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RESEARCH ARTICLE

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HIERARCHICAL CATALYST APPLIED TO PYROLYSIS OF PLASTIC WASTE AND RESIDUES FROM OIL INDUSTRY

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ABSTRACT

The hierarchical zeolites with ZSM-5 structure (HZ5) catalysts were obtained using a silanizing agent, the Phenyl-Amino-Propyl-Trimethoxysilane (PHAPTMS). The materials were synthesized by the hydrothermal method and characterized by X-ray diffraction, infrared spectroscopy, thermal analysis, surface acidity and scanning electron microscopy. The kinetic study by thermogravimetry of pure Atmospheric Residue of Petroleum (ATR) and High Density Polyethylene (HDPE) wastes were performed with and without catalyst. By using the model-free kinetic method applying the integral TG curves, we estimated the activation energy for degradation of waste in function of temperature. The kinetic study of HDPE and ATR showed a decreasing in the activation energy when the hierarchical material was used in the catalytic process, at 500, 475 and 450 °C. In thermalcatalytic pyrolysis of HDPE selectivity afforded products with added values, which can be used in the petrochemical industry. In thermalcatalytic pyrolysis of ATR, this material potentiated the formation of C₁-C₄ (liquid gas); C₅-C₁₂ (gasoline) C₁₃-C₁₉ (diesel), providing better loads in the process and reducing the waste generated during petroleum refining.

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INTRODUCTION

The oil industry is made up of human activities with great potential polluter. In refining, for example, they consume large amounts of water and energy, as well as produce large amounts of liquid waste, release various gases harmful to the atmosphere and produce solid waste that is difficult to treat and dispose. As a result of these facts, refineries have often major degraders of environment, as they have the potential to affect air, water, soil and, consequently, the entire biotic environment around it. Waste can be generated during the refining process, such as a example, AT, RV, as well as oil handling operations and treatment effluents, usually in the form of sludge, incinerator ash and sludge. Other residues, which have attracted attention in recent decades, are derivatives of the petrochemical industry, plastics, for example, have a slow process of degradation that can lead to soil, air and water contamination when they are not intended correctly (Castro et al., 2011; Lima et al., 2014; Figueiredo et al., 2016). On the other hand, with the current comforts of modern society, plastics have been an indispensable material in the life of humanity, as it is also notorious the growing demand for fossil fuels and petrochemicals. In this context, there is a need for both the recycling of this plastic waste as an alternative to avoid environmental and social problems, as well as to recover valuable products chemical residues derived from the oil industry, as well as residues generated during the refining process.

Due to this, in recent years the oil industry has sought to change the profile of its refineries, petrochemical sectors for the implementation of equipment and materials catalysts for heavy oil processing and waste disposal. And new strategies between refining and petrochemical activities have emerged. Thermocatalytic pyrolysis is a thermal process associated with the use of catalysts, which has become promising to increase the yield and selectivity of products in the hydrocarbon range desirable, which may be used as fuel, for example, for liquid fractions in the gasoline to diesel range recovered from petroleum residues (Araujo et al., 2016; Castro et al., 2011). For greater efficiency of the waste pyrolysis process, it is necessary to use an adequate catalyst that allows a better degradation performance of these residues at a lower temperature, as well as a better yield and product selectivity. Therefore, the use of an adequate catalyst is of fundamental importance. In recent decades, nanocrystalline zeolites with hierarchical porosity have shown to be very attractive as catalysts for reactions involving bulky molecules, such as in the waste pyrolysis process. The use of organosilanes has provided new routes for the preparation of zeolite materials with more accessible acidic sites (Serrano et al., 2008). This work aimed to synthesize, characterize the zeolite nanocrystalline crystals with hierarchical structures, using silanizing agent to obtain hierarchical structure, for applying in the degradation process of HDPE by thermal analysis.

