



Study of the conversion of low-density polyethylene over Nb₂O₅/HY composite materials

Estudo da conversão de polietileno de baixa densidade sobre materiais compósitos tipo Nb₂O₅/HY

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Due to the increase in the production of plastic waste, inadequate disposal and the long period of elimination of polymers, Brazil has been affected by serious environmental impacts. In order to avoid an expansion of the problem, catalytic pyrolysis has become a very attractive process in relation to the chemical treatment of these materials, promoting processes that require lower energy expenditure. Therefore, in this work, heterogeneous composite catalysts based on zeolite Y in acidic form, impregnated with different levels of calcined niobium oxide (10% Nb₂O₅/HY and 20% Nb₂O₅/HY) were developed via mechanochemistry. The obtained catalysts were characterized by X ray diffraction (XRD) and nitrogen adsorption at 77 K. Through these characterization techniques, it was possible to determine the structural and textural properties of the catalysts and thus be able to correlate them with their catalytic activity. The thermal and catalytic pyrolysis reactions of LDPE were carried out via Thermogravimetry (TG) at different heating rates (5, 10 and 20 °C.min⁻¹) using LDPE and LDPE + catalysts mixtures. Conversion data were correlated using the Flynn-Wall-Ozawa (FWO) and Vyazovkin (VZK) kinetic models. It was observed that the catalytic conversion curves presented lower temperature ranges than those proposed by the pure polymer and that the activation energies estimated by the two models were similar showing a good correlation of the data. As observed by the catalytic tests, the results indicated that the production of the Nb₂O₅/HY composite materials can be a good strategy to generate increased catalytic activity in the LDPE conversion process. Keywords: pyrolysis, Nb₂O₅/HY, LDPE.

Devido ao aumento na produção de resíduos plásticos, descarte inadequado e do longo período de degradação destes polímeros, o Brasil tem se deparado com sérios impactos ambientais. A fim de evitar uma ampliação do problema, a pirólise catalítica tornou-se um processo bastante atrativo em relação ao tratamento químico destes materiais, promovendo processos que demandem menores gastos energéticos. Desta forma, neste trabalho foram desenvolvidos via mecanossíntese, catalisadores heterogêneos compósitos a base da zeólita Y na forma ácida, impregnada com diferentes teores de óxido de nióbio calcinado (10 % Nb₂O₅/HY e 20 % Nb₂O₅/HY). Os catalisadores obtidos foram caracterizados por difração de raios X (DRX) e adsorção de nitrogênio à 77 K. Através destas técnicas de caracterização, foi possível determinar as propriedades estruturais e texturais dos catalisadores e assim poder correlacionar com sua atividade catalítica. As reações de pirólise térmica e catalítica do PEBD foram realizadas via Termogravimetria (TG) em diferentes taxas de aquecimento (5, 10 e 20 °C.min⁻¹) usando PEBD e misturas de PEBD + catalisador. Os dados de conversão foram correlacionados através dos modelos cinéticos de Flynn-Wall-Ozawa (FWO) e Vyazovkin (VZK). Foi observado que as curvas de conversão catalíticas apresentaram faixas de temperatura inferiores às apresentadas pelo polímero puro e que as energias de ativação estimadas pelos dois modelos foram similares indicando uma boa correlação dos dados. Conforme observado pelos testes catalíticos, os resultados indicaram que a produção do material compósito Nb₂O₅/HY pode ser uma boa estratégia para gerar aumento da atividade catalítica no processo de conversão do PEBD. Palavras-chave: pirólise, Nb₂O₅/HY, PEBD.

1. INTRODUCTION

Plastic waste has been a major problem for humanity over the years. Since, after being used, plastics are transformed into waste causing serious environmental problems [1]. Most of these residues are deposited in landfills and due to their chemical inertness and low biodegradability, these residues end up staying in the place for a long time, taking up a lot of physical space for the destination of the materials [2].

Faced with this problem, much has been discussed by the scientific community about ways to mitigate the problems caused by the disposal of plastic waste [3, 4]. Alternatively, there are methods of direct incineration, in which plastic waste is transformed into energy. However, this process produces toxic substances that are harmful to the environment [5]. Recycling and reusing of plastic are the best options, since in addition to reducing the amount of solid waste, saving energy and raw materials, they promote high process efficiency and increase the useful life of landfills [6].

There are different types of plastics, with a wide variety of characteristics and properties, which help in the numerous applications of these materials. The most widely used types of plastic are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyurethane (PU), polyvinyl chloride (PVC) and polyethylene terephthalate (PET) [7]. Among them, PE has stood out due to its unique properties, such as high molecular weight, semicrystalline structure (between 50-80 %), ease of processing, flexibility and chemical inertia, representing approximately 40 % of the applications of thermoplastic resins currently used [8], in addition to presenting constant works in the literature related to its use and reuse [9-11]. Although they have several industrial applications, their main use is in the production of plastic packaging, since they are inert against most chemicals due to their paraffinic nature and their high molecular weight.

Depending on the conditions of the system used, various types of polyethylene may be produced. This diversity is provided by the various existing polymerization processes [12]. Thus, the PE obtained can have different amounts and sizes of branches, varying degrees of crystallinity, in addition to different points of density and melting temperature, each type having specific applications according to their properties. The main commercial forms are high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) [13].

Among them, LDPE has a unique combination of properties: toughness, high flexibility and impact resistance, good processability, among others. When produced in the form of thin film, they have high transparency, which gives them efficiency in plastic bag applications [13]. Due to its remarkable electrical properties, as an insulator, it is widely used in the coating and insulation of electrical cables [6]. As LDPE has characteristics and properties that other types of PE do not have, there is a tendency to increase demand and study [10, 13, 14].

Valim (2015) [15] characterized the LDPE recycled with Al particulates from long-life packaging for the formation of composites. Bezerra (2016) [16] studied chemically recycled LDPE residues, using modified vermiculite as a catalyst for the final production of light hydrocarbons, which can later be used as raw material for the chemical and petrochemical industry. Coelho et al. (2010) [17] made a comparison between the thermal and catalytic degradations of LDPE and HDPE using catalysts based on transition metals (V, Zr and Ni) supported on zeolite Y (NaY and HY). The authors found that this structuring of the catalysts was able to promote the degradation process of polyethylene with varying efficiencies.

