Available online at www.sciencedirect.com
SCIENCE DIRECT
Catalysis Today 107–108 (2005) 507–512
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Thermo gravimetric kinetics of polypropylene degradation on ZSM-12 and ZSM-5 catalysts

José Geraldo A. Pacheco Filho [a,*], Emerson Cruz Graciliano [a], Antonio Osimar S. Silva [b], Marcelo J.B. Souza [b], Antonio Souza Araujo [b]

[a] *UFPE, Departamento de Engenharia Química, CTG, Av. Prof. Arturde Sá, S/N, Cidade Universitária, 50.740-521 Recife, PE, Brazil*
[b] *UFRN, Departamento de Química, CP1662, 59078-970 Natal-RN, Brazil*

Available online 22 August 2005

Abstract

The growth in waste plastics discarded each year is causing significant environmental problems. Polypropylene, mainly used to make car parts, pieces of furniture, fibers, fabric and film, represents 22 wt% of thermoplastic demand in the world. An alternative to this problem is chemical recycling in order to have a cheap source of useful chemicals and energy. In this work, the kinetics of catalytic thermo gravimetric degradation of polypropylene used in domestic furniture was investigated using ZSM-12 and ZSM-5 catalysts. The ZSM-12 catalyst demonstrated lower activation energy and higher activity in comparison with thermal degradation without a catalyst. A ZSM-12 zeolite content of 30 wt% in the mixture of polymer was sufficient to obtain high degradation conversions. The application of model-free Vyazovkin kinetics showed that to obtain 95% polypropilene degradation on ZSM-12 in 60 min required a temperature of 328 °C. This temperature was 55 °C lower than the thermal degradation for pure polymer. The ZSM-12 activity was more efficient than that of ZSM-5 under the same operational conditions.

Keywords: Catalytic degradation; Polypropylene; ZSM-12; ZSM-5; Model-free kinetics

1. Introduction

Polypropylene (PP) is mainly used to make car parts and domestic items of furniture by extrusion or injection, fibers, fabric, sorbents and film. Polypropylene has a high resistance to chemicals and a relatively high melting point, so it is useful for storing hot liquids. This polymer represents 22 wt% of the demand for thermoplastics in the world [5]. Plastic waste production is high because recycling is still inadequate. This kind of waste corresponds to 20% of landfill weight [1]. In order to recycle plastic waste, the material must be clean and of the same type of plastic, so this is not considered a long term solution [2]. An alternative to this problem is to incinerate plastic waste to obtain a source of energy. This, however, forms toxic flue gases due to the incomplete combustion of the solid particles [3]. A recent alternative is to transform this residue into hydrocarbons in order to produce chemicals or gasoline by thermal or catalytic degradation. In thermal cracking, the temperatures required are from 500 to 850 °C and the product obtained from this method has a very wide hydrocarbon distribution [4].

Catalytic degradation requires lower temperatures, from 350 to 550 °C, and the chemical distribution of the product is narrower than in thermal degradation, leading to the production of more valuable products [5]. Typical catalysts used for polymer degradation are acidic solids like amorphous silica-alumina, zeolites, mesoporous materials and activated carbon [6]. Polypropylene and polystyrene (PS) degradation on ZSM-5 produces a large quantity of aromatic compounds. Degradation by PS produces a large amount of coke on the surface of the catalyst [6]. Similar results were obtained when using PP degradation on natural

* Corresponding author.
E-mail address: gera@ufpe.br (J.G.A.P. Filho).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.07.065

zeolite clinoptilolite [4]. An important feature of catalytic degradation is the need for proper contact between the polymer and the catalyst to minimize degradation residues. The fluidized bed reaction displayed sufficient yields for polymer degradation, according to Luo et al. [2]. Aguado et al. [1] have carried out catalytic cracking of pure polyethylene (PE) and polypropylene on beta zeolite at a ratio of polymer/catalyst equal to 50:50, in a reactor at 400 °C, obtaining product distribution with 70 wt% in the gasoline range (C5–C12). Luo et al. [2] obtained 70–90 wt% of C5–C8 liquid hydrocarbons, 5–20% of gases and 5–10% of residue in the degradation of PE and PP on a silica-alumina in a fluidized bed at 475 °C. The degradation of PP and PS with ZSM-5 produces a large amount of aromatics, but the PS produces a large amount of coke on the surface of the catalyst [6].