MATERIALS AND METHODS

Preparation of the catalyst: The catalyst used in the current work is a hierarchical zeolite functionalized with organosilane. The procedure for obtaining the acid ZSM-5 was based on Costa *et al.*, 2011, synthesizing the material without organic template by the hydrothermal method, using silica gel (high-purity grade, pore size 60 Å, 200-400 mesh particle size, Sigma-Aldrich), sodium hydroxide microbeads (PA, Vetec), sodium aluminate anhydrous sodium (Riedel-de Haën) - 50-56% Al₂O₃ and 40-45% Na₂O and ultrapure water as a solvent. The precursor materials were combined in order to obtain amolar chemical composition for the synthesis gel in the following stoichiometric ratio: 12 Na₂O:2Al₂O₃:100 SiO₂:2500 H₂O, with the SiO₂/Al₂O₃ molar ratio of the gel equal to 25. The procedures for the synthesis of functionalized ZSM-5 zeolites by reaction with 15 mol% of Phenyl-Amino-Propyl-Trimethoxysilane (PHAPTMS), according to procedure described by Figueiredo *et al.*, 2016. The hydrogel was submitted to hydrothermal treatment in an autoclave at temperature of 180 °C, for 1 days. Then the material was cooled to room temperature, dried at 100 °C, then calcined at 500 °C, under nitrogen atmosphere by 4 h.

Characterization of the samples: The synthesized samples were characterized by powder X-ray diffraction, in order to confirm the crystalline structure proposal for the MFI type ZSM-5 zeolite (Mobil Five), in order to verifying the integrity of the zeolite structures (Caldeira *et al.*, 2016; Lima *et al.*, 2014). The diffractograms were obtained on Shimadzu equipment, model XRD 6000, using CuK α radiation, nickel filter, voltage of 30 kV and tube current 30 mA. The absorption spectra in the infrared region of the HZSM-5 samples with organosilane, calcined and not calcined, were obtained in the infrared range of 400-4000 cm⁻¹, using the KBr method, in a Bomem MB100-FTIR equipment. The Scanning Electron Microscopy (SEM) analysis performed on the samples with the purpose of identifying the morphology, size of the particles and homogeneity of the material. The micrographs of the samples were obtained in an electronic microscope PHILIPS model ESEM.

Thermocatalytic pyrolysis: The Atmospheric Residue of Petroleum (ATR) was obtained from Petrobras in Brazil, in the Exploration and Production Unit of Rio Grande do Norte and Ceará States (UNRNCE). The High Density Polyethylene (HDPE) was provided from Brasken Petrochemical Pole, in Camaçari, Bahia State. The pyrolysis of ATR and HDPE residues were performed in a pyrolyzer model PY-2020iS Control from Frontier LAB, coupled to a GC/MS, Shimadzu QP 2010 model, as shown in Figure 1.

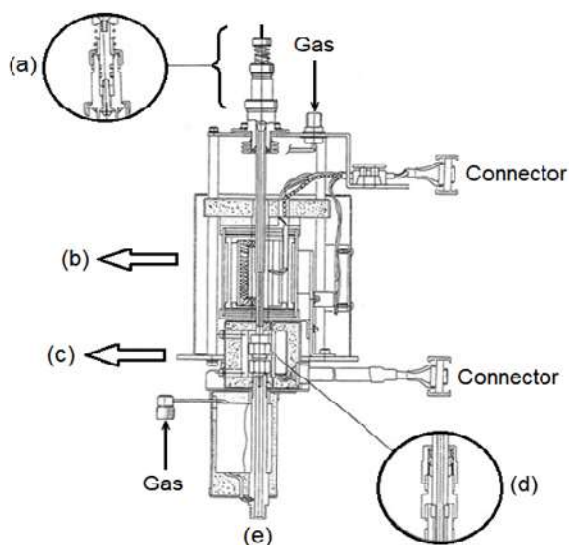


Figure 1. Pyrolysis reactor system coupled to the gas chromatograph and mass spectrometer (Py-GC/MS), where: (a) sample holder; (b) oven chamber; (c) connection of the reactor with the chromatographic column; (d) pyrolyzer interface with the chromatograph; (e) exit to GC/MS

