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Thermogravimetric study of the kinetics of degradation of polypropylene with solid catalysts

P. Carniti*, A. Gervasini

Dipartimento di Chimica Fisica ed Elettrochimica, Università degli Studi di Milano, Via Golgi 19, I-20133 Milano, Italy

Abstract

The degradation of polypropylene in the presence of solid catalysts of different acidity was studied by thermogravimetric analysis (TGA) employing three different heating rates. The temperatures of onset, T_{on}, of maximum-rate, T_{max}, as well as of end, T_{end}, of the degradation shifted to lower values as higher the acidity of the catalysts. A comparison among the catalytic activities has been performed on the basis of the apparent kinetic parameters, frequency factor and activation energy, obtained from the TG data. The maximum activity was observed for the more acidic catalysts (silica-aluminas). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polypropylene degradation; TGA; Solid catalysts; Kinetic parameters

1. Introduction

During the last decades, many studies have been devoted to the processes of degradation of polymers with the aim of recovering waste polymeric materials by conversion to chemicals and fuels. Such a recovering is a very attractive way to improve the waste disposal situation from ecological as well as economical point of view. The acceptance of landfilling and incineration of polymers as waste processes is decreasing. On the other hand, waste polymers could be employed as raw materials for industry to partially solve the expected shortage of natural resources (gas, oil, coal, etc.).

With the aim of governing the degradation of polymers to compounds having high synthetic value, studies on polymer pyrolysis in the presence of solid catalysts were undertaken by the authors [1–6]. The interest was devoted towards polyolefins (polypropylene (PP), polyethylene (PE), and polystyrene (PS)), which constitute a large part of both industrial and domestic wastes.

In the present work, the degradation of (PP) in the presence of solid catalysts of different acidity was studied by thermogravimetric analysis (TGA).

Many studies have been devoted to the evaluation of the kinetics of degradation of polyolefins by TGA. The complexity of the degradation mechanism and the difficulties in obtaining sound kinetic parameters by thermogravimetric (TG) data, in particular by data obtained in dynamic conditions, have been widely discussed [7–10].

By contrast, studies dealing with the degradation of polyolefins in the presence of solid catalysts followed by TGA are scarce. TGA experiments permit readily comparing the activity of different catalysts towards polymer degradation. Moreover, useful information on the kinetic parameters of the reaction can be obtained by interpreting TGA curves.

In previous studies [2–4], TG measurements were performed on the catalytic degradation of PP, PE, and PS by using as catalysts zeolites and silica-aluminas.

* Corresponding author. Tel.: +39-2-2660-3261; fax: +39-2-7063-8129.
E-mail address: paolo.carniti@unimi.it (P. Carniti).

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Mechanical mixtures of polymer and catalyst with a high amount of polymer (about 90% w/w) were employed. The results obtained were only useful for internal comparisons, as, in those conditions, the polymer degradation occurred not only on the catalyst surface, but also in the polymer bulk.

With the aim of eliminating the contribution of the bulk reaction, samples constituted by PP deposited on catalyst with a surface coverage lower than or equal to monolayer were used in the present work. Catalysts were chosen over a wider range of acidity.

A comparison among the activities of the catalysts has been performed on the basis of the kinetic parameters obtained from the TG data.

2. Experimental

Polypropylene (PP), MOPLEN FLF20-HIMONT, was supplied in powder form. The pyrolysis runs were carried out on PP deposited on catalysts of different acidity.

The catalysts employed, together with their characteristics, are listed in Table 1. The BET surface area of the catalysts was determined by nitrogen adsorption at 77 K. The surface acidity was measured by conventional *n*-butylamine titration employing Hammett indicators [6]. Before use they were activated in an oven at 500°C for 24 h in air.