In order to design an industrial unit to convert plastics into hydrocarbons, it is necessary to understand the kinetics of polymer degradation. The kinetics of PE degradation on SAPO were studied, using the model-free Vyazovkin method [7–9]. It should be noted that studies concerning the degradation of real plastics with additives used for producing useful pieces of furniture has not been well reported in the literature. The ZSM-12 is a unidimentional porous silica-rich zeolite with 5.5 Å × 5.9 Å diameter [14]. This zeolite has not been widely tested for polymer degradation. The paper sets out to study the kinetics of polypropylene degradation on ZSM-12 and ZSM-5 zeolites with different catalyst contents, with a view to providing data that can be used to design future industrial plants which will transform waste plastics into hydrocarbons.

2. Experimental

The ZSM-12 zeolite was synthesized by the hydrothermal method, using amorphous silica (Merk) as the source of silicon, sodium hydroxide (Merk), pseudoboehmite Catapal B (Vista Chemical, 70% Al_2O_3) as the source of aluminum and methiltriethylammonium chloride (98% MTEACl, Sigma) as the structural template. The precursors were added in stoichiometric proportion to obtain a gel with the following molar composition: $20MTEACl{:}10Na_2O{:}x\text{-}Al_2O_3{:}100SiO_2{:}2000H_2O$. The gel was heated at 140 °C for 144 h in a Teflon autoclave. After crystallization, the autoclave was cooled to room temperature and the solid phase was separated from the liquid phase by vacuum filtration, washed with distilled water and dried at 100 °C for 12 h. The solid was calcined and submitted to three successive ion exchange processes with 1 M NH_4Cl solution to obtain the acidic form HZSM-12 zeolite. HZSM-5 was synthesized in a similar way, using amorphous silica (Merk), sodium hydroxide (Merk), aluminum sulphate hexahydrate (Merk) and tetraproylammonium bromide (Merk) as the template. The gel obtained by means of stoichiometric proportion was heated at 150 °C for 168 h in a Teflon autoclave. The bulk structure of the zeolites was confirmed by XRD (Rigaku) analysis with Cu Kα radiation. The acidic properties of the catalysts were determined by using *n*-butylamine as the molecular probe, followed by TGA, according to procedures described in the literature [15]. The specific total surface area of the catalysts was measured using a BET apparatus (Micromeritics ASAP 2010). The micropore specific area was measured by the t-plot method [17]. The macropore and mesopore specific area was determined by the difference between the total area and the micropore area. The crystallite size was determined by SEM spectroscopy (Phillips).

A polypropylene sample SM-6100 from Polibrasil S/A with 12 wt% of calcium carbonate, for use in making domestic furniture, was used for kinetic measurements. The polymer has a density of 0.9×10^3 kg m^{-3}, a melting temperature (ASTM D-1525) of 152 °C and a melting index (ASTM D-1238, 230 °C, 16 kg) equal to 11.5 g/10 min. The sample was injected and mechanically pulverized to obtain a powder. The catalysts were thoroughly mixed with the polymer sample before the kinetics experiments, in a ratio of 10, 30 and 50 wt%. The degradation of the polymer was carried out using Mettler-TGA/SDTA851 TG equipment with a temperature range from 30 to 900 °C, under a nitrogen flow of 25 ml min^{-1} and different heating rates: 5, 10 to 20 °C min^{-1}. Five grams of polymer mixed with catalyst were used. The Vyazovkin model-free kinetics method was employed to obtain activation energies and polymer conversion data for different temperatures and reaction times.

