# Catalytic degradation of polyethylene: An evaluation of the effect of dealuminated Y zeolites using thermal analysis

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## Abstract

Commercial samples of high density polyethylene were degraded over Y zeolites with different Si/Al: ultrastable Y zeolite (USY) and three dealuminated Y zeolites (HY(4), HY(12) and HY(20)). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was used aiming to evaluate the apparent activation energy of polymer cracking. The results obtained show that the efficiency of different zeolites was due to their acidity. A high Si/Al ratio gave a greater acidity to zeolites and the onset degradation temperature of the polymer and related activation energy decreased. The sample residues obtained after an isothermic TGA, were analysed by DSC and it was observed that the crystallinity decreases with the acidity of zeolites. HY(20) zeolite was the most active catalyst due to the isolation of the residual Brønsted acid sites which promote their strong acidity. 

Keywords: Polymer; Microporous materials; Ageing; Thermogravimetric analysis

# Introduction

The dramatic plastic consumption in the second half of the twentieth century was accompanied by a drastic increase in plastic waste [1,2]. Plastic waste can be regarded as a potentially cheap source of chemicals and energy. In fact, the acceptance of the conventional waste process (landfill and incineration) is decreasing, while the use of waste

polymers as raw materials for industry can partially solve the problem of the shortage of natural resources expected in near future [3,4].

Polymer recycling becomes a better alternative to those methods. Thermal degradation methods to gas and liquid products show advantages compared to other polymer recycling methods. Pure thermal degradation of plastic wastes needs high temperatures and produces heavy products that need further processing for their quality to be upgraded. On the other hand, the presence of catalysts, such as zeolites, reduces the process temperature and forms hydrocarbon products in the motor fuel boiling range, which eliminates the need for further upgrading process steps [5,6].

Zeolites are tridimensional crystalline microporous aluminosilicates with the following formula in the synthesized form: $x\mathrm{M}_{2/n}\mathrm{O} \cdot x\mathrm{Al}_2\mathrm{O}_3 \cdot y\mathrm{Si}_2\mathrm{O} \cdot \mathrm{WH}_2\mathrm{O}$, where M either is a cation belonging to the group IA or IIA or an inorganic cation, while $n$ is the cation valence and W represents the water contained in the zeolite voids. The tridimensional structure of the zeolites produces solids with very high surface area and pore volume, which are capable of adsorbing great amount of hydrocarbons [7]. The important sites in zeolites are the Brønsted acid sites, which consist of hydrogen bonded to an oxygen atom that connects to the tetrahedral-coordinated $\mathrm{Si}^{4+}$ and $\mathrm{Al}^{3+}$ cations $[\mathrm{O} - \mathrm{Al} - \mathrm{OH} - \mathrm{Si} - \mathrm{O}]$. These sites are responsible for the strong acidic catalytic behaviour. On the other hand, the silanol groups $[\mathrm{O} - \mathrm{Si} - \mathrm{OH} - \mathrm{O}]$ observed in zeolites are Lewis acid sites with weakly acidic strength. The structures are present in Fig. 1 [7,8].

Y zeolites with high silica content are generally prepared by dealumination of the ammonium zeolites samples. In these zeolites, the catalytic activity depends of the decrease the Al content and the increase in the strength of residual Brønsted acid sites. It is known that the acid strength of a given site will increase when there is a decrease in the number of aluminium species in next nearest neighbour positions (NNN) of the aluminium which supports the acid site. A completely isolated aluminium tetrahedron will have zero NNN (ONNN) and will support the strongest type of framework Brønsted acid site [7,8].

