

점토광물에 의한 폴리프로필렌의 촉매분해

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Catalytic Degradation of Polypropylene using Clay Materials

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Introduction

Polymer wastes can cause serious pollution problems. Until recently, they have usually been discharged or incinerated. However, waste plastics, especially thermoplastics, can be regarded as being an abundant source of chemicals and energy. Furthermore, recycling of thermoplastics from waste products can contribute to the solution of pollution problems. Though several methods have been proposed for recycling of 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. One approach to chemical recovery 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 sources in fuels or chemicals [1].

In the thermal degradation of polyolefins, many hydrocarbons having a wide 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. Also, compared to thermal degradation, catalytic degradation has an advantage of a lower temperature of degradation. An excellent summary on the catalytic recycle of polymers was reported by Uemichi [2]. The most commonly used catalysts in the catalytic degradation of polymers are solid acids (zeolite, silica-alumina) and activated carbon.

However, very few works have been performed on the investigation of clay material and clinoptilolite as a catalyst for this process. Clinoptilolite has a pore structure of a monoclinic framework consisting of a 10-membered ring ($7.6 \times 3.0 \text{ \AA}$) and an 8-membered ring ($3.3 \times 4.6 \text{ \AA}$), and is a silica-rich member of the heulandite family. Halloysite, montmorillonite and pyrophyllite are clay materials having pore size of $7 \sim 40 \text{ \AA}$.

The objective of this study is to examine the performance of the natural zeolite and clay materials in the catalytic degradation of PP.

Experimental

Polypropylene (PP), in powder form, is an isotactic sample obtained by Honam Petrochemical Co. (in Yeacheon, Korea) as grade FC-150 (Melt Index=8.0g/10min, Density=0.90 g/cm³) with an average molecular weight (Mw) of 329700 and Mn=54300. The plastic samples of 60-150 mesh size were used for this study. Several types of solid acid catalysts such as natural halloysite (NH; $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$: 75~95 wt.%, Illite 5~20 wt.%, Kaolinite 0~5 wt.%, occurring in South-East area of Korea), natural clinoptilolite zeolite (NZ; occurring in Pohang area of Korea), prophyllite (NP; occurring in South-East area), montmorillonite (K30; reagent of Fluka) were evaluated through the degradation experiments of PP. NH, NP, K30 and NZ were ion-exchanged three consecutive times with

1M NH_4Cl solution at 70~80 °C for 20 h. The catalysts exchanged with NH_4^{4+} were dried at 125 °C for overnight, and then calcined in air at 500 °C to obtain the proton(H^+)-exchanged catalysts like HH, HP, HK30 and HNZ.

The catalytic degradation of the plastics was carried out in a semi-batch reactor where nitrogen is continuously passed with a flow rate of 30 mL/min. A mixture of 3.0 g of the plastics and 0.3 g of the catalyst was loaded inside a pyrex vessel of 30 mL and heated at a rate of 30 °C/min up to the desired temperature. The distillate from the reactor was collected in a cold trap (-10 °C) over a period of 2 h. The degradation of the plastic gave off gases, liquids and residues. The residue means the carbonaceous compounds remaining in the reactor and deposited on the wall of the reactor. The amount of coke deposit on the catalyst was calculated by measuring the desorbed amount of carbon dioxide during temperature programmed oxidation of used catalysts. 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 (Micromass Co., Auto spec.) with a capillary column (HP-5MS) and GC (HP6890) with a capillary column (HP-1MS). The physical properties and the composition of the liquids were also measured by a PONA (Paraffins-Olefins-Naphthenes-Aromatics) analyzer (DHA 2520).

Results and Discussion

First, chemical composition and physical properties of zeolite and clay minerals are presented in Table 1. Table 2 lists the gaseous, liquid products, and residues obtained in the thermal and catalytic degradation of PP at 400 °C for 2 h. The amount of gaseous products was calculated by subtracting the weight of liquid products, residues and catalyst from the total weight of PP sample and fresh catalyst initially loaded to the reactor. The residue means the wax-like material collected in the reactor and pipe wall, and its amount was measured by dissolving it with n-hexane. When the catalyst was used, liquid yield increased approximately 10 wt.%. We also observed the formation of carbon deposit (coke) on the used catalyst. The main degradation product was liquid oil. The analysis of gaseous products in this experiment showed the following relative amounts of each component; ethane (6.6 wt.%), propylene (29.7 wt.%), propane (5.3 wt.%), butene (46.6 wt.%), butane (7.5 wt.%) and pentane (4.3 wt.%).

Table 3 shows product distribution and physical properties of liquids for various catalysts at 400 °C for 2 h of PP degradation. Liquid products from catalytic degradation of PP contained quite a large amount of iso-paraffins, olefins, and aromatics, which constitute gasoline fraction. The formation of gasoline fraction seems to be advantageous for the utilization of the liquid products. The liquid products over NZ had much lower amount of olefins than HNZ. Therefore, the oligomers found in the case of NZ can be considered to be cracked mainly to olefins and iso-paraffin in the PP degradation over the HNZ.

