H-Gallosilicate-Catalyzed Degradation of Polyethylene into Aromatic Hydrocarbons Using Different Types of Reactors

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A fixed-bed flow reactor, in which melted polyethylene came into contact with H-gallosilicate catalyst, was highly effective in converting the polymer to aromatic hydrocarbons. The yield of aromatics was much lower when the degradation was performed by heating a mixture of the polymer and the catalyst in a batch reactor.

Catalytic degradation of polyolefins has received much attention as a key technology in plastics recycling. The existing method typically converts polyolefins into liquid fuels by the use of catalysts such as amorphous silica-alumina and zeolites.[1-6] One of the authors has recently developed a technology to break down polyethylene into valuable aromatic hydrocarbons, mainly benzene, toluene, and xylenes (BTX), by using H-gallosilicate as a catalyst.[7] This makes it possible to reuse polyolefinic waste chemically.

Research work on the degradation of polyolefins has mainly been performed by contacting melted polymer with catalyst in a fixed-bed flow reactor or by physically mixing polymer and catalyst powders and then heating the mixture in a batch reactor. Such a difference in the contact modes, resulting from different reactor systems, is expected to influence the composition of the degradation products. Therefore, particular attention should also be given to the contact mode or reactor system as well as catalyst to obtain a desired product distribution from the catalytic degradation of polyolefins.

In this paper, we report that the type of reactor system used, that is, how polyethylene is contacted with catalyst is quite important for effective utilization of the recently developed technology that uses a H-gallosilicate catalyst and converts polyethylene into aromatic hydrocarbons.

A powdered polyethylene with a low density of 0.915 g cm^{-3} was obtained from Aldrich Chemical Co. and used without further treatment. H-gallosilicate (Si/Ga = 25) powder obtained from N. E. CHEMCAT was pelletized without binder, crushed and sieved to 16-32 mesh granules. The catalyst was then calcined in air at 550 °C for 3 h and further treated in situ in a helium stream at the same temperature for 1 h just prior to use. Catalytic degradation of polyethylene was carried out by using flow- and batch-type reactors at 425-525 °C and under atmospheric pressure and a He stream (10 cm^3 min^{-1}). The down-flow tubular reactor holding a fixed catalyst bed of H-gallosilicate of 0.2 g was used, and 0.33 g of the polyethylene melted at 270 °C was fed into the reactor in 15 min (0.022 g min^{-1}) to give a catalyst/polyethylene weight ratio of 0.6. The details of the fixed-bed flow apparatus and procedures have been described elsewhere.[1] The degradation using the batch reactor was performed by physically mixing 0.5 g of polyethylene and 0.05-0.3 g of catalyst in the reaction vessel at room temperature and then heating the mixture by the use of an electric furnace with a prescribed temperature. It took 11-15 min to complete the catalytic degradation of polyethylene.

The degradation products were divided into gas (C_1-C_4), liquid (C_5 and higher hydrocarbons except wax), wax (greaselike hydrocarbons), and coke (carbonaceous deposit on the catalyst surface). Table 1 shows the yields of the products obtained from the thermal and catalytic degradation of polyethylene in both the flow and batch reactor systems. The table also includes the yields of aromatic hydrocarbons which are the products characterizing the catalysis by the gallosilicate. The thermal degradation at 450 °C mostly produced wax because of a low degradation rate in the absence of catalyst. The

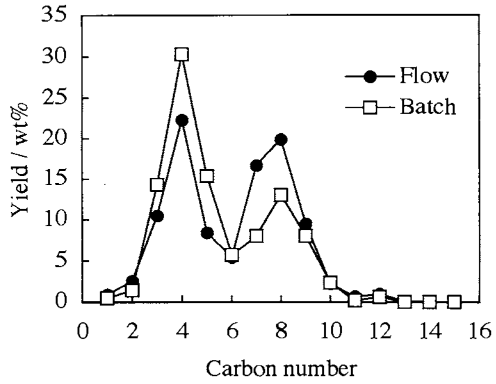

Figure 1. Carbon number distributions of the products from degradation of polyethylene using different reactors at 425 °C and a catalyst/PE ratio of 0.6.

