

Catalytic Properties in Polyolefin Cracking of Hierarchical Nanocrystalline HZSM-5 Samples Prepared According to Different Strategies

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Abstract

Two series of hierarchical nanocrystalline ZSM-5 zeolites prepared by different synthesis strategies (at low temperature and from silanized seeds) and with external surface areas ranging from 150 to 250 m² g⁻¹ were tested in the cracking of pure LDPE and HDPE at 340°C and of waste polyethylene at 360°C. Hierarchical zeolites showed quite higher activity, with values even 6 times higher than a standard nanocrystalline sample used as reference (n-HZSM-5). The activity values decreased from LDPE to HDPE due to the occurrence of some degree of branching in the former polymer, which act as preferential cracking sites. The major products were C₁ – C₄ hydrocarbons (in the range 30 – 70%, mostly C₃ – C₄ olefins) and C₅ – C₁₂ hydrocarbons (20 – 60%), whose share depends on both the polyolefin and the catalyst. The amount of C₁₃ – C₄₀ hydrocarbons was practically negligible (< 1%) due to the high acid strength of the zeolites which promotes end-chain cracking reactions. Likewise, hierarchical nanocrystalline HZSM-5 zeolites prepared from silanized protozeolitic units showed higher activities than the hierarchical nanocrystalline HZSM-5 samples synthesized at low temperature and atmospheric pressure. The differences were especially remarkable in the case of waste polyethylene cracking. These results were ascribed to the stronger acidity of the hierarchical zeolite samples prepared from silanized seeds.

Keywords: catalytic cracking, polyethylene, hierarchical ZSM-5, nanozeolites

1. INTRODUCTION

The production of plastic wastes in the European Union in 2007 was about 52.5 million tonnes [1]. Likewise, the amount of post consumer plastics wastes obtained in the EU that year was 24.6 million tonnes. Consequently, there is a growing social concern related to the management of the plastic wastes, which should proceed according to a hierarchical approach in agreement with the following order: waste minimization, reuse, recycling, energy recovery and landfilling [2]. In EU, landfilling is still the predominant choice for the management of plastic wastes (about 50%), although its share drops 2% annually due to the increase of recycling / energy recovery options. In this regard, catalytic cracking towards fuels and/or raw chemicals appears as a particularly promising option for treating high volumes of waste plastics. In this line, the largest liquefaction plant of plastic wastes based on catalytic cracking was built in Zabrze (Poland) with a capacity of 145,000 t / year [3]. The main components of the plastic waste stream are polyolefins: polyethylene (LDPE, LLDPE, HDPE) and polypropylene (PP). which account entirely for roughly 60% of the whole waste plastic stream.

The catalyst plays a key role in this type of processes since it allows the cracking temperature to be reduced as well as to address the selectivity towards more valuable products. Selectivity is determined by the acidity and porous structure of the catalysts. Different materials have been tested in the catalytic cracking of polyolefins: conventional zeolites (HZSM-5, HBeta, HY) [4-9], silica-alumina [10-12], fresh and spent FCC catalysts [13 – 17], mesostructured materials [18-20], nanozeolites and hierarchical zeolites [21-23]. A point to be taken into account in the catalytic cracking of plastics is the high viscosity and bulky nature of plastics that leads towards steric hindrances and mass transfer constraints. Thus, zeolites pose problems of accessibility for bulky polymers (e.g. PP) towards their internal acid sites due to their micropore size (0.4 – 0.75 nm). Then, higher activities are attained by using mesoporous catalysts and small crystal size zeolites (high external surface area), due to the presence of highly accessible acid

sites. This was proven in the catalytic cracking of PP over HMCM-41, SiO₂-Al₂O₃ and HZSM-5 [20]. Thus, 99.2% conversion was achieved over HMCM-41 instead of 11.3% over HZSM-5, due to the steric hindrances of PP, unable to enter the zeolite micropores. In addition, nanozeolites, due to their high share of external surface area with fully accessible acid sites, also showed remarkable performance in polyolefin cracking [21]. Hierarchical zeolites, which present a bimodal micro-mesoporous structure, are considered catalytic materials with high interest due to their improved mass transfer properties. In this line, hierarchical ferrierite obtained by desilication with NaOH, which showed 3-4 times higher mesopore surface area than the starting commercial sample, significantly enhanced the LDPE conversion [22]. Recently, a new method for the preparation of hierarchical zeolites through the addition of a seed silanization agent during the precrystallization step was reported [23]. This hinders the merge of the protozeolitic nanounits into bigger crystals giving rise to the formation of mesopores and therefore, to the generation of a bimodal (micro-mesoporous) material. In addition, the textural properties of the hierarchical zeolites may be tuned to some extent by choosing the adequate seed silanization agent or varying the amount of silanization agent [24].

In this work, the performance of hierarchical nanocrystalline ZSM-5 zeolites synthesized using three different seed silanization agents (3-aminopropyltrimethoxysilane, isobutyltriethoxysilane, and phenylaminopropyltrimethoxysilane) was investigated in the catalytic cracking of pure HDPE and LDPE. In addition, these materials were compared with hierarchical nanocrystalline HZSM-5 zeolites prepared by a low temperature method [25, 26]. Finally, the activity of the different hierarchical HZSM-5 samples was tested in the cracking of a real waste polyethylene. The goal was to determine the most adequate synthesis method of hierarchical nanocrystalline ZSM-5 for obtaining the highest activity in polyolefin cracking.

2. EXPERIMENTAL

2.1. Synthesis of the catalysts

a) Synthesis of hierarchical ZSM-5 from silanized protozeolitic units [23, 24].

The hierarchical nanocrystalline HZSM-5 samples were prepared by using three silanization agents (SSA): isobutyltriethoxysilane (IBTES, $(\text{CH}_3)_2\text{CHCH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$), 3-aminopropyltrimethoxysilane (APTMS, $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$) and phenylaminopropyltrimethoxysilane (PHAPTMS, $(\text{C}_6\text{H}_5)\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$).

Initially, a precursor solution of ZSM-5 zeolite was prepared using tetraethoxysilane, tetrapropylammonium hydroxide, aluminium isopropoxide and distilled water as reagents. A clear solution with the following molar composition was attained: 1 Al_2O_3 : 60 SiO_2 : 11.5 TPAOH: 1500 H_2O . This solution was precrystallized under reflux with stirring (100 rpm) at 90°C for 20 h. Subsequently, the seed silanization agent (SSA) was added in a fixed proportion (5 mol % with regard to the silica content of the gel) and left reacting for functionalizing at 90°C for 6 h. The final solution was crystallized in a Teflon-lined stainless steel autoclave at 170°C for 5 days. The solid products were separated by centrifugation, washed several times, dried overnight at 110°C and calcined in air at 550°C for 5 h. The synthesized samples were named as HZSM-5 (S), wherein S stands for the used SSA ($\text{S} \equiv \text{APTMS}$, IBTES or PHAPTMS).

b) Synthesis of hierarchical ZSM-5 by low temperature crystallization (LTC) method [25].

Hierarchical nanocrystalline HZSM-5 samples were also synthesized by a low temperature and atmospheric pressure method published elsewhere [25]. The samples were prepared at 90°C varying the synthesis time, which led to hierarchical HZSM-5 samples with different external surface areas. Two hierarchical HZSM-5 samples were synthesized, denoted as HZSM-5 (LTC)-1 and HZSM-5 (LTC)-2, respectively.

