

CATALYTIC DEGRADATION OF POLYPROPYLENE I. SCREENING OF CATALYSTS

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Abstract – The catalytic degradation of polypropylene has been investigated in this study. Solid acid catalysts, such as silica-alumina and zeolites (HZSM-5, natural zeolite, Mordenite etc.), were screened for polypropylene degradation in the range of 350-450 °C. The degradation products of polypropylene, especially a liquid fraction, formed over solid acid catalysts, were analyzed by GC/MS. The degradation products are distributed in a narrow range of carbon number compared with those obtained by thermal degradation. The liquid fraction contained large amounts of iso-paraffins and aromatics as are present in the gasoline fraction of petroleum. The natural zeolite catalyst (clinoptilolite structure, occurring in Youngil area of Korea) was an efficient catalyst for the polypropylene degradation. The acidity and characteristic pore structure of this zeolite appear to be responsible for the good performance. The effects of temperature and reaction time on the product distribution have also been studied in this work.

Key words: Polypropylene, Catalytic Degradation, Natural Zeolite, Waste Plastics

INTRODUCTION

Plastic waste disposal has been recognized as worldwide environmental problem. Even the manufacture of bio- and photo-degradable plastics cannot solve the problem, however, because these plastics have the limitation of long-term degradation and cause a different kind of environmental problem by the stabilizers introduced in their preparation [Mordi et al., 1994]. Therefore, in recent years, increased attention has been paid to the recycling of synthetic polymer waste. This can contribute to solving pollution problems and the reuse of cheap and abundant waste products [Jun et al., 1995; Kim, 1996].

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. 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 [Ohkita et al., 1993]. However, in the thermal degradation of polyolefin many hydrocarbons having a wide range distribution of the carbon atom number are formed. In contrast, the oils produced by catalytic degradation are known to contain a relatively narrow distribution of hydrocarbons. Catalytic degradation also has the advantage of a lower temperature of degradation when compared to thermal degradation.

The purpose of this study is to evaluate the performance of different types of solid acid catalysts in the catalytic degradation of polypropylene. Special emphasis has been placed

on a natural zeolite native to the Youngil area of Korea [Ha, 1987; Hwang et al., 1990].

EXPERIMENTAL

1. Material and Catalyst

Polypropylene (PP), in powder form, was obtained from Honam Petrochemical Co. (Yeacheon, Korea). Several types of solid acid catalysts, such as silica-alumina (grade135, Aldrich), ZSM-5 (JRC-Z5-27), Y zeolite (JRC-Z-Y 4.8), Mordenite (JRC-Z-M20), and natural zeolite (NZ) were evaluated through a catalyst screening test. Some of the catalysts were ion-exchanged three consecutive times with 1 M NH_4Cl for 20 h. The zeolites exchanged with NH_4^+ were dried at 110 for 16 h and calcined in air at 400 for 4 h to obtain the proton (H^+)-exchanged zeolite.

2. Apparatus and Procedure

The catalytic degradation of PP was carried out in a semi-batch reactor where nitrogen is continuously passed with a flow rate of 20 ml/min. The blending of the PP and the catalyst was performed in a ball mill. The catalyst concentration was 10 wt%. Samples were placed in a Pyrex vessel of 30 ml and heated, at the desired temperature, in the range of 300-450 °C. The distillate from the reactor was collected in a cold trap, usually over a period of 0.5-2 h.

3. Analysis

The degradation of the PP gave off gases, liquids and residues. The gases were analyzed by an on-line GC (HP 5890) with a Porapak Q column. The condensed liquid samples were analyzed by GC-MS (HP-5MS) with a capillary column. The physical properties and the composition of some of the liquids were also measured by a PONA analyzer (HP PONA). The acidic properties of the catalyst were determined by a con-

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ventional temperature programmed desorption (TPD) experiment of ammonia in the temperature range of 373 to 873 K at a constant heating rate of 5 K/min.