One of the treatment processes of these polymers is through the pyrolysis method, in which it is a process of thermal decomposition of organic materials through the breaking of C-C bonds, resulting in the formation of many chemical compounds and with several applications [18]. However, despite many studies, thermal degradation is a relatively more expensive process, requires high temperatures and controlled pressures, an inert atmosphere and the quality of the products obtained is still reduced, which ends up limiting the viability of the process [18]. One solution is to improve the process with the presence of appropriate catalysts, such as zeolites, providing a reduction in the degradation reaction temperature and an increase in the selectivity of products with greater added value [19-21]. Garcia et al. (2005) [21] studied and demonstrated the advantages of thermocatalytic degradation over thermal using HDPE and hybrid zeolites as

catalysts. Zeolites are highly crystalline aluminosilicates [22] and these materials have a great influence on the catalytic degradation of polymers due to their characteristics of strong acidity and ability to break down hydrocarbons, significantly reducing the temperature and reaction time of the process. These characteristics provide the obtainment of products with a better quality and in a greater range of hydrocarbons [23]. Several types of zeolites have been tested and studied as catalysts for catalytic pyrolysis processes [9, 11, 19]. Zeolite Y, for example, is widely used in adsorption and catalysis processes, due to its properties such as high specific surface area, acidity, excellent thermal stability and good activity and selectivity [11, 17, 24]. These materials act by differentiating the molecular size of the particles through their regular pores, thus leading to a molecular sieving effect [22]. In order to obtain materials with improved characteristics that can be applied in different processes, the development of multifunctional materials has been increasingly studied [25-27]. From this process, it is possible to combine materials with complementary properties, generating a single material that is more improved and efficient, with different properties from those of the original components that are not conventionally found. The structure can generate a solid compound that is attractive for industrial purposes, at a low cost, especially for catalysis applications [25]. Thus, some studies have used oxides to increase the surface area and catalytic activity of catalysts [26, 27]. Within this group, niobium-based compounds have exhibited special properties for different catalytic reactions, such as good selectivity and chemical stability, large surface area and strong interaction with other metals, which justifies its use as a catalyst [28]. In addition, Brazil is the world's largest producer of niobium, corresponding to 90 % of world demand. Thus, the proven catalytic properties of niobium and its availability make the great interest in studying the behavior of this material in different processes justified [28]. Tanabe and Okazaki (1995) [29], studied niobium compounds such as niobium pentoxide (Nb_2O_5), niobic acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$), niobium phosphate (NbOPO_4) and mixed oxides that contain niobium ($\text{Nb}_2\text{O}_5\text{-SiO}_2$; $\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3$), and have been shown to be useful as catalyst promoters and supports, and for selective oxidation catalysts. Nakajima et al. (2010) [30] studied the structure and acid catalysis of mesoporous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, and the results suggested that mesopores consisting of hydrophilic niobium oxide are advantageous for hydrophilic reactions, but not for hydrophobic reactions. Heitmann et al. (2016) [31] dispersed niobium oxyhydroxide (NbO_2OH) over the Poly(3-hydroxybutyrate) and studied the catalytic activity of the catalyst in the degradation of methylene blue dye ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$). The authors observed that the material showed excellent catalytic activity (degradation of approximately 100 %) for the oxidation of the dye, as well as, the polymer films were easily removed from the solution after the reaction and reused several times, maintaining its high activity.

Thus, this work addresses an interesting topic from the point of view of scientific, technological and environmental research, promoting the removal of environmental pollutants and the investigation of the energetic potential of catalytic materials aiming at obtaining products of high added value through the catalytic pyrolysis of LDPE. At the same time, due to the scarcity of scientific studies linked to the study of the catalytic activity of $\text{Nb}_2\text{O}_5/\text{HY}$ compounds, this work has the main objective of studying the efficiency of heterogeneous microporous catalysts (especially HY zeolite) impregnated with different ratios of niobium oxide (Nb_2O_5) for thermal and catalytic pyrolysis of low-density polyethylene (LDPE).

2. MATERIALS AND METHODS

2.1. Materials preparation

The zeolite Y used in the work was obtained from its sodium form (NaY, Sigma Aldrich). The HY zeolite was obtained by the ion exchange method adapted from literature [32]. Nb_2O_5 was obtained from hydrated niobium oxide (CBMM – Companhia Brasileira de Metalurgia e Mineração) and subjected to a calcination process at 300 °C in a Mufla oven (Quimis®) with a heating rate of 10 °C.min⁻¹ for 2 hours, obtaining the material calcined ($\text{Nb}_2\text{O}_5\text{-C}$). $\text{Nb}_2\text{O}_5\text{-C}$ was incorporated into HY zeolite through the mechanosynthesis process [33]. Composite catalysts of 10 % $\text{Nb}_2\text{O}_5/\text{HY}$ and 20 % $\text{Nb}_2\text{O}_5/\text{HY}$ (in mass proportions of $\text{Nb}_2\text{O}_5\text{-C}$) were also obtained via

mechanosynthesis, starting from the individual materials previously prepared (HY and Nb₂O₅-C), with uniform homogenization for 5 minutes. The obtained materials (HY, Nb₂O₅-C, 10 % Nb₂O₅/HY and 20 % Nb₂O₅/HY) were subjected to structural characterization and catalytic pyrolysis tests.

2.2. Characterization

The XRD analysis of the HY, Nb₂O₅-C, 10 % Nb₂O₅/HY and 20 % Nb₂O₅/HY catalysts were obtained by the powder method in a Panalytical Empyrean TCU 1000N diffractometer with CuK_α (1.5418 Å) radiation source, voltage 40 kV, current 40 mA, step 0.026° and scanning speed of 2°.min⁻¹ and an angular range of (2θ) was used from 5 to 55°. The diffractograms obtained were used for identification of the crystalline structure of the materials and identify the presence of contaminant phases by comparison with literature data [34]. The crystallinity degree of the materials was determined by comparison of the sum of the intensities of the most intense peaks of diffractogram at (2θ) = 6.23°; 15.67°; 18.69°; 20.38°; 23.67° and 27.08°, indexed to their respective crystallographic plans in relation to the Faujasite structure, and with sum of the intensities of the most intense peaks of a standard material (Faujasite structure).

