The effect of acidity behaviour of Y zeolites on the catalytic degradation of polyethylene

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Abstract

Thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses were used to investigate the effect of the acidity behaviour of Y zeolites on the catalytic degradation of polyethylene (PE). The acidity behaviour of these zeolites was modified by ion exchange treatments. Two Y zeolites with similar Si/Al atomic ratios were subjected to an ion exchange treatment using $NaNO_3$ for H-form (HY) and NH_4NO_3 for Na-form (NaY). The activity and the deactivation behaviour of the Y zeolites were determined in the samples by TGA measurements, using a polymer/catalyst ratio of 9:1. The sample residues obtained after an isothermic TGA, were analysed by DSC, in order to evaluate the crystallinity of each mixture. The HY zeolite, which has the strongest acidity, reduced the onset temperature resulting in more rapid degradation of the polymer. It is shown that the ion exchange treatment over Y zeolites enhances the selective catalytic degradation of polymer in detriment of the rapid deactivation.

Keywords: Y Zeolite; Ion exchange; Polymer degradation; Catalytic cracking; Deactivation

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]. Plastic waste can be regarded as a potentially cheap source of chemicals and energy. The conventional waste process (landfill and incineration) is becoming progressively expensive and often generates problems with unacceptable emissions. Polymer recycling has been suggested as the only sustainable solution to the problem of rapidly increasing amounts of plastic waste. Alternative processes for the conversion of plastic waste to useful products have attracted research in the area of thermal degradation [3,4]. Pure thermal degradation of plastic waste though requires high temperatures and produces heavy products. However, the thermal degradation of polymers to low molecular weight material has a major drawback in that a very broad product range is obtained. This method can be improved by using zeolites catalysts due to their characteristic strong acidity, which decrease the reaction temperature and produce valuable hydrocarbon products.

A large number of studies have been published using microporous materials on the catalytic degradation of polyethylene (PE) [4-6]. Manos's research group has performed several studies [7] concerning the catalytic degradation of PE over different zeolite structures. It was shown that zeolites possessing strong acid sites accelerated the PE degradation and the products obtained after degradation were identified.

Zeolites are crystalline microporous aluminosilicates with a well-defined pore structure formed by an array of corner-sharing SiO_4^{4-} or AlO_4^{5-} tetrahedral that are linked together through oxygen bridges. The framework of Y zeolite is based on sodalite cage that is joined by O-bridges between the hexagonal faces. Eight sodalite cages are linked leaving a large central cavity or supercage, with a diameter of 12Å. The supercages share a 12 -membered ring with an open diameter of 7.4Å. The catalytic properties of zeolites are mainly related to their acidic properties, and their acid strength can be controlled by the $\mathrm{Si/Al}$ ratio. The sites of major importance in zeolites are the Brønsted acid sites, which consist of aluminium and the charge compensating protons [8,9]. The most common modification in the acidity behaviour of Y zeolites is the ion exchange treatment.

This paper reports the effect of ion exchange treatments on the acidity behaviour of Y zeolites during the catalytic degradation of PE. Two Y zeolites with similar $\mathrm{Si/Al}$ atomic ratios were subjected to an ion exchange treatment using NaNO_3 for H-form (HY) and $\mathrm{NH}_4\mathrm{NO}_3$ for Na-form (NaY). The cracking activity and deactivation behaviour of the Y zeolites over PE was followed by thermal analyses.

Experimental

Materials and reagents

High density polyethylene (HDPE) in powder form, (Stamylan HD 2H 280) with an average molar mass of $60\mathrm{Kgmol}^{-1}$, was kindly supplied by DSM. The starting Y zeolites with similar Si/Al atomic ratios in powder form, Na-form (NaY - CBV100) and H-form (HY - CBV400) were obtained from ZEOLYST. Chemicals for ion exchange treatment (NaNO_3 and $\mathrm{NH}_4\mathrm{NO}_3$) were purchased from Aldrich.