The samples of PP deposited on the catalysts were prepared by impregnation starting from a solution of PP in toluene. The PP solution (1.52 mg/ml) was obtained putting 2 g of PP in 200 ml of toluene under reflux during 2 h and separating the PP residue by filtration. A weighed amount of catalyst was added to 25 ml of PP solution. Different quantities of each catalyst were added, as a function of the catalyst surface area, with the aim of obtaining a coverage of the catalyst surface close to, but lower than, monolayer. The monolayer extent was estimated on the basis of the hindrance of monomer (28.6×10^{-16} cm^2 per molecule corresponding to 0.244 mg/m^2). Afterward, the solvent was removed by rotoevaporation at 40°C and 200 mbar. The obtained powder was dried at 80°C and 200 mbar during about 70 h, homogenised in a mortar, and dried again at 80°C and 200 mbar overnight. The amount of PP on catalyst, determined by elemental analysis, ranged from 5 to 10% (w/w) — in particular, on SiO_2, 5.0%; SM, 6.5; ST, 6.4; MO, 10.2; SALA, 10.0; and SAHA, 7.5.

A Perkin-Elmer TGA 7 thermal analyser was used to follow the pyrolysis of PP on the various samples. Before each thermal degradative run, the sample (5–6 mg) was purged with nitrogen flowing at 60 ml/min at atmospheric pressure during at least 1 h. Constant heating rates (β) of 5, 10, and 20°C/min were used starting from 50 to 600°C. All the pyrolysis runs were carried out in inert atmosphere of nitrogen flowing at 60 ml/min at atmospheric pressure. The storage of data was made by Pyris software.

The weight loss of the single catalyst during a TG run, mainly due to loss of water, was evaluated by separate runs carried out on the catalyst without PP. The results were taken into account to perform a correction of the experimental data of the runs of catalytic pyrolysis of PP.

3. Results and discussion

The degradation of PP was performed on catalysts of different acidity. The catalysts were chosen to cover

Table 1
Characteristics of the employed catalysts

Catalyst	Type	Producer	Co-ion	Surface area (m^2/g)	Surface acidity	
					$pK_a \leq -3.7$	$pK_a \leq 1.5$
SiO_2[a]	Silica gel	Merck		342		
SM	Silica-magnesia	Grace	1.0% MgO	334	0.012	0.092
ST	Silica-titania	Grace	0.3% TiO_2	328	0.026	0.187
MO	Mordenite	Union Carbide	5.3% Al_2O_3	480	0.044	0.273
SALA	Silica-alumina	Akzo-ketjen	13.4% Al_2O_3	650	0.043	0.450
SAHA	Silica-alumina	Akzo-ketjen	24.4% Al_2O_3	512	0.064	0.479

[a] Inert reference material.

a wide range of acidity, in terms of both total ($pK_a < 5$) and strong ($pK_a < -3.7$) surface acidity (Table 1), with the following scale of acidity:

$$SM \leq ST < MO < SALA \leq SAHA.$$

As the quantity of PP deposited on catalyst for the degradation runs corresponded to a coverage of the catalyst surface close to monolayer, intimate contact between polymer and catalyst was achieved, minimising the parallel non-catalytic bulk pyrolysis.

A quite inert material (SiO_2) similar in surface area to the catalysts used was chosen as reference to evaluate PP degradation in the absence of catalytic action. Silica showed a quite negligible catalytic effect on PP degradation [1,4] as well as on polystyrene degradation [3–5] in terms of product yields and distribution. Moreover, quite an equal quantity of radicals was measured in the thermal degradation of polystyrene in the absence of any catalyst and with silica [5]. The amount of PP deposited on silica also corresponded to a coverage of the surface close to monolayer. Such reference sample was more adequate than pure PP, as the bulk degradation of polymer should be negligible with monolayer supported PP.

For each catalyst, runs were performed at three different heating rates (5, 10, and 20°C/min). Fig. 1 reports a typical example of thermogram of PP degradation on catalyst.

As expected, the thermograms shifted to higher temperatures as the heating rate increased from 5 to 20°C/min.

In each case, the temperatures of onset, T_{on}, of maximum-rate, T_{max}, as well as of end, T_{end}, of the degradation were evaluated on the basis of the derivative of the original thermogram. These temperatures are shown in Fig. 2.