2.2. Catalysts characterization

The crystallinity of the catalysts was checked by powder X-ray diffraction (XRD) in a Phillips X'PERT MPD diffractometer using Cu-K α radiation. XRD patterns within the 10 – 80° range were recorded with a step size and a counting time of 0.1° and 10 s, respectively. The silicon and aluminium contents of the catalysts were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) on a VARIAN Vista AX Axial CCD Simultaneous ICP-AES apparatus. Previously, the samples were digested by acid treatment with H₂SO₄ and HF. FTIR spectra were recorded in a Matson Infinity series spectrophotometer. The spectra were recorded with a resolution of 4 cm⁻¹ and 64 scans within the 400 – 4800 cm⁻¹ range.

Nitrogen adsorption-desorption isotherms at 77 K were performed in a Micromeritics Tristar 3000 apparatus. The samples were previously outgassed under vacuum at 210 °C for 6 hours. The surface areas were calculated by means of the BET equation. Pore volumes were determined from the nitrogen adsorbed volume at P/P₀ = 0.95. Micropore volumes and external surface areas were calculated by application of the t-plot method in a previously selected range of the adsorption branch of the isotherm. The mesopore size was calculated by application of the BJH procedure to the adsorption branch of the isotherm. Transmission electron micrographs (TEM) were collected on a Phillips TECNAI 20 microscope equipped with a LaB₆ filament under an accelerating voltage of 200 kV. Prior to the observation, the samples were dispersed in acetone, stirred in an ultrasonic bath and finally deposited over a carbon – coated copper grid.

The acid properties of the catalysts were determined by ammonia temperature programmed desorption (TPD) in a Micromeritics AutoChem 2910 system using He as carrier gas. Previously, the samples were outgassed under a helium flow (50 Nml min⁻¹) with a heating rate of 15°C min⁻¹ up to 560°C and kept at this temperature for 30 min. After cooling to 180°C, an ammonia flow of 35 Nml min⁻¹ was passed through the sample for 30 min. Once the physisorbed ammonia was removed by flowing helium at 180°C for 90 min, the chemisorbed ammonia was

determined by increasing the temperature with a heating rate of $15^{\circ}\text{C min}^{-1}$ up to 550°C , holding this temperature for 30 min. The ammonia concentration in the effluent helium stream was monitored with a thermal conductivity detector (TCD). High resolution ^{27}Al MAS-NMR spectra of the obtained samples were recorded at 104.1 MHz using a Varian Infinity 400 spectrometer. All the measurements were carried out at ambient temperature with a spinning frequency of 11 kHz and pulse width of 2.5 s.

2.3. *Plastics*

The polyolefins used in this work were pure low density polyethylene (LDPE, $M_w = 416,000$) and high density polyethylene (HDPE, $M_w = 188,000$) provided by REPSOL-YPF. Additionally, waste polyethylene from a garbage separation plant was also used as feed.

2.4. *Catalytic cracking experiments*

Catalytic cracking tests were carried out in a batch reactor provided with a helical stirrer. In a typical experiment, a mixture of 10 g of plastic and the suitable amount of catalyst (plastic / catalyst mass ratio was varied in the range 50 - 100) was loaded into the reactor. Subsequently, the reactor was heated with a rate of $6^{\circ}\text{C min}^{-1}$ up to the reaction temperature (340°C for pure polyethylenes and 360°C for waste polyethylene) that was hold for 2 or 3 h. The volatile products were swept from the reactor by a continuous nitrogen flow (35 Nml min^{-1}). Afterwards, the liquids were condensed in an ice trap and the gases were collected in a gas-bag. The analyses of both liquid and gaseous fractions were carried out by gas chromatography in a Varian 3800 GC using a 100 m length x 0.25 mm i.d. Chrompack capillary column. Conversions have been calculated taking into account only the products that leave the reactor with the N_2 stream (C_n , $n \leq 40$), the remaining residue being not considered as a reaction product. The activity was calculated as

(mass of plastic converted) (mass of aluminium in the catalysts)⁻¹ s⁻¹. Deviations in the mass balances were lower than $\pm 5\%$ in all experiments.

3. RESULTS AND DISCUSSION

3.1. *Properties of the catalysts*

The synthesis of hierarchical nanocrystalline zeolites from silanized seeds comprises three stages: precrystallization, silanization and crystallization [23,24]. Firstly, a precursor gel containing protozeolitic MFI nanounits (seeds) is prepared from clear solutions (precrystallization step). Secondly, the seed silanization agent (SSA) is added to the synthesis medium reacting with surface hydroxyls, being anchored onto the outer surface of the zeolite seeds (silanization step). The organic moiety over the external surface of these protozeolitic units precludes their aggregation into bigger crystals. However, some aggregation takes place as the nanounits may join each other by the points not sterically hindered by the SSA. Finally, the samples are crystallized at high temperature (170°C) under hydrothermal conditions (crystallization step). The materials finally obtained are formed by aggregates with sizes around 200 – 400 nm, consisting of ultrasmall ZSM-5 units. These materials show a bimodal pore structure (micro-mesoporous preferentially) due to the voids generated by the silanization agent after calcination [23]. Depending on the seed silanization agent employed, different external surface area and mesopore contributions could be achieved in the resulting materials [24].

The thorough characterization of the hierarchical nanocrystalline ZSM-5 samples synthesized by the seed silanization method was described elsewhere [23, 24]. Likewise, the complete characterization of the hierarchical ZSM-5 samples prepared by the low temperature and atmospheric pressure method can be found in reference [25]. Thus, only the most remarkable features of the characterization of the samples used in this work will be mentioned

henceforth. The crystallinity of the ZSM-5 zeolites was checked by means of XRD and FTIR. Figure 1 illustrates the XRD patterns of the calcined hierarchical HZSM-5 zeolites along with that of a standard nanocrystalline HZSM-5 sample (denoted as n-HZSM-5), included for comparison. The XRD patterns of all samples exhibit the classical features of ZSM-5 zeolite, neither other crystalline phase nor amorphous materials being detected. XRD patterns of hierarchical nanocrystalline HZSM-5 zeolites were less intense than those of the standard nanocrystalline n-HZSM-5. According to the Scherrer law, this is indicative of a decrease in the crystal size. On the other hand, the FTIR analyses (data not shown) indicate that all the samples show the occurrence of the 550 cm^{-1} band, characteristic of the asymmetric stretching of the five-member ring of ZSM-5 zeolites, which is not present in amorphous materials [27].

The BET and external surface area of the catalysts are summarized in Table 1. The different ZSM-5 samples prepared by the seed silanization and the low temperature method shows large surface areas due to the small size of their constituting nanounits. Thus, BET surface areas ranging within $480 - 575\text{ m}^2\text{ g}^{-1}$ and external surface areas around $160 - 240\text{ m}^2\text{ g}^{-1}$ are found in these samples. According to these data, ZSM-5 samples having comparable external surface areas have been prepared by both procedures. Additionally, the size of the secondary pores were very similar for both series of samples, showing a pore size distribution in the range $2.0 - 8.0\text{ nm}$, for hierarchical ZSM-5 prepared by the seed silanization method, and between 1.5 and 6.0 nm for the samples prepared by the low temperature procedure.

TEM micrographs of calcined hierarchical ZSM-5 samples indicate that they are formed by aggregates of small nanounits. Whereas the aggregates show sizes between 200 and 400 nm , the crystalline nanounits are really small with sizes in the range $5 - 20\text{ nm}$, depending on the sample. This can be clearly seen in Figure 2 wherein TEM micrographs of the HZSM-5 (PHAPTMS) sample are shown.