RESULTS AND DISCUSSIONS

1. Mass Balance in the Catalytic Degradation of PP

PP, alone or mixed with catalysts (silica-alumina, ZSM-5, Y-zeolite, Mordenite, natural zeolite), was degraded at 350, 400 and 450 °C. Table 1 lists the gaseous and liquid products and the residue from the degradation. After thermal degradation a large amount of residue was obtained. All the catalysts used showed less amount of residue than thermal degradation. ZSM-5, silica-alumina and natural zeolite (NZ) had practically no residue after catalytic degradation for 2 h above 400 °C. ZSM-5 and HZSM-5 catalysts produced much greater amount of gaseous product than any other catalysts. It is generally known that the pore structures in the zeolite can affect product distribution [Songip et al., 1993]. ZSM catalyst has MFI structure with intersecting $5.4 \times 5.6 \text{ \AA}$ and $5.1 \times$

5.5 \AA channels [Mordi et al., 1992]. Therefore, the initially cracked fragments can diffuse through the pore of ZSM and react further in the cavities created at the intersection of the two channels. Mordenite having one dimensional $6.1 \times 7.0 \text{ \AA}$ channels exhibited lower catalytic activity than ZSM catalyst. The natural zeolite is a silica-rich member of the heulandite family. Its pore structure is characterized by two main channels parallel to the c-direction, one formed by a 10-member ring ($7.6 \times 3.0 \text{ \AA}$) and the other by an eight-member ring ($3.3 \times 4.6 \text{ \AA}$) [Woo et al., 1996].

The proton exchanged zeolites such as HZSM-5, Z-HM20 and HNZ were more effective in the catalytic degradation of PP than their Na-form. Fig. 1 shows the TPD spectra of the natural zeolite used in this study. The area under the curves represents the total amount of desorbed ammonia molecules, which corresponds to the total amount of acid sites. The amount of desorbed ammonia molecules above 300 °C was regarded as that of strong acid sites of the catalysts [Woo et al., 1996]. The amount of total acid, especially that of strong acid, of HNZ was greater than Na-form natural zeolite. The

Table 1. Product distribution (wt%) in the catalytic degradation of PP

Catalyst	Gas (wt%)			Liquid (wt%)			Residue (wt%)		
	350 °C	400 °C	450 °C	350 °C	400 °C	450 °C	350 °C	400 °C	450 °C
NONE	6.7	13.7	16.2	9.0	75.3	81.1	84.3	11.0	2.8
ZSM-5	77.7	74.0	81.3	21.0	26.0	18.3	1.3	0	0.3
HZSM-5	79.3	66.7	69.3	18.1	33.3	30.7	2.7	0	0
SA	25.3	24.7	30.3	69.7	75.0	69.3	5.0	0.3	0.3
Z-Y4.8	13.0	27.0	21.3	20.7	68.3	78.7	66.3	4.6	0
Z-M20	5.3	19.0	23.0	3.7	25.0	77.0	91.0	56.0	0
Z-HM20	40.0	39.3	54.7	21.7	59.3	45.0	38.3	1.3	0.3
NZ	28.3	31.0	32.0	39.3	68.3	68.0	32.3	0.7	0
HNZ	30.3	25.7	24.3	51.0	74.3	75.7	18.7	0	0

(PP=3 g, Catalyst=0.3 g, Time=120 min)

