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有機廢棄物電漿氣化及
合成氣淨化程序之探討

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受委託機關（構）：國立中央大學

計畫主持人：陳郁文

核研所共同主持人：陳靖良（電漿專案計畫）

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中文摘要

本計畫目的為配合「電漿焚化熔融處理有害廢棄物產業化應用與發展」施政目標，開發可燃性廢棄物電漿氣化處理程序技術，以協助解決國內有機廢棄物所造成之環保問題。整體計畫為兩年期，第一年之主要工作內容包括：(1)建立有機廢棄物電漿氣化產物成分之定量分析技術；(2)篩選適當商用觸媒，進行有機廢棄物氣化反應催化觸媒技術研究；(3)探討有機廢棄物觸媒裂解機制；(4)進行有機廢棄物轉化成氣之操作條件與轉化效率實驗等。因為中央大學實驗室沒有電漿設備，因此本年度計畫先以一般電熱方式進行聚乙烯裂解之先期研究工作，以篩選出適當之商用觸媒並掌握初步反應條件，再於後續計畫中於核能研究所實際電漿爐設備中進行驗證。

觸媒裂解聚乙烯，一般所採用之觸媒為酸性沸石。經初步評估後，本計畫以 HY 及 HZSM-5 兩種商用沸石觸媒進行測試，此兩種沸石的酸性與孔洞結構均不相同，其性質以氮吸附、X 光繞射儀及元素分析鑑定。聚乙烯裂解採用二階段方式，聚乙烯先於第一個反應器中以 400~500 熱熔分解，再於第二個反應器中進一步觸媒裂解，反應產物以氣相色層分析儀分析。隨著溫度升高，氣相產物會變多，兩種觸媒都能產生 C5 至 C12 的產物，尤其是芳香烴，但溫度太高會有劇烈的結焦現象，因此目前尚無法反應產生足夠的合成氣。觸媒在反應後都發生結焦現象，變成黑色。積碳以熱重分析儀分析，發現 HY 沸石積碳現象嚴重很多，主要是 HZSM-5 沸石沒有巨孔洞，其孔徑均為直線，因而較不會積碳。另外，HZSM-5 沸石具有較高的矽鋁比，酸性較強，所產生的氣相產物也較多，對於氣化反應來說，可能是較佳的選擇。

關鍵詞：觸媒裂解、聚乙烯、聚烯烴、塑膠廢棄物

Abstract

Waste plastics, especially thermoplastics, can be regarded as being a cheap and abundant source of chemicals and energy. Recycling of thermoplastics from waste products can contribute to solving pollution problems associated with the land-filling incineration of plastics. In the thermal degradation of polyolefin, many hydrocarbons having a wide-range distribution of carbon atom numbers are formed. Compared to thermal degradation, catalytic degradation has the advantages of a lower temperature of degradation and a narrower distribution of hydrocarbons. In this study we investigated the catalytic degradation of polyethylene in a fixed bed reactor composed of a melter and a catalytic cracking bed. Solid acid catalysts such as HY and HZSM-5 were screened for polyethylene degradation in the range of 400-500 °C. The degradation products of PE, especially a liquid fraction, were analyzed by gas chromatography. The coke content in the used catalyst was determined by thermal gravimetric analysis using oxygen as the reactant. Compared to those obtained by thermal degradation, the catalytic degradation products were distributed in a narrow range of carbon numbers. In addition, HY zeolite produced more liquid products than HZSM-5. The product distribution was also strongly affected by the reaction temperature. However, HY zeolite always produced more liquid products than HZSM-5. The high gas product on HZSM-5 is essentially due to its higher acid strength of the active sites. Large amounts of isoparaffins and aromatics were present. The HZSM5 with high Si/Al ratio produced higher gas product and lower liquid product. It also produced less coke. HY zeolite was an efficient and cheap catalyst for the PE degradation. The acidity and pore structure of zeolite appear to be responsible for the good performance.

Keywords: catalytic degradation, polyethylene, polyolefin, plastic waste.

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Chapter 1. Introduction

In the 1990s, the recycling of residual plastics by combustion or pyrolysis has received significant attention in the world. Waste plastics, especially thermoplastics, can be regarded as being a cheap and abundant source of chemicals and energy. Furthermore, recycling of thermoplastics from waste products can contribute to solving pollution problems associated with the land-filling and incineration of plastics. Though several methods have been proposed for recycling waste plastics, it is generally accepted that material recovery is not a long term solution to the present problem, and that energy or chemical recovery is a more attractive one. Consequently, new technologies are being investigated for the chemical recycling of plastics waste. One approach is to employ inert gas pyrolysis to produce gasoline-like materials. In this method, the waste plastics are thermally or catalytically degraded into gases and oils, which can be used as resources in fuels or chemicals.

