Catalytic degradation of polyethylene over SAPO-37 molecular sieve

G.J.T. Fernandes, V.J. Fernandes, Jr., A.S. Araujo

Department of Chemistry, Federal University of Rio Grande do Norte, CP 1662, 59078-970 Natal RN, Brazil

Abstract

The degradation of high-density polyethylene (HDPE) was studied alone and in presence of silicoaluminophosphate type silicoaluminophosphate (SAPO-37) as catalyst. This material was synthesized by the hydrothermal method using tetrapropylammonium hydroxide and tetramethylammonium chloride as organic templates. The characterization by X-ray diffraction, infrared spectroscopy, thermogravimetry and scanning electron microscopy showed that typical faujasite structure for the SAPO-37 was obtained. The total acidity, determined by \( n \)-butylamine adsorption, it was equivalent to 0.558 mmol g\(^{-1} \), corresponding to moderate acid strength. For catalytic reaction, a physical mixture of 25%SAPO-37/HDPE was decomposed in a thermobalance at heating rates of 5, 10 and 20 \(^\circ\)C min\(^{-1} \), from 380 to 520 \(^\circ\)C. At the maximum degradation rate, the products were collected in a cold trap and analyzed by a coupled gas chromatograph/mass spectrometer. The degradation of HDPE without catalyst was carried out at the same conditions for comparison with the obtained data with SAPO-37. The HDPE alone suffers decomposition to a wide range of hydrocarbons (C\(_5\) – C\(_{25}\) ) while in the presence of catalyst, light hydrocarbons (C\(_2\) – C\(_{12}\) ) were obtained. By the application of the Vyazovkin model-free kinetic method, it was observed that the activation energy decreased from 290 kJ mol\(^{-1}\) for HDPE alone, to 220 kJ mol\(^{-1}\) for 25%SAPO-37/HDPE, evidencing that SAPO-37 is an effective catalyst for polyethylene degradation. © 2002 Published by Elsevier Science B.V.

Keywords: SAPO-37; Polyethylene degradation; Model-free kinetics

1. Introduction

Recently recycling of residual plastics by combustion or pyrolysis has received significant attention in the world [1]. Pyrolysis of plastics is of great interest because they are an alternative source of energy or chemical raw materials. This process is not well understood; however, the use of various solid acid catalyst is a promising way to improve the yield and selectivity to a desired hydrocarbon range. In addition, this process contributes to solve environmental problems.

Silicoaluminophosphate (SAPO) molecular sieves represent an important class of materials generated by the introduction of silicon into its aluminophosphate framework [2]. The SAPO-37 has faujasite structure and is an attractive material for catalytic application due to the presence of specific Brönsted and Lewis acid sites in its structure. The use of acid catalysts enhances the thermal degradation of synthetic polymers [3].

For designing recycling of plastics in large scale, the kinetics of decomposition must be known. Thermogravimetry (TG) and gas chromatography/mass spectrometry (GC/MS) have been used to investigate the performance of different catalysts on decomposition reactions of waste plastics (mainly polyethylene) [3]. In this work, we studied the catalytic degradation of high-density polyethylene over SAPO-37, using TG and GC/MS techniques. By using integral TG
curves and the Vyazovkin model-free kinetic method [4], the activation energy, the conversion rates and polymer degradation time as a function of temperature were estimated.

2. Experimental

The silicoaluminophosphate (SAPO-37) catalyst was prepared by the hydrothermal method, starting from precipitated silica, pseudobohemite, 85% phosphoric acid, water and the organic templates: 20% tetrapropylammonium hydroxide (TPAOH) and 25% tetramethylammonium chloride (TMACl). These reactants were mixed according to the following stoichiometry:

\[ \frac{1.0}{(TPA)_2O} \cdot \frac{0.025(TMA)_2O}{0.25SiO_2} \cdot \frac{1.0Al_2O_3}{1.0P_2O_5} \cdot \frac{120H_2O}{1} \]

The hydrogel was charged into a Teflon-lined vessel and autoclaved at 200 °C for a period of 24 h under autogonously pressure. The product was recovered by filtration, dried and calcined at 550 °C for 7 h, in air atmosphere flowing at 60 ml min⁻¹.

The SAPO-37 catalyst was characterized by several physicochemical techniques. The chemical composition was determined by X-ray fluorescence. The thermal behavior of the sample was investigated by thermogravimetry, using nitrogen flowing at 100 ml min⁻¹, in the temperature range 25–1000 °C. The infrared spectrum was obtained in the 4000–400 cm⁻¹ range using the KBr technique. X-ray diffraction was determined in the range of 2θ 10–40°, using radiation of Cu Kα. The shape and size of the crystals were evaluated by scanning electron microscopy. The acidity of the SAPO-37 was determined by n-butylamine adsorption in the range 340–460 °C.

3. Results and discussion

The characteristic properties of the SAPO-37 material were evaluated by means of several methods. From thermogravimetry, it was observed weight losses in well-defined temperature ranges, corresponding to water desorption (from room temperature to 150 °C), and thermal degradation of TPAOH and TMACl templates. The decomposition mechanisms involve complex steps; however, from 150 to 550 °C all organic materials were thermally decomposed, evidencing that the SAPO-37 should be calcined at 550 °C without affect its thermal properties [6].

X-ray analysis for the calcined SAPO-37 presents similar characteristics to that of faujasite structure [7], and from infrared spectra, it was observed vibration bands due to tetrahedral TO₄ (T = Al, Si, P) in the 1300–400 cm⁻¹ range. The morphology of the SAPO-37 crystals is visualized in Fig. 1.

From scanning electron microscopy, crystals with typical faujasite morphology were observed with good crystallinity. Concerning the acid properties of this material, the total acidity, as determined by n-butylamine adsorption in the range 340–460 °C, it was equivalent to 0.558 mmol g⁻¹, corresponding to moderate acid strength.

