

Catalytic cracking of polyethylene over zeolite mordenite with enhanced textural properties

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Abstract

Catalytic cracking of low density polyethylene (LDPE) has been investigated using different samples of mordenite zeolite as catalysts. In order to obtain materials with different textural properties, a new synthesis method based on the functionalization of the zeolite seeds with an organosilane was employed. Mordenite samples with BET and external surface areas in the range 385-485 m²/g and 9-57 m²/g respectively, were prepared. LDPE catalytic cracking reactions were performed at 420 °C for 2h in a batch reactor provided with a screw stirrer under a continuous nitrogen flow. Thermal cracking of LDPE leads to plastic conversion lower than 30%, while values of 40% are reached when traditional mordenite is used as catalyst. In contrast, when mordenite samples with enhanced textural properties were employed, a plastic conversion of 60% is attained, both gas (C₁-C₅) and gasoline (C₆-C₁₂) fractions being obtained as main products. On the contrary, gasoline fraction is not observed and a heavier hydrocarbon fraction in the range C₁₃-C₃₅ is detected when thermal cracking or even catalytic cracking over traditional mordenite samples are carried out. The formation of lighter hydrocarbon products (C₆-C₁₂) over mordenite samples with enhanced textural properties is assigned to the higher activity and accessibility of their acid sites, which promotes both end-chain and random scission cracking reactions of the polymer molecules.

Keywords: catalytic cracking; feedstock recycling; zeolites; mordenite; polyolefins.

1. Introduction

The worldwide polymer production has continuously grown in the last decades. In Western Europe the per capita consumption of plastics increased from 40 kg/inh-year in 1980, to 100 kg/inh-year in 2006, which implies an average growth higher than 3% per year [1]. The amount of post-use plastic wastes generated has increased in parallel to the growth of polymer production and consumption. Plastics wastes often ends-up in landfill, which implies the progressive depletion of the available space. Moreover, a used polymer is still a valuable raw material [2]. Energy recovery and mechanical or feedstock recycling are useful options for the management of plastic wastes. Every choice possesses advantages and disadvantages, and the use of a mix of all recovery methods may be necessary in order to divert the disposal of used polymers from land-filling [3].

Due to the high calorific value of polymeric wastes, incineration with energy recovery is an attractive strategy widely applied in some countries such as Switzerland and Denmark. Mechanical recycling of used thermoplastics allows important amounts of these plastic materials to be reintroduced in the consumption cycle. However, the potential growth of this technology is limited by the low quality of the goods made of mechanically recycled plastics. On the other hand, feedstock recycling transforms the plastic wastes into valuable chemicals or fuels [4]. Although currently being the option employed in the least extent, feedstock recycling is an area of increasing interest that could absorb a large amount of waste plastics [5].

Among the number of alternatives considered as feedstock recycling, catalytic cracking over different solid catalysts has attracted special attention in the last years. A variety of zeolites, fresh and spent FCC catalysts, aluminas, silica-alumina, aluminium pillared clays, mesostructured catalysts, hybrid zeolitic-mesoporous materials and

sulphated zirconia have been tested [6-14]. Particularly, zeolites have demonstrated to be efficient catalysts in the degradation of polyolefins into products with high commercial value [15-17]. Depending mostly on the acid strength of the catalyst, cracking proceeds mainly by either random (weak or medium acidity) or end-chain scission (strong acidity) giving rise to waxes and middle distillates (gasoil, gasoline) or light hydrocarbons (olefins), respectively. Subsequently, these primary cracking products may undergo oligomerization, cyclization or aromatization reactions [18,19]. The extent of these secondary processes depends on a variety of factors where the strength and nature of the acid sites and the textural properties of the catalysts play a key role. Additionally, it has been pointed out the importance of the proportion of external acid sites, fully accessible for the polymer macromolecules, on the catalyst activity [20]. A high share of external surface area promotes the cracking of polyolefins with remarkable activity even at low temperatures and high plastic/catalyst ratios ($P/C > 50$). Moreover, high values of external surface area results advantageous in the catalysts regeneration process, because the removal of coke from the external surface of the catalysts is easier and less aggressive than the combustion of the internal one [21].

