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Thermogravimetric kinetics of polyethelyne degredation over silicoaluminophosphate

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Abstract

In the current work, we investigated the Thermogravimetric kinetics of degradation of high-density polyethylene (HDPE) alone, and mixed with silicoaluminophosphate catalyst (SAPO-37/HDPE). To estimate the kinetic parameters of the polymer degradation, the Vyazovkin model-free kinetic method was applied. The activation energy (*E*) was calculated as a function of conversion (α) and temperature (*T*), providing an estimate of the time required for the degradation process at a given temperature. The products due to thermal and catalytic cracking of polyethylene were analyzed by gas chromatography/mass spectrometry (GC/MS). The SAPO-37 showed good catalytic activity, decreasing the activation energy for the process.

Keywords: Model-free kinetics; Polyethylene; Degradation; Silicoaluminophosphate; Thermogravimetry

1. Introduction

In the 1990s, the recycling of residual plastics by combustion or pyrolysis has received significant attention in the world [1,2]. Pyrolysis is known as a method to break complex organic materials such as synthetic polymers into relatively small molecules. This process is not well understood, but the use of various solid acid catalysts is a promising way to improve the yield and selectivity to a desired hydrocarbon range [3–5]. Pyrolysis of plastics is of great interest because it is an alternative source of energy or chemical raw materials. In addition, this process helps to solve environmental problems. For designing recycling of plastics in large scale, the kinetics of decomposition must be known. Thermogravimetry (TG) is the most important technique for this purpose [6,7]. TG and gas chromatography/mass spectrometry (GC/MS) have been used to investigate the performance of different catalysts in decomposition reactions of waste plastics (mainly polyethylene) [6–9].

Silicoaluminophosphate molecular sieves (SAPOs) represent an important class of adsorbents and materials generated by the introduction of silicon into its aluminophosphate framework [10]. The SAPO-37 has faujasite structure and is an attractive material for catalytic application due to the presence of specific Bronsted and Lewis acid sited in its structure. The use of acid catalysts can enhance the thermal degradation of synthetic polymers [11,12].

In this study, we investigated the Thermogravimetric kinetics for the degradation of high-density polyethylene (HDPE) under nitrogen atmosphere and different heating rates. By using integral TG curves and the Vyazovkin model-free kinetic method [13,14],

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the activation energy, the conversion rates and polymer degradation time as a function of temperature were estimated.

2. Experimental

SAPO-37 catalyst was prepared by the hydrothermal method, starting from inorganic sources of silicon (precipitated silica, Merck), aluminum (psuedobohemite, Condea), phosphorus (85% orthphosphoric acid, Merck), water, and the following organic templates: 20% tetrapropylammonium hydroxide (TPA, Aldrich) and 25% tetramethylammonuim chloride (TPA, Reidel). These reactants were mixed according to the stochiometry: 1.0 $(TPA)_2O$:0.025 $(TMA)_2O$:0.25 SiO_2:1.0 Al_2O_3:1.0 P_2O_5:120 H_2O. The hydrogel was charged into a Teflon-lined vessel and autoclaved at 200 °C for a period of 24 h under autogeneous pressure. The product was recovered by filtration, dried and calcined at 500 °C for 7 h, in air atmosphere flowing at 60 ml/min. The characterization of the calcined material by atomic absorption, infrared spectroscope, X-ray diffraction and scanning electron microscopy showed that a typical faujastic SAPO-37 structure was obtained with good crystallinity.

HDPE was purchased from Palmann of Brazil Company in powder form. The polymer was blended in Ball Mill. Then, the SAPO-37 catalyst was added to the HDPE at a concentration of 25 wt.%. The thermal degradation of HDPE alone and mixed with the catalyst (SAPO-37/HDPE) was carried out using a thermobalance Mettler-STGA 851, at a temperature range from 30 to 900 °C, under nitrogen flow (60 ml/min) and heating rates of 5, 10, and 20 °C/min. The Vyazovkin model-free kinetics method was applied to this process. In each experiment, ca. 10 mg of sample was used. In order to identify the hydrocarbon fractions resulting from the polyethylene degradation, the evolved products were collected in a cold trap and analyzed by a Shimadzu QP-5000 GC/MS, using a tenax adsorption packed column.

