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APPLICATION OF TG/FTIR TO THE STUDY OF THE REGENERATION PROCESS OF HUSY AND HZSM5 ZEOLITES

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The effect of regeneration conditions on the composition of the gases evolved during the catalytic pyrolysis of low density (LDPE) and high density polyethylene (HDPE) with HUSY and HZSM5 catalysts has been analysed by the TG/FTIR technique. When regenerated HUSY was employed, the evolution of the gases obtained was similar to that with fresh HUSY, indicating that the regeneration treatment did not affect its properties. Nevertheless with HZSM5, as the regeneration temperature was higher, the composition of the gases gradually became more similar to that evolved in the thermal process.

Keywords: *catalytic pyrolysis, HDPE, HUSY, HZSM5, LDPE, regeneration, TG/FTIR*

Introduction

Nowadays the catalytic pyrolysis constitutes one of the most promising methods of plastic waste recycling to be developed [1]. Depending on the process used the catalyst cycle life may vary from few seconds to several years. The main causes of the loss of catalytic activity are poisoning, fouling, thermal degradation, mechanical damage and corrosion/leaching [2]. In the case of zeolites, the deposition of carbonaceous compounds (coke) is the main deactivation mechanism. The coke can be eliminated by oxidative treatment at high temperatures. However, the high temperatures used in the regeneration processes can lead to dealumination and annealing of the catalyst structure [3]. The importance of the study of the regeneration to prolong the catalyst life is obvious.

In a previous article [4], the effect of regeneration temperature and time on the activity of HUSY and HZSM5 zeolites during the catalytic pyrolysis of LDPE and HDPE by TG was analysed. At that time the activity was defined as the ability of the catalyst to reduce the decomposition temperature of the polymer. This study showed that the possible changes in the activity of these zeolites are only related to the experimental conditions utilized during the regeneration process; while other parameters such as the previous deactivation process, the type of polymer used or the quantity of coke deposited do not affect the recovered activity. HUSY recovered all its initial activity independently of the regeneration conditions, indicating the great thermal stability of this zeolite. However in the case of HZSM5, for the higher regeneration temperatures a permanent loss of activity was observed.

On the other hand, Xie *et al*. [5] showed as the combination of the complementary techniques as TG/FTIR provides a versatile and complete analytical system to study reaction pathways for the formation of gaseous products and the degradation mechanisms of materials during pyrolysis and combustion processes. Recently, Marcilla *et al.* [6] have studied the deactivation process of HZSM5 and HUSY zeolites during the thermal and catalytic pyrolysis of polyethylene obtaining interesting results from the analysis of the evolution of the IR absorption bands. In the same way, Casu *et al.* [7] analyzed the pyrolysis of refuse derived fuels in order to characterize the incoming material and to establish the best condition of fuel gas production.

In the present work, the effect of the regeneration treatment of HUSY and HZSM5 catalysts on the gaseous products evolved during the catalytic pyrolysis of LDPE and HDPE has been studied by the TG/FTIR technique. The FTIR spectra registered provide valuable information about the different steps occurring in such processes.

Experimental

Materials

Two commercial polyethylene samples were utilized: low density polyethylene LDPE 780R supplied by DOW (LDPE) and high density polyethylene HDPE HD3560UR supplied by BP (HDPE). Both polymers were supplied in powder form with a maximum particle size of 500 μm. The melt flow indexes (MFI) at 190°C were 20 g·10 min^{-1} for LDPE and 6 g·10 min^{-1} for HDPE. LDPE is a branched polymer and has a smaller density (0.923 g cm^{-3}) as HDPE, which is linear (0.935 g cm^{-3}).

