Catalytic cracking of ethylene-vinyl acetate copolymers: comparison of different zeolites

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Abstract

In this work, five catalysts (three zeolites and two ordered mesoporous aluminosilicates, MCM-41) were tested for the pyrolysis of two samples of commercial ethylene-vinyl acetate (EVA) copolymers with different vinyl acetate percentage and different melt flow index. This study was carried out by using a thermobalance under nitrogen atmosphere and with a heating rate of 10 °C min^{-1}. As can be expected, the preliminary analysis of TG curves shows differences depending on the chemical and structural characteristics of the polymer and of the catalyst used: (i) despite that the temperature of maximum decomposition rate is always the same for the first decomposition step (acetic acid loss), the presence of catalyst makes this step less selective, thus occurring within a wider range of temperatures, especially for those catalysts with high external surface areas; (ii) the catalysts produce a reduction of the temperature of the second decomposition step (cracking of the residue from the first step) which is always lower than that of the thermal process; (iii) it seems that the greater decrease of the maximum decomposition rate temperature occurs when Hβ zeolite is added and is followed by the addition of Al-MCM-41 (however, the effect of the addition of catalyst depends on its percentage); and (iv) the comparison of TG curves corresponding to the addition of Hβ and Al-MCM-41 (which have high external surface areas), and of HY and H-ZSM-5 (with much lower external surface areas) reveals the importance of the accessibility to the active sites in the behavior of the catalyst.
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1. Introduction

Accumulation of enormous amounts of plastic waste produced all over the world has negative implications on the environment. Therefore, recycling plays an essential role in developing a sustainable economy and must be considered in any plastic application. The pyrolysis of organic materials has received renewed attention due to the possibility of converting these wastes into useful energetic products or into valuable chemicals [1,2], and a number of plastic pyrolysis pilot plants and demonstration schemes have been developed worldwide [2]. Among these plastic wastes, ethylene-vinyl acetate (EVA) copolymers represent the largest volume segment of the ethylene copolymer market. The properties of EVA copolymers depend on their vinyl-acetate contents, and products ranging from 2 to 40% of vinyl acetate (VA) are commercialized for different purposes [3].

Several authors have studied the influence of different catalysts on the mechanism of thermal decomposition of different waste products as well as on the values of the corresponding kinetic parameters [4–14]. The addition of a catalyst could not only improve the quality of products obtained from pyrolysis of plastic wastes and lower the temperature of decomposition, but could also enable a given selectivity to a certain product to be achieved [6,15]. Solid acid catalysts, such as zeolites, favor hydrogen transfer reactions due to the presence of many acid sites [15]. The access of molecules to catalyst reactive sites is limited to the pore size as well as the growth of end products inside the pores. Therefore, zeolite catalysts may produce molecular sieving and shape selectivity [15]. Thus, further developments in the process of feedstock recycling of plastics have included the use of these catalysts as a way of producing a highly aromatic product for the production of gasoline or as a chemical feedstock or for the production of fine chemicals [2].

The influence of the factors which govern the activity and selectivity of zeolites and other silica-alumina materials (mainly acidity of active sites, pore structure and accessibility) is a subject of study nowadays. As an example, Garforth et al. [1] show that the catalytic degradation of polyolefins may be investigated using thermogravimetric analysis (TGA) as a potential method for screening catalysts and found that the presence of catalyst led to a decrease in the apparent activation energy. These authors compare two types of TGA experiments (isothermal runs at several temperatures and dynamic runs at different heating rates) for the evaluation of mesoporous (MCM-41) and microporous (ZSM-5) catalysts in the degradation of high-density polyethylene (HDPE). The comparison of activation energies for the catalytic degradation of HDPE using different catalysts shows the following order: no catalyst > MCM-41 (pure silica) > silica-alumina > HSZM-5 > HY > HUSY > Al-MCM-41. In this case, the authors explain this order by the restricted access to the zeolitic materials, which probably means that the initial degradation of high-molecular weight polymers occurs predominantly at the external surface (i.e. that not due to the micropores) or at the pore mouths. Despite the fact that zeolites have a large internal surface area, a great number of the catalytic sites are initially unavailable for the degradation of large molecules such as polymers. However, smaller cracked products may enter in the zeolitic channels and then give rise to

different product distributions due to differences in pore systems, which influence product selectivity. On the other hand, the mesoporous materials such as the siliceous MCM-41 may allow the polymer to reach most of the active sites.

