

## **KINETIC PARAMETERS OF POLYETHYLENE DEGRADATION BY THE NATURAL ZEOLITE CHABAZITE**

*V. J. Fernandes Jr.<sup>1\*</sup>, A. S. Araujo<sup>1</sup>, R. A. Medeiros<sup>1</sup>, J. R. Matos<sup>2</sup>,  
L. P. Mercuri<sup>2</sup>, A. O. Silva<sup>1</sup> and D. M. A. Melo<sup>1</sup>*

<sup>1</sup>Department of Chemistry, Federal University of Rio Grande do Norte, CP 1662  
59078-970, Natal, RN

<sup>2</sup>Institute of Chemistry, University of São Paulo, São Paulo, SP, Brazil

### **Abstract**

High-density polyethylene (PE) was subjected to thermal degradation alone and in the presence of an ammonium-exchanged zeolite chabazite (CHA/PE). The processes were carried out in a reactor connected online to a gas chromatograph/mass spectrometer in order to analyse the evolved products. Polymer degradation was also evaluated by thermogravimetry, from room temperature up to 800°C, under a dynamic nitrogen atmosphere, with multiple heating rates. From the TG curves, the activation energy relating to the degradation process was calculated by using the Flynn and Wall multiple heating rate kinetic model for pure PE and for CHA/PE. The exchanged chabazite exhibited good selectivity for the catalytic degradation of PE to low molecular mass hydrocarbons.

**Keywords:** chabazite, Flynn and Wall kinetic model, polyethylene degradation

### **Introduction**

Chabazite was one of the first naturally occurring zeolites to be extensively studied. Chemically, it displays a large variability of the Si/Al ratio, and exchangeable cations [1–5]. These properties are influenced by the framework charge density and therefore by the Si/Al ratio [6]. Because of the great affinity for the ammonium ion, it is possible to obtain the ammonium form of chabazite by ion exchange [7]. The applications and use of natural zeolites have attracted much attention, and considerable progress has been made in the utilization of sedimentary zeolites. They have unique crystalline structures, which give them many unusual and useful qualities. The cation exchange properties of zeolites have been mostly used to modify the zeolite properties for some specific application, e.g. in detergents, the treatment of nuclear waste, adsorbents, etc.

Pyrolysis methods for the catalytic recycling of waste are a promising means of converting polymer materials into low molecular mass chemicals which can be used as raw materials for the chemical and petrochemical industry. The catalytic pyrolysis of polyolefins is of great interest because of their potential use as fuels or chemical sources [8–12]. The catalysts mainly used are zeolite molecular sieves [13, 14]. Additionally, the recycling of polymers from waste products can contribute to the solu-

\* Author for correspondence: e-mail: valterjr@uol.com.br

tion of pollution problems. The use of acid catalysts can enhance the thermal degradation of synthetic polymers [15, 16]. This study may be monitored by thermogravimetry [17–19].

In the present work, the degradation of high-density polyethylene (PE) was investigated in the presence of chabazite and the results of catalytic and thermal degradation were compared.

## Experimental

The catalyst H-chabazite was obtained by exchanging the natural zeolite, from Brejui Mine (Currais Novos, RN, Brazil), with a 0.5 M ammonium chloride solution and subsequent calcination at 550°C for 4 h. The sample was characterized by atomic absorption, X-ray diffraction, thermogravimetry, IR spectroscopy and scanning electron microscopy.

High-density PE was obtained from Palmman of Brazil, in powder form. The polymer and catalyst, previously activated at 450°C for 4 h, were blended in a ball mill. The catalyst was then added to the PE in a concentration of 10 wt%. The sample (10% catalyst/PE) was transferred to a tubular quartz microreactor fitted with a 3-way valve and heated from 400 to 600°C, under a static nitrogen atmosphere. The reactor was connected online to a Shimadzu GC14-A gas chromatograph coupled to a QP-500 mass spectrometer. A tenax packed adsorption column was used. The detailed procedure has been described elsewhere [21, 22].

