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Effect of the catalyst MCM-41 on the kinetic of the thermal decomposition of poly(ethylene terephthalate)

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Abstract The aim of this work is to determine the activation energy for the thermal decomposition of poly (ethylene terephthalate)—PET, in the presence of a MCM-41 mesoporous catalyst. This material was synthesized by the hydrothermal method, using cetyltrimethylammonium as template. The PET sample has been submitted to thermal degradation alone and in presence of MCM-41 catalyst at a concentration of 25% in mass (MCM-41/PET). The degradation process was evaluated by thermogravimetry, at temperature range from 350 to 500 °C, under nitrogen atmosphere, with heating rates of 5, 10 and 25 °C min^{-1}. From TG, the activation energy, determined using the Flynn–Wall kinetic method, decreased from 231 kJ mol^{-1}, for the pure polymer (PET), to 195 kJ mol^{-1}, in the presence of the material (MCM-41/PET), showing the catalyst efficiency for the polymer decomposition process.

Keywords Poly(ethylene terephthalate) · MCM-41 · Flynn–Wall kinetic model · Thermogravimetry

Introduction

Since the plastics conquered the packing market, its fraction in the urban solid residues increased significantly. In addition, plastic residues have low biodegradability along the time. Thus, the recycling appeared as one of the more promising study fronts for this end. Globally, recycling of commercial plastics is a very important way to reduce the volume of plastic waste that is sent to landfills and to conserve non-renewable petroleum resources. The route consists on the reprocessing of waste plastics in order to obtain more valuable chemical products. The concept of thermal or chemical recycling is used to transform waste plastic into chemical products, such as monomers, that can be used in the polymerization using catalytic routes.

A kinetic model is essential for evaluation the efficiency of economically conversion technologies. The properties and thermal degradation of some polymers such as PE (polyethylene) [1, 2], polycarbonate [3], ABS (acrylonitrile–butadiene–styrene) terpolymer [4] and polyolefins-oil mixtures [5] have been reported.

The application of mesoporous M41S material opened new perspectives in the absorption and catalysis fields because they present an organized structure and specific mesopore system [6]. They can be applied to conversion of molecules of voluminous size like polymers. Recent studies show the application for mesoporous MCM-41 as active catalyst for polymer degradation [7]. The degradation of polymer was done, aiming the use of polymeric residues as a source of energy to reduce the carbon monoxide concentration, providing a reduction of toxic gases, allowing the obtaining of hydrocarbons of commercial interest, specifically the range of fuels (liquefied gases, gasoline and diesel oil).

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The use of catalysts can enhance the thermal degradation of synthetic polymers which may be monitored by thermogravimetry [8–11]. In this work, the degradation of poly(ethylene terephthalate) (PET) was processed in the presence for MCM-41 and the thermal properties were investigated. The kinetics of the process was monitored by TG, using integral dynamic curves at multiple heating rates, and the activation energy was estimated from the Flynn–Wall kinetic model [12].

Experimental

The MCM-41 material was synthesized by the hydrothermal treatment of a gel with molar composition: SiO_2:$4Na_2O$:CTMABr:$200H_2O$, where CTMA represents the cethytrimethylanninioum bromide (CTMABr) as surfactant [13, 14]. In a typical synthesis, a mixture containing sodium silicate (Riedel de Haën), silica gel (Riedel de Haën) and distilled water were homogenized at 60 °C, for 2 h, under continuous stirring. To this mixture, an aqueous solution of CTMABr (Merck) was added and stirred for 1 h at room temperature. The reactive hydrogel were placed into the autoclave and submitted to a hydrothermal treatment at 100 °C for a period of 4 days. Each day, the pH was adjusted to 10 with 30% acetic acid solution. For the structure stabilization, sodium acetate (Carlo Erba) was added to the product and the material was heated for 1 day more. The obtained material was washed with a 2% vol HCl/EtOH solution, recovered by filtration and dried at 100 °C for 2 h, and then calcined at 550 °C with nitrogen for 1 h, and for an additional time of 1 h in air, at a heating rate of 2.5 °C/min.