The content and state of aluminium is of paramount importance regarding the catalytic application of these materials in cracking reactions. Table 1 shows the Si/Al atomic ratios of the samples determined by ICP-AES measurements. The hierarchical nanocrystalline samples show Si/Al atomic ratios in the range 40 – 65, values which are lower than that initially loaded in the synthesis medium (about 30). In contrast, the standard n-HZSM-5 sample exhibits a Si/Al ratio similar to that loaded in the synthesis gel. The acidity of the samples was determined by means of ammonia TPD measurements. The standard n-HZSM-5 sample shows a temperature for the peak maximum of the ammonia desorption placed around 350°C and acidity of 0.48 meq NH₃ g⁻¹. The three hierarchical nanocrystalline samples prepared from silanized seeds, HZSM-5 (APTMS), HZSM-5 (IBTES) and HZSM-5 (PHAPTMS), exhibit temperatures for the ammonia desorption maxima within the range 330 – 345°C and acidities around 0.25 – 0.30 meq NH₃ g⁻¹, due to their lower aluminium contents. Hierarchical HZSM-5 zeolites prepared at low temperature exhibit lower T_{max} values (300 – 312°C) and lower content of acid sites than the samples synthesized from silanized seeds. This is a clear indication of the lower acid strength of the hierarchical nanocrystalline HZSM-5 samples prepared using the low-temperature method.

Figure 3 illustrates the ²⁷Al MAS NMR spectra of the calcined HZSM-5 (PHAPTMS) and n-HZSM-5 samples. The spectra show a main signal centered at $\delta \sim 52$ ppm corresponding to tetrahedral aluminium (Al^{IV}), incorporated into the framework, and a much smaller one at $\delta \sim 3$ ppm corresponding to octahedral aluminium (Al^{VI}) which is outside the framework. The ²⁷Al MAS NMR spectra of all the hierarchical nanocrystalline samples, regardless of the synthetic method used, were very similar to those shown in Figure 3. In this regard, Table 1 shows the share of octahedral Al, determined from ²⁷Al MAS NMR spectra, of the different hierarchical HZSM-5 samples. It can be observed that this parameter represents always a low percentage, below 12%, for all the samples. Therefore, the majority of the aluminium presents tetrahedral coordination, being incorporated into the framework (> 80%). This is an important fact since octahedral

aluminium, assigned to extraframework aluminium species, generates Lewis acid sites while tetrahedral aluminium, incorporated into the framework is mostly of Brönsted acid site nature. Consequently, most of the aluminium sites present over these catalysts is of Brönsted nature, being expected to be the main responsible for the catalytic activity in plastic cracking reactions.

The cracking experiments have been carried out over the hierarchical nanocrystalline HZSM-5 samples using three different plastics: pure low-density polyethylene (LDPE), pure high density polyethylene (HDPE) and waste polyethylene. The reaction conditions, conversions and product distribution so obtained are shown in Table 2. Significant differences are observed among the samples in terms of plastic conversion. However, it must be taken into account that the Al content of the samples, which is directly related to the concentration of active sites, presents important variations from one catalyst to the other. Moreover, the reaction conditions (time and plastic/catalyst ratio) are not exactly the same for all the tests. Accordingly, the conversion results cannot be used directly to compare the performance of the hierarchical HZSM-5 samples. Thereby, the activity corresponding to each catalyst has been calculated as the amount of plastic converted per unit of time and per unit of Al weight in the catalyst. This parameter is subsequently used for comparing the catalytic behaviour of the different zeolite samples.

3.2. Catalytic cracking of pure LDPE and HDPE

i) Catalytic conversion of LDPE

Figure 4 shows the activity obtained in the catalytic cracking of LDPE at 340°C over the studied catalysts. All the values corresponding to the hierarchical HZSM-5 materials are higher than that of the reference n-HZSM-5 sample (0.2 s^{-1}). It should be taken into account that this reference catalyst is a nanocrystalline HZSM-5 zeolite which has shown in earlier works much higher activity than conventional standard micrometer HZSM-5 zeolites [20]. The activity for LDPE

cracking increases with the external surface area of the catalysts, reaching at best (HZSM-5 (PHAPTMS) sample) a value six times higher than that of the reference n-HZSM-5. These activities are especially remarkable since they were obtained at a cracking temperature as low as 340°C. On the other hand, the activity of the hierarchical HZSM-5 samples, depicted in Figure 4, point out other interesting facts. Firstly, the activity values corresponding to the hierarchical nanocrystalline zeolite samples synthesized by the low temperature method are lower (0.3 - 0.7 s⁻¹) than those of the materials prepared by the seed silanization method (0.5 – 1.2 s⁻¹) of similar external surface area. This comparison is especially remarkable between samples HZSM-5 (LTC)-2 and HZSM-5 (PHAPTMS), since despite the slightly lower external surface area of the latter (242 vs 225 m² g⁻¹), it exhibits 70% more activity. This striking difference can be ascribed to the higher acidity of the samples synthesized by the seed silanization approach (around 20-30°C difference in the temperature maxima of TPD data) as can be seen in Table 1.

The increase of activity with the external surface area is also related to the structure of the polymer. LDPE is formed by linear chains with some branching. The branches act as points of preferential cracking since they allow tertiary carbocations, more reactive for cracking, to be formed. However, this branching also prevents the polymer from entering the zeolite micropores making the external acid sites the main ones for cracking due to their full accessibility towards the polymers molecules.

Table 2 shows the selectivity data by groups obtained in LDPE cracking over hierarchical HZSM-5 samples. Catalytic cracking over HZSM-5 zeolite is meant to occur through an end chain cracking mechanism wherein the primary products are gaseous C₁ – C₄ hydrocarbons. The main components of this C₁ – C₄ fraction are C₃ – C₄ hydrocarbons (> 90%), the amount of methane being practically negligible and the concentration of C₂ hydrocarbons being rather low. Another point of interest is the makeup of the C₁ – C₄ gaseous fraction since it is formed by 60 – 70% of olefins (propylene, 1-butene and isobutylene). This is of particular interest considering that these

gaseous olefins are useful feedstocks for petrochemistry (e.g, in oligomerization and polymerization reactions), widening the range of potential applications of the obtained products from just fuels. Other products, mainly gasoline range hydrocarbons ($C_5 - C_{12}$), are obtained either by means of secondary reactions of oligomerization, cyclization and aromatization of these primary olefins or by direct catalytic cracking of the polymer. The major products over all the catalysts are $C_3 - C_4$ and $C_5 - C_{12}$ hydrocarbons, whereas the amount of $C_{13} - C_{40}$ hydrocarbons attained is practically negligible ($< 1\%$), which may be related to the high acid strength of the HZSM-5 zeolite. Thus, the selectivity towards $C_1 - C_4$ hydrocarbons varied within the 36 – 66% range for hierarchical nanocrystalline HZSM-5 samples, being lower than the maximum obtained over the reference n-HZSM-5 (76%). The selectivity towards $C_5 - C_{12}$ followed an opposite trend, reaching a maximum for HZSM-5 (IBTES) (62%). No clear trend between the selectivity and the external surface area of the catalysts can be envisaged.