Table 1. Yields of products obtained from thermal and catalytic degradation of polyethylene

	Reactor	Temperature / °C	Time / min	Catalyst/PE (wt/wt)	Yield / wt%					
					Gas	Liquid	Wax	Coke	Aromatics	BTX
Thermal	Batch	450	60	–	7.0	10.3	82.7	trace	trace	trace
H-gallosilicate	Batch	425	15	0.6	46.6	52.6	0.3	0.5	26.3	15.4
H-gallosilicate	Flow	425	15[a]	0.6	36.2	63.6	0	0.2	50.6	35.7

[a] Time on stream.

gallosilicate greatly promoted the degradation of polyethylene even at a lower temperature of 425 °C to give gas and liquid fractions as major products. They were obtained in almost comparable yields (Table 1) and distributed in the same carbon numbers of 1-14 (Figure 1) regardless of the types of the reactors used. These results indicate that the cracking of polyethylene over H-gallosilicate occurred to almost the same extent in both the reactor systems. However, the composition of the liquid product obtained was quite different; the aromatic hydrocarbons mainly consisting of BTX were much more produced when the flow reactor was used than the batch reactor, as shown in Table 1. The aromatization was apparently suppressed and aliphatic hydrocarbons were mainly produced in the latter despite an inherently excellent performance of H-gallosilicate catalyst for dehydrocyclization.

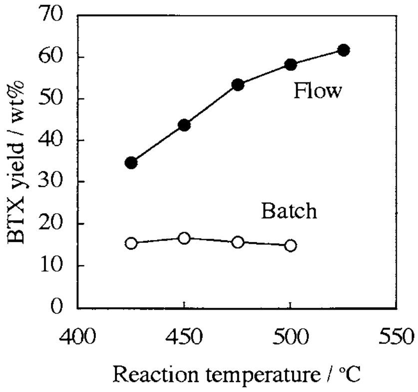

Figure 2. Effect of reaction temperature on the yield of BTX at a catalyst/PE ratio of 0.6.

Figure 2 shows the effect of reaction temperature on the yield of BTX. Since a high temperature is favorable for undergoing aromatization, the BTX yield increased with reaction temperature in the flow system, but no increase was observed in the batch system. Consequently, the difference in the yield between the two reactor systems became progressively greater as reaction temperature was increased. The yield value obtained in the flow system was about 2 and 4 times that in the batch system at 425 and 500 °C, respectively. The aromatics were also not so much produced in the batch system if the weight ratio of catalyst/polyethylene was increased. The BTX yield at 425 °C increased slightly from 11.2 wt% at the ratio of 0.1 to 15.4 wt% at 0.6. Further increase in the ratio probably brings about no favorable results and it is impractical to increase the ratio too high. The batch reactor system used in the present study was thus found to be difficult to produce aromatics selectively from the degradation of polyethylene.

The formation of aromatics in the catalytic degradation of polyethylene can be explained by a consecutive mechanism,[8] in which the cracking of polyethylene first takes place and then the resulting decomposed fragments undergo dehydrocyclization to aromatic hydrocarbons. This mechanism suggests that the secondary reactions involved in the polyethylene degradation predominantly determine the product distribution. The fixed-bed flow reactor, in which melted polyethylene comes into contact with the gallosilicate, is favorable for promoting the secondary reactions, because all the decomposed fragments primarily produced from polyethylene flow downward in the reactor and pass through the catalyst bed where they can convert into the aromatics. In the batch system, however, the volatile fractions among the primarily decomposed fragments having different boiling points escape from the reactor without sufficient contact with the catalyst. This results in a suppression of the secondary reactions and thereby a low yield of aromatics.

The insufficient contact of the primarily decomposed fragments with the catalyst in the batch system is probably responsible for little effect of reaction temperature on the BTX yield (Figure 2). Increasing reaction temperature generally makes it possible to accelerate both the rates of cracking and aromatization. However, the decomposed fragments more readily volatilize and escape from the reactor at higher temperatures. This means that residence time becomes shorter with increasing reaction temperature. For these opposite effects, the yield of BTX produced in the batch system scarcely depended on the reaction temperature.

The batch reactor system like that used in the present study has extensively been applied to the degradation of polyolefins because of its simple configuration and easy operations. However, it gave no satisfactory selectivity to aromatics in the degradation of polyethylene using H-gallosilicate. The down-flow tubular reactor holding the fixed catalyst bed of H-gallosilicate was highly suitable for converting the polymer into aromatic hydrocarbons, the process of which is a new option recently established for reusing polyolefinic waste chemically. The present study strongly suggests that reactor design, as well as the choice of catalyst, is also of prime importance in the development of chemical recycling technologies for plastic waste.

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