The thermal degradation of PE alone and with the catalyst (CHA/PE) was studied by TG, using a Shimadzu TG-50H thermobalance. The Flynn and Wall multiple heating rate kinetic model was applied. Sample degradation was carried out from room temperature up to 800°C, at heating rates of 5.0, 10 and 20 K min<sup>-1</sup>. The TG analysis was performed in a dynamic atmosphere of nitrogen flowing at 60 ml min<sup>-1</sup>. Approximately 10 mg was used for each experiment.

## Results and discussion

TG curves for PE and CHA/PE are shown in Fig. 1. Two well-defined mass change states may be observed for PE, and three for CHA/PE. The initial mass loss from the materials is attributed to the removal of weakly interacting molecules on the surface of the materials. The second stage involves almost total decomposition of PE and chain-end and cleavage. In the TG curve of CHA/PE, the third stage is probably due to PE degradation on the strong acid sites in the cavities of the chabazite.

Although reactions conducted in the bulk involve more serious problems of heat transfer than those observed for small TG samples, the influence of the catalyst on PE degradation could readily be explored by carrying out TG experiments, allowing useful internal comparisons. The loss in mass of the mixture (CHA/PE) was measured as a function of temperature up to 800°C, and the results were compared with those obtained without catalyst. Differential TG curves allowed the determination of  $T_i$ ,  $T_m$  and  $T_f$ , the temperatures corresponding to the initial mass loss, the maximum rate of mass loss, and the final constant mass, respectively, as reported in Table I. It was observed that the presence of chabazite decreased the  $T_i$ ,  $T_m$  and  $T_f$  values.

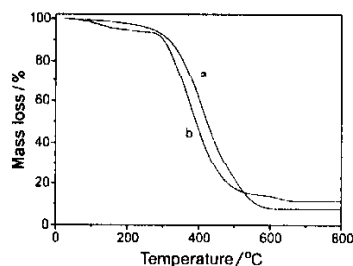


Fig. 1 TG curves of PE decomposition: a – PE without catalyst; and b – CHA/PE

Table 1 Values of  $T_i$ ,  $T_m$  and  $T_f$  for degradation of polyethylene alone (PE) and with catalyst (CHA/PE), determined by TG analysis, in a dynamic nitrogen atmosphere of  $30 \text{ cm}^3 \text{ min}^{-1}$

Sample	$T_i/^\circ\text{C}$	$T_m/^\circ\text{C}$	$T_f/^\circ\text{C}$
PE	292.2	413.0	540.4
CHA/PE	269.3	388.8	498.4

Chromatographic analysis demonstrated that thermal degradation of PE with and without catalyst gave rise to products distributed over a wide range of carbon atom numbers, as shown in Fig. 2. PE alone undergoes degradation to products containing 5 to 26 carbon atoms. The catalytic reaction led to lighter products ( $\text{C}_2$ – $\text{C}_{10}$ ), predominantly  $\text{C}_2$  (14.5%),  $\text{C}_5$  (17.6%),  $\text{C}_8$  (16.5%) and  $\text{C}_{10}$  (18.8%). This behaviour may be due to the Brönsted and Lewis strong acid sites of the exchanged chabazite, which can promote polymer chain cracking. The selectivity for products with 2, 5, 8 and 10 carbon atoms was attributed to the specific channel and cavity system of the chabazite.

The use of solid catalysts for polymer degradation requires information concerning the kinetic parameters, and mainly the energy activation relating to the process. Reliable methods for determining the activation energy by using dynamic integral TG curves at several heating rates have been proposed by Ozawa [20] and Flynn and Wall [23]. Software based on these methods was used to treat the TG data, allowing evaluation of the apparent activation energy. A detailed mathematical procedure em-

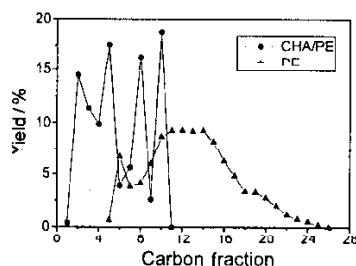


Fig. 2 Distribution of the products in relation to each carbon atom fraction, on degradation of PE and CHA/PE

ployed for better software comprehension has been reported by Fernandes *et al.* [24–26], where it was demonstrated that the heating rate and the absolute temperature can be related as follows.