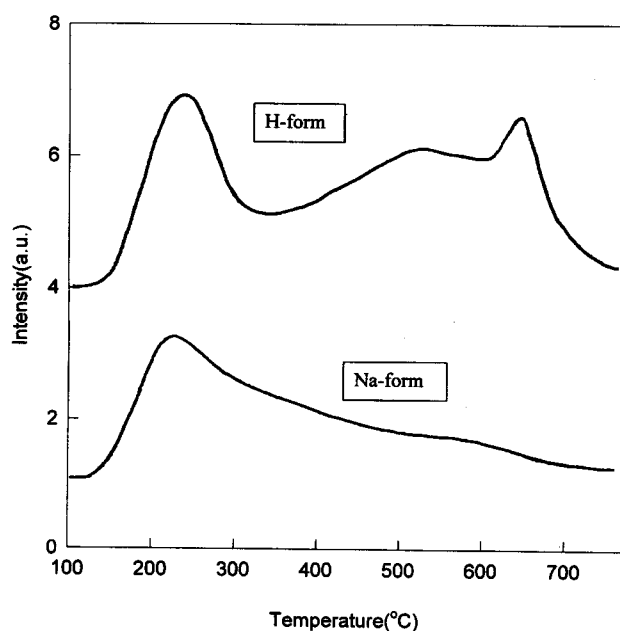


Fig. 1. TPD chromatograms of NH_3 on the clinoptilolite zeolite.

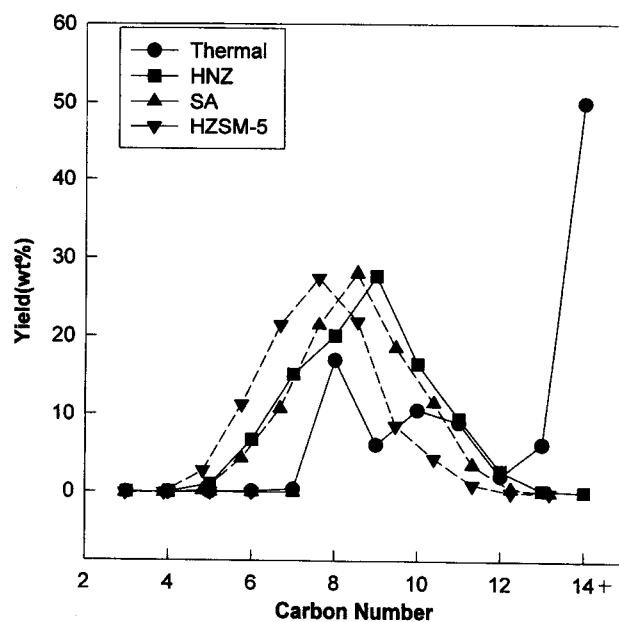


Fig. 2. Product distribution of liquid formed in degradation of PP at 400 °C.

Table 2. Distribution of liquid product in catalytic degradation of PP at 400 °C

Catalyst	n-Paraffin	i-Paraffin	Olefin	Naphthene	Aromatic	RON ^(a)
SA	0.9	21.1	45.7	9.6	22.7	90.4
HZSM-5	2.7	9.7	36.6	6.9	44.1	94.3
HNZ	3.1	15.9	47.9	12.7	20.4	90.3

(a) RON: research octane number [Lovasic et al., 1990]

acidic property of catalyst is known to be closely related to the catalytic activity of the degradation of polypropylene [Lovasic et al., 1990]. It is interesting to note that natural zeolite (HNZ), abundant and easily available in Korea, showed almost the same distribution of gaseous and liquid products as silica-alumina. This natural zeolite has been used for the first time in the catalytic degradation of polypropylene. Therefore, for the purpose of its commercial use, special emphasis was placed on the HNZ in the following experiments.

2. Composition of Liquid Products

In Fig. 2 the distribution of liquid products obtained by catalytic degradation is compared with that obtained by thermal degradation. There is a clear difference between the products of thermal and catalytic (HZSM-5, HNZ, SA) degradation. HZSM-5 and HNZ catalysts remarkably accelerated the degradation of polypropylene, and the relative yield of C₃-C₈ fraction was greater than 40 %. Thermal degradation products were distributed over a wide range of carbon number from C₃ to C₂₆ or higher. The weight percent in Fig. 2 at C₁₄₊ for the thermal degradation means the sum of weight % for all the liquid product which has carbon number of over C₁₄.

