

Catalytic degradation of polystyrene using albite and montmorillonite

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Abstract—The performance of albite and montmorillonite clay in the catalytic degradation of polystyrene (PS) was investigated in this study. The degradation was carried out in a semi-batch reactor with a mixture of PS and catalyst at 400–450 °C. Untreated montmorillonite (Mont), aluminium pillared montmorillonite (Al-PILMont), and albite (HA) showed good catalytic activity for the degradation of PS with very high selectivity to aromatic liquids. Al-PILMont has bigger pore volume and surface area than untreated Mont as a result of pillaring. The amount of residue decreased as HA>Mont>Al-PILMont, which is consistent with the order of pore volume and surface area. The effect of reaction temperature and contact time on the distribution of aromatics is also discussed for HA catalyst.

Key words: Catalytic Degradation, Polystyrene, Albite, Montmorillonite, Pillaring

INTRODUCTION

Plastic waste disposal has been recognized as worldwide environmental problem since the total amount of plastic wastes generated by our society is growing rapidly. The low biodegradability of plastic creates a serious environmental problem that is directing the governments to propose a solution to solve the problem based on source reduction, reuse and recycling [1]. Therefore, in recent years, chemical or feedstock recycling is growing in importance. In this way plastic wastes are converted into monomers, fuels or valuable chemicals for petrochemistry [2].

One approach to chemical recovery is to employ inert gas pyrolysis to produce gasoline-like materials. Traditional thermal and catalytic cracking-hydrocracking processes can be applied to transform both thermoplastics and thermosets into gases, liquid hydrocarbons, and solid residue. Thermal cracking and hydrocracking have been investigated at laboratory and pilot plant level and some semicommercial installations have been built for the treatment of mixed plastic wastes, even those containing chlorine [3-7].

However, thermal cracking yields low value unstable hydrocarbons within a very broad range of boiling points. Catalytic cracking operates at lower temperatures than thermal cracking and produces better quality products with the corresponding economical improvement. There are different methods for carrying out the catalytic cracking of polymers: catalytic cracking of plastic wastes and liquid streams mixtures, thermal cracking plus catalytic upgrading, catalytic cracking of plastic wastes by direct contact with the catalyst, and hydrocracking [2].

A large number of laboratory studies have been conducted for the direct catalytic cracking of different type of plastics [8-11]. An excellent summary of the catalytic recycle of polymers was reported by Uemichi [1]. In contrast to polyethylene (PE) and polypropylene (PP), PS can be thermally depolymerized to obtain styrene monomer with a high selectivity.

Natural clays are known to possess a high ability to catalyze re-

actions in either polar or nonpolar media. Acid activation of clay materials is one of the most effective methods to produce catalysts with high acidity, surface area, porosity and thermal stability [12,13]. Montmorillonite is a good example of clay materials.

In our previous works [14,15], we studied the degradation of polystyrene using several catalysts such as natural clinoptillorite zeolite and ultra stable Y zeolite. The objective of this study is to compare the performance of untreated and aluminium pillared montmorillonite clay, and albite mineral in the catalytic degradation of polystyrene.

EXPERIMENTAL

1. Material and Catalysts

PS, in powder form, was supplied by LG Chemical Co. (Grade 50IS, Mn=98,000-99,000, melt index=7.5 g/10 min, density=1.03 g/cm³). Albite (NA; Na₂O·Al₂O₃·6SiO₂) was supplied by Buyeo Materials Co., and it was ion-exchanged three consecutive times with 1 M NH₄Cl solution at 70-80 °C for 20 h. The catalysts exchanged with NH₄⁺ were dried at 120 °C overnight, and then calcined in air at 500 °C to obtain the proton (H⁺)-exchanged albite HA. Untreated montmorillonite (Mont) and aluminium pillared montmorillonite (Al-PILMont) were purchased from Fluka.