Ion exchange treatment in starting Y zeolites

Two Y zeolites with similar $\mathrm{Si/Al}$ atomic ratios were used as the starting materials: NaY ($\mathrm{Si/Al}$ ratio $= 2.83$) and $\mathrm{HY}(\mathrm{Si/Al}$ ratio $= 2.80)$. The ion exchange and subsequent calcinations were repeated on time for each starting Y zeolites using the same experimental conditions. Two modified samples were prepared by exchanging 10 g aliquots of Y zeolites with 250 ml (25 ml of solution/g zeolite) of 1.0 M solutions of the appropriate nitrate ($NaNO_3$ for HY and NH_4NO_3 for NaY) in a 500 ml erlenmeyer flask with a stirrer, at room temperature, during 24 h . The modified zeolites were separated by filtration, washed with deionised water and dried in an oven at 333 K for 8 h . The starting Y zeolites were previously calcined at 773 K during 12 h under a dry air stream and the modified zeolites were calcined in the same conditions. The samples obtained after the ion exchange treatment and subsequent calcinations were designated H(Na)Y from HY and Na(H)Y from NaY .

Preparation of the samples for degradation

Four samples of HDPE and Y-zeolites were prepared by mixing at room temperature the polymer powder with NaY, HY and the modified Y zeolites, using a polymer/catalyst ratio of 9:1. The ratio used in this study has been kept constant and equal to 9 , as was shown in a previous work [10] that was the best ratio for this type of study. In order to homogenise the particles of the polymer with the different catalysts, the samples were prepared using a meltblending process in a twin-screw extruder (prototype) at a screw speed of 50 rpm and temperature of 463 K .

Characterization

Elemental chemical analyses were performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using Philips ICP spectrometer (PU 7000) on samples previously dissolved by alkaline fusion. Si, Al and Na were quantitatively determined after dissolution of known quantities of zeolite material in acid solutions. The method involves the use of lithium metaborate as fluxing agent, which guaranties the thermal stabilization of elements during the fusion stage conducted at 1323 K . The phase analysis was performed by XRD using Philips PW1710 diffractometer. Scans were taken at room temperature in a 2θ range between 4 and 80°, using $CuK\alpha$ radiation.

The thermogravimetric analysis was carried out using TGA 50 Shimadzu instrument under high purity helium supplied at a constant $50 ml min^{-1}$ flow rate. Two types of experiments were performed: (i) dynamic experiments where the polymer/catalyst was heated between 300 and 800 K with a constant heating rate of $10 K min^{-1}$ and (ii) isothermic experiments were performed at 473 K during 8 h . The thermal behaviour of degraded samples was evaluated using a PerkinElmer DSC 7 differential scanning calorimetry. Samples of ca. 4 mg were heated from 303 to 423 K , at a heating rate of $10 K min^{-1}$, under a constant $20 ml min^{-1}$ flow rate of nitrogen, in order to estimate the crystallinity of each sample with the same thermal history.

Results and discussion

Changes in morphology, structure and chemical composition during ion exchange treatments in starting Y zeolites

To obtain the structural information, the relative crystallinity and the unit cell parameters of both starting Y zeolites and the modified samples was obtained by X-ray diffraction

(XRD). Table 1 summarizes the Si/Al atomic ratios, the crystallinity and the number of acids sites of Y zeolites.

The unit cell parameters were calculated from the (533), (642) and (555) reflection peak positions that were determined using the (101) reflection of the quartz ($2\theta = 26.64582$) as an internal standard by ASTM D 3942-80. The framework Si/Al ratio was obtained from the calculated unit cell parameters by using the Breck and Flanigen equation [11]. The bulk Si/Al ratio was determined by inductively coupled plasma emission spectroscopy (ICPAES).