Plastic waste disposal has been recognized as a worldwide environmental problem. Even a manufacture of bio- and photodegradable plastics cannot solve the problem because these plastics have the limitation of long-term degradation and caused a different kind of environmental problem by the stabilizers introduced in their preparation. Therefore, in recent years, increased attention has been paid to the recycling of synthetic polymer waste. This can be contributed to solving pollution problems and the reuse of cheap and abundant waste products. The energy or chemical recovery is an attractive method.

In the thermal degradation of polyolefin, many hydrocarbons having a wide range distribution of carbon atom numbers are formed. In contrast, the oils produced by the catalytic degradation are known to contain a relatively narrow distribution of hydrocarbons. Compared to thermal degradation, catalytic degradation also has advantages of a lower temperature of degradation [1-4].

The most commonly used catalysts in the catalytic degradation of polymers are solid acids, such as zeolite, silica-alumina and activated carbon.

Pyrolysis is known as a method to break complex organic materials such as synthetic polymers into relatively small molecules. This process is not well understood, but the use of various solid acid catalysts is a promising way to improve the yield and selectivity to a desired hydrocarbon range [4-6]. Pyrolysis of plastics is of great interest because it is an alternative source of energy or chemical raw materials. In addition, this process helps to solve environmental problems. For designing recycling of plastics in large scale, the kinetics of decomposition must be known. Most of studies used thermal gravimetric (TG) method to study the kinetics of both thermal and catalytic degradation [1-3]. However, TG method only can give the information of conversion versus temperature, and by Arrhenius plot, one can get activation energy. The experiment is much easier and time-saving. However, it is difficult to get the product distribution.

The waste plastics are thermally or catalytically degraded into gases or oils, which can be used as resources in fuels or chemicals. Catalytic degradation of polyolefins could not only improve the quality of products obtained from pyrolysis of plastics wastes and lower the temperature of decomposition, but could also enable a given selectivity to a certain product to be achieved. Several authors [2-5] have reported the use of solid acid catalysts in this process. However, the effects of the type of zeolites on the performance of the catalysts in degradation of polyethylene have not been studied in detail.

In this study, we carried out screening test of several solid acid catalysts for the degradation of polyethylene. The reaction mechanisms of catalytic degradation of polyethylene and polypropylene are very similar. In this study, PE was chosen as the material because it is cheaper and commercially available in Taiwan. Some authors have used the mixture of plastics as the feedstock, such

as ethylene-vinyl acetate copolymers. However, the mechanism of degradation is very complicate and very difficult to get conclusive results. Mesoporous molecular sieves have been tested as the catalysts. However, their structures would be collapsed upon exposed to moisture and the price is high. Therefore, they were not studied in this project. Special emphasis has been placed on the HY zeolite and HZSM-5 for its potential as a catalyst in PE degradation. HY and HZSM-5 are cheap and commercially available.

Chapter 2. Experimental

2.1 Materials

Low density PE in powder form, from local vendor, was used. NH_4Y ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.2$, CBV500) and HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$, CBV3020E) zeolites were obtained from Zeolysts Co. Both were in the form of NH_4 -zeolite. They were calcined at 500 °C for 4 h to convert to H-zeolite. HY zeolite has FAU structure and the pore size is 7.4 angstrom. HZSM-5 zeolite has MFI structure with intersecting 5.4×5.6 and 5.1×5.5 angstrom channels.

2.2 Nitrogen sorption

The specific surface area of the catalyst was measured by a Brunauer-Emmett-Teller (BET) apparatus (Micromeritics ASAP 2010). The surface areas of the samples were obtained from the analysis of nitrogen adsorption and desorption isotherms carried out at -196 °C in a volumetric apparatus. Sets of nitrogen adsorption-desorption isotherms were analyzed using a cylindrical mode and the Kelvin equation. The samples were outgassed at 350 °C for 12 h until the vacuum pressure was below 0.1 mPa before measurements were performed. Then, the sample cell was filled with helium, weighed, and attached to the measurement port. After determination of the void volume, the sample was evacuated again at room temperature to ensure that all helium is removed from the pores. A Baratron (0.001-10 Torr) pressure transducer was used for low pressure measurements, and measurements have been corrected for the thermal transpiration effect. At each isotherm point, the saturated vapor pressure of liquid nitrogen was measured in reference cell.