Mordenite is an industrially important solid acid catalyst widely used in cracking, alkylation, hydroisomerization and hydrocracking processes. Mordenite is a one-dimensional large-pore zeolite, which implies that under typical reaction conditions reacting molecules may suffer significant diffusion constraints in regard to bi- or tri-dimensional zeolites. Moreover, deactivation by pore blockage may occur easily in this one-dimensional structure [22,23]. In order to overcome these problems dealumination techniques creating intracrystal mesopores, or nanometer-sized mordenite synthesis strategies, increasing external surface areas, have been applied [24-26]. Recently, our group has developed a novel synthesis method based in the crystallization of silanized

seeds in order to modify the textural properties in zeolites [27]. This new strategy has led to the synthesis of a variety of zeolites (ZSM-5, ZSM-11 and Beta) having enhanced both overall and external surface areas [28].

In this work, mordenite has been chosen to be investigated as a catalyst in the conversion of polyethylene. By means of the aforementioned new synthesis method [27], different mordenite samples with enhanced textural properties have been prepared, testing and comparing their activity in the catalytic cracking of low density polyethylene (LDPE) with a traditional mordenite.

2. Experimental

2.1. Catalysts

Mordenite samples used in this work were synthesized adapting a new synthesis strategy published elsewhere [27,28]. Zeolitic catalysts were prepared from gels with the following molar composition: $20 \cdot \text{SiO}_2 : \text{Al}_2\text{O}_3 : 7.5 \cdot \text{Na}_2\text{O} : 900 \cdot \text{H}_2\text{O}$. Thereby, the required amounts of the silica source, Ludox AS-40 (Aldrich), sodium aluminate (Riedel-de Haën), sodium hydroxide (Panreac) and distilled water were properly mixed following a procedure previously described in the literature [25]. The final mixture was aged at room temperature for 20h. The solutions were then precrystallized in teflon-lined stainless-steel autoclaves under autogeneous pressure and static conditions at 170 °C for 1 day. Subsequently, the autoclaves were cooled down to room temperature and the mixture so obtained was functionalized by reaction with phenylaminopropyltrimethoxysilane (PHAPTMS; Aldrich) [27,28]. Different samples were prepared by adding the organosilane to the precrystallized solution in a proportion of 0-15 mol% with respect to the total silica content in the gel. The final crystallization was carried out in teflon-lined autoclaves under hydrothermal conditions at 170 °C for 7

days. The solid products obtained were finally separated by centrifugation, washed with distilled water, and dried overnight at 110 °C. At this point, a Na-form mordenite was obtained.

Thereafter, the sample was ion exchanged into the NH₄-form. According to the literature [29,30], ammonium nitrate was selected as exchange cation and a two-stage procedure was applied for the ion-exchange treatment. Finally, the zeolite was calcined in air at 550 °C for 5 hours in order to obtain the H-form mordenite and to remove the organosilane present in the samples prepared by means of organofunctionalization of the precrystallized solutions.

The crystallinity of the samples was checked by X-Ray diffraction (XRD) measurements collected in a Philips X'PERT MPD diffractometer using Cu K α radiation. Both, aluminum and sodium content of the synthesized samples were determined by means of atomic emission spectroscopy with induced coupled plasma (ICP-AES) collected in a Varian Vista AX instrument. In order to ascertain the acid properties of the catalysts, temperature-programmed desorption of ammonia (NH₃ TPD) measurements were carried out 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°C min⁻¹ up to 550°C, keeping constant this temperature for 30 min. The ammonia concentration in the effluent helium stream was monitored with a thermal conductivity detector (TCD). Nitrogen adsorption-desorption isotherms at 77 K were obtained in a Micromeritics ASAP 2010 apparatus equipped

with a vacuum turbo-molecular pump. Previously, the samples were outgassed at 300 °C under vacuum for 5 h. Surface areas were calculated by means of the BET equation. Micropore volume and external surface area of the catalysts were determined by application of the *t*-plot method. TEM images were obtained in a PHILIPS TECHNAI 20 electron microscope operating at 200 kV. The organic content of the samples was determined by elemental analysis using an Elementar Vario EL III analyzer equipped with a thermal conductivity detector, while TG measurements were obtained in a SDT 2960 Simultaneous DSC-TGA equipment.

2.2. *Plastic*

The plastic used in this work was pure low density polyethylene (LDPE) commercially produced by Repsol-YPF (Spain). The plastic was supplied in the form of pellets and was used as received.