3. Results

As can be seen from Figs. 1 and 2, the DRX analyses of synthesized HZSM-12 and HZSM-5 showed that these catalysts were highly crystalline without contaminant phases. Textural and physical–chemical characteristics for both catalysts as a Si/Al ratio, a specific surface area, acidity and crystallite size are illustrated in Table 1. Both zeolites show very similar acidity. The HZSM-12 showed a slightly

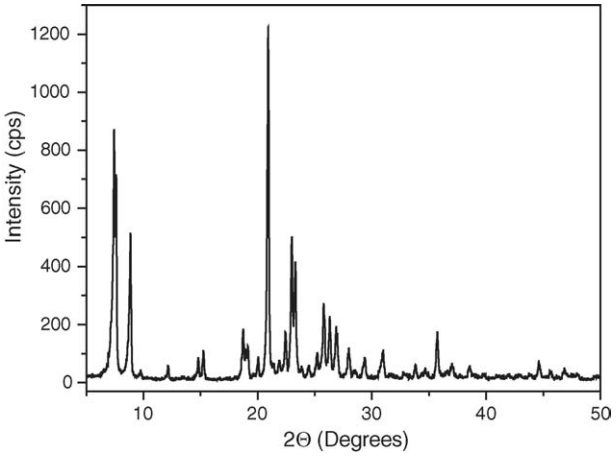

Fig. 1. X-ray diffraction pattern of the HZSM-12 catalyst.

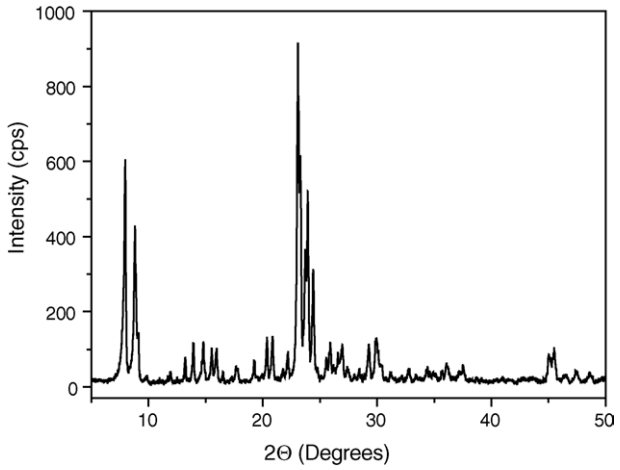

Fig. 2. X-ray diffraction pattern of the HZSM-5 catalyst.

higher Si/Al ratio and a smaller specific area than the HZSM-5. The crystallite diameter of the HZSM-12 is much smaller than that of the HZSM-5. The morphology of the catalysts crystals by SEM micrographics is illustrated in Fig. 3. The SEM pictures confirm that the catalysts are crystalline and that HZSM-5 crystallites sizes are much higher than those of ZSM-12 ones.

Fig. 4 shows the thermo gravimetric curves (TG) of pure polypropylene, containing 30 and 50 wt% of HZSM-12 catalyst, respectively. Fig. 4 displays that in the absence of catalyst, the polymer degradation pattern showed a very steep decrease, while in the presence of a catalyst, polymer degradation occurred more slowly. The loss of mass in the presence of HZSM-12 began at 320 °C and the loss of mass without catalyst started at 410 °C. This indicates that the catalytic PP degradation occurred at a lower temperature than in thermal degradation. Kim et al. [4] observed hydrocarbon production in the range C6–C12 at 350 °C for the catalytic PP degradation. Carniti and Gervasini [16] observed PP catalytic degradation at temperatures as low as 300 °C. Aguado et al. [1] also observed a significant increase in PP conversion in the presence of beta zeolite, in comparison to thermal conversion alone. Fig. 4 also shows that the initial temperature of degradation decreased when the HZSM-12 concentration was increased from 30 to 50 wt%. These results agree with those observed by Marcilla et al. [5] and Manos et al. [12] that the higher the concentration of the catalyst, the lower the PP degradation temperature, up to a minimum limit value. Manos et al. [12], in their study on PE degradation on Y zeolite, suggested the possible existence of a limiting step over the whole reaction process. Those authors assumed that large macromolecules had to react on the external surface of the zeolite catalyst first, which could be the limiting reaction step. Smaller cracked fragments can subsequently diffuse into the zeolite pores and undergo further reactions with zeolite. The more that zeolite was added, the more that polymers were in contact with it and more polymers participated in the initial degradation step [12].