Two different commercial zeolites were chosen as catalysts: HZSM5 and HUSY provided by

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Table 1 Characteristics of the zeolites employed

Zeolite	HZSM5	HUSY
SiO_2/Al_2O_3/mass%	22.2	4.8
Pore size/nm	0.55	0.74
BET surface area/$m^2\ g^{-1}$	341	614
External surface area^a/$m^2\ g^{-1}$	37.6	28.1
Pore volume^b/$cm^3\ g^{-1}$	0.18	0.35
Micropore volume^a/$cm^3\ g^{-1}$	0.16	0.29
Acidity^c/mmol $NH_3\ g^{-1}$	1.15–0.88	2.12
T_{max}/ºC	166–416	154

[a] obtained by application of the *t*-plot method,
[b] measured at p/p_0=0.99496, [c] from ammonia TPD

GRACE-Davison. Table 1 shows the main characteristics of the fresh zeolites. As can be seen, their properties are quite different in spite of their both being microporous catalysts.

Methods

The regeneration process over zeolites was performed in a Netzsch TG 209 thermobalance. TG/FTIR analysis was performed coupling the thermobalance to a Bruker Tensor 27 FTIR spectrometer through a transfer line heated to 200ºC to prevent condensation of the decomposition products. The spectra of the gases evolved were acquired at 4 cm^{-1} resolution in the range 4000–500 cm^{-1}. Infrared scans were taken from the onset of pyrolysis at every 2.8ºC (approx. 16.5 s) temperature interval.

Initially, the polymer degradation with fresh catalyst was carried out. In this experiment, powder sample masses of around 9 mg were heated from 30 to 550ºC at 10ºC min^{-1} in a nitrogen atmosphere with a flow rate of 45 mL min^{-1}. In all experiments, the catalyst to polymer ratio was 1/10. Polymer and catalyst were thoroughly mixed prior to experiments in order to obtain a good reproducibility. The coked zeolites obtained were regenerated at 600, 700, 800 and 900ºC for 15 min in an air atmosphere with a flow rate of 30 mL min^{-1}. The catalytic activity recovered was evaluated by repeating the catalytic experiment described above but using the regenerated zeolite. To compare the activity of zeolites, the thermal pyrolysis of LDPE and HDPE was also studied.

The nomenclature employed in the catalytic experiments is the following: the first two letters in each run corresponds to the polymer, 'LD' or 'HD' for LDPE and HDPE respectively. The third letter 'Z' or 'U' corresponds to the zeolite employed, HZSM5 or HUSY, respectively. When regenerated zeolite was employed 'Z' or 'U' is followed by 600, 700, 800 and 900 indicating the regeneration temperature.

Results and discussion

Figure 1 shows the FTIR spectra obtained at the temperature of maximum decomposition rate in the thermal pyrolysis of LDPE, and in the catalytic process with fresh HUSY and HZSM5 zeolites. In order to provide an easier comparison between the spectra, the LDPE and the mixture of LDPE with HZSM5 (LD-Z) spectra have been moved some relative absorbance units upwards. Table 2 shows the assignment of IR bands to vibrational modes of the different functional groups present in the main volatile products evolved in the pyrolysis processes studied. As can be seen in Fig. 1, all spectra show the same IR bands, although the relative intensity of some bands observed in the spectra obtained in the thermal and the catalytic processes is different. This fact indicates that the compo-

Table 2 Assignment of IR bands to vibrational modes of the different functional groups [15]

Group	Vibrational mode	Assigned wavenumber/cm^{-1}
mononuclear aromatic hydrocarbons	C–H stretching	3078
$=CH_2$	olefinic C–H stretching	3015
$–CH_3$	C–H asymmetrical stretching	2964
$–CH_2–$	C–H asymmetrical stretching	2934, 2926
$–CH_3$	C–H symmetrical stretching	2883
$–CH_2–$	C–H symmetrical stretching	2855
C=C	stretching	1647
mononuclear aromatic hydrocarbons	skeletal vibrations	1625–1475
$–CH_3$	C–H asymmetrical bending	1470–1430
$–CH_2–$	scissoring	1460
$–CH_3$	C–H symmetrical bending	1388
mononuclear aromatic hydrocarbons	in–plane C–H bending	1250–950
=CH	out-of-plane olefinic C–H bending	1000–650
mononuclear aromatic hydrocarbons	out-of-plane C–H bending	900–650
$–CH_2–$	rocking	720