The samples were placed in a steel crucible stainless steel (Ecocup SF) with a volume of 50 μ L. Samples of pure waste and with catalysts were prepared by mechanical mixing in the proportions of 10% of catalyst. The analyzes were carried out under a helium gas atmosphere with a flow of 3.0 mL/min, pyrolyzer temperature at 500, 475 and 450 °C, split ratio of 200:1 and pyrolyzer-GC interface temperature of 300 °C. The products from pyrolysis were separated on a UA5-30M-0.25F capillary chromatography column (5% diphenyl, 95% dimethyl-polysiloxane) 30 m length, 0.25 mm in diameter and stationary phase thickness of 0.25 μ m. The column pressure was maintained at 116.7 kPa, with a flow rate of 2.20 mL/min and a linear velocity of 53.2 cm/s. The GC/MS interface temperature was maintained at 300 °C. The detection range in the mass spectrometer was maintained between 20 to 600 m/z; the sweep interval was 0.50 s. The different constituents present in the pyrolysis products of the residues through the NIST library database (National Institute of Standards of Technology) of the software attached to the GC/MS analysis system.

RESULTS AND DISCUSSION

From X-ray diffractograms (Figure 2) was observed that the synthesized materials present the structure pattern of crystalline MFI type, as proposed by International Zeolite Association (IZA), with five characteristic peaks referring to the Miller indices [(101), (200), (501), (151), (133)], as previously reported (Caldeira, 2016, Figueiredo *et al.*, 2016; Serrano, *et al.*, 2011). The diffractograms of the calcined samples evidence that the structure of the ZSM-5 zeolite does not change due to the thermal treatment, only an increase in the intensity of the peaks and crystallinity. The main diffraction peaks are clearly differentiated, in the samples with silanization.

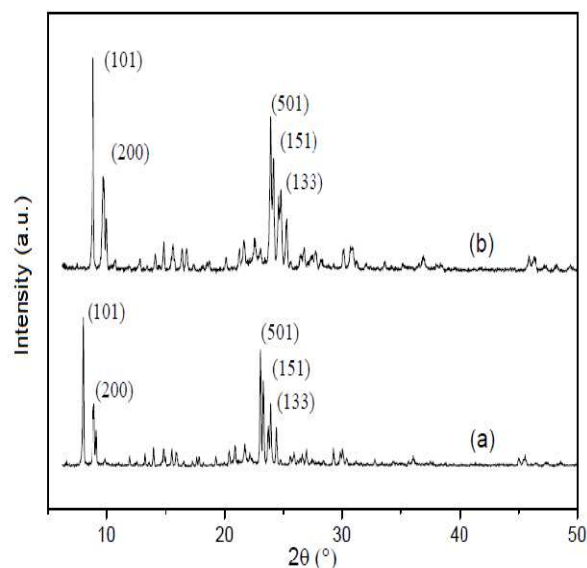


Figure 2. X-ray diffractograms of HZ5 materials: (a) uncalcined and (b) calcined sample

The crystal size was determined from the X-ray diffraction spectrum using Scherrer relation, and a composite distribution was found between 19-32 nm in crystal sizes for silanizing calcined sample. This value are in agreement with Xue *et al.*, 2012 and Aguado *et al.*, 2008. The FT-IR spectra for the samples are shown in Figure 3. The infrared spectrum of functionalized material shows signs of vibration close to 2934 and 1504 cm⁻¹, which indicate the presence of interactions of the organosilane molecules, since these vibrations are not present in the spectra of ZSM-5 in the calcined form, as observed in Figure 3. The vibration band close to 2934 cm⁻¹ indicates a symmetrical stretching of the C-H bond of the methyl group. Scanning electron microscopy analysis was performed with the aim of to identify the morphology and homogeneity of hierarchical HZ5 zeolite, as viewed in the Figure 4.

