THERMAL AND CATALYTIC CRACKING OF A LDPE-EVA COPOLYMER MIXTURE

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ABSTRACT

Catalytic cracking of a plastic mixture consisting of LDPE and EVA copolymer (86/14 w/w) over mesoporous Al-SBA-15 and Al-MCM-41 materials as well as nanocrystalline HZSM-5 zeolite (crystal size ~ 35 nm) has been carried out in a batch reactor at 400 - 420°C. The release of acetic acid formed from the EVA decomposition was observed within the temperature range 350 - 400°C. The most active catalyst was nanometer size HZSM-5 that led to complete conversion of the plastic mixture at 420°C whereas both Al-MCM-41 and Al-SBA-15 were meaningfully less active. In addition, the polymer mixture was more difficult to be cracked both thermally and catalytically than pure LDPE. This result has been ascribed to the occurrence of crosslinking reactions leading to a fast deactivation by coke fouling especially over mesoporous catalysts (Al-MCM-41 and Al-SBA-15) because of their open structure. A high selectivity towards C_1 - C_5 hydrocarbons (~ 75 %) was attained over nanometer size HZSM-5, most of them being valuable C_3 - C_4 olefins. PIONA analyses of the C_6 - C_12 hydrocarbon fraction obtained at 420°C indicates that olefins were the main components whereas a significant amount of aromatics was also obtained both thermally and catalytically (> 15 %).

Keywords: LDPE, EVA, cracking, nanocrystalline-HZSM-5 zeolite, Al-SBA-15, Al-MCM-41
1. Introduction

Plastics have become essential materials in our everyday life. As a result, their consumption has been growing continuously during the last decade leading to a parallel increase in the amount of plastics wastes, that reached 18.8 million of tonnes only in the European Union in 2000. Despite the significant advances of the last years, landfilling still remains as the preferred choice of plastic waste management in Europe (64 %) [1]. This situation is regarded as unacceptable under the premises of sustainable development for it leads to a loss of potential raw materials and unwanted environmental pollution. Other alternative of increasing implementation is energy recovery although it is questioned by the public opinion due to the possible emission of highly toxic compounds to the atmosphere such as PAH (polyaromatic hydrocarbons), dioxins, furans, etc. Recycling is an environmentally interesting alternative since it tries to obtain either plastics (mechanical recycling) or products useful as fuels or as raw chemicals, for instance the starting monomers (feedstock recycling) [2]. Mechanical recycling has almost double its share in Europe in the last decade because it is an easy recycling technology for being implemented (just by melting and molding the wastes). However, mechanical recycling is limited to thermoplastics. In addition, the progressive loss of plastic properties, the low quality of the recycled plastics coming from polymer mixtures due to the low compatibility of the resins, as well as the colour of the recycled material make it an intermediate treatment. In contrast, feedstock recycling is becoming a more attractive alternative as the technical and cost problems posed by the necessary sorting treatments among different plastics and from other residues are beginning to be solved due to the appearance of low - cost automatic separation systems and above all, the cooperation of public opinion with the popular container for plastic wastes. However, feedstock
recycling still requires significant technical improvement, although some technologies as gasification appears to be completely mature [3].

Feedstock recycling of polyolefins (LDPE, HDPE, PP) by thermal and catalytic cracking has been a subject of increasing worldwide research in the last years [4-12]. The reason of this interest lies in that these polymers account for roughly 60 % of the total plastic wastes. In addition, catalytic cracking allows the product distribution to be addressed towards more valuable hydrocarbon mixtures compared to the thermal cracking. Catalytic cracking of polyolefins have been carried out over different acid catalysts (zeolites, amorphous silica-alumina, mesoporous solids, clays) and even used FCC catalysts [13]. Mesoporous materials such as Al-MCM-41 and Al-SBA-15 as well as nanometer size HZSM-5 zeolite (crystal size < 100 nm) have shown remarkable performance relative to conventional catalysts [14,15]. The presence of uniform mesopores in the formers (pore diameter > 2.0 nm) and the high content of fully accessible external acid sites of the latter allow these catalysts to surpass the steric and diffusional hindrances found over the micropores of conventional zeolites (D_p < 0.8 nm) and caused by the bulky nature of the plastic molecules. In addition, nanocrystalline HZSM-5 yields high amounts of valuable C_3 - C_5 hydrocarbons (> 60 %), most of them olefins, due to both its microporous structure and great acid strength [14]. In contrast, Al-MCM-41 and Al-SBA-15 leads towards roughly 80 % of middle distillate hydrocarbons because of its mesoporous structure as well as medium acid strength [15].