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

On insertion of the  $R$  value of  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ , the expression obtained for  $E$  is

$$E \cong -4.35 \frac{\partial \log \beta}{\partial (1/T)} \quad (2)$$

Thus, it is possible to calculate the activation energy relating to the thermal degradation of a polymer by using the slope of the logarithmic heating rate curve as a function of reciprocal temperature. The activation energy observed for the degradation of PE was  $277.8 \text{ kJ mol}^{-1}$ , as compared with  $197.3 \text{ kJ mol}^{-1}$  for CHA/PE. This indicates that the zeolite may act as a cracking catalyst for PE, enhancing the generation of light products of potential industrial use.

\* \* \*

This work was supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP).

## References

- 1 J. H. Smith, *Zeolites*, 4 (1984) 309.
- 2 M. A. S. D. Barros, N. R. C. F. Machado, F. V. Alves and E. F. S. Aguiar, *Braz. J. Chem. Eng.*, 14 (1997) 233.
- 3 E. Passaglia, *Amer. Mineral.*, 55 (1970) 233.
- 4 R. M. Barrer, *Bull. Soc. Fr. Miner. Crystallogr.*, 97 (1974) 99.
- 5 R. M. Barrer, J. A. Davis and L. V. C. Rees, *J. Inorg. Nucl. Chem.*, 31 (1969) 219.
- 6 R. M. Barrer and J. Klinowski, *J. Chem. Soc. Faraday Trans.*, 68 (1972) 1956.
- 7 G. Sijaric, B. Tomazovic and T. Ceranic, *Zeolites*, 16 (1996) 301.
- 8 W. Kaminski, J. Janning and H. Sinn, *Fur. Rubber J.*, 15 (1979) 161.
- 9 R. C. Poller, *J. Chem. Tech. Biotechnol.*, 30 (1980) 152.
- 10 R. C. Mordi, J. Dwyer and R. Fields, *Polym. Degrad. Stab.*, 46 (1994) 57.
- 11 R. C. Mordi, R. Fields and J. Dwyer, *J. Anal. Appl. Pyrol.*, 29 (1994) 45.
- 12 W. C. McCaffrey, M. R. Kamal and D. G. Cooper, *Polym. Degrad. Stab.*, 47 (1995) 133.
- 13 Y. D. M. Simard, M. R. Kamal and D. G. Cooper, *J. Appl. Polym. Sci.*, 58 (1995) 843.
- 14 W. E. Farneth and R. J. Gorte, *Chem. Rev.*, 95 (1995) 615.
- 15 A. Lucchesi, G. Maschio and P. Giusti, *Polioplasti*, 288 (1981) 73.
- 16 G. Audisio, A. Silvani, P. L. Beltrame and P. Carlini, *J. Anal. Appl. Pyrol.*, 7 (1984) 83.
- 17 Y. Uemichi, Y. Kashiwaya, M. Tsukidate, A. Ayame and H. Kanoh, *Bull. Chem. Soc. Jpn.*, 55 (1983) 2768.
- 18 Y. Uemichi, Y. Kashiwaya, A. Ayame and H. Kanoh, *Chem. Lett.*, 1 (1984) 41.
- 19 V. J. Fernandes Jr., A. S. Araujo and G. J. T. Fernandes, *Stud. Surf. Sci. Catal.*, 105 (1997) 941.
- 20 T. Osawa, *Bull. Chem. Soc. Jpn.*, 38 (1965) 1881.
- 21 V. J. Fernandes Jr., A. S. Araujo and G. J. T. Fernandes, *J. Thermal Anal.*, 49 (1997) 255.
- 22 V. J. Fernandes Jr., A. S. Araujo, D. M. A. Melo and A. O. Silva, *Anais da ABQ*, 44 (1995) 1.
- 23 J. H. Flynn and W. A. Wall, *Polym. Lett.*, 4 (1969) 323.
- 24 V. J. Fernandes Jr., DSc. Thesis, Universidade de São Paulo, 1991.
- 25 V. J. Fernandes Jr. and A. S. Araujo, *Química Nova*, 18 (1995) 11.
- 26 V. J. Fernandes Jr. and A. S. Araujo, *Thermochim. Acta*, 255 (1995) 273.