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# CATALYTIC DEGRADATION OF WASTE HIGH-DENSITY POLYETHYLENE INTO LIQUID PRODUCT

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**Abstract** : Liquid-phase catalytic degradation of waste high-density polyethylene (HDPE) over ZSM-5 (powder type (PW)) and ZSM-5+binder (granule type (GR)) has been investigated with a stirred semi-batch operation at 400°C. Two ZSM-5 catalysts with a different crystal size were synthesized and also each ZSM-5 (25%) Catalyst was mixed with a same binder (kaolin: silica sol: alumina = 55%:10%:10%). The performance of prepared catalysts that has different physicochemical properties was discussed with the cumulative amount distribution, molecular weight distribution and also paraffin, olefin, naphthene and aromatic (PONA) distribution in liquid product. These liquid product quality and distributions were changed depending on the physicochemical properties of the catalyst. Moreover, the characteristic of ZSM-5 in the catalyst was strongly influenced on the activity and PONA distribution in liquid product.

**Key Words** : catalytic degradation, waste HDPE, catalyst type (powder, granule), ZSM-5 crystal size, liquid product composition

## INTRODUCTION

In order to dispose waste plastics, the methods such as landfill and incineration are facing a great social resistance due to the air pollution and soil contamination, and also the economical resistance by the increase of a space and disposal cost.[1] As a conventional method, mechanical recycling method is limited to treat the mixed waste plastic by technical problem, difficulties in maintaining the product quality and adequate price.[2] Thus, as the recycling of waste plastics the chemical recycling such as the thermal or catalytic degradation of polymer has been recognized as an ideal approach, in order to recover fuel oil and hydrocarbon feedstock.[3~5] By the way, the thermal degradation yields the low-quality hydrocarbon products with a very broad range of molecular weight, whereas the catalytic degradation operates at low temperature as compared to the thermal degradation and produces high-quality products.[6] In our previous work,[7] we compared the thermal degradation with the catalytic degradation of waste HDPE using spent fluid catalytic cracking (FCC) catalyst. Here the catalytic degradation using spent FCC catalyst was proved to be a better process than thermal degradation.

For the catalyst used in this study, two ZSM-5 catalyst prepared with different crystal size were used as a powder type and also each ZSM-5 catalyst was mixed with the same binder as a granule type. They had different physicochemical properties. The physicochemical properties of the catalyst were very influenced on

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the reactivity of heavy hydrocarbons and also product quality and distribution obtained.[8~11] The comparison of catalytic performance over these catalysts was discussed with the cumulative amount distribution as a function of reaction time, initial degradation rate into liquid product and PONA distribution of liquid product. Accordingly, the focus of this study is the relationship between the catalysts containing ZSM-5 with different crystal size and liquid product characteristic.

# EXPERIMENTAL

Waste HDPE was used as a raw material and palletized 1/8 inch (O.D.) x a few mm (L), which was supplied by recycling company (Duck Shin Co., Daejeon). Its average molecular weights of number and weight were $2.3 \times 10^4$ and $3.7 \times 10^5$, respectively, and its melting point was 133°C. Two ZSM-5 catalysts with a small (PW-S) and large crystal size (PW-L) was synthesized as a powder type and it was mixed with binder as a granule type(GR-S(PW-S+ binder), GR-L(PW-L+binder)), respectively, which has 25 weight% of ZSM-5 in mixed catalyst. Here, the binder contained in the catalyst is the weight percentage of kaolin: silica sol: alumina = 55%:10%:10%. In order to ensure the ZSM-5 prepared, X-ray diffraction (XRD) was performed using Rigaku D/MAX-IIIB with Cu K$\alpha$ radiation. For the samples, the specific BET surface areas and total pore volumes were determined from the adsorption/desorption isotherms of nitrogen recorded using the procedure described previously.[7] The distinction between the micropore and the mesopore area was made using the T-plot method. Also, the crystal size of ZSM-5 was measured by particle size analyzer (Mirotrac Co. S3000 Model). The physical properties of the catalysts are shown in Table 1. The acidic properties of the catalysts were investigated using an ammonia temperature-programmed desorption (TPD) method within a temperature range of 100-800°C at a constant heating rate of 10°C/min.