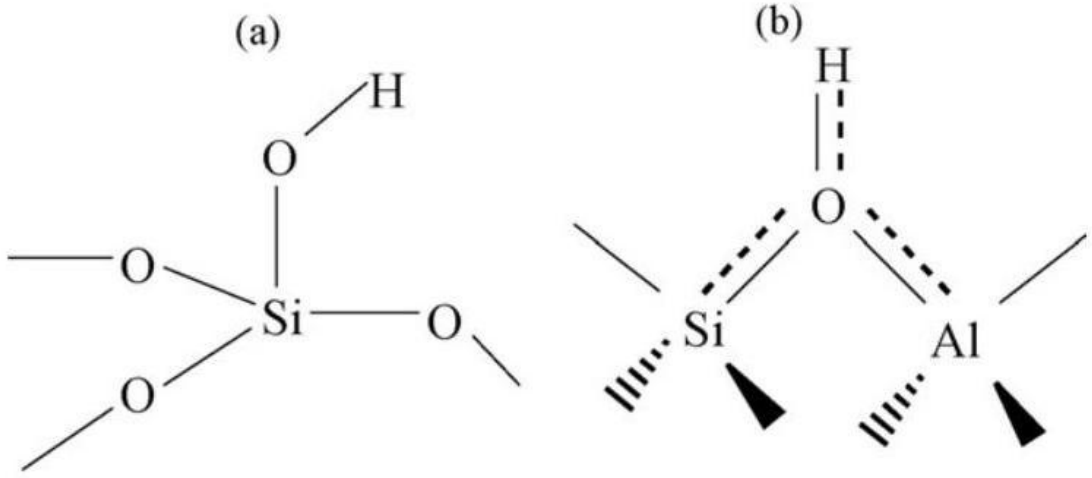


Fig. 1. Schematic representation of: (a) silanol and (b) zeolitic Brønsted acidic hydroxyl [7,8].

In a previous work we have reported the effect of ion exchange treatments on the acidity behaviour of Y zeolites during the catalytic degradation of PE [9]. Our results show the suitability of ion exchange treatment over Y zeolites for the catalytic cracking of plastic waste. The present study is concerned with the catalytic degradation of a commercial high density polyethylene (HDPE) catalysed by Y zeolites with different silica contents: ultrastable Y zeolite (USY) and three dealuminated Y zeolites (HY(4), HY(12) and HY(20)). The dealumination process can promote porous structure modifications which may improve some interesting properties of zeolites, such as thermal and hydrothermal stability, acidity, catalytic activity, resistance to ageing and low coking rate [10].

The stability of the polymer samples with the same amount of Y zeolites was estimated on the basis of the results obtained from thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses. Although the process of catalytic degradation of PE is far from an elementary reaction, kinetic information derived from thermogravimetric analyses, such as apparent activation energies, can be used for internal comparison of catalysts [11]. Hence, the polymer samples were subjected to dynamic thermogravimetric analyses in order to estimate the activation energy of the process. The samples residues obtained after an isothermal TGA were analysed by DSC to determine the polymer crystallinity of each mixture.

# Experimental

## Materials and reagents

High density polyethylene (HDPE) in powder form (Stamylan HD 2H 280) with an average molar mass of $60 Kgmol^{-1}$ was kindly supplied by DSM. The Y zeolites USY (CBV 500), HY(4) (CBV 400), HY(12) (CBV 712) and HY(20) (CBV 720), were obtained from ZEOLYST with the specific surface area of $730 - 780\ m^2\ g^{-1}$, were used in powder form. All zeolites were previously calcined at 773 K during 8 h under a dry air stream. The zeolites USY and HY(12) were available in the ammonium form and after heating they decomposed into $NH_3$ and $H^+$. The $NH_3$ desorbs and the presence of the protons increases the number of acid sites. The other zeolites were available in the proton form.

## Preparation of the samples for degradation

Four samples of HDPE and the dealuminated Y zeolites were prepared by mixing at room temperature the polymer powder with USY, HY(4), HY(12) and HY(20) using a polymer/catalyst ratio of 9:1. The ratio used in this study has been kept constant and equal to 9 , as shown in a previous work [12] to be the best ratio for this type of study.