The adsorption isotherms of the materials were obtained through the adsorption and desorption of nitrogen at 77 K, in a Micromeritics equipment, model ASAP 2020. For the analysis of the samples, about 0.15 g of the materials were previously dried at 350 °C, under vacuum, for 3 hours, to then be subjected to nitrogen adsorption. The adsorption/desorption isotherms of N₂ for the samples were obtained in the relative pressure range P/P_0 from 0.015 to 0.995. Through isotherms, through the volume of adsorbed gas and correlation via mathematical models by the methods of Brunauer et al. (1938) [35] and Lippens and Boer (1965) [36], textural properties were determined, such as pore volume and specific surface areas.

2.3. LDPE conversion

The LDPE thermal and catalytic pyrolysis tests were performed on a thermal analysis equipment TG/DTG from Shimadzu model DTG-60H, under an inert and dynamic N₂ atmosphere, with a flow of 50 mL.min⁻¹, at heating rates of 5, 10 and 20 °C.min⁻¹. The LDPE sample used in this work was obtained from Sigma Aldrich in powder form. The thermogravimetric curves were obtained by heating the pure LDPE (thermal pyrolysis) and the LDPE mixed with the catalysts HY, Nb₂O₅-C, 10 % Nb₂O₅/HY and 20 % Nb₂O₅/HY (catalytic pyrolysis) via the mechanical mixture, in a weight's ratio of 80% of the polymer and 20% of the catalysts. The studies were carried out in the temperature range of 30 to 900 °C, using approximately 10 mg of sample for each test. From the non-isothermal kinetic models proposed by Flynn-Wall-Ozawa (FWO) [37] and Vyazovkin (VZK) [38], the activation energies of the LDPE thermal and catalytic degradation reactions were determined.

2.4. Kinetic method

For the realization of kinetic were used the FWO [37] and VZK [38] models. The FWO model assumes that the thermal decomposition kinetics obeys a first order equation, using thermogravimetric analysis and constant heating rates. The expression for the FWO model is given by equation 1.

$$\log(\beta) = -0.4567 \left(\frac{E_{\alpha}}{RT} \right) - 2.315 + \log \left(\frac{AE_{\alpha}}{Rg(\alpha)} \right) \quad (1)$$

This equation is widely used in kinetic studies of thermal degradation. For a process where a sample is subjected to controlled heating, under a certain heating rate β , the slope of the lines obtained for $\log(\beta)$ versus $1/T$ is equal to $-0.4567(E_{\alpha}/R)$ and T is the temperature to reach a

certain degree of conversion. Starting from each slope it is possible to obtain the apparent activation energy. In the VZK model (equation 2) for the determination of E_α through the slopes of the linear regression of the graphs of $\ln(\beta/T^2)$ versus $1/T$, for all conversion values [38]. In this equation the slope is given by $-E_\alpha/R$ and is used to obtain the apparent activation energy to each conversion.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{RA}{E_\alpha g(\alpha)}\right) - \frac{E_\alpha}{RT} \quad (2)$$

3. RESULTS AND DISCUSSION

Figure 1 shows the X ray diffractogram for the HY zeolite obtained in this study. The structure shown in the diffractogram is similar to zeolite taken as a comparison standard reported in Treacy and Higgins (2007) [34]. Well-defined and narrow peaks are observed indicating that zeolite is characterized by high crystallinity and purity. Comparing all reflections of the diffractogram of the HY zeolite with a standard 73-2310 file from the database of the Joint Committee for Powder Diffraction Studies - International Center for Diffraction Data (JCPDS - ICDD), and with data from the literature [32, 34], it can be seen that the sample is formed by a material with a faujasite type structure. This diffractogram shows intense diffraction peaks at angles $2\theta = 6.23^\circ$; 10.15° ; 11.91° ; 15.67° ; 18.69° ; 20.38° ; 22.82° ; 23.67° ; 25.82° ; 27.08° ; 29.66° ; 30.79° ; 31.42° ; 32.48° ; 34.13° and 37.97° , indexed to their respective crystallographic plans in relation to the Faujasite structure [34].

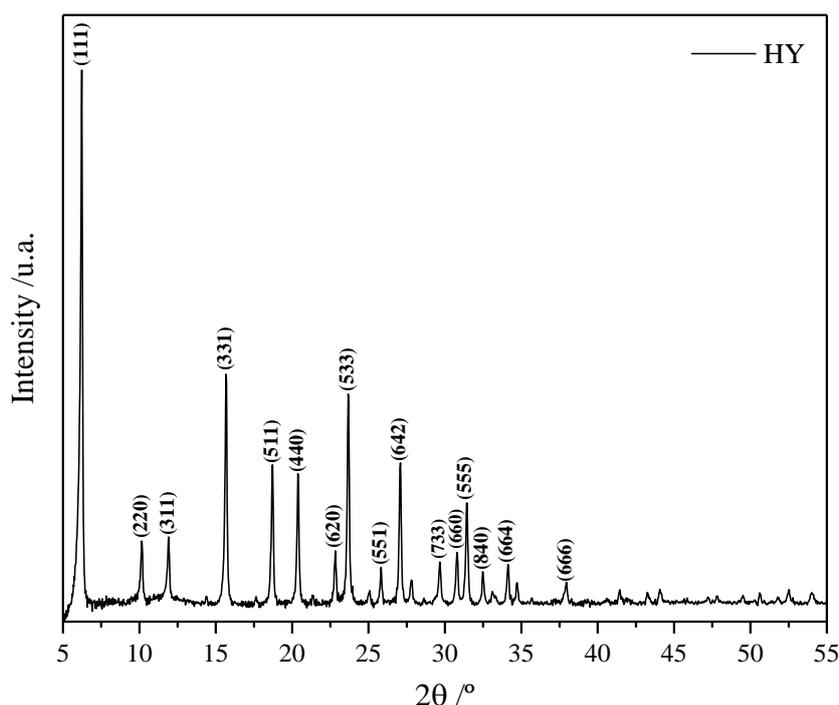


Figure 1: X ray diffractogram of the HY zeolite.

