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Deactivation of US-Y zeolite by coke formation during the catalytic pyrolysis of high density polyethylene[1]

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Abstract

Catalytic pyrolysis of waste polymers over zeolitic catalysts has the potential to recover valuable hydrocarbons. Thermogravimetric analysis has been used as a tool to characterise the activity, regenerability and deactivation behaviour of zeolite US-Y in the degradation of high density polyethylene (HDPE). Deactivation of the catalyst occurs due to the deposition of coke. Analysis of the TGA results allowed a relationship between catalyst activity and coke content to be derived. The catalyst activity was found to fall exponentially with coke content. © 1997 Elsevier Science B.V.

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1. Introduction

Polymer waste is a cause of increasing environmental concern in the developed world [1–4]. In view of their biodegradability, most polymers are felt unsuitable for landfill disposal. Polymer manufacture is a significant consumer of fossil fuels, and the recovery of the energy/raw material value of waste polymer is attractive [2]. The production of liquid hydrocarbons from polymer degradation would be beneficial in that liquids are easily stored, handled and transported. However, these aims are not easy to achieve. Few industrially important synthetic polymers are readily converted back to their monomers. Pyrolysis, i.e. thermal cracking of the polymers to give low molecular weight materials, is attractive, but unfortunately gives a very broad range of products – from coke to hydrogen. It also requires high temperatures, typically 400–600°C [3]. This approach has, for example, been adopted by BP in the construction of a fluidised bed thermal cracker for mixed polymer wastes. However, the BP process is believed to be uneconomic to the extent of £100 per tonne, processed at the price levels of 1994 [4].

Catalytic pyrolysis is being investigated as a means to address these problems. Suitable catalysts can both control the product range from pyrolysis and substantially reduce the reaction temperature, potentially leading to a cheaper process with more valuable products. Some recent studies of polymer catalytic pyrolysis are summarised in Table 1.

Of course, there are problems with the use of catalysts. Coke formation occurs during the reaction, and the catalysts gradually deactivate. Zeolite catalysts can be regenerated by burning off the coke, but this can result in a loss of activity. In many ways, the problems are similar to those associated with catalytic refining operations in the petroleum industry.

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This paper reports laboratory studies of the use of ultrastable-Y zeolite (US-Y) for the catalytic degradation of high density polyethylene. In order to determine kinetic parameters for the degradation, TGA and standard data analysis methods can be used. One objective of this work was to develop a protocol for the screening of other potential catalysts for their activity, deactivation behaviour and regenerability. While Audisio et al. [20] used TGA to compare polymer decomposition kinetics for various catalysts, the method has until now not been used to investigate catalyst deactivation behaviour and regenerability.

A problem in the interpretation of TGA results is quantification of the deactivation behaviour. Changes in the rate of weight loss could be due either to catalyst deactivation or to changes in the composition of the polymer residue during a run. In an attempt to decouple these two effects, a method was adopted which involved the addition of fresh polymer to catalyst samples which had already been coked to different levels. If polymer passes through the same composition profile during TGA degradation, the influence of composition difference is eliminated, and the effect of coke can be determined. Of course, this is a crude assumption, but as will be shown, it does lead to an effective means of separating the two effects. The approach is preferred to the addition of different amounts of polymer to fresh catalyst, as with higher amounts of polymer it is believed that significant proportions of the polymer are degraded thermally, without ever coming into contact with the catalyst.

Table 1
Some studies of catalytic pyrolysis of polymers using solid acid catalysts

Catalyst(s)	Polymer(s)	Reaction system	Reference
Zeolites H-ZSM5, H-Mordenite, H-mordenite, H-theta-1	LDPE	Direct contact in batch reactor at 350°C	[5,6]
Al_2O_3, Y-Al_2O_3, silica-alumina, silica, zeolites Na-Y, H-Y, RE-Y	Polypropylene, polyethylene and polystyrene	Direct contact in batch reactor at 200–600°C	[7–9]
Zeolite Na-Y	Polyethylene	Direct contact in batch reactor at 180–300°C	[10]
Silica-alumina, zeolite Ca-X	Polypropylene	Direct contact in continuous feed fixed-bed reactor at 477°C	[11]
Silica-alumina and H-ZSM5	Polyethylene, polypropylene	Pyrolysis of polymer at 400–450°C with vapours passed through catalyst bed at 420°C.	[12,13]
Zeolite H-HZMS5, silica-alumina, alumina carbon, various metal oxides	LDPE	Pyrolysis at 400°C, with vapours passed through catalyst bed	[16]
Silica-alumina, zeolites Na-Y, Na-X, Ca-A, Ca-X, Na-A	Polyethylene	Direct contact in batch reactor at 420–580°C	[17]
Silica-alumina	LDPE, HDPE	Direct contact in batch reactor and continuous fixed catalyst beds at 180–320°C	[18]
Silica-alumina	Polypropylene	Direct contact in batch reactor at 180–300°C	[19]
Alumina, silica, silica-alumina, zeolites Na-Y- H-Y, RE-Y	Polypropylene, polyethylene, polystyrene	Direct contact in batch reactor at 200–600°C and TGA	[20]