2.3. *Catalytic cracking experiments*

Cracking reactions of LDPE were carried out in a stainless steel batch reactor provided with a screw stirrer [21]. In a typical experiment, a mixture of 7.5 g of plastic and 0.15 g of catalyst (P/C = 50) were loaded into the reactor, being purged with nitrogen at 45 mL·min⁻¹ for 10-15 minutes. This nitrogen flow was maintained until the end of the reaction in order to ensure an inert atmosphere and swept the volatile products from the reactor. Subsequently, the reactor was heated with a rate of 6 °C·min⁻¹ up to the reaction temperature, the experiments being carried out at 420 °C and atmospheric pressure for 2 hours. The volatile products leaving the reactor were separated as follows: liquids were condensed in an ice trap, while gases were collected in a gas-bag. The analysis of both gas and liquid fractions were carried out by gas

chromatography in a Varian CP-3800 GC using a 100 m length x 0.25 mm i.d. Chrompack CP SIL PIONA capillary column and FID detector. The chromatograms were interpreted using a Varian Detailed Hydrocarbon Analysis (DHA) *Star* software for product identification and quantification. In this way, only hydrocarbons having a C atom number lower than 15 could be detected. Thereby, in order to characterize heavier hydrocarbons in both the liquid and wax fractions, a Varian CP-3900 GC was employed provided with a 15 m length x 0.25 mm i.d. Factor Four VF-1ms capillary column and FID detector. Liquid and wax samples were injected after dilution in carbon disulphide (CS₂).

Conversions have been calculated taking into account only the products that leave the reaction system with the N₂ stream, the remaining residue inside the reactor being not considered as a product. Turnover frequency (TOF) was calculated as (grams of plastic converted) · (grams of aluminium in the catalyst)⁻¹ · (reaction time)⁻¹.

3. Results and Discussion

3.1. Catalysts characterization

XRD patterns of zeolite samples synthesized with one day of precrystallization time and different organosilane (PHAPTMS) content are shown in Figure 1. Samples are labelled as MOR (IZA three letters code for mordenite zeolite), followed by the PHAPTMS proportion (0, 8, or 15 mol%) added to the precrystallized solution in regard to the total initial silica content in the gel. All the samples exhibit XRD patterns with diffraction peaks coincident with the pure phase MOR structure. The high crystallinity of the samples is demonstrated by the absence of the broad bottom reflection characteristic of amorphous phases. A significant reduction in the intensity of the diffraction peaks when PHAPTMS is added during the synthesis is clearly observed.

According to the Scherrer law, this fact could be related to a decrease in the crystal size of the samples.

Figure 2 illustrates the N₂ adsorption-desorption isotherms of this series of samples synthesized with different proportion of PHAPTMS. The sample synthesized without PHAPTMS exhibit the typical isotherm of microporous materials. Only an important steep jump at very low relative pressures ($P/P_0 < 10^{-2}$) is observed, which corresponds to the N₂ adsorption in the mordenite micropore system. No significant adsorption is registered at neither medium, nor high relative pressures. Mordenite samples synthesized by organofunctionalization of the precrystallized solutions show N₂ isotherms with three different adsorption zones. Additionally to the adsorption at very low partial pressures, associated with the zeolitic micropore system, an enhancement of the N₂ adsorption occurs mainly at relative pressures between 0.1-0.2. This adsorption zone could be related with adsorption in additional micropores (supermicropores) of higher size than the zeolitic ones. Moreover, the N₂ adsorption extends at higher pressures and a slight continuous slope at medium relative pressures arises from the N₂ adsorption on the external surface of the zeolite particles. A steep jump is also observed at high relative pressures ($P/P_0 > 0.8$), describing a hysteresis cycle, which indicates the presence of interparticular porosity.

The textural properties of the catalysts are summarized in Table 1. The mordenite samples presents BET surface areas ranging from 384 to 485 m²/g. As a general trend an enhancement in the external, micropore and BET surface area is noticed when the proportion of organosilane added after the precrystallization stage increases. External surface area represents about 2% of the BET surface area in the sample synthesized without PHAPTMS, while it is about a 12% for MOR-15 zeolite, which is synthesized adding 15 mol% of organosilane.

Table 1 also includes the Si/Na and Si/Al ratios for the ion exchanged zeolites. All the samples were synthesized with close Si/Al atomic ratios (7-10). However, an enhancement in this ratio is appreciated in the materials synthesized when the amount of PHAPTMS added to the precrystallized solutions during the synthesis increases. Interestingly, MOR-15 sample (Si/Al = 10.2) possess a Si/Al ratio significantly higher than MOR-8 (Si/Al = 8.3). This fact implies that the number of Al atoms per gram of catalyst available in MOR-8 sample is a 21% higher than in MOR-15. On the other hand, it can be concluded that the ion exchange process has been carried out satisfactorily because of the high Si/Na atomic ratios attained for all the samples. Previously to the ion exchange, Si/Al ratios between 7 and 10, and Si/Na atomic ratios close to 5 were measured for all the zeolites.

