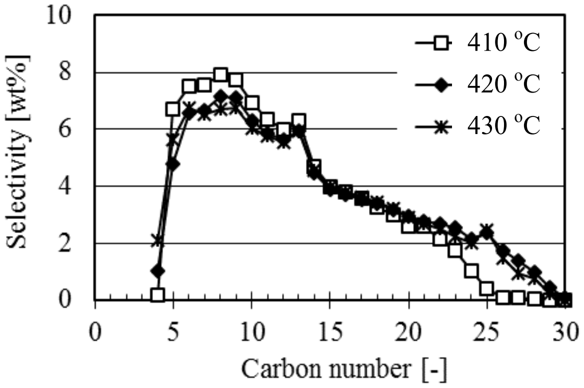

Fig. 7 Carbon number distribution of the product from PE cracking.

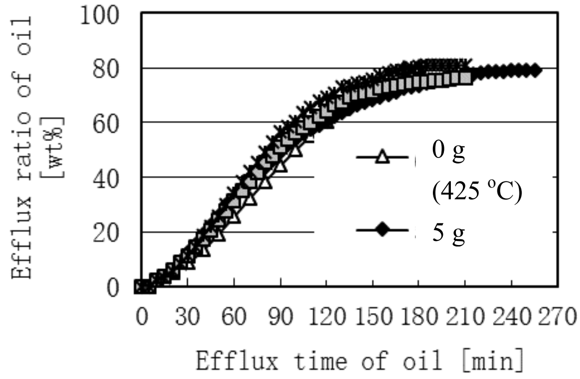

Fig. 8 Effect of catalyst concentration on the PE cracking (reaction temperature: 420 °C (FCC (U)) and 425 °C (non-catalytic); PE (H): 75 g).

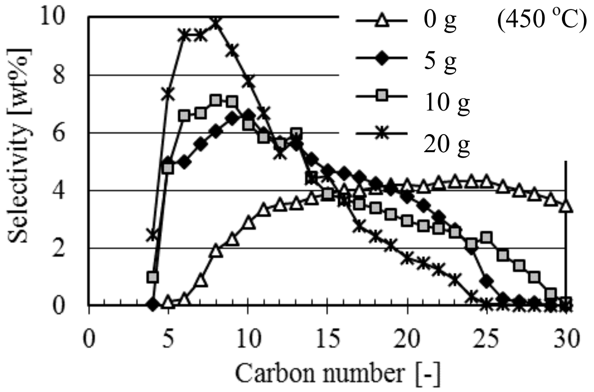

Fig. 9 Carbon number distribution of cracked oil from PE cracking with various amount of catalyst.

Figs. 8 and 9 show the effects of the catalyst concentration. It is obvious that although the lager amount of the catalyst promoted the cracking of plastics only slightly, the product pattern shifted markedly to lower carbon number side with increasing catalyst concentration. Under conditions of low catalyst concentration, the reaction is assumed to be the mixture of the catalytic reaction and the non-catalytic one. This concept is supported by the fact that the product pattern is in between the non-catalytic and the catalytic reaction with high catalyst concentration.

3.4 The Stability of the Catalyst

These tests were conducted by repeated batch-wise reaction experiment. Once the cracking reaction is finished (the stop of the oil effusion), new sample (PE (H), 75g) was introduced to the reactor while keeping the used catalyst and residue in the reactor. Results obtained by the 14 times-repeated experiments, are shown in Figs. 10 and 11. Fig. 10 shows that the yield of effused oil increased from 70% (1st experiment) to almost 97% (8th to 12th experiments) and then decreased. The gaseous product expressed by the amount of methane (CH_4) increased with run times from about 1.5 wt% to 3.3 wt%. Total material balance is shown in Table 4. Fig. 11 shows the product pattern of the oil showing that the 1st experiment oil was quite rich in C_{10}-hydrocarbons and the highest product was C_{28} hydrocarbon. However, the product of 3rd experiment shifted to higher side, which distributed mainly over C_{10}-C_{20}, nonetheless, the higher limit was still C_{30}. This pattern was almost constant from the 3rd experiment to the 14th experiment. It is still quite different from that of the non-catalytic system. Also, the apparent of product oil was quite different, showing the pale-clean liquid whereas the product of the non-catalytic one was light

