

KINETIC PARAMETERS OF POLYMER DEGRADATION BY SAPO-37

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Abstract

High density poly(ethylene) has been submitted to thermal degradation alone, and in the presence of silicoaluminophosphate SAPO-37. The processes were carried out in a reactor connected on line to a gas chromatograph/mass spectrometer in order to analyze the evolved products. Polymer degradation was also evaluated by thermogravimetry, from room temperature until 800°C, under nitrogen dynamic atmosphere, with multiple heating rates. From TG curves, the activation energy related to degradation process was calculated using the Flynn and Wall multiple heating rate kinetic model for pure polymer (PE) and for polymer in the presence of catalyst (PE/S37). SAPO-37 showed good selectivity for low molecular mass hydrocarbons in PE catalytic degradation.

Keywords: Flynn and Wall kinetic model, poly(ethylene) degradation, SAPO-37

Introduction

Silicoaluminophosphate molecular sieves (SAPO's) are an important class of adsorbents and catalytic materials, generated by the introduction of silicon into its respective aluminophosphate framework [1–4]. SAPO-37 was first described by Lock *et al.* in 1984 [5] and has become the focus of great attention because it has the same structure of Y zeolite, suggesting a potential application to catalytic/adsorption processes.

Actually, the most important Y zeolite industrial process is the catalytical cracking. A material as SAPO-37, with the same FAU structure, but with phosphorous element in the frame, creates possibilities to enhance catalytic cracking processes [6, 7].

The pyrolysis method for the catalytic recycling of waste is a promising way to convert polymer materials into low molecular mass chemicals which can be used as raw materials for the chemical and petrochemical industry. Catalytic pyrolysis of poly(olefins) is of great interest because of their potential use as fuels or chemical resource. The most used catalysts used are zeolite molecular sieves [8, 9]. In addition,

recycling of polymers from waste products can contribute to solve pollution problems.

In this work the degradation of high density poly(ethylene) (PE) was processed in the presence of SAPO-37 and the results of catalytic and thermal degradation were compared.

Experimental

The SAPO-37 catalyst was synthesized by the hydrothermal method, starting from inorganic sources of precipitated silica, pseudoboehmite (Condea), 85% orthophosphoric acid (Merck), and water. Tetra-propylammonium hydroxide solution in water-TPA 20% (Aldrich) and tetra-methylammonium solution in water-TMA 25% (Riedel) were used as the organic templates. The reactants were mixed in the following stoichiometric molar composition:



The reactive hydrogel was charged into a PTFE vessel and autoclaved at 200°C for a period of 24 h, under pressure. The product was washed, dried, and calcined at 500°C for 7 h with dry air.

The sample was characterized by atomic absorption, X-ray diffraction, thermogravimetry, IR spectroscopy and scanning electron microscopy.

High density poly(ethylene) (PE) was obtained from Palmman of Brazil, in powder form blending of polymer and catalyst, previously activated at 450°C for 4 h, was carried out in a ball mill. Then, the catalyst was added to the PE, at a concentration of 25% (mass/mass) – (PE/S37). Each sample was transferred to a Shimadzu TGA-50H and heated from 40 to 800°C temperature range, under a dynamic nitrogen atmosphere, connected on line, through a cool trap, to a Shimadzu GC14-A gas chromatograph coupled to a QP-5000 mass spectrometer. A Tenax adsorption packed column was used.

Also, thermal degradation of PE alone (PE) and with catalyst (PE/S37) was studied by thermogravimetry, using the Flynn and Wall multiple heating rate kinetic model. Sample degradation was carried out from room temperature up to 800°C, with heating rates of 5.0; 10 and 20°C min⁻¹. The thermogravimetric analysis was performed in dynamic atmosphere of nitrogen flowing at 60 mL min⁻¹. 0.01 g of sample was used for each experiment.

Results and discussion

Thermogravimetric curves for PE and PE/S37 are shown in Fig. 1. For the PE sample without catalyst, a continuous mass loss relative to polymer decomposition is observed, while in PE/S37, there are three mass losses. In the TG curve of PE/S37, the initial mass loss (from 30 to 281°C) is attributed to the removal of some weakly interacted molecules on the surface of the materials; the second stage (281 to 506°C) is at-

tributed to the PE decomposition and chain end cleavage. The third stage (506 to 650°C) is probably due to PE degradation on the Lewis acid sites in the catalyst.

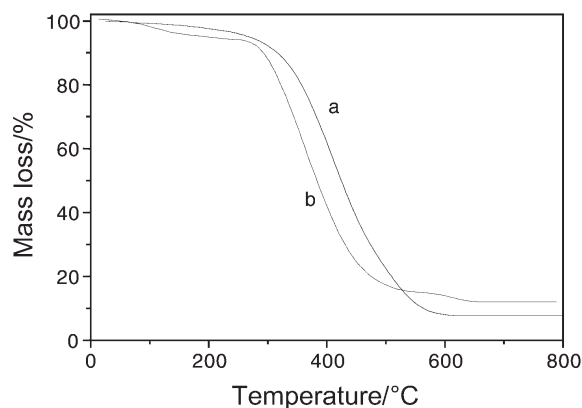


Fig. 1 TG curves of the PE decomposition: a – PE without catalyst; and b – PE/S37

Although reaction conducted in bulk involves more serious problems of heat transfer than those observed in TG small samples, the influence of the catalyst on PE degradation could be readily explored by carrying out thermogravimetric experiments, allowing useful internal comparisons. The mass loss of the mixture (polymer with SAPO-37) was measured as a function of temperature up to 800°C, and the results were compared with that obtained without a catalyst. Using differential TG curves it was possible to determine T_i , T_m and T_f , which refer to the temperatures corresponding to the initial mass loss, maximum rate of mass loss, and final constant mass, respectively, as reported in Table 1. It was observed that the presence of the catalyst decreased the T_i , T_m and T_f values.