Table 1
Structural and chemical analysis of zeolite samples

Samples	Si/Al bulk ^{a}	Si/Al framework	Relative crystallinity (%)	$nA_1 \times 10^{20}$ (sites.g g^{-1})^{b}	σ(%)
HY	2.80	4.05	74.0	14.0	-
H(Na)Y	2.94	4.19	81.0	12.5	32.5
NaY	2.83	2.63	100	2.8	-
Na(H)Y	2.89	3.09	80.0	16.1	65.0

The Si/Al atomic ratios for both zeolites did not change substantially upon ion exchange treatment which indicates that no dealumination occurred during the treatment. However, for the zeolites HY and H(Na)Y, the framework Si/Al ratio is higher than the bulk Si/Al ratio, indicating the presence of extra-framework alumina species. In the case of NaY , the Si/Al ratios of the bulk and the framework were similar before and after ion exchange treatment. This indicates that the Si/Al atomic ratios were uniformly distributed throughout each zeolite particle and excluded the presence of extra-framework alumina species.

The relative crystallinity was estimated by comparing the intensities of the ion exchanged of the samples with those of NaY as a standard sample (100 % crystalline). The total intensities of the six peaks assigned to (331), (511), (440), (533), (642) and (555) reflections were used for the comparison according to ASTM D 3906-80 method. It was found that the XRD patterns of starting and the modified zeolites were very similar. After the ion exchange treatment, the modified zeolites maintained over 80 % of crystallinity as compared to the respective standard NaY zeolite (Table 1). The ion exchange treatment used in this work for the starting Y zeolites did not modify significantly the zeolite structure.

However, this treatment modified the acidity behaviour of the starting Y zeolites. The differences in the theoretical number of acid sites reflect the selectivity of Y zeolites for cation exchange, as it has been observed the selectivity is $NH_4 > Na$ [12]. Each cation compensates the negative charge arising from an Al atom in the framework. The acidity increases when the sodium-type Y zeolites (NaY) are transformed into proton-type zeolites Na(H)Y. In the case of HY, the starting zeolite lost 10% of acidity sites when a sodium salt solution is used to transform to proton-type zeolite (HY) in the sodium-type Y zeolites H(Na)Y.

These modifications change the properties of *Y* zeolites and thereby affect the catalytic performance of the final Y zeolites based catalysts.

Thermal stability studies of the polymer/catalyst samples

A comparison of the activity of various catalysts at a weight ratio of 9:1 (plastic to catalyst) in TGA experiments is shown in Fig. 1.