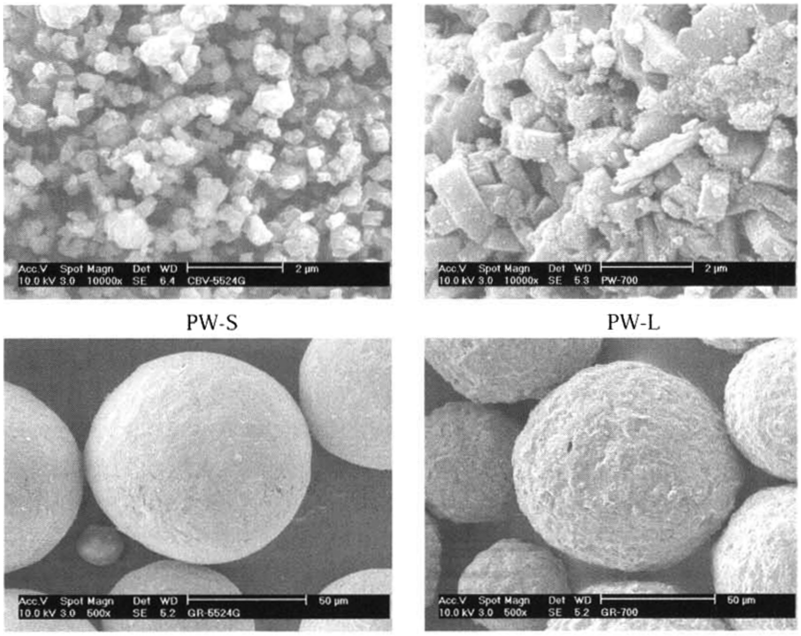
The degradation experiment using waste HDPE was carried out in a stirred semi-batch reactor (volume 1.1 liter) at 400°C under atmospheric pressure.[7] The experiment conditions were as follows: a reactant amount of 200 g, a catalyst amount of 20 g, a nitrogen stream of 20 cc/min, a speed of 200 RPM and heating rate of about 9°C/min up to 400°C. The gas products were vented after cooling by a condenser to 7°C. The liquid products were measured by weight, as a function of lapsed time. Each component of the liquid products was quantified and qualified by gas chromatography, using FID and MS detectors. For this analysis method, a detailed explanation was described previously.[12]

# RESULTS AND DISCUSSION

## Characterization of Catalyst

The catalyst was prepared as both a powder type catalyst (100%ZSM-5) and a granule type catalyst (ZSM-5 (25wt%) + binder (75wt%)). The morphology of various catalysts was determined from the SEM micrographs, as shown in Figure 1. The crystallites in the powder type catalyst showed a regular rectangular shape with different crystal size, whereas the granule type catalyst had a sphere shape with big size. The mean crystal size of powder type catalysts is given in Table 1. PW-S catalyst was about four times as small crystal size as PW-L catalyst. The crystal size in powder type catalyst had very influenced on the external surface pattern of particle in the preparation of granule type catalyst. GR-S catalyst prepared by PW-S that has a small crystal size showed much smoother surface than GR-L catalyst. In XRD analysis over powder type catalysts, two prepared ZSM-5 catalysts showed very similar peaks pattern in each catalyst, as shown in Figure 2.

Also, each catalyst had different physicochemical properties, as shown in Table 1. As a comparison of the physical properties of various catalysts, the powder type catalyst showed mainly micropore surface area, whereas that of granule type that was consisting of both ZSM-5



PW-S PW-L

GR-S GR-L

Figure 1. Scanning electron microscopy (SEM) over four catalysts.

Table 1. Physical properties of four catalysts

| Catalyst Type | Si/Al atomic ratio | Surface Area ($m^2/g$) | | | Total Pore Volume ($cm^3/g$) | Mean Crystal Size (µm) |
|---|---|---|---|---|---|---|
| | | BET | Micro- | Meso- | | |
| GR-S | 2.25 | 131.4 | 76.9 | 54.5 | 0.1612 | |
| PW-S | 23.89 | 427.0 | 381.0 | 46.0 | 0.1575 | 0.38 |
| GR-L | 1.96 | 130.5 | 48.9 | 81.6 | 0.1926 | |
| PW-L | 23.31 | 389.7 | 376.6 | 13.1 | 0.1848 | 1.63 |

