Catalytic degradation of high density polyethylene over microporous and mesoporous materials

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Abstract

High-density polyethylene (HDPE) was converted to a mixed of lower and higher hydrocarbons over micro (ZSM-11 zeolite with MEL structure) and mesoporous (MCM-41) modified materials. The main liquid hydrocarbons (LHC) were: benzene, toluene, xylenes (BTX), using Zn-, Mo-, and H-containing MEL-zeolites as catalysts. The Zn-zeolite exhibited the highest levels of LHC (>57 wt%) with BTX selectivity of 47 wt%. H-zeolite gave a higher fraction of gaseous hydrocarbons (C1–C4) than Mo- and Zn-zeolites. Zn–MCM-41 produced mainly C5–C16 products. LPG (C3–C4) levels were interesting for all the samples. Thermo gravimetric analyses studies of mixtures catalyst/polymer, have been used to investigate the performance of different catalysts on degradation reactions of the polymer. The catalytic transformation of the polyolefin occurs at lower temperature with respect to thermodecomposition of the pure HDPE (500 °C). A one-pass reactor in the temperature range of 410–500 °C and atmospheric pressure was employed. We observed the complete conversion of HDPE, in the range of temperatures studied (410–500 °C). The synthesized and modified samples after cation incorporation were characterized by TG–DSC, XRD, TPD-FID, FTIR and surface area by BET, in order to verify and to confirm the crystallinity (for microporous materials) and regularity (for mesoporous materials) of the structures, stability and the type of active sites. The reactant was characterized by FTIR, XRD and TG–DSC. Reaction products were analyzed by gas chromatography. By means of development of a competitive catalytic system, we determine the feasibility of the process of degradation of HDPE remainders towards the synthesis of gaseous and liquid hydrocarbons.
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Keywords: HDPE; Catalytic degradation; ZSM-11; MCM-41; Products composition

1. Introduction

In view of their versatility and relatively low cost, the consumption of plastic materials has been growing steadily. Plastic is a very useful commodity consumed in many aspects of human life in large volumes, although the disposal of waste plastics constitutes a severe environmental problem mainly due to their chemical inertness and low biodegradability. Nowadays, governments and environmental foundations have to take into consideration, more and more, the generation of large amounts of waste plastics as they cause serious pollution. Most waste plastics are disposed of by landfill or incineration resulting in the loss of their energy content. During the past few years recycling of plastics has been recognized as a necessity. Polymer recycling methods can be grouped as follows:

(1) Mechanical reprocessing of the used plastics (into a second-generation product) form new products. This method is not generally applicable, because of the low quality of the new products.

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(2) Plastics incineration to recover energy. This method only shifts a solid waste problem to one of air pollution.

(3) Thermal and/or catalytic degradation of plastic waste to gas and liquid products, which can be utilized as fuel oils or advanced chemicals.

Thermal degradation depends, in principle, on the type of the plastic to be recycled. Condensation polymers such as PET and nylon can be broken down into their monomer units by several depolymerization processes [1,2]. On the other hand, vinyl polymers such as polyethylene and polypropylene are very difficult to decompose to monomers because of random scission of the carbon–carbon bonds of the polymer chains, producing by thermal degradation a broad product range requiring high operating temperatures, typically more than 500 °C and even up to 900 °C [3,4]. Further processing requires for their quality to be upgraded.

Catalytic degradation, on the other hand, yields a much narrower product distribution of carbon atom number and reducing the reaction temperature. Such a mixture of hydrocarbons can be used as a fuel. There have been a number of publications reporting the use of molecular sieves and amorphous silica–alumina catalysts for the cracking of polymers into a range of hydrocarbons. The molecular sieve-based catalysts as mordenite, SAPO, faujasite, REY and ZSM-5, give small aliphatic compounds and aromatics depending on the catalyst structure and temperature [5–8].