The thermal and catalytic degradation for HDPE and SAPO-37/HDPE, respectively, was evaluated by thermogravimetry, at heating rates of 5, 10 and 20 °C min⁻¹. For thermal degradation of HDPE, no significant decomposition occurred until ca. 420 °C; however, by the addition of SAPO-37 catalyst, the decomposition started at ca. 380 °C. Also, it was observed that the samples exhibit a well-pronounced weight loss in the 370-550 °C temperature range. This range was selected for kinetic studies, and plots of conversion in function of temperature were obtained, as shown in Figs. 2 and 3, for HDPE and SAPO-37/HDPE, respectively.
Fig. 1. Scanning electron micrography of the SAPO-37 crystals.

Fig. 2. Conversion of HDPE as function of temperature. From left to right: 5, 10 and 20 °C min⁻¹.
The conversion of the HDPE over SAPO-37 occurs with less energy. This is evident by the plots of degree of conversion versus time, as shown in Figs. 4 and 5, respectively. For complex reactions, such as polymer degradation, the nth-order algorithm causes unreasonable kinetic data. Applying the Vyazovkin model-free kinetic method, accurate evaluations of complex reactions can be performed, as a way of obtaining reliable and consistent kinetic information about the overall process [4]. The theory is based on

$$\frac{\partial \alpha}{\partial T} = k e^{-E/RT}$$

where $\alpha$ is the conversion, $T$ the temperature; $k$ the rate constant (s$^{-1}$) and the activation energy $E$ is constant for a certain conversion (iso-conversion method). A chemical reaction is measured at least at three different heating rates and the respective conversion curves are calculated out of the TG measured curves. The estimated activation energy for HDPE degradation process was ca. 290 kJ mol$^{-1}$, whereas for SAPO-37/HDPE, this value decreased to 220 kJ mol$^{-1}$, evidencing the catalytic activity of the SAPO in the process.

The catalytic conversion of polyethylene as a function of time, for different temperatures, it was...
estimated, noting that the time decreases considerably as a function of temperature. Also, it was possible to estimate the temperature for the polymer degradation allowing to estimate the time required for the process at a given temperature, as summarized in Table 1. It was observed, for instance, that for 90% of polyethylene degradation in a period of 5 h, it is necessary to process at 424 °C, whereas for the same time, the temperature required for processing 90% of SAPO-37/HDPE is 406 °C.

Regarding the product characterization, the GC/MS analysis demonstrated that thermal degradation of HDPE gave rise to products distributed over a wide range of carbon atoms, C5–C26 [3]. The catalytic reaction (SAPO-37/HDPE) led to lighter products, mainly C1–C12, distributed as the following carbon fractions and wt.%—C1: 8.0%; C3: 18.4%; C5: 12.8%; C6: 19.6%; C7: 3.6%; C8: 11.5%; C9: 9.2%; C10: 2.4%; C11: 7.4% and C12: 7.1%. This catalytic activity may be due to presence of acid sites in the SAPO-37, which can promote polymer chain cracking. The selectivity for products with 3, 5, 6, 8 and 12 atoms of carbons was attributed to the specific channel system of the faujasite structure of the SAPO-37.

### Table 1
Iso-conversion kinetic parameters for HDPE and SAPO-37/HDPE

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Kinetic parameter (°C) at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10% 25% 50% 75% 90% 95%</td>
</tr>
<tr>
<td><strong>HDPE</strong></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>– – – – – – – – – – – – –</td>
</tr>
<tr>
<td>60</td>
<td>415.1 429.9 437.9 443.5 447.5 449.8</td>
</tr>
<tr>
<td>120</td>
<td>405.0 419.3 428.2 433.6 437.3 439.5</td>
</tr>
<tr>
<td>180</td>
<td>399.2 413.8 422.7 427.9 431.5 433.6</td>
</tr>
<tr>
<td>240</td>
<td>395.2 409.9 418.8 423.9 427.4 429.5</td>
</tr>
<tr>
<td>300</td>
<td>392.1 407.0 415.8 420.9 424.3 426.3</td>
</tr>
<tr>
<td><strong>SAPO-37/HDPE</strong></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>– – – – – – – – – – – – –</td>
</tr>
<tr>
<td>60</td>
<td>389.9 404.7 415.4 422.6 430.2 436.7</td>
</tr>
<tr>
<td>120</td>
<td>377.4 393.1 404.3 411.6 419.6 426.5</td>
</tr>
<tr>
<td>180</td>
<td>370.3 386.4 397.9 405.3 413.5 420.7</td>
</tr>
<tr>
<td>240</td>
<td>365.3 381.8 393.5 400.9 409.3 416.6</td>
</tr>
<tr>
<td>300</td>
<td>361.5 378.3 390.1 397.6 406.1 413.5</td>
</tr>
</tbody>
</table>

4. Conclusions

The SAPO-37 molecular sieve synthesized by hydrothermal treatment showed to be a promising catalyst for the high-density polyethylene degradation. From TG analysis and by the application of the Vyazovkin model-free kinetic method, it was demonstrated that the activation energy for degradation of HDPE without catalyst decreased from 290 to 220 kJ mol⁻¹ for SAPO-37/HDPE. For a given degree
of conversion of polyethylene, it was possible to estimate the time and temperatures required for the process. The monitoring of the obtained products by GC/MS showed that the HDPE degradation produces a wide range of hydrocarbons from C\textsubscript{5} to C\textsubscript{25}, whereas in presence of the SAPO-37, it was obtained from C\textsubscript{1} to C\textsubscript{12}.

Acknowledgements

Financial support was provided by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

References