Chemical catalysed recycling of polypropylene over a spent FCC catalyst and various commercial cracking catalysts using TGA

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Abstract

Thermogravimetric analysis (TGA) has been used as a tool to characterise the activity, regenerability and deactivation behaviour of spent FCC commercial catalyst (FCC-s1) in the degradation of polypropylene. The FCC-s1 catalysts and amorphous silica–alumina (SAHA) significantly reduced the activation energy as compared with thermal process, and zeolites (ZSM-5 and HUSY) further reduced the activation energy. However, silicalite catalysts gave very minimal effect on PP degradation at a temperature similar to that of thermal cracking. Analysis of the TGA results allowed a relationship between catalyst activity and coke content to be derived. The activity of FCC-s1 catalysts was found to fall exponentially with coke content, and it could be recover most its initial value. The results represent an interesting alternative to have significant impact on the economics of a catalytic polymer degradation process employing post-use FCC commercial catalysts of zero market value.
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1. Introduction

The recycling of polymer waste is important in the conservation of resources and the environment [1]. The destruction of wastes by incineration is prevalent, but is expensive and often generates problems with unacceptable emissions. It is also undesirable to dispose of waste plastics by landfill due to high costs and poor biodegradability. 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 [2]. An alternative strategy is that of chemical recycling, which has attracted much interest recently with the aim of converting waste polymers into basic petrochemicals to be used as hydrocarbon feedstock or fuel oil for a variety of downstream processes [3].

Two main chemical recycling routes are the thermal and catalytic degradation of waste polymers. In thermal degradation, the process produces a broad product range and requires high operating temperatures, typically more than 500 °C and even up to 900 °C [4–8]. These facts strongly limit their appli-

cability and especially increase the higher cost of feedstock recycling for waste plastic treatment. Therefore, catalytic degradation provides a means to address these problems [9,10]. The addition of catalyst is expected to reduce decomposition temperature, to promote decomposition speed, and to modify the products. The catalytic degradation of polymeric materials has been reported for a range of model catalysts centred around the active components in a range of different model catalysts, including amorphous silica–aluminas, zeolites Y, mordinite and ZSM-5 [11–16] and the family of mesoporous MCM-41 materials [17–19]. However, these catalysts have been used that even if performing well, they can be unfeasible from the point of view of practical use due to the cost of manufacturing and the high sensitivity of the process to the cost of the catalyst. Another option for the chemical recycling of polymer wastes by using fluidized catalytic cracking (FCC) catalysts is attractive [20–22]. Therefore, an alternative improvement of processing the recycling via catalytic cracking would operate in mixing the polymer waste with fluid catalytic cracking (FCC) commercial catalysts.

Additionally, from an economic point of view and taking into account the reaction conditions needed, a process could be the most favourable solution if the catalyst cost is practically zero for the catalytic conversion of polymer waste [23–25]. To date, the catalyst used in the FCC process comprises 5–40% zeolite

dispersed in a matrix of synthetic silica–alumina, semi-synthetic clay-derived gel, or natural clay. These catalysts increase significantly the commercial potential of a recycling process based on catalytic degradation, as cracking catalysts could cope with the conversion of plastic waste co-fed into a refinery FCC unit. A more interesting approach is that of adding polymer waste into the FCC process, under suitable process conditions with the use of zero value of spent FCC catalysts, a large number of waste plastics can be economically converted into valuable hydrocarbons. Moreover, there are problems with the use of this kind of cracking catalysts; in particular, coke formation occurs during the reaction and the catalysts gradually deactivate. Considering that the FCC process follows an operation based on the equilibrium between the coke combustion and its consumption by cracking reactions, the yield of coke from the polymers deserves special consideration, since it is significant and could govern the implementation of this option. The objective of this work is to explore the capabilities of TGA system in the catalytic degradation of polypropylene for the development of several concepts intended to investigate the spent FCC catalyst for its activity, deactivation behaviour and regenerability, and specifically for the comparison of other commercial cracking catalysts involved to enhance the potential benefit of catalytic polymer recycling.