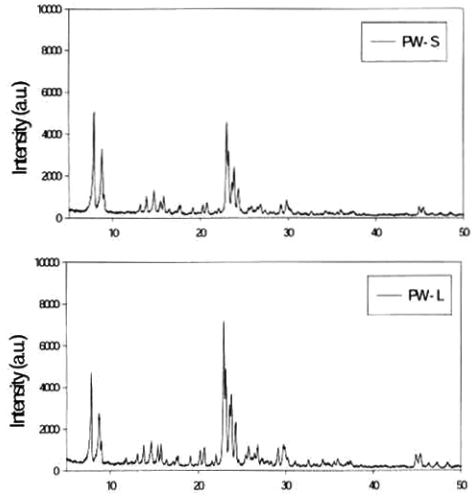


Figure 2. XRD analysis of two prepared ZSM-5 catalysts.

and binder had mesopore and micropore surface area simultaneously. In powder type, PW-S catalyst having a small mean crystal size showed the development of the mesopore as a relative high mesopore surface area, compared to PW-L with a large crystal size. This result was well agreed with that of Cambler et al..[13)] It was reported that a small crystal size in the Beta zeolite had a high mesoporosity, due to the development of interparticle void. On the other hand, in granule type the GR-L catalyst showed the blockage of micropore with relatively low micropore surface area, as compared with the GR-S catalyst. The pore size distribution of catalyst is important in determining the activity and product distribution from the catalytic degradation of heavy molecules, due to the difference in the diffusion of the reactant inside pores of catalyst and the reactivity on the active sites within pores. The initial degradation of heavy hydrocarbons is occurred on the external surface of the catalyst and then the intermediates formed would diffuse into the pore of the catalyst where further reaction takes place. Accordingly, the pore size distribution of various catalysts will be discussed with the cracking reaction of large molecules.

The acidic properties of catalyst have a great influence on the reactivity of heavy molecules. The acidity over four catalysts containing ZSM-5 with a different crystal size was shown in Figure 3, appearing the ammonia-TPD profiles. The catalysts exhibited three desorption peaks at a low temperature (below 250°C), mild temperature (250°C - 600°C) and high temperature (above 600°C). The desorption peaks observed at a low temperature were attributed to weak acid sites, produced from physically adsorbed ammonia, whereas those at a high temperature were attributed to strong acid sites. Here the temperature of the maximum peak reflected the acid strength and also the size of each peak depended on the number of acid sites. For the peak at high temperature, PW-S catalyst was appeared at about 450°C whereas PW-L catalyst at about 300°C. It means that PW-S catalyst with a small crystal size showed higher acid strength than PW-L catalyst. In granule type catalysts, two peaks appeared at below 600°C showed much smaller number of acid sites as a comparison of powder type catalyst, whereas that at above 600°C was formed as a new peak and probably occurred from the binder in mixed catalyst.

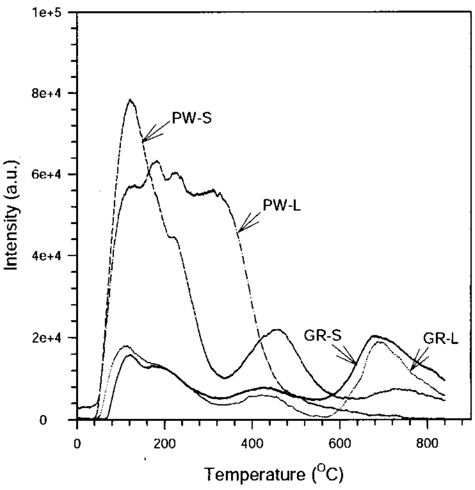


Figure 3. Ammonia-TPD spectra over four catalysts.

## Activity

Figure 4 shows the cumulative amount distribution of the liquid products from the degradation of waste HDPE over four catalysts under the same experimental conditions. The yield of liquid product over the catalyst containing ZSM-5 was relatively low, because of the overcracking of heavy molecule into gas products as shape selectivity.[14] Furthermore, the powder type catalyst (PW-S) had lower yield of liquid product than the granule type catalyst (GR-S). However, the comparison of liquid yield on both GR-L and PW-L catalysts was difficult, because the liquid product of two cases was not completely obtained after about 350 min of lapse time. The performance of the catalysts can be explained by the initial degradation rate, calculated from the slope of the cumulative

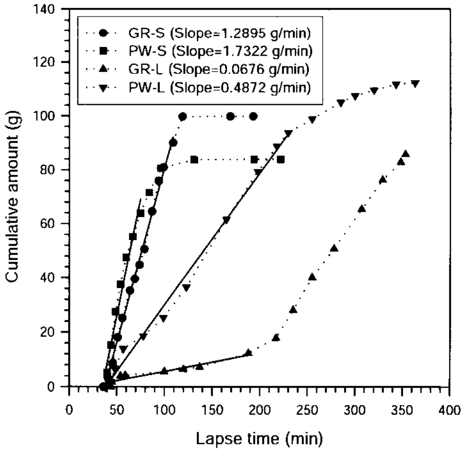


Figure 4. Cumulative amount distribution of liquid product for catalytic degradation of waste HDPE using various catalysts at 400°C (catalyst amount=4.76wt%).