2. Experimental

Experiments were carried out using an STD-2960 simultaneous TGA-TDA system. Temperature and sample weight were recorded at 10 s intervals. The materials used were zeolite US-Y (H form, Si/Al 5.7 Crossfield Chemicals, Warrington, UK) and pure high density polyethylene (destabilised, MW $\approx$ 20000, $\rho = 960.3 \mathrm{kgm}^{-3}$, ref HLMJ-200 MJ-8, BASF).

Two types of experiment were carried out: polymer degradation and catalyst regeneration. During polymer degradation, the sample was swept with nitrogen at a fixed rate (30 ml/min). The temperature was raised from ambient to 500°C at a constant rate (in the 5–20°C/min range, depending on the purpose of the experiment). In all experiments, catalyst and polymer were present in equal weights, the total weight (catalyst plus polymer) being about ~10–15 mg. A previous work [14] showed that at these catalyst/polymer ratios the values of activation energy and reaction order determined from experiments (at least for fresh catalyst) were almost independent of the exact catalyst/polymer ratios. This gives some confidence that the results were not being biased by the influence of mixing and mass transfer in the molten polymer. During the experiments it was found that, if polymer and catalyst were unmixed, significantly higher (50–100°C) degradation temperatures were required. However, mixing of catalyst and polymer before the start of each run ensured that results were reproducible to within ±2°C. This supports the view that contact between polymer and catalyst is essential to obtaining intrinsic (i.e. not mass-transfer limited) kinetic parameters. Thorough mixing of catalyst and polymer was carried out prior to all experiments.

During catalyst regeneration, the coked catalyst was cooled from 500° to 300°C under nitrogen, and then heated in air (30 ml/min) from 300° to 600°C at 10°C/min. The temperature was maintained at 600°C for 10 min before cooling.

3. Results

Three sets of experiments carried out, as follows:

(i) Experiments were carried out at four heating rates, using fresh catalyst. The method of Ozawa [15] was used to obtain the kinetic parameters for fresh catalyst. Experimental results are shown in Fig. 1. These data ignore the initial loss of weight due to water evaporation, which is essentially complete by 130°C. Complete weight loss (i.e. 0% residue) refers to the final nonvolatile residue of catalyst and coke, and does not imply that polymer was completely decomposed. The activation energies determined by Ozawa's method at different levels of conversion from 5–95% were in the 87–115 kJ mol^{-1} range, with a mean value of 101 kJ mol^{-1}. The apparent reaction order was 2.

(ii) The regenerability of catalyst was investigated. Coked catalyst was regenerated and cooled, before a further amount of polymer (equal in weight to the catalyst) was added. Fig. 2 shows the degradation weight loss curves for fresh catalyst (RO) and the catalyst which had been used and regenerated between one and four times (R1 to R4). The greatest loss in activity was during the first regeneration, with smaller losses during subsequent regeneration.

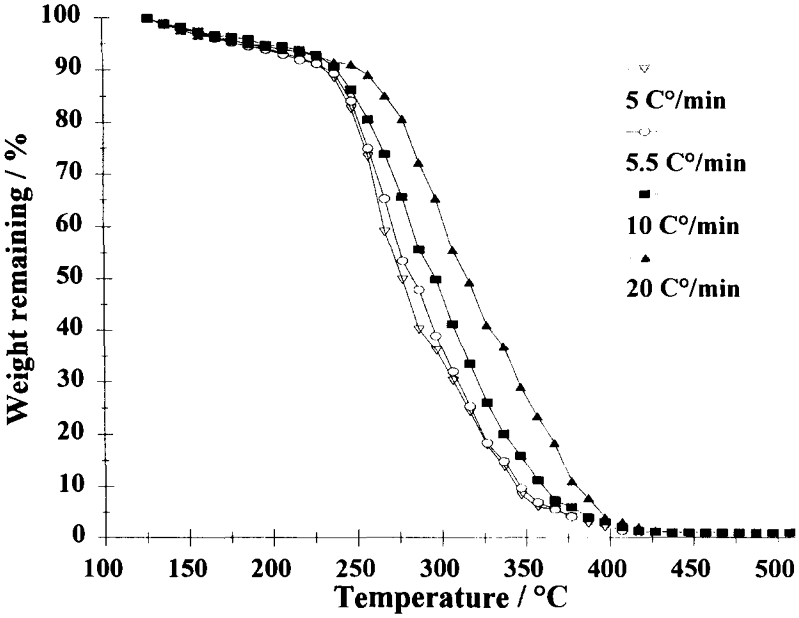

Fig. 1. Weight loss curves for HDPE in the presence of US-Y at various heating rates.

