

Production of hydrocarbons by catalytic degradation of low density polyethylene over Co-ZSM-5 and H-ZSM-11

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Introduction

Huge amounts of plastic wastes are generated every year due to the increasing variety of uses of plastics. Consumption of polymers in Europe between 2000 and 2002 increased by 6%, resulting in a 5% increase in plastic residues which were mainly eliminated by landfill and incineration. This causes severe environmental problems because of chemical inertness and pollutants [1]. Chemical recycling is an important technique to convert these wastes into gas and liquid hydrocarbons [2]; moreover, the addition of catalysts improves the thermal process [3] because it permits more valuable products to be obtained than in thermal processes at low temperatures and at lower reaction time.

In this work we show activity results using H-ZSM-11 and Co-ZSM-5 as catalysts, analyzing temperature effect and active sites in the degradation of LDPE.

Materials and Methods

The Na-ZSM-11 and Na-ZSM-5 zeolites were synthesized by hydrothermal crystallization in Na₂O-Al₂O₃-SiO₂ systems, using tetrabutylammonium hydroxide and tetrapropylammonium hydroxide respectively, as structure director agent, according to known methods [4]. The NH₄-zeolites were prepared by ion-exchange with 1 M ammonium chloride solution. Co-ZSM-5 was obtained by ion-exchange from NH₄-ZSM-5 with CoCl₂ solution.

The catalysts were characterized by several physicochemical techniques: XRD, FTIR, Surface area (BET) and AA. The feed was analyzed by FTIR and thermal analysis TG-DSC. The reaction products were studied by gas chromatography equipped with a FID detector, using a HP-1 capillary column for liquid and Porapak Q packed column for gaseous products, and gas chromatography/mass spectrometry. Measurements of catalytic activity were evaluated using a single-pass flow reactor of quartz with an inner diameter of 9 mm and 300 mm long, at atmospheric pressure and temperature range between 400-500°C with N₂ as carrier gas.

Results and Discussion

DSC results show an endothermic signal around 112°C related with the melting point (Figure 2). The polymer degradation in the presence of modified zeolites occurred at much lower temperatures and at more gradual rate, allowing the cracking rate of polyethylene. We can see a diminution of the temperature decomposition of pure LDPE from 470°C to 415 and 323°C, employing Co- and H-zeolites, respectively (Figure 1 and 2).

Polymer conversion was 100% towards liquid (liquid HC), gas (gaseous HC) and solid residues (unconverted LDPE + Coke) from the catalytic LDPE degradation experiments at different temperatures (Table 1).

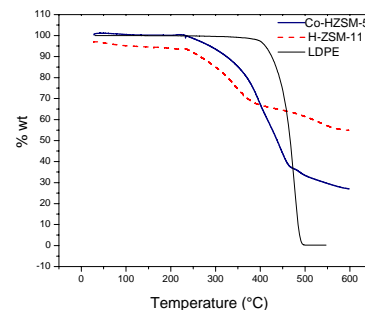


Figure 1. TG curves of pure LDPE and mixtures of catalysts/polymer

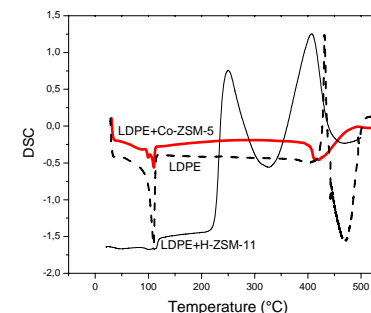


Figure 2. DSC curves of pure LDPE and mixtures of catalysts/polymer

Table 1. Product yields in the catalytic degradation of LDPE

Catalysts*	T (°C)	LHC (wt %)	GHC (wt %)	Solid residues (wt %)	Lewis/Brønsted (mmol/g)***
					FTIR
H-ZSM-11	400	44.91	51.96	3.13	0.14
H-ZSM-11	450	48.12	48.33	3.55	
H-ZSM-11	500	57.01	39.00	3.99	1.33
Co-ZSM-5**	400	36.75	61.71	1.54	
Co-ZSM-5**	450	40.12	57.35	2.53	
Co-ZSM-5**	500	51.91	45.19	2.90	

* Crystallinity >98 % by XRD and FTIR, Surface area 392-377 m²/g by BET

** Co 0.75 wt % by AA.

*** Lewis/ Brønsted ratio by FTIR of pyridine (mmol/g) retained at 400°C and 10⁻⁴ Torr.

According to the results shown in Table 1, LDPE is converted mainly to liquid and gaseous hydrocarbons. The increase of the temperature improves the LHC products for the both catalysts used. Liquid fraction was slightly higher for the H-ZSM-11, the catalyst with major presence of Brønsted acid sites.

References

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