ii) Catalytic conversion of HDPE

Figure 5 illustrates the activity obtained in the cracking of pure HDPE at 340°C over the six investigated catalysts. It can be observed that the activity values are lower for all the samples than those attained previously with LDPE in the same conditions. This fact can be ascribed to the absence of branching (precursors of tertiary carbocations) in HDPE chains due to its linear structure, what makes its cracking more difficult than in the case of LDPE [20]. The activities obtained over the hierarchical nanocrystalline HZSM-5 samples are higher than that corresponding to the reference n-HZSM-5 catalyst (0.12 s^{-1}), reaching at best 0.66 s^{-1} for the sample HZSM-5 (APTMS). This indicates that the increase in external surface area and the reduction in the diffusional constraints, that takes place in hierarchical zeolites, lead towards improved activities, allowing the cracking to be performed to a greater extent. Again, the hierarchical nanocrystalline HZSM-5 samples prepared by seed silanization exhibited higher

activities than the equivalent zeolites with similar external surface area synthesized by the low temperature method. However, the differences were shortened with regard to the results previously obtained with LDPE. Thus, HZSM-5 (PHAPTMS) presented an activity value of 0.48 s^{-1} , while HZSM-5 (LTC)-2 exhibits an activity of 0.41 s^{-1} , a 17% lower. Whereas there is a clear trend of increasing activities with growing external surface area for hierarchical nanocrystalline zeolites prepared by the low temperature method, this does not occur with hierarchical HZSM-5 synthesized from silanized seeds because of the results with HZSM-5 (APTMS). This catalyst showed the highest activity (0.66 s^{-1}) despite of its lower external surface area ($166 \text{ m}^2 \text{ g}^{-1}$) versus $225 \text{ m}^2 \text{ g}^{-1}$ for HZSM-5 (PHAPTMS). The remarkable performance of HZSM-5 (APTMS) can be explained considering the structure of the HDPE and the features of the catalyst itself. HDPE is a linear polymer so its cracking takes place not only over the external surface area but also to some extent over the internal surface area. Then, the true accessible surface area does not coincide solely with the external surface area. On the other hand, HDPE requires more acid strength for its cracking due to its linear structure. In this regard, HZSM-5 (APTMS) shows the strongest acid sites among the hierarchical samples ($T_{\text{max}} \sim 346^\circ\text{C}$), which is probably the main reason of its higher activity with this polymer.

The selectivity data by groups obtained in pure HDPE cracking are shown in Table 2. The reference n-HZSM-5 catalyst yielded mostly gaseous $\text{C}_1 - \text{C}_4$ hydrocarbons (73.5%). Likewise, the hierarchical nanocrystalline HZSM-5 samples gave rise chiefly to both $\text{C}_1 - \text{C}_4$ and $\text{C}_5 - \text{C}_{12}$ hydrocarbons and only in the case of HZSM-5 (IBTES), a 7% of $\text{C}_{13} - \text{C}_{40}$ hydrocarbons were attained. This is in agreement with an end-chain cracking mechanism, predominantly by β -scission, typical of the HZSM-5 zeolite. HZSM-5 (LTC)-1 and HZSM-5 (LTC)-2 samples yielded 70 – 80% of $\text{C}_1 - \text{C}_4$ hydrocarbons (60 - 70% $\text{C}_3 - \text{C}_4$ olefins) and 20 – 30% of $\text{C}_5 - \text{C}_{12}$ hydrocarbons. In this case, a maximum in $\text{C}_1 - \text{C}_4$ selectivity is appreciated for HZSM-5 (PHAPTMS), with a value of 76.6%; while the corresponding maximum in $\text{C}_5 - \text{C}_{12}$ selectivity

(67.2%) is observed for HZSM-5 (APTMS). It seems that samples with large activity give rise to higher amounts of $C_5 - C_{12}$ hydrocarbons, indicative of the larger extent of oligomerization reactions of the $C_2 - C_4$ olefins obtained as primary products by end-chain cracking reactions. On the other hand, the amount of olefins within the $C_1 - C_4$ fraction obtained over hierarchical nanocrystalline zeolites from silanized seeds rises to roughly 90%, higher than in the case of LDPE.

Figure 6 compares the selectivity per atom carbon number obtained in the cracking of the two pure polyolefins (HDPE, LDPE) over the hierarchical sample prepared by the seed silanization method with the highest external surface area (HZSM-5 (PHAPTMS)). The selectivity data indicate that, for both LDPE and HDPE, a major maximum placed at C_4 is appreciated. In addition, the amount of C_4 is considerably higher for HDPE than for LDPE (54.6 vs 29.0%), which is related to the higher reactivity of LDPE as a consequence of the presence of branching. On the other hand, the product distribution resulting from both polymers exhibit a minor peak in the range $C_6 - C_9$. It is remarkable that no hydrocarbons heavier than C_{16} were obtained with any of the polyolefins, due to the high acid strength of the HZSM-5 zeolite since the cracking proceeds chiefly according to an end-chain cracking mechanism.

Figure 7 illustrates the PIONA analyses of the $C_6 - C_{12}$ fraction obtained in the cracking at 340°C of LDPE and HDPE over the hierarchical HZSM-5 (PHAPTMS) sample. For HDPE, the main products in this fraction were olefins with a share close to 40%, followed by isoparaffins (30%), whereas the proportion of aromatics is not very high, just 13.7%. For LDPE, the share of olefins and isoparaffins decreased slightly with regard to HDPE (34.6 and 26.1%, respectively) and the amount of naphthenes augmented meaningfully to 19.2%.

3.3. Catalytic cracking of waste polyethylene

The ultimate goal of the present research is the assessment of the performance of the hierarchical HZSM-5 zeolite samples in the cracking of a real polyethylene waste in order to determine the possible subsequent application of the catalysts. This is a more complex case than the cracking of pure polyolefins due to the presence of a variety of impurities: metals, different additives, other plastics such as residual PVC, etc. which can poison the catalysts leading to its further deactivation. Accordingly, a sample of waste polyethylene coming from a garbage separation plant located at "Comunidad de Madrid" (Spain) was subjected to cracking with the synthesized catalysts.

Figure 8 depicts the DSC analyses of both waste polyethylene and pure HDPE for comparison. The waste polyethylene DSC shows a main peak placed at 133°C assigned to the melting of high density polyethylene chains. A small peak can also be appreciated at 112°C, likely corresponding to the melting of LDPE domains present in the waste polyethylene sample. Considering the relative share of both peaks in the DSC analyses, it points out that the waste polyethylene contains about 85% HDPE and 15% of LDPE.

The metal content of both waste polyethylene and pure HDPE were determined by means of ICP-AES measurements (see Table 3). In pure HDPE, the total metal content is very low and accounts for less than 0.03 wt %. In contrast, the metal content in waste polyethylene is much higher and accounts for roughly 0.4 wt %. The main metals present were Cu and Ti with a share of 0.162% and 0.151%, respectively.

The cracking of waste polyethylene was carried out at 360°C instead of the 340°C used in the experiments developed with pure polyolefins (LDPE, HDPE). This temperature was chosen taking into account that similar activities were achieved in the cracking at 360°C of the waste polyethylene and at 340°C of the pure HDPE with the reference n-HZSM-5 catalyst. The need of a higher temperature is a consequence of the increasing difficulty for cracking waste polyethylene. This can be due to both the effect of the impurities present in the polymer or to a

structural change of the plastics during its use (e.g. crosslinking) that make its cracking more difficult.