There have been many reports on the thermal and catalytic degradation of high-density polyethylene (HDPE) as it is one of the main polymers in municipal solid wastes [9–11]. We have showed an important breakthrough in the difficult problem of reusing polyolefinic (low density polyethylene (LDPE)) waste chemically by using H, Ga and Zn-containing MEL and BEA zeolites as catalysts, converting selectively the feed to aromatic hydrocarbons [12]. In this work, we studied the thermal-catalytic transformation of HDPE over Zn-, Mo-, and H-, ZSM-11 and MCM-41 materials.

2. Experimental

The Na–ZSM-11 zeolite (Si/Al = 17) was prepared using the following reactants [12]: TEOS (tetraethylorthosilicate), as the source of silicon and $NaAlO_2$ (sodium aluminate) for aluminum. TBAOH (tetrabutylammonium hydroxide) as template, following the next steps: (a) Al source dissolved in water was added to TEOS solution at 0 °C. The clear solution obtained was stirred for 60 min. (b) The final solution of step a converts into a solid co-gel by addition of the corresponding template at room temperature. The xerogel obtained was dried at 110 °C overnight. (c) The xerogel obtained in step b was impregnated with the adequate template solution by wetness impregnation. The incipient wet SiO_2/Al_2O_3 was loaded to a Teflon-lined autoclave and crystallized at 170 °C for 60 h. The final product was filtered, washed with distilled water, dried at 110 °C and calcined at 540 °C for 12 h.

The Na–MCM-41 (Si/Al = 20) mesoporous material was obtained by sol–gel technique [13]: TEOS and $NaAlO_2$ were vigorously mixed for 30 min. Then, a 10 wt% solution of HTMABr (hexadecyltrimethylammonium bromide) in ethanol was added drop wise under stirring at room temperature. TEAOH (tetraethylammonium hydroxide) was added to the resultant solution and stirring was continued during 5 h. TEAOH and water were further dripped into the milky solution. The mixture was heated at 80 °C for 30 min to remove ethanol used in the solution and produced in the hydrolysis of TEOS. The final gel was heated in a static Teflon-covered reactor under autogenous pressure at 100 °C for 10 days. The solid reaction product was extracted from the autoclave, filtered, washed with distilled water and dried at 60 °C overnight. The post-synthesis thermal treatment evaluated to remove the template was: heating rate of 1 °C/min under N_2 flow of 5 ml/min to 500 °C maintaining also this temperature for 6 h.

The ammonium form of the catalyst was prepared by ion-exchange with 1 M ammonium chloride solution at 80 °C for 40 h. Zn–ZSM-11 and Zn–MCM-41 samples, with 2.8 and 3 wt% of Zn respectively, were obtained by ion-exchange of NH_4-samples with 0.5 M zinc nitrate solution by refluxing for 20 h. Mo–ZSM-11 was prepared by impregnating NH_4-zeolite with aqueous ammonium heptamolybdate solution to yield a 1 wt% of Mo. Finally, the samples were dried at 110 °C and calcined at 500 °C under nitrogen flow and then under an oxidizing atmosphere for 20 h.

The catalysts were characterized by several physicochemical techniques. X-ray powder diffraction patterns were collected in air at room temperature on a Philips PW-1700 equipment, using Cu Kα radiation of wavelength 0.15418 nm. Diffraction data were recorded from 0.5 to 50° 2-theta, at an interval of 0.01° and scanning speed of 2°/min. Infrared measurements were performed on a JASCO 5300 FTIR spectrometer. For structure characterization in the lattice vibration region, the samples were mixed with KBr at 0.05% and pressed forming a wafer. Pyridine adsorption experiments of the samples H-, Zn- and Mo-materials were carried out using a thermostatized cell with CaF_2 windows connected to a vacuum line, and with a self-supported wafer. Surface area studies by BET were obtained using a Micromeritics ASAP 2000.