3. Results and discussion

The TG curved for HDPE and SAPO-37/HDPE at different heating rates is shown in the Figs. 1 and 2, respectively. For thermal degradation of HDPE, no significant decomposition occurred until ca. 420°. With the addition of SAPO-37 catalyst, the decomposition started at 375 °C. This indicated that SAPO-37 catalyst, with Bronsted and Lewis acid sites, was effective for degradation of HDPE at the reaction conditions used.

It is observed that both samples exhibit a pronounced weight loss in the 370–550 °C temperature range. This range was selected for kinetic studies. Figs. 3 and 4 show the degree of conversion as a function of the temperature relative to degradation of

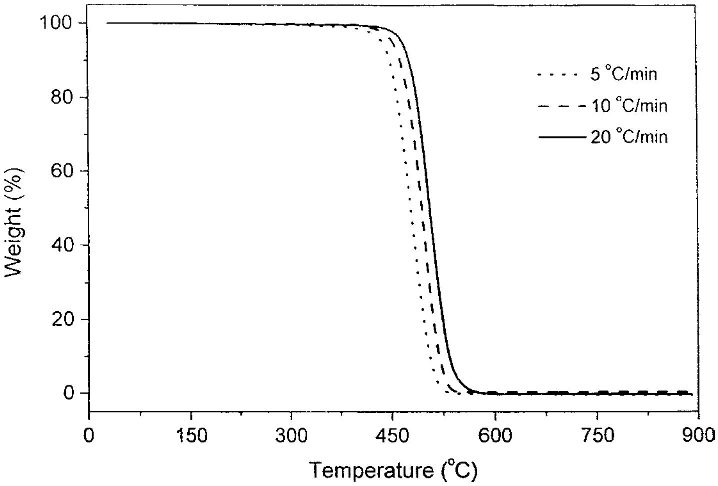

Fig. 1. TG curves of HDPE at different heating rates.

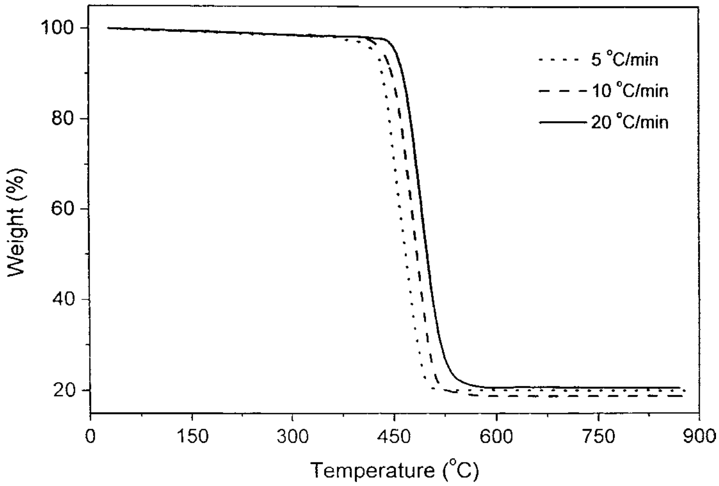

Fig. 2. TG curves of SAPO-37IHDPE at different heating rates.

HDPE and SAPO-37/HDPE, respectively. It is clearly noted that the degradation of the HDPE over SAPO-37 occurs with less energy. This is even more evident when examining the plots of degree of conversion versus time, as shown in the Figs. 5 and 6, for HDPE and SAPO-37/HDPE.

The reaction rate of the thermal and catalytic reaction depend on conversion (α), temperature (*T*), and time (*t*). For each process, the reaction rate given as a function of conversion, *f*(α), is different for each process, and must be determined from experimental data. For single reactions, the evaluation of *f*(α) with nth order is possible. For complex reactions, such as polymer degradation, the function of *f*(α) is complicated and in general unknown. In these cases the nth order algorithm causes unreasonable kinetic data. Applying the model-free kinetics method, accurate evaluations of complex reactions can be performed, as a way to obtain reliable and consistent kinetic information about the overall process [14].