The lowering of both the T_{on} and T_{max} values obtained with the various catalysts with respect to those with the inert material ($-\Delta T_{on}$ and $-\Delta T_{max}$) is shown in Table 2. The values of $-\Delta T_{on}$ were similar to those of $-\Delta T_{max}$ for each catalyst with little dependence on β. Moreover, they grew up with the acidity of the catalyst. A less marked decrease in T_{max} was observed in a previous work [4] with SALA and SAHA ($-\Delta T_{max}$, 95 and 55°C for SALA and SAHA, respectively), due to the occurrence of the parallel bulk degradation of polymer.

The values of T_{on} and T_{max} are correlated with the kinetics and the mechanism of the degradation. Thus, even if $-\Delta T_{max}$, as well as $-\Delta T_{on}$, can be regarded as a good direct measure of the catalytic effect, the influence of the catalyst on PP degradation can be also, and

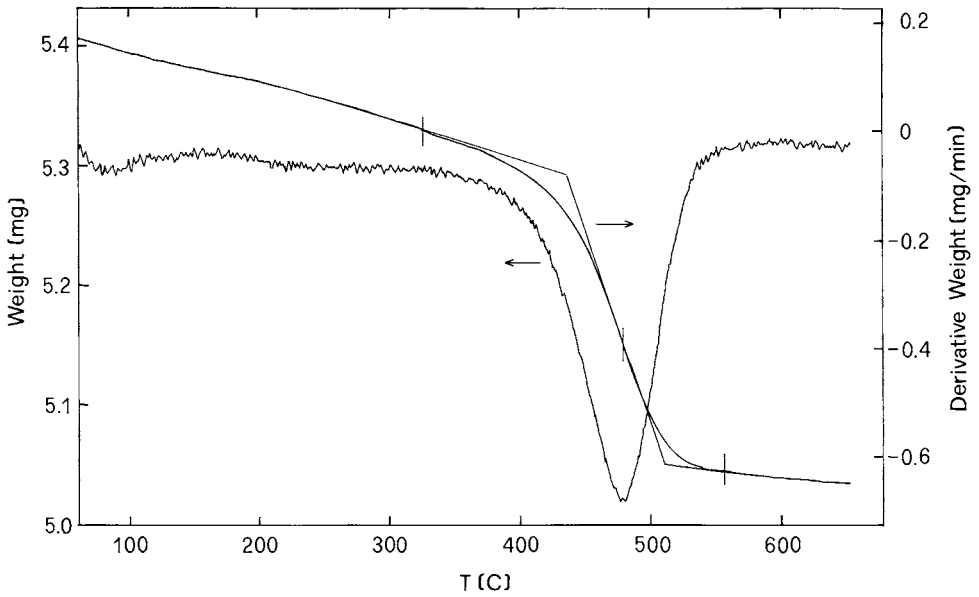

Fig. 1. A typical example of thermogram of PP degradation on catalyst. Catalyst, ST; heating rate, 20°C/min.

