Catalytic Degradation of Polypropylene into Liquid Hydrocarbons Using Silica-Alumina Catalyst

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(Received December 4, 1995)

The degradation of polypropylene (PP) was carried out at 380 °C by batch operation using silica-alumina catalyst in 1) liquid phase contact and 2) vapor phase contact. For liquid phase contact, the liquid hydrocarbon products with a yield of 69 wt% had a boiling points (BP) range of 36 to 270 °C, equivalent to the BP of normal paraffins n-C_6 to n-C_{15}. For vapor phase contact, the yield of liquid products was much lower (54 wt%) and the rate of liquid recovery was much slower.

There have been many reports on the catalytic degradation of plastics over solid acid catalysts aiming at the conversion of waste plastics into liquid hydrocarbons.[1-4] From the type of reaction apparatus and the method of operation used in these studies it is not clear which steps of the thermal degradation process the solid catalyst worked on. Uemichi et al.[1-2] conducted the degradation of polypropylene at 420-550 °C in a flow type reactor using solid acid catalysts, so that the gaseous hydrocarbons were predominant in the products. Saito[3] reported a two step polyethylene degradation process: the thermal degradation using a natural zeolite at 450 °C followed by the degradation with a synthetic zeolite at 300 °C. In the 1st step catalytic degradation a wax like product (C_5-C_{43}, 87 wt% yield) was obtained and the 2nd catalytic degradation produced liquid hydrocarbons with a overall yield of 74 wt%. Degradation of polyethylene with silica-alumina reported by Ohkita et al.[4] was actually the catalytic cracking of volatile compounds in the thermally degraded polyethylene at 400 °C. In order to investigate the catalytic steps of solid catalyst in polymer degradation, this work compares the catalytic effects on polypropylene (PP) degradation process 1) when the melted PP was brought into contact with solid catalysts (liquid phase contact) and 2) when the thermally degraded hydrocarbon vapors from PP were brought into contact with solid catalyst particles (vapor phase contact). The yields of product gas, liquid and residues; recovery rate of liquid products, and boiling point composition of liquid products of catalytic degradation were compared with those of non-catalytic thermal degradation.

The catalysts employed in this study, silica-alumina (SiO_2/Al_2O_3: 8/2, specific surface area: 420 m^2/g) was obtained from Mizusawa Chemical Industries. Polypropylene pellet (4.0 mm in size) having a molecular weight of 16000 was supplied by UBE Chemical Industries. Thermal degradation of PP was carried out in a glass reactor(35 mm i.d. and 350 mm length) under atmospheric pressure at 380 °C by batch operation. 10 g of PP pellet was loaded into the reactor for thermal degradation and 10 g of PP mixed with 1.0 g of catalyst (1.0 mm in size) was loaded into the reactor for the catalytic degradation (liquid phase contact). For catalytic degradation in vapor phase contact, catalysts were placed on a stainless steel net 10 cm from the bottom of the reactor. In a typical run, after the reactor was set, air remaining in the reactor was purged with N_2 at a flow rate of 30 ml/min. The reactor was then heated to 120 °C in 60 min (1.7 °C/min) and held at 120 °C for 60 min in order to drive off the absorbed water from the catalyst and the PP sample. Nitrogen flow was then cut off and the temperature was increased from 120 °C to 380 °C at a heating rate of 3 °C/min. The degradation products were classified into three groups: gases (products which were not condensable at water cooling temperature), liquid hydrocarbons and residues. The amount of gaseous products was determined by subtracting the weight of liquid products and residues from the plastic sample feed. The term residue refers to both the carbonaceous and the waxy compounds remaining in the reactor after the degradation run. Products of degradation were analyzed using two gas chromatographs: liquid products with an ov-101 capillary column and gaseous products with a Porapak QS column.

Table 1. Product yield (wt%) for thermal and catalytic degradation of polypropylene at 380 °C[a]

Contact phase of catalysts	Non-cata. (thermal)	Silica-alumina (vapor phase)	Silica-alumina (liquid phase)
Product Yields			
Liquid (L)	64.9	54.5	68.8
Gaseous (G)[b]	24.7	35.0	24.8
Residues (R)	10.4	10.5	6.4
Bromine number of liquid products (g-Br/100g sample)	66.7	90.3	94.0

[a] Product yields for non-catalytic, and catalytic vapor phase contact (after 800 min); and liquid phase contact (after 350 min).
[b] G = 100 - (L +R).

The yield of product gases, liquids and residues obtained from the thermal degradation and catalytic degradation (in liquid phase and vapor phase contact) of PP were shown in Table 1. For catalytic degradation in vapor phase contact, the yield of residues did not differ significantly from that of thermal degradation, however, the yield of liquid products decreased and that of gaseous products increased. These results imply that in vapor phase contact, thermally degraded hydrocarbon underwent further decomposition into gaseous products over silica-alumina catalyst. On the other hand, for catalytic degradation in liquid phase contact, the yield of gaseous products did not differ much from that of thermal degradation, but the yield of liquid products increased at the expense of yield of residues. Gaseous products from the catalytic degradation consisted of mainly butene (57 wt%) and propylene (30 wt%), whereas the gaseous products from thermal degradation consisted of propylene (70 wt%) and ethane (28 wt%). The above results indicate that in liquid phase contact the waxy residues (heavier hydrocarbons) decomposed into lighter liquid hydrocarbons over silica-alumina catalyst resulted in the higher yield of liquid products than the case of

