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Catalyzed pyrolysis of plastics: A thermogravimetric study

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Thermal or catalytic pyrolysis processes have attracted much attention for the conversion of plastic wastes to a mixture of their basic hydrocarbons, which can be valuable either as fuels or as raw chemicals. The effect of different catalysts on the thermal degradation of propylene (PP) has been studied by thermogravimetric analysis (TGA). TGA experiments were used to compare the activity of different catalysts towards PP degradation. All the hydrocracking (HC) catalysts enhanced the pyrolysis of PP. The reaction rates were found to increase with increasing catalyst fraction, acidity of catalyst and decreasing particle size. The temperatures of onset (T_{on}), of maximum-rate (T_{max}) and of end (T_{end}) of the degradation also shifted to lower values. Among HC catalysts, it seems that Z-713 performed better at all three weight fractions; Z-713 reduced both T1% and T99% better than others. On the other hand, the FCC catalyst (RCD-8) performed poorly for the degradation of PP. Various titania based catalysts prepared in our laboratory, performed well. The number of acid sites and catalyst pore size along with impregnation with transition metals such as W/ Ni and Ni/ Mo are found as the key factors for the energy efficient degradation of polymers. The details of the research are presented in this paper.

Key words: Thermogravimetric analysis (TGA), DSC, pyrolysis, catalytic degradation, polypropylene, waste plastics, catalysts.

INTRODUCTION

The applications of plastic materials are continually increasing in the modern world. Presently, plastics are manufactured for various uses such as: consumer packaging, wires, pipes, containers, appliances, electrical/electronics parts and automotive parts. The increase in plastic materials consumption has led to a parallel rise in the generation of plastic wastes. As not all waste plastic are not recyclable and biodegradable, the disposal of these wastes has become a major social concern. Therefore, measures have to be implemented to reduce plastic wastes for negative impact on the environment. Land filling of plastic waste is not the right solution due to the danger of leaching and soil impregnation of plastic additives, such as various dyes and phthalates and polluting ground water. Moreover, the number of landfill sites is decreasing. Incineration process is also not acceptable because it produces

several pollutants that are dangerous to the environment. Moreover, both processes do not allow the recovery of the organic content of plastic waste, which should be part of the organic life-cycle (Pinto et al., 1999). Feedstock recycling of plastic wastes is regarded currently as a promising alternative for the management of plastic wastes. In such process, plastics transform to their constituent monomers or their basic hydrocarbon feed stock. Thermal or catalytic cracking of plastic wastes yields a mixture of their basic hydrocarbons, which can be valuable either as fuels or as raw chemicals (Serrano et al., 2000). The energy consumption during the thermal cracking (pyrolysis) is very high and the molecular weight distribution of the products obtained is quite broad, varying with the conditions used (Marcilla et al., 2001). However, the selectivity of the product obtained can be controlled by the use of suitable catalysts (catalytic cracking) under appropriate conditions of temperature, pressure and atmosphere (N_2, H_2 or air). Catalytic cracking of plastics requires lower energy consumption (temperatures from 350 to 550°C) and the chemical distribution of the product is narrower than in thermal

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process, leading to the production of more valuable products (Ali and Siddiqui, 2005). Typical catalysts used for polymer degradation are acidic solids like amorphous silica-alumina, zeolites, mesophorous materials and activated carbon (Kim et al., 2000). The number of acid sites and pore size of catalysts are described as the two key factors in the degradation of polymers. Many researchers have studied the use of various zeolites, such as ZSM-5, Y, beta and mordenite (Aguado et al., 2007). Owing to its strong acidity, ZSM-5 has been investigated most intensively. The application of ZSM-5 to the pyrolysis of waste plastics, however, has revealed several technical problems, such as the relatively high quantity of gas products and coke formation near the pore entrance. Mesoporous zeolites, such as, MCM-41 was found to have a high potential for use as a pyrolysis catalyst for waste plastics because of its high surface area, tunable uniform mesopores (from 20 to 100 °A) and moderate acid strength (Geraldo et al., 2005). The kinetics of degradation of polyolefins by thermogravimetric analysis (TGA) in the presence of solid catalysts of different acidity was reported by Carniti and Gervasini (2001).

In the present work, the activity of different hydrocracking catalysts and a composite titania-alumina and USY zeolite catalyst (prepared by us) has been studied by thermogravemetric analysis. A comparison of the activities of these catalysts, performed under similar experimental conditions, has been evaluated on the basis of TGA data. The information thus collected can be used for feedstock recycling of plastic waste. PP has relatively high melting point and a high resistance to chemicals; and the demand for polypropylene (PP) in the world is about 25 wt% of thermoplastic and is steadily increasing. Consequently PP, being one of the largest parts of both industrial and domestic wastes, is selected for this study.