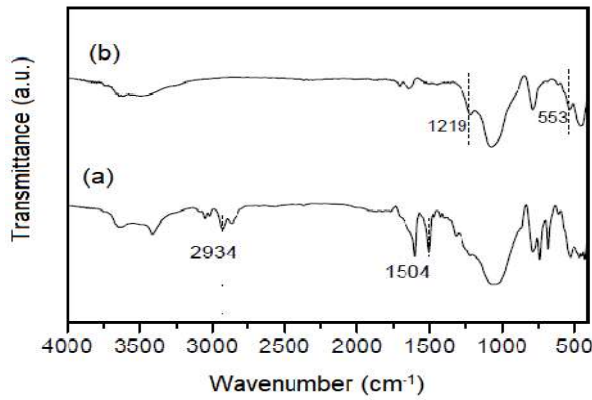


Figure 3. FT-IR spectra of HZ5 materials: (a) uncalcined and (b) calcined sample

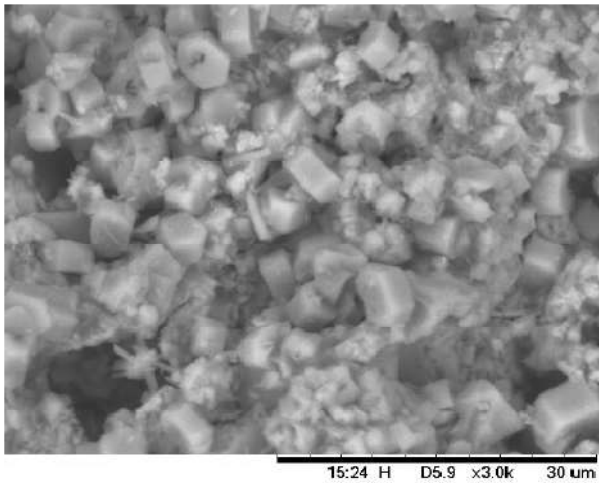


Figure 4. Scanning electron micrograph of silanized ZSM-5 zeolite (HZ5)

The micrograph was obtained with magnification of 3,000 times and measurement of the 30 μm scale bar. The functionalized sample showed typical morphology of MFI zeolite even after functionalization with 15 mol% of PHAPTMS. It was observed compact aggregates consisting of an oval shape with the presence of some larger crystals. A mixture of larger crystals and fragments of crystalline materials, in agreement with what is reported in the literature (Xue *et al.*, 2012).

Physicochemical characterization of waste: The results regarding the characterization of the ATR, such as: determination of density, viscosity, amount of saturated, aromatic, resins and asphaltenes (SARA), infrared spectroscopy are presented in Table 1. The data for HDPE is given in Table 2.

Table 1. Analyzes performed for the ATR

Property	Value
Density at 20°C (g/cm^3)	0.8767
API Density	29.9
Dynamic viscosity at 40°C (mPa.S)	1006.2
Kinematic viscosity at 40°C (mm^2/s)	1090.8
Sulfur (% m/m)	0.43
Nitrogen (% m/m)	0.22
Carbon (% m/m)	85.3
Hydrogen (% m/m)	12.7
Oxygen (% m/m)	1.35
C/H (molar ratio)	0.61
SARA Distribution	
- Saturated (% m/m)	17.0
- Aromatics (% m/m)	29.2
- Resins (% m/m)	37.0
- Asphaltenes (% m/m)	16.8

Table 2. Data informed by the Braskenfor characteristics of HDPE

Property	ASTM	Value
Melt index ($\text{g}/10 \text{ min}$)	D 1238	0.43036
Density (g/cm^3)	D 792	0.961
Tensile strength (MPa)	D 638	22
Thermal deflection 0.455MPa	D 648	79 °C

The petroleum residues are normally constituted of fractions considerably heavy, resulting in a complex chemical composition. The density found in the RAT was $0.8767 \text{ g}/\text{cm}^3$ indicates that this residue consists of light fractions in their chemical composition. The values determined for dynamic and kinematic viscosities were 1006 mPa.S and $1091 \text{ mm}^2/\text{s}$, respectively is probably attributed to the constituents present in the sample related mainly with temperature. The SARA analysis indicated a significant presence of aromatics in the ATR sample, corroborating with the data found for density and viscosity. Since the RAT is a fraction of a process, in which most of the lighter constituents have already been removed, i.e. justifies the strong presence of resins, aromatics and asphaltenes, with complex chemical substances, since in great part promote the formation of coke. In general, resins and asphaltenes are compounds that have high molecular mass and molecular size, being formed by polyaromatic rings, thus making it difficult to convert to fractions of low molecular weight. However, the ATR presents a relative percentage of the fraction of saturated in their composition. By elemental analysis (CHNSO), the percentages by mass reveal a high carbon content, followed by hydrogen, as expected for a petroleum residue, whose main constituents are hydrocarbons, in addition to other small amounts appear as organic compounds that contain other elements such as nitrogen, oxygen and sulfur. The TG and DTG curves for decomposition of HDPE with and without catalyst are shown in Figures 5 and 6, respectively. The TG/DTG curves at different heating rates for ATR and HZ5/ATR are shown in Figures 7 and 8, respectively.