The Fig. 5 shows the polymer degradation conversion as a function of temperature for pure PP and in the presence of 30 and 50 wt% of HZSM-12. It was observed that polymer degradation was more efficient in the presence of the catalyst. Similar results were observed by Araujo et al. [9] for polyethylene degradation in the presence of SAPO catalyst.

The conversion rates of polymer degradation depend on reaction time and temperature. These are different for each type of catalyst and have to be determined to aid the design of industrial reactors. For complex reactions like the polymer degradation, the mathematical model of the

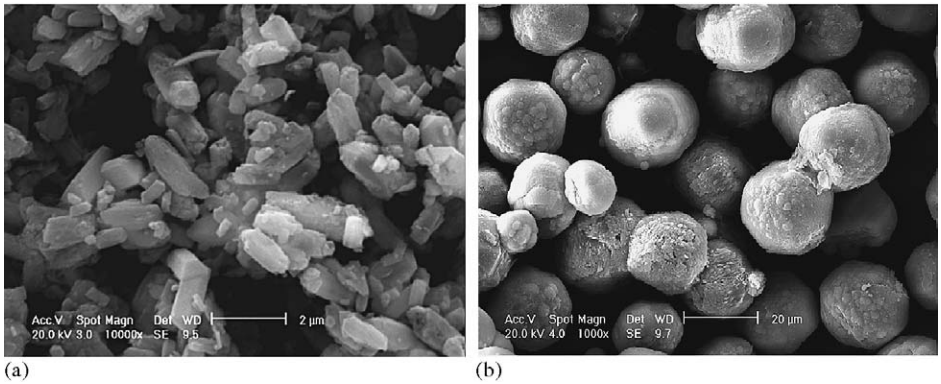

Fig. 3. Scanning electron micrographs of the HZSM-12 (a) and HZSM-5 (b) crystals.

Table 1
Textural and physico-chemical properties of the catalysts HZSM-12 and HZSM-5

Sample	Si/Al ratio	Total BET area ($m^2\ g^{-1}$)	Micropore area ($m^2\ g^{-1}$)	Macropore + mesopore area ($m^2\ g^{-1}$)	Acidity (mmol g^{-1})	Crystallite size (μm)
HZSM-12	29.3	297	271	26	0.53	2
HZSM-5	23.7	343	330	13	0.56	27

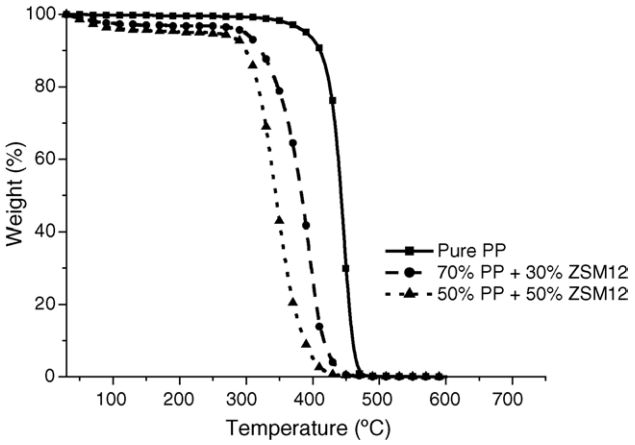

Fig. 4. Thermo gravimetric curves heated at the rate of 10 °C min^{-1} with different catalyst concentrations: 0, 30 and 50 wt%.

