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Kinetic study of low density polyethylene degradation on the silicoaluminophospate SAPO-11

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Abstract Degradation of low density polyethylene (LDPE) was studied for the pure polymer and mixed with silicoaluminophosphate SAPO-11 catalyst. SAPO-11 was synthesized by hydrothermal method using di-isoprolpylamine as structure template, and characterized by XRD and SEM. From X-ray diffraction, it was observed that SAPO-11 was obtained with high crystallinity. Using the model-free kinetics, proposed by Vyazovkin, the activation energies were determined for the process of polymer degradation. It was found that the degradation process of 90% of LDPE mixed with SAPO-11 over a period of 1 h, occurred at a temperature of 378 °C, while for the pure LDPE, the temperature was increased to 434 °C in the same period of time and conversion, indicating that SAPO-11 was an effective catalyst for the degradation of LDPE. The activation energy for the degradation of pure LDPE was equivalent to 251 kJ mol^{-1}. Also, when the SAPO-11 was mixed with the polymer, this value was decreased to 243 kJ mol^{-1}.

Keywords Degradation · Polyethylene · SAPO-11 · Thermogravimetry · Model-free kinetic

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Introduction

In order to obtain fuels and materials from plastic rejects, a considerable number of researches have been realized in the last decades, aiming to minimize the problem of solid residues accumulation, where plastic residues can be converted in valuable products through thermal or catalytic degradation [1]. Consequently, polymer degradation became an increasing and important method to convert plastic residues into chemical products such as fuel and petrochemicals [2, 3] and fractions used in materials engineering [4, 5].

In general, catalytic degradation of polymers requires temperatures in the range of 350–550 °C and the chemical products are hydrocarbons mainly gasoline and diesel [6]. Typical catalysts used for polymer degradation are acid solids such as silica–alumina, zeolites, and mesoporous materials [7].

The silicoaluminophosphates (SAPOs) are molecular sieves that represent an important class of materials produced by the introduction of silicon in the structure of aluminophosphate [8]. It was already observed that the microporous molecular sieves, such as ZSM-5 zeolite, present potential use as acid catalyst, for its uniform microporous structures and strong acidity [9]. The SAPO-37 with faujasite structure is an attractive material for catalytic application due to the presence of Brönsted and Lewis acid sites located in its structure [10]. The use of acid catalysts can enhance the thermal degradation of synthetic polymers which may be monitored by thermogravimetry [11, 12]. In this study, the thermogravimetric kinetics for the degradation of low density polyethylene (LDPE) under nitrogen atmosphere and different heating rates was investigated. Using integral TG curves and the kinetic method proposed by Vyazovkin [13, 14], the activation energy, the conversion rates, and time of polymer

degradation as a function of temperature were also estimated.

Experimental

The SAPO-11 silicoaluminophosphate was synthesized by the hydrothermal method of a mixture containing pseudo-bohemite (Captal-B) as aluminum source, acid phosphoric (Vetec), silica gel (Aldrich), di-isopropilamina (Riedel de Häen) as structural template, and distilled water as solvent [15]. The precursors had been added in the following molar composition: $1DIPA:1Al_2O_3:0{,}5SiO_2:1P2O:80H_2O$. The resulting solution was transferred to a stainless steel Teflon-lined autoclave and heated in on oven at temperature of 170 °C for 72 h under autogeneous pressure. The resultant solid was recovered by filtration, washed with distilled water and dried at 100 °C for 6 h. The removal of the diisopropylamine from the pores of the synthesized samples was carried out by calcinations at temperature of 550° for 12 h under atmospheres of nitrogen for 4 h, then dry air for 8 h. The characterization of the calcined material was carried through by the X-ray diffraction (Shimadzu model XRD-600 using Cu K_α radiation in the range 2θ angle from 5° to 45°) and scanning electron microscopy (Philipps model XL30-ESEM). These techniques were used to confirm the crystalline properties and morphology of the crystals, respectively.

In order to evaluate the process of degradation of polyethylene, initially, the LDPE was physically mixed to the SAPO-11, in concentracion of 50% in mass. The thermal degradation of LDPE alone or mixed with the catalyst (LDPE/SAPO-11) was carried out on a thermobalance TGA/SDTA 851 from Mettler, at the temperature range from 30 to 900 °C and heating rates of 5, 10, and 20 °C min^{-1}, using nitrogen flowing at 25 mL min^{-1}. The kinetic method proposed by Vyazovkin was used to determine the parameters of activation energies relative and conversion data at different temperatures and reaction times. The calculations were performed using a Mettler-Toledo STARe software.