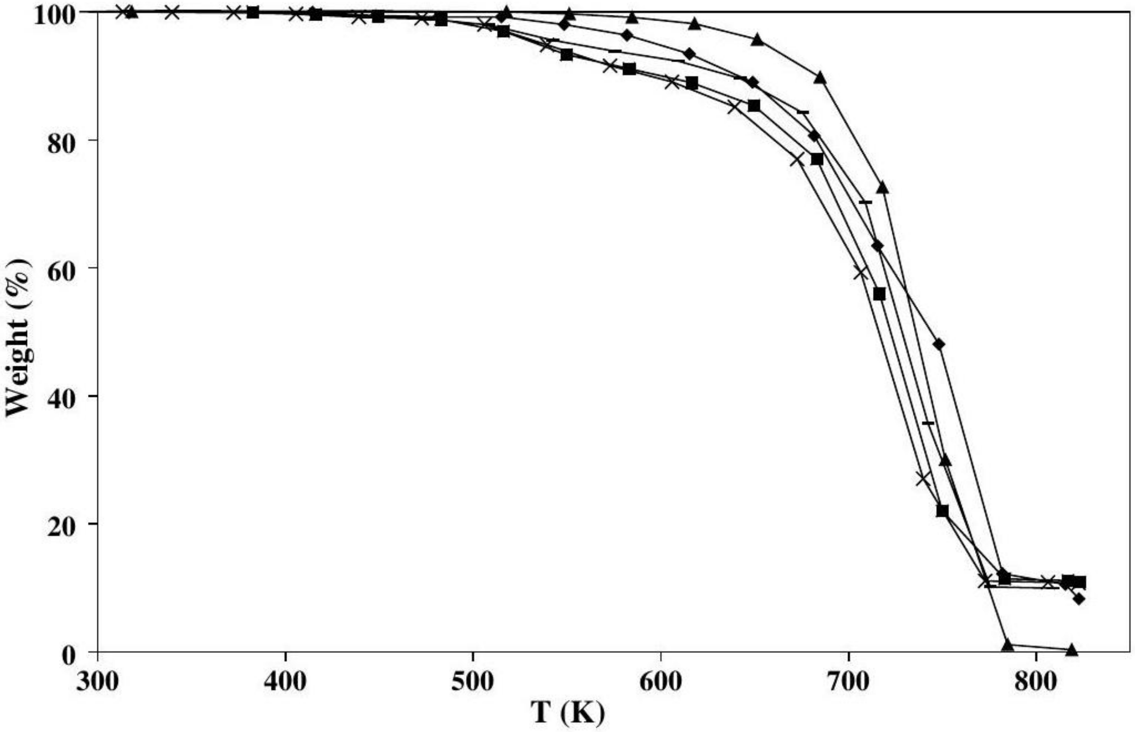

Fig. 1. Dynamic thermogravimetric curves obtained for the samples: (**Δ**) PE , (■) PE + HY, (×) PE + H (Na) Y , (**Δ**) PE + NaY and (-) PE + Na(H)Y.

As it can be observed, the onset temperature of polyethylene, evaluated according to [13], is the highest in comparison with all the modified samples. The values of onset temperature and the number of sodium ions per unit cell drawn from the unit cell formula of the FAU-zeolites are shown in Table 2.

The lowest value of onset temperature degradation is observed for HY and the highest for NaY . This behaviour is due to the difference of the strength acidity sites of the starting Y zeolites (Table 1). However, the ion exchange treatment in Y zeolites modified the onset temperature on the catalytic degradation of PE. The addition of sodium to HY increases the onset temperature and, on the other hand, the addition of protons to NaY decreases the onset temperature. The most pronounced effect of these treatments was observed over Na(H)Y due to the increase of number of acid sites (Tables 1 and 2).

Table 2
Number of sodium ions per unit cell and the onset temperatures obtained for the polymer/zeolite samples

Samples	Na/UC[a]	T onset (K)
PE	-	518.7
PE + HY	10.7	370.3
PE + H(Na)Y	12.3	375.7
PE + Na(H)Y	15.3	385.1
PE + NaY	47.2	397.3

In order to evaluate the catalytic performance of the samples along reaction time, an isothermic TGA experiment was carried out. Fig. 2 shows the behaviour of the polymer over Y zeolites during the catalytic degradation of PE at 473 K for 8 h .

As expected, no weight loss was observed for PE. During the first five minutes of reaction time, the weight of starting Y zeolites and the modified Y zeolites decreases rapidly resulting in more rapid polymer degradation. At a longer time scale, the catalysts becomes stable most probably due to the blocking of the active sites. After this period of time (5 min) the weight of NaY decreases more slowly than the other catalysts and the more efficient catalyst was HY.

In order to understand the mode of deactivation of Y zeolites during the catalytic degradation of PE, the residual activity [14] of the zeolites $A_R (A_R = a_t)\ a_0$, where a_t is the activity along degradation time t and a_0 is the initial activity 5 min after the beginning of the polymer catalytic degradation) was determined using the data of Fig. 2 and the results are shown in Fig. 3.

