

## 몬모릴로나이트 촉매를 이용한 폴리스티렌의 분해

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### Catalytic Degradation of Polystyrene Using Montmorillonite Clays

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#### Introduction

Waste plastics can be converted into fuel oils by thermal or catalytic process. The oils produced by catalytic degradation are known to contain a relatively narrow distribution of hydrocarbons, lower amount of olefins and higher amount of aromatics compared to the oils from the thermal degradation. An excellent summary of the catalytic recycling of polymers was reported by Uemichi[1]. In contrast to polyethylene (PE), polypropylene (PP) and polystyrene (PS) can be thermally depolymerized to obtain the styrene monomer with a high selectivity[2,3]. 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. Acid activation of clay minerals is one of the most effective method that has been used to produce active materials for adsorption and catalysis proposes[4,5]. Montmorillonite is a good example of natural clays. Acid-treated montmorillonites can be purchased from a variety of commercial sources.

In the present work, we investigated the performance of the K-series montmorillonite clays (K5, K10, K20, K30), purchased from Fluka AG, in the degradation of PS to fuel oils.

#### Experimental

K-montmorillonites are produced by Süd Chemie AG from raw clays of Bavaria, Germany, and laboratory quantities are commercially available from Fluka. Polystyrene (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>). PS samples of

60-150 mesh size were used for this study. 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 a desired temperature. The distillate from the reactor was collected in a cold trap (-5 °C) over a pre-determined time.

The composition of the K-montmorillonite was determined by a X-ray fluorescence analysis (Philips PW2400). The acidic properties of the catalysts were determined by a conventional temperature programmed desorption (TPD) experiment of ammonia in the temperature range of 373-973 K at a constant heating rate of 5 K/min. The specific surface area and pore size of the catalysts were measured by a BET apparatus (Micromeritics ASAP 2010). 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 a GC-MS (Micromass Co., Auto spec.) with a capillary column (HP-5MS).

### **Results and Discussion**

Table 1 shows chemical compositions of K-series catalysts measured by a X-ray fluorescence(XRF). Si/Al ratio increases from K5 to K30 due to the increase of the dealumination. The distribution of acid sites for the K-catalysts was studied by the chemisorption of ammonia from gas phase. In order to have more precise information on the acid sites, the TPD method developed by Niwa et al.[6] was applied to the catalysts. After adsorbing NH<sub>3</sub> at 100 °C on the cleaned surface, water vapor was injected to the K-catalysts and then evacuated to remove weakly-held ammonia which is known to be unnecessary to analyze the acidic property[7]. According to the NH<sub>3</sub>-TPD results, four K-catalysts had very similar acid site distributions : the maximum peak temperatures (T<sub>m</sub>) for the weak, medium, and strong acid sites were 150 °C, 400 °C, and 570 °C respectively. K5 showed the highest total amount of acid sites, especially it had the biggest strong acid sites. The other three K-catalysts showed about the same acid site distributions. Table 2 shows BET surface area, pore volume, and the amount of desorbed ammonia in TPD of the K-catalysts. Pore volume and BET surface area increased as K5 < K10 < K20 < K30. Taking into account of the surface area, the total acid sites per unit surface area decreased as K5 > K10 ~ K20 > K30.

PS was degraded in the presence of K-catalysts for 2 h. Table 3 lists the gases, liquids, residues and cokes on the catalyst from the degradation experiments. The amount of gases products was calculated by subtracting the sum of weights for liquids, residues and catalyst with coke from the total weight of PS sample and fresh catalyst initially loaded to the reactor. Carbonaceous compounds adhering to the reactor wall were dissolved in *n*-hexane and were measured as degradation residues. In all cases, the liquid oils were main products. Although the amount of acid sites of K5 was higher than that of K30, K5 showed higher amount of residue than K30 did at all the three temperatures. This could be explained by higher surface area and pore volume of K30 compared to K5. Large pores of K30 may facilitate the approach of the degraded fragments to the catalyst surface.

The production of liquid from PS degradation for K30 was faster than K5, probably due to higher pore volume of K30. Since aromatic hydrocarbons are main products, over 94 wt.% of the liquid products, they are analyzed in detail. Table 4 shows the distribution of aromatic components of the liquid products for K-catalysts at 450 °C for 2 h. The main product in C<sub>16</sub>-C<sub>21</sub> is styrene dimer(C<sub>16</sub>) and that in C<sub>22</sub>-C<sub>30</sub> is trimer(C<sub>24</sub>). All the catalysts showed over than 10 wt.% of styrene dimer. K5 produced the highest amount of styrene and the lowest amount of ethylbenzene among all the K-series catalysts. Styrene and ethylbenzene are known to be produced by different reaction pathway[3]. Compared to K5, large pore and surface area of K30 seems to promote the production of ethylbenzene.

