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FORMATION OF AROMATIC HYDROCARBONS IN DEGRADATION OF POLYETHYLENE OVER ACTIVATED CARBON CATALYST

Yoshio UEMICHI,* Yasunori KASHIWAYA, Akimi AYAME, and Hisao KANOH
Department of Industrial Chemistry, Muroran Institute of Technology, Mizumoto-cho, Muroran 050

Catalytic effects of activated carbon on the degradation of polyethylene were investigated. Activated carbon was highly effective for the formation of normal alkanes (C_1-C_5 fractions) and aromatics (C_6-C_8). Experimental results were explained in terms of high cracking and cyclization activities of the catalyst.

Increased attention is being paid to the degradation of plastic wastes because of their potential use as chemical resources or fuels.1) Thermal degradation of polyethylene has already been reported, but it yields many products. In this respect catalytic degradation will be superior to the thermal degradation. However, little is known about catalytic effects on the degradation of polyethylene except for the use of solid acid catalysts.2,3) In the present study activated carbon was found to be effective for the degradation of polyethylene because of the preferential formation of aromatic hydrocarbons.

Activated carbon (4-8 mesh, Diasorb-G, Mitsubishi Chem. Ind. Ltd.) made from coconut was used as a catalyst. It was treated with 1 mol dm^{-3} nitric acid, washed with distilled water and then dried at 110 °C. Finally, the catalyst was evacuated at 600 °C for 3 h. A platinum (1 wt%) catalyst was prepared by impregnating silica-alumina (5 mmϕ, 13.5% Al_2O_3, N631-L, Nikki Chem. Co., Ltd.) or alumina (2-4 mmϕ, KHA-24, Nishio Ind. Co., Ltd.) with an aqueous solution of platinum(IV) ammonium chloride. The catalyst was reduced by hydrogen at 530 °C and then washed with ammonium hydroxide to remove chlorine. Low-density polyethylene (Ube Ind. Ltd.) was used as a sample; its density was 0.90 g cm^{-3} and molecular weight (M_v) 1.3×10^4. The catalytic degradation was carried out at 526 °C using a fixed-bed flow system4) and 3.0 g of each catalyst was used in a run. A reactor packed with glass beads was used in thermal degradation. Polyethylene sample was melted in a melter at 300 °C under an atmosphere of nitrogen. The melt of polyethylene was introduced into a reactor through a capillary of inside diameter of 2 mm. The feed rate of polyethylene was controlled by both the temperature of the capillary and the pressure of the nitrogen in the melter. They were kept constant through a run at given levels in the range of 340-360 °C and 0.3-0.4 kg cm^{-2} G, respectively. The degradation products were collected at 20 min intervals and were analyzed by capillary column gas chromatography using methylcyclohexane as internal standard.[5)]

The distribution of carbon number in the products over activated carbon is shown in Fig. 1, in which the results of thermal degradation and those of catalytic degradation with silica-alumina[3)] are also presented. H.B.P indicates high-boiling-point products. They were not detected with the gas chromatograph under the present conditions, but were estimated to be hydrocarbons with carbon numbers of greater than 24.[5)] In Fig. 1 the reaction over the activated carbon gave a narrow distribution of carbon number, compared with thermal degradation, and C_6-C_7 fractions were preferentially formed. On the reaction over silica-alumina the distribution was also narrow, but the products were rich in C_3-C_5 fractions.

Results on the further survey of products are summerized in Table 1, which also includes results on the reaction over supported platinum catalysts. Apparently activated carbon was very effective for the preferential formation of normal alkanes in C_1-C_5 fractions and that of aromatics in C_6-C_8 fractions. This narrow distribution of carbon number and the high yield of aromatics would be attributable to the catalytic effect of activated carbon on the C-C bond scission of polyethylene and the subsequent cyclization of straight-chain intermediates. As previously reported, silica-alumina catalyst produced aromatics, the yield of which was only 10 wt%.[3)] This fact means that the silica-alumina