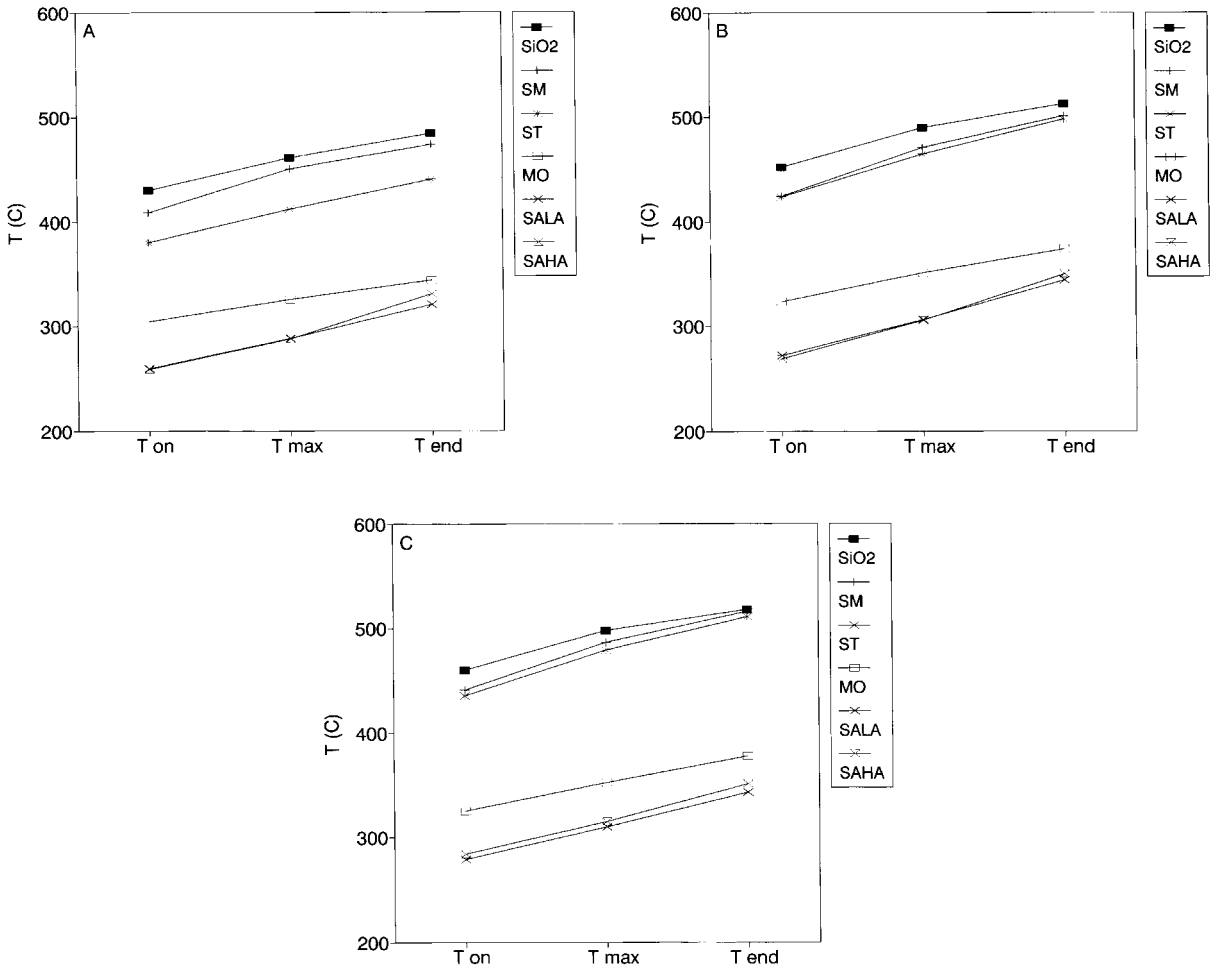

Fig. 2. Temperatures of onset, T_{on}, of maximum-rate, T_{max}, and of end, T_{end}, of the degradation for PP degradation on different catalysts. Heating rate: (A) 5°C/min; (B) 10°C/min; (C) 20°C/min.

better, discussed on the basis of kinetic parameters derived from a kinetic interpretation of the TG data, as performed in the following.

Analysing the thermograms of PP degradation obtained in the presence of the various catalysts, a regular decreasing of weight versus temperature was observed both before the onset-temperature and after the end-temperature. Such weight loss occurred with quite constant rate; even if the rate could be different at the beginning and at the end of the thermogram. An analogous continuous decrease in weight before T_{on} and after T_{max} was not observed in runs carried out by employing PP without catalyst. These observations evidenced that a minor, but not negligible, loss of weight attributable to the catalyst, mainly due to a release of physical and structural water, occurred beside the major weight loss of the sample due to the degradation of PP.

To evaluate the weight variation relevant to the catalyst, thermal analyses were performed on each catalyst in the absence of polymer. The weight loss was relatively small and quite linear with temperature for the less acidic catalysts, SiO_2, SM, and ST, while with the more acidic ones, MO, SALA, and SAHA, the loss was globally more important and it was higher in the range of temperatures up to 300°C.