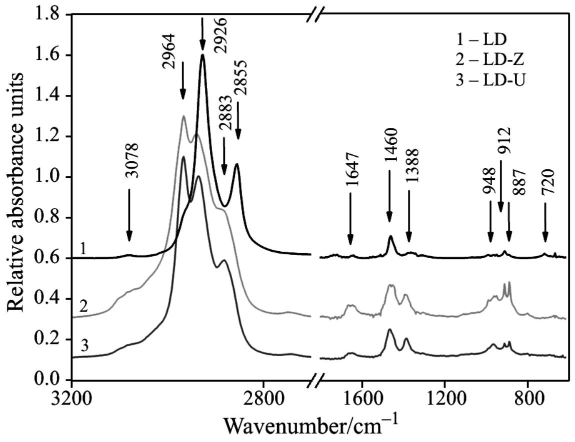

Fig. 1 FTIR spectra obtained at the temperature of maximum decomposition rate in the thermal pyrolysis of LDPE and in the catalytic pyrolysis with fresh HZSM5 and HUSY

sition of the gases evolved during these processes is different. The presence of alkene compounds is indicated by the IR bands at 3015 cm^{-1}, typical of =C–H stretching vibrations; at 1647 cm^{-1}, corresponding to C=C functional group; and the group of bands situated in the region from 1000 to 850 cm^{-1}, due to the =C–H stretching and deformation vibrations. The bands between 3000–2800 and 1500–1350 cm^{-1} are an indication of the presence of aliphatic species such as $-CH_3$ and $-CH_2-$. On the other hand, the presence of the band at 3078 cm^{-1}, and the bands in the region of 1625–1475 and 1000–650 cm^{-1}, reveal the existence of aromatic compounds. In the spectrum originated in the thermal pyrolysis of polyethylene, the characteristic bands indicate that the composition of the gases obtained is made up of a mixture of volatile hydrocarbons such as alkanes and alkenes, whereas the presence of aromatic products is negligible. The most important IR bands are those corresponding to the $-CH_2-$ group (2926 and 2855 cm^{-1}), indicating that products of relative long molecular chain are obtained during the degradation process, a fact confirmed by the band at 720 cm^{-1}. This behaviour has been previously reported by different authors [8, 9]. On the other hand, in the spectra obtained in the presence of catalysts, the most intense band corresponds to the $-CH_3$ group (2964 cm^{-1}). These results confirm that the catalyst favours the cracking process increasing the yield of shorter and/or more branched hydrocarbons. Apart from the change in the chain length, the presence of the catalyst also produces an increase of olefinic and aromatic products, especially with HZSM5. The hydrophobic character of HZSM5 favours the yield to olefins, which are polar compounds, since these molecules are not adsorbed by the catalyst. Instead, as olefins are strongly retained in HUSY, secondary reactions are favoured increasing the concentration of paraffins in the composition of volatile products obtained [10, 11]. As was shown [6], similar results were obtained for HDPE.

Figures 2–5 show the evolution *vs.* the temperature of the intensity of the main absorbance bands obtained in the processes studied. At the top and at the bottom of these figures, the catalytic processes with fresh catalysts and the thermal behaviour, respectively, are shown while curves at the centre of the figures correspond to the catalytic process employing regenerated catalysts at the indicated temperatures. This arrangement allows the similarities and differences to be observed between the evolution of the gases obtained with regenerated zeolites and those corresponding to the catalytic process with fresh zeolite and to the thermal one. The range of temperatures at which the gases are evolved can be observed as well as the displacement of the temperature of maximum gas evolution rate.