# 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 the elements during the fusion stage conducted at 1323 K .

Phase analysis was performed by XRD using a Philips PW1710 diffractometer. Scans were taken at room temperature in a $2\theta$ range between 4 and 80°, using Cu$K\alpha$ radiation. The degree of crystallinity was estimated by comparing the reflection intensities of the peaks ( 331 ), ( 511 ), ( 440 ), ( 533 ), ( 642 ) and (555) of the sample and that of the sample taken as reference, NaY ( 100% crystalline) according to ASTM D 3906-80 method. The unit cell parameters were calculated from the (533), (642) and (555) reflection peak positions and determined using the (101) reflection of the quartz ($2\theta = 26.64187$) as an internal standard by ASTM D 3942-80 method.

Thermogravimetric analyses (TGA) were carried out using a 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 were subjected to different heating rates of 5 , 10 and 20 K $min^{-1}$, between 300 and 800 K in order to estimate the activation energy of the catalytic degradation process and (ii) isothermal experiments were performed at 473 K during 8 h . The thermal behaviour of degraded samples was evaluated using a Perkin-Elmer 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

## Morphology and chemical composition of starting *Y* zeolites

The data obtained by X-ray diffraction (XRD) analysis were used to provide structural information of the different Y zeolites. The framework Si/Al ratio was obtained from the unit cell parameters calculated using the Breck and Flanigen equation [13] and the bulk Si/Al ratio was determined by inductively coupled plasma emission spectroscopy (ICP-AES). The changes in the Si/Al atomic ratio, the relative crystallinity and the theoretical number of acids sites of ultrastable Y (USY) and dealuminated Y zeolites (HY(4), HY(12) and HY(20)) are presented in Table 1.

The Si/Al atomic ratio is different for the ultrastable Y zeolite and the dealuminated Y zeolites. The framework Si/Al ratio is higher than the bulk Si/Al ratio indicating the presence of extra-framework alumina species (EFAL). The EFAL species are formed during the dealumination processes of Y zeolites and can

Table 1
Characteristics of the Y zeolite samples used in PE degradation

| Samples | Si/Al bulk | Si/Al framework | Unit cell formula | Relative crystallinity (%) | EFAL [a] | $n\,A_1 \times 10^{20}$ ( sites $g^{-1}$ |
|---|---|---|---|---|---|---|
| USY | 3.0 | 3.9 | $H_{39.3}Na_{0.7}Al_{40}Si_{153}O$ | 80 | 11 | 20.5 |
| HY(4) | 2.8 | 4.1 | $H_{27.3}Na_{10.7}Al_{38}Si_{154}$ | 77 | 17 | 14.0 |

| | | | | | | |
|---|---|---|---|---|---|---|
| HY(12) | 4.7 | 9.7 | $H_{16.5}Na_{1.5}Al_{18}Si_{174}O$ | 68 | 19 | 8.6 |
| HY(20) | 13.0 | 16.6 | $H_{10.6}Na_{0.3}Al_{11}Si_{181}O$ | 63 | 3 | 5.5 |

[a] EFAL is the number of extra-framework aluminium species drawn from the framework Si/Al ratio of the zeolites.
[b] $n\,A_1$ is the theoretical number of acid sites drawn from the unit cell formula of the zeolites.

contribute to the rapid deactivation of the zeolites [14]. However, the dealumination process of Y zeolites affects their crystallinity. As shown in Table 1, a loss of 30% of the crystallinity for the three dealuminated Y zeolites was observed when compared to the respective standard NaY zeolite. The ultrastable Y zeolite maintained over 80% of the crystallinity.

The dealumination process changed the acidity behaviour of the Y zeolites. The differences in the theoretical number of acid sites reflect the decrease in the acid species with high Si/Al ratio. Although HY(20) presents the lower number of acid sites, its strength is more important due to the isolation of the Brønsted sites [7,8].

# Thermal stability studies of the polymer/zeolites samples

From thermal analysis the catalytic degradation of polyethylene was studied in the presence of Y zeolites with different silica contents: an ultrastable Y zeolite (USY) and three dealuminated Y zeolites (HY(4), HY(12) and HY(20)) in order to determine the effect of the dealumination process on catalytic degradation.

Fig. 2 shows the weight loss of the samples polymer/zeolites as a function of the temperature, obtained at 5 K $min^{-1}$. The onset temperatures [15] obtained under the same experimental conditions are shown in Table 2.

