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Catalytic degradation of high density polyethylene: An evaluation of mesoporous and microporous catalysts using thermal analysis[1]

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Abstract

Catalytic degradation of waste polymers offers the potential for the selective recovery of useful chemical fractions by influencing the product distributions. Thermogravimetric analysis has been used to investigate the activity of various aluminosilicate catalysts in the degradation of high density polyethylene (HDPE). Amorphous silica–alumina significantly reduced the apparent activation energy as compared with uncatalysed thermal processes. Zeolites Y and ZSM-5 further reduced the activation energy resulting in more rapid degradation. Aluminium containing MCM-41 was found to be active in the degradation of HDPE at a rate similar to that of HZSM-5, confirming the potential of this family of materials in the cracking of heavier hydrocarbons. © 1997 Elsevier Science B.V.

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1. Introduction

The recycling of polymer waste is important in the conservation of resources and the environment. Thermal degradation has been studied to characterise and determine the stability of polymers [1,2]. Unfortunately, the products of thermal degradation from many polymers are distributed over a wide range of carbon numbers and their commercial value is low, requiring upgrading for effective utilisation.

On the other hand, catalytic degradation offers the potential for selective recovery of useful chemical fractions by influencing the product distribution. Catalytic degradation of polyethylene, PE, and polypropylene, PP, has been reported to be more facile than thermal degradation giving very different product distributions [3–12]. Good gas and liquid yields have been reported using both static and flow reactors at temperatures between 200° and 600°C for a range of catalysts, including amorphous silica–aluminas, activated carbons, and zeolites Y and ZSM-5.

Catalytic degradation of polyolefins has also been investigated using thermogravimetric analysis as a potential method for screening catalysts [13,14] and it was found that the presence of catalysts led to a decrease in the apparent activation energy from 270 kJ mol^{-1} for thermal cracking to 40–190 kJ mol^{-1}. In this paper, a comparison of two types of TGA experiments has been considered, one using isothermal runs at several temperatures and the other using different heating rates [15] over the 30–600°C range.

To date, the catalytic degradation of polymeric materials has centred around the active components in commercial fluidised catalytic cracking, namely, zeolites Y and ZSM-5. One problem with polymer

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degradation over these catalysts is the limited access to the active catalytic sites via windows with diameter 0.74 nm in zeolite Y and 0.55 × 0.51 nm in ZSM-5. The new extra-large pore material MCM-41 [16] with pore openings between 2–20 nm offers interesting possibilities while considering heavier feedstocks, such as 'bottoms cracking' [17]. A thermogravimetric comparison of the aluminium and silicon forms of MCM-41 in the degradation of high density polyethylene is reported in the present paper.

2. Experimental

High density polyethylene (HDPE) in powder form, Grade HMLJ200MJ8 (average molecular weight 20 000) was obtained from BASF. The catalysts employed are listed in Table 1 and, with the exception of the MCM-41 materials, were activated before use in a flowing stream of dry nitrogen (BOC) at 450°C for 4 h. Both siliceous MCM-41 and MCM-41 incorporating tetrahedral aluminium were activated by calcination at 420°C in nitrogen for 1 h, cooled to 350°C and then calcined further in air at 540°C for 12 h.

The polymer and zeolite powders were sieved to ensure that particle sizes were not less 125 {μ}m and then blended by grinding an equal amount of catalyst and polymer together. The catalytic degradation of HDPE was investigated in a flowing nitrogen environment using a thermal analysis instrument (TA Instruments SDT 2960 simultaneous DTA–TGA). Samples were subjected to a constant heating rate while the temperature and weight were measured and recorded. Two types of pyrolysis experiments were performed; firstly, polymer/catalyst mixtures were heated at 15°C min^{-1} to 275°, 300° and 325°C and held isothermally for 120 min, and secondly, polymer/catalyst mixtures were heated to 600°C at constant heating rates of 5°, 5.5°, 10° and 20°C min^{-1}.

Table 1
Catalysts used in polyethylene degradation

Catalyst	Commercial name	Si/Al
Silica–alumina (SAHA)	Synclyst 25 [a]	2.7
HY	H-Y zeolite [a]	2.6
HUSY	H-Ultrastabilised Y zeolite [a]	6.0
HZSM-5 (17)	HZSM-5 zeolite [b]	17
HZSM-5 (70)	HASM-5 zeolite [b]	70
MCM-41 (Al)	— [c]	17.5
MCM-41 (Si)	— [c]	>600 [d]

[a] Crosfield chemicals (Warrington, UK).
[b] BP chemicals (Sunbury-on-Thames, UK).
[c] Synthesised by procedure outlined by Beck [18,19].
[d] As determined by the experimental limits of elemental analysis for Al and Si.