It is known that thermal degradation occurs by radical mechanism and offers many oligomers by hydrogen transfer from tertiary carbon atoms along the polymer chain to the radical site [Audisio et al., 1984]. However, catalytic degradation generally takes place by an ionic mechanism and produces various isomers [Audisio et al., 1984]. Table 2 shows product distribution of liquids for SA, HZSM-5 and HNZ at 400 °C for 2 h of degradation. Liquid products from catalytic degradation of polypropylene contained a large amount of iso-paraffines and aromatics which constitute the gasoline fraction. The formation of gasoline fraction seems to be advantageous for a utilization of the products. Among the catalysts tested HZSM-5 produced the highest amount of aromatics and the least amount of olefins. SA and HNZ showed about the same distribution of paraffines, olefins, naphthenes and aromatics. The unsaturated structures are principally of aromatic type in case of degradation over HZSM-5, and of an olefinic type for SA and HNZ catalysts. This fact is in good accordance with the results of Vasile et al. [Vasile et al., 1988]. HZSM-5 is well known to have high selectivity for the transformation of n-alkanes due to the steric effect and for the aromatization processes [Vasile et al., 1984]. Therefore, it can be assumed that

Table 3. Composition of aromatics formed at 400 °C for 2 h

Aromatics	SA	HZSM-5	HNZ
Benzene	2.7	2.2	3.8
Toluene	0	18.9	0
Ethylbenzene	11.9	5.0	13.0
Xylenes	14.0	35.2	14.8
Ethyltoluenes	39.4	23.3	38.4
Trimethylbenzene	21.3	13.0	18.9
Tetramethylbenzenes	6.1	0.5	7.3
C ₁₀ Aromatics	4.4	1.4	3.2
Methyl naphthalene	0.1	0.1	0.6
Dimethyl naphthalenes	0		0

HZSM-5 accelerates aromatization via dehydrocyclization compared to olefin formation. SA and HNZ preferentially increase iso-paraffine formation and hydrogenation of olefins by hydrogen transfer.

Detailed composition of aromatics in relative weight percent is shown in Table 3. C₁₀ and higher aromatics were obtained only in limited amounts. Therefore, it is reasonable to assume that aromatics were mainly formed by the dehydrocyclization of the C₆-C₉ decomposed fragments such as mono- and di-methyl alkane and their unsaturated derivatives. Demethylation of tri-methyl benzene is known to occur on the metal-free catalyst [Uemichi et al., 1985]. Main aromatic products varied with the type of catalysts. SA produced mainly ethyltoluene, trimethylbenzene and xylene. Xylene, ethyltoluene and toluene were the main aromatics for HZSM-5. HNZ did not produce toluene like SA. The amount of aromatics in HNZ decreased as ethyltoluene > trimethylbenzene > xylene. At the present stage of this study, however, a detailed mechanism is not clear. All the three catalysts showed higher than a 90 research octane number (RON). The research octane number (RON) was used as an index of the quality of the liquid products. The higher the octane number, the higher the tendency for the liquid to burn evenly and completely. This value was calculated according to the method proposed by Lovasic and coworkers [Lovasic et al., 1990].

3. Effect of Reaction Temperature

The effects of reaction temperature over HNZ catalysts were studied at 350, 400, 450 °C. Table 4 shows the distribution of liquid product for 2 h of degradation. When the reaction tem-

Table 4. Effects of reaction temperature on product composition for HNZ catalyst

Temp. (°C)	n-Paraffin	i-Paraffin	Olefin	Naphthene	Aromatic	RON
350	0.8	22.3	41.8	10.2	25.0	90.2
400	3.1	15.9	47.9	12.7	20.4	90.3
450	0.9	18.6	51.4	10.2	18.9	91.0