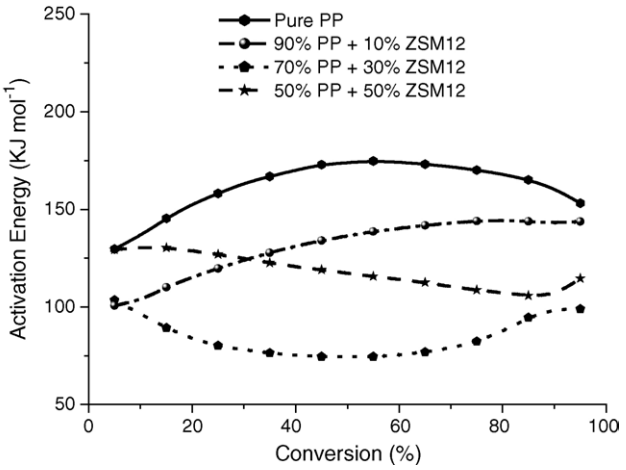

Fig. 6. Activation energy for polypropylene degradation for pure polymer and polymer containing 10, 30 or 50 wt% of ZSM-12 catalyst.

reaction rate is very difficult to obtain. In this case, model-free Vyazovkin kinetics [13] is suitable to simulate the polymer conversion as a function of temperature without requiring an explicit mathematical model.

The integral method of Vyazovkin kinetics [10,11] was developed on the premise that the activation energy can be constant for an isoconversion. In this method, the activation energy and conversion are determined as a function of time and temperature reactions, from experimental polymer thermo gravimetric degradation data, using Eq. (1).

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

where α is the degradation conversion; T_α the reaction temperature (K) in a constant isoconversion α; β the heating rate dT_α/dt (units: K s^{-1}); t the reaction time (s); R the ideal gas constant (kJ mol^{-1} K^{-1}); k_0 the pre-exponential factor of the Arrhenius equation (reaction rate constant) (s^{-1}); E_α the activation energy for an isoconversion (kJ mol^{-1}) and $g(\alpha)$ is the integrated form of the reaction rate kinetic model as a function of the conversion.

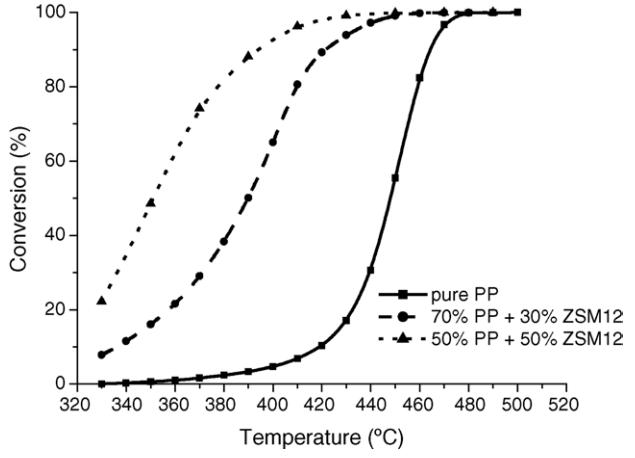

Fig. 5. Polypropylene conversion curves heated at the rate of 10 °C min^{-1} as a function of temperature at different catalyst concentration.

From polypropylene thermo gravimetric degradation data at three different heating rates 5, 10 and 20 °C min^{-1}, for each conversion α, the values of $\ln(\beta/T_\alpha^2)$ were plotted in function of $1/T_\alpha$ to estimate the equation parameters E_α and k_0. The degradation activation energy as a function of PP conversion, for pure PP or PP containing 10, 30 or 50 wt% of ZSM-12 is shown in Fig. 6. PP degradation activation energy can be observed to diminish when the catalyst concentration is increased from 10 to 30 wt%. However, using 50% of catalyst leads to activation energy greater than that with 30% of catalyst. The PP degradation with 30% of ZSM-12 diminishes the activation energy from 150 to 100 kJ mol^{-1} for an isoconversion of 95%, in comparison with degradation without a catalyst, confirming the influence of the catalyst on the activation energy of degradation.