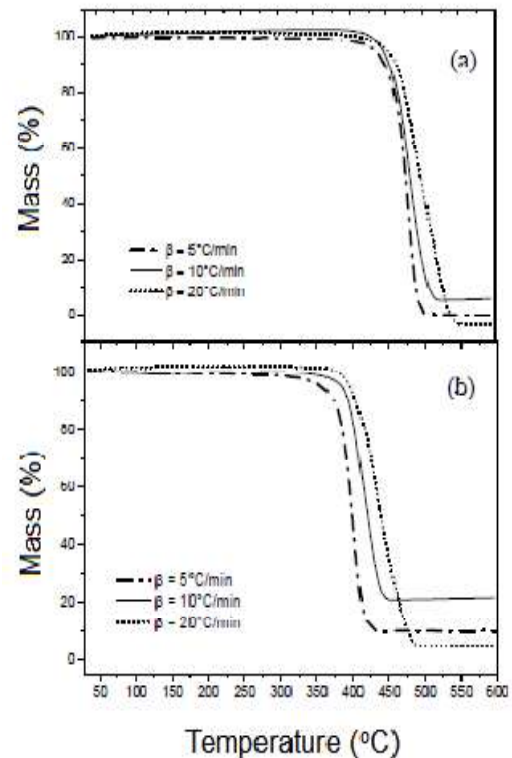


Figure 5. TG curves for degradation of: (a) HDPE and HZ5/HDPE at different heating rates

Analyzing the TG and DTG curves for HDPE, it was possible to observe the thermal behavior, generated by the performance of the

HZ5 material in the decomposition of high-density polyethylenedensity. It was observed that when the pyrolysis process of HDPE is applied, the degradation begins around 420 °C, and the effect of temperature is decreased to 350 °C when HZ5 catalyst is employed in the process, with a DTG peak temperature of 476 °C.

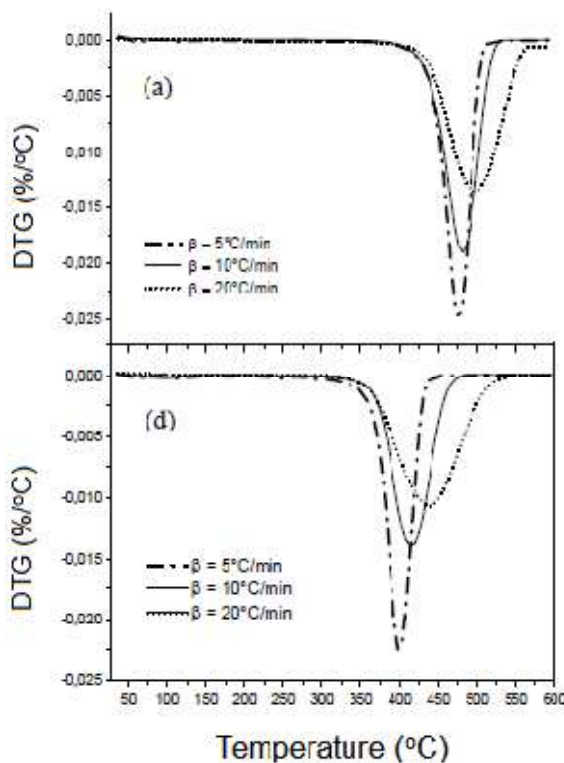


Figure 6. DTG curves for degradation of: (a) HDPE and HZ5/HDPE at different heating rates