Ammonia TPD spectra of the different ion-exchanged mordenite samples are depicted in Figure 3. Broad spectra, which seem to be the sum of several overlapped TPD peaks, are observed for all the H-form mordenites, indicating that desorption may proceed simultaneously from sites of different types. The component peak at lower temperatures (< 325 °C) is controversial and it has been ascribed to desorption of ammonia bound to weak acid Brönsted [31], or Lewis sites [32], or even to silanol groups [33]. More recently it has been reported that low temperature peaks may represent NH_3 desorption from $\text{NH}_4^+ \cdot n\text{-NH}_3$ associations [34,35]. On the other hand, the component peak at higher temperatures can be assigned to desorption from strong Brönsted and Lewis sites. Independently of the TPD peak assignation, the different ion-exchanged mordenite samples exhibit a similar desorption profile, indicating that they possess a similar acid nature.

TEM images of different mordenite samples prepared with and without addition of PHAPTMS are shown in Figure 4. All of them are constituted by micrometer-size

particles, although meaningful differences can be appreciated among them. Zeolites synthesized without PHAPTMS are formed by uniform crystals with sizes within the micrometer size, while in the samples prepared by organofunctionalization of precrystallized solutions the micrometer-size particles are really formed by agglomeration of a number of closely packed needle-like crystals of 50-200 nm in width. This is in agreement with the decrease in the intensity of the XRD diffraction peaks previously described for the organofunctionalized samples. Moreover, the enhancement in the textural properties could be also related with the decrease in the zeolite crystal sizes as it was reported elsewhere [36].

3.2. Plastic cracking experiments

Table 2 summarizes the results obtained in the cracking of LDPE over the different catalysts, as well as those corresponding to the thermal cracking experiment. Thermal cracking of LDPE leads to plastic conversion lower than 30%, while values of 40% are reached when a traditional mordenite sample (MOR-0) is used as catalysts. Conversion values increase to 57% by using the mordenite samples with enhanced textural properties (MOR-8 and MOR-15), which were synthesized by PHAPTMS functionalization of the precrystallized solution.

Similar conversion values are obtained with MOR-8 and MOR-15 samples, but they possess different Al contents. Accordingly, the comparison should be made in terms of turnover frequency (TOF). The TOF value attained over the improved mordenite samples (MOR-8, 0.064 s^{-1} ; MOR-15, 0.078 s^{-1}) was significantly higher than the value achieved on the reference zeolite (0.039 s^{-1}). The differences detected in the activity (TOF) of the catalysts can be related with their respective textural properties. Moreover, Figure 5 shows that TOF values achieved with the different samples

correlates well with their external surface area. The catalysts having higher external surface area present superior activity. High external surface area implies a higher proportion of external acid sites not limited by steric or diffusional problems, which explains the high activity obtained over the mordenite samples with enhanced textural properties. Moreover, a direct relationship has been previously observed between the activity in polyolefin cracking and the external surface area of other zeolitic structures [16,20]. In the case of the mordenite, an enhancement in the activity of the samples is also observed when their textural properties are improved.

The product yields obtained in the cracking experiments are also shown in Table 2. A higher amount of gas (C_1-C_5), gasoline (C_6-C_{12}) and diesel ($C_{13}-C_{35}$) hydrocarbon fraction were obtained when the catalytic cracking reactions were carried out over mordenite catalysts in regard to the thermal cracking. A significant enhancement (from 6.6% to 14.1%) in the yield of the $C_{13}-C_{35}$ fraction was detected, when comparing the catalytic reaction over the reference mordenite (MOR-0) with the thermal cracking. The catalytic process over the zeolite promotes the scission of the polymeric chains to proceed at a larger extent, and a higher amount of hydrocarbons with chains lower than 35 carbon atoms were swept by the nitrogen flow from the reactor.

When catalytic cracking was performed over zeolites with enhanced textural properties (MOR-8 and MOR-15) the highest increase was observed over the C_6-C_{12} fraction. Yields in the gasoline fraction (C_6-C_{12}) with values around 21% were achieved when cracking proceeds over these samples, while only a slight 0.7% was attained when thermal cracking was carried out. The differences detected in the product yields of the catalysts can be related with their respective textural properties. Enhanced textural properties zeolite samples, with a high proportion of external surface area, possess an elevated number of acid sites accessible to the voluminous polymeric chains. This fact

favours long-chain polymer scission reactions, and a highly cracked product with shorter hydrocarbon chains is obtained.