Results and discussion

Figure 1 presents the XRD pattern of calcined SAPO-11. The position and intensity of diffraction peaks showed that the studied material presented a well-defined AEL structure [16, 17]. No additional peaks in XRD patterns were observed indicating that the sample was obtained with high crystallinity.

From scanning electron microscopy, it was observed in Fig. 2 that SAPO-11 sample showed a morphology with

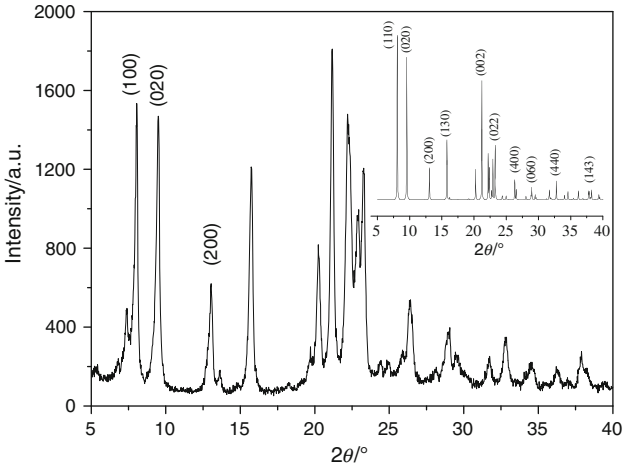

Fig. 1 X-ray diffractogram of the SAPO-11 microporous materials

spherical crystals that prevail when compared with the presence of small traces of orthorhombic crystals. This behavior is similar to the micrographs presented in the literature [17–19]. The spherical shape of the crystals is good for maximizing the contact with the polymer, and consequently increasing the kinetics of its degradation.

The TG/DTG curves for LDPE and LDPE/SAPO-11 at different heating rates are shown in Figs. 3 and 4, respectively. For thermal degradation of LDPE, a mass loss in the range of temperature from 400 to 510 °C was observed, due to the thermal degradation of the polymer. However, by the addition of SAPO-11 catalyst do the LDPE, the decomposition started at 340 °C, and finished at ca. 400 °C. This temperature difference between the two samples evidenced the catalytic effect of the microporous SAPO-11 material, indicating that the acid sites had been efficient for the degradation of the LDPE in the pre-established conditions. Also, a dehydration process was observed from 40 to 110 °C for SAPO-11. In the literature have also observed a reduction in degradation temperature of LDPE when added SAPO-37 catalyst [20].