The deactivation was more pronounced in the case of HY with a larger number of acid sites. In contrast, the H(Na)Y reduced the deactivation and NaY remained unchanged throughout the degradation of PE. The decrease in cracking activity is much more pronounced for HY than for NaY. The Na(H)Y and H(Na)Y zeolites present an intermediate behaviour, of that starting Y zeolites. The differ-

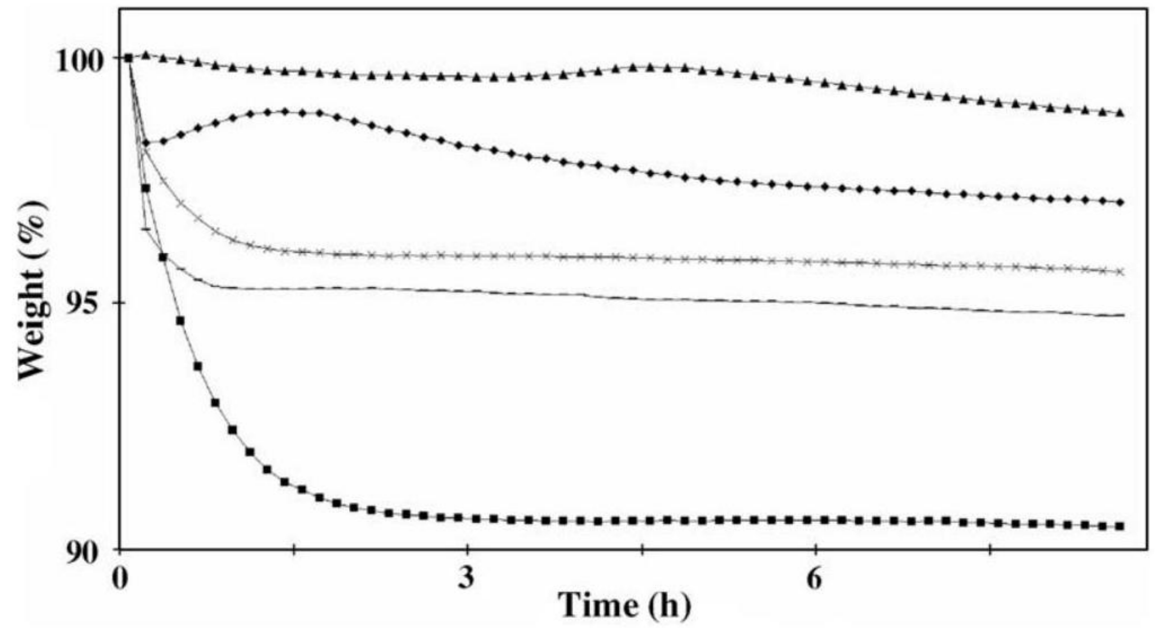

Fig. 2. Isothermic thermogravimetric curves obtained for the samples: (Δ) PE , (■) PE + HY, (×) PE + H(Na)Y, (Δ) PE + NaY and (-) PE + Na(H)Y.