The mass of coke deposited on the catalysts after the degradation of HDPE was determined by reheating the catalysts to 600°C in air at 10°C min^{-1} in the thermobalance.

2.1. Data analysis

TGA data from isothermal experiments at 275°, 300° and 325°C were analysed by using a least squares fitting of the integrated rate equation (Eq. (1)) to the experimental data:

$$P_t = [P_{t=0}^{n-1} + (n-1)kt]^{1/1-n} \qquad (1)$$

Since the polymer mass (P) is 1 at time (t) = 0, then Eq. (1) can be reduced to

$$P_t = [1 + (n-1)kt]^{1/1-n} \qquad (2)$$

This equation applies to a system in which conversion can be attributed entirely to weight loss. As pointed out later, catalytic processes produce 'coke' and the picture is more complicated.

In the fitting of the three curves, each was assumed to have its own rate constant (k), but the reaction order (n) was assumed the same for all three temperatures. Thus, in the data fitting there were four variables, the three rate constants and the order, n.

Data from the experiments to 600°C using different heating rates was treated using Ozawa's method [15]. In both cases, the apparent activation energies for the catalysts used were estimated from the Arrhenius temperature dependence using the value for k.

3. Results and discussion

3.1. Effect of catalyst

Although the process of catalytic degradation of HDPE is far from an elementary reaction, kinetic information derived from thermogravimetric analysis, such as apparent activation energies, can be used for

Table 2
Comparison of activation energies (E_{act}) determined for the catalytic degradation of HDPE using two different mathematical models

Catalyst	Integrated rate equation E_{act}/kJ mol^{-1}	Ozawa model E_{act}/kJ mol^{-1}
HZSM-5 (17)	105	118
HZSM-5 (70)	113	114
HY	103	119
HUSY	95	118
MCM-41 (Al)	77	74
MCM-41 (Si)	201	209
Silica–alumina (SAHA)	147	128
No catalyst	—	255

internal comparisons of catalysts. As shown in Table 2, the presence of catalysts leads to a decrease in the apparent activation energies. The average activation energy for the thermal degradation of HDPE was in agreement with previous literature values (250–305 kJ mol^{-1}) [20,21].

As expected, amorphous silica–alumina significantly reduced the activation energy as compared with thermal processes, and zeolites further reduced the activation energy (95–110 kJ mol^{-1}) resulting in more rapid degradation.

Both mathematical treatments of the data give similar values for activation energies for the reaction over various catalysts; however, the mathematical treatment of data from isothermal runs at 275°, 300° and 325°C appear to show a larger difference between silica–alumina and the zeolite catalysts.

3.2. *Effect of acidic character*

Acid-catalysed degradation of hydrocarbons is known to proceed via carbonation mechanisms, initiated either by proton donation (Brønsted acid sites) or by hydride abstraction (Lewis acid sites). Our preliminary infrared studies revealed the acidity of the silica–alumina catalysts to be over 90% Lewis in character and this could account for the differences in the activation energy of this catalyst, compared with that of the zeolites, ZSM-5 and Y, where catalytic sites are almost entirely Brønsted acid sites when activated at temperatures of 350°C and below [22].

3.3. *Effect of pore architecture*

Although a slight difference was observed in the activation energies for the zeolite catalysts, ZSM-5 and Y, the much higher coke levels for both Y catalysts (Table 3) reflect the larger pore opening of zeolite Y (0.74 nm) and the presence of supercages within the structure of $\approx$1.3 nm diameter. On the other hand, ZSM-5 has narrower pore openings, $\sim$ 0.55$\times$ 0.51 nm, and no supercages. Therefore, bulky feed molecules have restricted access to the internal active catalytic sites and spacial restrictions within the pore system tend to inhibit the bimolecular processes leading to 'coke' production. Consequently, ZSM-5 catalysts show much lower coke levels.

The restricted access to the zeolitic materials probably means that the initial degradation of high molecular weight polymers predominantly occurs on the outer surface or at the pore openings. Since zeolites have a very large internal surface area, a great number of the catalytic sites are initially unavailable for the degradation of large molecules, such as polymers. However, smaller cracked products may gain entry to the zeolitic channels, and then give rise to differing product distributions due to differences in pore systems which influence product selectivities with zeolite catalysts.