Table 1 Values of T_i , T_m and T_f to degradation of polyethylene alone (PE) and with catalyst (PE/S37), determined by thermogravimetric analysis, in dynamic nitrogen atmosphere of $60 \text{ cm}^3 \text{ min}^{-1}$

| Sample | $T_i/^\circ\text{C}$ | $T_m/^\circ\text{C}$ | $T_f/^\circ\text{C}$ |
|--------|----------------------|----------------------|----------------------|
| PE | 322 | 424 | 573 |
| PE/S37 | 281 | 374 | 506 |

Chromatographic analysis showed that thermal degradation of PE with and without a catalyst gave rise to volatilized products distributed over a C_1 to C_{12} range of carbon atom numbers, as shown in Table 2. The catalytic reaction led to a mixture of lighter products. This behavior may be due to the Brønsted and Lewis strong acid sites of the exchanged SAPO-37, which can promote the polymer chains cracking. The selectivity of products with 3, 5, 6 and 8 carbon atoms was attributed to the specific channel and cavity system of SAPO-37.

Table 2 Product distribution % (mass/mass) in the degradation of HDPE carried out without and with catalyst, in dynamic nitrogen atmosphere

| Fraction | PE | PE/S37 |
|----------|-------|--------|
| C1 | 6.07 | 8.00 |
| C2 | – | – |
| C3 | 18.40 | 18.40 |
| C4 | 1.95 | – |
| C5 | 14.70 | 12.80 |
| C6 | 2.35 | 19.60 |
| C7 | 21.90 | 3.62 |
| C8 | 1.94 | 11.50 |
| C9 | 9.96 | 9.17 |
| C10 | 7.20 | 2.40 |
| C11 | 11.50 | 7.39 |
| C12 | 4.03 | 7.12 |

The use of solid catalysts for polymer degradation requires information concerning the kinetic parameters, mainly the energy activation relative to the process. Reliable methods for determining the activation energy using dynamic integral TG curves at several heating rates have been proposed by Ozawa and Flynn and Wall. A software based on these methods was used to treat the TG data, allowing the evaluation of the apparent activation energy. A detailed mathematical procedure employed for a better software comprehension has been reported by Fernandes *et al.* [10–12], where it was demonstrated that the heating rate and the absolute temperature can be related as follows:

$$\frac{\partial \log \beta}{\partial 1/T} \cong - \left[\frac{0.457}{R} \right] E \quad (1)$$

and, inserting the R value $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, an expression obtained for E

$$E \cong -435 \frac{\partial \log \beta}{\partial 1/T} \quad (2)$$

Thus, it is possible to calculate the activation energy related to thermal degradation of a polymer, using the slope of the logarithmic heating rate curves as a function of reciprocal temperature. The activation energy observed for the polymer degradation without a catalyst was 286 kJ mol^{-1} against 223 kJ mol^{-1} in the presence of SAPO-37. These results indicate that silicoaluminophosphate may have acted as a cracking catalyst for the PE, enhancing the generation of light products of potential industrial use.

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References

- 1 S. T. Wilson, B. M. Lok and E.M. Flanigen, U. S. Patent 4,310,440, 1982.
- 2 B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannon and E. M. Flanigen, U. S. Patent 4,310,440, 1982.
- 3 C. A. Messina, B. M. Lok and E. M. Flanigen, U. S. Patent 4,544,143, 1985.
- 4 S. T. Wilson and E. M. Flanigen, U. S. Patent 4,567,029, 1986.
- 5 B. M. Lok et al., J. Am. Chem. Soc., 106 (1984) 6092.
- 6 G. C. Edwards, J. P. Gilson and C. V. McDaniel, Eur. Pat. 0209793, 1987.
- 7 J. A. Herbst, F. G. Dwyer and A. Huss, Eur. Pat. 02008409, 1987.
- 8 Y. D. M. Simard, M. R. Kamal and D. G. Cooper, J. Appl. Polym. Sci., 58 (1995) 843.
- 9 W. E. Farneth and R. J. Gorte, Chem. Rev., 95 (1995) 615.
- 10 V. J. Fernandes Jr. and A. S. Araujo, Thermochim. Acta, 255 (1995) 273.
- 11 V. J. Fernandes Jr., A. S. Araújo and G. J. T. Fernandes, Stud. Surf. Sci. Catal., 105 (1997) 941.
- 12 V. J. Fernandes Jr., A. S. Araujo and G. J. T. Fernandes, J. Therm. Anal. Cal., 56 (1999) 1279.