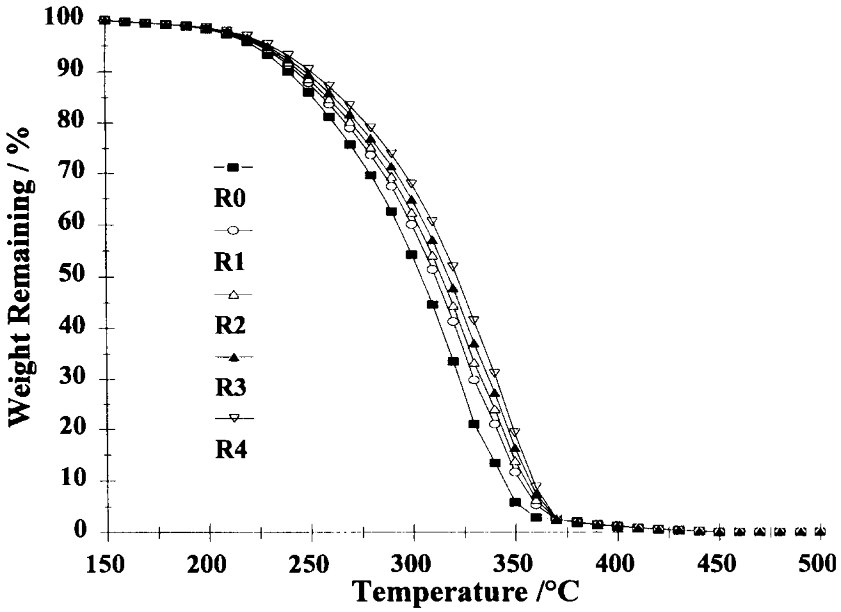

Fig. 2. Polymer weight loss curves for HDPE using fresh and regenerated US-Y catalysts.

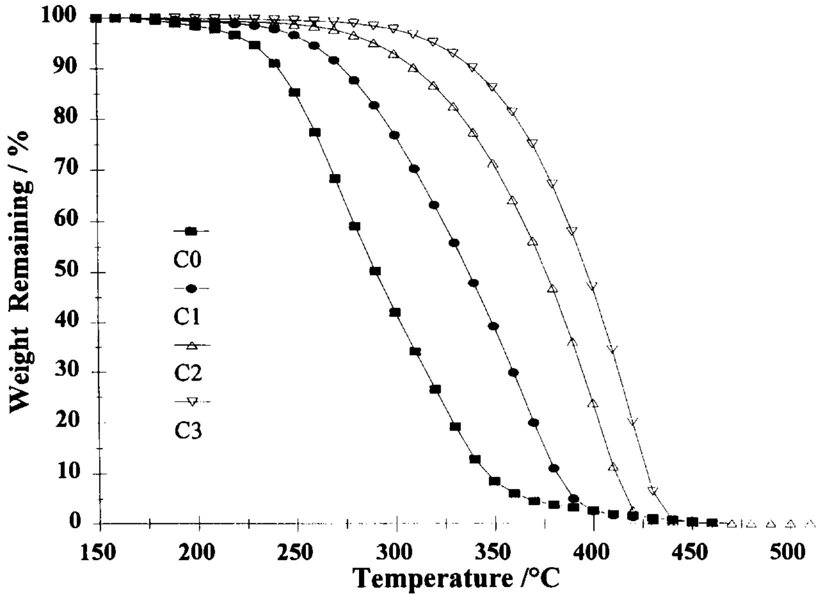

Fig. 3. Polymer weight loss curves for HDPE using fresh and pre-coked US-Y catalyst.

(iii) The change in activity of the catalyst with increasing levels of coke was investigated. Instead of regenerating the catalyst, fresh polymer – equal to the initial fresh catalyst – was added to coked catalyst. These were well mixed and a further degradation run was carried out. This procedure was repeated to find weight loss curves for catalyst which carried the coke from one, two or three degradation runs (C1, C2 or

Table 2
Coke content after various numbers of polymer degradation runs

Number of fresh polymer additions	Coke content at end of run (%w/w of catalyst)
0	7.13, 7.13
1	11.35, 11.97
2	13.87, 14.34
3	15.21, 15.78

C3). Fig. 3 shows these results plotted together with the weight loss for fresh catalyst (CO).

