

## 점토광물을 이용한 폴리스티렌의 분해

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### Performance of Clays in Catalytic Degradation of Polystyrene

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#### INTRODUCTION

Recycling of polymer wastes can contribute to the solution of pollution problems and the reuse of cheap and abundant source of chemicals. 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 degradation temperature. 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 [3-5].

Natural untreated clays possess a very low ability to catalyze reactions in either polar or non-polar media. However, the structural properties of these materials can be modified by various activation methods in order to produce catalysts with high acidity, surface area, porosity and thermal stability.

Several solid acids such as clay materials (Halloysite, Pyrophyllite, Montmorillonite K-30, Albite) are screened for their performances in the catalytic degradation of polystyrene. We investigated the catalytic degradation of polystyrene in a semi-batch reactor with a mixture of polystyrene and catalysts

at 400~450°C. The catalysts showed good catalytic activity for the degradation of PS with high selectivity to aromatics liquids. Styrene is the major product in the liquid product. The objective of this study is to compare the catalytic property of the clay materials.

## **EXPERIMENTAL**

PS, in powder form, was supplied by LG Chemical Co. (Grade 50IS, Mn=98000-99000, melt index=7.5 g/10 min, density=1.03 g/cm<sup>3</sup>). Several types of solid acid catalysts such as natural halloysite (NH; Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·4H<sub>2</sub>O) and pyrophyllite (NP; Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>), occurring in south-east area of Korea, montmorillonite (K-30; reagent of Fluka) and albite (NA; Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·6SiO<sub>2</sub>, occurring in Buyeo area of Korea) were evaluated through the degradation experiments of PS. NH, NP and NA were ion-exchanged three consecutive times with 1M NH<sub>4</sub>Cl solution at 70~80°C for 20 h. The catalysts exchanged with NH<sub>4</sub><sup>+</sup> were dried at 120°C overnight, and then calcined in air at 500°C to obtain the proton(H<sup>+</sup>)-exchanged catalysts like HH, HP and HA.

The catalytic degradation of PS 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 PS 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 condensed liquid samples were analyzed by a GC (HP6890) with a capillary column (HP-PONA).

## **RESULTS AND DISCUSSION**

Table 1 shows chemical compositions of clay catalysts measured by XRF analysis. SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are main components of the four clay catalysts with minor amount of Na<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub> and others. The Si/Al ratio increased from HH <HP <HA <K-30. Table 2 lists the gaseous, liquid products, and residues obtained in the catalytic degradation of PS 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 PS 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. In all cases, the liquid oils were main products. The effect of temperature on the PS degradation was studied using HH, HP, K-30 and HA catalysts. Table 3 shows the mass balance in product distribution. As the temperature increased the amount of liquid products increased, while that of the residues decreased.

Composition of some major liquids products, formed in the degradation of PS at 400 °C for 2 h is

presented in Table 4. The catalytic degradation over HA exhibited the highest selectivity of styrene(65.67%) and the lowest selectivity of ethylbenzene(7.33%) and benzene(0.14%) compared to the degraded aromatic products with HH(styrene 56.79%, ethylbenzene 13.27%), HP(styrene 58.80%, ethylbenzene 12.37%) and K-30(styrene 43.52%, ethylbenzene 21.10%). One can also see that the amount of styrene dimer and trimer of HA is the lowest among the four clay catalysts. The increase of pore volume and specific surface area resulted in an increase of ethylbenzene and a decrease of styrene. The large pore may be considered to facilitate the hydrogenation of styrene fragment to produce ethylbenzene [6]. When the degradation temperature increased from 400 to 450°C, the production of styrene increased, but that of ethylbenzene decreased.

Table 1. Chemical compositions of clay catalysts.

Catalyst	Composition (wt. %)						Total	Si/Al ratio
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	Others	LOI		
HH	53.3	33.7	1.4	0.9	4.4	6.0	99.7	2.7
HP	74.3	21.1	0.1	0.3	1.8	2.0	99.6	6.0
K-30	78.0	10.5	0.2	2.2	2.3	5.9	99.1	12.7
HA	73.4	14.4	6.3	0.0	3.9	1.7	99.7	8.6

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

Catalyst	Gas (wt.%)	Liquid (wt.%)	Residue (wt.%)
HH	9.1	78.3	12.6
HP	5.1	78.5	16.4
K-30	10.2	79.0	10.8
HA	10.6	78.2	11.2

Table 3. Effect of temperature on the yield of product (wt.%) in the catalytic degradation of PS for 2 h.

Catalyst	Temperature	Product(wt.%)		
		Gases	Liquids	Residues
HH	400°C	9.1	78.3	12.6
	425°C	7.6	82.2	10.2
	450°C	4.8	90.2	5.0
HP	400°C	5.1	78.5	16.4
	425°C	6.7	83.8	9.5
	450°C	5.9	88.3	5.8
K-30	400°C	10.2	79.0	10.8
	425°C	9.7	83.2	7.1
	450°C	1.0	94.5	4.5
HA	400°C	10.6	78.2	11.2
	425°C	8.0	82.1	9.9
	450°C	4.8	88.8	6.4

Table 4. Selectivity of some major products formed in the degradation of PS at 400°C for 2 h.

Aromatics	HH	HP	K-30	HA
Benzene	0.21	0.15	2.99	0.14
Toluene	8.35	8.12	8.22	10.23
Ethylbenzene	13.27	12.37	21.10	7.33
Styrene	56.79	58.80	43.52	65.67
<i>iso</i> -Propylbenzene	2.65	2.64	5.02	1.36
$\alpha$ -Methylstyrene	9.60	9.69	8.59	9.76
<i>n</i> -Propylbenzene	0.14	0.14	0.17	0.14
Others <sup>a</sup>	0.65	0.63	1.34	0.96
C <sub>11</sub> -C <sub>15</sub>	1.08	0.76	2.81	0.60
C <sub>16</sub> -C <sub>21</sub>	6.53	6.41	6.12	3.09
C <sub>22</sub> -C <sub>30</sub>	0.73	0.29	0.12	0.72

<sup>a</sup> Other aromatic compounds having C<sub>5</sub>-C<sub>10</sub>

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### **REFERENCES**

1. H. Ohkita, R. Nishiyama, T. Tochiyama, T. Mizushima, *Ind. Eng. Chem. Res.*, **32(12)**, 3112 (1993).
2. Y. Uemichi, *Catalysis (Japan)*, **37(4)**, 286 (1995).
3. R.C. Mordi, R. Field, J. Dwyer, *J. Anal. Appl. Pyrol.*, **29**, 45 (1994).
4. G. Audisio, A. Silvani, P.L. Beltrame, P. Carniti, *J. Anal. Appl. Pyrol.*, **7**, 83 (1984).
5. P.L. Beltrame, P. Carniti, G. Audisio, F. Bertini, *Polym. Degrad. Stab.*, **26**, 209 (1989).
6. U. Flessner, D.J. Jones, J. Roziere, J. Zajac, L. Storaro, M. Lenarda, M. Pavan, A. Jimenez, E. Rodriguez-Castellon, M. Trombetta, G. Busca, *J. Mol. Catal. A.*, **168**, 247(2001).