Thermal and catalytic cracking of ethylene-vinyl acetate copolymers (EVA) has not received so much attention so far, probably due to the low amount produced of this polymer with regards to the aforementioned polyolefins [16]. However, as they are used for the manufacture of
greenhouse films, they are highly concentrated on agriculture plastic wastes along with pure polyethylenes. In Almeria (Southern Spain), a high amount of film wastes are collected every year (> 20,000 tonnes) for the lifetime of these films is just roughly 1-2 years due to its degradation by solar radiation, oxidation, etc. The highly polyethylene content of this film wastes (> 85 %) turn them into a potential material amenable to degradation by catalytic cracking. This work reports the results obtained in the thermal and catalytic cracking of a LDPE + EVA copolymer mixture (86/14 w/w), with a composition similar to that found in real film wastes. The performance of the different catalysts indicates that the mixture is more difficult to be cracked than the pure LDPE although nanocrystalline HZSM-5 is capable of degrading completely the plastic mixture.

2. Experimental

2.1. Catalysts

All the catalysts used in this work were synthesized in our laboratory according to procedures published in literature [15,17,18]. The samples were characterized by different techniques that confirmed its complete purity. The crystallinity of the samples was checked by X-ray diffraction (XRD) in a Philips X’Pert MPD diffractometer using Cu Kα radiation. The Si/Al atomic ratio of the samples was determined by inductively coupled plasma espectroscopy (ICP) with a Varian VISTA-AX CCD apparatus. Nitrogen adsorption-desorption isotherms at 77 K of the calcined catalysts were obtained with a Micromeritics ASAP 2010 instrument. Previously, the samples were outgassed under vacuum at 200ºC for 5 h. Surface areas were calculated by means of the BET equation whereas pore size distribution were determined by the BJH method applied to the adsorption branch of the isotherm. Cylindrical pore geometry was assumed for the
calculations and the Jura-Harkins equation was used to determine the thickness of the adsorbed layer. Micropore volume and external surface area of the catalysts were determined by application of the t-plot method.

The incorporation of aluminum into the catalysts was checked by $^{27}$Al-MAS-NMR spectra of the calcined catalysts. The spectra were obtained at 104.26 MHz using a Bruker MSL-400 spectrometer equipped with a Fourier Transform unit. The external standard reference was [Al(H$_2$O)$_6^{3+}$] and all measurements were carried out at ambient temperature with a spinning frequency of 4000 cps and time intervals of 5 s between successive accumulations.

The acid properties of the catalysts were determined by ammonia temperature programmed desorption (TPD) in a Micromeritics 2910 (TPD/TPR) equipment. Previously, the samples were outgassed under an He flow (50 Nml min$^{-1}$) by heating with a rate of 15ºC min$^{-1}$ up to 560ºC and remaining at this temperature for 30 min. After cooling to 180ºC, an ammonia flow of 35 Nml min$^{-1}$ was passed through the sample for 30 min. The physisorbed ammonia was removed by flowing He at 180ºC for 90 min. The chemically adsorbed ammonia was determined by increasing the temperature up to 550ºC with a heating rate of 15ºC min$^{-1}$, this temperature being maintained for 30 min. The ammonia concentration in the effluent He stream was monitored by a thermal conductivity detector.
2.2. Plastics

The plastic mixture used in this work contains 86 wt % of pure LDPE ($M_w = 416,000$) and 14 wt% of an ethylene-vinyl acetate copolymer (EVA, $(-\text{CH}_2\text{-CH}(\text{O}_2\text{CCH}_3))-x(-\text{CH}_2\text{-CH}_2)-y$), 33 wt% vinyl acetate) which were provided by REPSOL-YPF. Both plastics were mixed and homogenized by cryogenic grinding until reaching a particle size below 0.25 mm in a Retsch ZSM-100 ultracentrifuge mill.

Thermogravimetric analyses of the pure polymers and their mixtures were carried out in a TA SDT simultaneous DSC-TGA apparatus under inert atmosphere (100 Nml min$^{-1}$ of nitrogen). The sample was heated from room temperature up to 600ºC with a rate of 5ºC min$^{-1}$.