From the thermogravimetric results it can be observed that the onset temperature of the degradation was lowered in the presence of all Y zeolites. Moreover, the decrease of the onset temperature was lower for the sample with USY zeolite and higher for the sample with HY(20). This behaviour can be explained by the reduction of the number of the acid sites observed after the dealumination process of Y zeolites. The diminution of $Al^{3+}$

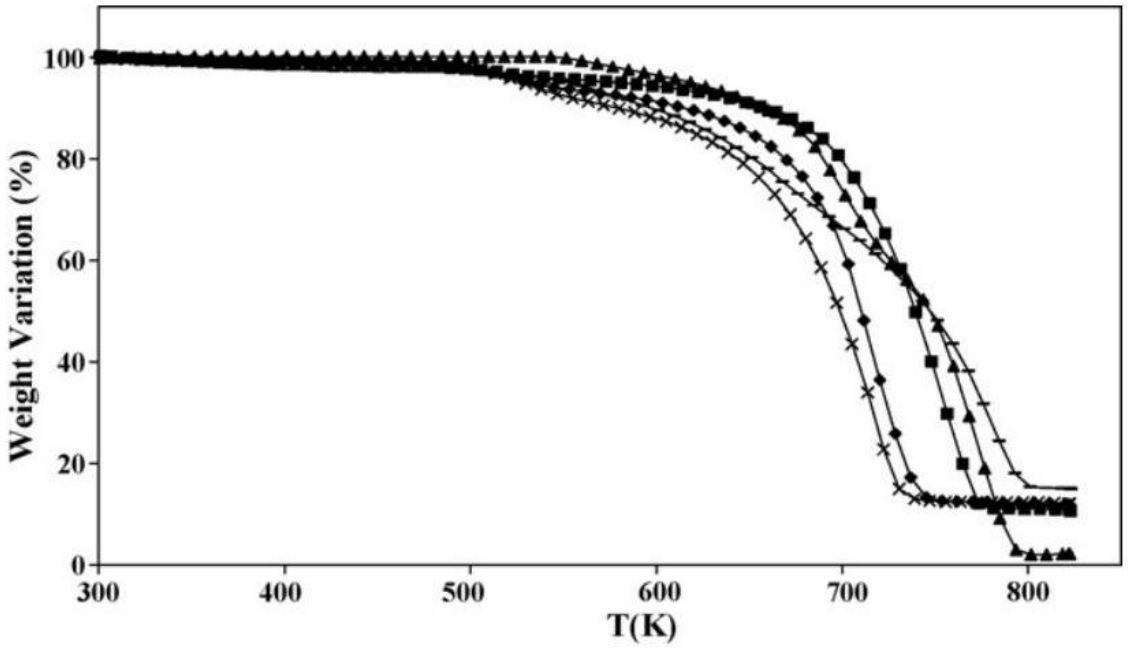


Fig. 2. Dynamic thermogravimetric curves obtained for the samples: ( Δ ) PE, (■) PE + USY, (-) PE + HY (4), ( ∧ ) PE + HY (12) and ( × ) PE + HY (20).

Table 2
Parameters obtained for the polymer/zeolites samples from TGA results

| Samples | *T* onset (K) [a] | Activation energy ( $kJmol^{-1}$ ) [b] |
|---|---|---|
| PE | 715.0 | 131.2 |
| PE+USY | 696.4 | 110.0 |
| PE+HY(4) | 665.2 | 100.0 |
| PE + HY(12) | 677.0 | 71.0 |
| PE + HY(20) | 664.5 | 69.2 |

[a] Onset temperatures obtained at 5 K $min^{-1}$.
[b] Average activation energies calculated by the Ozawa model.
cations in the neighbouring positions provides strong Brønsted acid sites due to their isolation [7,8].