Figure 2 shows the evolution corresponding to the experiments of LDPE with HUSY. At the bottom of the figure, it can be seen that the tendency observed previously for the thermal degradation of LDPE at the temperature of the maximum decomposition rate stays constant in all the range of temperatures where the gases are evolved. The band of the $-CH_2-$ group is

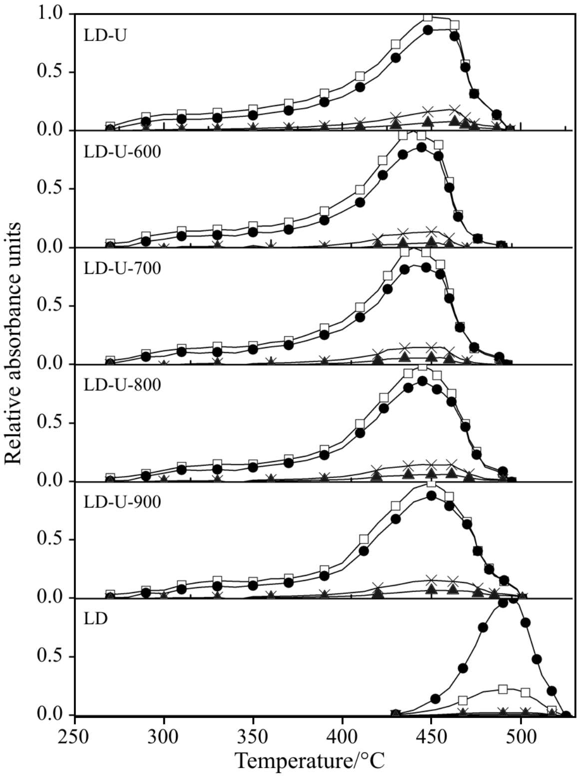

Fig. 2 Evolution with the temperature of the bands characteristic of alkanes ($-CH_3$ and $-CH_2-$ asymmetrical stretching), alkenes (3015 cm^{-1}) and aromatics (3078 cm^{-1}) obtained during the thermal and catalytic pyrolysis of LDPE with fresh and regenerated HUSY zeolite, □ – alkane (CH_3), ● – alkane (CH_2), × – olefin, ▲ – aromatic

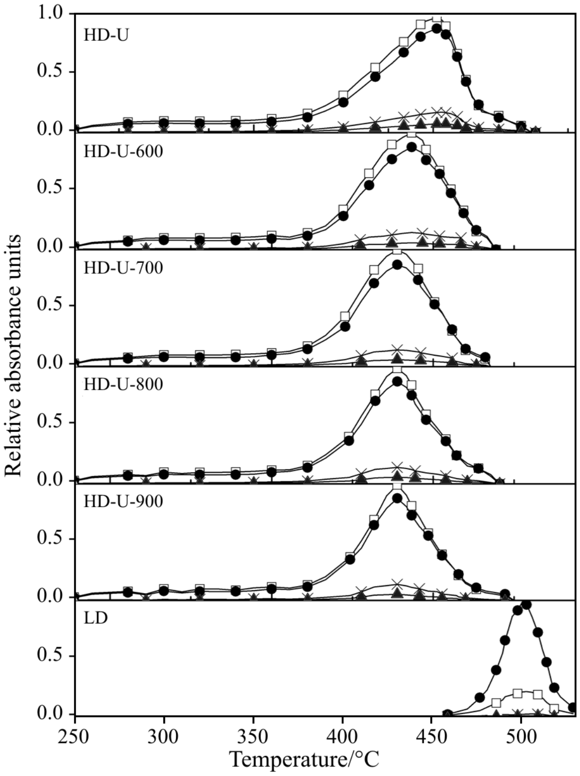

Fig. 3 Evolution with the temperature of the bands characteristic of alkanes (–CH_3 and –CH_2– asymmetrical stretching), alkenes (3015 cm^{-1}) and aromatics (3078 cm^{-1}) obtained during the thermal and catalytic pyrolysis of HDPE with fresh and regenerated HUSY zeolite, □ – alkane (CH_3), ● – alkane (CH_2), × – olefin, ▲ – aromatic