The interest of all these studies about the catalytic cracking of polyolefins over acid solids as zeolites supports the interest of their extension to the case of EVA copolymers. The thermal decomposition of EVA copolymers can be considered as a two-step process. First, acetic acid is evolved from the acetate, followed by the second step which corresponds to the main chain degradation. Munteanu and Turcu [3] suggested a mechanism for the first step of EVA copolymer decomposition. According to these authors, in the grafted chains, the decomposition of the acetoxy groups is favored by the tendency to form (via hydrogen bonds with active methylene groups) a six-ring transition state. The activated complex decomposes thermally, eliminating acetic acid. According to McGrattan [16], at around 367 °C, acetate pyrolysis occurs, leaving a polyunsaturated linear hydrocarbon. A competing reaction also produces CO, CO_2 and CH_4, but acetate pyrolysis is the favored reaction. A second reaction, at approximately 470 °C, breaks the polyunsaturated hydrocarbon to give either an alkane, or an alkene or a 1,n-diene as final products.

The ability of siliceous mesoporous materials to act as catalysts in the degradation of EVA has been demonstrated by Marcilla et al. [13] who pyrolyzed six samples of commercial EVA copolymers with different VA with and without an MCM-41 acid catalyst in a TG apparatus at 10 and 40 K min^{-1} and under inert atmosphere (N_2), showing that the catalytic pyrolysis of this copolymer can be considered as the combination of the pyrolysis of three fractions: the decomposition of VA domains, that seemed to be unaltered by the presence of the catalyst, the decomposition of the corresponding polyene residue after its evolution and the decomposition of PE domains, with an increase of the effect of the catalyst as the amount of VA decreases in the copolymer.

Early studies on the degradation of EVA copolymers showed that the initial step in the thermal degradation involves the formation of acetic acid and that this was enhanced with increasing VA content, although according to McGrattan [16], also a competing reaction produces CO, CO_2 and CH_4. The second step involves degradation of the main chain with little evidence of interaction between the ethylene and VA units [17]. This secondary decomposition was shown to be much more complex reaction than one simply producing ethylene and 1-butene, generating all volatile hydrocarbon chains from C_8 to C_{26} [16]. On the other hand, several authors have studied the influence of the catalyst in the pyrolysis of polyolefins [18–20], showing different product distributions depending on the zeolitic catalyst selected (shape selectivity), demonstrating that the choice of a suitable zeolite structure is an important factor. Thus, in this work, the influence of five acid materials (three zeolites and two ordered mesoporous aluminosilicates, MCM-41) with different structural characteristics in the catalytic pyrolysis of two samples of commercial EVA copolymers with different VA percentage have been studied using a thermobalance as a method for catalyst screening, relating the differences between the catalysts with their structural and acidic properties.

2. Experimental

2.1. Materials

Table 1 shows the main characteristics (as provided by the supplier) of the two commercial EVA analyzed and the notation used in this work, and Table 2 shows the main characteristics of the five catalysts. The three zeolites were prepared by conventional hydrothermal synthesis as described elsewhere [21]. The zeolites were ion-exchanged with 1 M NH_4NO_3 for 24 h and calcined at 550 °C to obtain the acid form (H-zeolite). Al-MCM-41a was prepared by hydrolysis of tetraethoxysilane (TEOS) in a basic solution of hexadecyltrimethylammonium bromide (CTAB). Sodium aluminate was added as Al source to the synthesis solution. The final material was calcined at 550 °C in order to remove the surfactant. These materials were characterized by XRD, FTIR, SEM, N_2 adsorption at 77 K and elemental analysis. Al-MCM-41b was synthesized by Escola [22]. Table 2 shows some of the main properties of the materials studied.