2. Experimental

2.1. Materials and TGA experiments

The polymer used in this study was pure polypropylene (PP; isotactic, $\rho = 853.6 \, kg m^{-3}$, MW $\approx 332,000$, Aldrich). The catalysts employed are described in Table 1. Prior to use, all the catalysts were pelleted, crushed and sieved to give particle sizes ranging from 75 to 180 μm. In the case of the spent FCC catalyst, it normally holds a certain amount of coke, and air is needed to burn it off at high temperature before further application [22]. During catalyst regeneration, the FCC catalyst was dried by heating under air from 120 to 520 °C at 60 °C h^{-1} for 2 h, and then heated in flowing nitrogen to 550 °C at a rate of 120 °C h^{-1} to reactive the catalyst. Other catalysts were

dried by heating in flowing nitrogen (50 ml min^{-1}) to 120 °C at 60 °C h^{-1}. After 2 h the temperature was increased to 520 °C at a rate of 120 °C h^{-1} to active the catalyst for 5 h. Before TG experiments were started, both catalyst (75–125 μm) and polymer (75–180 μm) were chosen with several fluidisation runs at ambient temperature and pressure were performed to meet the need of mixing reproducibility. Additionally, a higher flow rate of nitrogen gas (100 ml min^{-1}) were used in all TG runs to improve the external heat transfer between the molten polymer and the outside of the catalyst particles after well purging the analyzer to inert the atmosphere inside. The polymer and catalyst powders were sieved to ensure that particle sizes were not more 180 μm and then blended by grinding an equal amount of catalyst and polymer together. The catalytic degradation of PP was investigated in a flowing nitrogen environment using a thermogravimetric 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. In all experiments, catalyst and polymer were present in equal weights, the total weight (catalyst plus polymer) being at about 10 ± 1 mg. Although TGA is a useful tool for the screening of potential catalysts in related to their kinetic parameters for polymer catalytic degradation, an extensive investigation of catalyst deactivation with several cycles of polymer addition may introduce a limit in the use of polymer/catalyst ratios. The FCC-s1 catalyst used in this study is a spent equilibrium catalyst obtained from a commercial FCC unit with different levels of metal contamination and a mixture of Y zeolite, a silica–alumina matrix and binder, which indicates that a high amount of catalyst can be used, mainly when compared with FCC processes working with quite higher plastic/catalyst ratios.

Two types of TGA experiment were carried out: polymer degradation and catalyst deactivation. During polymer degradation, only one stage of dynamic experiment was performed. Polymer/catalyst mixtures were heated to 770 K at constant heating rates of 3, 5, 10 and 20 K min^{-1}, and held isothermally for 120 min to crack unconverted fragments further by catalytic cracking and/or thermal cracking. During catalyst deactivation,

Table 1
Catalysts used in the catalytic degradation of polypropylene.

Catalyst	Si/Al	Surface area (cm²/g)			Pore size (nm)	Acidity[a] (μmol Py/g catalyst)		Commercial name
		BET[b]	Micro	External		Brønsted	Lewis	
FCC-s1	2.1	147	103	44	–[c]	4.8	3.7	Equilibuium catalysts[d]
ZSM-5	17.5	391	263	128	0.55 × 0.51	39.1	26.1	ZSM-5 zeolite[e]
HUSY	13.6	547	429	118	0.74	33.4	19.8	Ultrastabilised Y zeolite[d]
SAHA	3.6	268	21	247	3.28[f]	1.9	22.6	Amorphous silica–alumina[d]
Silicalite	>1000	362	297	65	0.55 × 0.51	–[g]		Synthesized in-house

[a] Measured by IR spectroscopy and adsorption–desorption of pyridine (Py) at 573 K for the amount of adsorbed Py (μmol/g) on both acid sites of catalysts.
[b] Total surface area (BET).
[c] The FCC-s1 catalyst used was a spent (coked) equilibrium catalyst obtained from a commercial FCC unit with different levels of metal (Ni and V) contamination and a mixture of Y zeolite, a silica–alumina matrix and binder, not determined.
[d] Chinese Petroleum Corp., CPC, Taiwan, ROC.
[e] BP Chemicals, Sunbury-on-Thames, UK.
[f] Single-point BET determined.
[g] The siliceous form of ZSM-5 with very few or no catalytically active sites, not determined.

the coked catalyst was cooled from 770 to 520 K under nitrogen, and then heated in air (30 ml min^{-1}) from 520 to 870 K at 10 K min^{-1}. The temperature was maintained at 870 K for 20 min before cooling. Owing to the limit of TG experiments, only the low boiling point reaction products formed by the cracking events occurring at the end of the chain will come out from the reactor, while the products with longer chains will stay in the reactor being available for potential cracking processes. Therefore, the PP can be cracked at 770 K with or without the catalysts, and the content of coke can be determined using TGA by the change weight at 870 K after burning off. The mass of coke deposited on the catalysts (coke content) after the degradation of polymer was then determined. The change in activity of the catalyst with increasing levels of coke was also investigated. Instead of regenerating the catalyst, fresh polymer (equal to the initial fresh catalyst) was added with well mixed and a further degradation run was carried out to coke catalyst.