Figure 9 illustrates the activity values obtained in the cracking at 360°C of waste polyethylene over the five hierarchical HZSM-5 zeolites and the reference n-HZSM-5 catalyst. In contrast with the results obtained with pure polymers, the hierarchical HZSM-5 samples prepared by the low temperature method show similar activities than that of the reference n-HZSM-5 sample ($\sim 0.15 \text{ s}^{-1}$). However, hierarchical HZSM-5 samples prepared by the seed silanization method present activities clearly above this value, reaching at best (sample HZSM-5 (PHAPTMS)) an activity seven times higher (1.07 s^{-1}). In addition, the activity increases with the amount of external surface area of the catalyst. These differences in activity are really remarkable taking into account that all the catalysts are hierarchical and/or nanocrystalline HZSM-5 and highlight the importance of the synthesis procedure. The origin of the low activity of HZSM-5 (LTC)-1 and HZSM-5 (LTC)-2 samples can be ascribed to their weaker acidity. The waste polyethylene is more difficult for being catalytically degraded so it requires, along with accessible surface area, strong acidity. In this regard, the hierarchical nanocrystalline HZSM-5 (APTMS), HZSM-5 (IBTES) and HZSM-5 (PHAPTMS) samples exhibit not only large external surface area but stronger acidity, this combination being especially suitable for the cracking of the waste polyethylene.

Table 2 summarizes the selectivity by groups obtained in the cracking of waste polyethylene at 360°C. Both the reference n-HZSM-5 and the low-temperature hierarchical HZSM-5 (LTC)-1 and HZSM-5 (LTC)-2 samples yielded mostly $C_1 - C_4$ hydrocarbons (70 – 93%). In this regard, the highest amount of $C_1 - C_4$ hydrocarbons was attained over the n-HZSM-5 (LTC)-1 sample (92.3%). Hierarchical HZSM-5 samples prepared by the seed silanization method provided the higher amounts of $C_5 - C_{12}$ hydrocarbons (30 – 40%). In addition, the selectivity towards the $C_{13} - C_{40}$ fraction is practically negligible over all the catalysts, confirming that an

end-chain cracking mechanism, typical of HZSM-5 zeolite, takes place during the waste polyethylene cracking. Figure 10 illustrates the selectivity by carbon atom number obtained in the catalytic cracking of waste polyethylene over HZSM-5 (PHAPTMS) and HZSM-5 (LTC)-2 samples. A maximum is observed at C₃ for HZSM-5 (LTC)-2 (~ 45%) while for HZSM-5 (PHAPTMS) the maximum is placed at C₄ (32%). Hydrocarbons higher than C₅ are not detected in the cracking of waste polyethylene over HZSM-5 (LTC)-2. In contrast, over HZSM-5 (PHAPTMS) a meaningful content of C₅ – C₁₂ hydrocarbons can be observed in the product. The gaseous products are of remarkable interest considering they are chiefly made up of olefins, which constitute potential feedstocks for petrochemistry. Likewise, another advantage of the hierarchical nanocrystalline ZSM-5 samples, coming from their enhanced textural properties, is their easier regeneration, due to the better removal of the coke deposited located over the external surface and inside the mesopores [28]. Consequently, it can be concluded that hierarchical HZSM-5 samples prepared by the seed silanization method are promising catalysts for the catalytic cracking of waste polyethylene due to their suitable combination of textural and acid properties.

4. CONCLUSIONS

Hierarchical nanocrystalline HZSM-5 zeolite samples were tested in the cracking of pure LDPE and HDPE at 340°C, showing higher activity than the reference nanocrystalline n-HZSM-5 (external surface of 78 m² g⁻¹), due to their larger values of external surface area. For LDPE and HDPE, activity values reached at best 1.2 and 0.7 s⁻¹ over hierarchical nanocrystalline HZSM-5 (PHAPTMS) and HZSM-5 (APTMS) samples, respectively, six times higher than the value corresponding to the reference n-HZSM-5 sample (0.2 and 0.12 s⁻¹, respectively).

Likewise, hierarchical HZSM-5 samples prepared by the seed silanization method showed higher performance than the hierarchical nanocrystalline HZSM-5 materials of similar

external surface area prepared by the low temperature method due to their larger acidity. The calculated activity values were higher with LDPE than with HDPE, due to the presence of certain degree of branching in LDPE. In addition, far larger activities were observed in the cracking at 360°C of a waste polyethylene, roughly formed by 85% HDPE and 15% LDPE, over the hierarchical nanocrystalline HZSM-5 prepared by the seed silanization method.

Regarding selectivity data, the major products were C₁ – C₄ hydrocarbons (30 – 70%), followed by C₅ – C₁₂ hydrocarbons (20 – 60%), their relative proportion depending on the polyolefin and the employed catalyst. The amount of C₁₃ – C₄₀ hydrocarbons was practically negligible (< 1%) due to the high acid strength of this zeolite which promotes an end-chain cracking mechanism. The main hydrocarbon fraction was C₄ for both LDPE and HDPE, a minor peak being appreciated at C₇ – C₉. For HDPE and LDPE, olefins were the major components in both gaseous and liquid fractions, which are compounds of high interest for being used as raw chemicals rather than as fuels.

In summary, hierarchical HZSM-5 samples prepared by the seed silanization method can be viewed as promising catalysts for waste polyethylene cracking as they possess a right combination of accessibility and acid strength.

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Table 1. Physicochemical properties of the calcined HZSM-5 catalysts.

Samples	(Si/Al) _{zeolite}	S _{BET} (m ² g ⁻¹)	S _{EXT} (m ² g ⁻¹) ^a	T _{max} (°C) ^b	Acidity (meq NH ₃ g ⁻¹) ^b	Octahedral Al (Al ^{VI} , %) ^c
n- HZSM-5	32	459	78	354	0.480	3.0
HZSM-5 (APTMS)	51	489	166	346	0.300	8.8
HZSM-5 (IBTES)	65	518	203	334	0.258	12.0
HZSM-5 (PHAPTMS)	58	573	225	330	0.288	11.2
HZSM-5 (LTC)-1	47	513	171	312	0.210	7.8
HZSM-5 (LTC)-2	41	501	242	305	0.262	8.0

^aCalculated by the t-plot method

^bDetermined from ammonia TPD measurements.

^cDetermined from ²⁷Al MAS NMR spectra

Table 2. Conversion and selectivity data obtained in the cracking of LDPE, HDPE and waste polyethylene over different HZSM-5 catalysts.

LDPE (340°C)						
Catalyst	t (min)^a	P/C^b	Conversion (%)	C₁ – C₄	C₅ – C₁₂	C₁₃ – C₄₀
n-HZSM-5	180	100	31.6	76.0	24.0	0
HZSM-5 (LTC)-1	120	100	24.1	58.9	40.3	0.8
HZSM-5 (LTC)-2	180	100	79.7	62.6	36.5	0.9
HZSM-5 (APTMS)	120	100	34.1	66.2	33.8	0
HZSM-5 (IBTES)	120	50	78.2	36.7	62.1	1.2
HZSM-5 (PHAPTMS)	120	100	65.3	48.7	50.9	0.4
HDPE (340°C)						
n-HZSM-5	180	100	18.8	73.5	26.5	0
HZSM-5 (LTC)-1	120	100	15.0	82.0	18.0	0
HZSM-5 (LTC)-2	180	100	48.6	71.6	28.4	0
HZSM-5 (APTMS)	120	100	43.1	31.3	67.2	1.5
HZSM-5 (IBTES)	120	100	22.6	55.7	37.3	7.0
HZSM-5 (PHAPTMS)	180	100	41.0	76.6	23.3	0.1
Waste polyethylene (360°C)						
n-HZSM-5	120	100	16.7	71.4	28.2	0.4
HZSM-5 (LTC)-1	120	100	8.1	92.3	7.7	0
HZSM-5 (LTC)-2	120	100	11.4	81.3	18.7	0
HZSM-5 (APTMS)	120	100	47.9	66.8	33.2	0
HZSM-5 (IBTES)	120	100	47.7	65.6	34.3	0.1
HZSM-5 (PHAPTMS)	120	100	60.2	57.4	42.4	0.2

^aReaction time; ^bPlastic / catalyst mass ratio

Table 3. Metal contents of pure and waste plastics.

