Thermogravimetric Study of Polyethylene Catalytic Degradation by Zeolites

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Abstract

Commercial samples of high density polyethylene were decomposed over faujasites (FAU) type zeolites (Y-type) using thermal gravimetric analysis (TGA). The catalytic activity and behavior of the FAU-zeolites catalysts were determined. It was found that the degradation temperature of polymer strongly depends on the catalytic acidity of the zeolites. HY zeolite was identified as the most active catalyst due to its strong acidity. The results showed that the activation energy decrease with the amount of catalyst added.

Introduction

Nowadays, plastic waste is one of the major concerns for the scientific community as well as environmentalists. In 2000 the plastic consumption was 45 Mt in Europe, and the consumption is growing annually by 4 – 8%. On the other hand, the amount of waste from plastics was about 30 Mt in 2000 [1,2]. Polymer recycling has been suggested as the only sustainable solution to the problem of rapidly increasing amounts of plastic waste. Among the various polymer recycling methods, thermal and/or catalytic degradation of plastic waste to fuel show the highest potential for a successful future commercial polymer recycling process. However, this method can be improved by using zeolites catalysts due to their characteristic strong acidity, which decrease the reaction temperature. Zeolites are crystalline microporous alumino-silicates whose structure is formed by an array of corner-sharing $SiO_4{}^{4-}$ or $AlO_4{}^{5-}$ tetrahedral that are linked together through

oxygen bridges. The faujasite (FAU) zeolite is based on sodalite cage that are joined by O bridges between the hexagonal faces. Eight such sodalite cages are linked leaving a large central cavity or supercage, with a diameter of 12.5Å. The supercages share a 12 - membered ring with an open diameter of 7.4Å. The catalytic properties of zeolites are mainly related to their acid character as seen by their uses in industrial chemical transformation mainly in cracking. The acidity of zeolites is caused by the presence of Brönsted acid sites. H-form zeolites are highly acidic species and were once considered to be the solid equivalents of superacids [3,4].
This work reports the catalytic degradation of a commercial high density polyethylene (HDPE) catalysed by faujasite zeolites, NaY and HY . Polymer samples with different amounts (5, 7 and 10 %) of Y zeolites were subjected to thermogravimetric analysis to estimate the activation energy of the process.

Experimental

Materials. High density polyethylene (HDPE) (Stamylan HD 2H280) with an average molar mass of 60 $\mathrm{kg\ mol^{-1}}$, was kindly supplied by DSM was used in powder form. The FAU-zeolites, NaY and

HY in powder forms, were obtained from Aldrich. The FAU-zeolites were calcinated at $500\,^{\circ}\mathrm{C}$ during 8 hours under a dry air stream prior to use.
The molar Si/Al ratio and the number of acids sites estimate from the protons number of FAUzeolites obtained by bulk chemical analysis are presented in Table 1.

FAU-zeolites	Si /Al	Unit cell formula	$nA_1 \times 10^{20}[\text{ sites. } g^{-1}]^a$
NaY	2.37	$Na_{53.5}H_{3.5}Al_{57}Si_{135}O_{384}$	1.70
HY	2.51	$Na_{9.6}H_{45.1}Al_{54.7}Si_{137.3}O_{384}$	23.2

$^a nA_1$ is theoretical number of acid sites drawn from the chemical formula of the FAU-zeolites

Table 1- Characteristic of the FAU zeolite samples
Several samples of HDPE and FAU-zeolites were prepared by mixing at room temperature the polymer powder with NaY and HY , using the latter with different amounts (Table 2).

Instrumentation. Thermogravimetric analyses of mixture without further treatment were carried out using TGA 50 Shimadzu instrument under high purity helium supplied at a constant 50 $\mathrm{mL\ min^{-1}}$ flow rate. The sample holders used were 70μ L crucibles of alumina oxide, supplied by Shimadzu, in which approximately 5 mg sample was degraded. The samples were subjected to different heating rates of 5,10,15 and 20 $\mathrm{K\ min^{-1}}$, between 300 and 800 K , in order to estimate the activation energy of the process.

Results and Discussion

Typical TG curves of HDPE and HDPE-zeolite mixtures (NaY and HY) obtained at $20\ \mathrm{K\ min^{-1}}$ are shown in Fig. 1.