2. Apparatus and Procedure

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 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 PS 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

The chemical composition of HA, Mont, and Al-PILMont is re-

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Table 1. Chemical compositions of catalysts

Catalyst	Composition (wt%)							Si/Al ratio
	SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	Others	LOI	Total	
HA	73.4	14.4	6.3	0	3.9	1.7	99.7	8.6
Mont	59.2	18.5	0.2	5.6	6.9	8.7	99.1	5.4
Al-PILMont	62.8	23.6	0.04	0.9	3.2	9.1	99.6	4.5

Table 2. Pore volume distribution and surface area

Catalyst	Micro-pore volume ^a (cm ³ /g)	Total pore volume ^b (cm ³ /g)	BET surf. area (m ² /g)
HA	0.00045	0.0040	0.45
Mont	0.013	0.244	147
Al-PILMont	0.074	0.314	260

^at-plot method.^bmeasured at P/Po=0.99.**Table 3. Yield (wt%) of product in the catalytic degradation of PS at 400 °C for 2 h**

Catalyst	Gas (wt%)	Liquid (wt%)	Residue (wt%)
None	3.8	82.3	13.9
HA (400 °C)	10.6	78.2	11.2
HA (425 °C)	8.0	82.1	9.9
HA (450 °C)	4.8	88.8	6.4
Mont	6.2	83.2	10.6
Al-PILMont	8.1	81.6	10.3

ported in Table 1. SiO₂ and Al₂O₃ are the main components of the three catalysts with a minor amount of Na₂O, Fe₂O₃ and others. The Si/Al ratio increased from Al-PILMont<Mont<HA.

The BET surface areas, pore volumes and micropore volumes of the Mont, Al-PILMont, and HA are summarized in Table 2. Albite has very small surface area and pore volume. Montmorillonite is a clay having layered structure; therefore, it shows much higher mesopore volumes than albite. Al-PILMont has 260 m²/g of BET surface area and 0.314 cm³/g of total pore volume, bigger than those of Mont. One can see that surface area and pore volume increased substantially as a result of aluminium pillaring.

Table 3 lists the gaseous and liquid products, and residues obtained in the catalytic degradation of PS 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 is a 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. Compared to non-catalytic thermal degradation, all the catalysts showed lower amount of residue and higher amount of gaseous products. The amount of residue decreased as HA>Mont>Al-PILMont, which is consistent with the order of pore volume and surface area. It means that Al-PILMont can increase the approach of the intermediately degraded fragments of polystyrene for their cracking to lower carbon number aromatics.

Selectivity of some major liquids products, calculated from mass

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

Aromatics	HA			Mont	Al-PILMont
	400 °C	425 °C	450 °C	400 °C	400 °C
Benzene	0.14	0.16	0.20	0.77	1.30
Toluene	10.23	9.43	7.97	7.93	8.40
Ethylbenzene	7.33	6.10	5.23	9.43	14.08
Styrene	65.67	65.71	65.90	59.89	52.52
<i>iso</i> -Propylbenzene	1.36	0.93	0.63	1.57	2.22
α -Methylstyrene	9.76	7.84	6.21	7.63	8.30
<i>n</i> -Propylbenzene	0.14	0.15	0.14	0.14	0.05
Others ^a	0.96	1.41	1.16	1.21	1.90
C ₁₁ -C ₁₅	0.60	1.06	1.02	1.22	1.63
C ₁₆ -C ₂₁	3.09	6.02	9.46	8.31	8.05
C ₂₂ -C ₃₀	0.72	1.19	2.08	1.90	1.55

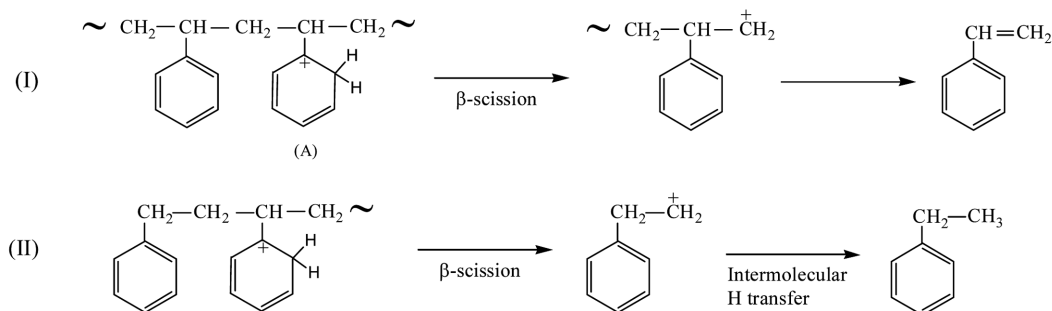
^aOther aromatic compounds having C₅-C₁₀.