Figure 6 compares the product distributions per carbon atom number obtained in the catalytic cracking of LDPE over the different mordenite samples. The product distribution obtained in the thermal cracking is also included with comparative purposes. A major maximum is observed for all the experiments corresponding to the gaseous C₄ fraction, being this maximum higher than 26% in the absence of catalyst. When zeolites with enhanced external surface area are employed, total gas fraction (C₁-C₅) selectivity diminishes a 30% in regard to the thermal process. At the same time, a significant enhancement in the light liquid fraction (C₆-C₁₂) with a second maximum between C₇ and C₁₀, is detected. Moreover, a high similarity in the atom carbon number distributions of both zeolites with enhanced textural properties can be observed. In the absence of catalyst, the overall gasoline fraction (C₆-C₁₂) selectivity is lower than 3%, while values nearly 40% are attained in the catalytic reactions over zeolites with enhanced textural properties. In the case of the traditional mordenite, having low external surface area, a large proportion of heavy hydrocarbons in the region C₁₃-C₃₅ is formed, a maximum for the C₁₆ fraction being observed with a value around 6%. In fact, the atom carbon number distribution attained in the cracking reaction over the conventional mordenite sample is relatively similar to that of the thermal cracking. However, the maximum corresponding to the C₁₆ fraction is lower (3%) and less clearly perceived in the latter case, and a broader distribution with a maximum between the C₁₆ and C₁₈ fractions is observed. Summarizing, both thermal and catalytic cracking over the zeolite sample with low external surface area, allows both C₁-C₅ and C₁₃-C₃₅ fractions to be formed as main products, while C₁-C₅ and C₆-C₁₂ are the main fractions

when catalytic reactions are carried out over the mordenite sample with enhanced textural properties.

PIONA GC analyses were used to determine the proportion of paraffins, olefins, isoparaffins, naphthenes and aromatics in the products generated from the thermal and catalytic conversion of LDPE at 420 °C. Figures 7-A, and B, illustrate the composition by hydrocarbon types of the gas (C₁-C₅), and gasoline (C₆-C₁₂) fractions, respectively.

Figure 7-A shows that the gaseous products (C₁-C₅) obtained in both thermal and catalytic cracking of LDPE were mainly olefins (80%). Propylene, 1-butene and isobutene were the main products (45-50%), which may be interesting feedstocks in the petrochemical industry. Paraffins and isoparaffins are also present in the gas fraction, although representing around 10% each only.

According to Figure 7-B the composition of the slight amount of C₆-C₁₂ hydrocarbons obtained in LDPE thermal cracking are mainly paraffins (89%). The 2.3% yield of this fraction achieved over the reference mordenite (MOR-0) consisted mainly of aromatics (41%), while paraffins, olefins, isoparaffins and naphthenes were also present in a lesser proportion. The meaningful amount of C₆-C₁₂ hydrocarbons obtained in the catalytic experiments over mordenites with enhanced textural properties was composed by a variety of paraffins, olefins, naphthenes and aromatics. In this case, some significant differences are observed between MOR-8 and MOR-15.

Reactions over MOR-8 generated mainly olefins (45%) and n-paraffins (31%), as well as a lower proportion of aromatics (11%), isoparaffins (8%) and naphthenes (5%). When catalytic cracking was carried out over MOR-15, a decrease in the proportion of olefins (28%) and paraffins (22%) was noted, increasing at the same time the percentage of aromatics (25%), isoparaffins (15%) and naphthenes (10%). These results suggest that the primary cracking products, generated by both random and end-

chain scission, suffer subsequent secondary cyclization, oligomerization or aromatization reactions [18]. Although the enhancement in the textural properties of MOR-15 with regard to MOR-8 is not enough to generate differences in the selectivity by carbon atom number, secondary reactions are favoured in a slightly large extent when the zeolite with higher both overall and external surface area (MOR-15) is employed. Secondary reactions are promoted by the zeolitic acid sites, which may be located on the external surface or inside the pore system of mordenite. In any of both cases, higher overall and external surface area should favour secondary reactions, due to the existence of a higher proportion of easily accessible acid sites, and less diffusional constraints.

Figure 7-C illustrates the distribution between n-paraffins, α -olefins, and other compounds (isoparaffins, linear and non-linear olefins, naphthenes and aromatics) of the heavier fraction. Both, thermal and catalytic cracking performed over the zeolite with low external surface area generated a high amount of unreacted n-paraffins which are the main hydrocarbons present in the C₁₃-C₂₄ fraction, reaching percentages close to 80%. However, in the diesel fraction produced over mordenites with higher external surface area, the fraction labelled as others is the predominant (> 50%), being formed by a mixture of non-linear paraffins and olefins, as well as cyclic and aromatic compounds. At the same time, a proportion of n-paraffins lower than 30%, and a percentage of α -olefins higher than 10% was attained. This behaviour is related again to the higher proportion of external acid sites on the modified zeolites, which favours secondary reactions to take place at a large extent from the primary cracking products.