Catalytic reactions were performed using a single-pass flow reactor, made of quartz with an inner diameter of 9 mm and 300 mm long, operating at atmospheric pressure, at a temperature range between 400 and

550 °C with N_2 as carrier gas and time-on-stream TOS = 20 min. The mechanical mixture of catalyst/polymer deposited over a bed of micro-spheres of quartz was employed. The reactor was connected to a liquid condenser and gas collection bag. The residues which remained with the catalysts and liquid product were weighed after the completion of the experiment. The gas weight was calculated by difference.

The thermal degradation of HDPE alone and mixed with the catalysts (catalyst/polyolefin = 2) was investigated using a thermal analysis instrument (TA Instruments 2920 TGA–DSC). Samples were subjected to a constant heating rate of 10 °C/min from ambient temperature to 600 °C under flow of nitrogen (50 ml/min).

Feed (HDPE) was analyzed by FTIR (JASCO 5300) and XRD (Phillips PW-1700). The reaction products were analyzed by a gas chromatograph (HP5820) equipped with an FID detector, using a 30 m Methyl Silicone capillary column for liquid and 2.2 m Porapak Q column for gaseous products.

3. Results and discussion

Table 1 lists the total surface area, Bronsted/Lewis acid sites ratio, crystallinity and regularity of the catalytic materials used in this work.

In Fig. 1 are shown the FTIR results of the HDPE employed in the reactions. Peaks are assigned as follows: CH stretching peak in the range 2850–2950 cm^{-1}, CH vibration 1460–1470 cm^{-1} and CH rocking 700–730 cm^{-1} [14]. XRD data are consistent with published HDPE (Fig. 2) [15].

Fig. 3 shows thermal analyses results. The polymer degradation pattern (TGA equipment) showed a very deep diminution above 450 °C, without any weight loss at lower temperatures, indicating that no volatile products were formed until then. DSC results show an endothermic signal around 120 °C related with the melting point. The polymer degradation in the presence of modified zeolites occurred at much lower temperatures and
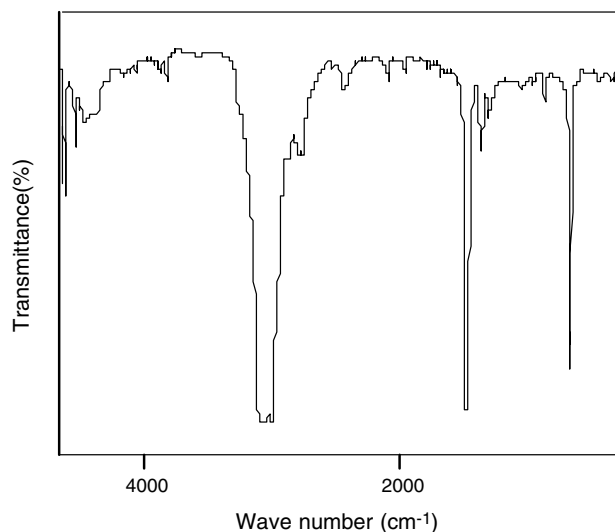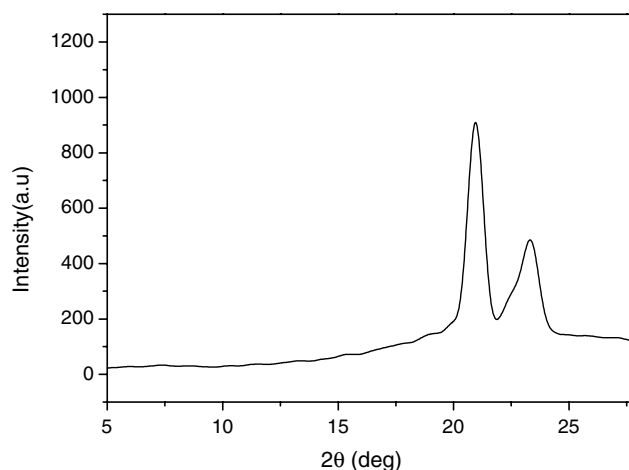