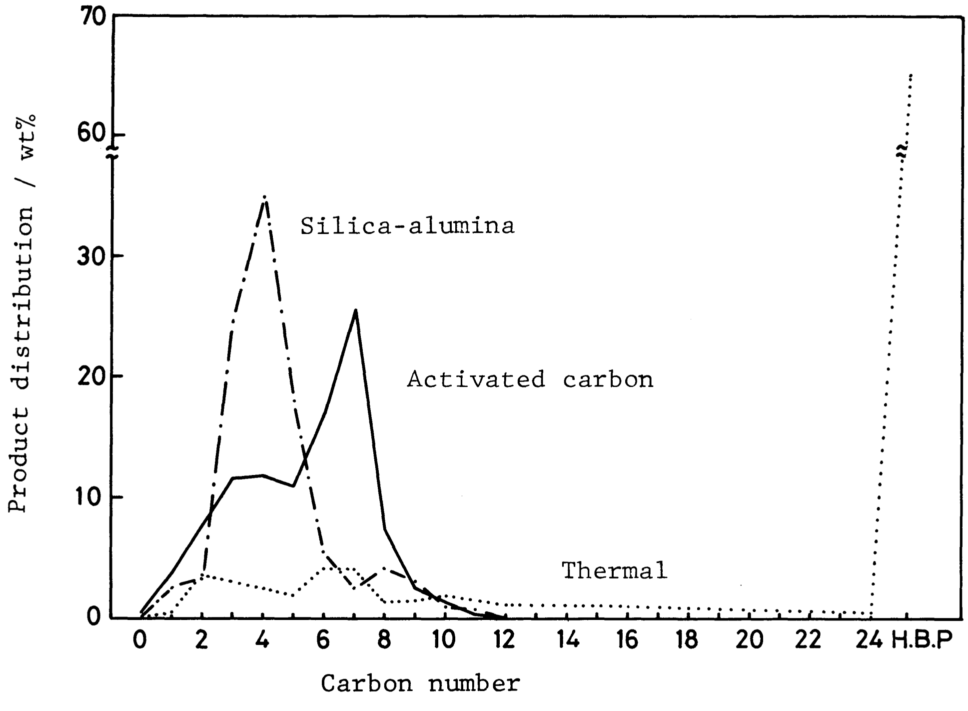

Fig. 1. Product distribution as a function of carbon number in catalytic and thermal degradations at 526 °C. Feed rate of polyethylene: 0.097(silica-alumina), 0.095(activated carbon) and 0.060 g min^{-1}(thermal).

catalyst is lack in the cyclization activity for the preferential formation of aromatics.

Supported platinum catalyst has widely been used in catalytic reforming process, in which cyclization is the most important reaction to increase the octane number. So, the degradation of polyethylene was attempted over platinum catalysts supported on silica-alumina and alumina. In Table 1 the product distributions on the reaction over the platinum catalysts were largely dependent on the cracking activity of the supports used. On the use of silica-alumina having high cracking activity, considerable amounts of aromatics were formed, but the yield of aromatics was less than the case of activated carbon. When platinum was supported on alumina which had relatively low cracking activity, the platinum catalyst was less active and yielded a mixture of hydrocarbons with a wide range of carbon number. These results support the conclusion that

Table 1. Composition (wt%) of degradation products[a]

	Activated carbon				Pt/SiO_2-Al_2O_3	Pt/Al_2O_3[b]
Carbon No.	Alkanes	Alkenes	Aromatics	Total		
H_2				0.5	2.2	3.0
1	3.8			3.8	2.1	7.1
2	7.1	0.6		7.7	1.9	3.7
3	10.0	1.6		11.6	17.4	4.0
4	10.7	1.1		11.8	23.8	5.9
5	9.5	1.3		10.8	14.2	6.0
6	9.5	1.2	6.7	17.4	7.3 (0.8)[c]	8.0 (2.0)[c]
7	4.2	0.4	20.8	25.4	9.2 (7.0)	9.7 (3.6)
8	1.0	0.1	6.3	7.4	11.5 (10.2)	7.4 (4.2)
9	0.4		1.9	2.3	5.5 (5.0)	4.9 (3.0)
10	0.1		1.2	1.3	1.0 (0.9)	4.6
11			0.2	0.2	0.3 (0.2)	1.8
12					0.3 (0.3)	1.9
13-21					0.3	4.4
H.B.P					3.0	27.8
Total	56.3[d]	6.3	37.1	100.2	100.0 (24.4)	100.2 (12.8)
Yield of products/wt%	81				79	71
Feed rate of polyethylene/ g min^{-1}	0.095				0.078	0.081

a) Composition was obtained at the initial stages of the reaction.

b) Aromatics having higher carbon number than 9 could not be identified.

c) Values in parentheses indicate the amount of aromatics.

d) Isoalkanes (about 3 %) are included.

catalytic activity for cracking and that for cyclization must be well balanced each other for the selective formation of aromatics. In this respect activated carbon is highly satisfactory as a catalyst in the degradation of polyethylene.

As a radical mechanism has been proposed for reforming of naphtha and cracking or dehydrogenation of pure hydrocarbons over activated carbon catalyst,6-8) the degradation of polyethylene would probably proceed through radical intermediates. This view is supported by the very low yield of branched alkanes and alkenes, because if carbonium ions are predominant intermediates, large amounts of branched hydrocarbons are expected to be formed.9) On the other hand, the formation of large amounts of alkanes would be ascribed to the hydrogenation of alkenes by hydrogen released in a cyclization process, thus resulting in the formation of small amounts of alkenes.

In conclusion, activated carbon catalyst has high cracking and cyclization activities in the degradation of polyethylene to produce aromatic hydrocarbons in significant amounts. The present finding provides a basis for the selective recovery of such useful fractions as benzene and its homologs from plastic wastes.

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