# Chemical recycling of poly(ethylene) by catalytic degradation into aromatic hydrocarbons using H-Ga-silicate

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**H-Ga-silicate exhibits excellent catalytic activity towards the formation of aromatic hydrocarbons, mainly benzene, toluene and xylenes (BTX), in the degradation of poly(ethylene), indicating its high potential as a catalyst for the advanced chemical recycling of polyolefins.**

It is currently very important to recycle waste plastics from the standpoints of environmental protection and conservation of energy. A chemical method that converts plastics into valuable chemical feedstocks or fuels is of great interest because it provides a viable means to contributing to the solution of problems caused by waste disposal. The conversion of plastics can be achieved thermally or catalytically. Since thermal degradation of polyolefins, the main components of waste plastics, is a low selectivity reaction, successful application of catalysts to these conversion processes would be a key step towards the development of the plastic recycling technologies.

Catalytic degradation of polyolefins has mostly been carried out with a view to obtaining valuable hydrocarbon mixtures as fuels.[1–4] There have been only a few reported studies on chemical recycling (otherwise termed feedstock recycling, raw material recycling or tertiary recycling) which aims to yield chemical feedstocks.[5–7] To achieve chemical recycling, polyolefins must be decomposed in high yield into useful feedstocks. This step is usually more difficult than conversion into fuels. In other words, chemical recycling requires cracking catalysts with selectivities much higher than those required for fuel recovery. This is the reason why catalytic chemical recycling of polyolefins has not been developed. Here we report that H-Ga-silicate is highly effective as a catalyst for producing aromatic hydrocarbons selectively in the degradation of poly(ethylene). This successful result means that chemical recycling of polyolefins is now a feasible operation.

Catalytic degradation of low-density poly(ethylene) (Aldrich LDPE, density 0.915 g $cm^{-3}$) has been carried out using a flow reactor at 400–525 °C, at atmospheric pressure and under a He stream (10 $cm^3$ $min^{-1}$). The poly(ethylene) melt, 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 min. The degradation products were classified into gas ($C_1$ to $C_4$), liquid ($>C_5$) and coke (carbonaceous deposit on the catalyst surface). The composition of the gaseous and liquid products was analysed by gas chromatography. The details of the reaction procedures have been given elsewhere.[1] A commercially available H-Ga-silicate (Si/Ga = 25, N. E. CHEMCAT) was pressed into a disk, crushed and sieved to 16–32 mesh granules, and finally calcined at 500 °C for 3 h in air. The Ga catalyst was compared with H-ZSM-5 (Si/Al = 15, N. E. CHEMCAT) and amorphous silica–alumina (Si/Al = 5.4, Nikki Chemical N631L). These alternatives have been extensively used for the conversion of polyolefins into liquid fuels. The acidic properties of the catalysts were evaluated from their catalytic activities for three model reactions: *n*-hexadecane cracking was carried out at 400 °C, using 1 mg of catalyst, cumene dealkylation at 250 °C and 10 mg, and propan-2-ol dehydration at 175 °C and 3 mg. In each case, a pulse reactor loaded with the powdered catalyst was operated under flowing He (30 $cm^3$ $min^{-1}$).

Fig. 1 shows the activities of the catalysts for the acid-catalysed model reactions. The highest conversions were shown by H-ZSM-5, followed by H-Ga-silicate. The Ga catalyst was much more active than silica–alumina for the cracking of cumene and *n*-hexadecane, which occurs on strong acid sites, while both catalysts showed almost the same activity for the dehydration of propan-2-ol, which proceeds on weakly acidic sites. It is suggested from these results that H-Ga-silicate is less acidic than H-ZSM-5, but has acid sites that are significantly stronger than those on silica–alumina, which exhibited low cracking activities.