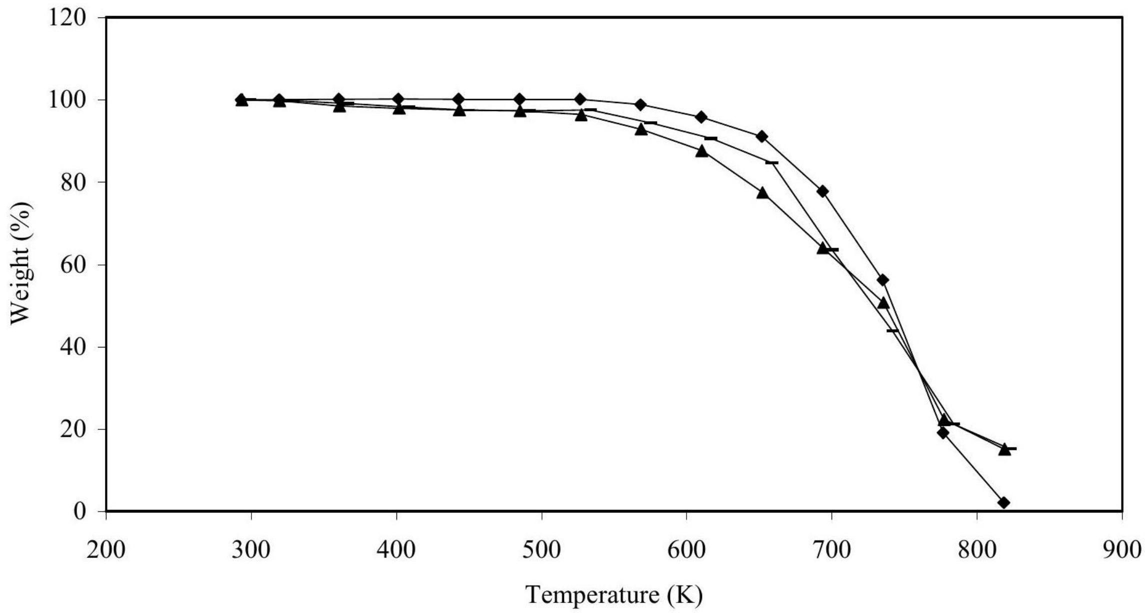

Fig. 1- TGA curves of the polymer weight vs. temperature for: (ϕ) HDPE; (-) HDPE +10%NaY; (Δ) HDPE + 10%HY

It is clear that, with the same loading amount of FAU-zeolites, different onset degradation temperatures can be observed. For HDPE, HDPE with NaY and HDPE with HY the onset temperatures are 715, 691 and 682 K , respectively. These results can be explained by the fact that, in spite of the Si/Al ratio of both zeolites is very similar, the more efficiency occurs to a larger extent in the HY due to the higher number of acid sites. These results are in agreement with other authors, who observed that polyethylene degrades at much lower temperature in the presence of both catalysts and HY was the most active catalyst [5]. Since the order of the activity of HY is higher than NaY, HY was selected to study the influence of the catalyst amount on the thermal degradation of HDPE process. The amount of polymer and HY used in this work is shown in Table 2.

Sample	1	2	3	4
HDPE	100	95	93	90
HY	0	5	7	10

Table 2- Composition of the samples.

Fig. 2 shows the weight loss of the samples as a function of the temperature. As it can be observed, the onset temperature of the degradation decreases as the percentage of HY increases.