Metal	Pure HDPE (wt%)	Waste polyethylene (wt%)
Al	0.002	0.015
Ca	0.001	0.070
Cr	0.004	0.003
Cu	0.000	0.162
Fe	0.000	0.003
Mg	0.000	0.003
Na	0.001	0.013
Pb	0.000	0.009
Ti	0.000	0.151
Zn	0.021	0.006

FIGURE CAPTIONS

Figure 1. XRD patterns of calcined hierarchical nanocrystalline HZSM-5 samples.

Figure 2. TEM micrographs of the hierarchical nanocrystalline HZSM-5 (PHAPTMS).

Figure 3. ^{27}Al MAS NMR spectra of the calcined hierarchical nanocrystalline HZSM-5 (PHAPTMS) and n-HZSM-5 samples.

Figure 4. Activity values obtained in the LDPE cracking at 340°C over different hierarchical nanocrystalline HZSM-5 samples (P/C = 100).

Figure 5. Activity values obtained in the HDPE cracking at 340°C over different hierarchical nanocrystalline HZSM-5 samples (P/C = 100).

Figure 6. Selectivity per atom carbon number obtained in the catalytic cracking of LDPE and HDPE over hierarchical HZSM-5 (PHAPTMS) at 340°C (P/C = 100).

Figure 7. PIONA analyses of the C₆ – C₁₂ fraction obtained in the cracking of LDPE and HDPE over HZSM-5 (PHAPTMS) at 340°C.

Figure 8. DSC analyses of virgin and waste polyethylenes.

Figure 9. Activity values obtained in the waste polyethylene cracking at 360°C over hierarchical nanocrystalline HZSM-5 samples (P/C = 100).

Figure 10. Selectivity per atom carbon number obtained in the cracking of waste polyethylene at 360°C over HZSM-5 (LTC)-2 and HZSM-5 (PHAPTMS) catalysts.

FIGURE 1

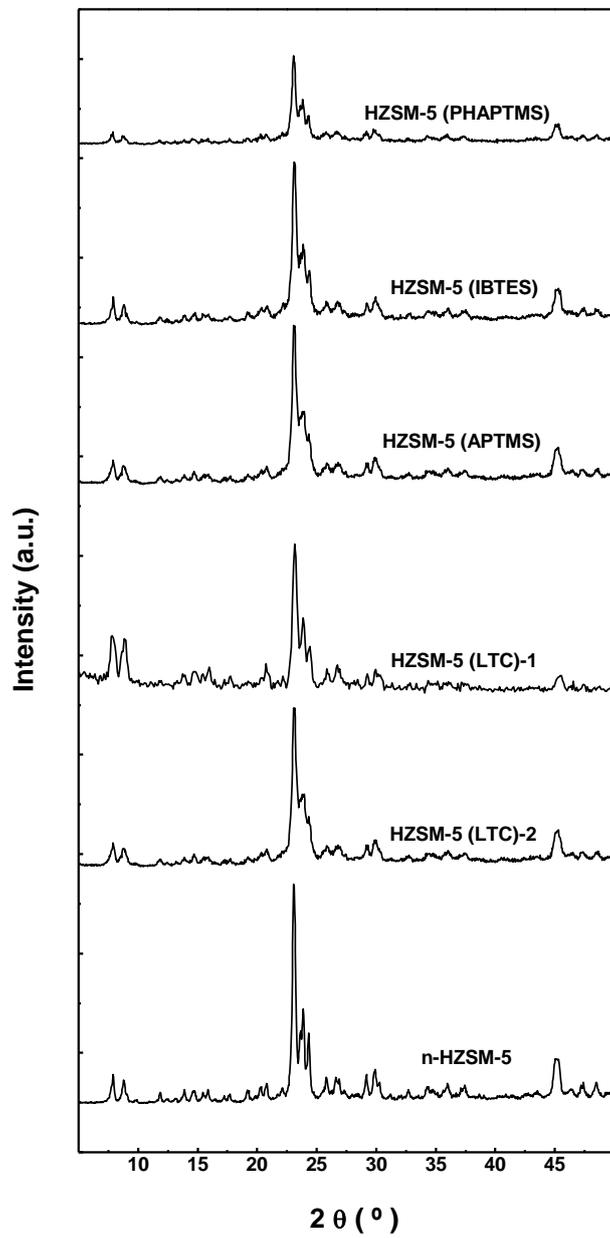


FIGURE 2

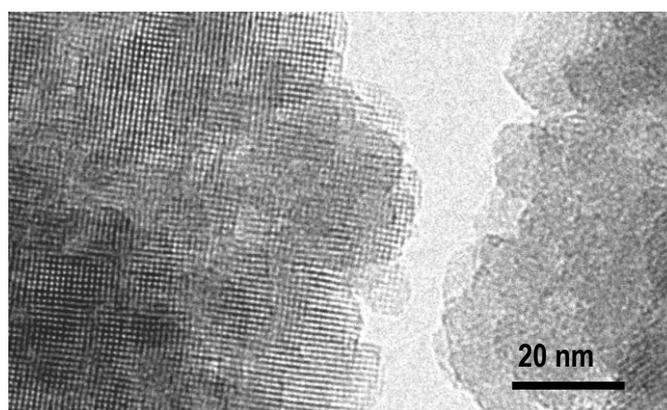
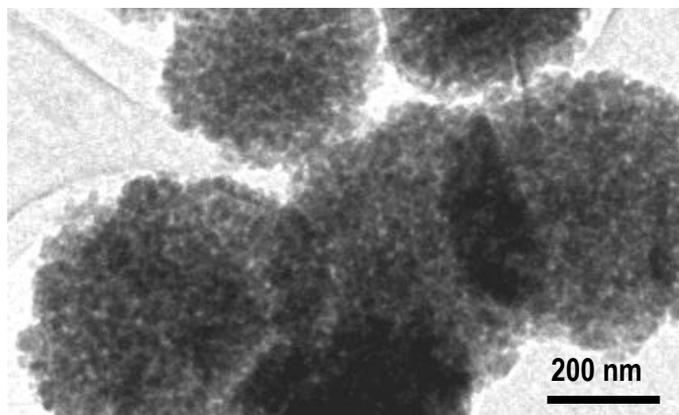