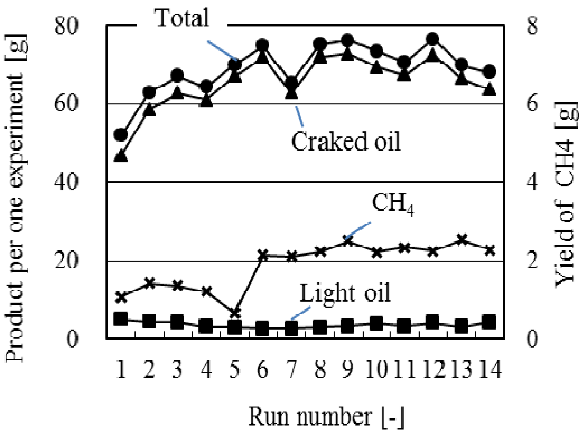

Fig. 10 Experimental results of repeated runs (PE (H): 75 g (repeated 14 times); FCC (U): 10.0 g (no exchange); reaction temperature: 420 °C).

Table 4 Material balance of 14 times of reaction.

Product	Recovery/g
Cracked oil (1st trap)	916.6
Light oil (2nd trap)	50.9
CH_4	26.5
Residue	38.7
Coke	3.5
Material balance	98.6 wt%

* Reaction conditions: T = 420 °C; catalyst; FCC (U) = 10.0 g; same experiment as in Fig. 10.

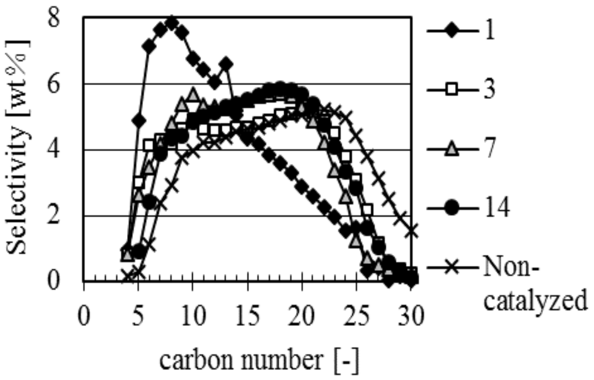

Fig. 11 Carbon number distribution of cracked oil.

brown-colored solid. The reason of this difference will be discussed later.

3.5 Chemical Structure of the Cracked Product

As already described, the product oil of the catalytic reaction was clear liquid whose carbon number distributed from C_5 to C_{30} whereas that of the non-catalytic system was solid material (fluid point was higher than 40 °C) in spite of the carbon number being rather similar to the catalytic reaction product. Table 2 shows the typical chemical composition of the cracking product [10]. It is clear that the main product of the catalytic reaction was aromatic hydrocarbons and iso-paraffins, whereas that of the non-catalytic one was strait chain paraffins (n-paraffins) and strait chain olefins (n-olefins). The main products C_{20}-C_{30} of the non-catalytic reaction were n-paraffins and α-olefins (decided by GC-MS). The melting point of iso-paraffins and aromatic hydrocarbons C_5-C_{20} is usually below 0 °C, and that of n-paraffins is higher than 0 °C. The different of fluid point of the product of catalytic and non-catalytic systems, of the similar carbon number distribution can be reasonably explained by the different chemical structure of the product (Table 2). The low fluid point is favorable from the stand point of the product handling.

3.6 Coke Deposition on the Catalyst

TGA-DTA analysis in air was conducted for the used catalysts which had been subjected to the reaction for one time (7.5 times by weight) and 14 times (100 times by catalyst weight) are shown in Fig. 12. Samples were subjected to the analysis after washing with toluene to remove oily material. The total weight loss was about 20 wt% and 30 wt% for sample 1 and sample 14, respectively. This means that the quick coking at the early time of the reaction occurred, and that the successive coking proceeded rather slowly probably because of the selective poisoning of the coking site by the deposited coke and the weakening of the acid sites of the catalyst by the repeated reaction and regeneration (in the FCC plant). This phenomenon is well agreed with the fact that the first run gave lower oil yield which was followed by higher and stable oil yield during the repeated runs from 2nd to 14th, giving rather similar carbon-number distribution but different chemical composition of the product.