Figure 2 shows the diffractograms of calcined Nb_2O_5 and $\text{Nb}_2\text{O}_5/\text{HY}$ catalysts in both proportions (10 % $\text{Nb}_2\text{O}_5/\text{HY}$ and 20 % $\text{Nb}_2\text{O}_5/\text{HY}$). It is observed that no crystalline peak was formed in the diffractogram of the Nb_2O_5 calcined at 300°C , showing a totally amorphous structure, as reported in the literature [25]. The diffractograms of the 10 % $\text{Nb}_2\text{O}_5/\text{HY}$ and 20 % $\text{Nb}_2\text{O}_5/\text{HY}$ catalysts showed diffraction peaks characteristic of the HY zeolite (Figure 1), thus confirming that after the mechanosynthesis process, the zeolite structure in the catalyst was maintained. XRD of Nb_2O_5 highlight the absence of peaks, as well as the presence of a halo

centered at 2θ close to 26° , which is typical of amorphous materials. In parallel, no XRD pattern related to any Nb_2O_5 species was observed for the current $\text{Nb}_2\text{O}_5/\text{HY}$ catalysts, suggesting a high dispersion of this oxide over the zeolite structure, regardless of the niobium oxide load [25].

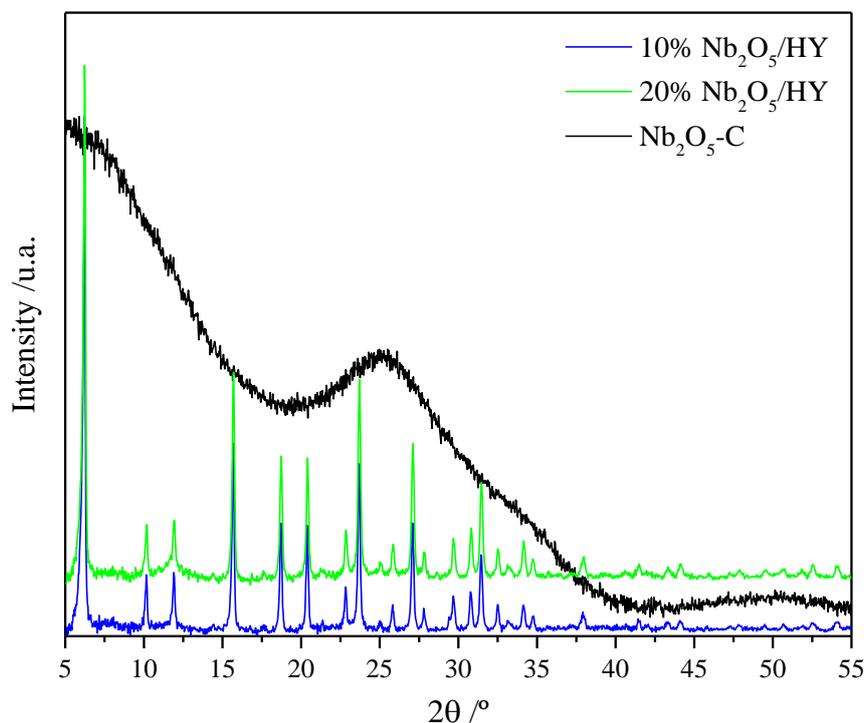


Figure 2: X ray diffractogram of samples obtained from calcined Nb_2O_5 and $\text{Nb}_2\text{O}_5/\text{HY}$ in different proportions.

The nitrogen adsorption/desorption isotherms at 77 K of the prepared samples are shown in Figure 3. According to the International Union of Pure and Applied Chemistry (IUPAC), the isotherms of the samples containing the HY zeolite presented a type I profile, characteristic microporous materials. In addition, a small cycle of hysteresis type IV is observed over a wide range of P/P_0 (0.450-0.995), relative to the pore size distribution in the region from micro to mesoporous [39]. For the Nb_2O_5 sample, the isotherm exhibited a profile between types I and IV, characteristic of micro and mesoporous materials. However, this profile was not evidenced in the isotherms of the $\text{Nb}_2\text{O}_5/\text{HY}$ materials, reinforcing the greater effect of the HY zeolite compared to the oxide (as evidenced too in XRD analyzes) [24, 40].

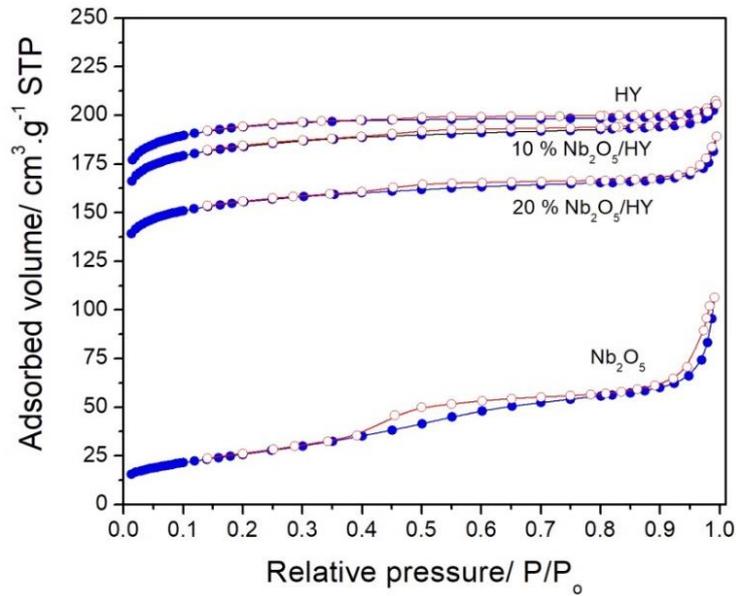


Figure 3: Adsorption/desorption isotherms of N_2 at 77 K from HY, Nb_2O_5 and Nb_2O_5/HY catalysts in different proportions.

From these analyzes, the textural characteristics of the materials were determined, as showed in Table 1. The materials containing the zeolite showed high specific areas, with a reduction the surface area (S_{BET}) and the volume of micropores (V_{MIC}) as the content of niobium oxide incorporated in the catalyst structure is increased, similar results have been reported in the literature [24].