2.2. Equipment

Thermogravimetric runs were performed in a Netzsch TG 209 thermobalance. The experiments for the determination of the thermal decomposition temperature were carried out with an initial sample mass of around 15 mg and at a heating rate of 10 °C min^{-1}. All samples were in powder form and the study was carried out using initial mixtures with around 10–15% of catalyst. The samples were placed in open Al_2O_3 pans. The carrier gas was N_2 (99.99% minimum purity) at a flow rate of around 0.5 cm^3 STP s^{-1}.

To ensure the measurement of the actual sample temperature, a calibration of the temperature was performed by repeating each run twice. In the first run, only the sample was placed in the sample holder, while in the second the weight loss of the sample together with three metals, used as standards, was registered. In this case, a magnet surrounded the oven and sample. The metals used (alumel, nickel and perkalloy) lose their magnetic properties at a specific temperature (Curie-point transition at 163, 354 and 596 °C, respectively). In all cases, the temperatures were correct (error below 5 °C) thus assuring the reliability of the temperature measurement as well as a very good reproducibility.

Table 1
Characteristics of the two commercial EVA copolymers studied

Commercial name of polymer	VA%	MFI[a]	Hardness	Nomenclature
EVA BASF LUPOLEN U-3510-K	13	4	84	EVA0
EVA ESCORENE UL15028CC	27.5	145	69	EVA1

[a] MFI, melt flow index (g (10 min)$^{-1}$).

Table 2
Characteristics of the five catalysts studied

Zeolite	Pore size (Å)	Shape of pores	SiO_2/Al_2O_3	Specific area ($m^2 g^{-1}$)	Origin
H-ZSM-5	5.1×5.5, 5.3×5.6	Cylinders and zigzag channels	30	500	Synthesized for present work
HY	7.4	Cages	12	750	Synthesized for present work
Hβ	5.6, 7.7×6.6	Cylinders	25	625	Synthesized for present work
Al-MCM-41a	27	Cylinders	42.7	1360	Synthesized by Escola [22]
Al-MCM-41b	20	Cylinders	25	1100	Synthesized for present work

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3. Results and discussion

Figs. 1 and 2 show TGA curves obtained for the two EVA copolymers with the five catalysts. As can be seen, most of them exhibit the common behavior of the catalytic pyrolysis with this kind of catalyst and a decrease of the temperature for the main decomposition process appears. As Marcilla et al. [13] observed, the temperature of maximum weight loss for the first process, i.e. that corresponding to VA elimination, suffers almost no modification and appears approximately at the same temperature despite the presence of the catalyst, whereas the second weight loss is clearly affected by the different catalysts. As can be seen, the influence of the catalyst is different depending on the type of zeolite–polymer set selected. Several factors must be considered to explain these different behaviors, some concerning the catalysts and some the polymer. With relation to the catalyst, the following considerations may be taken into account:

i)   The activity of a solid acid catalyst increases when the number and/or the strength of the acid sites increase [18–20]. In some cases, as with Al-MCM-41, higher Si/Al ratios indicate a lower acid site concentration and so lower catalytic activity.