Table 2
Differences between onset-temperatures (ΔT_{on}) and between maximum-rate temperatures (ΔT_{max}) for PP degradation on catalyst and on SiO_2 (inert reference material)

Catalyst	β (°C/min)		
	5	10	20
	$-\Delta T_{on}$ (°C)		
SM	22	28	19
ST	50	28	24
MO	126	129	135
SALA	171	180	181
SAHA	171	183	176
	$-\Delta T_{max}$ (°C)		
SM	11	19	11
ST	49	25	19
MO	136	139	146
SALA	173	184	188
SAHA	173	184	183

The catalyst weight was subtracted from the experimental thermograms, taking also into account the weight variation of the catalyst, in order to obtain thermograms relevant only to PP. However, as the release of water from catalyst could be in some extent hindered by the presence of PP, the correction introduced cannot be considered exact. It is acceptable only for a limited weight loss of the catalyst.

Considering the total weight loss attributable to PP, it was observed that such weight variation did not correspond to the initial amount of PP present in the sample in any run with catalyst. A certain quantity of organic or carbonaceous material was still present on the catalyst also at temperatures so high as 500–600°C. The formation of carbonaceous residue was favoured by lowering the heating rate and it was more evident on the more acidic catalysts, MO, SALA, and SAHA. With these catalysts, the sample was always black at the end of the pyrolysis. Elemental analyses of pyrolysed samples obtained with heating rate of 10°C/min showed the presence of amounts of C residue of 2.2, 1.7, and 1.5% (expressed as PP equivalent) with MO, SALA, and SAHA, respectively, being the initial PP amounts 10.2, 10.0, and 7.5%, respectively.

Considering that the correction for the weigh loss of the catalyst is less accurate in the initial part of the reaction and that the formation of carbonaceous residues did not allow the reaction to reach 100% of PP degradation, only data in the range 25–75% of degradation were utilised for a kinetic interpretation. The data in such interval, expressed in terms of fractional degradation versus temperature are depicted in Fig. 3.

In spite of the complexity of the polymer degradation process, the kinetic model most frequently used for the interpretation of TG data relevant to thermal degradation of polymers, assumes that the degradation rate (r) can be expressed by a simple kinetic relationship:

$$r = -\frac{dW}{dt} = kW^n = AW^n \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where W is the residual weight fraction, attributable to PP, n the reaction order, and an Arrhenius-like temperature dependence for the rate coefficient k is assumed. Such a simplified approach permits one to obtain quickly the apparent kinetic parameters of the overall process.

The kinetic parameters could be obtained applying Eq. (1) and considering constant heating rate by the classical Freeman and Carroll method [11]. However, the values of E_a and n estimated by this method can vary widely with heating rate, also because of error-propagation effects resulting when ratios between experimentally determined quantities are employed [7]. A preliminary kinetic interpretation of the experimental data showed that Freeman and Carroll's method was inadequate to give rise to sound reaction orders. On the other hand, in a previous work [4], the reaction orders obtained by this procedure starting from TG data of PP catalytic degradation were so low as 0.03–0.34 and they were difficult to be justified.

In the present interpretation, the order n was assumed equal to one, as suggested by Chan and Balke [7]. On the other hand, a first-order kinetics for the overall thermal degradation reaction of PP is often found or assumed [12]. Thus, Eq. (1) can be rewritten as

$$\frac{r}{W} = k = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

The ratio r/W (reaction rate/residual fraction) at each temperature can be regarded as the rate coefficient (k). Reporting r/W versus temperature the expected