The characterization of the material was carried out from X-ray diffraction (Rigaku), thermal analysis (TG-SDTA model 2960, TA Instruments), scanning electron microscopy (Stereoscan-440), and nitrogen adsorption isotherm analysis (Micromerities–ASAP 2000). These techniques are frequently used for determine the typical MCM-41 mesoporous structure [6].

Poly(ethylene terephthalate), in powder form (50 mesh), was obtained from Recipet of Brazil. The kinetic parameters for decomposition of the PET alone and with catalyst (PET/MCM-41) were determined in a simultaneous TG/DTA (model 2960, TA Instruments), in the temperature range from 300–500 °C, with heating rates of 5, 10 and 20 °C/min and atmosphere of nitrogen flowing at 100 mL min^{-1}. Applying the Flynn–Wall multiple heating rate kinetic model, the values of activation energy for the processes were determined. The calcined MCM-41 was added to the PET at a concentration of 25 wt%.

Results and discussion

The X-ray difractogram of the MCM-41 synthesized material is shown in Fig. 1. This technique shows that the hexagonal structure of mesoporous MCM-41 was formed after calcination of the material. The XRD pattern shows five peaks of the reflection planes (100), (110), (200), (210) and (300). The presence of a very intense peak of the reflection plane (100) already shows the formation of mesopores structure. However, the presence of five peaks confirms the obtaining of a high quality material with well-defined structure of mesopores and a mesoporous parameter (a_0) equivalent to 4.25 nm.

Figure 2 shows the isotherms of adsorption and distribution of pore size diameters obtained for MCM-41. It can be observed that the isotherm was type IV, characteristic of mesopore materials. The value of surface area of the material, performed correlating the data of nitrogen adsorption isotherms from the BET method at 77 K in the range P/P_0 from 0.05 to 0.20, was equivalent to 835 m^2g^{-1}. The distribution of pore diameter was obtained correlating the values of adsorbed volume as a function of relative pressure (P/P_0) of pores in the range 10 to 100 Å, obtaining a value of 2.3 to 2.6 nm.

The analysis by scanning electron microscopy was carried out in order to observe the morphology of the material. It can be observed in Fig. 3 that the sample of MCM-41 showed the level of particulate microstructure predominantly of small particles in the range of 0.5–1.5 µm. The morphologies of the particles were similar among themselves, mostly uniform, giving the appearance of small plaques, some of them connected and others similar to grains of rice, indicating that the obtained phase corresponds to MCM-41, as verified by XRD analysis and adsorption of nitrogen.