MATERIALS AND METHODS

Plastics

The model plastics that were chosen in this study included low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS). These plastics were used in the same form as received from the Saudi Basic Industries Corporation (SABIC), Riyadh, KSA.

Catalysts

The four commercially available catalysts were used because of their known selectivity towards the hydrocracking reactions. Catalyst C-1 was prepared by us.

Preparation of catalyst # 1 (C-1)

Catalyst # 1 was prepared using a method of mixing, metals impregnation, drying and calcinations according to method described by Ali and Asaoka (2008). The supports used were titania-alumina composite, alumina and USY zeolite. Cataloid AP-1 was used as a binder to prepare extrudates. Titania-alumina composite was prepared by impregnating titania-alumina powder, having 150 micron particle size (*extrudates*), with Ni-Mo metal pair solution. 3.1 g of nickel nitrate hexahydrate [$Ni(NO3)2.6H2O$] in 3.2 ml of water was prepared. Similarly, a solution of 2.9 g (hexaammonium heptamolybdate tetrahydrate) [$(NH4)6Mo7O24.4H2O$] in 3.2 ml of water was prepared and heated to 50 °C to dissolve the solid. The two solutions were mixed and quickly added to the *extrudates* and mixed well to provide homogeneous impregnation of the solution on the solid material. The impregnated powder was dried overnight at room temperature, then dried at 120 °C for 5 h and calcined at 550 °C for 2 h. The impregnated titania-alumina powder thus obtained was mixed with 4 g cataloid AP-1 and 8 g USY zeolite; deionized water was added to make a thick paste in a polyethylene bag. The sample was dried overnight at room temperature, then dried in an oven at 120 °C for 5 h and calcined at 550 °C for 2 h.

The catalysts were characterized for surface area, porosity characteristics and acidity. The BET surface area, pore volume and pore size distribution were obtained from nitrogen adsorption-desorption isotherms measured at 77K by a Quantachrome, NOVA 1200 porosimeter, using the BJH method. The total acidity was determined in the temperature range 180 to 800 °C by ammonia adsorption-desorption method.

Thermal analysis (TGA)

The non isothermal thermo gravimetric analysis was performed on a TA Instruments SDT Q600, simultaneous TGA-DTA-DSC analyzer. The experiments were conducted under flowing atmosphere of nitrogen at a purge rate of 200 ml/min. The samples were studied in the fine powder form. A quantity of 3.5±0.3 mg was placed in an open ceramic sample pan. The sample was then equilibrated to 200 °C before being heated to 550 °C at different heating rates (3 to 10 °C/min). The actual heating rate was calculated from temperature measurements made during the period of polymer degradation. In this study, this analysis serves primarily as an assessment tool in the screening of various potential catalysts for polyolefin pyrolysis. An assessment of the catalyst performance prior to use in a reactor reduces cost.

TGA sample preparation

For the catalytic pyrolysis study by TGA, the samples were prepared by mixing dried proportions of PP and catalysts (dry mixing). PP was first frozen in liquid nitrogen and crushed into a very fine powder before mixing with an appropriate amount of very fine catalyst.

## RESULTS AND DISCUSSION

Catalyst characterization

The properties of catalysts are given in Table 1.

Catalyst(s) weight loss

The thermal stability of catalysts was assessed by recording weight loss during TGA runs on all five catalysts (Figure 1). Calcium oxalate monohydrate was

Table 1. Properties of catalysts.