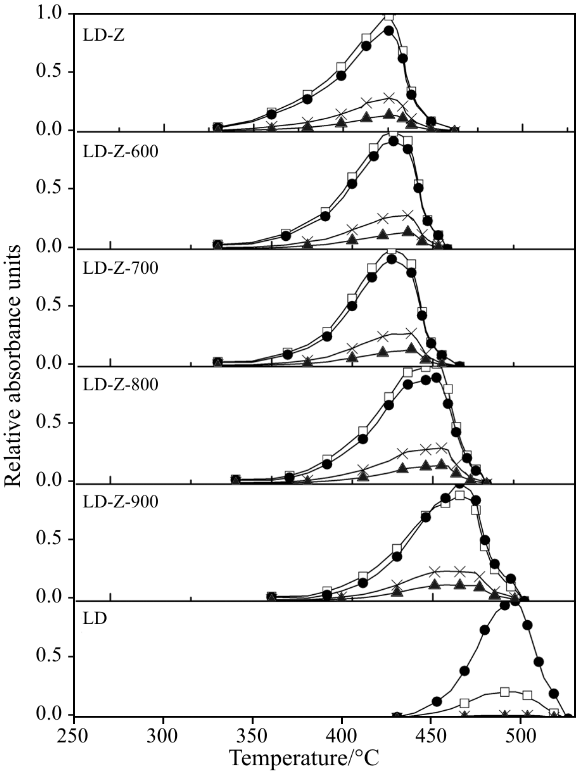

Fig. 4 Evolution with the temperature of the bands characteristic of alkanes (–CH_3 and –CH_2– asymmetrical stretching), alkenes (3015 cm^{-1}) and aromatics (3078 cm^{-1}) obtained during the thermal and catalytic pyrolysis of LDPE with fresh and regenerated HZSM5 zeolite, □ – alkane (CH_3), ● – alkane (CH_2), × – olefin, ▲ – aromatic

the most intense during all the degradation process, whereas the relative intensity of the bands related to aromatics and alkenes is negligible.

In the presence of the HUSY zeolite the evolution of the curves changes. In this way, the degradation process starts at temperatures as low as 270ºC, but the decomposition process extends over a wide range of temperatures. Two different events of generation of gases can be observed. From the initial temperature to about 400ºC, the decomposition takes place at a low rate and the composition of the gases evolved stays constant. In this range of temperatures, the band of –CH_3 is the most intense although the difference of intensity between this band and that of the –CH_2– group is not very important. From 400ºC to the temperature of maximum gas evolution rate, the degradation rate is higher and the intensity of all curves increases, mainly those corresponding to alkanes. From that temperature to the end of the process, the intensity of bands decreases quickly. In this last stage, the intensity of the –CH_2– group with respect to the –CH_3 increases slightly. On the other hand, the contribution of olefinic and aromatic compounds is more important than that observed in the thermal process. Apparently there are no differences between the spectra of fresh and regenerated HUSY at the different regeneration temperatures employed.

For HDPE (Fig. 3), the evolution of the IR bands is similar to that of LDPE. The FTIR analysis shows that the composition of the gases evolved during all catalytic processes is identical independently of the regeneration conditions and the type of polymer used. These results agree with those obtained with thermogravimetric analysis [4]. According to Nassionou *et al.* [12] a large part of coke formed in zeolites with a structure similar to that of HUSY was located near the outer surface of the crystallites, where the coke elimination by the regeneration treatment is facilitated. This fact explains that at a low regeneration temperature such as 600ºC, all the coke was eliminated and the catalyst recovered all its initial activity. HUSY also shows a high thermal stability even at regeneration temperatures as high as 900ºC, keeping its initial catalytic properties. On the other hand, the polymer structure does not influence the process [13].

Figure 4 shows the corresponding curves of HZSM5 with LDPE. The behaviour with fresh HZSM5 changes with respect to that with HUSY. The