2.2. TGA data analysis

TGA data from the experiments to 770 K (ramped temperature) using different heating rates (3, 5, 10 and 20 K min^{-1}) was estimated using Ozawa's method [26]. If it is assumed that the reactions can be modelled by a single nth-order reaction, the weight loss curve can be expressed as

$$-\frac{\mathrm{d}w}{\mathrm{d}t} = kw^n \tag{1}$$

where w is the weight percentage of remaining polymer, t is the time, k is the rate constant and n is the reaction order. Although the polymer cracking process is a complex one often the kinetic model used for interpretation of TGA data assumes that the overall degradation rate can be expressed by a simple kinetic equation. It is also derived from the simple nth order model used for isothermal experiments combined with Arrhenius given in the following equation

$$-\frac{\mathrm{d}w}{\mathrm{d}t} = A \exp\left(\frac{-E_a}{RT}\right) W^n \tag{2}$$

Since $T = T_0 + at$ at a constant heating rate of a, $\mathrm{d}T = a \times \mathrm{d}t$ which can be substituted into Eq. (2) and integrated to give an infinite series as shown in the following equation

$$-\int_{w_0}^{w} \frac{\mathrm{d}w}{w^n} = \frac{A}{a} \int_{T_0}^{T} \exp\left(\frac{-E_a}{RT}\right) \mathrm{d}T$$
$$= \frac{AE_a}{aR} \left[\frac{\exp(-E_a/RT)}{E_a/RT} + \left(\ln\frac{E_a}{RT} - \frac{E_a}{RT} + \ldots\right) \right] \tag{3}$$

By integration and using Doyle's approximation [27], the function P can be approximated by Eq. (4) and therefore Eq. (3) becomes Eq. (5)

$$\log P\left(\frac{E_a}{RT}\right) = c + m\left(\frac{E_a}{RT}\right) \tag{4}$$

$$-\int_{w_0}^{w} \frac{\mathrm{d}w}{w^n} = \left(\frac{AE_a}{aR}\right) P\left(\frac{E_a}{RT}\right) \tag{5}$$

where c and m are constants whose values are estimated by Doyle. For a given weight fraction the right-hand side of Eq. (5) is constant as shown in the following equation

$$\left(\frac{AE_a}{a_1R}\right) P\left(\frac{E_a}{RT_1}\right) = \left(\frac{AE}{a_2R}\right) P\left(\frac{E_a}{RT_2}\right) = \ldots \tag{6}$$

Using the approximation given by Doyle and taking the logarithm, a linear equation can be written

$$-\int_{w_0}^{w} \frac{\mathrm{d}w}{w^n} = -\log a_1 - 0.4567\left(\frac{E_a}{RT_1}\right)$$
$$= -\log a_2 - 0.4567\left(\frac{E_a}{RT_2}\right) = \ldots \tag{7}$$

The use of a more precise approximation for the function P in Eq. (5) has been reported elsewhere [28]. Further increase in precision of the integral methods can be accomplished by using numerical corrections [29] or by directly performing numerical integration [30]. As reported previously [31], during the TG experiments, it was found that, if polymer and catalyst were unmixed, significantly higher (50–100 K) degradation temperatures were required. Mixing of catalyst and polymer before the start of each run ensured that results were reproducible to within 2 K. Therefore, well mixing of catalyst and polymer was carried out prior to all experiments. This provides the view that contact between polymer and catalyst is essential to obtaining intrinsic (i.e. not mass-transfer limited) kinetic parameters.