2.3 X-ray diffraction

The bulk structure of the zeolite was confirmed by X-ray diffraction analysis with Cu-K α radiation. XRD analysis was conducted on a computer-controlled Siemens D500 diffractometer employing nickel-filtered Cu-K α radiation ($\lambda = 0.15418$ nm). The X-ray tube was operated at 40 kV and 30 mA. Spectra were scanned at 0.02° step size and 1 sec step time from 1° to 80°. Fluorophlogopite mica (Standard Reference Material 675, National Bureau of Standards) was used as an external standard in order to protect the detector from the high energy of the incident X-ray beam.

2.4 Catalytic degradation

The catalytic degradation of PE was carried out in a fixed bed semibatch reactor where a stream of nitrogen (100-150 mL/min) was continuously passed. The gas flow was controlled by a mass flow controller (Brooks MFC 5850E). The PE sample was melted and cracked in the first part of the reactor, and then the thermally degraded fragments were passed to the catalyst bed by using nitrogen as the carrier gas. The catalyst concentration was 10 wt. % of the PE amount. PE samples and the catalysts were placed separately in a 30-mL Pyrex vessel and heated at the desired temperature in the range of 400-500 °C. The degradation of PE was usually carried out over a period of 1 h. The degradation products from the reactor were separated into gas and liquid fractions in a cold trap maintained at -5 °C.

The degradation of PE gave off gases, liquids and solid residues. The residue means the carbonaceous and waxy compounds remaining in the reactor and deposited on the reactor wall. The gases were analyzed by an on-line GC with a Porapak QS column. The condensed liquid samples were analyzed by a GC with a capillary column HP-5MS (0.25 mm \times 30 m). The compositions of some of

liquids were also measured by a PONA (Paraffins-olefins-naphthalenes-aromatics) analyzer (HP PONA).

The amount of coke deposited on the catalyst was calculated by measuring the desorbed amount of carbon dioxide during temperature programmed oxidation (TPO) of the used catalysts. In TPO, the used catalyst was first treated by helium at 423 K, and then it was cooled down to 313 K before passing a mixed gas of 1 vol. % oxygen and the balance helium. The temperature was increased up to 873 K with a heating rate of 10 K/min, and the produced carbon dioxide peaks are measured.

The coke content in the used catalyst was also examined by thermal gravimetric analysis using oxygen as the reactant gas. Thus HZSM-5 with Si/Al ratio of 23 contains more acidic sites than that with Si/Al ratio of 60. However, the HZSM-5 with Si/Al ratio of 60 has higher acidic strength. The HZSM-5 with Si/Al ratio of 60 produced a higher gas fraction and a higher amount of aromatics in the liquid products.

Table 1. Various Y zeolites from Zeolysts Corporation

| Zeolyst™ Product | SiO ₂ /Al ₂ O ₃ Mole Ratio | Nominal Cation Form | Na ₂ O (Weight %) | Unit Cell Size (Å) | Surface Area (m ² /g) |
|---------------------|--|---------------------------|---------------------------------|-----------------------|--|
| CBV 100 | 5.1 | Sodium | 13.0 | 24.65 | 900 |
| CBV 300 | 5.1 | Ammonium | 2.8 | 24.68 | 925 |
| CBV 400 | 5.1 | Hydrogen | 2.8 | 24.50 | 730 |
| CBV 500 | 5.2 | Ammonium | 0.2 | 24.53 | 750 |
| CBV 600 | 5.2 | Hydrogen | 0.2 | 24.35 | 660 |
| CBV 712 | 12 | Ammonium | 0.05 | 24.35 | 730 |
| CBV 720 | 30 | Hydrogen | 0.03 | 24.28 | 780 |
| CBV 760 | 60 | Hydrogen | 0.03 | 24.24 | 720 |
| CBV 780 | 80 | Hydrogen | 0.03 | 24.24 | 780 |
| CBV 901 | 80 | Hydrogen | 0.03 | 24.24 | 700 |

Table 2. Various ZSM-5 zeolites from Zeolysts Corporation

| Zeolyst™ Product | SiO ₂ /Al ₂ O ₃ Mole Ratio | Nominal Cation Form | Na ₂ O (Weight %) | Surface Area (m ² /g) |
|---------------------|--|---------------------------|---------------------------------|-------------------------------------|
| CBV 2314 | 23 | Ammonium | 0.05 | 425 |
| CBV 3020E | 30 | Hydrogen | 0.10 | 400 |
| CBV 3024E | 30 | Ammonium | 0.05 | 400 |
| CBV 5524G | 50 | Ammonium | 0.05 | 425 |
| CBV 8014 | 80 | Ammonium | 0.05 | 425 |
| CBV 28014 | 280 | Ammonium | 0.05 | 400 |