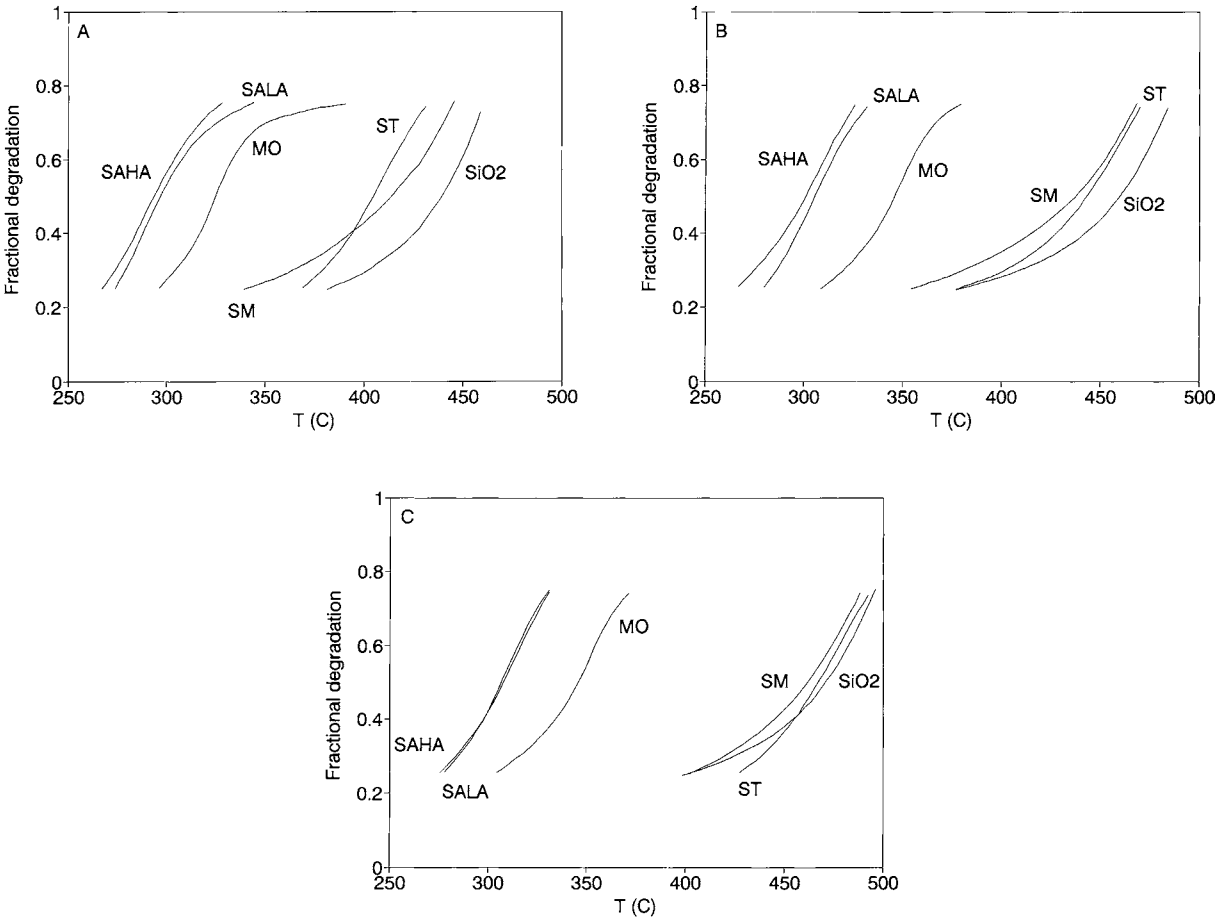

Fig. 3. PP degradation on different catalysts in the range 25–75% of degradation. Heating rate: (A) 5°C/min; (B) 10°C/min; (C) 20°C/min.

increasing trends were observed up to 50–60% of degradation with all the catalysts. Afterward, with the more acidic ones and particularly with the lowest heating rate, the r/W ratio ($=k$) decreased because the formation of less- or non-reactive residue on the catalyst surface (Fig. 4). In these cases, non-negligible carbonaceous residue was observed at the end of the reaction, as above-mentioned.

Considering the increasing region of k versus T, Arrhenius plots were drawn and the kinetic parameters, $\ln A$ and E_a, were calculated by linear regression of $\ln k$ versus $1/T$. The resulting values are shown in Table 3. No unique trend was observed for $\ln A$ and E_a versus β. In fact, both $\ln A$ and E_a were increasing with β for SM, ST, SALA, and SAHA, while they were decreasing for MO and did not follow any trend for SiO_2. Moreover, the deviation from the means values did not exceed in any case 17% for $\ln A$ and 14% for E_a. Considering also that only apparent overall kinetic parameters can be derived by the employed procedure, the values obtained with different β for each catalyst could be averaged to give an acceptable estimate of the parameters.