However, another new information was suggested by the DTA analysis, that the repeated PE cracking makes different types of coke (aged) which is oxidized by air at higher temperature (400-500 °C), than that of the freshly deposited coke (fresh) which is oxidized by air at 300-400 °C.

3.7 The Physical Steps and Chemical Mechanism of the Catalyzed Polyolefin Cracking in the Molten Polymers

The system of this reaction can be assumed to be as in Fig. 13 and the chemical phenomena on the spent FCC catalyst are assumed to be as in Figs. 14 and 15.

Polyolefin is one of the long-chains hydrocarbons that are synthesized from small molecular weight

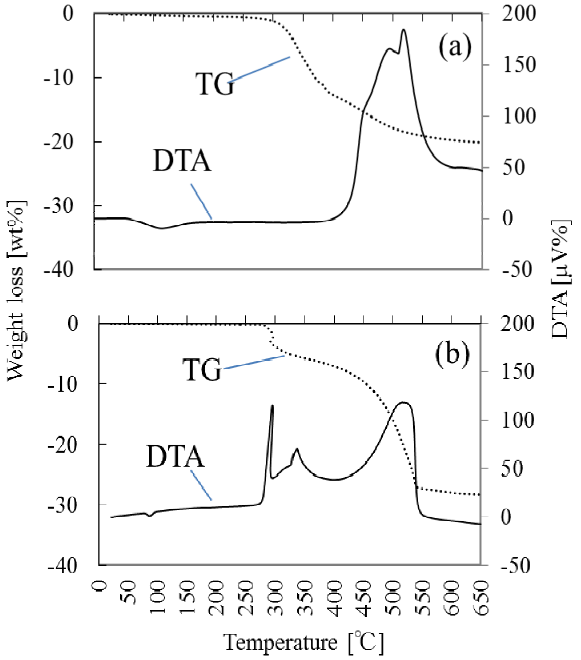

Fig. 12 TGA-DTA analysis of FCC (U) after reaction in air ((a) After 7.5 g-PE/g-cat processed; (b) After 105 g-PE/g-cat processed).

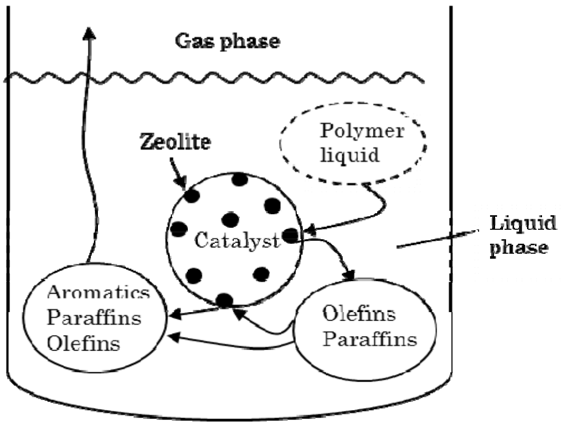

Fig. 13 Image of FCC catalyzed polyolefins.

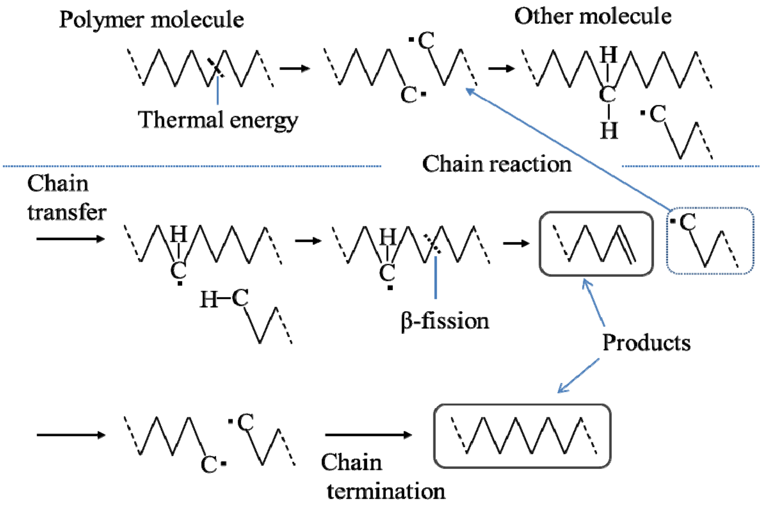

Fig. 14 Thermal reaction mechanism of PE cracking.