ii) An important factor related to the ability of a porous acid solid to act as a catalyst is its pore size and shape [1,15,19,20]. In fact, the catalytic role of the acid centers will only be emphasized if the reactant molecules may access to the active sites located in the inner surface of the solid. Thus, if the structure of the pores does not permit the access of the polymeric chain to the acid sites, the
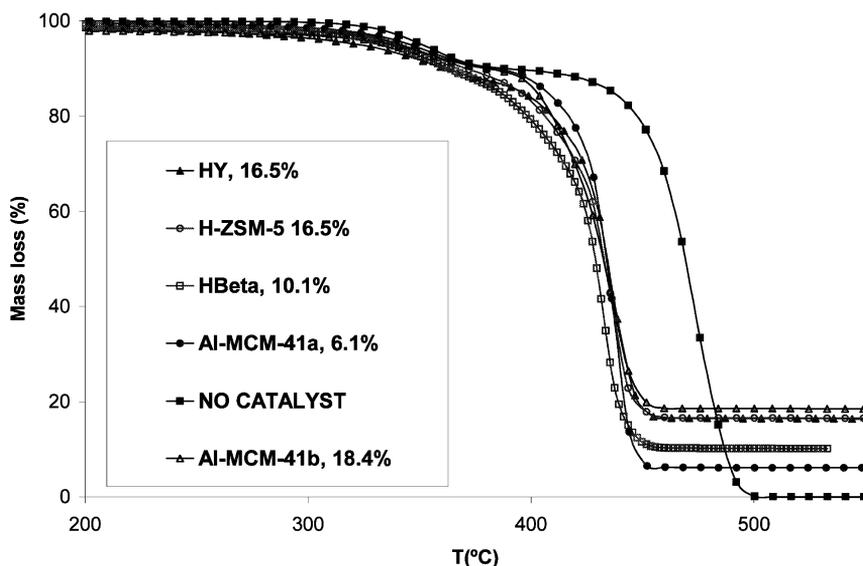

Fig. 1. TGA curves obtained for the catalytic pyrolysis of EVA0 with the five catalysts studied in this work.
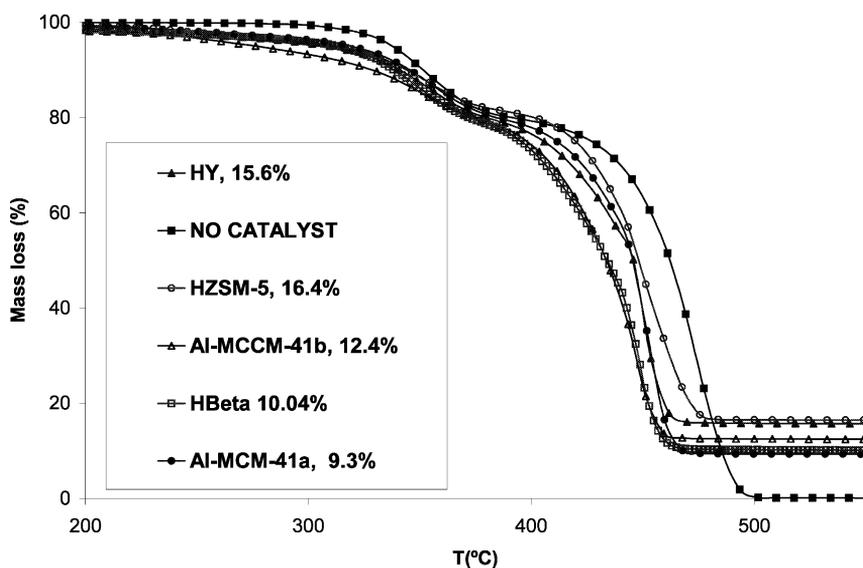
Fig. 2. TGA curves obtained for the catalytic pyrolysis of EVA1 with the five catalysts studied in this work.

reaction cannot be accelerated. On the other hand, if there is no enough space to permit the formation of the intermediate species of the reaction or of the final reaction products, the reaction will not be accelerated either.

iii) Another contribution to the global activity of the catalysts comes from their external surface, determined by the size of the catalyst particles [20]. If the pores of the material are restricted to the access of the reactant molecules, but the external surface is high enough to allocate an adequate number of acid centers, the catalyst may still exhibit catalytic properties. In this sense, the lower the catalyst particle size, the higher its external surface and, consequently, its catalytic activity.