Name	Description and composition	Surface area (m²/g)	Pore volume cc/g	Total acidity	Wt. loss Prior 100°C	Wt. loss after 100°C
C-1	NiMo loaded on [TiO₂+alpha alumina+AP-1+USY] extrudates	359.0	0.42	1.48	3.26	7.36
C-11	KC-2710 (AKZO Nobel)	182.0	0.23	0.85	2.96	8.40
C-12	Z-713 (Zeolyst international)	221	0.34	1.15	1.45	4.57
C-13	HC-100 (UOP)	231	0.25	1.20	3.67	9.73
C-14	RCD-8 (UOP)	210	0.21	1.50	2.19	6.28
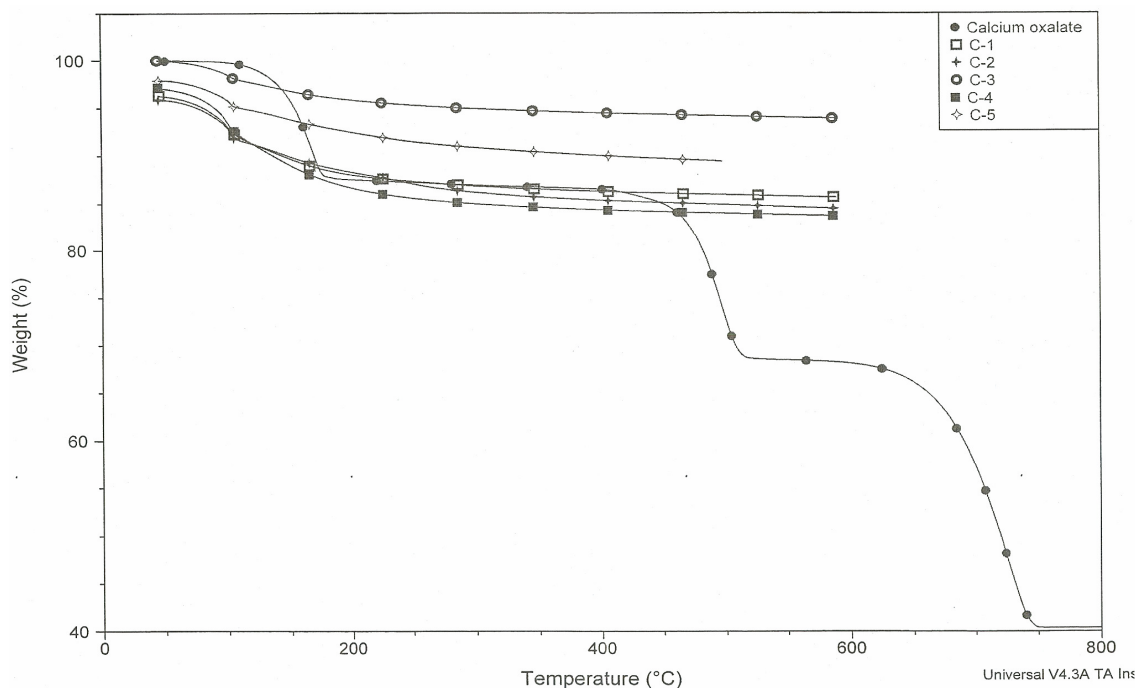
Figure 1. Weight loss % for five catalysts and calcium oxalate monohydrate.

used as a calibration standard. This material has become popular for demonstrating thermobalance performance, as its TG gives three distinct weight losses over a wide temperature range. The measured losses (Figure 1) are with in the agreeable limits with theoretical losses, according to the usual scheme:

$$CaC_2O_4.H_2O \cdot CaC_2O_4 \cdot CaCO_3 \rightarrow CaO$$
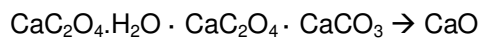
The curve gives a value of 18.50% lost, when compared with the theoretical value of 19.2%, for the decomposition of the anhydrous oxalate to calcium carbonate around 500°C. This is due to the disproportionation of carbon monoxide to carbon dioxide and carbon [2CO → C + CO₂]. The residual calcium oxide was pale grey due to the carbon deposited.

All five catalysts showed weight loss around 100°C, which indicates water loss. The weight change is observed to be more pronounced for the hydrocracking catalysts C-2 and C-4. The catalyst prepared by us (C-1)

also showed a relatively high loss.