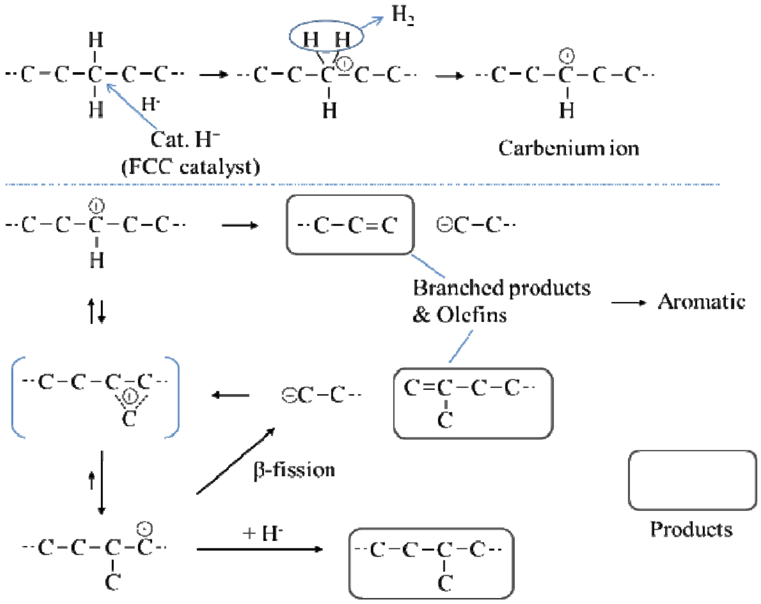

Fig. 15 Acid catalyzed ion mechanism of PE cracking.

hydrocarbons as such as ethylene, propylene and styrene. Therefore, the catalytic cracking of polyolefins using FCC catalyst should follow the catalytic reaction involved in the FCC process. The FCC process gives gasoline rich product from heavy petroleum fractions (higher molecular weight hydrocarbons), that is explained by activity of FCC catalyst as solid acid catalyst [8-10].

First step should be the adsorption of polymer molecules on the outer surface of the catalyst. Because of the large size of the polymer molecule, neither the inside surface of the zeolite cavity nor the zeolite surface inside of the particle can be accessed by the polymer molecule. The primary product of the reaction will be paraffins and olefins (mainly branched molecule), which leave the catalyst surface and migrate in the polymer melt. Some of the cracking products come out of the liquid to gas phase as the vapor and come out of the reactor and trapped as the liquid product. Because of the slow diffusion and the strong affinity of the product for the polymer liquid, the primary products may stay in the liquid for a certain period and are subjected to secondary reactions such as secondary cracking, aromatization, coking and hydrogen transfer [8-11]. The higher fraction of C_5-C_{10} products under the presence of fresh catalyst or the high concentration of catalyst could be attributed to the higher contribution of secondary reaction. The large fraction of C_{20}^+ product and lower fluid point of the products on the used (deactivated catalyst) can be explained by the higher yield of iso-paraffins of C_{15}^+ hydrocarbons, because the isomerization to branched hydrocarbon proceeds faster than their cracking to lower molecules.

It has already been pointed out that the product obtained without catalyst is solid at ambient temperature. For the non-catalyzed system, the skeletal isomerization is not easy because of the character of intermediate (free radical). Probably the chain transfer of the free radical reaction inside of the same huge molecule makes large primary product with strait chain. The product shows usually higher melting point and higher fluid point.

5. Conclusions

Polyethylene and other polyolefins were subjected to the catalytic cracking in the molten state by using spent FCC catalyst. Among polyolefins tested, polyethylene was most hard to be cracked. The catalytic cracking of polyethylene was promoted by spent FCC catalyst at around 400 ^oC, giving naphtha fraction and middle distillate as the major product. The activation energy of the catalyzed reaction was about 74 kJ/mol, which was much lower than the non-catalyzed system. The molecular structure of the cracked product (from polyethylene) was iso-paraffins, olefins and aromatic hydrocarbons, which lead to the low fluid temperature (< -20 ^oC) while the major products of the non-catalyzed system were straight chain paraffins and α-olefins.

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