2.3. Catalytic degradation experiments

The experimental installation used in the present study for the plastic cracking experiments is shown in Figure 1. It consists of a batch reactor provided with a helicodal stirrer. In a typical experiment, 10 g of the plastic mixture and 0.2 g of catalyst (plastic / catalyst mass ratio = 50) were loaded into the reactor. Subsequently, the reactor is heated at a rate of 6ºC min$^{-1}$ up to the reaction temperature (400 - 420ºC) that was maintained for 2 h. The volatiles products are swept from the reactor by a continuous nitrogen flow (25 Nml min$^{-1}$). Subsequently, the liquids are condensed in an ice trap and the gases are collected in a gas bag. The analyses of both the liquid and gaseous fractions were carried out on a Varian 3800 GC. PIONA GC analyses (Paraffins, Isoparaffins, Olefins, Napthenes and Aromatics) of the gasoline fraction was carried out using a 100 m length x 0.25 mm i.d. Chrompack capillary column. Conversion was calculated
as follows: (mass of hydrocarbons C_n < 20 + mass of acetic acid released) (mass of plastic mixture loaded)^{-1} \times 100. Selectivity data were calculated exclusively on the basis of the obtained hydrocarbon fraction so the amount of acetic acid collected in every experiment was discounted from the total mass of products. The mass balances were closed in every experiment within a ± 5 wt % error.

3. Results and discussion

3.1. Catalysts

The main physicochemical properties of the catalysts used in this work are shown in Table 1. Al-SBA-15 and Al-MCM-41 are mesoporous materials with pore sizes above 2.0 nm. However, Al-SBA-15, unlike Al-MCM-41, also exhibits a significant amount of micropores (micropore volume ~ 0.05 cm^3 g^{-1}). n-HZSM-5 zeolite is a microporous material which possesses a high external surface area (85 m^2 g^{-1}, almost 20 % of the total BET area) due to its nanometer crystal size (35 nm). The presence of mesopores in both Al-MCM-41 and Al-SBA-15 and the high proportion of external surface area of n-HZSM-5 allow a better access of the bulky polymer macromolecules towards their acid sites.

All the catalysts were synthesized with close Si/Al atomic ratios (25 - 40) in order to get a similar content of acid sites. ^{27}\text{Al-MAS-NMR} spectra of the three calcined catalysts before reaction show a distinct peak at 52 ppm corresponding to tetrahedral aluminum and a fairly smaller one placed at ~ 0 ppm assigned to octahedral (extraframework) aluminum. These results bear out the high degree of incorporation of aluminum into the catalyst frameworks.
The acid properties of the different catalysts, determined from ammonia TPD curves, are summarized in Table 1 whereas their respective TPD curves are depicted in Figure 2. Mesoporous Al-MCM-41 and Al-SBA-15 catalysts present similar medium acid strength distributions since their temperature maxima for ammonia desorption are placed around 250ºC. In contrast, nanometer size HZSM-5 exhibits a temperature maximum at 357ºC confirming the presence of the strong acid sites typical of this zeolite.

3.2. TG experiments

Figures 3.a and b show the TG analyses under nitrogen flow corresponding to both plastics, LDPE and EVA copolymer, respectively. LDPE shows a steep weight loss with a maximum in the derivative curve placed at 464ºC whereas for the EVA copolymer two distinct jumps are observed placed at 340ºC and 458ºC, respectively. The former corresponds to the release of acetic groups coming from the acetate grains and its amount (24 %) agrees well with the vinyl acetate content of the copolymer. The second jump arises from the main chain degradation taking place at a temperature close to that of the LDPE decomposition.

3.3. Cracking experiments

Figure 4 shows the results obtained in the thermal and catalytic cracking of the plastic mixture at 400 and 420ºC. The most active catalyst at both temperatures was n-HZSM-5 zeolite that was able to degrade completely the raw plastic mixture at 420ºC. Catalytic cracking over both mesoporous Al-MCM-41 and Al-SBA-15 led to similar conversions at 400ºC to that of
thermal cracking. The activity of these materials increases at 420ºC although still far from n-HZSM-5 zeolite. Al-SBA-15 gave a slightly higher conversion than Al-MCM-41, probably due to its higher content of accessible acid sites according to the TPD measurements.

Several additional reactions were performed with the pure polymers under identical experimental conditions in order to find out the role played by the different plastics present in the mixture. Figure 5 shows the conversions obtained in the thermal and catalytic cracking over Al-MCM-41 and n-HZSM-5 zeolite at 420ºC with both LDPE and EVA, along with those of the plastic mixture. It can be observed that LDPE is the easiest plastic to be cracked either thermally or catalytically. Both n-HZSM-5 zeolite and Al-MCM-41 are capable of degrading LDPE completely. In contrast, the ethylene-vinyl acetate copolymer (EVA), that contains 33 wt% of vinyl acetate, is a more difficult plastic to be cracked. The presence of EVA in the raw mixture affects drastically the activity of the catalysts compared to pure LDPE [16].