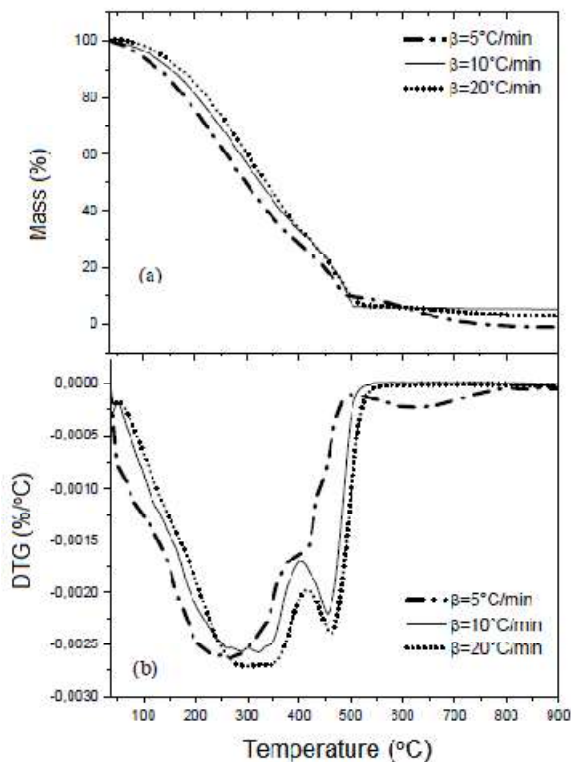


Figure 7. (a) TG curves and (b) DTG curves for ATR at different heating rates

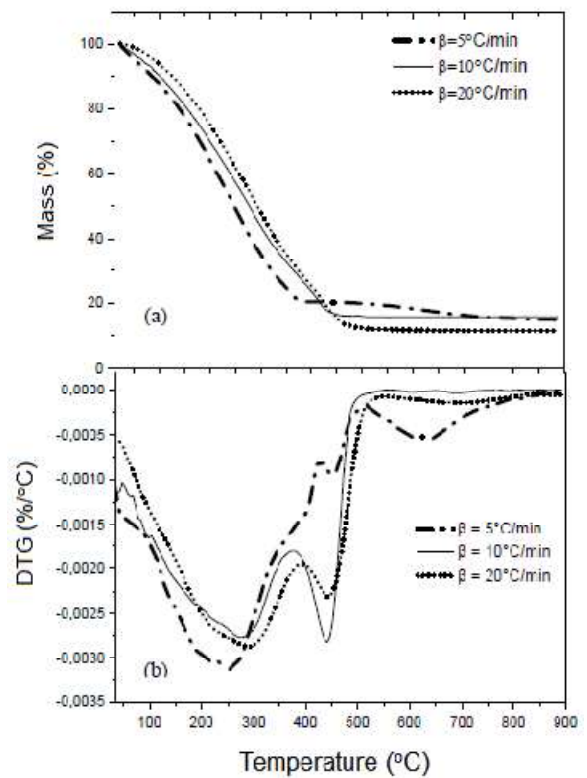


Figure 8. (a) TG curves and (b) DTG curves for HZ5/ATR at different heating rates

For the development of the kinetic study, the selected temperature ranges were between 416–528 °C and 373–466 °C, for pure HDPE and HZ5/HDPE, respectively. Applying the Vyazovkin model-free kinetic model (Vyazovkin; Wright, 1999), the conversion as a function of temperature in the time periods studied. Thus, it was observed that the most efficient degradation process was observed for the HZ5/HDPE over a period of 16 h, so that with lower activation of 150 kJ/mol was required for degradation of the polymer. This behavior is possibly attributed to the greater external area of the catalyst associated to accessibility to active sites and the Brønsted acidity, making the effect observed catalytic in the form of lower temperature and lower activation energy, when compared with other catalysts studied (Xue *et al.*, 2012; Saha; Ghoshal, 2007). It was determined, for example, for pure HDPE to achieve 80% degradation it is necessary to heat it at 460 °C for 20 min, whereas for the HZ5/HDPE, to achieve the same conversion at the same time, a temperature of 373 °C is required.

Analyzing the Figures 7 and 8, for thermal degradation of ATR, it was possible to observe two mass loss events for both samples: one between 150–400 °C, another between 400–550 °C for pure ATR. For the mixture HZ5/ATR a mass loss event between 100–374 °C, and another at 374–500 °C. The behavior of these curves were close similar. Furthermore, a relatively rapid decay was observed in the distillation zones and cracking, respectively, thus being able to correlate with the high API degree of this residue, as well as the amount of constituents present, when evaluating the decomposition in each temperature range: the first stage can be attributed to the decomposition of light and medium hydrocarbon fractions of saturates and some constituents of aromatics, and in the second stage to the heavy fractions, related to resins and asphaltenes, investigated by the composition of the SARA analysis (Gonçalves *et al.*, 2010). The kinetic study was also carried out using the model proposed by Vyazovkin. For the degradation of ATR and HZ5/ATR, the apparent activation energy (E_a) found was 353 kJ/mol and 120 kJ/mol, respectively. For low conversion zone including light and medium fractions in HZ5/ATR, the E_a was ca. 86 kJ/mol and in the component ranges referring to the highest fractions conversions, around 127 kJ/mol, evidencing a significant effect in lowering the apparent activation energy in both regions. The kinetic study is a criterion that reveals the main phenomena involved in the thermal behavior of a raw