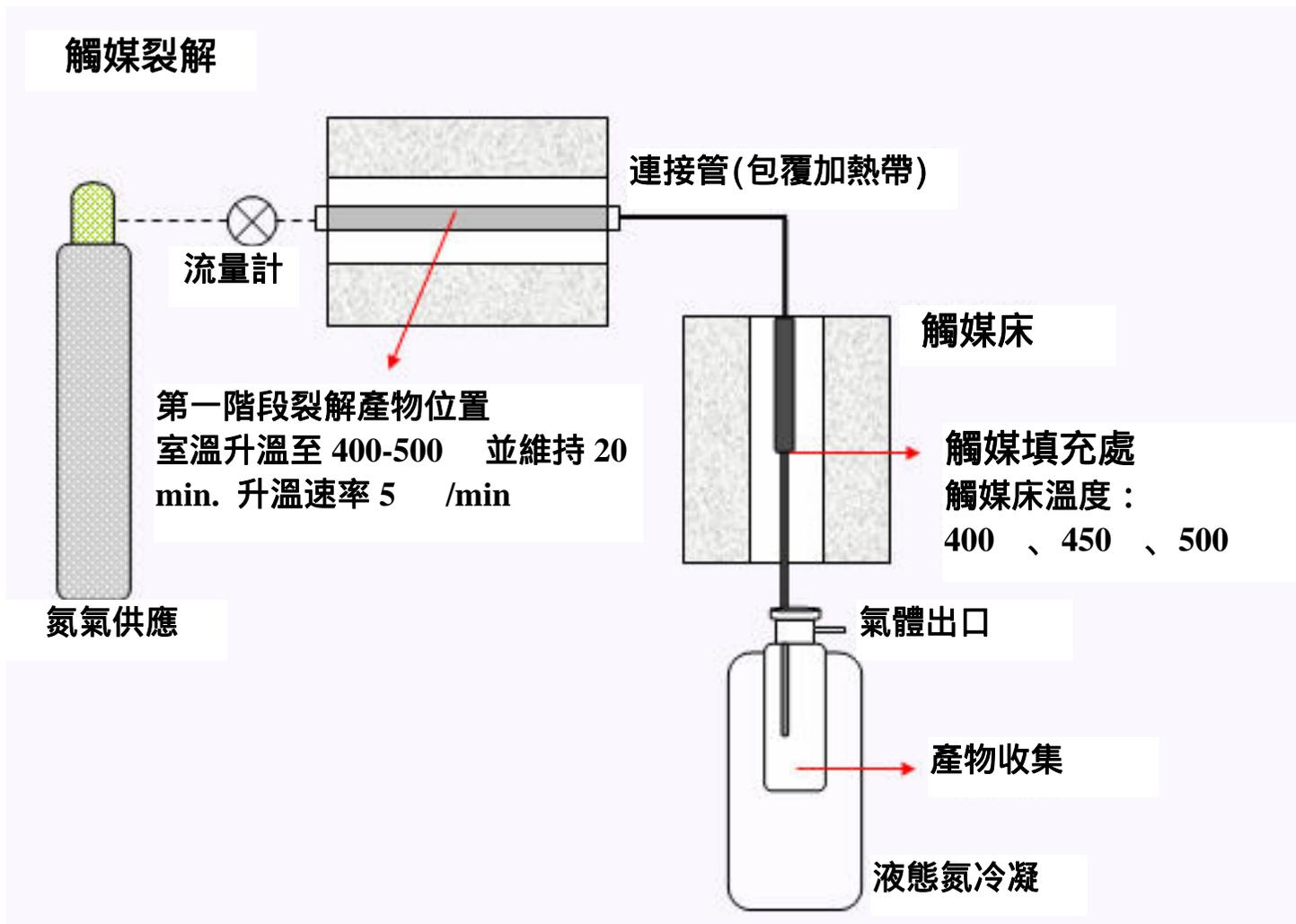


Figure 1. Reaction setup.

Chapter 3. Results and Discussion

3.1 Characteristics of catalysts

Table 3 shows BET surface area and microporous surface area. The microporous surface area was determined by the t-plot method. HZSM-5 has a BET surface area of 398 m²/g and HY zeolite has a even higher BET surface area of 520 m²/g. Both zeolites have very large microporous surface areas of about 83% of the BET surface areas, indicating that the major pores are micropores in both zeolites, as expected.

3.2 Effect of the type of zeolite and reaction temperature

PE, along with the catalysts (HY and HZSM-5 zeolites) in the cracking bed was degraded at 420-480 °C. Table 4 lists the gaseous and liquid products and the residue from the degradation. The amount of gaseous products was calculated by subtracting the weight of liquid products and the residues from the PE sample weight. Carbonaceous and waxy compounds adhering to the reactor wall were dissolved in n-hexane and were measured as degradation residues.