Selectivity by groups obtained in the thermal and catalytic cracking of the plastic mixture at 420ºC is shown in Figure 6 while the corresponding selectivity by carbon atom number is depicted in Figure 7. Thermal cracking give mainly rise to gaseous C$_1$ - C$_5$ hydrocarbons. n-HZSM-5 zeolite exhibited a a very high selectivity (~ 75 %) towards gaseous C$_1$ - C$_5$ hydrocarbons, most of them being valuable C$_3$ - C$_5$ olefins with a maximum at the C$_4$ fraction (> 30 %). This selectivity pattern is related to both the presence of strong acid sites and the microporous structure of this catalyst (~ 0.55 nm) that leads to a carbocationic end-chain cracking mechanism, mostly by β-scission reactions [14]. Mesoporous catalysts (Al-SBA-15 and Al-MCM-41) provided a great amount of gasoline hydrocarbons (C$_6$ - C$_{12}$) with a selectivity in the range 40 - 54 %. These results agree well with the medium acid strength and fully accessible mesoporous
structure of both catalysts. The larger mesopore size in Al-SBA-15 explains the selectivity increase towards C₆ - C₁₂ hydrocarbons. In Figure 8, selectivity by groups obtained in both thermal and catalytic cracking at the lowest temperature (400°C) is depicted. Al-MCM-41 selectivity was fairly similar to that of thermal cracking whereas Al-SBA-15 seems to be able to carry out some degree of catalytic cracking or reforming of the thermal cracking products since a meaningful amount of C₆ - C₁₂ hydrocarbons was obtained. In contrast, n-HZSM-5 zeolite presents a selectivity pattern very similar to the one obtained over this same catalyst at higher temperature (420°C).

PIONA analyses of the C₆ - C₁₂ hydrocarbon fractions (Figure 9) obtained at 420 ºC with the plastic mixture point out that olefins were the major components, surpassing 25 wt % in all cases. On the other hand, in the case of thermal cracking, a significant content of aromatics (~ 15 %) is also detected. This is a remarkable difference relative to pure LDPE thermal cracking wherein n-paraffins and 1-olefins are the major products. In addition, irrespective of the used catalyst, the aromatic content of the liquids obtained in the catalytic cracking is always higher than 20 %.

The observed performance of the different catalysts may be originated from the combination of two simultaneous phenomena. Firstly, the acetic acid released from the decomposition of the EVA domains may cause catalyst dealumination affecting negatively the catalyst activity. An additional experiment was carried out to check this possibility. Pure EVA copolymer was heated up to the reaction temperature (420°C) without loading any catalyst in the medium so as to release completely the acetate as acetic acid. Subsequently, the temperature was dropped to 250 ºC and a continuous nitrogen flow was passed through the reactor for 3 h to
ensure the total elimination of the acetic acid. Finally, after cooling to room temperature, n-HZSM-5 zeolite was added leaving the whole system to react as before. Surprisingly, the conversion (82 %) was identical to that obtained when the catalyst is present in the reaction medium from the very beginning. In addition, $^{27}$Al-MAS-NMR spectra of the n-HZSM-5 zeolite retrieved after the reaction carried out with pure EVA copolymer and the zeolite from the beginning and calcined again indicates a low degree of dealumination since the peak of octahedral aluminum only represents around 10 % of the total area. This result suggests that catalyst dealumination, at least in the case of n-HZSM-5 zeolite, does not take place in a great extent, while its effect on the catalyst performance seems to be negligible.

Secondly, according to Munteanu et al [19], the polyene structure remaining into the reactor after the elimination of acetic acid have a trans configuration that favours cross-linking though oligomerization reactions. These highly crosslinked structures might lead to the facile formation of polycondensed structures far more difficult to be cracked than the polyolefinic chains. In addition, these structures are likely aromatic and coke precursors giving rise to a fast catalyst deactivation, especially at lower temperatures, since bimolecular hydrogen transfer reactions leading to coke formation are favoured [20]. The high aromatic content observed in the C$_6$ - C$_{12}$ fraction with the PIONA analyses seems to support this hypothesis. Deactivation by coking should be favoured over mesoporous Al-SBA-15 and Al-MCM-41 because of both their lower acid strength and uniform mesopore size that allows the growth of coke deposits. In contrast, n-HZSM-5 is less prone to this phenomenon because of the presence of some type of shape selectivity over the external acid sites of this catalyst. It is known that HZSM-5 zeolite shows a high resistance to coke deactivation due to its micropore size (~ 0.55 nm), that prevents the growth of coke precursors. In addition, its higher acid strength and carbocationic end-chain
cracking mechanism allow to crack the polyene structures effectively at lower temperature than the other catalysts.