Table 4 shows the distribution of aromatics products for the hydrocarbons of $\text{C}_6\text{--C}_{13}$. Clay materials generated the aromatics of higher molecular weight than zeolite. The aromatics from the thermal degradation contained somewhat higher amount of high carbon number aromatics, such as dimethylethylbenzene. However, for HNZ and NZ catalysts tested, the amount of ethyltoluene was the highest. The amount of aromatics in HNZ decreased as ethyltoluene > propylbenzene > trimethylbenzene. Thermal degradation showed C_{11} and higher aromatics were produced only in limited amounts except HH catalyst. Therefore, one can assume that aromatics were mainly formed by the dehydrocyclization of the C_6 to C_{10} decomposed fragments, which were mainly alkylpentane, alkylhexane, alkylheptane, and their unsaturated derivatives. Aromatics can also be produced by the dealkylation of higher carbon number

aromatics. However, this step is presumed to be multi-stage reactions consisting of dehydrocyclization to five-membered ring compounds and their ring expansion [3].

It is well known that acidic property is necessary to form the carbenium ion for the catalytic degradation of PP. The distribution of liquid products for the protonated catalysts shifted to lower carbon number hydrocarbons and lighter aromatics are produced with these catalysts. From this fact, it may be concluded that the catalytic degradation of PP did not only depend on the proper distribution of acid sites but also on the pore structure. The work of Sakata et al. [4] supports this supposition. They reported high degradation acidity of a mesoporous silica (KFS-16), which was comparable to that of silica-alumina, even though KFS-16 had no acidic site at all on the surface. High degradation temperature offered lighter hydrocarbons by accelerating the cracking reactions.

Acknowledgement

The authors wish to acknowledge the financial support of the Korea Science and Engineering Foundation (R02-2000-00336).

References

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Table 1. Physical properties of catalysts used in this study.

Sample Name	Mineral Type	Fomular	Pore/Layer Size (Å)	S _{BET} (m ² /g)
HNZ	Clinoptilolite/Zeolite	Ca ₄ [Al ₈ Si ₂₈ O ₇₂]·24H ₂ O	7.6×3.0	271
			3.3×4.6	
HH	Halloysite/Clay	Al ₂ O ₃ ·2SiO ₂ ·4H ₂ O	7~10	27
HP	Pyrophyllite/Clay	Al ₂ O ₃ ·4SiO ₂ ·6H ₂ O	10~20	20
K30	Montmorillonite/Clay	Al ₂ O ₃ ·4SiO ₂ ·6H ₂ O	14~40	330

Table 2. Yield (wt.%) of product in the catalytic degradation of PP at 400 °C for 2 h.

Catalyst	Gas (wt.%)	Liquid (wt.%)	Residue (wt.%)	Coke (wt.%)
None	13.7	75.3	11.0	-
None(450 °C)	20.7	77.5	1.8	-
NZ	10.9	87.4	0.83	0.89
HNZ	13.8	84.3	0.33	1.6
NH	11.9	86.4	1.2	0.50
HH	10.4	88.2	1.2	0.20
K30	13.0	85.6	0.88	0.49
HK30	14.1	84.7	0.54	0.69
NP	10.0	74.3	4.9	0.80
HP	16.3	81.7	1.6	0.32

Table 3. Distribution (wt.%) of liquid product in the catalytic degradation of PP at 400 °C for 2 h.

Catalyst	n-paraffins	iso-paraffins	olefins	naphthenes	aromatics	RON
NZ	1.0	22.70	37.89	10.38	27.96	90
HNZ	0.62	18.86	51.0	9.78	19.74	91
NH	2.30	22.28	47.85	8.08	19.48	91
HH	2.71	15.99	53.61	10.57	17.11	90
K30	2.34	14.17	62.69	8.12	12.68	91
HK30	1.63	17.34	59.0	8.93	13.09	91
NP	3.67	16.39	46.36	17.40	16.18	90
HP	3.20	17.67	48.43	10.14	20.55	90

Table 4. Composition of major aromatics (wt.%) formed in the degradation of PP at 400 °C for 2 h.

Aromatics	Thermal	HNZ	HH	HK30	HP
Benzene	0	2.22	3.75	4.13	6.38
Toluene	0.29	0	1.10	8.14	5.18
Ethylbenzene	21.68	7.61	9.10	16.96	8.56
Xylenes	2.59	8.69	12.71	9.82	13.52
Propylbenzene	9.43	14.88	6.98	5.94	3.84
Ethyltoluene	1.22	22.5	8.74	12.52	11.85
Trimethylbenzene	0.67	11.06	9.62	8.65	11.42
Butylbenzene	0	3.47	0.64	2.21	2.47
Methylpropylbenzene	1	9.84	13.78	8.56	7.48
Diethylbenzene	0.75	4.76	8.53	4.61	9.23
Dimethylethylbenzene	53.68	8.42	16.86	7.88	14.19
Tetramethylbenzenes	1.88	4.3	3.26	4.08	3.71
Methylindan	2.07	1.85	2.65	5.21	1.09
Naphthalene	4.76	0.37	2.26	1.29	1.08