2.3. Catalytic fluidised-bed reaction experiments

The information of product distribution for the catalytic degradation of polypropylene (PP) over spent FCC commercial equilibrium catalyst (FCC-s1) is necessary because its contribution could be significant for further comparison and detailed discussion of the reaction kinetics. The experimental system for catalytic conversion of commingled polymer waste into hydrocarbons over various catalyst in a fluidised-bed reactor is given elsewhere [32] and modified to meet the need for PP degradation over FCC-s1 catalyst. A calibration cylinder containing 1% C_1–C_5 hydrocarbons was used to help identify and quantify the gaseous products. Gaseous hydrocarbon products were analysed using a gas chromatograph equipped with (i) a thermal conductivity detector (TCD) fitted with a 1.5 m × 0.2 mm i.d. Molecular Sieve 13X packed column and (ii) a flame ionisation detector (FID) fitted with a 50 m × 0.32 mm i.d. PLOT Al_2O_3/KCl capillary column. The remaining solid deposited on the catalyst after the polymer degradation was deemed "residues " and contained involatile products and coke. The amount and nature of the residues was determined by TGA (calculated as described in Section 2.1 by heating the deposited catalyst to 870 K in 30 ml min^{-1} air). Products (P) are grouped together as hydrocarbon gases (<C_5), gasoline up to C_9 (C_5–C_9), liquids (condensate in condenser and filter) and residues (coke and
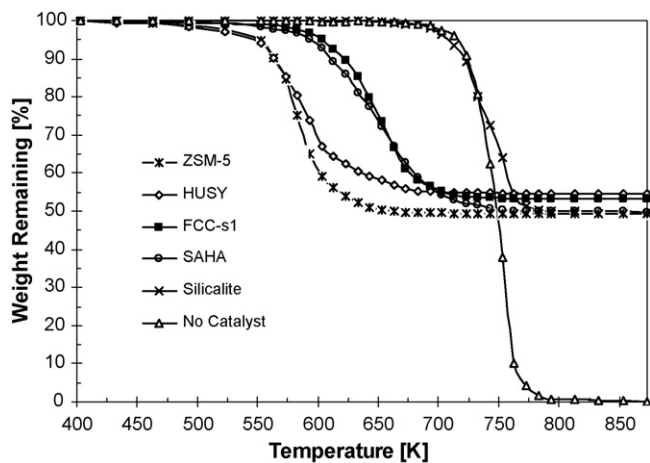
Fig. 1. Comparison of TG curves for the thermal and catalytic pyrolysis of polypropylene at a 10 K/min heating rate under nitrogen stream.

Fig. 2. Weight loss curves for PP degradation in the present of spent equilibrium fluidised catalytic cracking commercial catalyst (FCC-s1) at various heating rate.

products, deposited on catalyst) to enable the overall pyrolysis processes to be described more easily.

3. Results and discussion

3.1. Degradation of PP over a spent FCC catalyst in TGA

TGA curves for the reactions of PP degradation with and without the presence of catalysts at 10 K min⁻¹ heating rate are also shown in Fig. 1. Due to nonvolatile products with high molecular weight materials formed and consequently deposited in the catalyst system, it is difficult to take them away during the TG process with nitrogen carried gas used, and this results in some degree of increasing the weight percentage remaining. Since the pore structure of the catalyst is an important factor for the cracking process, the TG runs for PP degradation over HUSY and FCC-s1 catalysts gave higher weight remaining than ZSM-5, silicalite and SAHA catalysts. As shown in Fig. 1, it appears that the PP can be cracked at 770 K with or without the catalysts, and the content of coke can be determined using TGA by the change weight at 870 K after burning off. Comparing the two curves of PP degradation with silicalite and without catalyst, it is observed both are practically identical. The siliceous form of ZSM-5, silicalite, containing very few or no catalytically active sites, gave very minimal effect on PP degradation at a temperature similar to that of thermal cracking. As expected, clear differences observed have shown a remarkable effect of the presence of spent fluid catalytic cracking catalyst (FCC-s1) compared to catalyst free. However, with the strong acidity zeolites (ZSM-5 and HUSY) the degradation of 90% polymer takes place at considerably lower temperatures and is complete at a temperature at which in both FCC-s1 and SAHA catalysts just half of the original PP has been degraded. Although TGA is a useful tool for the screening of potential catalysts in related to their kinetic parameters for polymer catalytic degradation, an extensive investigation of catalyst deactivation with several cycles of polymer addition may introduce a limit in the use of polymer/catalyst ratios. The use of this reaction system coped with a spent FCC catalyst can be a better option since it can gives
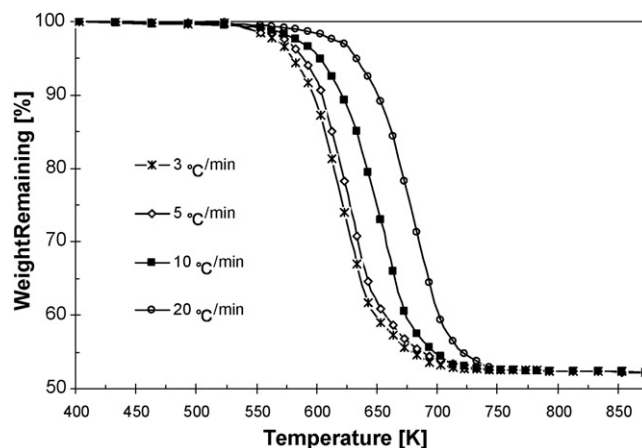
a good conversion compared with silicalite, and even its activity is lower than that of the ZSM-5, HUSY and SAHA catalysts, this can be compensated by increasing the catalyst to PP ratio.