TGA study of plastics

The thermogravimetric (TG) curves for HDPE, LDPE, PP, PS, PET and PVC are depicted in Figure 2. As is evident from figures, the degradation behaviors of HDPE, LDPE and PP are similar, but PET and PS are different. The behavior of PE or PP and PET or PS shows one main distinct weight loss step, which show that all of them have a constant degradation behavior at the involved temperature range. Degradation is completed in the temperatures between 420 and 490°C. However, the TG behavior of PVC shows a completely different behavior due to loss of chlorine in the form of HCl and other organo halogen compounds. The differences in TG curves of different plastic types could obviously be attributed to the different macromolecular structure and pyrolysis mechanism. These results clearly indicate the
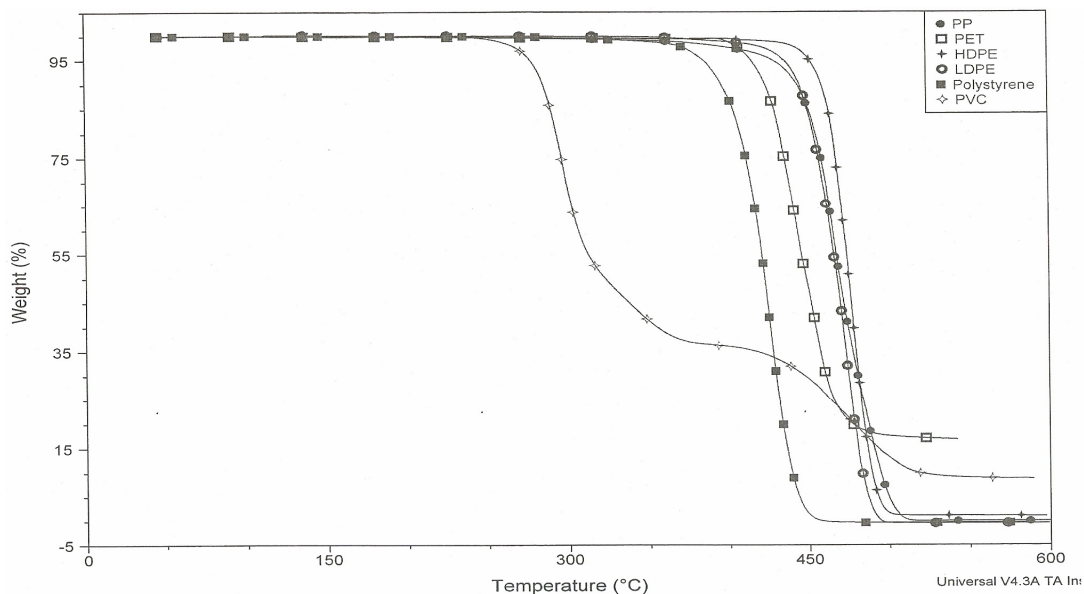
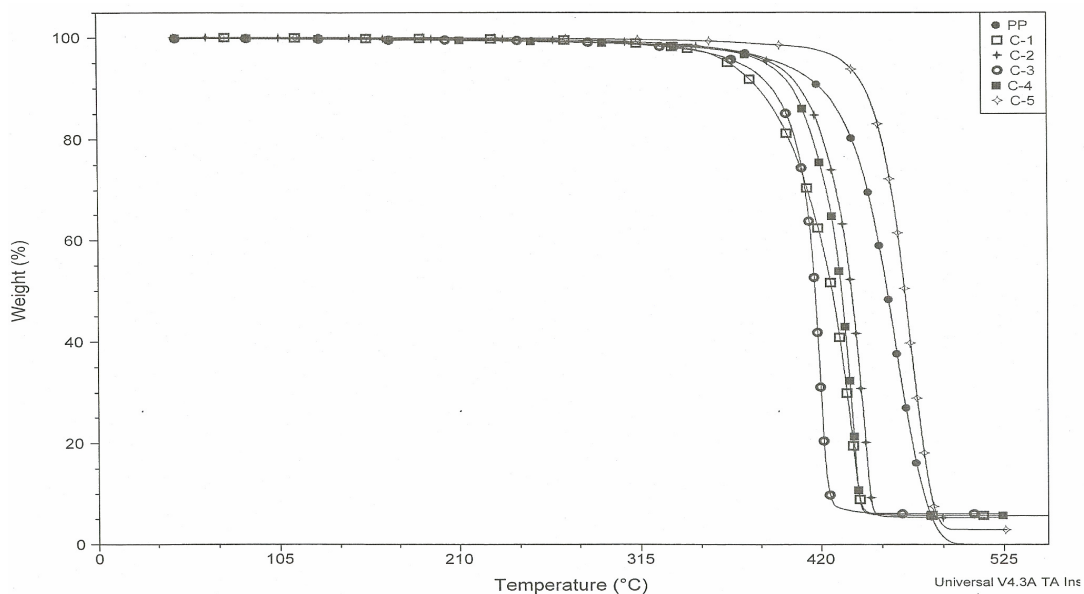**Figure 2.** TGA thermograms for virgin plastics.

Figure 3. TG degradation curves for virgin PP and PP containing 5% catalysts.

usefulness of TG analysis for the identification of different plastic types in samples collected from municipal wastes.

Catalytic degradation of polypropylene

The shape of the TGA curve represents a qualitative evaluation of the polymer degradation and is typically influenced by certain factors such as particle size, sample amount and heating rate. In this study, the following parameters are used in assessing the effectiveness of

various catalysts: (1) temperature at 1% conversion (T1%); (2) temperature at maximum rate of conversion (Tmax); (3) temperature at 99% conversion (T99%).