With respect to the influence of the characteristics of the polymer on the catalytic pyrolysis, the following may be stated:

iv) If a polymer–catalyst set is selected in such a way that the shape and the size of the catalyst pores are able to permit the access of the terminal groups of the chains to the acid sites, the catalyst activity will increase when the possibilities to initiate the degradation reactions of the polymer chains increase, that is, when more terminal groups are in the chain, i.e. (a) when the polymer is more branched and (b) when the polymer chains are shorter [14].

v) The length of the polymer chains not only affects the terminal group's number, but also determines the viscosity of the melted polymer (i.e. the melt flow index, MFI). The shorter the polymer chains, the lower the viscosity of the melted polymer and the higher its MFI, probably enhancing the mixing and diffusion

within the solid particles of the catalyst and access to the acid centers of the external surface or the penetration in the pores.

vi) The polymer branching degree is also important due to the eventual steric hindrances, which, once a polymer chain is linked to an active site, may make difficult the access of other macromolecules to the neighboring sites.

vii) Obviously, for copolymers such as EVA, as VA content decreases, the behavior of the catalytic pyrolysis of the copolymer resembles more that of PE [13].

Considering the previous aspects, a qualitative interpretation of TG curves of Figs. 1 and 2 may be provided. The presence of certain catalysts clearly modifies the behavior of the first process (VA elimination) that starts earlier and proceeds over a wider temperature range (Figs. 3 and 4 show a magnification of this zone). The most effective catalysts in this respect are HY (EVA0) and Al-MCM-41b (EVA1). This premature initiation of the decomposition may be related to the presence of the acid sites in the external catalyst surfaces: zeolite HY shows the lower Si/Al ratio and Al-MCM-41b, with a mesoporous structure, exhibits much more accessible active sites than the other microporous materials and more acid centers than Al-MCM-41a (see Si/Al ratios in Table 2). Another aspect that is clearly observed is that these effects are more marked in the case of EVA1 sample that may be due to the lower viscosity of this polymer (see Table 1), which could favor the mixing process with the catalyst and the diffusion within the pores. This high accessibility to the active sites, helped by the pore structure of the catalyst as well as by the polymer characteristics, may be the reason for the marked effect of Al-MCM-41b catalyst shown in Fig. 4.
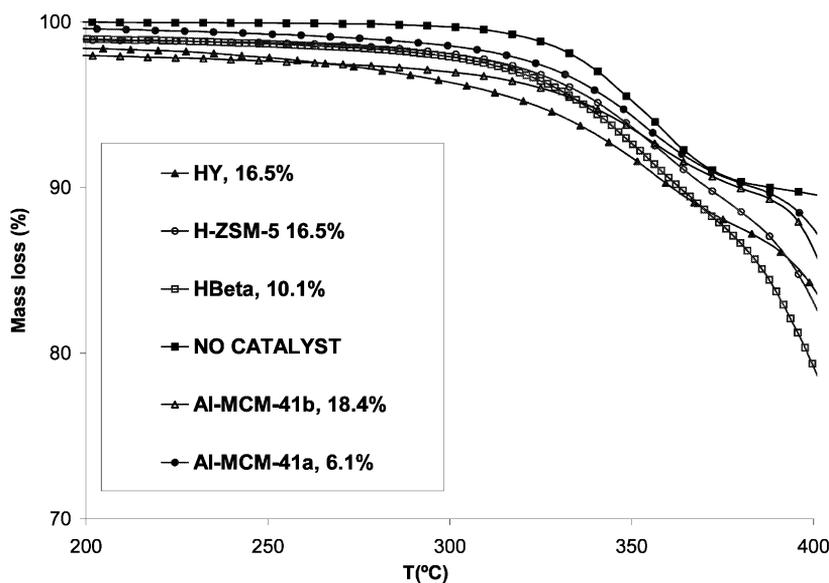