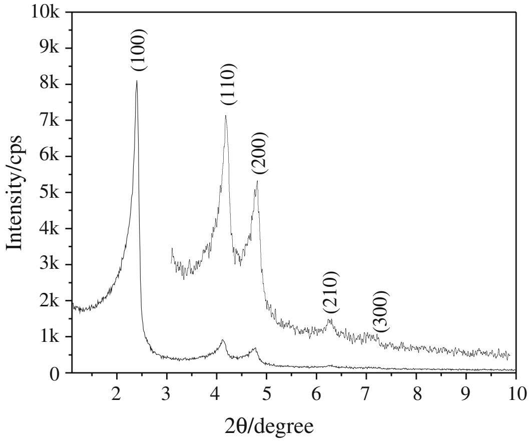

Fig. 1 X-ray diffractogram of the MCM-41 nanostructured material

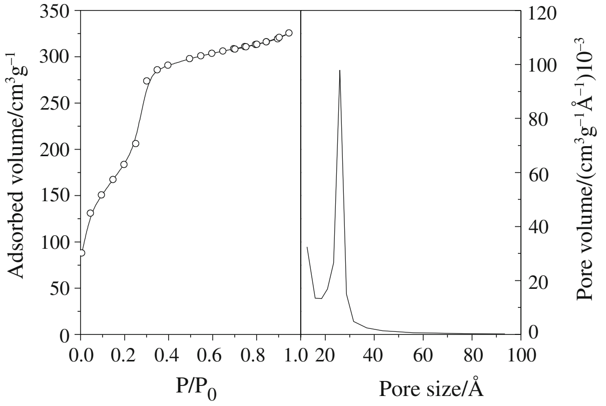

Fig. 2 Nitrogen adsorption isotherm and pore size distribution for MCM-41

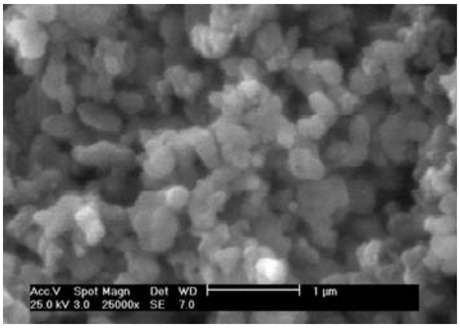

Fig. 3 Scanning electron micrography of the MCM-41

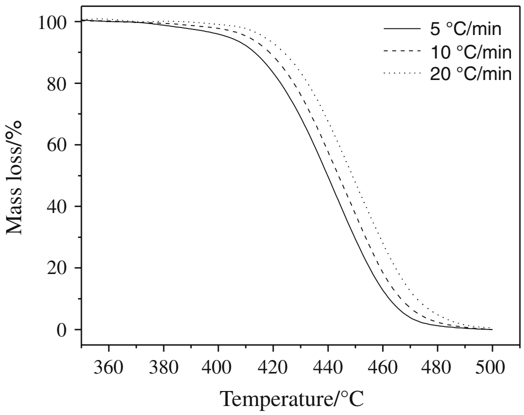

Fig. 4 TG curves for decomposition of PET without catalyst

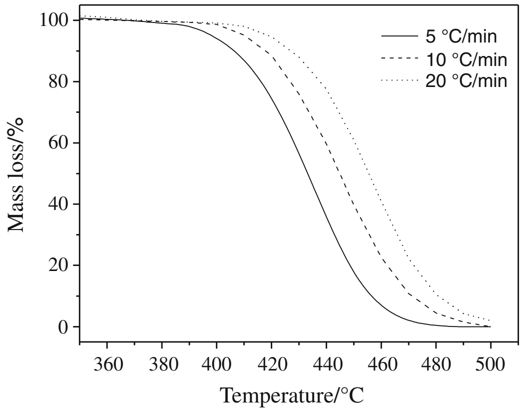

Fig. 5 TG curves of decomposition of PET mixed with MCM-41 catalyst

The global determination of the kinetic parameters for the decomposition of PET using the Flynn–Wall model based on thermogravimetric data is receiving considerable attention. The determination of an activation energy parameter from a single integral thermogravimetric analysis curve needs repeated regression analysis. Differential method based on Flynn–Wall mode is able to present a quick, simple method for determining activation energies directly from mass loss versus temperature at several heating rate. In summary, this method for determining the activation from thermogravimetric plots involves only the reading of the temperature at a constant weight loss from TG curves at different heating rates [15].

The kinetic study of the thermal decomposition of the materials by thermogravimetry (TG) has been a useful tool for estimate polymer half-life in certain conditions, as well as it allows calculating the kinetic parameters involved in the process. Some factors are decisive for these parameters calculation, as the experimental conditions (sample mass, type of sample support, heating rate and atmosphere) and the calculation method employed. Once the calculated parameters are dependent on the calculation method used, integral methods were chosen in this work based on Osawa–Flynn–Wall method [15–18]. This method limitation is that it is only applicable to samples with a single decomposition stage and whose kinetics should be of first order.

The velocity of the catalyst cracking of polymer, depends on the conversion (α), temperature (T) and time of reaction (t). In each process, the reaction velocity is given as a function of conversion f(α) and can be determined from experimental data.