Besides measuring the polymer weight loss, the residual coke in catalysts exposed to one to four degradation runs, was measured by regeneration in air. Table 2 shows the coke contents measured during two sets of experiments. For each of the coke determinations of Table 2, a corresponding polymer weight loss curve had been measured. This allowed the relationship between catalyst activity and coke content to be quantified. The method used for this is described in the following section.

4. Analysis of the effect of coke on activity

To be able to quantify the change in activity of catalyst at different levels of coke, it was expedient to make some assumptions regarding the mechanism of deactivation: that the effect of coke was to obstruct active sites, and that the uncovered sites would give rise to the same reaction mechanism, and should thus give the same apparent reaction order and activation energy as had been determined using Ozawa's method. The only kinetic parameter to be affected would thus be the pre-exponential factor. By modifying the pre-exponential factor, the predicted weight loss curve could be shifted until it was as close as possible, or become coincident with the experimental curve. The criterion for coincidence was minimum sum of square differences between measured and model weight loss curves. By this method, the apparent pre-exponential factor A_i could be determined for each of the i different initial levels of coke. The catalyst activity was then defined as:

$$\eta = A_i/A_0 \qquad (1)$$

where A_0 is the pre-exponential factor determined for fresh catalyst.

A further complication is that the coke content clearly changes over the course of a polymer degradation. Thus, the activity η as defined here refers to a value intermediate between the initial and final coke contents. The mean coke content for a TGA run was taken as that corresponding to the average activity over a particular run.

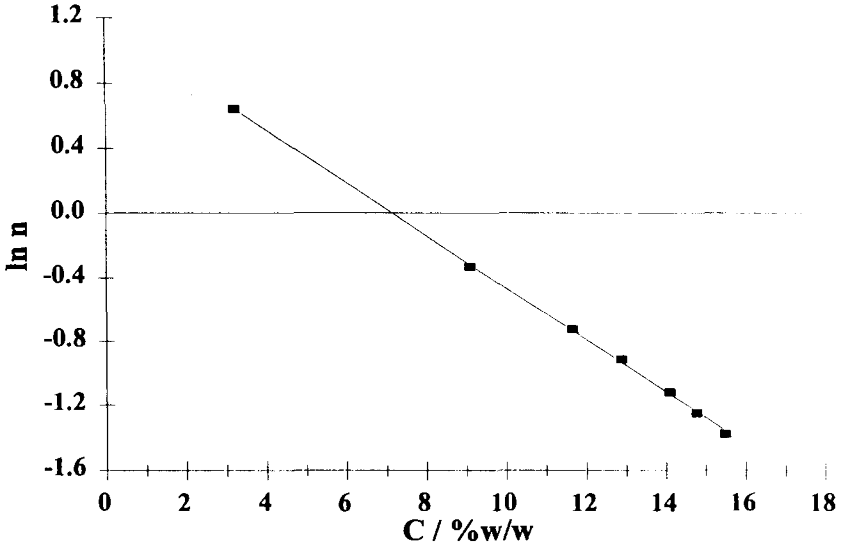

Fig. 4. Catalyst activity as a function of coke content.

Fig. 4 shows the activity defined by Eq. (1) plotted against the mean coke content during each run. The relationship between coke content and activity is found to be well represented by:

$$\eta = e^{-kC} \tag{2}$$

where k is the constant and C the coke content of the catalyst. For US-Y degrading HDPE, the value of k was found to be 0.163 $(\%w/w)^{-1}$.

5. Conclusions

TGA provides a powerful tool for the rapid investigation of catalysed polymer degradation kinetics, the rate of catalyst deactivation and catalyst regenerability. It will provide a useful screening tool allowing the comparison of a range of materials for their effectiveness in this application. While the assumptions made are necessarily crude, they do provide a convenient way of assigning activity and deactivation behaviour.

It has been found that HDPE in the presence of zeolite US-Y is degraded with an apparent activation energy of 101 kJ mol^{-1}. The reaction, apparently, was of the second order. Activity was found to decline exponentially with coke content, the catalyst losing approximately half of its activity with a coke content of 4.24%. The catalyst regained most of its initial activity on regeneration, and could be regenerated several times.

6. Nomenclature

A	Pre-exponential factor/ (min^{-1} conc)
C	Coke content/(%w/w)
k	Rate of activity loss with coke content/$(\%w/w)^{-1}$
η	Activity
subscript	
i	ith coke content
0	Initial coke content

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