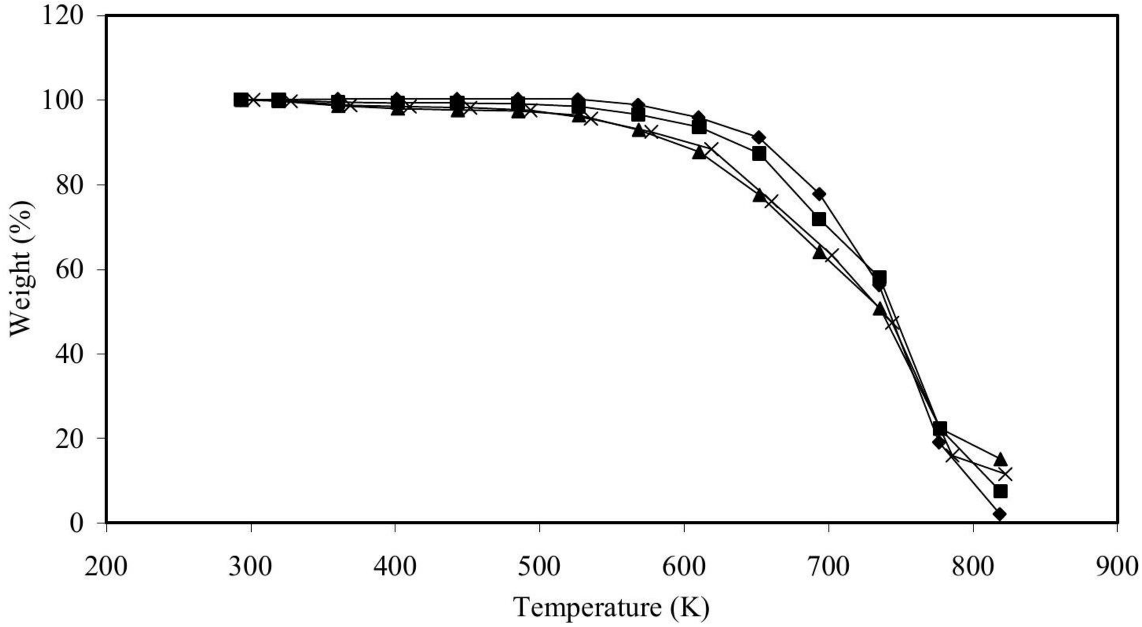

Fig. 2- TGA curves obtained for the samples indicated in Table 1: (·) sample 1, (■) sample 2, (×) sample 3 and (Δ) sample 4.

The Ozawa method was chosen to determine the activation energy of the polymer decomposition using multiple heating rates. This method is considered more appropriate to obtain kinetic parameters than the single heating rate ones [6]. From the TGA curves at each heating rate the temperature is estimated for a specific conversion level. Figs 3 a and 3 b presents two examples of the plot of the logarithms of the heating rates against the reciprocals of the corresponding values of the absolute temperatures that produce a straight line whose slope is proportional to the activation energy.

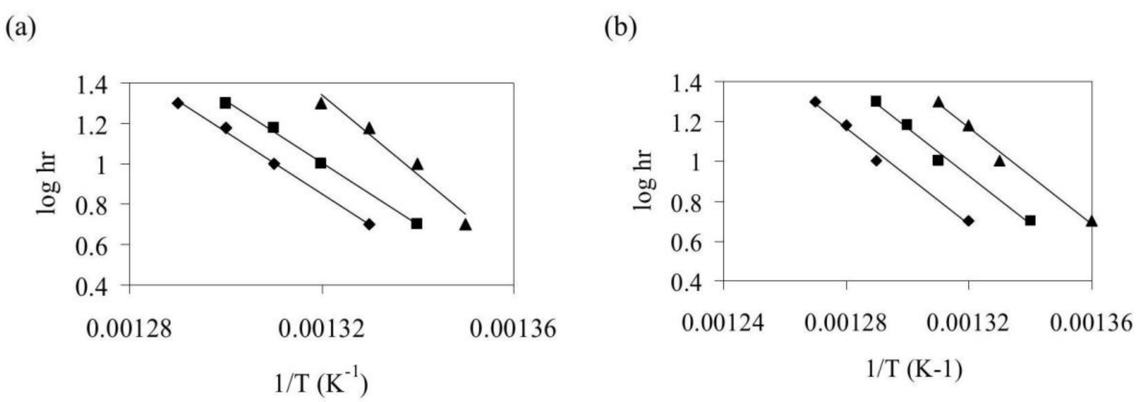

Fig. 3- Plots of the logarithm of the heating rate vs. reciprocal temperature during polymer degradation at various conversion levels for sample 1 (a) and sample 4 (b): (ϕ) 80%, (■) 70% and (Δ) 60%.

The gradients of the various lines are very similar resulting in analogous values of the activation energy at different residual weights and can be accepted as an indication of the accuracy of the method. The average values of the apparent activation energies are presented in Table 3. As it can be seen the lowest value was obtained for sample 4, with 10% of HY zeolite.

Sample	1	2	3	4
Average activation energy $[kJmol]^{-1}]$	127	119	105	96

Table 3- Average activation energy values of HDPE degradation over HY catalysts.

Conclusion

TGA provides a useful and convenient tool for comparing a wide range of materials for the catalytic degradation of polymers. The kinetic analysis using a dynamic model explained well the catalytic degradation of HDPE using HY zeolite.
The accuracy of the method was confirmed as the values of activation energy at different residual weights show small deviations among each other. The activation energy of the reaction decreases as the amount of zeolite increases.

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