A Novel Technology for Chemical Recycling of Low-Density Polyethylene by Selective Degradation into Lower Olefins Using H-Borosilicate as a Catalyst

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Catalytic degradation of low-density polyethylene to lower olefins over H-borosilicate has been proposed as a novel technology for chemical recycling of polyolefins.

The development of an effective technology to recycle waste plastics is becoming increasingly important. Polyolefins, the major constituents of the plastics, have been recycled in part by reuse after remelting and shaping, energy recovery through combustion, conversion to fuels, and utilization as a reductant in the iron manufacturing. The combustion of the waste plastics and their derived products means a loss of potential for use as resources. Recently, an alternative that converts waste plastics to feedstocks has received much attention, because the new option is expected to contribute to conservation of our limited natural resources.

We have recently developed a technology for chemical recycling of polyolefins by conversion into aromatic hydrocarbons using H-gallosilicate.[1,2] Here, we propose a new catalytic process to recycle polyolefinic waste chemically. The proposed method uses H-borosilicate as a catalyst that can break down low-density polyethylene (LDPE) into lower molecular weight olefins.

Catalytic degradation of LDPE (Aldrich, density 0.915 g cm^{-3}) was carried out similarly to a previous work[2] by using a flow reactor at 400–575 °C, at atmospheric pressure and under a N_2 stream (10 cm^3 min^{-1}). The melt of LDPE, heated at 270 °C was fed at a feed rate of 0.02 g min^{-1} into the reactor loaded with 0.2 g of catalyst for 15 or 30 min. The gaseous and liquid products were analyzed by gas chromatography. Grease-like hydrocarbons that adhered to the wall of the outlet of the reactor and carbonaceous deposit on the catalyst surface were defined as wax and coke, respectively, and determined by weighing. The H-borosilicate powder from N. E. CHEMCAT was pressed into a disk, crushed and sieved to 16–32 mesh granules, and used as a catalyst after calcination at 550 °C for 3 h in air. The XRD and ICP analyses showed that the borosilicate has an MFI structure and a Si/B ratio of 70, and contains low concentrations of Al and Fe atoms (Si/Al > 1300 and Si/Fe > 10000). The catalytic properties of the borosilicate were compared with those of H-ZSM-5 (Si/Al = 150, N. E. CHEMCAT) and amorphous silica-alumina (Si/Al = 5.4, Nikki Chemical N631L), which have been used extensively as catalysts for the degradation of polyolefins.[3,4] To evaluate the acidic properties of the catalysts, cumene dealkylation at 250 °C using 10 mg of catalyst and 2-propanol dehydration at 175 °C and 3 mg were carried out by the use of a pulse reactor. Helium was flowed as a carrier gas at 30 cm^3 min^{-1} and 0.2 µL of reactant was injected into the helium stream in each pulse.

The yields of products obtained from thermal and catalytic degradation of LDPE are shown in Table 1. The thermal degradation mainly produced waxy components, while the catalysts used greatly promoted the degradation of LDPE to yield lighter hydrocarbons of the carbon numbers less than 14. The composition of the products largely depended on the catalyst type. H-borosilicate was found to show a very high selectivity for C_3–C_5 olefins, while the paraffins with the same carbon numbers were formed in small quantities. Such a product composition is apparently different from that observed over the conventional catalysts. H-ZSM-5 produced less olefins than the H-borosilicate. Much lower olefin selectivities have been reported in the degradation with the ZSM-5 of a lower Si/Al ratio of 15 because of major formation of aromatics and paraffins.[2] Silica-alumina also showed a low selectivity for the C_3–C_5 olefins.

Table 1. Yields of products obtained from degradation of LDPE at 525 °C

	Catalyst			
	H-B-silicate	H-ZSM-5	SiO_2-Al_2O_3	Thermal
Yield / wt%				
H_2	0.1	0.3	0.2	tr.[a]
C_1+C_2	3.9	9.4	1.3	2.5
C_3-C_5 olefins	75.5	40.2	53.3	5.1
C_3-C_5 paraffins	5.2	21.9	9.7	1.7
C_6+ aliphatics	12.2	7.4	27.8	11.4
Aromatics	3.0	20.8	6.8	tr.[a]
Wax	0.2	0	0	79.3
Coke	tr.[a]	tr.[a]	0.9	tr.[a]

[a] Less than 0.05%.