4. Conclusions

The results obtained in the present work point out the importance of the textural properties of the mordenite zeolite for its use in the catalytic cracking of polyolefins (LDPE). Mordenite samples with different textural properties and external surface areas have been synthesized by means of a novel method based on the silanization of precrystallized zeolite nuclei. The enhancement in the textural properties of zeolites has been proven to be advantageous in reactions where voluminous molecules are involved. The highest activities are obtained for the zeolites possessing enhanced textural properties, because they present an elevated proportion of external acid sites fully accessible to the voluminous polymeric chains.

The use of mordenite samples with enhanced textural properties favour the generation of liquid hydrocarbons with boiling points in the range of the gasoline fraction (C₆-C₁₂). In this way, lighter hydrocarbons are obtained when cracking reactions take place over the modified mordenite samples with respect to the thermal process or the catalytic cracking over a traditional mordenite. These results suggest that primary cracking products produced by both end-chain and random scission reactions may undergo subsequent cracking reactions over the high proportion of easily accessible acid sites on the mordenite samples with higher values of external surface area. Moreover, secondary cyclization, oligomerization or aromatization reactions are promoted by the zeolitic acid sites.

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Table 1. Composition and textural properties of the mordenite samples.

Sample	Si /Al ^a	Si/Na ^a	PHAPTMS (mol%) ^b	S _{BET} (m ² /g)	S _{EXT} (m ² /g)	S _{MIC} (m ² /g)
MOR-0	7.8	1103	0	384	9	375
MOR-8	8.3	780	9	419	31	388
MOR-15	10.2	680	22	485	57	428

^a from ICP-AES; ^b from CHN elemental analyses

Table 2. Cracking of LDPE over different mordenite catalysts ($T = 420^{\circ}\text{C}$; g LDPE/g catalyst = 50; time = 2 h).

Sample	Conversion (wt%)	Product yields (wt%)			TOF (s^{-1})
		$\text{C}_1 - \text{C}_5$	$\text{C}_6 - \text{C}_{12}$	$\text{C}_{13} - \text{C}_{35}$	
No catalyst	27.9	20.6	0.7	6.6	-
MOR-0	38.5	22.1	2.3	14.1	0.039
MOR-8	56.6	25.6	21.2	9.8	0.064
MOR-15	57.1	25.8	21.0	10.3	0.078

Figure captions:

Figure 1: XRD patterns of as-synthesized mordenite materials with different PHAPTMS silanization agent contents.

Figure 2: N₂ adsorption-desorption isotherms at 77 K of ion exchanged mordenite materials synthesized from different PHAPTMS silanization agent contents.

Figure 3: NH₃ TPD spectra of ion exchanged mordenite samples.

Figure 4: TEM micrographs of ion exchanged mordenite samples; a), b) MOR-0 material, and c), d) MOR-15 material.

Figure 5: Comparison of activity (TOF) and external surface area of the different mordenite catalysts.

Figure 6: Selectivity by carbon atom number obtained in the LDPE cracking reactions.

Figure 7: Composition by hydrocarbon type of: (A) C₁-C₅, (B) C₆-C₁₂, and (C) C₁₃-C₂₄ fractions, respectively, obtained in the LDPE cracking reactions.

Figures:

Figure 1

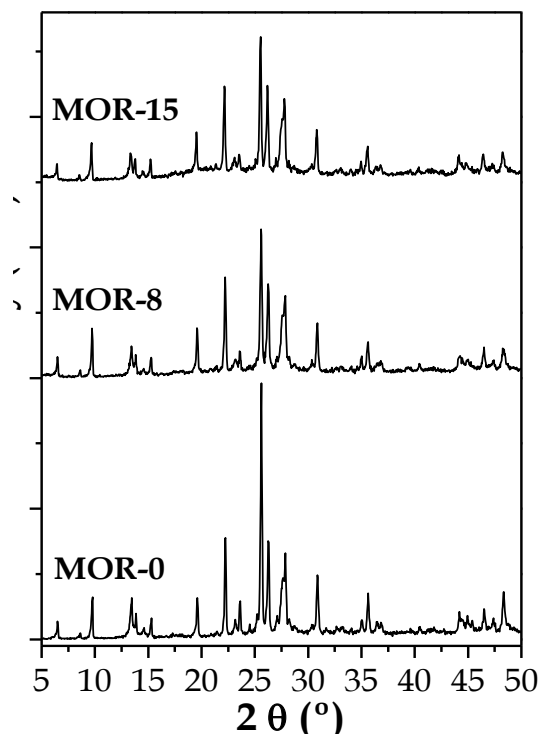


Figure 2

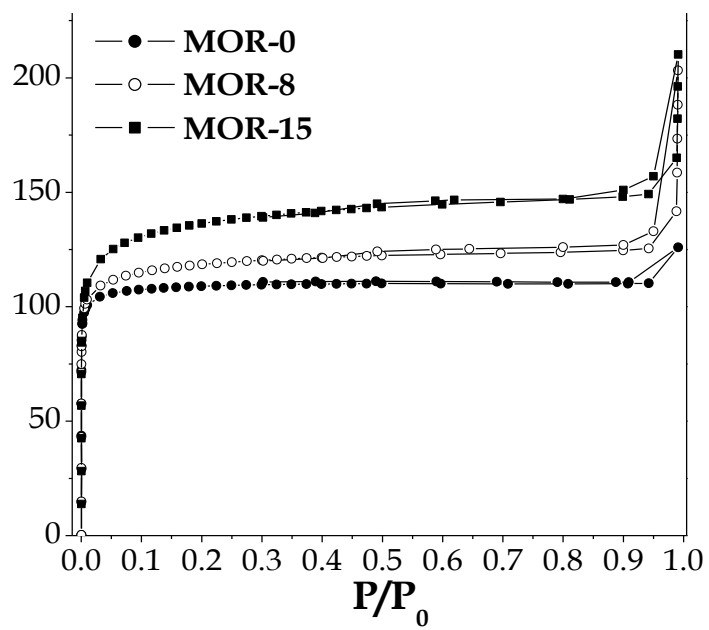


Figure 3

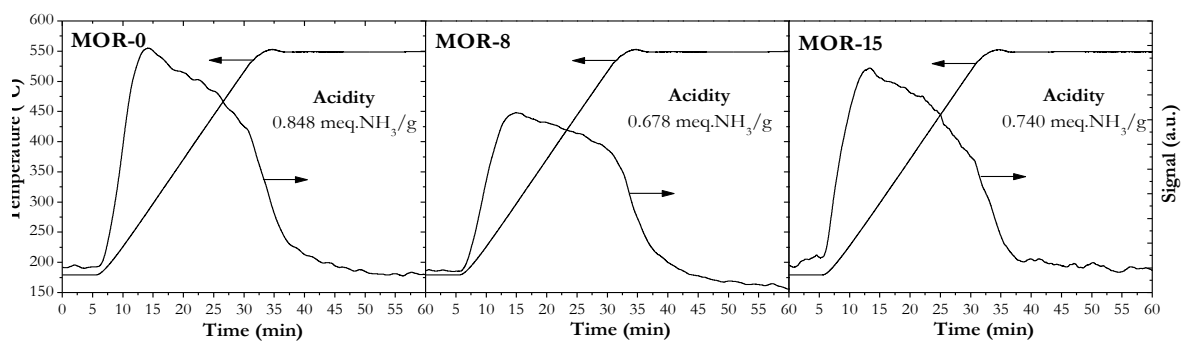