material inside a refinery. The effect of thermal and thermocatalytic pyrolysis of HDPE on HZ5/HDPE was studied at temperatures 450, 475 and 500°C. The pyrograms relative to HDPE and ATR without and with catalyst are shown in Figures 9 and 10, respectively.

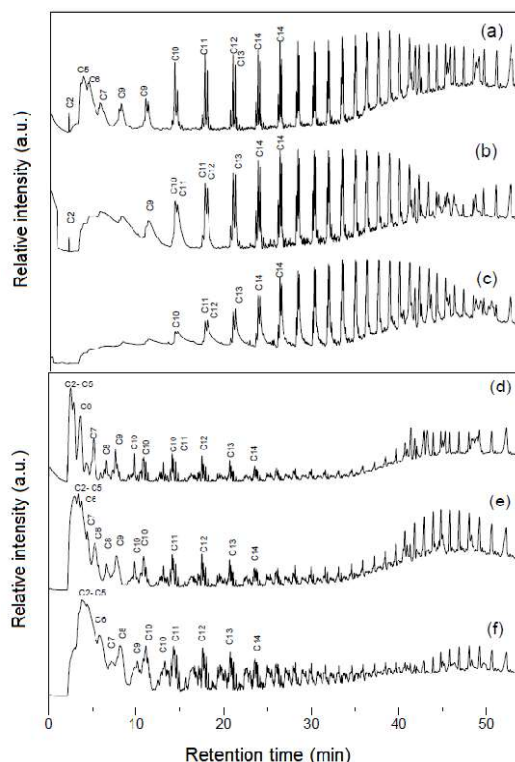


Figure 9. Pyrograms at different pyrolysis temperatures of pure HDPE: (a) 500°C; (b) 475°C and (c) 450°C; and for HZ5/HDPE at: (d) 500°C; (e) 475°C and (f) 450°C

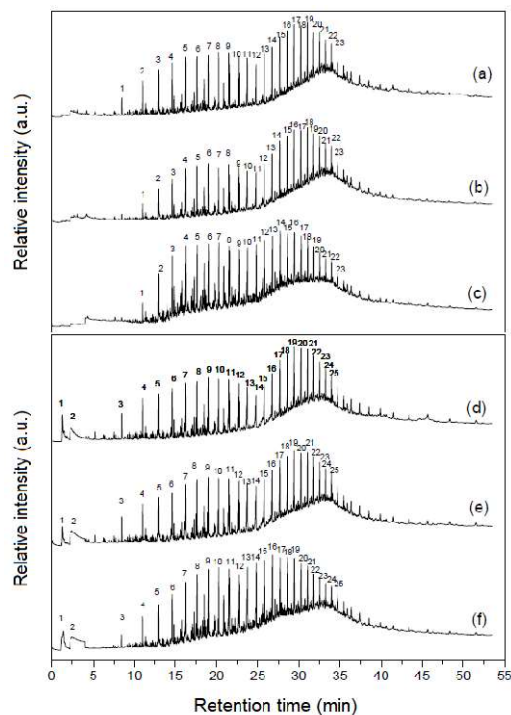


Figure 10. Pyrograms at different pyrolysis temperatures of pure HZ5/HDPE: (a) 500°C; (b) 475°C and (c) 450°C; and for HZ5/HDPE at: (d) 500°C; (e) 475°C and (f) 450°C

According to the results of the samples of HDPE with catalyst, there was a significant concentration of lighter products in retention time of 0 to 15 minutes, when compared to the sample of HDPE without catalyst, mainly in the hydrocarbon ranges of C₂-C₄ and C₅-C₁₂. This behavior was also noticed by Burange et al., 2015; Serrano et al., 2010.