A TG analysis on the performance of all five catalysts in the catalytic pyrolysis of PP was carried out using 3, 5 and 8 wt% of each catalyst. TGA runs at 8 wt% of all five catalysts were repeated to check for repeatability of the TGA data. It was concluded that the data is reproducible within experimental limits.

Figure 3 shows the results obtained in the runs performed with PP and PP mixed with the catalyst

Table 2. Temperature and conversion at maximum rate of degradation of PP.

Name	T_{max} (°C)	$-\Delta T_{max}$ (%)	C_{max} (%)
Virgin PP	470	0	55
(C3) 3 wt% Z 713	424	9.8	86
(C3) 5 wt% Z 713	419	11	82
(C3) 8 wt% Z 713	409	13	80
(C2) 3 wt% AKZOKC	457	2.8	93
(C2) 5 wt% AKZOKC	437	7	86
(C2) 8 wt% AKZOKC	419	11	87
(C4) 3 wt%UPOHC	448	4.7	93
(C4) 5 wt%UPOHC	434	7.7	86
(C4) 8 wt%UPOHC	406	13.6	85
(C1) 3 wt% CAT-1	449	4.5	88
(C1) 5 wt% CAT-1	432	8	82
(C1) 8 wt% CAT-1	418	11	80
(C5) 3 wt% RCD-8	470	0	76
(C5) 5 wt% RCD-8	468	0	74
(C5) 8 wt% RCD-8	460	2	70

prepared by us (C-1), the hydrocracking (HC) catalysts C-2, C-3 and C-4 and the FCC/ RFCC catalyst C-5, all of them with about 5% of catalyst. The temperature at the maximum rate of conversion (T_{max}) and conversion maximum weight loss (C_{max}) with the addition of the various catalysts and with increasing catalyst weight fractions are shown in Table 2. However, no significant correlation between C_{max} and the catalyst type and amount was observed, although a distinct increase in conversion percent occurred with increasing catalyst weight fraction. Figure 3 and Table 2 also show that all catalysts except the FCC/RFCC catalysts (C-5) enhanced the degradation of PP. Zeolyst Z-713 catalyst (C-3) was found to be most effective in reducing the T_{max} for degradation of PP. The FCC/RFCC catalysts (C-5) had almost no effect. Although AKZO 2710 (C-2) is also a Ni/W catalyst, it is less effective than Z-713 in its catalyzing the degradation of PP. The number of acid sites on a solid catalyst plays a key role in the catalytic degradation rate of polyolefins. This number increases with increasing aluminum incorporation into the zeolite crystal. This may explain that AKZO 2710's reduced catalytic activity (Al/Si = 1.15) in comparison to the Z-713 catalyst (Al/Si = 6.5). Another influence on polyolefin degradation using microporous materials is the catalyst pore size. Z-713 is relatively large pore zeolite and high acidity, whereas the base-zeolite of HC catalysts is characterized by medium pores and relatively low acidity. Given that PP molecules are much larger than the pore size of other catalysts, the degradation of the primary decomposition products (large olefin molecules) occurs preferably over the surface of Z-713 catalysts, forming smaller molecules that can be permitted into the pores of the other HC catalysts for further cracking. Thus, larger pore of Z-713 will permit for further degradation of PP within its pore, unlike medium pore catalysts. The total acidity of the other HC catalysts was found to have lower values (0.84 mmol/g) as compared to the Z-713 (1.3 mmol/g). The metal loading on the titania-alumina in catalyst C-1 was found to increase the acidity of titania-alumina from 0.84 to 1.1 mmol/g. However, impregnation with the metals (Ni/ Mo) of silica-alumina base (catalysts C-1) was less effective than the metals Ni/ W (catalysts C-2 and C-3) and Ni/Mo (catalyst C-4). This direct influence of catalyst acidity and pore size on the catalytic degradation of PP was also observed in the literature of Durmus and Kaşgöz (2005).

Figures 4 and 5 show the TGA runs performed with PP and PP mixed with 3 and 8% of catalysts C-1 to C-4. Table 2 presents the temperature of the maximum decomposition rate (T_{max}). As it can be seen from the Figures 4 and 5 and in the Table 2, the catalytic effect is remarkable and T_{max} is lowered with increasing catalyst weight for all the four catalysts employed. The number of acid sites that are available for polymer cracking increases with the catalyst amount, thereby, enhancing the degradation reactions. From the plots, it is evident that all the HC catalysts enhanced the degradation of PP.