Both catalysts showed a high yield of gaseous and liquid products, and practically no residue after degradation. However, all of them had more than 50% residue at a temperature less than 400 °C. HZSM-5 catalyst produced a greater amount of gaseous product than HY zeolite. HZSM-5 zeolite has MFI structure with intersecting 5.4×5.6 and 5.1×5.5 angstrom channels. Therefore, the initial cracked fragments can diffuse through the pores of HZSM-5 and react further in the cavities created at the intersection of the two channels, yielding more gaseous products. HY zeolite was easily deactivated by coking because it had large supercages with its crystallites. In Table 4, the liquid products on HY zeolite are greater than those on HZSM-5 zeolite. Both catalysts had very low coking.

In Tables 5-7, the carbon number distribution of liquid products obtained by catalytic degradation of PE is compared with that obtained by thermal degradation. There is a clear difference between the products of thermal versus catalytic degradation. HY and HZSM-5 greatly accelerated the degradation of PE. The liquid products over both zeolites contained a narrow distribution of carbon numbers. Thermal degradation products were distributed over a wide range of carbon numbers. Thermal degradation produced a large amount of oligomers. The SEM studies indicated that for mixture of polymer/catalyst particles, at temperature around 573 K, the molten polymer was drawn into the space between particles and hence to active sites at the external surface of zeolite catalysts, if sufficiently volatile, can either diffuse through the polymer film, as products, or react further in the pores of zeolites. Since HZSM-5 has appropriate zeolite structure, it produced more aromatics than other catalysts.

Both zeolites had very low coke deposit. The results demonstrated that these catalysts have very good stability. It should be noted that the low coke content is essentially due to the high acidity and unique pore structure of the zeolites. HY zeolite has a big supercage (about 1.3 nm) in the intersection of pore channels. However, due to its high acidity, coke was not generated in this supercage. HZSM-5 is well-known for its low coke in the oil refinery applications. The linear shape of PE may also play some role in the low coke.

Tables 5-7 show the product distribution of liquids for both catalysts. The values of liquid product distributions are weight percentages. Thermal degradation produces large amount of hydrocarbons with carbon number > 20. In contrast, catalytic degradation of PE over HY and HZSM-5 solid acid zeolites produced very small amount of hydrocarbons with carbon number > 20. The major products are the hydrocarbon with carbon number between C5 and C12. It means that the major products by catalytic degradation on HY and HZSM-5 zeolites are in the gasoline range. Some products in diesel oil range were also

produced.

HZSM-5 seemed to have lower coke even at high temperature, due to its unique pore structure. Although HZSM-5 had strong acid sites than HY, its pore opening is smaller. This may result in the lower activity due to the difficulty of reactants diffusing into the zeolite structure. In addition, HY zeolite produced more liquid products than HZSM-5. The product distribution was also strongly affected by the reaction temperature. However, HY zeolite always produced more liquid products than HZSM-5. The high gas product on HZSM-5 is essentially due to its higher acid strength of the active sites. The acidic properties and the pore structure of zeolite play important roles in this reaction. One may conclude that zeolite HY is a good catalyst for degradation of PE over the temperature range 420-480 °C. It also produced large amount of hydrocarbons in the gasoline range. Large amounts of isoparaffins and aromatics were present.

Liquid products from thermal degradation of PE contained linear olefins and aromatics. In contrast, liquid products from catalytic degradation of PE contained large amount of isoparaffin and aromatics. In addition, HZSM-5 produced much more aromatics than HY and thermal degradation of PE. Since HZSM-5 has many Brønsted acid sites, aromatization seems to be favorable on the Brønsted acid sites, and hydrogen consumed in the aromatization reaction may be consumed for the hydrogenation of olefins. HZSM-5 showed more than 75% of aromatics. HY produced more paraffins than HZSM-5.

The acidity of zeolite is known to be closely related to the catalytic activity of the degradation of PE and PP. ZSM-5 catalysts were used to study the effect of Si/Al ratio on the PE degradation. Two ZSM-5 zeolites of different Si/Al ratios were tested for PE degradation at 723 K for 1 h. It is well-known that a higher Si/Al ratio of HZSM-5 zeolite means a lower amount of acid sites, since acid sites are closely related to the existence of the aluminum atom in the zeolite

structure. However, the acid strength increased with an increase of Si/Al ratio, since the acidic strength is related to the number of silicon atoms in the neighborhood of aluminum atom in the zeolite structure. As shown in Table 9, the HZSM5 with higher Si/Al ratio produced higher gas product and lower liquid product. As expected, it also produced more coke [4].