Table 2. Paraffin, olefin, naphthene and aromatic distribution of liquid product over four catalysts

| Catalyst Type | Paraffin | Olefin | Naphthene | Aromatic |
|---|---|---|---|---|
| GR-S | 1.50 | 32.25 | 8.76 | 57.48 |
| PW-S | 1.85 | 51.91 | 8.04 | 38.21 |
| GR-L | 20.42 | 73.30 | 3.45 | 2.83 |
| PW-L | 18.83 | 78.88 | 0.64 | 2.15 |

amount distributions like shown in Figure 4. The initial degradation rate was obtained from the change of cumulative amount of liquid product as a function of reaction time in the range of initial reaction time. These values have a proportion relation with the activity of catalyst, because if the catalyst has better cracking performance for reactant, higher initial degradation rate will be obtained. The initial degradation rate was clearly differed over four catalysts and its order was PW-S>GR-S>PW-L>GR-L. Their activity is depending on the physicochemical properties of the catalyst. Powder type catalyst that has large active sites existing on external surface area due to a high external surface area per catalyst gram and also high content of ZSM-5 showed higher initial degradation rate than granule type catalysts. In the powder type, the PW-S catalyst that has high mesoporosity and high acid strength showed the improvement of activity as a comparison of PW-L catalyst. This result showed a similar tendency over the granule type catalyst. That is, the granule type catalyst containing PW-S with a high activity had higher initial degradation rate than that with PW-L catalyst. Furthermore, GR-L catalyst showed the lowest activity among four catalysts, because of the low activity of PW-L catalyst contained in GR-L catalyst and also the micropore blockage of GR-L catalyst.

## Liquid Product Distribution

The molecular weight and PONA distributions of the liquid product obtained over four catalysts were shown in Figure 5. The liquid products were mainly obtained in the gasoline range. The molecular weight distribution of liquid PONA products showed a difference, according to the characteristic of catalysts. The molecular weight distribution of liquid PONA products over two ZSM-5 catalysts with a different crystal size was clearly differed, whereas that between the granule and powder type catalyst having a same ZSM-5 catalyst showed a similar tendency. It is evident that the liquid product distribution is much more influenced by the characteristic of ZSM-5 in prepared catalysts.

In powder type catalysts, the PW-S catalyst had a short molecular weight distribution in the gasoline range with mainly liquid olefin and aromatic products, whereas the PW-L catalyst showed a wide molecular weight distribution containing heavy products, due to its low activity. For straight hydrocarbon distribution in liquid products, the PW-S catalyst with a higher activity was obtained mainly the light olefin products by the carbenium ion mechanism involving the $\beta$-cleavage of the carbenium ions,[15] compared to that of PW-L catalyst. On the other hand, over PW-L catalyst with a low activity the liquid paraffin products showed a wider molecular weight distribution and lower fraction than the liquid olefin products. From these results, it is supposed that saturated hydrocarbons in the catalytic degradation of a heavy molecule are much cracked into light olefin products, by means of high reactivity of the catalyst. PW-S catalyst that has a good physicochemical property showed the improvement of aromatic products, rather than that of olefin products. It shows that the olefin product formed in the first cracking reaction undergoes catalytic aromatizing reaction, increasing the quantities of aromatic compounds in the liquid products.