The results for TG reactions of polypropylene degradation at a definite temperature over spent FCC commercial catalysts (FCC-s1) at four heating rates are shown in Fig. 2. The differences in deviation from TG curves for the degradation of PP is associated with both the nature of reaction mechanism and the use of different heating rates used in this study. The latter is a general characteristic of dynamic reaction. The former leads to production of a variety of volatile products. It is seem that the activation energy increases with the degree of conversion within the range of 10–90% weight loss curves calculated by the iso-conversion plot and the values as presented in Table 2. This effect could be ascribed to the nature of scission degradation in the presence of various cracking catalysts and the differences in deviations from the effect of volatile fragment diffusion at different level of coke content, as well as the relation of transient change in catalytic activity to catalyst deactivation. Although the process of catalytic degradation of PP 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 determined for the thermal and catalytic degradation of PP in nonisothermal TG weight loss curves at different heating rates (3, 5, 10 and 20 K min⁻¹) by using Ozawa method

Weight remaining (wt%)	Activation energy (E_a/kJ mol⁻¹)		
	FCC-s1	Silicalite	No catalyst
90	80.7	130.4	142.7
80	82.7	135.5	134.9
70	85.4	134.0	132.7
60	87.4	138.4	133.5
50	89.1	139.7	144.5
40	88.5	146.7	152.4
30	89.3	149.3	157.2
20	89.6	155.7	161.5
10	91.5	160.6	167.9
Mean	87.1	143.4	147.5

internal comparisons of catalysts. As can be seen in Table 2, the average activation energy for the thermal degradation of PP was in agreement with previous literature values, while silicalite catalysts gave only a slight reduction in the average of activation energy (143.4 kJ mol^{-1}) compared with thermal experiments (147.5 kJ mol^{-1}) [33–35]. Both Saha et al. [35] and Vyazovkin et al. [36,37] have applied the advanced isoconversional analysis called model-free kinetics to reduce a systematic error appeared in the integral method. In the case of thermal cracking of PP using a similar molecular weight range by Saha et al. [35], the value of activation energy (120–170 kJ mol^{-1}) is consistent with the present result (133–168 kJ mol^{-1}). However, the activation energy (150–250 kJ mol^{-1}) obtained by Vyazovkin et al. [36] and Peterson et al. [37] are larger than those calculated in this work. The existing differences in the activation energy might be due to different molecular weights of the PP polymer employed as well as due to the variation of model-free kinetic analysis used for those cases.

For noncatalytic decomposition, activation energy (133–168 kJ mol^{-1}) is a slowly increasing with degradation extent in the 20–90% range. Studies of Filho et al. [38] on variation of activation energy (130–175 kJ mol^{-1}) with degradation extent for PP decomposition are compared with the present results in the same trends along with a minor deviation of each value to that observed by us. Since the difference in deviation of activation energies for PP degradation is associated with the nature of polymer structures related to their molecular weights, the type of TG runs and their model-fitting methods, the values calculated by Vyazovkin et al. [36] and Peterson et al. [37] are larger than those obtained in this work. The results indicate that a generation of secondary reaction and oligomerisation is followed by a faster formation of unzipped intermediates via thermal cracking reactions, within the different degree of reaction temperature used in TG runs, to give relatively different amounts of volatile and nonvolatile products in different level of weight loss varied with the changes of activation energies. The value of activation energy for PP/silicalite decomposition at different fraction residual weights showed relatively comparable deviation among each other may be associated with the reaction mechanism occurring at a temperature with each degree of thermal conversion. The activation energies determined by Ozawa's method at different levels of conversion from 10 to 90% were in the 80.7–91.5 kJ mol^{-1} range, with a mean value of 87.1 kJ mol^{-1}. It is also observed that the difference in activation energy between FCC-s1 and silicalite catalysts is slowly increasing with function of degradation extent. The average of activation energy for PP degradation over FCC-s1 catalyst is much lower than those for both silicalite or noncatalytic cases. However, the comparison is not straightforward as reaction conditions are not perfectly matched: polymer structure, particle sizes, ratios of polymer to catalyst and internal voidage of polymer/catalyst mixture will be different, and the composition of catalysts are different. The average of activation energy for PP degradation over FCC-s1 catalyst is much lower than those for both silicatlte or noncatalytic cases. Similar type of reduction of activation energy is obtained in the present case with various cracking catalysts in comparison to zeolitic catalysts used by
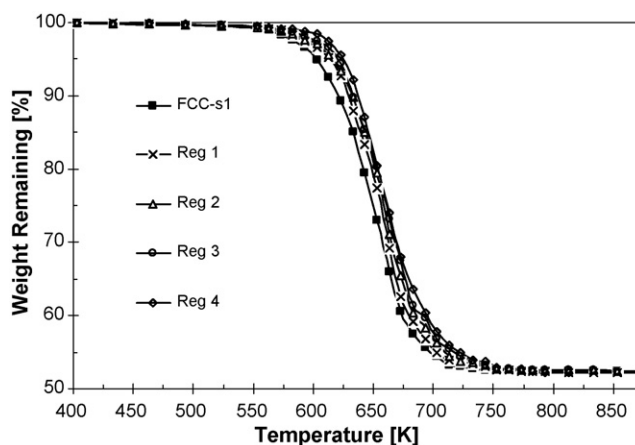

Fig. 3. TG weight loss curves for PP degradation using FCC-s1 and regenerated catalysts.