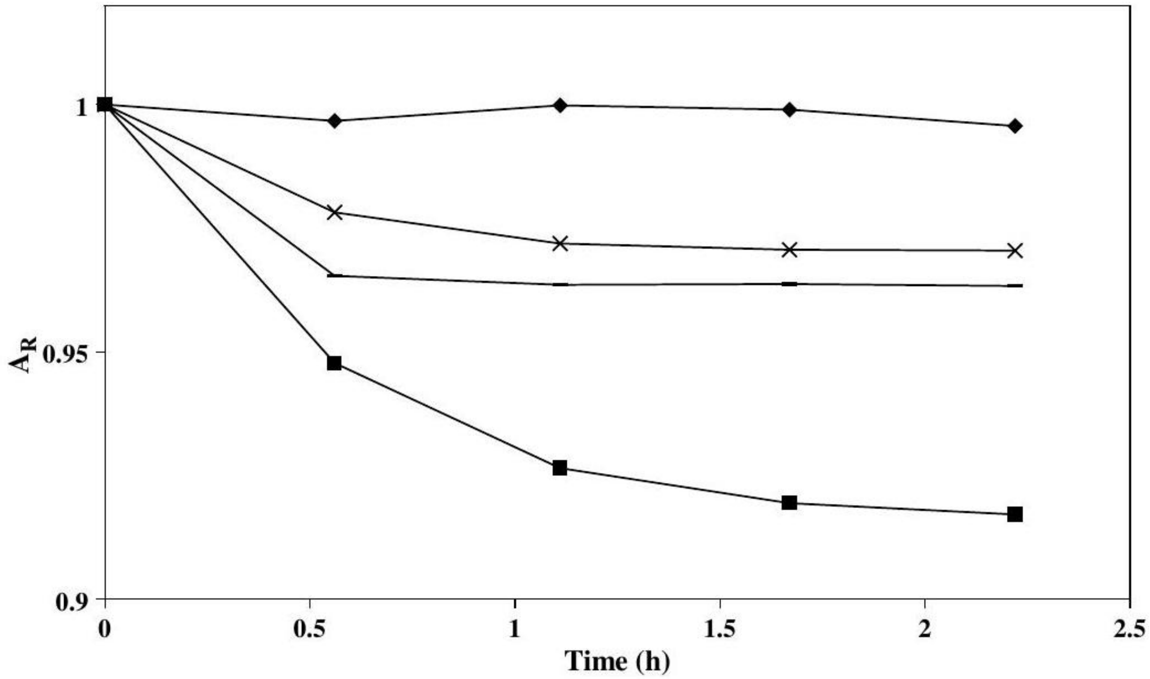

Fig. 3. Change in the residual activity A_R of (■) PE + HY, (×)PE + H(Na)Y, (ϕ)PE + NaY and (-) PE + Na(H)Y.

ences in the cracking activities of the Y zeolites can be explained by the differences in acidity. It was shown that the ion exchange treatment with sodium over HY zeolite decreases the density of Brønsted acid sites and has a positive effect in deactivation [14]. This was explained considering that the strongest Brønsted acid sites are more active for catalyzing undesired reactions mainly leading to undesired molecules (coke). In this case, the low density of acid sites obtained for Na(H)Y and H(Na)Y favours the selective catalytic degradation of PE in detriment of undesired reactions.

The ion exchange treatment affects the mode of deactivation of Y zeolites. It is well known that zeolites have a very large internal surface area with a great number of catalytic sites that are initially unavailable for the degradation of large molecules, such as polymers [5]. However, after the cracking of the first molecules of PE, the molecules can diffuse into the zeolite structure producing coke. In the case of HY zeolite the polymer cracking leads to obstruction of the pores structure and the coke molecules are formed rapidly on the very strong Brønsted acid sites. Then, the coke molecules increase very slowly. This increase is due not only to the formation of new coke molecules but also to the growth in size of the molecules already formed [15]. In the modified zeolites, due to the decrease of the number of acid sites, the obstruction of structure is partial and the access to acid sites occurs more easily.

The residues obtained after the isothermic TGA experiment described in Fig. 2 were analysed by DSC in order to determine the effect of zeolites in