Tables 2 and 3 show, respectively, the degradation temperature of pure polypropylene and the polymer containing 30% of ZSM-12 as a function of the reaction time for each isoconversion. This data was calculated using model-free Vyazovkin kinetics, Eq. (1). We note that the degradation time diminishes significantly when the reaction temperature is increased. From Table 2, we observe that for pure PP degradation with 95% conversion in 60 min, the

Table 2
Pure polypropylene degradation temperatures (°C) related to conversion rates and reaction time

Time (min)	Conversion (%)						
	5	10	20	50	70	90	95
30	335.03	352.63	368.44	386.92	392.76	397.68	399.23
60	319.03	336.53	353.26	372.79	378.21	381.92	382.64
120	303.85	321.23	338.79	359.25	364.28	366.88	366.85
180	295.33	312.63	330.64	351.59	356.40	358.40	357.96
240	289.43	306.68	324.98	346.27	350.93	352.52	351.80
300	284.94	302.15	320.66	342.21	346.75	348.04	347.11
360	281.32	298.49	317.18	338.92	343.38	344.42	343.33

Table 3
Polypropylene (containing 30 wt% of HZSM-12) degradation temperatures (°C) related to conversion rates and reaction time

Time (min)	Conversion (%)						
	5	10	20	50	70	90	95
30	252.97	264.09	275.52	297.85	312.30	339.19	349.81
60	237.91	247.36	255.49	273.64	288.29	318.07	327.97
120	223.69	231.64	236.87	251.40	266.16	298.37	307.61
180	215.73	222.87	226.57	239.22	254.01	287.43	296.32
240	210.23	216.84	219.51	230.90	245.72	279.93	288.58
300	206.06	212.26	214.17	224.64	239.46	274.25	282.71
360	202.70	208.58	209.90	219.64	234.46	269.69	278.02

required reaction temperature is 383 °C. Compared to another type of polymer studied by Fernandes et al. [8], pure polyethylene degradation in the same condition requires a temperature of 450 °C [8], indicating that non-catalytic degradation of polypropylene is easier than polyethylene. These results agree with those of Aguado et al. [1] who observed that the non-catalytic degradation of polypropylene has a conversion rate eight times greater then polyethylene, probably due to the high proportion of tertiary carbons in the polypropylene that may favor breakage of the C–C bonds.

From Table 3, we observe that the simulation of a 95% conversion of polypropylene degradation containing 30% of ZSM-12 in 60 min requires a reaction temperature of 328 °C. This temperature is 55 °C, lower than for the degradation of pure polypropylene.

The Fig. 7 shows the thermo gravimetric degradation curves of pure polypropylene containing 50% of ZSM-12 and 50% ZSM-5 for comparison purposes. We observe that the ZSM-12 catalyst is more active than the ZSM-5 for the degradation of polypropylene. Fig. 8 shows that the activation energy for degradation of polypropylene with ZSM-12 catalyst is smaller than with ZSM-5 for higher

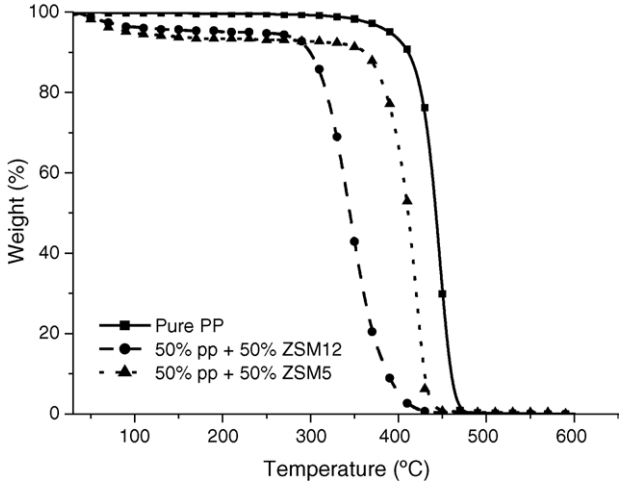

Fig. 7. Thermo gravimetric degradation curves of pure polypropylene and for polypropylene containing 50% of ZSM-12 or 50% of ZSM-5, with heating rate of the 10 °C min^{-1}.