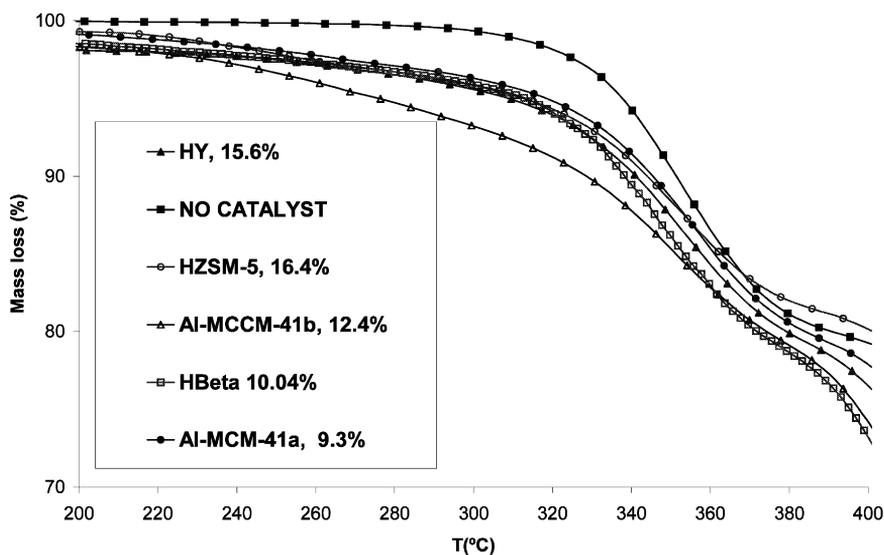Fig. 3. Magnification of the first decomposition step shown in Fig. 1.

Fig. 4. Magnification of the first decomposition step shown in Fig. 2.

On the other hand, the second weight loss, corresponding to the decomposition of PE domains and of the polyene residue after the evolution of VA, is affected differently by the presence of each catalyst and a shift to lower temperatures can be observed. As expected, the preliminary analysis of TGA curves shows the main differences in the second decomposition step [13], depending on the chemical and structural characteristics of the polymer and of the catalyst used. Figs. 1 and 2 show that the greater decrease of the maximum decomposition rate temperature appears when Hβ zeolite is added and is followed by the addition of Al-MCM-41b. However, the effect of the addition of a catalyst depends on its percentage. Thus, a proper comparison would require the same zeolite concentration in all the cases. Apparently, the lower decrease in temperature is due to H-ZSM-5 zeolite. For both copolymers, the order of influence of the catalysts in the second step of decomposition is the following: non-catalyzed < H-ZSM-5 < HY < Al-MCM-41a;Al-MCM-41b;Hβ.

For EVA1 in the cases of Al-MCM-41b and Hβ, both catalysts produce the same decrease of the temperature, but Hβ with a lower percent of catalyst. Interestingly, both materials are those with the higher external surface area. Thus, the activity order of the catalysts observed may be summarized as follows: H-ZSM-5 and HY zeolites are the less active, Hβ zeolite exhibits the greater activity and mesoporous Al-MCM-41 has an intermediate behavior. The good performance of Hβ zeolite versus H-ZSM-5 can be attributed not only to the existence of greater channels in Hβ structure, which makes easier the access to the active sites (in this case, the Si/Al ratios are similar; see Table 2), but also to the amount and acidity of the accessible active sites. Thus, Hβ which has a significant external surface area (of about 200 m^2 g^{-1} as deduced from its N$_2$ isotherm) and high acidity is the most active material.

