

## Gasoline Range Chemicals from Zeolite-catalysed Thermal Degradation of Polypropylene

Raphael C. Mordi,\*† Roy Fields and John Dwyer

*Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, UK*

The thermal degradation of polypropylene over zeolite catalysts (H-ZSM-5, H-mordenite and H-theta-1) has been studied; GC analysis of the product fractions revealed that 70–80% were of the gasoline range hydrocarbons.

Over the last few decades, there has been increasing concern regarding the environmental problem caused by plastic waste disposal. Recently, plastic waste disposal has been tackled from several angles; for example, by plastics recycling, but this accounts for only 1%, and the manufacture of photo- and bio-degradable plastics. The degradation of these plastics however depends on several factors, such as composition, physical characteristics of the polymer and environmental conditions including moisture and oxygen content, temperature and light. The degradation of these plastics has been questioned on the basis of uncertainty over the degradation byproducts, and whether the additives in the materials would present health problems. Another approach involves incineration of these plastics, but problems with this method include environmental and health hazards from the release of toxic materials, together with the loss of fuel and chemicals available from the plastics.

In this communication, we report a process whereby polymers are degraded as model compounds, in the presence of zeolite catalysts to gasoline range chemicals. In a typical

experiment performed under static conditions, H-ZSM-5 (0.20 g) and polypropylene pellets (1.00 g) were placed in a Pyrex reaction glass tube (300 ml), which was evacuated (water pump), sealed, put into a metal guard tube and placed in a preheated furnace at 350 °C. After 2 h the guard tube was removed from the furnace and allowed to cool to room temperature, and then opened to a vacuum line. The emerging gas was trapped at –45 °C (CO<sub>2</sub>-chlorobenzene), Fraction A; at –196 °C (liquid nitrogen), Fraction B; and on a previously activated charcoal at –196 °C, Fraction C. A liquid residue remained in the reaction tube, Fraction D. The relative proportions (by weight) of these fractions are in Table 1. The conversion was taken as 100%, since no solid polymer remained at the end of the reaction. At 300 °C, the degradation was much slower as a solid mass of polymer was recovered with about 80% (by weight) conversion to Fractions A–D with a relatively lower conversion to Fractions B and C. Under similar conditions in the absence of zeolite very little reaction occurred as only resolidified polymer was recovered.

Fractions A–D were analysed using gas chromatography and the products identified by comparison of their retention times with those of authentic compounds (n-alkanes and n-alkenes) in a calibration mixture of known composition. Fraction C contained only methane; Fraction B contained a

† *Present address:* Department of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK.

**Table 1** Product fractions from polypropylene degradation over zeolites at 350 °C for 2 h

Fraction	H-ZSM-5	H-mordenite	H-theta-1 <sup>a</sup>
A	15	43	34
B + C	59	24	47
D	12	15	13

<sup>a</sup> The Si : Al content of H-theta-1 was 35.

mixture of C<sub>1</sub>–C<sub>7</sub> hydrocarbons as expected for a catalysed reaction.<sup>1</sup> This fraction was then treated with bromine in chloroform and analysed. The chromatogram was similar to that of the unbrominated mixture, evidence that the original fraction contained mainly saturated hydrocarbons of which the C<sub>3</sub> and C<sub>4</sub> components comprised more than 70% (by area) of this mixture. Product analysis of Fraction A showed the mixture to contain aliphatic hydrocarbons in the C<sub>6</sub>–C<sub>11</sub> range, together with aromatic compounds (mainly benzene, toluene and the xylenes).

It should be noted that in these reactions the polymer and the zeolite were used in a 5 : 1 ratio. As the amount of polymer used is greater than that of the zeolite and yet there was a reasonable conversion to products, we conclude that the process is catalytic and that the cracking takes place inside the zeolite cavities. However, we believe that the cracking process is initiated on the surface-active sites of the zeolite.

Other acidic zeolites investigated under similar conditions were H-mordenite and H-theta-1. In both cases at 350 °C for 2 h the conversion was 100% as defined above. However, we noted that lower proportions of Fractions B and C were obtained (Table 1), whereas higher proportions of Fraction A were obtained. The analyses of the fractions using gas chromatography showed that components were essentially aliphatic hydrocarbons, with no aromatic components, with Fraction D showing products up to C<sub>22</sub>. These results are consistent with pore sizes and the acid sites of the three zeolites. It is known that acid sites are related to catalytic activity<sup>1</sup> and for a given zeolite as the Si/Al ratio increases the

relative catalytic activity increases,<sup>2</sup> even though activity per acid site remains constant at higher Si/Al ratio. Therefore, for our degradation reactions, H-ZSM-5 (Si/Al = 17) would be expected to have a higher activity than H-mordenite (Si/Al = 8). The pore structures in the zeolites can affect product distribution;<sup>3</sup> the initially cracked fragments can diffuse through the pore of H-ZSM-5 (MFI structure with intersecting 5.4 × 5.6 and 5.1 × 5.5 Å channels<sup>4</sup>) and react further in the cavities created at the intersection of the two channels but not in the channels of H-mordenite (MOR structure with one-dimensional 6.1 × 7.0 Å channels<sup>4</sup>) or H-theta-1 (TON structure with one-dimensional 5.3 × 5.5 Å channels<sup>5</sup>), where there are no cavities for further reaction, hence the higher proportion of Fractions B and C in the H-ZSM-5 catalysed reaction.

In conclusion, the zeolite H-ZSM-5 is an efficient catalyst for the conversion of polymer to gasoline range chemicals. By fine-tuning the process, any additives within the polymer which may become toxic during incineration could be made safe by making use of the known properties of the zeolites.

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