A more quantitative view of this analysis, considering the temperatures at 1% (T1%) and 99% (T99%) conversion is presented in Table 3. Also shown in this table are the percent decreases (-Δ T %) in the PP
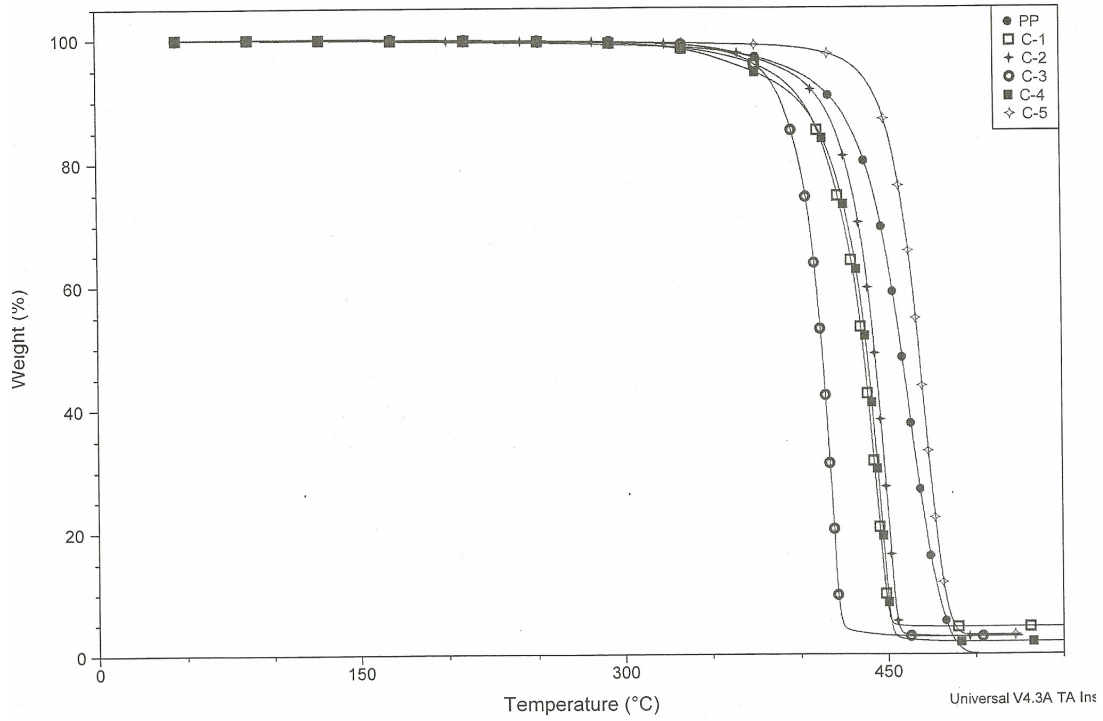
Figure 4. TG degradation curves for virgin PP and containing 3% catalysts.
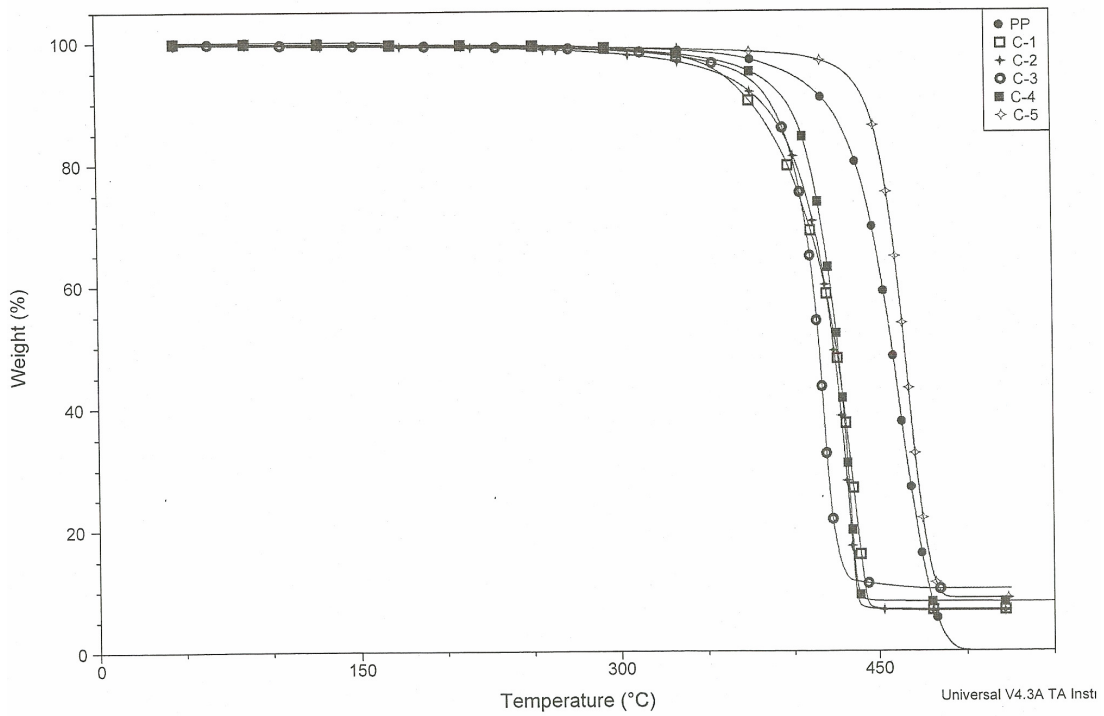