The carbon number distributions of the olefins, paraffins and aromatics obtained over H-borosilicate are shown in Figure 1. A highly selective formation of olefins was clearly illustrated. Propylene (32%), butenes (29%) and pentenes (14%) accounted for most of the olefins produced. Paraffins and aromatics were produced in limited amounts, and rather evenly distributed in each carbon number fraction. It is well known

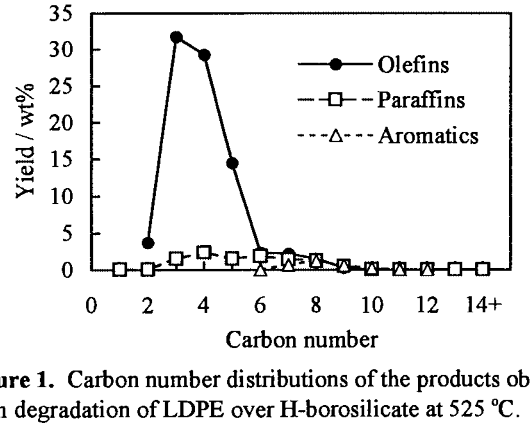

Figure 1. Carbon number distributions of the products obtained from degradation of LDPE over H-borosilicate at 525 °C.

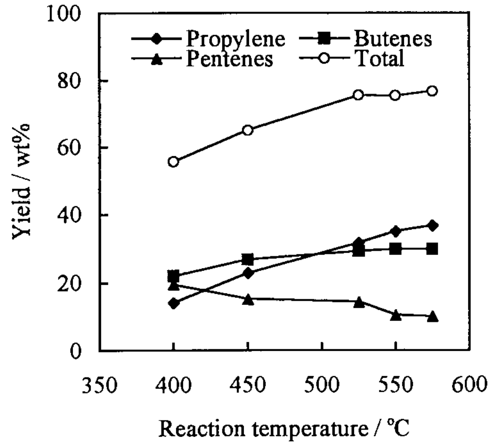

Figure 2. Effect of reaction temperature on the yields of C_3-C_5 olefins obtained from degradation of LDPE over H-borosilicate.

that C_3–C_5 fractions are the main products in the acid-catalyzed degradation of polyolefins. However, it has been quite difficult to yield the olefins selectively without any significant formation of the paraffins. Pyrolysis is known to be a reaction for producing lower olefins from LDPE, but usually needs temperatures higher than 700 °C.[5,6] The degradation of LDPE over H-borosilicate can proceed even at lower temperature of around 500 °C to give high selectivities for C_3–C_5 olefins. They could be used as monomers for the production of polyolefins and/or raw materials for various chemicals. The borosilicate is thus a potentially interesting catalyst for possible industrial application to the chemical recycling of plastic waste.

The effect of reaction temperature on the yields of C_3–C_5 olefins obtained over H-borosilicate is shown in Figure 2. Upon an increase in the temperature, much more propylene and a little more butenes were produced, while the yield of pentenes slightly decreased at higher temperatures. These observations indicate a shift of product distribution to the fractions of lower carbon numbers and a higher temperature is favorable for producing propylene selectively.

Figure 3 shows the catalytic activities for 2-propanol dehydration and cumene dealkylation, which are thought to occur on weakly and strongly acidic sites, respectively. Among the catalysts used, the borosilicate showed the lowest activities for both the reactions, indicating the least acidity. This is consistent with the literature.[7–9] It is difficult to prove no influence of Al impurity on the generation of acidic sites on the borosilicate. However, a very low Al concentration (Si/Al > 1300) makes it possible to assume that the acidity of the H-borosilicate mainly results from the presence of framework boron.

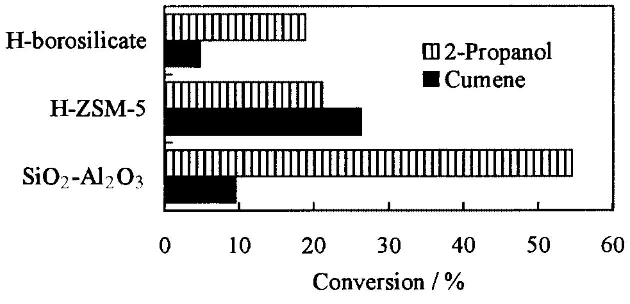

Figure 3. Catalytic activities for acid-catalyzed model reactions.

The degradation of LDPE probably initiates thermally despite the presence of the borosilicate. LDPE can undergo thermal decomposition at above 400 °C[10,11] to yield unsaturated fragments. Their further cracking is likely to occur on H-borosilicate because the unsaturates are readily activated even on weak acid sites by protonation to form carbenium ion intermediates. An extensive occurrence of the β-scission of the carbenium ions produces the olefins with carbon numbers of 3–5. The degradation of LDPE generally involves various reactions such as dehydrocyclization and hydrogen transfer, which lead to the formation of aromatics, paraffins, and carbonaceous deposit. They frequently occurred on the sufficiently acidic H-ZSM-5 and silica-alumina catalysts and thereby lowered the olefin selectivity. On the other hand, little occurrence of the undesirable reactions in the LDPE degradation over the H-borosilicate with weak acidity leads to an excellent olefin selectivity.

The results represented here clearly indicate that the proposed technology using H-borosilicate catalyst is highly promising as a new option for chemical recycling of polyolefins.

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