Table 10 shows that HZSM-5 with higher Si/Al ratio produced higher amount of aromatics. Acidity is one of the key factors for the initialization to form carbenium ion from PE. In addition, it is also the most important property to accelerate the aromatization of primary degraded fragments. However, the number of acid sites and the strength per acid sites are all important. By regulating the Si/Al ratio, one is able to optimize the acidity of zeolite, which again can influence the product distribution of PE degradation.

The space velocity of nitrogen could influence the product distribution. As shown in Table 11, the liquid product increased and the gas product and coke decreased with an increase of space velocity in any reaction temperature.

3.3 Reaction mechanism

It is known that thermal degradation occurs by a radical mechanism, and it offers many oligomers by hydrogen transfer from the tertiary carbon atom along with the polymer chain to the radical site. However, catalytic degradation of PE is known to proceed by carbenium ion mechanism. The initial step of the degradation reaction is considered to occur by either the abstract of the hydride ion (by Lewis acid sites) from the PE molecule or the addition of a proton (by Brønsted acid sites) to the C-C bonds of the PE molecule or thermally degraded olefins. Successive scission of the main chain occurs to produce fragments having lower molecular weights than that of PE. The resulting decomposed fragments are further cracked or dehydrocyclized in the subsequent steps.

Table 3. The BET surface area and microporous surface area of HZSM-5 and HY zeolites.

| sample | BET surface area (m ² /g) | Microporous surface area (m ² /g) |
|--------|--------------------------------------|--|
| HZSM-5 | 398 | 332 |
| HY | 520 | 432 |

Table 4. Product distribution of catalytic degradation of PE.

| Rxn. Temp. () | <u>Gas (wt. %)</u> | | | <u>Liquid (wt.%)</u> | | | <u>Coke (wt. %)</u> | | |
|----------------|--------------------|------|------|----------------------|------|------|---------------------|-----|-----|
| | 420 | 450 | 480 | 420 | 450 | 480 | 420 | 450 | 480 |
| HY | 25.6 | 43.7 | 48.3 | 73.2 | 55.2 | 50.7 | 1.2 | 1.1 | 1.0 |
| HZSM-5 | 53.4 | 61.2 | 66.9 | 46.4 | 38.7 | 33.0 | 0.2 | 0.1 | 0.1 |

Table 5. Product distribution of degradation of PE at 420 .

| Catalyst | Gas (wt. %) | Coke (wt. %) | Liquid (wt. %) | C5-C12 (wt. %) | C13-C20 (wt. %) | >C20 (wt. %) |
|----------|----------------|-----------------|-------------------|-------------------|--------------------|-----------------|
| Thermal | - | - | 100.0 | 11.7 | 65.7 | 22.6 |
| HY | 25.6 | 1.2 | 73.2 | 55.4 | 13.4 | 4.4 |
| HZSM-5 | 53.4 | 0.2 | 46.4 | 15.5 | 28.2 | 2.7 |

Table 6. Product distribution of degradation of PE at 450 .

| Catalyst | Gas (wt. %) | Coke (wt. %) | Liquid (wt. %) | C5-C12 (wt. %) | C13-C20 (wt. %) | >C20 (wt. %) |
|----------|----------------|-----------------|-------------------|-------------------|--------------------|-----------------|
| Thermal | - | - | 100.0 | 12.8 | 63.2 | 24.0 |
| HY | 43.7 | 1.1 | 55.2 | 42.7 | 8.1 | 4.4 |
| HZSM-5 | 61.2 | 0.1 | 38.7 | 34.0 | 3.5 | 1.2 |

Table 7. Product distribution of degradation of PE at 480 .

| Catalyst | Gas (wt. %) | Coke (wt. %) | Liquid (wt. %) | C5-C12 (wt. %) | C13-C20 (wt. %) | >C20 (wt. %) |
|----------|----------------|-----------------|-------------------|-------------------|--------------------|-----------------|
| Thermal | - | - | 100.0 | 10.4 | 56.5 | 33.1 |
| HY | 48.3 | 1.0 | 50.7 | 37.7 | 10.3 | 2.7 |
| HZSM-5 | 66.9 | 0.1 | 33.0 | 28.2 | 3.1 | 1.7 |

Table 8. Distribution of liquid products of degradation of PE at 450 for 1 h.