Figure 5. TG degradation curves for virgin PP and PP containing 8% catalysts.

degradation temperatures as a result of the respective catalysts.

Table 4 shows that all hydrocracking (HC) catalysts (C-2, C-3 and C-4) were effective in lowering the onset of

Table 3. Performance of catalysts at 1% and 99% conversion of PP.

Name	1% Conversion		99% Conversion	
	$T_{1\%}$ (°C)	-Δ T (%)	$T_{99\%}$ (°C)	-Δ T (%)
Virgin PP	377	0	490	0
(C3) 3 wt% Zeolyst - 713	345	8	450	8
(C3) 5 wt% Zeolyst - 713	309	18	441	10
(C3) 8 wt% Zeolyst - 713	268	30	421	14
(C2) 3 wt% AKZOKC	343	9	465	5
(C2) 5 wt% AKZOKC	320	15	446	9
(C2) 8 wt% AKZOKC	271	28	431	12
(C4) 3 wt%UPOHC	347	8	465	5
(C4) 5 wt%UPOHC	328	13	451	8
(C4) 8 wt%UPOHC	283	25	441	10
(C1) 3 wt% CAT-1	358	5	470	4
(C1) 5 wt% CAT-1	332	12	456	7
(C1) 8 wt% CAT-1	305	19	436	11
(C5) 3 wt% RCD-8	370	2	485	1
(C5) 5 wt% RCD-8	350	7	482	2
(C5) 8 wt% RCD-8	334	10	479	4

Table 4. Activation energy (Ea) for catalytic degradation of PP.

| Catalyst	Catalyst[a] (% w/w)	Ea (kJ/mol)	Regression for line used for Ea
Nil	0	306.8	0.993
C-1	5	115.1	0.995
C-11	5	116.1	0.989
C-12	5	120.8	0.987
C-13	5	112.5	0.972
C-14	5	230.8	0.992

[a]Measured weight fraction.

degradation. At 3 wt% catalyst, HC catalysts lowered T1% by approximately 8 to 9%, whereas titania/alumina catalyst (C-1) lowered T1% by about 5%. Similarly, T99% decreased with increasing catalyst weight fraction for all the catalysts. Thus, the degradation temperature range is significantly reduced with the addition of the HC catalysts.

Furthermore, it appears that the Z-713 catalyst is most effective and FCC/ RFCC catalyst (C-14) is least effective. Figure 6 shows only degradation endothermic peaks (single peaks) by DSC for the virgin PP and PP/catalysts blends with PP content of over 92%. PP is the continuousphase in all these blends. For the PP/catalysts blends the degradation temperatures for HC catalysts (C-1, C-3 and C-4) are lower than the degradation endothermic peak of PP (480°C). However, there is no change for the PP/RDC catalyst (C-5). Also, the endothermic peak for PP/ Z-713 (C-3) is lowest (420°C). Thus, DSC results further confirm our earlier findings.