FIGURE 3

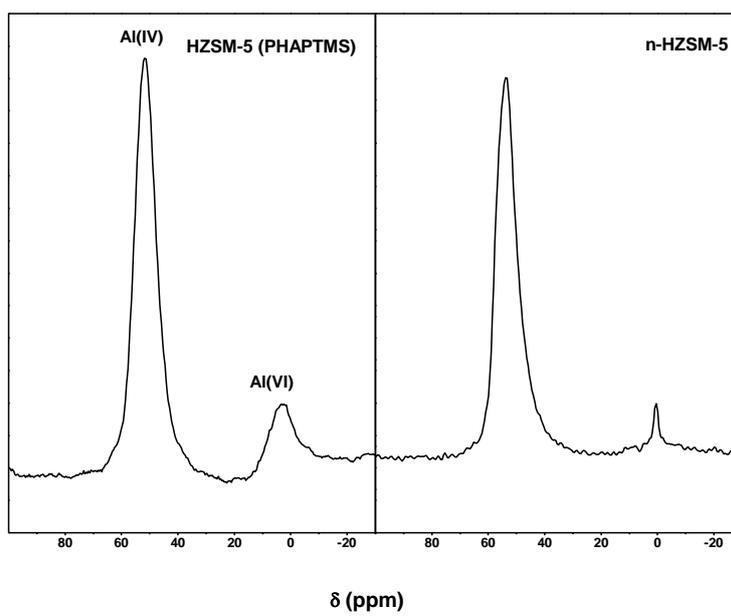


FIGURE 4

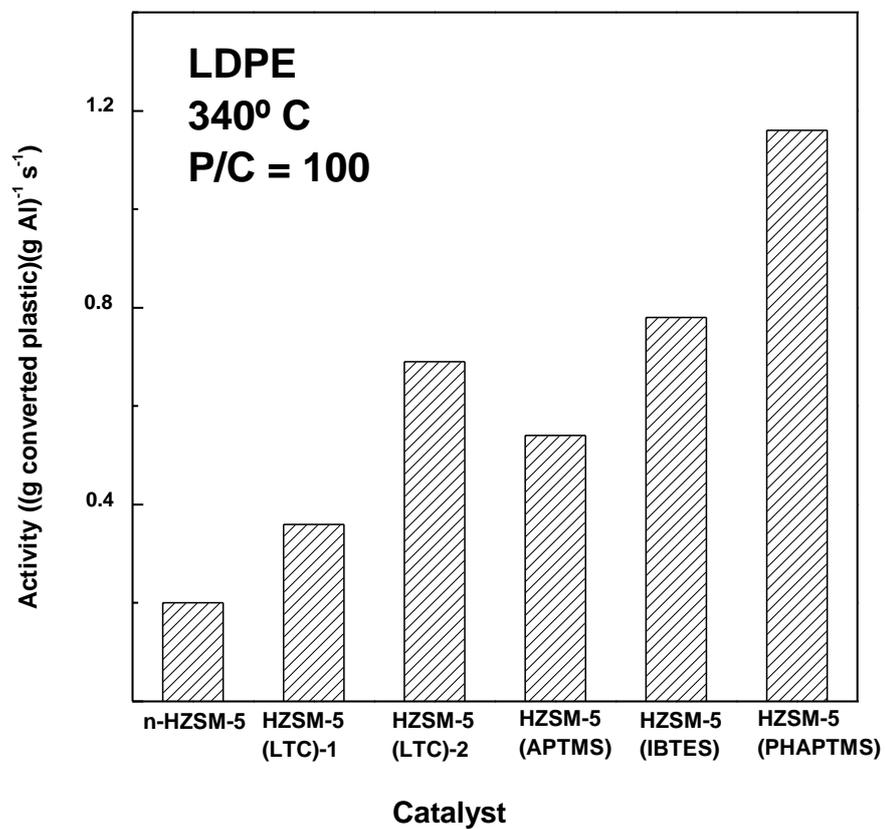


FIGURE 5

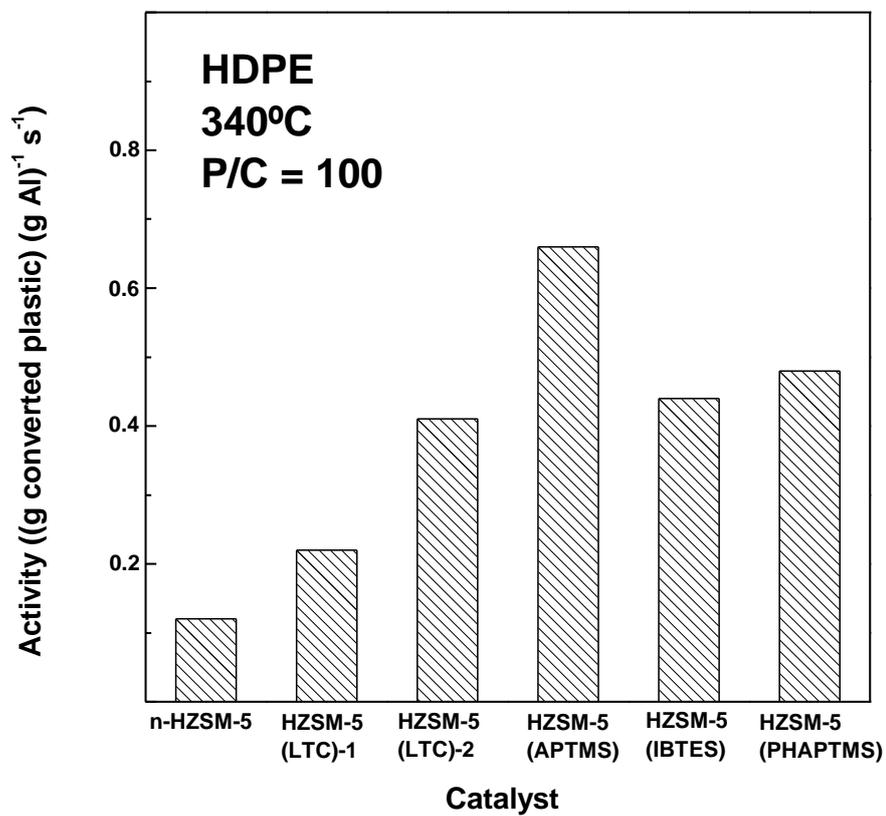


FIGURE 6

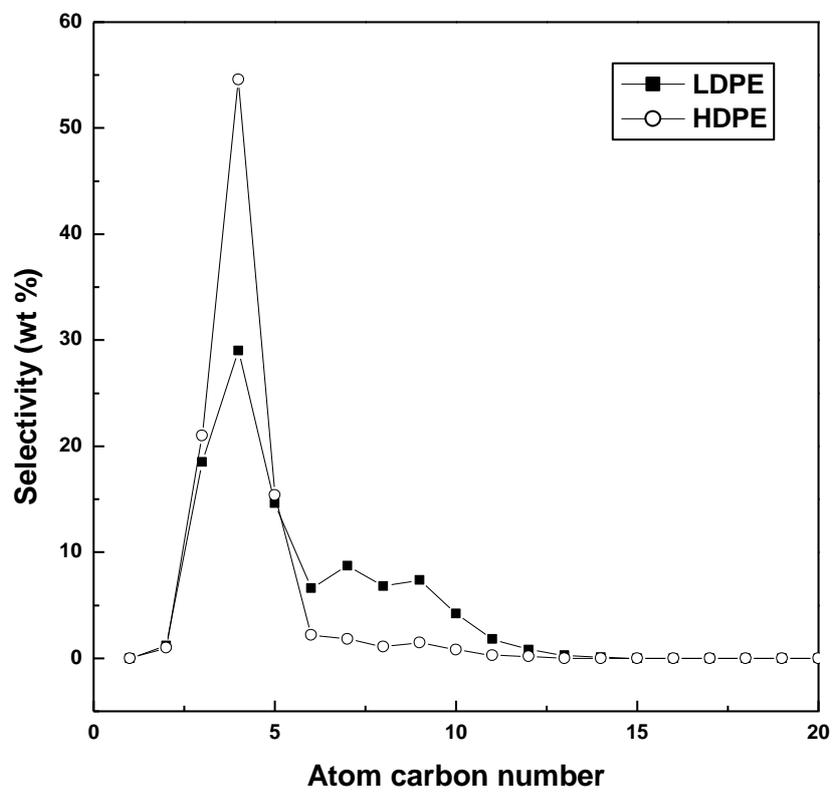