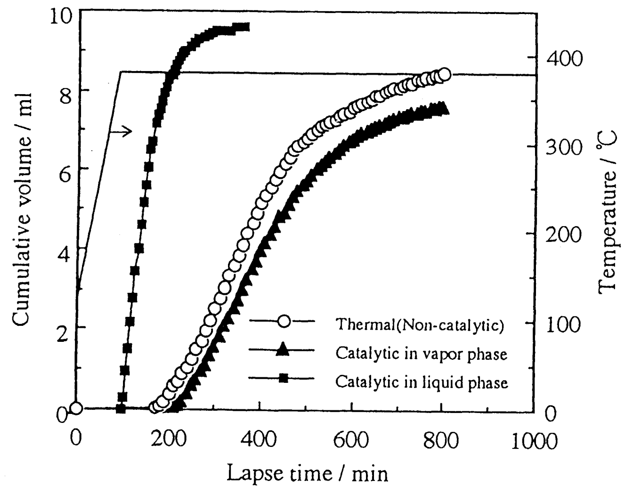

Figure 1. Cumulative volume of liquid product from thermal and catalytic degradation of PP at 380 ℃.

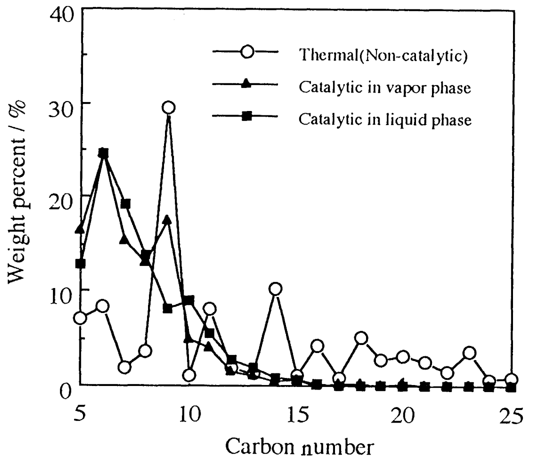

Figure 2. NP-grams of liquid product from thermal and catalytic degradation of PP at 380 ℃.

thermal degradation.

Figure 1 shows the cumulative volume of liquid products in the graduated cylinder and the temperature in the reactor as a function of lapsed time. The count of lapsed time was started when the heating of the sample from 120 °C to the reaction temperature started. The initial rate of degradation of PP over silica-alumina catalyst in liquid phase contact was 1.2 g(products) g(residual liquid)$^{-1}$ h^{-1} which is ca. 4 times faster than that of non-catalytic thermal degradation and catalytic degradation in vapor phase contact. These results suggest that acid sites of silica-alumina in contact with the PP melt (liquid phase) accelerated the degradation of PP significantly. Our unpublished data on thermal and catalytic (liquid phase contact) degradation of polyethylene revealed that for catalytic degradation, when PE was heated at 430 °C (for a certain time) the molecular weight distribution (determined by Gel Permeation Chromatography) of the residual liquid in the reactor was shifted to a lower molecular weight range than that for thermal degradation. This result also indicate that the solid acid catalyst in direct contact with melted plastic polymers promotes the degradation of plastic polymers into lower molecular weight compounds.

The liquid products were characterized by a Normal Paraffin gram (NP-gram) proposed by Murata et al.[5] Figure 2 shows the NP-gram (carbon number distribution) of liquid products obtained from catalytic and thermal degradation of PP at 380 °C. The carbon numbers of abscissa in Figure 2 were obtained by analyzing the gas chromatogram of the liquid products. These carbon numbers are equivalent to retention values of the corresponding normal paraffins and indicate a range of boiling points in which the boiling points of the hydrocarbons are distributed. For thermal degradation, the liquid hydrocarbon products were distributed in a wide range of equivalent hydrocarbons with boiling points ranging over 36-405 °C (C_5-C_{25}). Murata et al.[5] have reported a similar result for the thermal degradation of PP at 390 °C, characterized with a comb-like peaks at n-C_6, n-C_9, n-C_{11}, n-C_{14} and n-C_{16}, and so on. On the other hand, for the PP degradation over silica-alumina in both liquid and vapor phase contact, the liquid products were predominant in carbon fractions of n-C_5 to n-C_{15} compounds equivalent to hydrocarbon with boiling points ranging over 36-270 °C. The bromine number of the liquid products, which is a measure of unsaturation in liquid hydrocarbons, was determined in order to compare the degree of total unsaturation in liquid products from the thermal and catalytic degradation of PP (see Table 1). Bromine numbers of liquid products were 66.7 and 90-94 (g-Br/100 g liquid product), for thermal and catalytic degradation, respectively, indicating catalytically degraded products have a higher degree of total unsaturation than the non-catalytic thermally degraded products. From results we suggest that the silica-alumina (solid acid) catalyst breaks the long polymeric chain from ends into small units. As a result, the amount of unsaturated hydrocarbon (olefins) increases in the products. It is well known that the thermal degradation of polyolefinic polymers occurs by the random scissoning of the long polymeric chain and the products of degradation are distributed in a wide range of molecular weights. Therefore, the amount of total unsaturation per gram of liquid products for thermal degradation is lower than that for catalytic degradation.

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