Based on this problem, Vyazovkin [12,13,15] developed and integral method where any model is selected (model-free kinetics) and allows one to evaluate both

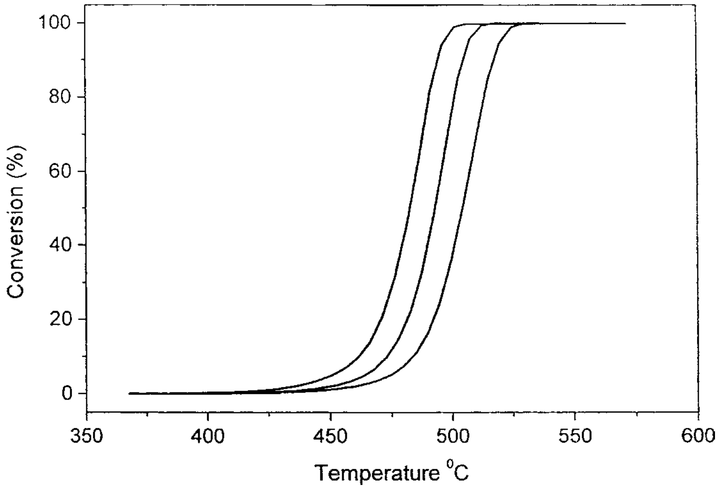

Fig. 3. Conversion of HDPE in function of temperature. From left to right: 5, 10 and 20 °C/min.

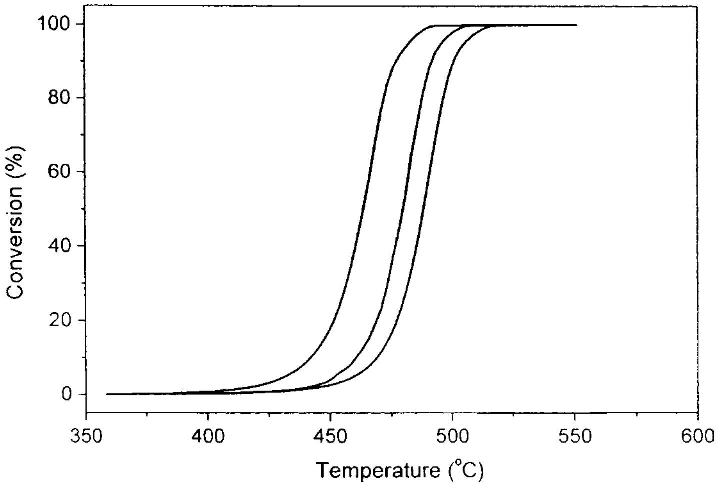

Fig. 4. Conversion of SAPO-37/HDPB in function of temperature. From left to right: 5, 10 and 20 °C/min.

single and complex reactions, using multiple heating rates.

The theory is based on the idea that, and the activation energy, $E(\alpha)$, is constant for a certain conversion (isoconversion method).A chemical reaction is measured at least three different heating rates (β) and the respective conversion curves are calculate out of the TG measured curves.

For each conversion α, ln $\beta/T^2\alpha$ is plotted against $1/T\alpha$, giving rise to a straight line with slope $-E\alpha/R$, therefore providing the activation energy as a function of conversion.

Taking the rate equation, presented as $f(\alpha)$, and dividing by the heating rate $\alpha = \mathrm{d}T/\mathrm{d}t$:

$$\frac{\partial\alpha}{\partial t} = kf(\alpha) \rightarrow \frac{\partial\alpha}{\partial T} = \frac{k}{\beta}f(\alpha) \qquad (1)$$

where $\partial\alpha/\partial t$ is the reaction rate (s^{-1}); k the rate constrant (s^{-1}); α the conversion and β is the heating rate (K^{-1}).

Replacing k by the Arrhenius equation, $k = k_0 \mathrm{e}^{-E/RT}$

$$\frac{1}{f(\alpha)}\partial\alpha = \frac{k_0}{\beta}\,\mathrm{e}^{-E/RT}\partial T \qquad (2)$$

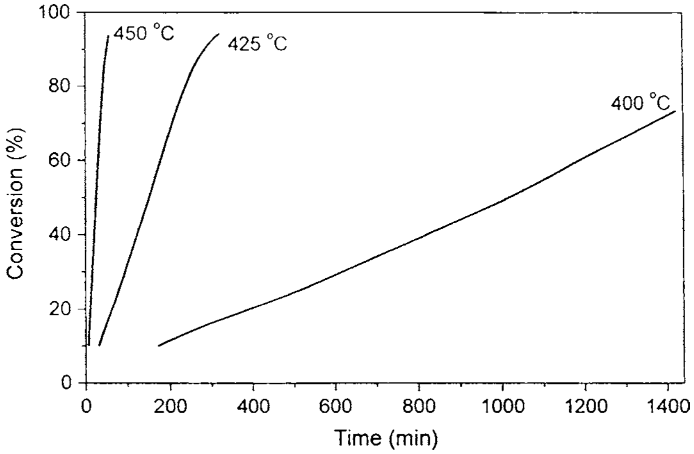

Fig. 5. Conversion of HDPE in function of time for different temperatures.