Filho et al. [38]. Similar trends for catalytic runs for any value of degradation extent can be obtained due to the fact that similar reaction mechanism might be followed for those cases of degradation to give small cracked products. The apparent reaction order was 2. In this study, much lower apparent activation energy values were observed for FCC-s1 catalysts compared to silicalite catalysts. This indicates that the presence of spent FCC catalyst may allow the primary converted polymer to diffuse to the majority of the active sites, and consequently lead to the relatively low apparent activation energy. Coked catalyst was regenerated and cooled, before a further amount of polymer (equal in weight to the catalyst) was added. Fig. 3 shows the degradation weight loss curves for fresh catalyst (F1) and the catalyst that had been used and regenerated between one and four times (R1–R4). Slightly loss observed in activity was during the first regeneration, with only a few considerable losses during subsequent regeneration. It is indicates that the catalyst can regain most its initial activity on regeneration, and could be regenerated several times.

3.2. Relation of coke formation to spent FCC catalyst deactivation in TGA

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. Besides measuring the polymer weight loss, the residual coke in catalysts exposed to one to four degradation runs, was measured by regeneration in air. This procedure was repeated to find weight loss curves for catalyst that carried the coke from one, two or three degradation runs (Coke 1, Coke2 or Coke 3). Fig. 4 shows these results plotted together with the weight loss for fresh catalyst (Fresh FCC-s1). If polymer passes through the same composition profile during TGA degradation, the influence of composition difference is eliminated, and the effect of
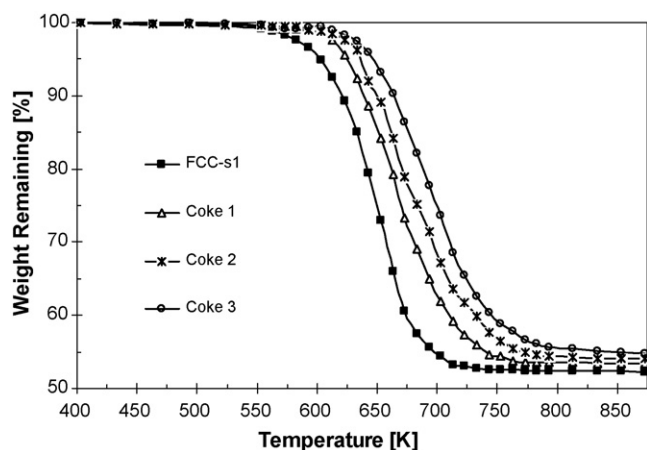
Fig. 4. TG weight loss curves for PP degradation using FCC-s1 and the pre-coked catalysts.

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. The change in activity of the catalyst with increasing levels of coke was also investigated. Instead of regenerating the catalyst, fresh polymer (equal to the initial fresh catalyst) was added with well mixed and a further degradation run was carried out to coke catalyst. Table 3 shows the coke contents and half-degradation temperature measured during two sets (set A and set B) of experiments. The degradation temperature of 50% weight loss was about 650 K for fresh PP cracking over a FCC-s1 catalyst, and it shifted to a high temperature with an increase in the level of coke deposition along with the number of polymer addition. As shown in Table 3, the value of half-degradation temperature increases with the degree of coke content for two parallel sets of each cycle under four PP additions. The value of half-degradation temperature increases with the degree of coke content for two parallel sets of each cycle under four PP addition runs. Higher half-degradation temperatures obtained in set B indicating that PP can be cracked at or close to the external surface of the catalysts and therefore, the controlling catalytic factors will be associated with the number of accessible spaces in related to the value of coke content deposited on the catalyst and the total number of acid sites.