For a comparison of powder type and granule type catalysts, the granule type catalysts have lower activity than powder type catalysts like

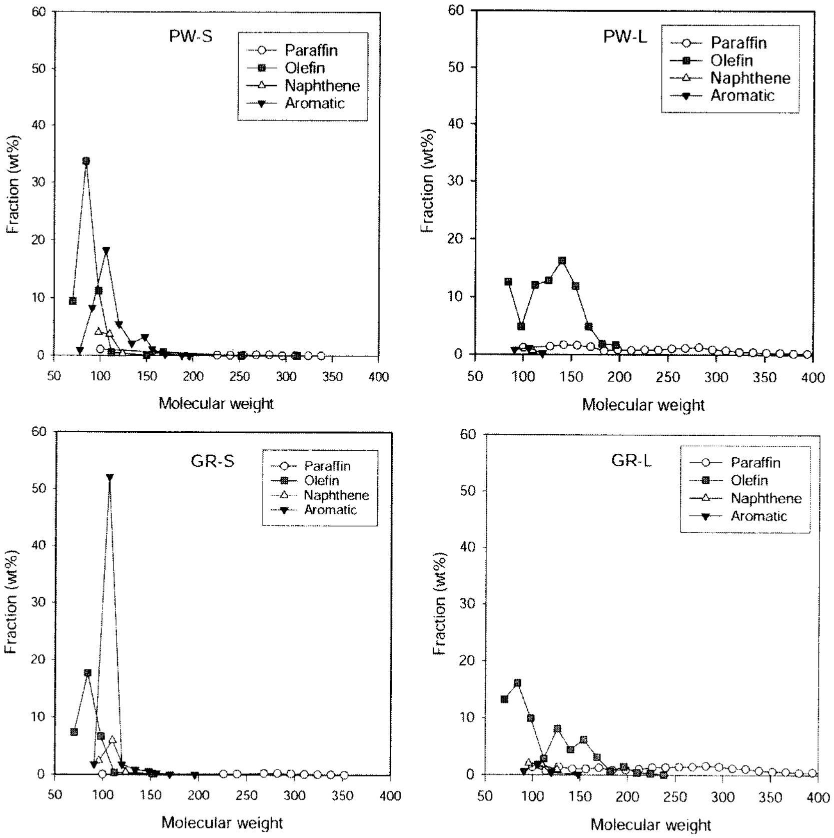


Figure 5. Molecular weight distribution of liquid PONA products for catalytic degradation of waste HDPE using various catalysts at 400°C (catalyst amount=4.76wt%).

appeared in Figure 4, but they showed roughly similar molecular weight distribution and PONA distribution. A little difference of liquid product distribution in their catalysts is the olefin and aromatic product distribution. Compared to PW-S catalyst, GR-S catalyst showed the increase of aromatic products with big kinetic diameter by decreasing the olefin products, due to the cyclization of light olefin intermediates. It seems that the development of mesopore in GR-S catalyst has an influence on the improvement of aromatic products, although GR-S catalyst has low content of ZSM-5. Furthermore, the GR-S catalyst showed much more augment of aromatic products with eight carbon numbers, from about 20% (PW-S) to about 50% (GR-S), whereas decreasing the light olefin product with six carbon numbers, from about 35% (PW-S) to about 20% (GR-S). It can be explained that the reaction mechanism over the catalyst with development of mesopores was the improvement of $C_8$ aromatic products by means of the cyclization and alkylation of both $C_6$ olefins and also $C_2$ intermediates.

## CONCLUSIONS

The performance of four catalysts, which was two ZSM-5 with a different crystal size as a powder type (PW-S, PW-L) and also its mixed with the same binder as a granule type (GR-S, GR-L), respectively, was compared for catalytic degradation of waste HDPE.

These catalysts had a different pore size distribution and acid properties. For powder type catalysts, PW-S catalyst, compared to PW-L catalyst, showed the development of mesopore and good acid properties. Also, powder type catalyst had mainly the micropore, whereas granule type catalyst had the micropore and mesopore simultaneously. These results were very influenced on the product characteristics and especially PONA distribution in liquid product. Powder type catalysts showed lower liquid yield by the reactivity of reactant into gas products as the shape selectivity than granule type catalysts. The catalysts containing PW-S catalyst that has a good pore structure and acid properties showed high initial degradation rate into liquid product and also the increase of aromatic products by means of the decrease of olefin and paraffin products, due to the cyclization of olefin and paraffin intermediates. Also, GR-S catalyst having development of mesopores produced more $C_8$ aromatic products with big kinetic diameter by means of cyclization and alkylation of $C_6$ olefin and $C_2$ intermediates than PW-S catalyst. From these results, it was concluded that a physicochemical properties of catalyst are very important to control the characteristic of liquid product in the catalytic degradation of heavy hydrocarbons.

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