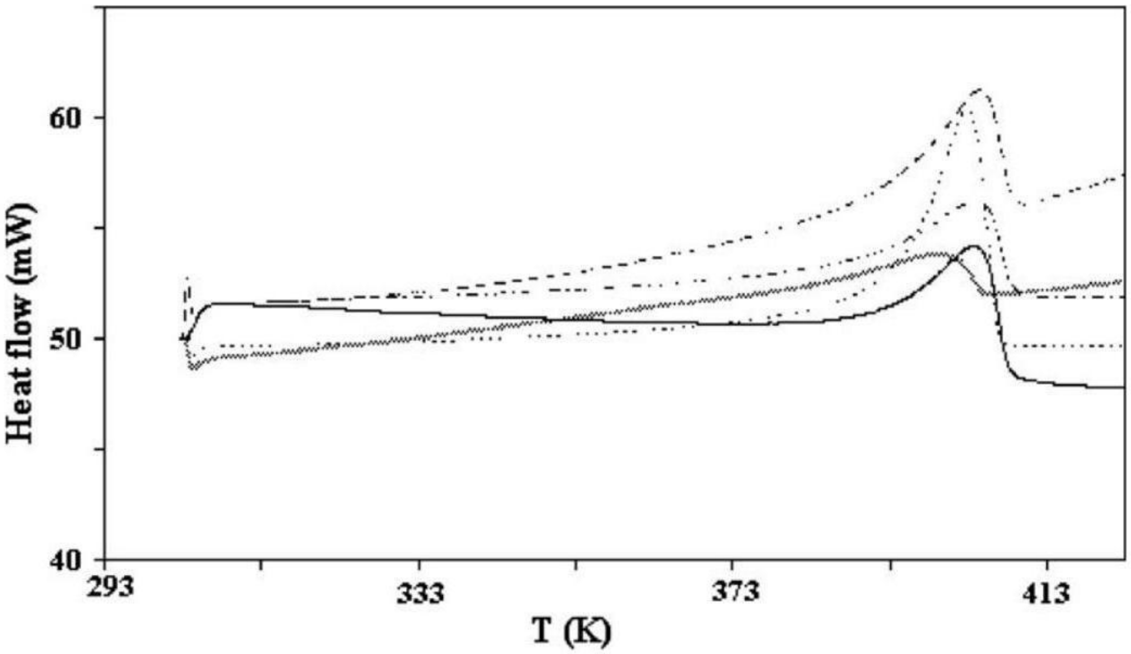

Fig. 4. DSC curves obtained for the samples: $(\cdots)$PE, $(\mathrm{M}\wedge\wedge)$PE + HY, $(-)$PE + H(Na)Y, $(-.-.-)$PE + NaY and $(---)$PE + Na(H)Y.

Table 3
DSC results obtained for the polymer/zeolite samples

Samples	ΔH_f (J/g)	χ (%) [a]
PE	161.6	58.3
PE + HY	91.8	33.1

PE + H(Na)Y	123.9	44.7
PE + NaY	118.5	42.8
PE + Na(H)Y	91.7	33.1

[a] The degree of crystallinity was calculated considering that, for polyethylene, the theoretical heat of fusion (ΔH_f) was $277.1 \mathrm{Jg}^{-1}$ [17].

the polymer crystallinity. The thermal behaviour of PE and PE with zeolites samples is illustrated in Fig. 4.

It can be observed that the melting temperature range slightly decreases with the presence of the zeolites, being more pronounced in the case of the HY zeolites, which have higher acidity. Values in Table 3 indicate that the heat of fusion decreases when a zeolite is added, and that the higher acidity of the zeolites leads to a diminution of the crystallinity degree of the polymer.

Probably the zeolite particles dispersed in polymer may not act as nucleation agents decreasing the crystallinity degree of the polymer samples [16]. The differences observed can be attributed to the diversity of the products obtained after PE catalytic degradation due to the presence of the zeolites.

Conclusions

TGA provides a useful and convenient tool for comparing a wide range of materials for the catalytic degradation of polymers. The starting Y zeolites showed a different catalytic activity. The degradation reaction with HY was faster than with NaY , most probably due to the presence of the strong acid sites which leads to higher acidity in the former zeolite. Moreover, in the presence of the modified zeolites, the polymer degraded with an intermediate rate of the individual starting catalysts. The results obtained clearly confirm the suitability of ion exchange treatment over Y zeolites for the catalytic cracking of plastic waste.

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[a] Determined from ICP-AES analysis.
[b] nA_1 is theoretical number of acid sites drawn from the unit cell formula of the FAU-zeolites.

[a] Number of sodium ions per unit cell drawn from the unit cell formula of the FAU-zeolites.