Table 1: Textural properties obtained from the adsorption/desorption of N_2 at 77 K.

	S_{BET} ($m^2.g^{-1}$)	S_{MIC} ($m^2.g^{-1}$)	S_{EXT} ($m^2.g^{-1}$)	V_T ($cm^3.g^{-1}$)	V_{MIC} ($cm^3.g^{-1}$)	V_{MESO} ($cm^3.g^{-1}$)
HY	739	652	87	0.312	0.261	0.051
Nb_2O_5	88	-	88	0.114	-	0.114
10 % Nb_2O_5/HY	698	602	96	0.306	0.242	0.064
20 % Nb_2O_5/HY	588	496	92	0.267	0.199	0.068

Where: S_{BET} is the BET surface area, S_{EXT} is the t -plot external surface area, S_{MIC} is the micropore surface area, V_T is the total pore volume, V_{MIC} is the t -plot micropore volume and V_{MESO} is the mesopore volume. $S_{BET} = S_{MIC} + S_{EXT}$ and $V_T = V_{MIC} + V_{MESO}$.

Research results obtained by Figueiredo et al. (2016) [41] showed promising results in LDPE pyrolysis using zeolites. Figures 4, 5 and 6 shows the TG/DTG curves for thermal and catalytic pyrolysis of LDPE using the different catalysts, with heating rates of 5, 10 and 20 $^{\circ}C.min^{-1}$, respectively.

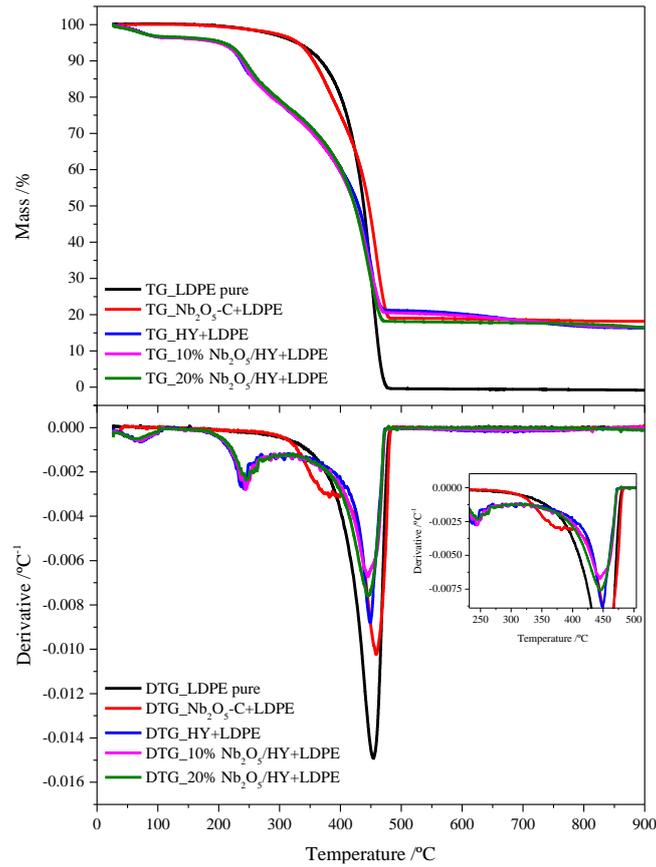


Figure 4: TG/DTG curves of thermal and catalytic pyrolysis of LDPE over the heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

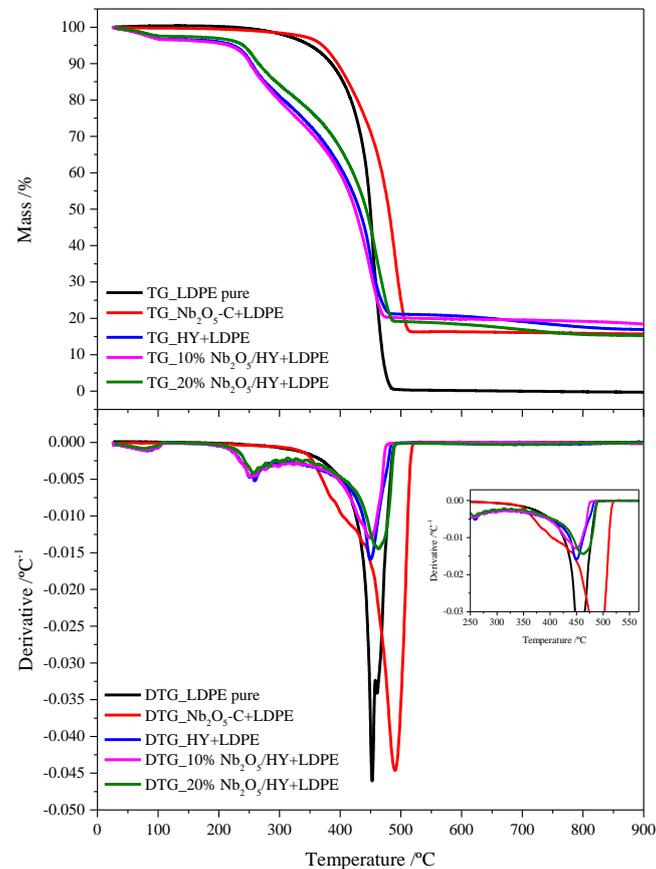


Figure 5: TG/DTG curves of thermal and catalytic pyrolysis of LDPE over the heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