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. The mechanism involved is associated with the diffusion of bulky fragments for the unreacted or partially reacted polymer softened by dissolution of low molecular species deposited on the catalyst. Since the coking mechanism related to catalyst deactivation in each cycle of regeneration times for the catalytic degradation of PP can be assumed with the same apparent activation energy, 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. Hence, 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. 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

$$\eta = \left(\frac{A_i}{A_0} \right) \tag{8}$$

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. The activity η as defined here refers to a value intermediate between the initial and final coke contents. Thus, the mean coke content for a TGA run was taken as that corresponding to the average activity over a particular run. Fig. 5 shows the activity defined by Eq. (8) plotted against the mean coke content during each run. The relationship between coke content and FCC-s1 activity is found to be well represent by:

$$\eta = (\exp^{-\alpha C}) \tag{9}$$

where α is the constant and C is the average coke content of the FCC-s1 catalyst. For spent FCC degrading PP, the value of α was found to be 0.084 (% w/w)$^{-1}$. It can be obtained that the FCC-s1 catalyst loses approximately half of its activity with a coke content of 5.4%.

Table 3
Half-degradation temperature and coke content determined at the end of each reaction after two parallel sets of each cycle under four PP additions

Number of fresh polymer additions	Set A		Set B	
	Half-degradation temperature (K)[a]	Coke content (% w/w)	Half-degradation temperature (K)	Coke content (% w/w)
0	648.7	5.68	651.2	5.68
1	672.1	8.42	679.5	9.98
2	687.1	11.29	695.3	12.62
3	703.7	13.71	709.4	14.91

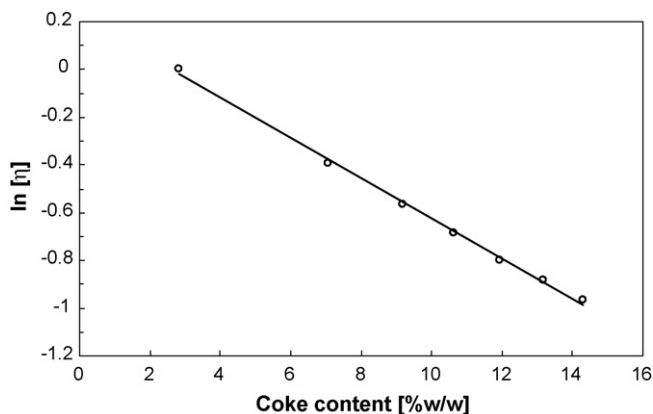[a] The degradation temperatures determined by the weight loss of 50% PP in the TG curves.

Fig. 5. Catalyst activity as a function of coke content for the catalytic degradation of two parallel sets of PP additions over FCC-s1 catalysts.

3.3. Comparison with other commercial cracking catalysts in TGA and fluidised-bed reactions

In order to further study the catalytic effect in the course of the reaction for pp degradation, the activation energies with various commercial cracking catalysts were also determined. Acid-catalysed degradation of hydrocarbons is known to proceed via carbonation mechanisms, initiated either by proton donation (Brφsted acid sites) or by hydride abstraction (Lewis acid sites). As can be seen in Table 1, 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 FCC-s1 catalysts where catalytic sites are containing both Brφsted and Lewis acid sites and also the FCC matrix may provide potentially extra cracking ability. As also shown in Table 4, FCC-s1 catalysts reduced the activation energy (87.1 KJ mol^{-1}) as compared with amorphous silica–alumina (SAHA) (91.7 KJ mol^{-1}). Since the spent FCC catalysts possess much milder acidity than zeolites and have a bimodal pore structure including mesopores as well as micropores are initially available for the degradation of large molecules. The smaller cracked products obtained for pp degradation over FCC-s1 catalysts may gain entry to the bimodal channels, and then give rise to differing product distributions due to differences in pore systems. Zeolite-based catalysts with a very strong acidity with almost entirely Brφsted acid sites resulted in decreasing

a significant lowering of the apparent activation energy (ZSM-5 = 72.5 KJ mol^{-1}; HUSY = 76.4 KJ mol^{-1}). Although a slight difference was observed in the activation energy for the zeolite catalysts (ZSM-5 and HUSY), the much higher coke level for HUSY catalyst (Table 4) reflects the larger pore opening of zeolite Y (0.74 nm) and the presence of supercages within the structure of 1.3 nm diameter. The relatively low coke content in FCC-s1 (5.6–5.7% w/w) than with HUSY catalysts (7.7–8.2% w/w) may indicate possible constraints on the diffusion of liquid polymer into the pores, although the differences in the nature of the sites may also be relevant. However, ZSM-5 with narrower pore openings (0.55 nm × 0.51 nm) and no supercages, the bulky feed molecules have restricted access to the internal active catalytic sites and special restrictions within the pore system tend to inhibit the bimolecular processes leading to coke production (=0.1% w/w). The amount of coke obtained from TG reactions for PP degradation over various cracking catalysts was typically HUSY > FCC-s1 > SAHA > ZSM-5 ≈ silicalite (Table 4).