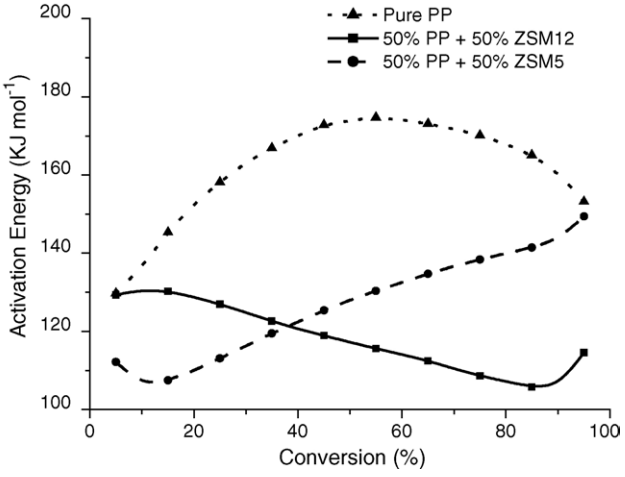

Fig. 8. Influence of the conversion on the activation energies for degradation of pure polypropylene and for polypropylene containing 50% of ZSM-12 or 50% of ZSM-5.

conversions, confirming the higher activity of the ZSM-12 catalyst. Uddin et al. [3] observed that the polypropylene and polyethylene degradation on the ZSM-5 catalyst takes place due to the presence of zeolite acidic sites. They also concluded that the activity of the FSM catalyst is due to its hexagonal structure because it is active for degradation and it has no acidic sites. According to these authors, the radicals produced during the thermal degradation of the polymer may stay for a period in the pores of the catalyst working like small reactors, thus accelerating the degradation process.

In this study, the performance of the ZSM-12 catalyst for PP degradation was more efficient than that of the ZSM-5. These catalysts showed similar acidity, as can be seen in Table 1. Thus, the performance difference may not be due solely to the acidity. The crystallite size of the ZSM-12 (Table 1) is much smaller than that of the ZSM-5. This fact indicates that the external macropore and mesopore surface of the HZSM-12 catalyst is greater than that of the HZSM-5 due to the particles having formed from small size crystallites. Thus, the HZSM-12 catalyst may act more efficiently in the reaction of cracking the large polymer molecules on its external surface, resulting in a better conversion, which is in accordance with the experimental results shown in Figs. 7 and 8. This agrees with Aguado et al. [1] who observed more efficient degradation activity with small size beta zeolite crystallites than with larger ones.

Another cause for the superior activity of the ZSM-12 catalyst may be the diameter of its channel, formed by a 12 ring member with 5.6 Å × 6.0 Å, somewhat larger than the HZSM-5 channels that are formed by a 10 ring member with 5.3 Å × 5.6 Å. If the degradation starts on the external surface, large polymer fragments are cracked, forming smaller molecules that diffuse into the zeolite pores. In the pores, the small molecules may be cracked or submitted to other reactions like isomerization and oligomerization. Then larger pore size zeolites such as the ZSM-12 are more active for polymer degradation.

4. Conclusion

The HZSM-12 and HZMS-5 catalysts showed high crystallinity and a similar specific total area, acidity and Si/Al ratio. The average diameter of the crystallite size of the HZSM-12 was much smaller than that of the HZSM-5. The polypropylene degradation in the presence of the catalyst HZSM-12 took place at lower temperatures than in thermal degradation. The temperature of PP degradation decreased and the conversion increased when the HZSM-12 concentration was increased from 30 to 50 wt%.