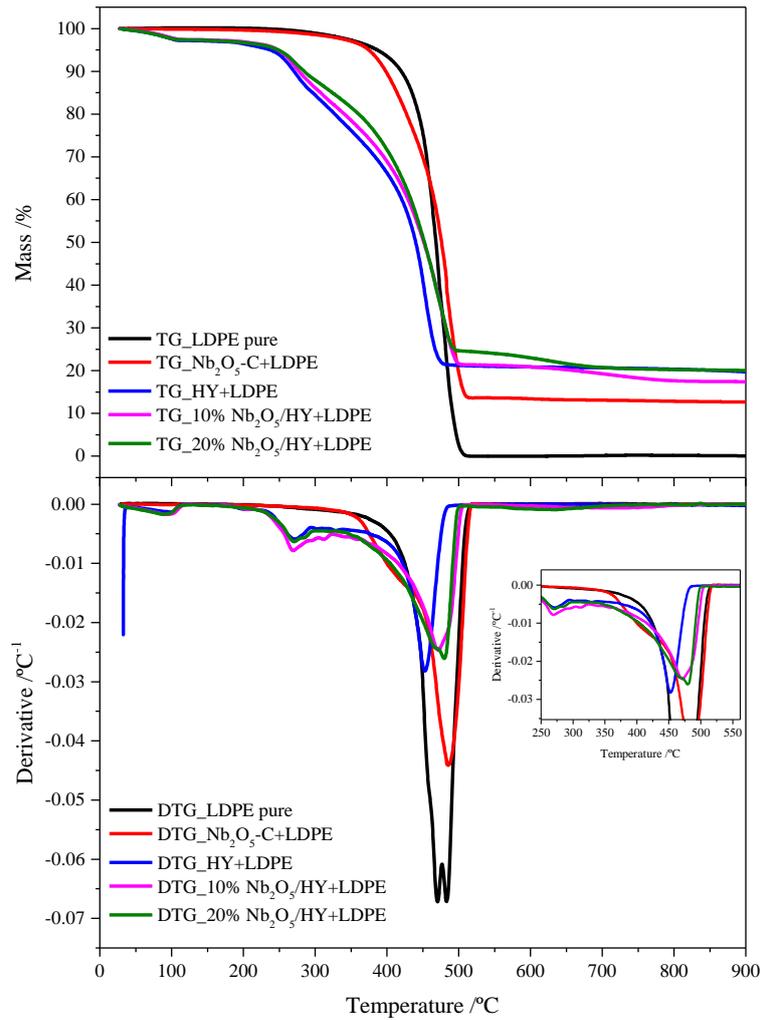


Figure 6: TG/DTG curves of thermal and catalytic pyrolysis of LDPE over the heating rate of $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

Typically the thermal pyrolysis curves of pure LDPE show only one decomposition event and the variation in the heating ratio causes significant differences in the initial, final and maximum peak degradation temperatures in the DTG curves and in the percentage of residual mass. The samples undergo a complete thermal degradation in the temperature range of 476 to 513 $^{\circ}\text{C}$, for the different heating rates. Thus, it is concluded that the entire polymeric mass was degraded at the end of the tests, leaving no residues. Similar results for the thermal degradation of pure LDPE have been found in the literature [42, 43]. The curves for the catalytic pyrolysis tests showed one to three mass loss events. For the first event, there is about 2 to 5 % of loss of mass between 30 and 107 $^{\circ}\text{C}$, attributed to the evaporation of physically adsorbed water. The second event, in the range of 173 to 327 $^{\circ}\text{C}$, begins to reduce the molecular weight related to the elimination of structural hydroxyls from zeolite Y, with about 7 to 11 % reduction in mass. And finally, the third event, with about 80% loss of mass in the temperature range between 292 to 517 $^{\circ}\text{C}$, referring to the dominant process of depolymerization of LDPE over catalysts [16]. For all tests using catalysts at different heating rates, at the end of the process, the percentage of mass remaining in the sample crucible was in the range of 14 to 25 %, with a residual average of 19.8 %. All values for temperatures and relative mass losses of the main degradation events are shown in Table 2.

Table 2: Values of temperatures and relative mass losses of the main events of thermal and catalytic pyrolysis of LDPE, at different catalysts and heating rates.

Sample	β (°C.min ⁻¹)	Event II				Event III					
		ΔT (°C)	T_{onset} (°C)	T_{peak} (°C)	$m_{T_{peak}}$ (%)	ΔT (°C)	T_{onset} (°C)	T_{peak} (°C)	$m_{T_{peak}}$ (%)	$R_{dT_{peak}}$ (%)	R_d (%)
LDPE	5	-	-	-	-	311-476	311	454	75.4	24.6	-
	10	-	-	-	-	338-487	338	458	69.1	30.9	-
	20	-	-	-	-	373-513	373	477	65.9	34.1	-
Nb ₂ O ₅ -C	5	-	-	-	-	292-480	292	459	63.2	36.8	19.2
	10	-	-	-	-	330-517	330	490	63.2	36.8	16.3
	20	-	-	-	-	350-516	350	485	64.0	36.0	13.6
HY	5	173-270	173	239	10.8	316-470	316	449	65.1	34.9	21.4
	10	197-282	197	259	11.5	319-482	319	450	63.2	36.8	21.3
	20	226-294	226	271	10.3	359-482	369	453	62.1	37.9	21.4
10 % Nb ₂ O ₅ /HY	5	179-274	179	244	11.7	337-471	337	445	64.0	36.0	20.7
	10	185-327	185	258	11.7	327-474	327	449	66.5	33.5	20.4
	20	215-323	215	269	8.4	323-503	323	471	62.5	37.5	21.4
20 % Nb ₂ O ₅ /HY	5	190-267	190	245	10.8	322-470	322	445	65.9	34.1	18.4
	10	206-313	206	257	8.3	345-488	345	463	65.8	34.2	19.2
	20	217-298	217	270	7.8	340-498	340	480	68.2	31.8	24.7

Definitions: β is the heating rate; ΔT = temperature range; T_{onset} is the initial degradation temperature; T_{peak} is the maximum peak temperature; $m_{T_{peak}}$ is the residual mass at maximum peak temperature; $R_{dT_{peak}}$ is the residue at maximum peak temperature; R_d is the final waste.

As a comparative effect, Figure 7 show the overlapping of the conversion curves α of LDPE as a function of temperature using the different catalysts, at heating rates of 5, 10 and 20 °C.min⁻¹, respectively. The conversion curves were determined from the difference between the initial and final masses of the sample, derived from the TG curves, and they represent a more simplified way of comparatively analyzing the total polymer conversion thermal behavior.