This evidence shows the catalytic effect on the formation of products, which is a result of a greater fragmentation of pyrolysis products promoted by acidic sites in the catalyst, as well as the presence of nano-scale crystals, the mesopores intercrystalline, greater external surface area, which results in greater accessibility improved to active sites.

In thermocatalytic pyrolysis, as the temperature was increased from 450-500 °C it was observed that there was a slight reduction in yield in the distribution of products in the C₅-C₁₂ range and a significant increase in yield in the C₂-C₄ range. This behavior was also found (Bagri; Williams, 2002) when studying the catalytic pyrolysis of polyethylenes at different temperatures.

On the other hand, thermocatalytic pyrolysis at 475°C showed a higher 71% selectivity in the C₂-C₁₂ range. The thermocatalytic pyrolysis at 450 and 500 °C showed selectivity of about 62%, and the catalytic effect can be verified potentiated in this range of hydrocarbons, as well as showing selectivity in numbers of carbon atoms. In general, the main products found in the catalytic pyrolysis of polyethylene are: ethene, butene, benzene, toluene, and p-xylene. These compounds are reported can be obtained from pyrolysis thermal at elevated temperatures of 600 and 900 °C (Blazsó, 2005; Deng et al., 2006). It is shown that it is possible to find them in temperatures below 600 °C, from catalytic pyrolysis (Dimitrov et al., 2013; Figueiredo, 2016). Therefore, the products disclosed for the pyrolysis of pure HDPE at studied temperatures, 500, 475 and 450 °C, were a series of olefins, chain paraffinic hydrocarbons long, however the pyrolysis of HZ5/HDPE showed olefinic chains of smaller sizes, even more branched isomers, and aromatic compounds, such as benzenes, toluenes and xylenes for the three studied temperatures. For ATR, the distribution of pyrolysis products into hydrocarbon are distributed in the range of C₂-C₄, and an increase in the range between (C₅-C₁₂) when compared with thermal pyrolysis of RAT at the same temperatures. In thermocatalytic pyrolysis, as the temperature was increased from 450-500 °C it was noticed that there was a small reduction in yield, referring to distribution of products in the C₅-C₁₂ range and an increase related to yield in the range of C₂-C₄. From the ATR load, even lighter fractions can be obtained, (Alvarez et al., 2011) typically C₁-C₄ gas (Liquefied Petroleum Gas), middle distillates C₅-C₁₀ (gasoline), C₁₁-C₁₂ (kerosene), C₁₃-C₁₇ (diesel), C₁₈-C₂₅ (heavy diesel) and C₂₆-C₃₈ (lubricating) according to Caldeira, et al., 2016. Fractions in the C₁-C₄ hydrocarbon range refer to low conversion needing lower activation energy, whereas the fractions of middle and heavy distillates refer to high conversion requiring a high activation energy (Gonçalves et al., 2008; Gonçalves et al., 2010).

CONCLUSION

The current work proposed the development of a methodology to obtain hierarchical materials for application as catalyst for conversion of plastics and residues from petroleum industry, in order to obtain valuable hydrocarbon products. Based on the characterization techniques employed in this work, the hierarchical zeolites were successfully synthesized by the hydrothermal method in the absence of organic template, using the PHAPTMS as a silanizing agent. This generated a significant effect on the acidity of the materials, being possible to change the concentrations of Bronsted and Lewis acid sites of the materials. The adding the silanizing agent did not destroy the zeolite structure, as proved from XRX, FT-IR and SEM. At observations made by the SEM of the MFI (PHAPTMS) produced aggregates with different particle sizes. The material presented catalytic potential for conversion of HDPE and ATR residues, due to intercrystalline mesoporosity, with improved accessibility to acid sites of large molecules. The addition of 10% in mass of catalyst mass to HDPE or ATR waste produced a decrease in degradation temperature. These data were complemented with the results of lowering in activation energy, obtained from the model non-isothermal kinetics proposed by Vyazovkin. The analysis of products from pyrolysis indicates that these the silanized catalyst can be used for upgrade in raw materials in the petrochemical industry, obtaining fractions of LPG (C₁-C₄), gasoline and diesel products.

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