Figure 4

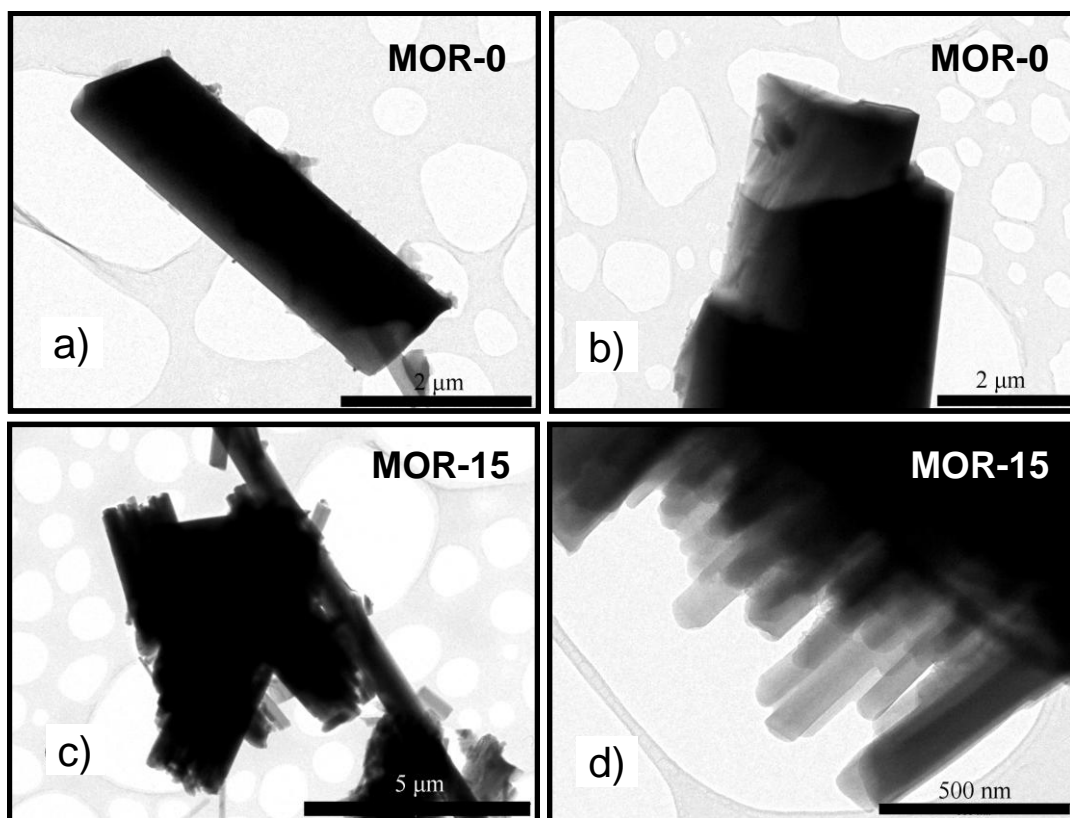


Figure 5

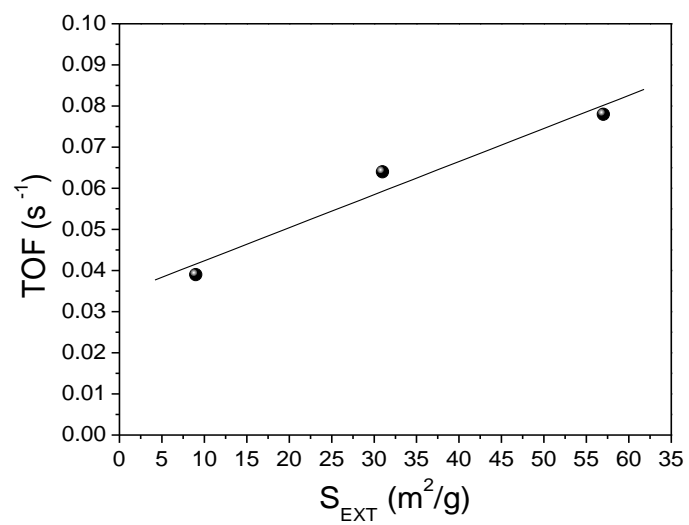


Figure 6

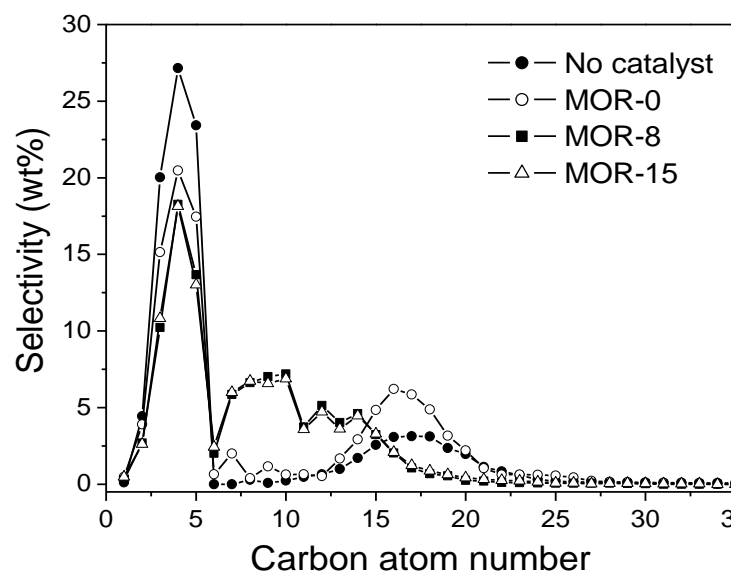


Figure 7