Note that the behavior of the pure LDPE and Nb₂O₅+LDPE curves are similar, however when the process is conducted with the other catalysts there is a great difference in the profile of these curves. At the same time, it is observed that at the heating rate of 5 °C.min⁻¹ there is a greater conversion, that is, as in this step the sample is heated gradually, the conversion occurs more completely for all samples. Analyzing the conversion curves for Nb₂O₅+LDPE, it is observed that the change in the heating rate from 10 to 20 °C.min⁻¹ did not result in considerable changes in the polymer conversion, showing that for this material it is necessary to gradually increase the temperature for an effect on conversion. For samples containing zeolite HY, for the same heating rate, it is verified that as the amount of zeolite in the material structure increased, there was an acceleration in the degree of polymer conversion, in addition to these conversions having started in advance.

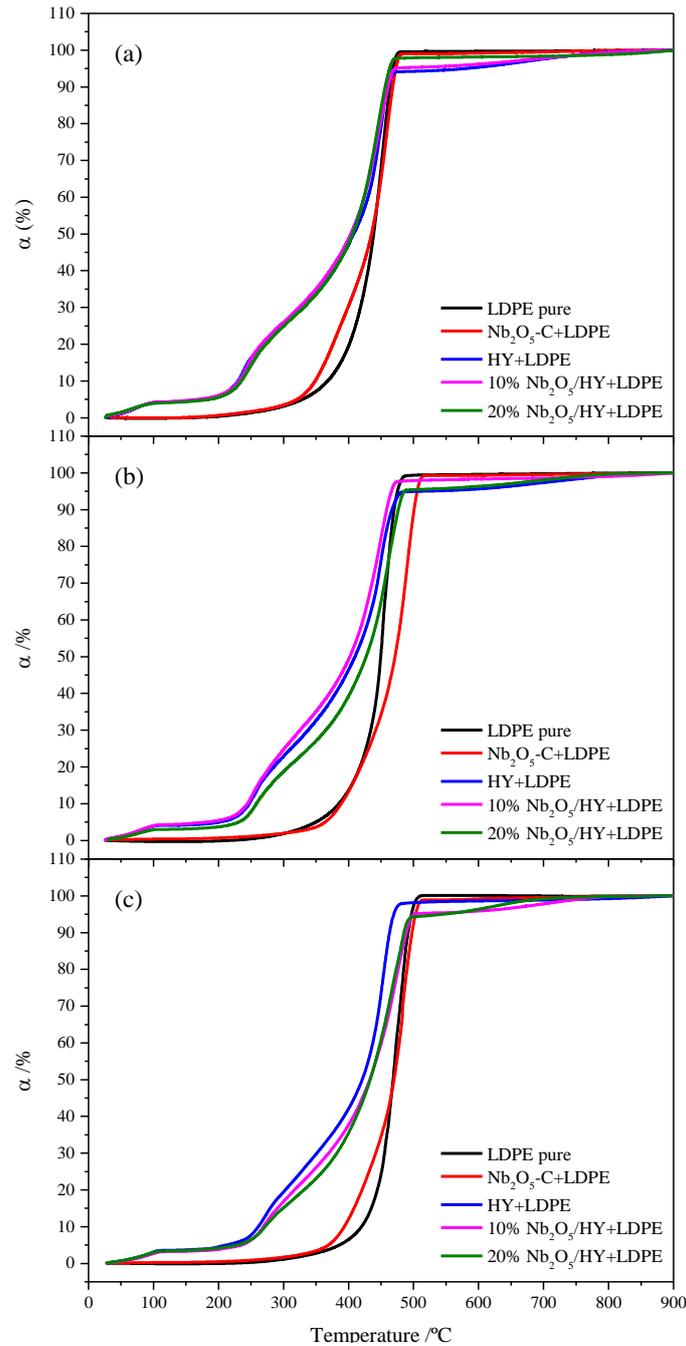


Figure 7: Overlapping of the conversion curves versus temperature for different samples: a) 5 °C.min⁻¹, b) 10 °C.min⁻¹ and c) 20 °C.min⁻¹.

The FWO [37] and VZK [38] non-isothermal kinetic models were applied to the study of LDPE thermal and catalytic pyrolysis. In the isoconversional equations proposed by the models for the determination of kinetic parameters, integral data of the TG curves were used at different heating rates (5, 10 and 20 °C.min⁻¹), where the E_α values were estimated for each degree of conversion (α) selected from the TG curve. Thus, the polymer decomposition speed depends on parameters such as conversion (α), temperature (T) and reaction time (t), where in each process the reaction speed is given as a function of the conversion $f(\alpha)$ [44]. For the FWO model, E_α is obtained from the slope of the $\log(\beta)$ graph (K.min⁻¹) versus $1/T$ (K⁻¹) in a fixed value of α , with a minimum of three different heating ratios. For the Vyazovkin method, the log curve $\ln(\beta/T^2)$ (K⁻¹.min⁻¹) versus $1/T$ (K⁻¹) allows the determination of the apparent E_α from any selected value

of α . The integral temperature approximations are obtained under the assumption that the activation energy does not depend on the degree of conversion.

Figure 8 shows the for example isoconversional lines of the FWO and VZK models obtained for pure LDPE. It is observed that the lines for each degree of conversion are manifested adjacent and parallel, which indicates that a similar kinetic behavior is achieved and, consequently, small variations in E_α are generated in relation to the degree of conversion (α). The proximity between the lines (α : 0.4-0.9) implies the possibility of a simple reaction mechanism.