| Catalyst | n-Paraffins | Iso-Paraffins | Olefins | Naphthalenes | Aromatics |
|----------|-------------|---------------|---------|--------------|-----------|
| Thermal | 36.8 | 4.7 | 29.8 | 9.6 | 19.1 |
| HY | 15.7 | 24.0 | 23.0 | 8.0 | 29.3 |
| HZSM-5 | 9.3 | 3.3 | 7.7 | 4.0 | 75.6 |

Table 9. Product distribution of catalytic degradation of PE at 450 .

| Catalyst | Si/Al Ratio | Gas (wt. %) | Coke (wt. %) | Liquid (wt. %) |
|----------|-------------|-------------|--------------|----------------|
| HZSM-5 | 23 | 34.2 | 0 | 65.8 |
| HZSM-5 | 60 | 53.4 | 0.2 | 46.4 |

Table 10. Distribution of liquid products of degradation of PE at 450 for 1 h.

| Catalyst | Si/Al Ratio | n-Paraffins | Iso-Paraffins | Olefins | Naphthalenes | Aromatics |
|----------|-------------|-------------|---------------|---------|--------------|-----------|
| Thermal | - | 36.8 | 4.7 | 29.8 | 9.6 | 19.1 |
| HZSM-5 | 23 | 17.6 | 4.9 | 20.0 | 4.8 | 52.7 |
| HZSM-5 | 60 | 9.3 | 3.3 | 7.7 | 4.0 | 75.6 |

Table 11. Effect of space velocity on the product distribution on HY catalysts.

| Rxn. Temp. N ₂ flow rate | 420 (wt%) | | | 450 (wt%) | | | 480 (wt%) | | |
|--|-------------|-------|------|-------------|------|------|-------------|-------|------|
| | Liquid | Gas | Coke | Liquid | Gas | Coke | Liquid | Gas | Coke |
| 100 mL/min | 56.6 | 41.95 | 1.45 | 51 | 47.7 | 1.35 | 49.8 | 48.95 | 1.25 |
| 200 mL/min | 72.2 | 26.46 | 1.34 | 55.2 | 43.7 | 1.09 | 54.3 | 44.73 | 0.97 |

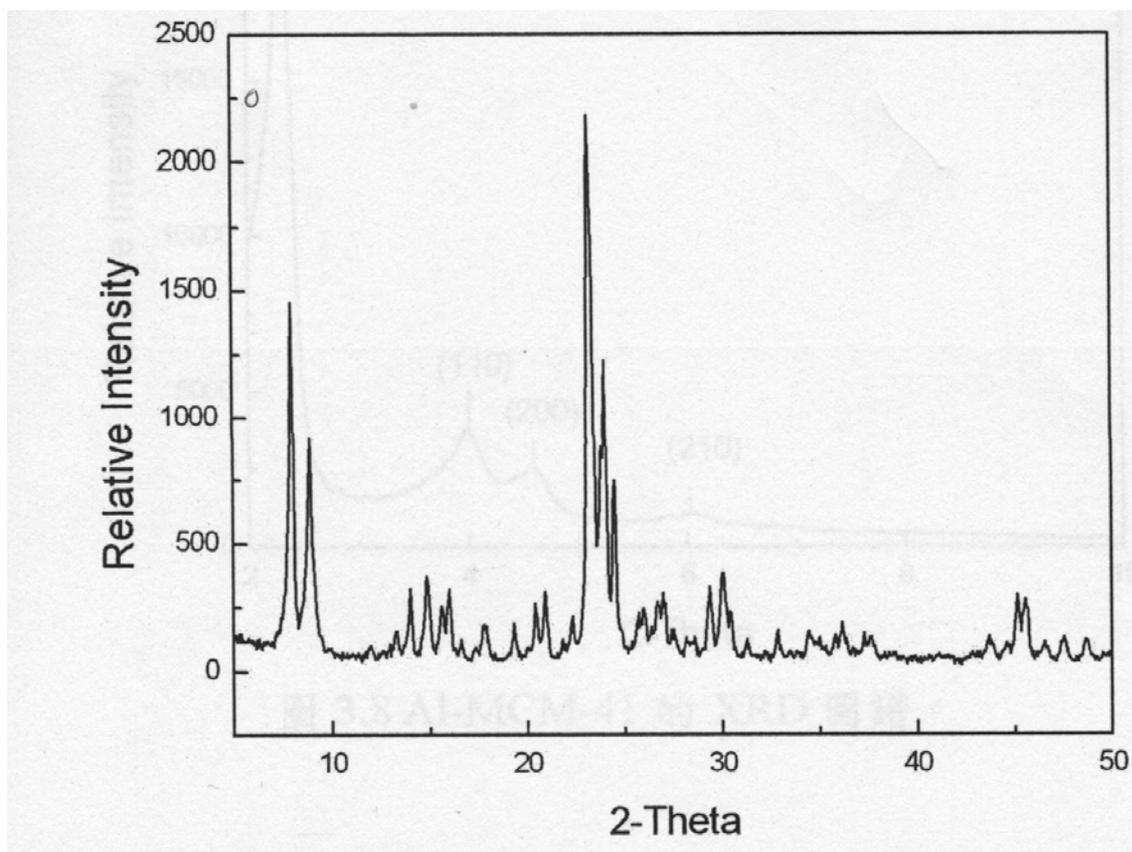


Figure 2. XRD pattern of HZSM-5.