Plots of mass loss versus temperature of PET and mixture MCM-41/PET at three different heating rates, using nitrogen flowing at a rate of 20 mL min^{-1} are shown in Figs. 4 and 5. Each sample has a typical mass loss region. Thermal decomposition occurred in the range of 400–490 °C for PET and at 380–480 °C for PET/MCM-41. This temperature difference between the two samples evidenced the catalytic effect of the mesoporous MCM-41 material for the process of PET decomposition.

On the basis of the results of thermogravimetric analysis of samples, apparent energies of activation for overall degradation of polymer can be determined by considering rate of mass loss curves against temperature. Since the

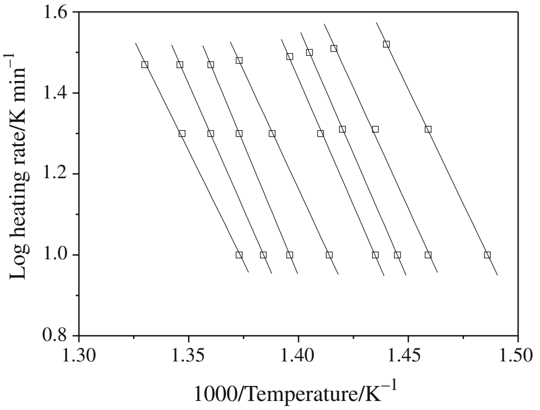

Fig. 6 Curves for determination of the activation energy using the Flynn–Wall kinetic method for PET without catalyst

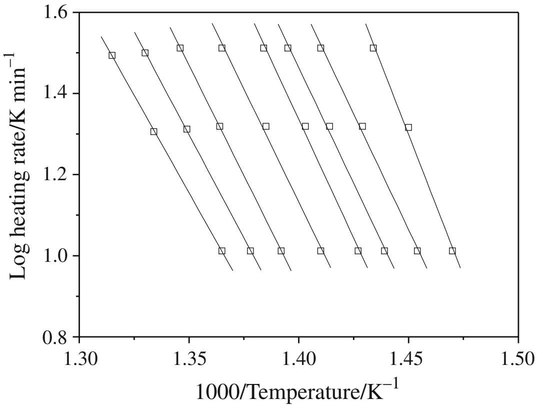

Fig. 7 Curves for determination of the activation energy using the Flynn–Wall kinetic method for PET mixed with MCM-41 catalyst

mass loss is indicative of the scission of the chemical bonds leading to volatilization, it is clear from Figs. 4 and 5 that even at the lowest heating rate, this process becomes noticeable only above de 360 °C.

The activation energies (E_a) in kJ mol^{-1} for the thermal degradation of the PET and MCM-41/PET were determined from the slope of the logarithm of heating rate curve as a function of reciprocal temperature, as visualized in the Figs. 6 and 7. The linearity, function for the thermal degradation rates confirms that the adopted kinetic model can be used to evaluate the polymer degradation.

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

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

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

$$E \cong -18.2\frac{\partial \log \beta}{\partial 1/T} \qquad (2)$$

Thus, it was 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.

It can be stated that Flynn–Wall methods work well in any conversion grade. The activation energy observed for the degradation of PET was 231.0 kJ mol^{-1}, compared with 195.7 kJ mol^{-1} for MCM-41/PET, evidencing that the mesoporous MCM-41 acted as a catalyst for degradation of PET.

Conclusions

The MCM-41 material was well synthesized and characterized by XDR, SEM, and BET surface area. The effect of the material on the kinetic of the thermal decomposition of PET was evidenced by a decreasing on the activation energy of the process when the MCM-41 was used as catalyst. The nanoporous MCM-41 material exhibits surface properties, such as specific area and pore size adequate for application as catalyst for polymer recycling. Thermogravimetry was the main technique, which can be used in satisfactory way to monitor the effective participation of the MCM-41 catalyst on the process. The linearity, function for the thermal decomposition rates confirms that the adopted kinetic model can be used to evaluate the polymer degradation.

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