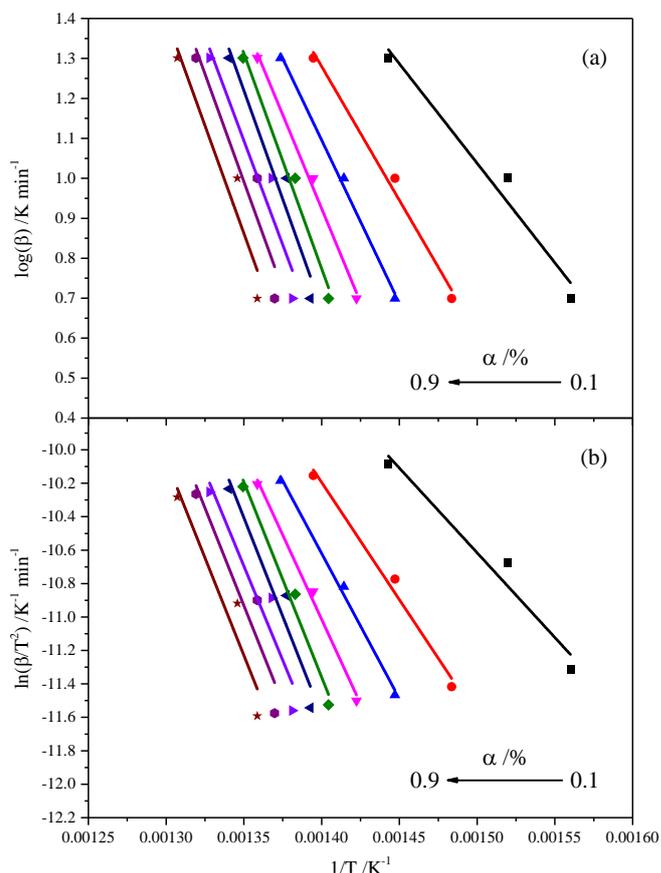


Figure 8: Isoconversional graphs of FWO (a) and VZK (b) for TG data from pure LDPE obtained at different heating rates. Conversion rate (α).

With the values of the slopes of the straight lines it was possible to calculate the E_α by the FWO and VZK methods, using the angular coefficients of equations 1 and 2. The E_α estimated by the FWO method for the LDPE decomposition reaction varied between 90.70 and 196.26 kJ mol^{-1} , depending on the degree of conversion (α) and type of material, with average values of $\bar{E}_\alpha \cong 167.67 \text{ kJ.mol}^{-1}$. For the Vyazovkin method, the E_α varied between 84.28 and 193.18 kJ.mol^{-1} , with mean values of $\bar{E}_\alpha \cong 164.33 \text{ kJ.mol}^{-1}$. These values were of the same order of magnitude as other works published in the literature [45, 46]. It appears that there was a reduction in the values of apparent activation energy compared to that presented by pure LDPE for both models ($E_{\alpha_FWO} = 167.67 \text{ kJ.mol}^{-1}$ and $E_{\alpha_VZK} = 164.33 \text{ kJ.mol}^{-1}$), for all materials (with the exception of the HY zeolite in which the formation of composites may have occurred and thus, generated a blockage of the pores and the deactivation of the active sites of the zeolite. In this way, it caused a diffusional effect on the reaction and, consequently, an excessive increase in the resistance to mass transport and the activation energy of the system. Table 3 shows the Values of the average activation energies (E_α) resulting from the application of the isoconversional FWO and VZK models for the thermal and catalytic pyrolysis of LDPE.

Table 3: Values of the average activation energies (E_{α}) resulting from the application of the isoconversional FWO and VZK models for the thermal and catalytic pyrolysis of LDPE.

Sample	LDPE	LDPE + Nb ₂ O ₅ -C	LDPE + HY	LDPE + 10 % Nb ₂ O ₅ /HY	LDPE + 20 % Nb ₂ O ₅ /HY
Model	$\bar{E}_{\alpha}/\text{kJ.mol}^{-1}$				
FWO model	167.67	114.21	502.82	113.90	148.07
VZK model	164.33	108.23	517.83	108.74	144.65

The most efficient degradation process was observed when used the catalysts Nb₂O₅-C and 10% Nb₂O₅/HY, so that they occurred with the lowest average activation energies (for FWO model $\bar{E}_{\alpha} = 114.21 \text{ kJ.mol}^{-1}$ and $113.90 \text{ kJ.mol}^{-1}$, respectively, and for model VZK $\bar{E}_{\alpha} = 108.23 \text{ kJ.mol}^{-1}$ and $108.74 \text{ kJ.mol}^{-1}$, respectively) required for polymeric degradation, showing the effect of catalysts on the process. This behavior can be attributed to the large external area of these materials (Table 1) and better accessibility to the active sites. At the same time, when analyzing the profiles for Nb₂O₅/HY catalysts with different proportions, the effect of Nb₂O₅ on the materials is evident, since when compared to the profile observed in the HY zeolite profile, there was no increase in activation energy. This effect may be due to the Nb₂O₅ incorporated in the zeolite to behave as a reaction promoter, stabilizing the action of the zeolite and thus favoring the reaction pathway. This catalytic effect is observed in the form of reduced temperature and activation energy, when compared with the other studied catalysts.

4. CONCLUSIONS

HY zeolite obtained in this work is similar to as a comparison standard literature with well-defined and narrow peaks and the calcined Nb₂O₅ has a totally amorphous structure. The Nb₂O₅/HY catalysts (10 % Nb₂O₅/HY and 20 % Nb₂O₅/HY), maintaining the crystalline structure of the HY zeolite in the catalyst.

The isotherms adsorption/desorption of N₂ at 77 K of the samples containing the HY zeolite (HY, 10 % Nb₂O₅/HY and 20 % Nb₂O₅/HY) presented a type I profile and with a type IV hysteresis cycle, characteristic of microporous materials. And the surface area for these materials decreases as the niobium oxide content in the samples increases. For the Nb₂O₅ sample, the isotherm exhibited a profile between types I and IV and a much lower surface area than other materials.

The catalytic potential of all materials was studied by catalytic LDPE pyrolysis. For the polymer degradation process, the initial and final degradation temperatures, respectively, were 311 and 476 for the heating rate of $5 \text{ }^{\circ}\text{C.min}^{-1}$, 338 and 487 for the heating rate of $10 \text{ }^{\circ}\text{C.min}^{-1}$, and 373 and 513 for the heating rate of $20 \text{ }^{\circ}\text{C.min}^{-1}$. For catalytic pyrolysis, all catalytic curves showed lower temperature ranges than pure LDPE. These results demonstrate that the catalysts are promising for pyrolysis applications. The isoconversional models FWO and VZK were adequate to estimate the kinetic parameters of the LDPE pyrolysis reaction, presenting similar profiles of E_{α} behavior as a function of conversion α . These results indicate that the mathematical models enabled a good representation of the data.

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