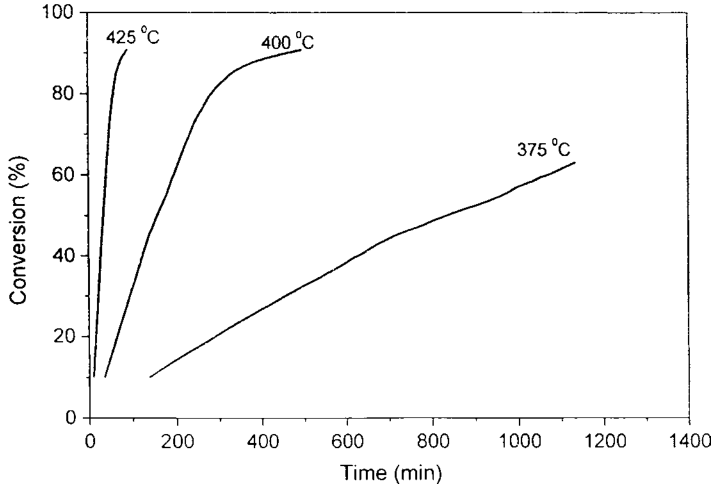

Fig. 6. Conversion of SAPO-37/HDPE in function of time for different temperatures.

Integrating up to conversion α (at the temperature T):

$$\int_0^{\alpha} \frac{1}{f(\alpha)} \partial\alpha = g(\alpha) = \frac{k_0}{\beta} \int_{T_0}^{T} e^{-\frac{E}{RT\partial T}} \quad (3)$$

Since E/2T >> the whole temperature can be estimated by:

$$\int_{T_0}^{T} e^{-\frac{E}{RT\partial T \approx \frac{R}{E} T^2 e^{-\frac{E}{RT}}}} \quad (4)$$

Substituting the whole temperature, and applying logarithm:

$$\ln \frac{\beta}{T_{\alpha}^2} = \ln\left[\frac{Rk_0}{E_{\alpha} g(\alpha)}\right] - \frac{E_{\alpha}}{R}\frac{1}{T_{\alpha}} \quad (5)$$

This equation is defined as a dynamic equation, which is used for determination of the activation energy for all conversion values. The activation energy for thermal and catalytic decomposition of HDPE is shown in Fig. 7. For HDPE, the E is ca. 290 kJ/mol whereas for ASPO-37/HDPE, this value decreased to ca. 220 kJ/mol, providing evidence of catalytic activity of the silicoaluminophosphate in the process.

The thermal and catalytic conversion of polyethylene as a function of time, for different temperatures, was estimated, noting that the time decreases considerably as a function of temperature. Also, it was possible to estimate the temperature for the HDPE

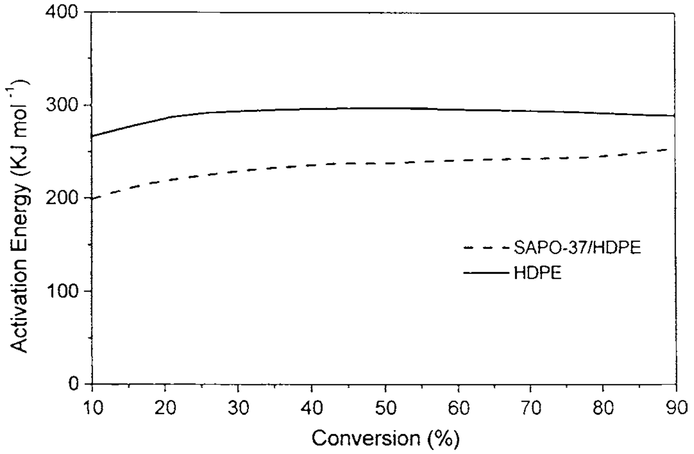

Fig. 7. Activation energy of HDPE and SAPO-37/HDPE, according to model-free kinetic method.