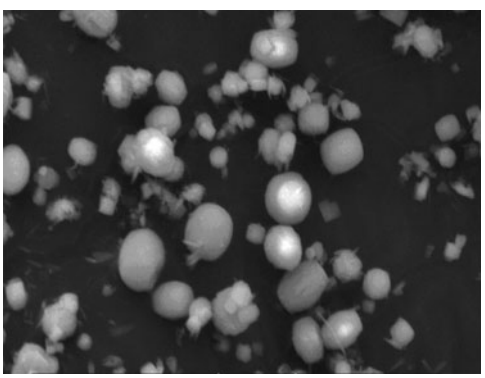

Fig. 2 Scanning electron micrography of the SAPO-11

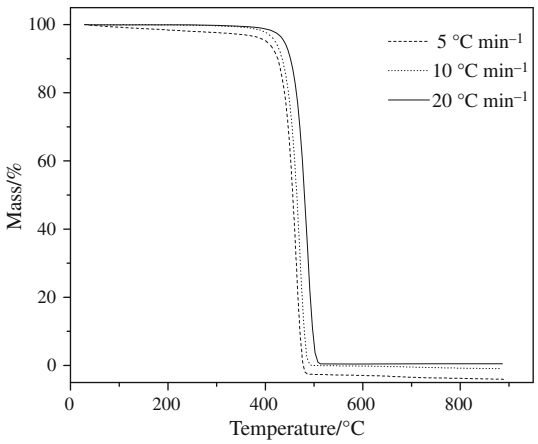

Fig. 3 TG curves for LDPE at different heating rates

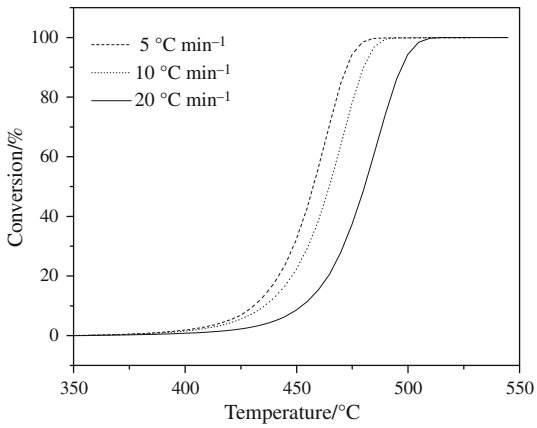

Fig. 5 Conversion of LDPE as a function of temperature

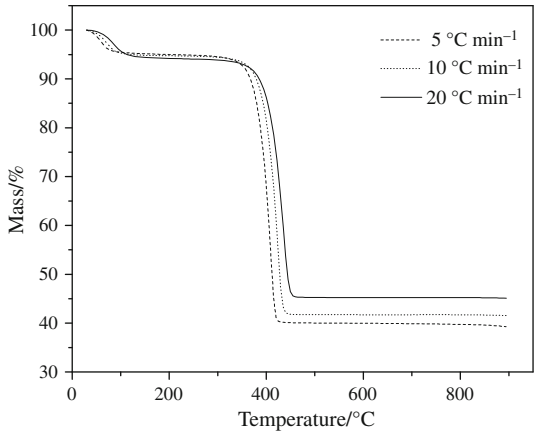

Fig. 4 TG curves for LDPE/SAPO-11 at different heating rates

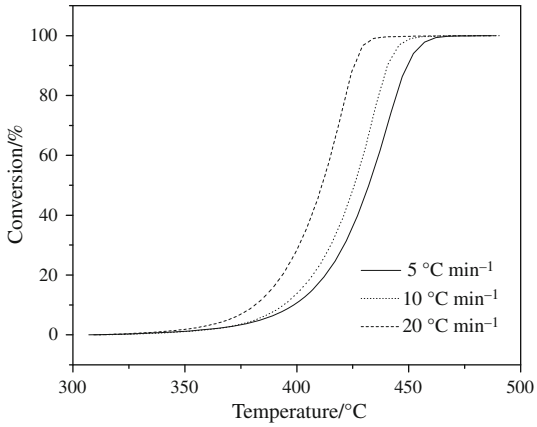

Fig. 6 Conversion of LDPE/SAPO-11 as a function of temperature

For the kinetic studies, the selected ranges of temperature ranges were 391–500 °C for pure LDPE, and 342–465 °C, for LDPE/SAPO-11. These ranges were selected for kinetics studies. The Figs. 5 and 6 show the degree of conversion as a function of temperature relative to the degradation of LDPE and LDPE/SAPO-11, respectively. It was observed that for this LDPE polymer, the process of degradation was more efficient when this was mixed with the catalyst, occurring with less energy. Similar results occurred on degradation of polypropylene with the HZSM-12 catalyst [21].

It is known that the reaction rate of a thermal or catalytic reaction depends on conversion (α), temperature (T), and time (t). For each process, the reaction rate as a function of conversion, $f(\alpha)$, is different and must be determined from experimental data. For single reactions, the evaluation of $f(\alpha)$ with nth order is possible. For complex reactions, for instance degradation of LDPE, the evaluation of $f(\alpha)$ is complicated and, in general unknown. In this case, to obtain reliable and consistent kinetic information about the overall process, the model-free kinetics was applied based on the Vyazovkin theory. This theory is based on an isoconversional computational technique that calculates the effective activation energy (E_a) as a function of the conversion (α) of a chemical reaction, $E = f(\alpha)$. The chemical reaction is measured at least in three different heating rates (β) and the respective conversion curves are calculated out of the TG curves [22–25]. The methods that make use of the isoconversional principle states that at a constant extent of conversion, the reaction rate is a function only of the temperature so that:

$$\left[\frac{\mathrm{d}\ln(\mathrm{d}\alpha/\mathrm{d}t)}{\mathrm{d}T^{-1}}\right] = -\frac{E_a}{R}. \quad (1)$$

In Eq. 1, E_a is Arrhenius parameters (apparent activation energy), R is the gas constant, T is the temperature, t is the time, and α is the extent of conversion, which can be determined from analysis of TG [23].

The catalytic conversion presented in the curves of the Figs. 4 and 5 is more evident when examining the plots of degree of conversion versus time, as shown in Figs. 7 and 8 for LDPE and LDPE/SAPO-11, respectively, which were

obtained from model-free kinetic data [25]. Those graphs show comparative curves between the pure polyethylene and mixed with the catalyst on different sets of temperatures in the degradation steps. It was observed that the time for the degradation of LDPE and LDPE/SAPO-11 decreased considerably as a function of temperature.