Al-MCM-41 has the highest accessible surface (more than 1000 m^2 g^{-1}) but poor acidity. HY-type and H-ZSM-5 zeolites are poorly active, despite their high acidity, probably because these sites cannot be reached by the polymer. Related to the external surface area of these materials, for H-ZSM-5 it is very low (around few m^2) in comparison with the micropores area, and it is difficult for its determination from the N$_2$ isotherm. However, Hβ zeolite, due to its structural characteristics of the growth and mixing of the crystals, has an important external surface area, which may be easily obtained and which converts this zeolite into an interesting material for several purposes. In Al-MCM-41 case, perhaps their external surface area is low, but since it is a mesoporous material, the majority of the surface area is accessible to the reactant agents.

Another interesting conclusion drawn from the observation of Fig. 2 is the fact that the decrease of temperature for the second decomposition step is higher for Al-MCM-41b than for Al-MCM-41a, probably due to the higher activity of Al-MCM-41b related with its higher Al content and, thus, higher acidity. According to the bibliography, higher activity appears when more acid sites are available in the catalyst [1,2,18,20] and in some cases, reducing the Si/Al ratio serves to increase the acidity of the catalyst [1,2,18]. Thus, the comparison of TGA curves corresponding to the addition of Al-MCM-41a and Al-MCM-41b reveals the importance of the catalyst properties (in this case SiO$_2$/Al$_2$O$_3$ ratio) in the behavior of the catalyst.

The curves shown in Fig. 2, and mainly that corresponding to HY case, exhibit the existence of two different zones in the second decomposition step. This fact was also observed by Marcilla et al. [13] and attributed to the existence of two different domains in the polyene chain resulting from the first decomposition step: PE domains in the original polymer and the residue of the decomposition of VA domains, which interact differently with the active sites. As can be expected, this fact is less evident for EVA0, because of its lower VA content (Fig. 1), which correspondingly subtracts importance to the influence of VA decomposition polyene domains. Regarding the polyene formation after the acetate groups evolution in the first decomposition step, one may expect, erroneously, that the size of the pores was not as important as in other cases, because the side groups which may hinder the internal diffusion of the chains and cause steric effects had already disappeared by chemical reactions. But according to the ideas of Munteanu and Turcu [3], who suggested that in the first step of EVA copolymer pyrolysis, the decomposition of the acetoxy groups in the grafted chains is favored by the tendency to form—via hydrogen bonds with active methylene groups—a six-ring transition state, may be these cyclic structures which are partly responsible for the steric effects, if their formation in the small channels of 5.5 A of ZSM-5 zeolite is hindered.

4. Conclusions

In this work, the influence of five catalysts (three zeolites and two mesoporous aluminosilicates, Al-MCM-41) with different structural characteristics in the catalytic pyrolysis of two samples of commercial EVA copolymers with different

VA percentage have been studied using a thermobalance under nitrogen atmosphere and with a heating rate of 10 °C min^{-1}. As can be expected, the preliminary analysis of TGA curves shows differences depending on the chemical and structural characteristics of the polymer and of the catalyst used:

- In spite of the fact that the temperature of maximum decomposition rate is always the same for the first decomposition step (acetic acid loss), the presence of catalyst makes this step less selective, thus occurring within a wider range of temperatures, especially for those catalysts with more accessible pore structure and higher number of acid centers.
- In all cases, the catalysts produce a reduction of the temperature of the second decomposition step (cracking of the residue from the first step) which is always lower than the thermal one.
- It seems that the greater decrease of the maximum decomposition rate temperature appears when Hβ zeolite is added, and is followed by the addition of Al-MCM-41. However, the effect of the addition of catalyst depends on its percentage. Thus, a proper comparison requires the same zeolite concentration in all the cases. Apparently, the lower decrease of temperature is due to H-ZSM-5 and HY-type zeolites, which, despite the high acidity of their actives sites, are mostly not accessible.
- The comparison of TG curves corresponding to the addition of Al-MCM-41a and Al-MCM-41b reveals the importance of the catalyst properties (in this case SiO_2/Al_2O_3 ratio) in the behavior of the catalyst.

These effects are more noticeable in the case of EVA1 sample where lower viscosity may favor the mixing process with the catalyst and the diffusion within the pores.

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