Table 1
Applied kinetics: *iso*-conversion parameters for HDPF

Time (min)	0 °C (%)	10 °C (%)	25 °C (%)	50 °C (%)	75 °C (%)	90 °C (%)	95 °C (%)
0	–	–	–	–	–	–	–
60	371.60	415.07	428.88	437.85	443.50	447.53	449.76
120	362.11	404.99	419.27	428.19	433.57	437.34	439.46
180	356.69	399.22	413.77	422.66	427.89	431.51	433.57
240	352.90	395.19	409.92	418.79	423.91	427.43	429.45
300	–	392.09	406.97	415.82	420.86	424.30	426.28
360	–	389.59	404.57	413.41	418.38	421.77	423.72
420	–	387.48	402.56	411.39	416.30	419.64	421.57
480	–	385.67	400.82	409.64	414.51	417.80	419.71
540	–	384.08	399.30	408.11	412.94	416.19	418.08
600	–	382.66	397.95	406.75	411.54	414.76	416.64
660	–	381.39	396.72	405.52	410.28	413.47	415.33
720	–	380.23	395.61	404.40	409.13	412.29	414.14
780	–	379.16	394.59	403.38	408.08	411.21	413.05
840	–	378.18	393.65	402.43	407.10	410.22	412.05
900	–	377.27	392.78	401.55	406.20	409.29	411.12
960	–	376.42	391.96	400.73	405.36	408.43	410.25
1020	–	375.62	391.20	399.96	404.57	407.62	409.43
1080	–	374.87	390.48	399.24	403.83	406.86	408.66
1140	–	374.16	389.80	398.56	403.13	406.15	407.94
1200	–	373.49	389.16	397.91	402.47	405.47	407.25
1260	–	372.86	388.55	397.30	401.84	404.82	406.60
1320	–	372.25	387.97	396.72	401.24	404.21	405.98
1380	–	371.68	387.42	396.16	400.67	403.63	405.39
1440	–	–	–	–	–	–	–

Table 2
Applied kinetics: *iso*-conversion parameters for SAPO-37/HDPE

Time (min)	0 °C (%)	10 °C (%)	25 °C (%)	50 °C (%)	75 °C (%)	90 °C (%)	95 °C (%)
0	–	–	–	–	–	–	–
60	–	389.86	404.67	415.37	422.60	430.21	436.72
120	–	377.36	393.06	404.25	411.58	419.60	426.53
180	–	370.27	386.45	397.92	405.30	413.53	420.71
240	–	365.33	381.84	393.49	400.92	409.30	416.63
300	–	361.54	378.31	390.10	397.55	406.05	413.51
360	–	–	375.46	387.35	394.83	40341	410.97
420	–	–	373.06	385.05	392.54	401.20	408.84
480	–	–	371.00	383.07	390.58	399.30	407.01
540	–	–	369.19	381.33	388.85	397.63	405.40
600	–	–	367.58	379.78	387.31	396.14	403.97
660	–	–	366.13	378.39	385.93	394.80	402.68
720	–	–	364.82	377.12	384.67	393.58	401.51
780	–	–	363.61	375.96	383.52	392.47	400.43
840	–	–	362.50	374.88	382.46	391.44	399.44
900	–	–	361.47	373.89	381.47	390.48	398.51
960	–	–	360.50	372.96	380.55	389.59	397.65
1020	–	–	359.60	372.09	379.69	388.75	396.85
1080	–	–	–	371.28	378.87	387.97	396.09
1140	–	–	–	370.51	378.11	387.22	395.37
1200	–	–	–	369.78	377.38	386.52	394.69
1260	–	–	–	369.08	376.70	385.86	394.05
1320	–	–	–	368.42	376.04	385.22	393.44
1380	–	–	–	367.80	375.42	384.62	392.85
1440	–	–	–	–	–	–	–

degradation processes, providing an estimate of the time required to the process at a given temperature, as summarized in Tables 1 and 2, for HDPE and SAPO-37/HDPE respectively. It was observed, for instance, that, for 90% completion of the polyethylene degradation in a period of 10 h, it is necessary to process at 415 °C, whereas for the same conversion in the same time period for SAPO-37/HDPE, the temperature required is 396 °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. HDPE alone undergoes degradation to products containing C_5 to C_{26} [16]. The catalytic reaction (SAPO-37/HDPE) led to lighter products, mainly C_2 to C_{12}, predominantly C_3 (18.4%), C_5 (12.8%), C_6 (19.4%), and C_8 (11.5%). This behavior may be due to the acid sites of the SAPO-37, which can promote polymer chain cracking. The selectivity for products with 3, 5, 6, and 8 atoms of carbons was attributed to the specific channel and cavity system of the faujastic silicoaluminophosphate (SAPO-37).

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