The HZSM-12 catalyst is more active and has less activation energy than the HZSM-5 one for the degradation of polypropylene. The crystallite size of the HZSM-12 is much smaller than the HZSM-5 one, so its external macropore and mesopore surface is greater due to the particles formed from small size crystallites. This may help the cracking reaction of the large polymer molecules on its larger external surface. Another cause for the superior faster conversion of the HZSM-12 over the HZSM-5 catalyst may be because the diameter of its channel is greater which allows larger fragments of polymer to enter the channels to be cracked.

The kinetics of the polypropylene degradation was obtained by the model-free Vyazovkin method for pure polymer (thermal degradation) and 30 wt% ZSM-12 containing polymer. The degradation time diminished significantly when the reaction temperature was increased. The zeolite ZSM-12 performed well in the degradation of polypropylene that can be recycled from used domestic furniture. This kinetics can be used to design an industrial reactor to recycle used plastics by catalytic degradation to produce hydrocarbons for fuels and chemicals. For example, for the 95% conversion of polypropylene degradation containing 30% of ZSM-12 in 60 min, a reaction temperature of 328 °C is required. This temperature is 55 °C lower than that for the degradation of pure polypropylene.

Acknowledgements

The authors are grateful for the financial support for this project, which came from the Brazilian institutions CNPq and FINEP. Polibrasil supplied the polymers.

References

[1] J. Aguado, D.P. Serrano, J.M. Escola, E. Garagorri, J.A. Fernández, Polym. Degradation Stability 69 (2000) 11–16.
[2] G. Luo, T. Suto, S. Yasu, K. Kato, Polym. Degradation Stability 70 (2000) 97–102.
[3] M.A. Uddin, Y. Sakata, A. Muto, Y. Shiraga, K. Koizumi, Y. Kanada, K. Murata, Micropor. Mesopor. Mater. 21 (1998) 557–564.
[4] J.R. Kim, Y.A. Kim, J.H. Yoon, D.W. Parka, H.C. Woob, Polym. Degradation Stability 75 (2002) 287–294.
[5] A. Marcilla, A. Gomez, J.A. Reyes-Labarta, A. Giner, Polym. Degradation Stability 80 (2003) 233–240.
[6] J.-R. Kim, J.-H. Yoon, D.-W. Park, Polym. Degradation Stability 76 (2002) 61–67.
[7] V.J. Fernandes Jr., A.S. Araujo, G.J.T. Fernandes, Stud. Surf. Sci. Catal. 105 (1997) 941.
[8] G.J.T. Fernandes, V.J. Fernandes Jr., A.S. Araújo, Catal. Today 75 (2002) 233–238.
[9] A.S. Araujo, V.J. Fernandes Jr., G.J.T. Fernandes, Thermochim. Acta 392–393 (2002) 55–61.
[10] S. Viazovkin, A.I. Lesnikovich, Thermochim. Acta 128 (1988) 297.
[11] S. Viazovkin, C.A. Wight, Thermochim. Acta 340 (1999) 53.
[12] G. Manos, A. Garforth, J. Dwyer, Ind. Eng. Chem. Res. 39 (2000) 1203–1208.
[13] S. Viazovkin, V. Goriyachko, Thermochim. Acta 194 (1992) 221.
[14] W.M. Meier, D.H. Olson, Ch. Baerlocher, Atlas of Zeolite Structure Types, Elsevier, New York, 1996, p. 158.
[15] A.S. Araujo, V.J. Fernandes Jr., S.A. Verissimo, J. Therm. Anal. Calorim. 59 (2000) 649–655.
[16] P. Carniti, A. Gervasini, Thermochim. Acta 379 (2001) 51–58.
[17] J.H. De Boer, B.C. Lippens, B.G. Linsen, J.C.P. Broekhoff, A. Van Den Heuvel, T.V. Osinga, J. Colloid. Interface Sci. 21 (1966) 405.