Conclusions

Thermal and catalytic cracking of a standard mixture of LDPE and EVA copolymer (86/14) proceeds with lower conversion than the degradation of pure LDPE. However, nanometer size HZSM-5 was able to degrade it completely at 420ºC unlike mesoporous catalysts, that led to conversions below 70 %. In addition, n-HZSM-5 gave rise to a high selectivity towards valuable C$_3$ - C$_5$ hydrocarbons (~ 70 %), most of them olefins. Al-SBA-15 showed a slightly better performance than Al-MCM-41, probably due to its higher content of acid sites and larger pore size. The lower activity observed with regards to pure LDPE cracking has been related to crosslinking reactions of the polyenes structures formed from the EVA copolymer by the release of the acetic acid, leading to the formation of less degradable polycondensed compounds which are aromatic and coke precursors. This phenomenon is especially remarkable over mesoporous catalysts due to their lower acid strength and the presence of uniform mesopores that allow the growth of bulky coke molecules. In contrast, n-HZSM-5 is capable of degrading completely the plastic mixture because of its higher acid strength and some type of shape selectivity of its external acid sites. Therefore, n-HZSM-5 shows remarkable properties for the catalytic cracking of LDPE-EVA copolymer mixtures.
Acknowledgements

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References


Table 1. Physicochemical properties of the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>Pore Volume (cm$^3$ g$^{-1}$)$^a$</th>
<th>Pore Diameter (nm)</th>
<th>Crystal size (nm)</th>
<th>Si/Al</th>
<th>$T_{\text{max}}$$^b$ (°C)</th>
<th>Acidity$^b$ (mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-MCM-41</td>
<td>1240</td>
<td>0.83</td>
<td>2.1</td>
<td>-</td>
<td>40</td>
<td>254</td>
<td>0.254</td>
</tr>
<tr>
<td>Al-SBA-15</td>
<td>605</td>
<td>0.63</td>
<td>5.0</td>
<td>-</td>
<td>40</td>
<td>246</td>
<td>0.319</td>
</tr>
<tr>
<td>n-HZSM-5</td>
<td>430</td>
<td>0.16</td>
<td>0.55</td>
<td>35</td>
<td>25</td>
<td>357</td>
<td>0.324</td>
</tr>
</tbody>
</table>

$^a$measured at $p/p_0 = 0.99$; $^b$calculated from ammonia TPD measurements
FIGURE CAPTIONS

**Figure 1.** Scheme of the experimental cracking installation.

**Figure 2.** Ammonia TPD curves of the catalysts.

**Figure 3.** TGA under nitrogen of pure LDPE (3.a) and EVA (3.b) copolymer.

**Figure 4.** Conversions obtained in the thermal and catalytic cracking of the plastic mixture at different temperatures.

**Figure 5.** Conversions obtained in the thermal and catalytic cracking of pure polymers.

**Figure 6.** Selectivity by groups obtained in the thermal and catalytic cracking of the plastic mixture at 420°C.

**Figure 7.** Selectivity by carbon atom number obtained in the catalytic cracking of the plastic mixture at 420°C.

**Figure 8.** Selectivity by groups obtained in the thermal and catalytic cracking of the plastic mixture at 400°C.

**Figure 9.** PIONA analyses of the C₆ - C₁₂ hydrocarbon fraction obtained in the thermal and catalytic cracking of the plastic mixture at 420°C.
FIGURE 1
FIGURE 2

Signal (a.u.) vs. t/min plot for Al-SBA-15, Al-MCM-41, and n-ZSM5 samples. The temperature (T) in °C is shown on the right y-axis. The peaks at different times indicate the release of signals during the experiment.
FIGURES 3a) AND 3b)
FIGURE 4

Thermal Conversion (wt %)

- n-HZSM-5
- Al-SBA-15
- Al-MCM-41

Temperature: T = 400 °C and T = 420 °C
FIGURE 5

Conversion (wt %)
FIGURE 6

Selectivity (wt %)

- Thermal
- Al-MCM-
- Al-SBA-1
- n-HZSM-
Selectivity (wt %)

Thermal
Al-SBA-15
Al-MCM-41
n-HZSM-5

$C_1 - C_5$
$C_6 - C_{12}$
$C_{13} - C_{20}$
FIGURE 9

Selectivity (wt %)

- paraffins
- isoparaffins
- olefins
- naphtenes
- aromatics

Al-MCM-41
Al-SBA-15
n-HZSM-5