The activation energy (E_a) for the thermal and catalytic decomposition of the LDPE, estimated by the theory of model-free kinetics, is shown in the Fig. 9. For the pure LDPE, the relative activation energy was 252 kJ mol^{-1}. For the degradation of LDPE using SAPO-11, the E_a was equivalent to 243 kJ mol^{-1}, evidencing the effect of the catalyst of the molecular sieve in the degradation process of polyethylene.

Also, it was possible to estimate the temperature of the degradation process for LDPE and of LDPE/SAPO-11, predicted by the kinetic data, providing an estimation of the time required to the degradation reaction, as summarized in Table 1. It was observed, for instance, for LDPE to achieve 90% of degradation, is necessary to heat it at 434 °C for 60 min; whereas for LDPE/SAPO-11, to achieve the same conversion at the same time the temperature of 378 °C is required.

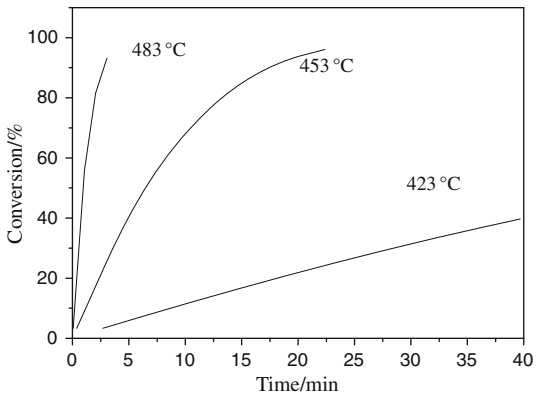

Fig. 7 Conversion of LDPE as function of time for different temperatures

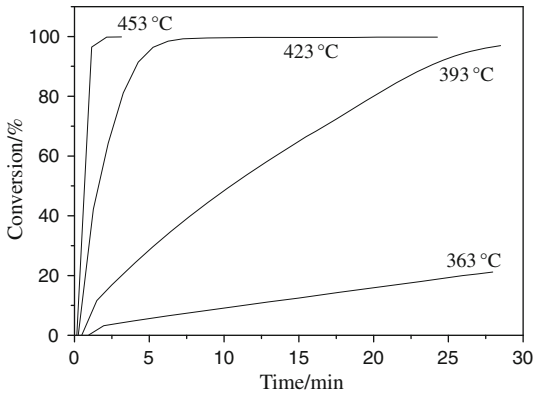

Fig. 8 Conversion of LDPE/SAPO-11 as function of time for different temperatures

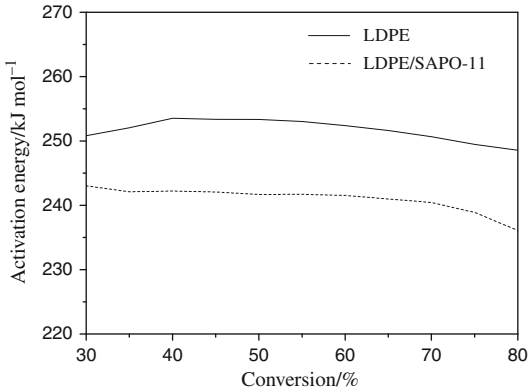

Fig. 9 Activation energy of LDPE and LDPE/SAPO-11 using the model-free kinetics

Table 1 Iso-conversion kinetic parameters for LDPE and LDPE/SAPO-11

Time/min	Conversion/%					
	10	30	60	**90**	95	99
LDPE						
10	421.2	437.9	450.2	461.6	464.8	478.6
30	405.8	422.3	434.5	444.6	447.5	460.5
60	396.5	412.8	424.9	**434.3**	437.0	449.6
90	391.1	407.3	419.5	428.4	431.0	443.3
120	387.4	403.5	415.6	424.3	426.8	438.9
LDPE/SAPO-11						
10	364.5	383.5	397.5	407.3	409.9	415.9
30	350.7	367.7	380.9	389.1	390.8	395.7
60	342.3	358.1	370.9	**378.1**	379.3	383.5
90	337.5	352.6	365.1	371.8	372.8	376.6
120	334.1	348.8	361.1	367.4	368.2	371.8

Conclusions

The SAPO-11 synthesized by the hydrothermal method and characterized initially for X-ray diffraction is a good catalyst for low density polyethylene degradation. The model-free kinetics applied in the research has proved to be an evaluation tool in the study of degradation of LDPE. From TG analysis and by the application of the kinetic method proposed by Vyazovkin, it has been demonstrated that the activation energy for the degradation process of polymer, decreased when SAPO-11 was added to LDPE. It was observed in the data of isoconversion that for different degree of conversion and different times, the temperature

was diminished when SAPO-11 was used, evidencing the catalytic effect of the material.

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