The averaged values of $\ln A$ and E_a obtained with the various catalysts are collected in Table 4. In Table 4, the ratios between the rate coefficients with catalyst and with SiO_2, calculated at different temperatures by employing the averaged kinetic parameters are also shown. These values are a direct indication of catalyst activity.

The apparent E_a obtained with SiO_2 is lower than most values reported in the literature, which range

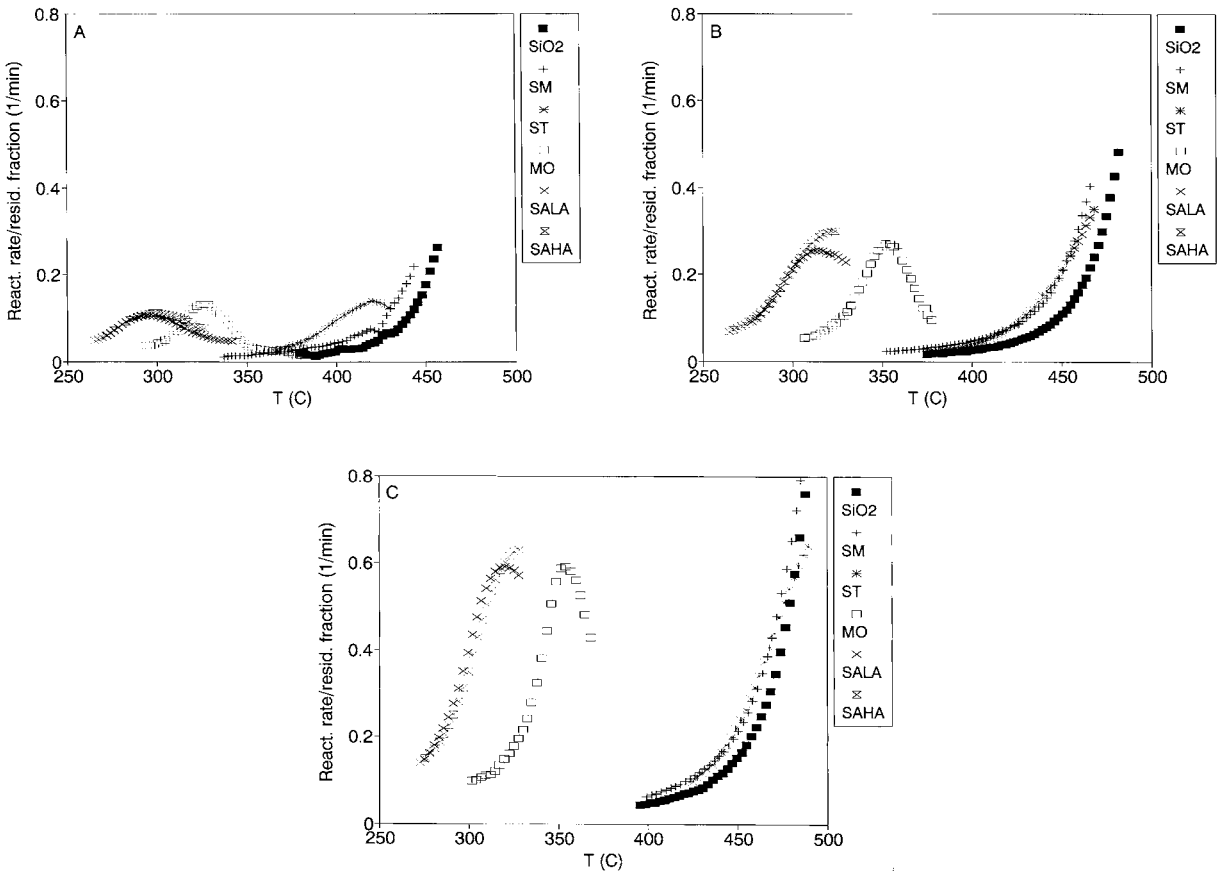

Fig. 4. Reaction rate/residual fraction for PP degradation on different catalysts as a function of temperature. Heating rate: (A) 5°C/min; (B) 10°C/min; (C) 20°C/min.

between 170 and 250 kJ/mol for first-order overall degradation of PP [12]. This is probably due to the monolayer distribution of PP on the support.