The bulk of the products observed with these acidic cracking catalysts (FCC-s1, ZSM-5, HUSY and SAHA) were in the gas phase with less than 5 wt% liquid collected (Table 5). Also, the differences in the product distributions between those catalysts can be seen with ZSM-5 producing a much more C$_1$–C$_4$ hydrocarbon gases (56 wt%) than FCC-s1, HUSY and SAHA catalysts. Some similarities were observed between FCC-s1 and SAHA with C$_1$–C$_4$ and C$_5$–C$_9$ yields, which were approximately 27–30 wt% and 53–54 wt%, respectively. Due to the long chain dimensions of the polymer and its high viscosity, it seems logical to assume that the polymer macromolecules break down first on the external catalytic surface and only small fragments can enter the catalyst pore structure to undergo further reactions. This phenomenon is consistent with the selectivity results reported previously [39] involving the catalytic conversion of post-consumer polymer waste into hydrocarbons over fluidised cracking catalysts in a fluidised-bed reactor. As also can be seen in Table 5, the yield of volatile hydrocarbons and the selectivity

Table 4
Comparison of the average value of activation energy and the value of coke content determined from TG weight curves for the catalytic degradation of PP

Catalyst type	Activation energy (E_a/kJ mol^{-1})[a]	Coke content (% w/w)[b]
FCC-s1	87.1	5.7
HUSY	76.4	8.2
ZSM-5	72.5	0.1
HAHA	91.7	0.6
Silicalite	143.4	0.2

[a] Calculated by the dynamic reaction at four heating rates of 3, 5, 10 and 20 K min^{-1}.
[b] Determined by heating the deposited catalyst to 870 K in 30 ml min^{-1} air described in Section 2.1.

Table 5
Summary of products of PP degradation over various commercial catalysts (reaction temperature = 400 °C, fluidising N$_2$ rate = 600 ml min^{-1}, polymer to catalyst ratio = 100% w/w, and total time of collection = 30 min)

Degradation results	Catalyst type				
	FCC-s1	HUSY	ZSM-5	SAHA	Silicalite
Yield (wt% feed)					
Gaseous	**81.2**	**88.3**	**89.7**	**83.1**	**15.3**
Liquid[a]	**5.4**	**2.4**	**3.5**	**3.7**	**2.6**
Residue[b]	**12.2**	**8.7**	**5.0**	**12.9**	**81.9**
Involatile residue	7.9	2.9	3.7	10.5	80.3
Coke	4.3	5.8	1.3	2.4	1.6
BTX[c]	**1.2**	**0.6**	**1.8**	**0.3**	**0.2**
Distribution of gaseous products (wt% feed)					
Hydrocarbon gases (ΣC$_1$–C$_4$)	**26.9**	**33.5**	**56.2**	**30.2**	**10.2**
Gasoline (ΣC$_5$–C$_9$)	**54.3**	**54.8**	**33.5**	**52.9**	**5.1**

[a] Liquid: condensate in condenser and captured in filter.
[b] Residue: coke and involatile products.
[c] BTX: benzene, toluene and xylene.

to gases hydrocarbons for PP degradation over zeolitic catalysts (ZSM-5 ≈ HUSY) gave higher yield than spent FCC commercial catalyst (FCC-s1) and non-zeolitic catalysts (SAHA) and the highest was obtained for ZSM-5 (nearly 90 wt%). Therefore, from a practical point of view, the use of spent commercial cracking catalyst from FCC units may lead to a cheaper process with valuable products and can be further used as an adequate approach for the catalytic recycling of polymer waste.

4. Conclusions

TGA provides a useful tool for the rapid investigation of catalysed polymer degradation kinetics, the rate of catalyst deactivation and catalyst regenerability. The silicelous form of ZSM-5, silicalite, show a slight catalytic effect for polymer degradation and the average value of activation energy is only comparable to that for thermal reaction. It has been found that PP in the presence of a spent FCC catalyst (FCC-s1) is degraded with the apparent activation energy of at about 87.1 kJ mol^{-1} and this can have the ability to convert polymer waste into volatile products with the potential to provide a cheaper process in industrial application.

Deactivation of the spent FCC catalyst occurs due to the deposition of coke. Activity of reused FCC-s1 catalyst was found to decline exponentially with coke content. While the assumptions made are necessary crude, they do provide a convenient way of assigning activity and deactivation behaviour. The apparent activation energies for PP degradation over various commercial cracking catalysts were in the following order: silicalite < SAHA < FCC-s1 < zeolites (ZSM-5 ≈ HUSY). The FCC-s1 catalyst regained most its initial activity on regeneration, and could be regenerated several times. It is also demonstrated that from a practical point of view, the use of spent commercial cracking catalyst can be a suitable solution for the catalytic recycling of polymer waste.

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