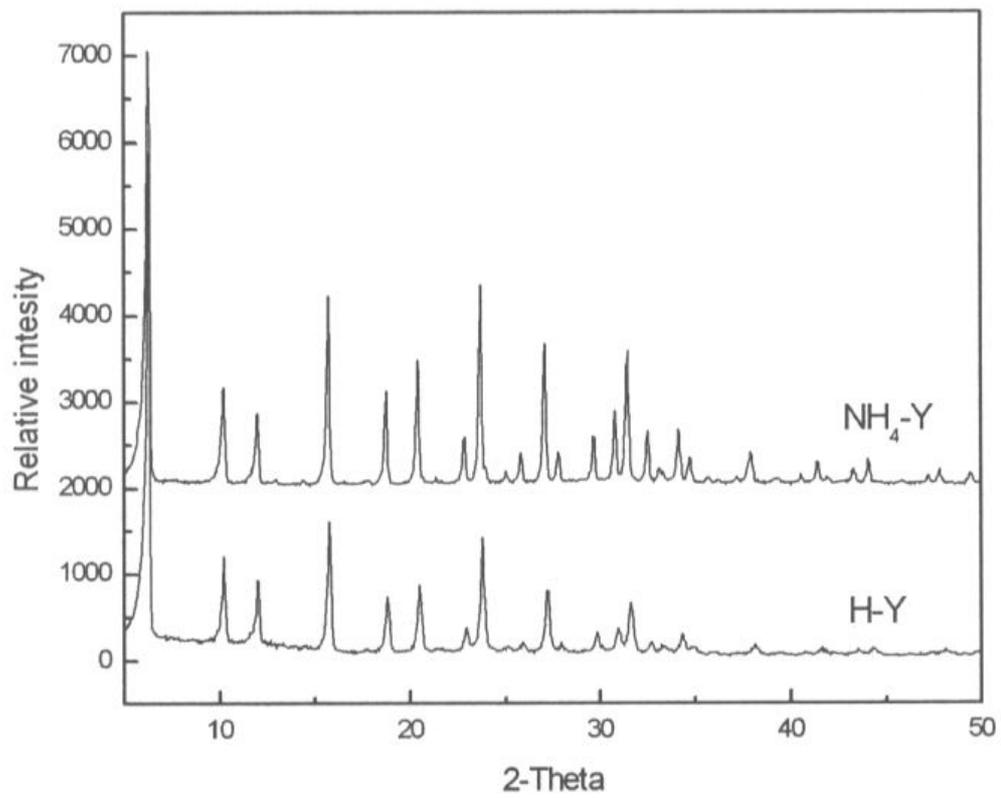


Figure 3. XRD patterns of NH₄Y and HY.

Chapter 4. Conclusion

Compared to thermal degradation, catalytic degradation has the advantages of a lower temperature of degradation and a narrower distribution of hydrocarbons. In this study we investigated the catalytic degradation of polyethylene in a fixed bed reactor composed of a thermal melter and a catalytic cracking bed. Solid acid catalysts such as HY and HZSM-5 were screened for polyethylene degradation in the range of 400-500 °C. The degradation products of PE, especially a liquid fraction, were analyzed by a gas chromatography. The coke content in the used catalyst was determined by thermal gravimetric analysis using oxygen as the reactant. Compared to those obtained by thermal degradation, the catalytic degradation products were distributed in a narrow range of carbon numbers. In addition, HY zeolite produced more liquid products than HZSM-5. The product distribution was also strongly affected by the reaction temperature. However, HY zeolite always produced more liquid products than HZSM-5. The high gas product on HZSM-5 is essentially due to its higher acid strength of the active sites. Large amounts of isoparaffins and aromatics were present. The HZSM5 with high Si/Al ratio produced higher gas product and lower liquid product. As expected, it also produced less coke. HY zeolite is an efficient catalyst for the PE degradation. It is also cheap and commercially available. The acidity and pore structure of zeolite appear to be responsible for the good performance.

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