In order to evaluate the activation energy of the polymer decomposition, the Ozawa method was chosen, using different heating rates of 5,10 and 20 K $min^{-1}$. This method was considered more appropriate to obtain kinetic parameters than the single heating rate ones [16]. From the TGA curves at each heating rate the temperature was estimated for a specific conversion level. As the plot of the logarithms of the heating rates against the reciprocals of the corresponding values of the absolute temperatures produce a straight line, it was possible to obtain the activation energy values, as they are proportional to the slopes [12]. The gradients of the various lines were 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 [17,18]. Fig. 3 presents the apparent activation energy values obtained as a function of the fractional residual weight for Y zeolites catalysts used in this work.

For PE a decreasing tendency on the activation energy with increasing the fractional residual weight was observed. This behaviour was similar in other studies [19-21] and the explanation provided was the influence of mass and heat transfer

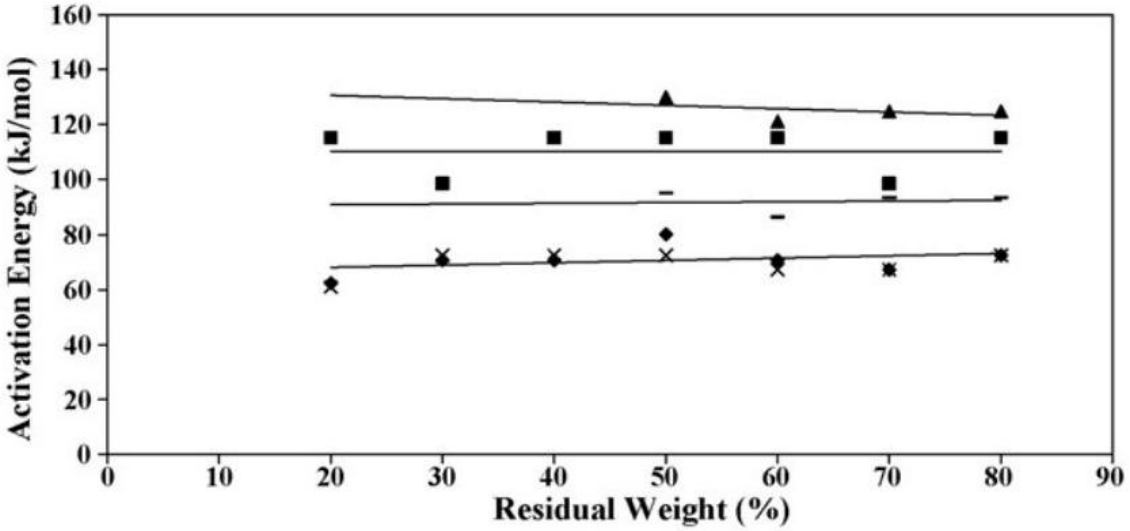


Fig. 3. Activation energy vs. residual weight for polymer degradation over zeolite catalysts: ( Δ ) PE , (■) PE + USY, ( - ) PE + HY (4), ( Δ ) PE + HY (12) and ( × ) PE + HY(20).

