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### Catalytic Degradation of Polystyrene Using Acid-Treated Halloysite Clays

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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].

Thermal degradation of waste plastics into fuel oils was studied extensively, but the oils obtained showed a wide-ranged distribution of carbon atom numbers and contained a significant fraction of olefins [2-4]. The olefins are not favorable for fuel oils because these are easily polymerized into unusable compounds during storage and transportation. In contrast, 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 [2]. The most commonly used catalysts in the catalytic degradation of polymers are solid acids and bases [3-8].

Plastic wastes for the catalytic degradation processes are mainly limited to polyolefinic wastes (polyethylene and polypropylene) and polystyrene (PS). In contrast to polyethylene and polypropylene, PS can be thermally depolymerized to obtain the monomer styrene with a high selectivity.

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. Montmorillonite and halloysite are good examples of natural clays. Compared to the montmorillonite, halloysite is less studied in the field of

catalysis. Halloysite is a kaolinite family and it has a composition of  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . In the present work, we investigated the performance of halloysite clay in the degradation of polystyrene to fuel oils. Special focus of this study will be placed on the effect of acid treatment of the clay on the distribution of liquid hydrocarbon products.

### **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>). PS samples of 60-150 mesh size were used for this study. The Na-form of the halloysite( $\text{NH}:\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ ) was ion-exchanged three consecutive times with 1 M  $\text{NH}_4\text{Cl}$  solution at 70-80 °C for 20 h. The halloysite exchanged with  $\text{NH}_4^+$  was filtered washed several times with distilled water, dried at 120 °C for overnight, and then calcined in air at 400 °C for 4 h. By this procedure the proton ( $\text{H}^+$ )-exchanged form halloysite HH was prepared. In order to modify the acidity of HH, it was refluxed with 1 M, 2 M, 3 M or 4 M hydrochloric acid solution at 80 °C for 24 h, and the catalysts were denoted as 1NHH, 2NHH, 3NHH, and 4NHH, respectively.

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-1MS).

### **Results and Discussion**

The chemical composition of all the catalysts are reported in Table 1.  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are main components of the halloysite catalysts with minor amount of  $\text{Na}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$  and others. As the HCl concentration increased, the ratio of Si/Al increased due to dealumination. Si/Al ratio of 4NHH was as high as 22.6. And as the severity of acid treatment increases from HH to 3NHH, pore volumes and surface area increase. However, 4NHH shows lower pore volume and surface area than 3NHH probably due to a partial destruction of active sites.

PS was degraded in the presence of various acid-treated halloysite catalysts at 400 °C for 2 h. Table 2 lists the gases, liquids, residues on the catalyst from the degradation experiment. 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. The amount of residue decreased and the amount of the liquid increased as the HCl concentration increased. However, 3NHH and 4NHH showed about the same amount of residue. Since aromatic hydrocarbons are main products, over 96 wt.% of the liquid products, they are identified in detail in Table 3. 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>25</sub>). Thermal degradation shows the highest amount of styrene (70.1 wt.%) and the lowest amount of ethylbenzene (8.8 wt.%). Thermal degradation of PS starts with a random initiation to form polymer radicals [9], the main products being styrene and its corresponding dimers and trimers. HH catalyst shows 56.50 wt.% of styrene, 14.32 wt.% of ethylbenzene, and 10.70 wt.% of  $\alpha$ -methylstyrene. The increase of HCl concentration resulted in an increase of ethylbenzene and a decrease of styrene. Since the specific surface area, pore volume, and weak acidic sites increased from 1NHH to 3NHH, the production of ethylbenzene seems to be related with these acidic surface areas.

The acid catalyzed cracking of PS is of carbenium nature [10]. 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 resulting carbenium may undergo  $\beta$ -scission followed by a hydrogen transfer. The possible production pathways of benzene, styrene, methlstyrene, toluene, ethylbenzene, isopropylbenzene and indane derivatives are reported by Audisio et al. [11]. From this fact, it may be concluded that the catalytic degradation of PS did not only depend on the proper distribution of acid sites but also on the pore structure.

The Halloysite catalysts showed good catalytic performance for the degradation of PS with selectivity to aromatics over than 99%. Styrene is the major product, and ethylbenzene is the second abundant one in the liquid product. The increase of acidity favored the production of ethylbenzene by promoting hydrogenation reaction of styrene. Therefore, a designed operation including acidity of catalyst will be necessary to control the product distribution between styrene monomer and ethylbenzene.

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Table 1. Chemical composition of dealuminated halloysite.

Sample	Composition (wt.%)							Si/Al <sup>a</sup> ratio	Total pore volume <sup>b</sup> (cm <sup>3</sup> /g)	BET surf. area (cm <sup>2</sup> /g)
	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	Total			
HH	53.3	33.7	1.4	0.9	4.4	6.0	99.7	2.7	0.143	27
1NHH	66.5	24.8	1.5	1.0	4.7	0.1	98.4	4.6	0.151	36
2NHH	74.3	16.2	1.2	0.7	6.2	2.4	98.7	7.8	0.197	106
3NHH	77.4	13.2	1.1	0.6	6.0	2.5	98.2	9.9	0.289	208
4NHH	88.7	6.7	0.4	0.4	1.9	0.1	98.3	22.6	0.209	141

a : silica / alumina molar ratio, b : P/Po ~ 0.99

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	8.94	73.70	16.86
1NHH	8.47	74.93	16.60
2NHH	8.74	76.73	14.53
3NHH	11.63	77.10	11.27
4NHH	10.50	78.10	11.40

Table 3. Selectivity of some major products formed in the degradation of PS at 400 °C for 2h.

Aromatics	NH	HH	1NHH	2NHH	3NHH	4NHH
Benzene	0.18	0.24	0.40	0.79	1.00	0.98
Toluene	9.56	9.86	9.84	8.94	8.62	8.46
Ethylbenzene	11.36	14.32	16.64	16.18	17.77	15.80
p-Xylene	-	-	-	-	-	-
Styrene	58.86	56.50	51.34	50.22	46.41	48.23
iso-Propylbenzene	2.39	2.81	3.41	3.35	3.79	3.32
α-Methylstyrene	9.60	10.70	10.50	9.65	9.15	9.41
n-Propylbenzene	0.19	0.18	0.17	0.15	0.13	0.14
Others <sup>a</sup>	0.84	0.89	0.81	1.02	1.38	0.85
C <sub>10</sub> -C <sub>15</sub>	0.99	1.55	1.67	2.00	1.97	2.06
C <sub>16</sub> -C <sub>21</sub>	4.85	2.33	5.01	7.43	9.47	10.37
C <sub>22</sub> -C <sub>30</sub>	1.19	0.65	0.21	0.27	0.27	0.36

a : C<sub>5</sub>-C<sub>9</sub>