balance of the products formed in the degradation of PS for different catalysts after 2 h, is presented in Table 4. At 400 °C, the catalytic degradation over HA exhibited the highest selectivity of styrene (65.67%) and the lowest selectivity of ethylbenzene (7.33%) compared to the degraded aromatic products with Mont (styrene 59.89%, ethylbenzene 9.43%), and Al-PILMont (styrene 52.52%, ethylbenzene 14.08%). The increase of pore volume and specific surface area by pillaring resulted in an increase of ethylbenzene and a decrease of styrene. The large pores may be considered to facilitate the hydrogenation of styrene fragments to produce ethylbenzene [16]. One can also see that an amount of styrene dimer and trimer was produced for all the three catalysts. In a separate experiment of thermal degradation of PS at 400 °C, the selectivity of high carbon number aromatic products (C₁₆-C₃₀) was 17.5%, much higher than that for the catalytic degradation. Therefore, one can confirm the increased degradation performance of the catalytic degradation using these three catalysts.

The effect of temperature on the PS degradation was studied by using HA catalyst. 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. The selectivity of aromatic hydrocarbons for HA catalyst at different temperatures is listed in Table 4. It is noteworthy that the highest selectivity to ethylbenzene (7.33%) is obtained at the lowest temperature (400 °C). However, the selectivity of styrene did not change significantly with increasing temperature.

Styrene and ethylbenzene are known to be produced by different reaction pathways as shown in Scheme 1 [17]. Therefore, at high temperatures, one can consider that reaction pathway I is dominant with respect to pathway II. Further hydrogenation of the produced styrene can also occur, but this reaction seems less important than pathway I at high temperatures. The increase of styrene selectivity and decrease of ethylbenzene selectivity at high temperature was also reported by Audisio et al. [17]. They explained this by relatively high stability of the polymeric ion (A) in pathway I.

The effect of contact time on the degradation of PS was studied with HA catalyst at four different nitrogen flow rates of 30, 60, 90 and 120 mL/min. Table 5 shows the distribution of aromatic prod-



Scheme 1. Reaction steps for the production of styrene and ethylbenzene.

Table 5. Selectivity of some major products formed in the degradation of PS with HA using different flow rate of nitrogen at 400 °C for 2 h

Aromatics	HA(30)	HA(60)	HA(90)	HA(120)
Benzene	0.14	0.10	0.08	0.08
Toluene	10.23	7.33	6.41	5.83
Ethylbenzene	7.33	6.22	5.51	4.99
Styrene	65.67	62.54	61.65	62.09
<i>iso</i> -Propylbenzene	1.36	0.96	0.81	0.68
α -Methylstyrene	9.76	6.82	6.33	5.75
<i>n</i> -Propylbenzene	0.14	0.12	0.10	0.09
Others ^a	0.96	0.88	0.74	0.65
C ₁₁ -C ₁₅	0.60	0.77	0.98	0.79
C ₁₆ -C ₂₁	3.09	11.71	13.95	14.53
C ₂₂ -C ₃₀	0.72	2.55	3.44	4.52

^aOther aromatic compounds having C₅-C₁₀.

ucts. An increase of ethylbenzene selectivity from 4.99% to 7.33% is observed with the increase of contact time by reducing the nitrogen flow rate from 120 to 30 mL/min. The selectivity of styrene increased slightly at nitrogen flow rate of 30 mL/min. With increasing contact time, the degraded styrene fragments will have more time to be further degraded to lower molecular weight aromatic or to participate in the hydrogenation reaction to produce ethylbenzene. The amount of aromatic products from C₁₆-C₃₀ (mainly dimers and trimers of styrene) decreased significantly as the contact time increased.

CONCLUSIONS

Albite and montmorillonite clays showed good catalytic performance for the degradation of PS with high selectivity to aromatics. Styrene was the major product, and ethylbenzene was the second abundant one in the liquid product. The increase of surface area and pore volume, caused by pillaring of aluminium to montmorillonite clay, enhanced the production of ethylbenzene by promoting further hydrogenation of the degraded styrene fragments. However, high degradation temperature decreased the selectivity to ethylbenzene. An increase of contact time by reducing nitrogen gas flow rate enhanced the selectivity to ethylbenzene, and reduced the amount of dimers and trimers of styrene.

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