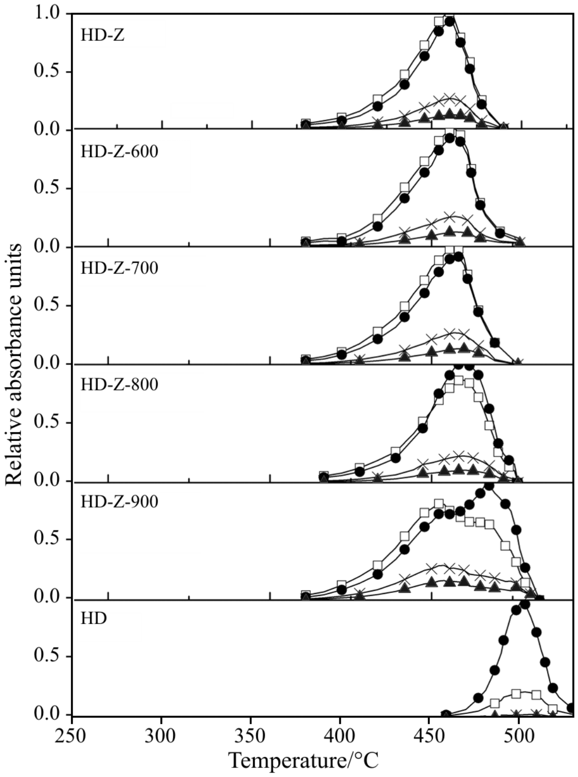

Fig. 5 Evolution with the temperature of the bands characteristic of alkanes (–CH_3 and –CH_2– asymmetrical stretching), alkenes (3015 cm^{-1}) and aromatics (3078 cm^{-1}) obtained during the thermal and catalytic pyrolysis of HDPE with fresh and regenerated HZSM5 zeolite, □ – alkane (CH_3), ● – alkane (CH_2), × – olefin, ▲ – aromatic

degradation process starts at higher temperatures (about 325ºC) and finishes at lower temperatures (about 470ºC) than with fresh HUSY. The evolution of the bands of aliphatics (–CH_3 and –CH_2–) is the same as with HUSY and as commented before the contribution of olefinic and aromatic compounds is higher than that for HUSY. This tendency changes gradually with the regenerated zeolites. When the regeneration temperature is low (600 and 700ºC), the behaviour is similar to that obtained for fresh HZSM5. For the regeneration temperature of 800ºC, the shape of the curves changes and apparently two overlapped processes are taking place. At 900ºC, a splitting of the curve can be observed, increasing the second peak at the expense of the first one. This behaviour is more pronounced for HDPE (Fig. 5). The second peak that appears gets closer to that corresponding to the thermal decomposition. In this second peak, the intensity of the –CH_2– band increases slightly and is more important than the –CH_3 band. This fact suggests that two different mechanisms during the pyrolysis process with HZSM5 regenerated at high temperatures take place. Initially, the composition of the gases evolved is similar to that corresponding to fresh HZSM5, but at higher temperatures this composition changes, becoming more similar to that obtained during the thermal process. Moreover, a progressive change of the temperature of maximum gas evolution rate towards higher temperatures can be observed. For HDPE an important widening of the range of temperatures can be observed, although the change of temperature of maximum gas evolution rate is not so important as for LDPE.

These results indicate that the high regeneration temperatures employed have affected the HZSM5 structure and that the activity of this zeolite depends on the type of polymer. According to Marcilla *et al.* [4], the thermal stability of the HZSM5 zeolite is lower than that of HUSY and the catalyst suffers a progressive dealumination during the regeneration process implying the loss of a greater number of weak and strong acid sites. The higher the regeneration temperature, the lower the number of available acid sites. In this way, the decomposition proceeds initially by the catalytic route until the acid sites available are exhausted, and from this stage the decomposition takes place by thermal mechanism. Serrano *et al.* [14] also observed that the strength and nature of the acid sites affect both the decomposition temperature and the products obtained in the cracking process as it has been observed in Figs 4 and 5.

Conclusions

The TG/FTIR technique has been successfully employed to study the effect of the regeneration conditions in catalytic pyrolysis of LDPE and HDPE. The FTIR analysis of the gases obtained when HUSY is employed as a catalyst showed that the composition of the volatile products evolved was independent of the regeneration process and the polymer structure. However, significant differences can be observed for regenerated HZSM5. A progressive change of the gases evolved can be observed when the regeneration temperature increases acquiring a composition more similar to that obtained during the thermal process. This change of the composition is higher with HDPE than LDPE, confirming the higher number of reaction initiation points for branched LDPE.

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