FIGURE 7

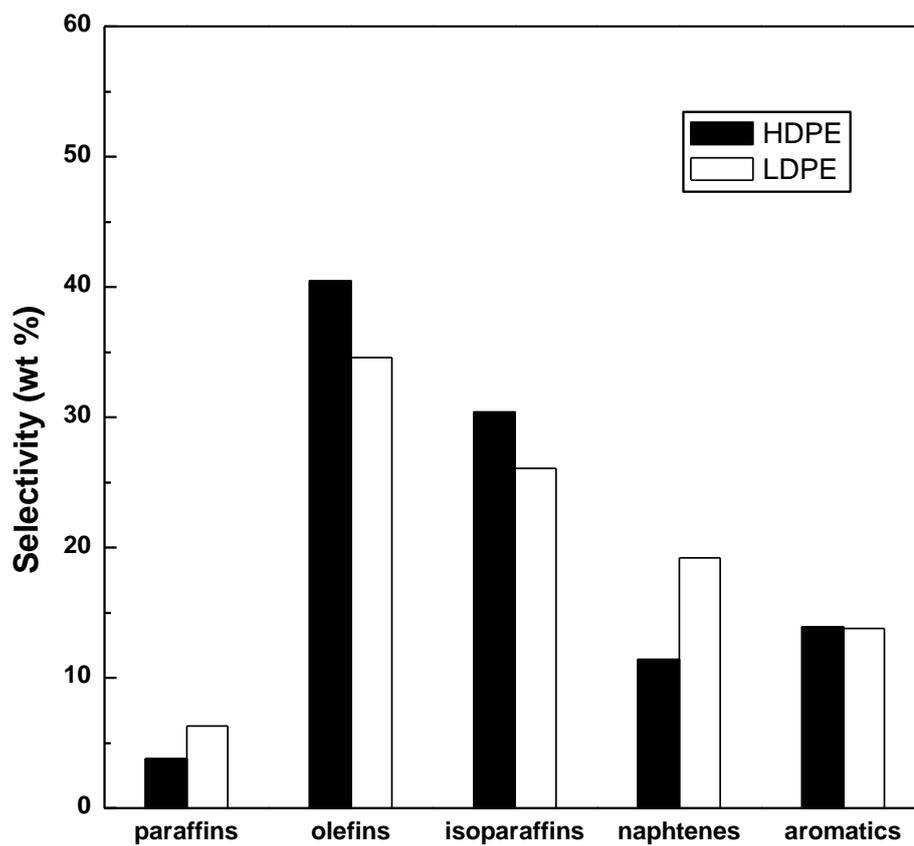


FIGURE 8

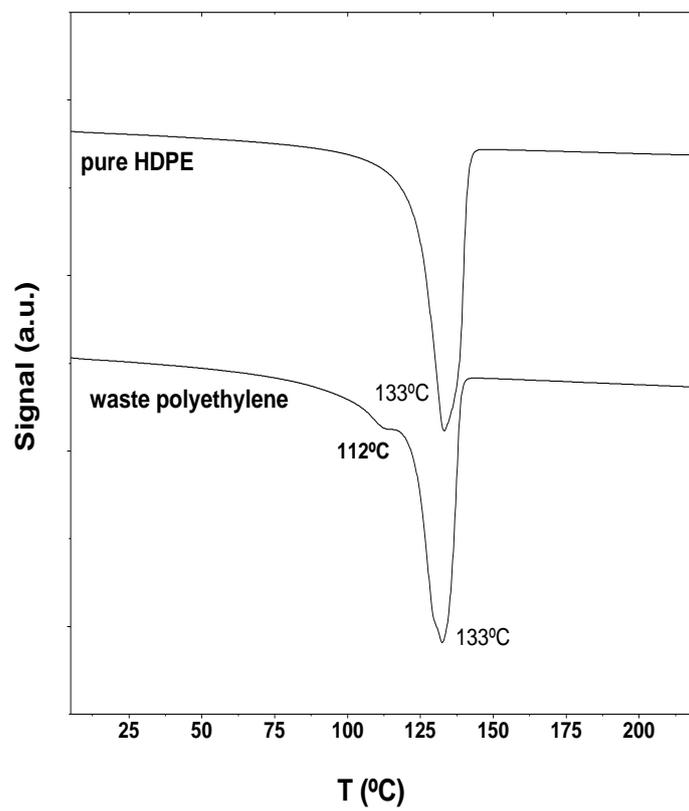


FIGURE 9

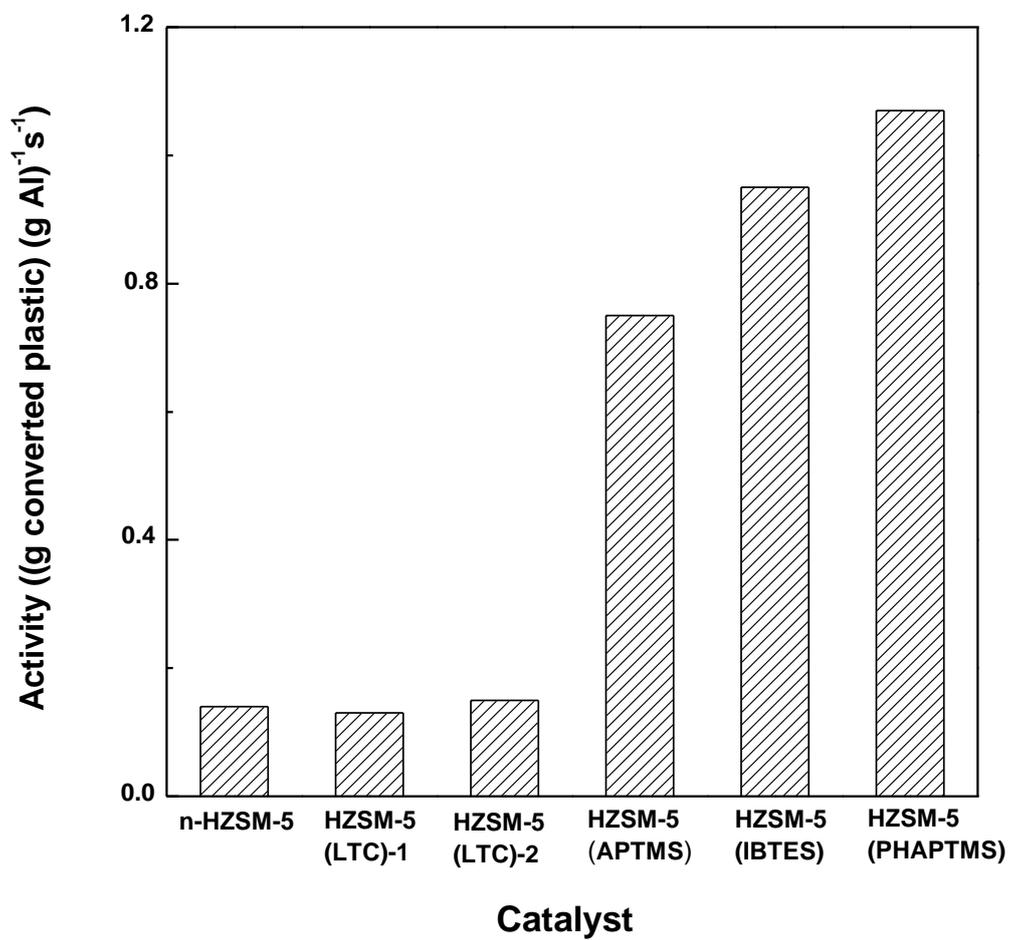


FIGURE 10