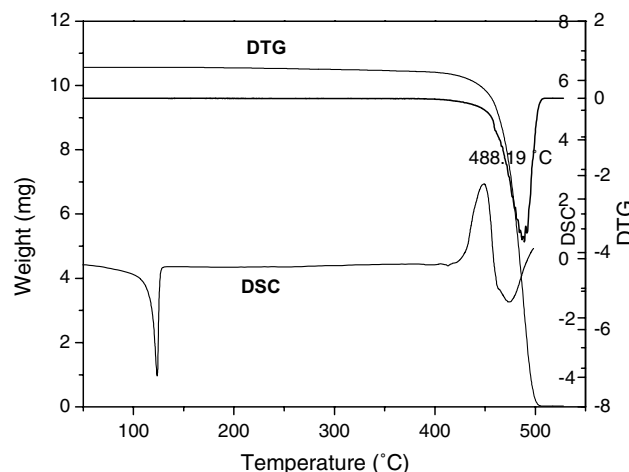Fig. 1. FTIR spectra of HDPE.

Fig. 2. XRD pattern of HDPE.

Fig. 3. Thermal analysis of HDPE.

Table 1
Samples physicochemical characterization

Catalysts	Surface area BET (m^2/g)	Crystallinity (%)		Bronsted/Lewis
		XRD	IR[a]	FTIR[b]
H–ZSM-11	392	100	>99	8
Mo–ZSM-11	386	>99	>98	3
Zn–ZSM-11	378	>98.050	>97	0.90
Zn–MCM-41	1060	–[c]	–[c]	0.13

[a] FTIR in the fingerprint zone of the materials (400–1200 cm^{-1}).
[b] Bronsted/Lewis ratio calculated by FTIR of pyridine (mmol/g) retained at 400 °C and 10^{-4} Torr.
[c] High hexagonal structure regularity without cubic phase, at long range by XRD and at short range by FTIR [13].
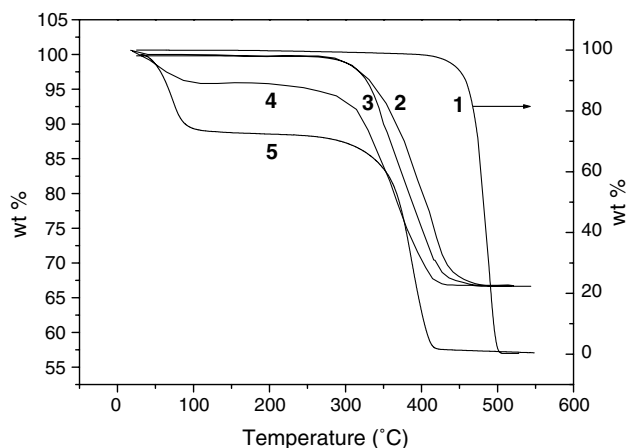
Fig. 4. TGA of pure HDPE (1) and physical mixture of HDPE/catalyst: H–ZSM-11 (2), Mo–ZSM-11 (3), Zn–ZSM-11 (4) and Zn–MCM-41 (5).

Table 2
Catalytic activity of the samples for HDPE degradation at $T = 500$ °C and 100% of conversion[a]

Products (wt%)	Catalysts		
	Zn–ZSM-11	Mo–ZSM-11	H–ZSM-11
Gaseous HC	**28.12**	**33.10**	**48.86**
Methane	3.10	2.41	6.65
Ethylene	1.20	2.21	6.65
Ethane	8.81	4.45	6.70
LPG	15.01	24.03	28.86
Liquid HC	**57.24**	**52.60**	**44.84**
Pentanes	0.32	0.42	0.86
BTX	47.73	38.14	24.71
C9+	9.19	14.04	19.27
Coke	**14.64**	**14.30**	**6.30**

Gaseous HC: Gaseous Hydrocarbons; Liquid HC: Liquid Hydrocarbons; LPG: Liquefied petroleum gas; BTX: benzene–toluene–xylenes; C9+: aromatics.