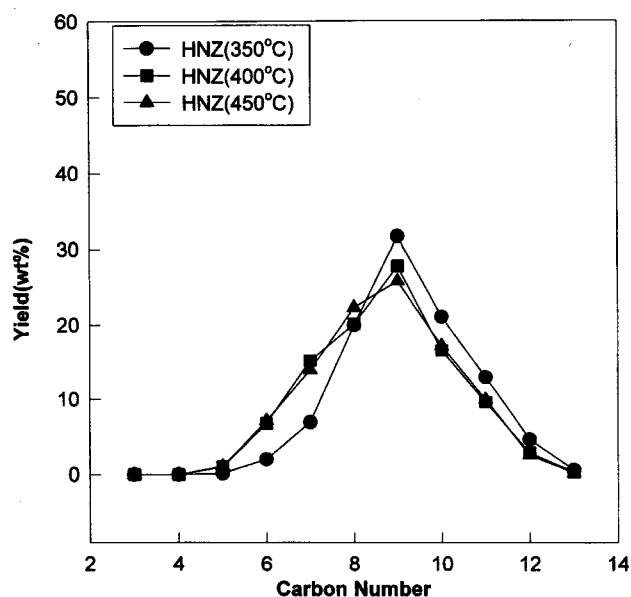


Fig. 3. Product distribution of liquid formed in degradation of PP over HNZ.

perature increased, the amount of aromatics and iso-paraffines was decreased, and that of olefins was increased. As shown in Fig. 3, the distribution of liquid product shifted to a lower number of carbon atoms with an increase of the temperature. The range of carbon atoms remained in a narrow range, from C_5 to C_{12} . The RON value was maintained nearly constant with temperature. One can see that high temperature was unfavorable for the cyclization and aromatization of unsaturated degradation fragments, even though it accelerates further degradation to lighter hydrocarbons.

4. Effect of Reaction Time

The effects of reaction time on the composition of the liquid products obtained over natural zeolite (HNZ) are shown in Table 5. A longer reaction time promoted further degradations of liquid fractions to give a small increase in the relative yield of gaseous fraction. The further degradation would be attributed to those of linear aliphatic hydrocarbons. Naphthenes and aromatics would hardly undergo further degradation because of their greater stability compared to linear aliphatic hydrocarbons. Therefore, the increase in the weight percent of naphthenes and aromatics in the liquid products, with the increase of reaction time, would be a reasonable result.

Product distribution in carbon number with different reaction time is shown in Table 6. The distribution of the prod-

Table 5. Distribution of liquid products at different reaction times

Product distribution	Reaction time		
	30 min	60 min	120 min
n-Paraffins	0.8	0.9	3.1
iso-Paraffins	18.5	18.3	15.9
Olefins	53.0	52.2	47.9
Naphthenes	8.9	9.4	12.7
Aromatics	18.8	19.2	20.4

(Catalyst=HNZ, T=400 °C)

Table 6. Distribution of carbon number at different reaction times

Carbon number	Reaction time		
	30 min	60 min	120 min
C-3	0	0	0
C-4	0.1	0.0	0
C-5	3.0	2.1	1.0
C-6	9.1	8.2	6.8
C-7	13.8	14.3	15.4
C-8	22.0	21.7	20.2
C-9	25.1	26.0	27.5
C-10	14.6	15.3	16.4
C-11	9.4	9.6	9.5
C-12	2.7	2.5	2.9
C-13	0.3	0.3	0.3

(Catalyst=HNZ, T=400 °C)

ucts shifted slightly to higher carbon numbers with increasing reaction time. This may be due to progressive deactivation of HNZ catalyst. Uemichi et al. [Uemichi et al., 1983] studied the deactivation kinetics of silica-alumina and CaX zeolite catalyst used in a continuous flow reactor where PP and catalyst are separated. They reported about 10-15 % of coke deposition after 3 h of PP degradation. Table 6 shows that even after 2 h, however, the products are concentrated on small carbon numbers. Therefore, the deactivation of HNZ catalyst was not so severe that it could be a good candidate for the catalytic degradation of polypropylene.

CONCLUSION

The silica-alumina, HZSM-5, and HNZ are efficient catalysts for the conversion of polypropylene to gasoline range chemicals. Among these catalysts used, HZSM-5 produced the highest amount of aromatics. SA and HNZ showed higher quantity of iso-paraffines and olefins than HZSM-5. The clinoptilolite type natural zeolite, abundant near to Pohang in Korea, could be a good candidate for its commercial application in the degradation of polypropylene. Further detailed kinetic studies would be necessary for a better understanding of the degradation mechanism and design of catalyst for proper uses of degraded products.

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