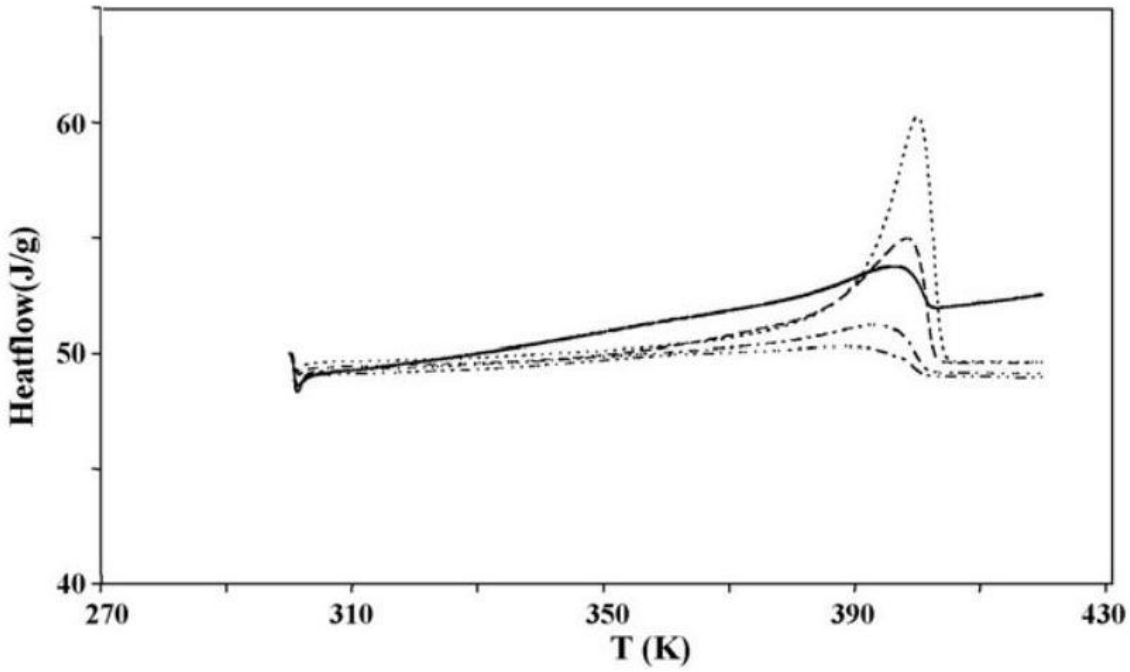

Fig. 4. DSC curves obtained for the samples: ( ⋯ ) PE, (--- ) PE + USY, ( ∧∧∧ ) PE + HY(4), (− ⋯ −)PE + HY(12) and (− ⋯ − ⋯ )PE + HY(20).

Table 3
DSC results obtained for the polymer/zeolites samples

| Sample | $\Delta H(\mathrm{Jg}^{-1})$ | $\chi(\%)^{a}$ |
|---|---|---|
| PE | 161.6 | 58.3 |
| PE+USY | 139.0 | 50.2 |
| PE + HY(4) | 91.8 | 33.1 |
| PE + HY(12) | 101.7 | 36.7 |
| PE + HY(20) | 94.6 | 34.1 |

[a] The degree of crystallinity was calculated considering that, for polyethylene, the theoretical heat of fusion ( $\Delta H_{\mathrm{f}}$ ) was $277.1\ \mathrm{J\,g^{-1}}$ [23]. phenomena. In all cases the presence of Y zeolites catalysts leads to a decrease in the activation energy (the average values are shown in Table 2), which explains the inflection points towards lower temperatures, observed in Fig. 2 [22]. As expected, the ultrastable Y zeolite (USY) reduces significantly the activation energy during the thermal process, and the dealuminated Y zeolites reduce even more the activation energy resulting in a more rapid degradation. For these dealuminated Y zeolites, it was shown that the maximal strength for the acid sites it obtained when the Brønsted acid sites are isolated [7].

In order to evaluate the crystallinity of the polymer in the presence of Y zeolites, a DSC analysis was performed after an isothermic TGA experiment at 473 K during 8 h . Fig. 4 presents the DSC curves obtained for the polymer/zeolites samples studied in this work. In all cases, a decrease in the $\Delta H$ was observed when a zeolite was added and consequently the degree of crystallinity ( $\chi$ ) obtained was lower (Table 3).

As expected, this behaviour is similar to the one observed for the onset temperatures, PE has the higher crystallinity, it decreases when a USY zeolite was added and decreases even more with the dealuminated Y zeolites.

# Conclusions

In this work, the catalytic degradation of PE over Y zeolites with different silica contents: an ultrastable Y zeolite (USY) and three dealuminated Y zeolites (HY(4), HY(12) and HY(20)) was studied by thermogravimetric analysis. Among several Y zeolites, used in the same amount, it was observed that HY(20) has the strongest effect on catalytic degradation of PE. Apparent activation energies for the catalytic degradation of PE, calculated on the basis of Ozawa mathematical model outlined in this paper were in the following order:HY(12) ≅ HY(20) > HY(4) > USY
When the dealuminated Y zeolites are added a significant decrease in the degradation temperature, activation energy and crystallinity can be detected due to the diminution of

$Al^{3+}$ cations in the neighbouring positions providing strong Brønsted acid sites due to their isolation.

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