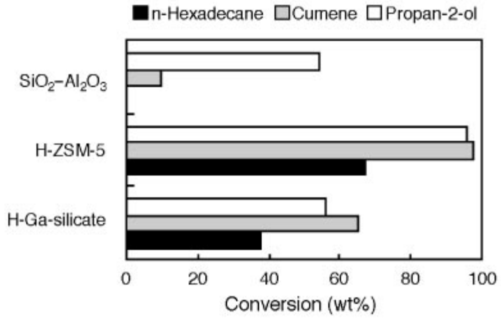

**Fig. 1** Catalytic activities for model reactions

The catalysts thus characterised showed quite different activities and selectivities in the degradation of poly(ethylene). The results are summarised in Table 1. H-Ga-silicate is highly effective as a catalyst for the production of aromatic hydrocarbons. A high temperature was favourable to producing the aromatics selectively. A yield of more than 70 wt% was obtained at 525 °C and the liquid product substantially consisted of aromatic hydrocarbons. Benzene, toluene and xylenes (BTX), important raw materials, accounted for most of the aromatics produced. H-ZSM-5 also produced considerable amounts of aromatics at 525 °C. However, the yield was lower than that obtained over H-Ga-silicate at 400 °C. On the other hand, silica–alumina was not suitable for producing aromatics. About 40 wt% yield of aromatics has also been reported in the degradation of poly(ethylene) over metal/carbon catalysts at 526 °C with longer contact times.[5] H-Ga-silicate gives superior results.

Fig. 2 shows the product distributions as a function of carbon number. The products obtained over H-Ga-silicate were distributed over carbon numbers 1–13. The proportion of $C_6$–$C_8$

**Table 1** Yields of products from degradation of poly(ethylene)

| | | Yield/wt% | | | | |
|---|---|---|---|---|---|---|
| Catalyst | $T$/°C | Gas | Liquid | Aromatics | BTX | Coke |
| H-Ga-silicate | 400 | 40.3 | 59.4 | 44.1 | 30.1 | 0.3 |
| H-Ga-silicate | 525 | 28.0 | 72.0 | 71.6 | 61.8 | —[a] |
| H-ZSM-5 | 525 | 58.0 | 42.0 | 40.8 | 33.5 | —[a] |
| $SiO_2$–$Al_2O_3$ | 525 | 57.2 | 42.1 | 9.5 | 3.7 | 0.4 |

[a] Less than 0.05%.

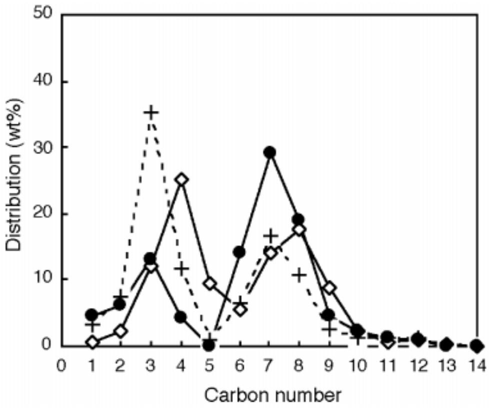

**Fig. 2** Carbon number distributions of the products: (+) H-ZSM-5 (525 °C), (◇) H-Ga-Si (400 °C) and (●) H-Ga-Si (525 °C)

components, mostly BTX, increased with reaction temperature, probably indicating greater aromatisation of the gaseous fractions at higher temperatures. The Ga catalyst showed good stability when reused, as expected from the very small amount of coke deposited on the catalyst surface (Table 1). The ZSM-5-type structure of H-Ga-silicate is likely to resist coke formation.

Ishihara *et al.*[8] reported that the degradation of poly(ethylene) over silica–alumina proceeds as follows: polymer→oligomer→liquid→gas. We believe the consecutive degradation mechanism is applicable to the present work and the aromatics are formed from the oligomer, liquid and/or gas, not directly from the polymer itself. That is, the aromatisation and cracking proceed competitively, and their relative contributions determine the product distributions. Cracking is probably a predominant reaction with H-ZSM-5, over which the liquid hydrocarbons corresponding to the aromatic precursors were converted into gaseous fractions. Thus, the cracking activity of H-ZSM-5 with strong acidity seems to be too high to give a good yield of aromatics. On the other hand, H-Ga-silicate has moderate cracking ability, whilst greatly enhancing aromatisation *via* the catalytic action of Ga species on the catalyst surface.[9,10] Aromatisation would predominate over cracking at high temperature and, hence, the yield of aromatics greatly increased with reaction temperature. It is therefore reasonable to consider that a good balance between cracking and aromatisation activities is the origin of the excellent catalytic performance of H-Ga-silicate. Both aromatisation routes, by direct dehydrocyclisation of the liquid intermediates and by oligomerisation of gaseous fractions and subsequent cyclisation, must be involved in the degradation over the Ga catalyst. The latter should be important at high temperature.

## Notes and References

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