The new mesoporous materials with pore sizes between 2 and 20 nm may allow the polymer to diffuse to the majority of the active sites. As expected, the siliceous form of MCM-41, containing virtually no aluminium, has a minimal effect on HDPE with degradation occurring at a temperature similar to that of thermal cracking. A slight reduction in the activa-

Table 3
Comparison of coke levels, determined by TGA, on catalysts after degradation of HDPE at 600°C

Catalyst	Coke level/wt%
HZSM-5 (17)	0.7
HZSM-5 (70)	0.3
HY	10.6 [a]
HUSY	9.4 [a]
MCM-41 (Al)	0.2
MCM-41 (Si)	<0.1
Silica–alumina (SAHA)	0.3

[a] These high coke levels make for additional difficulty in the simple rate treatment used.

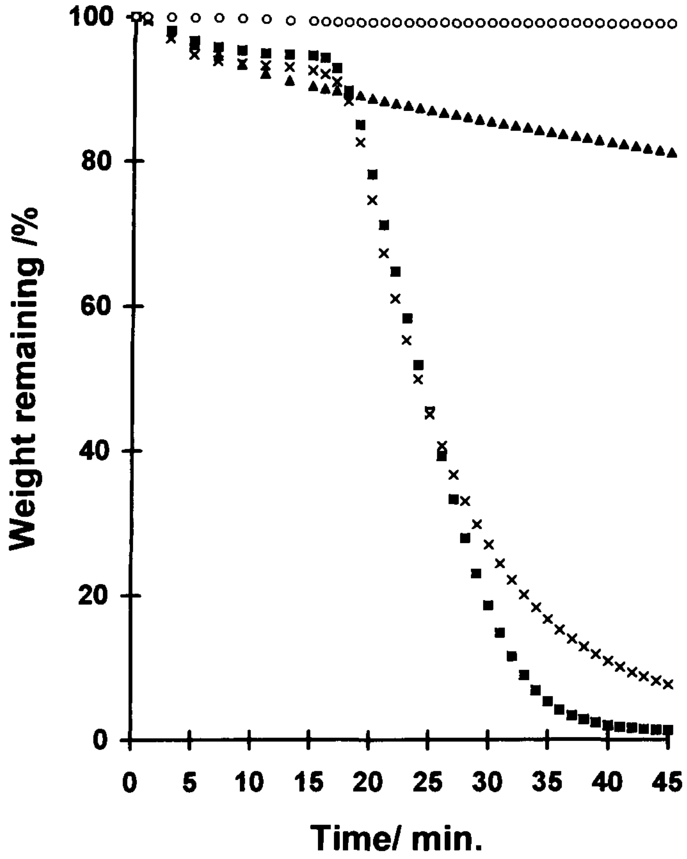

Fig. 1. Weight loss curves for HDPE in the presence of (■) – HZSM-5 (17), (x) – Al-containing MCM-41, (▲) – silica–alumina, and (○) – purely siliceous MCM-41.

tion energies compared with thermal degradation (Table 2) is observed and is comparable to that observed for amorphous silica used by other workers [13]. Incorporation of aluminium into zeolite frameworks typically generates acid sites (both Brønsted and Lewis), and a similar feature is expected within MCM-41 materials. This acidity, coupled with the larger pore openings of MCM-41 materials (sorption measurements indicate around 5.0 nm for this sample), leads to a significant lowering of the activation energy. Fig. 1 shows the comparable rates of degradation of HDPE for ZSM-5(17) and MCM-41 containing aluminium.

For zeolite catalysts, the apparent activation energies would appear to be associated with a rate determining step involving chemical reaction, presumably at active sites on the external surface. In the case of the MCM-41 containing aluminium, the relatively low apparent activation energy may indicate constraints on the diffusion of liquid polymer into the pores, although the differences in the nature of the sites (compared to zeolites) may also be relevant. If the pores of MCM-41 are readily accessible to the polymer, then the overall activity in polymer degradation appears to be roughly comparable to that of only the external acid sites of ZSM-5(17), based solely on TGA data obtained.

4. Conclusion

TGA provides a useful and convenient tool for comparing a wide range of materials for the catalytic degradation of polymers. Apparent activation energies for the catalytic degradation of HDPE, calculated on the basis of the two mathematical models outlined in this paper, were in the following order:

$$\text{MCM-41(Si)} < \text{SAHA} < \text{zeolites(ZSM-5, Y)} < \text{MCM-41(Al)}$$

New mesoporous materials, in particular MCM-41 containing aluminium, are reported to be of potential interest in the cracking of heavier feedstocks [17]. The results of the present study confirm this suggestion since these materials are active in the degradation of polyolefins.

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