Estimation of activation energy (Ea) for PP degradation

The kinetic parameters, activation energy (Ea) and the pre-exponential factor (A), were estimated for the catalytic pyrolysis of PP by the various catalysts. A comparison of the activities amongst the catalysts was thus, performed. The Freeman-Carroll differential approach, (Westerhout et al., 1997), was used to
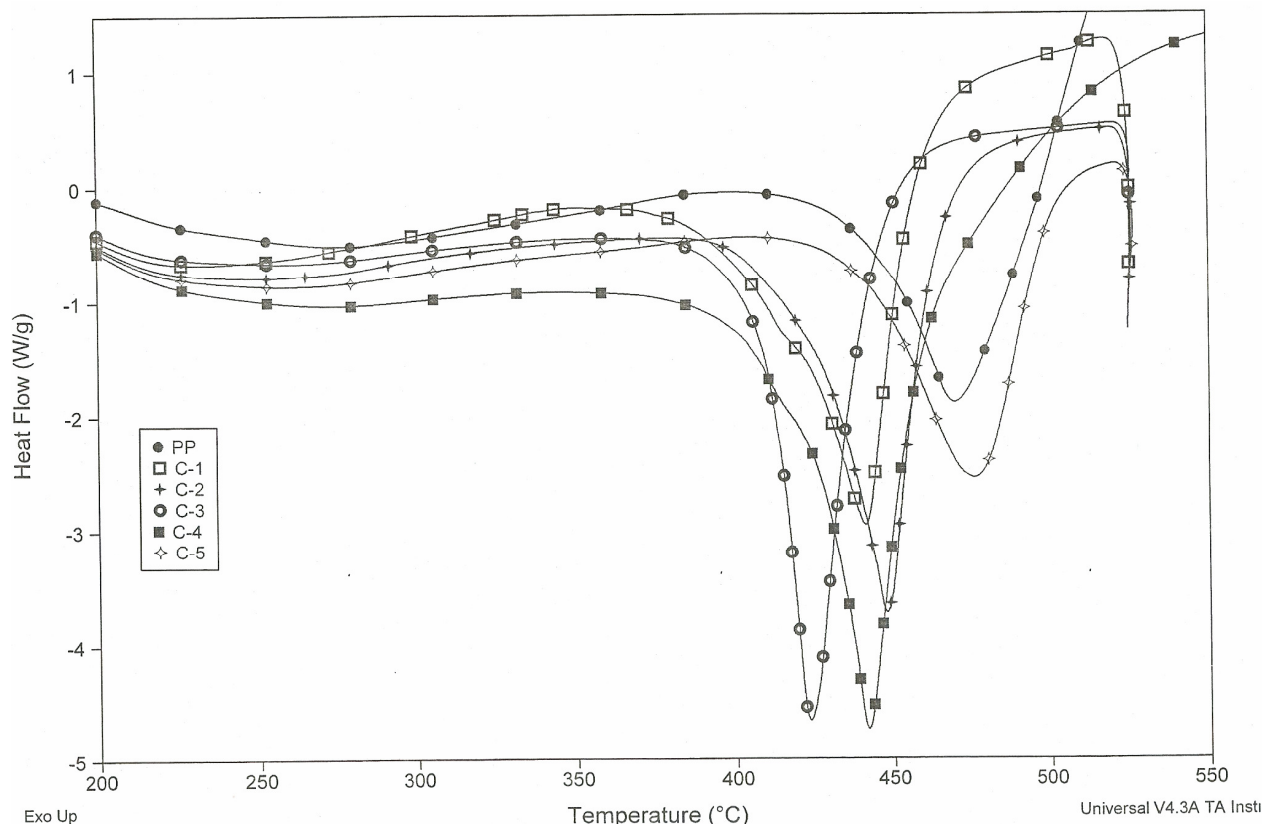
Figure 6. DSC analysis/curves of virgin PP and PP/catalysts blends.

determine kinetic parameters. The kinetic parameters were estimated for the samples containing 5 wt% of catalysts(C-1, C-11 – C-14) and Ea and regression for line used for Ea calculations were estimated by the Arrhenius equation. The results are shown in Table 4. The pyrolysis of virgin PP gave overall activation energy as 306.8 kj/mole. The activation energies for catalyzed decomposition of PP showed considerable lowering (values between 112.5 and 120.8 kj/mole) for HC catalysts. For RCD-8 (C-14), the activation energy was found to be relatively high (230.8 kj/mole), but still lower than that for PP without any catalyst.

Conclusions

The activities of five different catalysts for the decomposition of polypropylene were evaluated by TGA, DTA and DSC analysis. The maximum activity was observed for the more acidic catalyst loaded with Ni/W metals (zeolyst Z-713). The temperature of PP degradation decreased and the conversion increased when the Z-713 concentration was increased from 3 to 8 wt%. The RFCC catalyst (RDC-8) performed poorly for the degradation of PP. TG data was allowed to estimate activation energy (Ea) and the pre-exponential factor (A)

for the catalytic degradation of PP.

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