[a] According to the FTIR data of the reaction products (absence of the characteristic band of HDPE at 1470 cm^{-1}) and TGA results.

at more gradual rate, allowing the cracking rate of polyethylene (Fig. 4). We can see a diminution of the decomposition temperature of HDPE (200, 160 and 150 °C) in the presence of Zn, Mo and H-samples, respectively. In this way for zinc-containing samples, other weight lost at lower temperature due to water elimination (beginning about 50 °C), can be observed.

Table 2 shows the influence of the catalysts in the transformation of the HDPE in the reaction system. Polymer conversion was 100% towards liquid and gaseous products. Liquid fraction was 57 and 52 wt% for Zn–ZSM-11 and Mo–ZSM-11, respectively. BTX selectivity was 47 wt% for Zn-zeolite and 38 wt% for Mo-zeolite. These samples could act as an electron-donor–acceptor complex between carbenium intermediate species and unoccupied molecular orbital (LUMO)
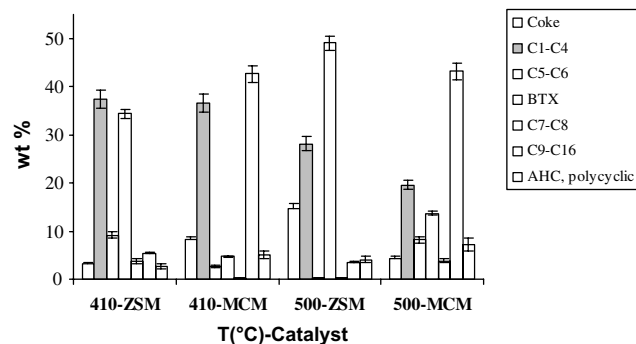

Fig. 5. Reaction products distribution for the catalytic degradation of HDPE over Zn–ZSM-11 and Zn–MCM-41 catalysts at 410 and 500 °C.

of the Zn/Mo sites present in the catalyst by hydride abstraction, since Lewis sites are present according to the IR data (Table 1) [16,17]. The higher activity or selectivity towards BTX of Zn-containing zeolites than Mo-zeolites is due to higher values of Lewis sites (Table 1). H-zeolite gave a higher gaseous fraction (>48 wt%), with light alkanes and olefins as main products. The reaction over H–ZSM-11 showed more cracking products by proteolysis of pentacoordinated carbonium ions due to the greatest values of Bronsted sites present in this sample (Table 1) [18]. Moreover, the LPG levels within the gaseous reaction products were higher than C1 and C2, for all of the samples studied.

Fig. 5 shows comparative activity results between ZSM-11 and MCM-41 materials modified with zinc, at different temperatures. Both materials contain principally Lewis acid sites but present different porous size and surface area (Table 1). Polymer was 100% converted (according to the FTIR data of the reaction products; absence of the characteristic band of HDPE at 1460–1470 cm^{-1}, and TGA results), towards liquid and gaseous products. The liquid products increase with increasing temperature. Aromatics selectivity was 47 wt% for Zn-ZSM and only 15 wt% for Zn-MCM catalyst, but C9–C16 hydrocarbons products were 5 and 45 wt%, respectively. These results are according to the shape selectivity present in MFI material and its narrow pores to access active sites. Meanwhile, in MCM material the larger pore size and channels allow the formation of higher hydrocarbon products.

4. Conclusions

Employing micro and mesoporous materials with Zn, Mo or H, as active sites and using a catalytic system as we described in this work, it is possible to use HDPE waste as a source of gaseous and liquid hydrocarbons products at the temperatures studied (410–500 °C). The selectivity to BTX obtained with Zn–ZSM-11 is higher than the reported data in the literature [19,20]

according to the higher proportion of Lewis sites. Zn–MCM-41 showed an important LHC fraction between C9–C16.

Acknowledgements

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