The presence of catalyst leads in every case to a lowering of E_a. The maximum lowering was observed for SAHA and SALA. However, the decrease of E_a is often partially compensated by a concurrent decrease of the frequency factor ($\ln A$), particularly for SAHA, SALA, and SM. In the case of MO, the activity of the catalyst can be attributed to both a decrease of E_a and an enhancement of $\ln A$.

The scale of activity of the catalysts, in terms of k/k_{SiO_2}, is in line with the scale of acidity. SM and ST display substantially the same low activity. The inversion of activity with the increase of temperature has to be attributed to the different activation energies. Also the activities of the more active catalysts, i.e. the two silica-alumina, are very similar, being SAHA a little more active. The PP degradation rates with these catalysts are some 600 times faster than with SiO_2 at T_{max} (around 300°C for both SAHA and SALA). The k/k_{SiO_2} ratio decreases with temperature. However, it continues to be high up to T_{end}. In fact, k/k_{SiO_2} of 158 and 179 at 375°C were obtained for SAHA and SALA, respectively, being T_{end} around 340–350.

The distribution patterns of products for PP degradation was observed to be different with strongly acidic catalysts, as silica-aluminas and acidic zeolites, with respect to degradation carried out with PP alone or in the presence of little acidic catalysts [1,4,13]. A different mechanism involving ionic species was

Table 3
Kinetic parameters for the PP degradation on different catalysts obtained at different heating rate by linear regression

Catalyst	PP[a] (% w/w)	β (°C/min)	ln A (A in min^{-1})	E_a (kJ/mol)	r[b]
SiO_2	5.0	5	24.9	162	0.985
		10	18.5	124	0.976
		20	20.8	136	0.978
SM	6.5	5	13.7	94	0.979
		10	14.7	99	0.974
		20	19.7	127	0.989
ST	6.4	5	19.0	120	0.993
		10	19.9	129	0.997
		20	21.1	137	0.997
MO	10.2	5	25.2	136	0.990
		10	22.0	121	0.993
		20	21.7	116	0.983
SALA	10.0	5	13.2	73	0.978
		10	16.8	88	0.989
		20	20.2	101	0.995
SAHA	7.5	5	13.6	75	0.985
		10	15.6	82	0.997
		20	18.6	94	0.997

[a] PP content in the sample.
[b] Linear correlation coefficient.

Table 4
Averaged kinetic parameters and rate coefficient ratios for the PP degradation on different catalysts

Catalyst	ln A[a] (A in min^{-1})	E_a[a] (kJ/mol)	k/k_{SiO_2}[b]		
			300°C	375°C	450°C
SiO_2	21.4 ± 2.7	140 ± 16	1	1	1
SM	16.1 ± 2.6	107 ± 15	5.5	2.4	1.3
ST	20.0 ± 0.9	129 ± 7	2.8	2.1	1.7
MO	23.0 ± 1.6	124 ± 8	136	92	68
SALA	16.7 ± 2.8	87 ± 12	647	179	64
SAHA	15.9 ± 2.0	84 ± 8	625	158	53

[a] Averaged values.
[b] Rate coefficient ratio calculated by using the kinetic parameters.

invoked in the presence of strongly acidic catalysts. Likely, such ionic species are radical cations generated by Lewis sites as in the case of polystyrene degradation [5,6].

4. Summary

In the present work, the degradation of polypropylene in the presence of solid catalysts of different acidity was studied by thermogravimetric analysis (TGA).

The quantity of PP deposited on catalyst for the degradation runs corresponded to a coverage of the catalyst surface close to monolayer. In such a way, intimate contact between polymer and catalyst was achieved, minimising the parallel non-catalytic pyrolysis.

In spite of the complexity of the degradation process, TG data allowed obtaining apparent activation energies and frequency factors for the catalytic degradation of PP. The overall degradation reaction was assumed to follow a first-order kinetics.

A comparison among the activities of the catalysts was performed on the basis of the apparent kinetic parameters. The maximum activity was observed for the more acidic catalysts (silica-aluminas).

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