In a separate experiment, thermal degradation of PS at 400 °C showed the highest amount of styrene (70.1 wt.%) and the lowest amount of ethylbenzene (8.8 wt.%). Thermal degradation of PS is known to start with a random initiation to form polymer radicals[8], the main products being styrene and its corresponding dimers and trimers. The acid catalyzed cracking of PS is of carbenium nature[9]. The most likely reaction pathway involves the attack of proton associated with a Brønsted acid site to the aromatic rings of PS, due to the reactivity of its side phenyl groups towards electrophilic reagents.

The effect of temperature on the PS degradation was also studied using K30. As shown in Table 3, when the temperature increased the amount of liquid product increased at the expense of the decrease of residue.

### **Acknowledgement**

This work is financially supported by the Ministry of Education and Human Resources Development(MOE) and the Ministry of Commerce, Industry and Energy(MOCIE) through the fostering project of the Industrial-Academic Cooperation Centered University.

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

Sample	Composition (wt.%)							Si/Al ratio <sup>a</sup>
	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 <sup>b</sup>	Total	
K5	64.2	18.1	0.11	3.73	3.30	10.2	99.8	6.01
K10	72.8	14.0	0.35	2.34	3.75	6.22	99.8	8.85
K20	74.9	13.2	0.22	2.40	2.92	6.13	99.7	9.66
K30	76.2	10.3	0.09	1.88	2.23	8.90	99.6	12.57

a : Silica / alumina molar ratio

b : loss on ignition

Table 2. BET surface area, pore volume, and the amounts of desorbed ammonia in TPD

Catalyst	BET area(m <sup>2</sup> /g)	Pore volume(cm <sup>3</sup> /g)	Temperature range			Total amounts
			100-300 °C	300-500 °C	500-800 °C	
K5	200	0.65	4.99E+05	5.67E+05	9.39E+05	20.1E+05
K10	220	0.93	4.08E+05	4.18E+05	8.97E+05	17.2E+05
K20	240	1.05	4.21E+05	4.60E+05	8.31E+05	17.1E+05
K30	330	1.23	4.67E+05	5.34E+05	8.55E+05	18.6E+05

Table 3. Yield(wt.%) of product in the catalytic degradation of PS at 400-450 °C for 2 h

Catalyst	Temperature (°C)	Product (wt.%)			
		Gases	Liquids	Residues	Cokes
K5	400	7.9	78.2	10.2	3.7
	425	7.8	82.1	8.0	2.1
	450	2.6	91.0	5.2	1.2
K10	400	8.6	78.8	9.5	3.1
	425	10.6	82.4	5.5	1.5
	450	2.7	91.3	4.9	1.1
K20	400	8.4	79.2	9.4	3.0
	425	8.7	83.5	6.2	1.6
	450	2.5	91.5	4.9	1.1
K30	400	10.2	79.0	8.4	2.4
	425	9.7	83.2	5.6	1.5
	450	1.0	94.5	3.6	0.9

Table 4. Distribution of major aromatics (wt.%) formed in the catalytic degradation of PS with different montmorillonite catalysts at 450 °C for 2 h

Aromatics	K5	K10	K20	K30
Benzene	1.25	1.81	2.51	2.72
Toluene	7.4	7.36	6.83	6.36
Ethylbenzene	10.88	12.09	12.22	12.69
Styrene	55.0	53.01	52.90	51.07
<i>iso</i> -Propylbenzene	1.87	2.49	2.25	2.30
$\alpha$ -Methylstyrene	7.31	7.37	6.85	6.27
<i>n</i> -propylbenzene	0.14	0.14	0.14	0.15
Others <sup>a</sup>	0.92	1.54	2.03	2.12
C <sub>11</sub> -C <sub>15</sub>	1.5	1.60	1.85	1.9
C <sub>16</sub> -C <sub>21</sub>	12.25	11.32	10.94	12.81
C <sub>22</sub> -C <sub>30</sub>	1.43	1.22	1.42	1.56

a : C<sub>5</sub>-C<sub>10</sub>