

# CATALYTIC DEGRADATION OF HIGH DENSITY POLYETHYLENE OVER NANOSTRUCTURED MATERIAL EVALUATED BY TG

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**Abstract:** The aim of the current work was evaluate the process of catalytic degradation of High Density Polyethylene (HDPE) using AlMCM-41 nanostructured catalyst. This study was carried out by thermogravimetry and pyrolysis coupled to gas chromatography. The AlMCM-41 material was synthesized from an hydrogel containing cethyltrimethylammonium bromide (CTMABr) as template, pseudoboemite, fumed silica, sodium silicate and distilled water as solvent. These reactants were mixed in order to obtain a gel with the following composition: 1CTMABr:4SiO<sub>2</sub>:0.04 Al<sub>2</sub>O<sub>3</sub>:1Na<sub>2</sub>O:200H<sub>2</sub>O. The kinetic relative to the process of HDPE degradation was evaluated using Flynn-Wall model, in order to verify the influence of the AlMCM-41 material on the process. Clear differences were observed in the thermogravimetry behavior of the samples. Results obtained shown a remarkable effect of the catalyst in the acceleration of the degradation processes. The kinetic parameters obtained revealed a reduction in the activation energy of the catalytic decomposition as compared to the thermal process.

**Keywords:** MCM-41 catalyst; polyethylene; pyrolysis; kinetics; Thermogravimetry

*:Resumo: No presente trabalho foi avaliado o processo de degradação catalítica de polietileno de alta densidade (PEAD) utilizando catalisadores nanoestruturados de AlMCM-41, por meio de análise térmica e pirólise acoplada a cromatografia gasosa. Estes materiais foram sintetizados a partir de hidrogel contendo brometo de cetiltetrametilamônio (CTMABr) como molde, pseudoboemita, sílica fumada, silicato de sódio e água destilada como solvente. Estes reagentes foram misturados para se obter um gel com a seguinte composição: 1CTMABr:4SiO<sub>2</sub>:0,04 Al<sub>2</sub>O<sub>3</sub>:1Na<sub>2</sub>O:200H<sub>2</sub>O. A cinética relativa ao processo de degradação do HDPE foi avaliada utilizando o modelo de Flynn-Wall, para verificar a influência dos materiais AlMCM-41 no processo. Foram observadas diferenças claras no comportamento termogravimétrico das amostras. Os resultados obtidos mostraram um efeito notável no catalisador na aceleração dos processos de degradação. Os parâmetros cinéticos obtidos revelaram uma redução na energia de ativação da degradação catalítica do PEAD em relação ao processo de degradação térmica.*

## Introduction

Plastic materials are considered part of solid urban waste, in which polyethylene from containers and packages represent around 60% of this type of waste. The composition on this residue is mainly polyolefins (high and low density polyethylene, polypropylene and polystyrene), accounting for around 70% of the total plastic waste [1].

The disposal of these polymeric wastes involves different problems. Apart from their non-biodegradable character which produces an aesthetical pollution lasting for years, their uncontrolled incineration can produce serious problems in the environment. For designing incinerators, the formation of products in such a process or their presence in waste materials must be considered [2-3].

Different alternatives have been studied for the recycling or disposal of such residues

[4], ranging from post-consumer recycling [5-7], biodegradable polymers [10] or controlled incineration with energy recovery [11], among others.

Another interesting alternative is the pyrolysis of such polymer materials which produces a mixture of hydrocarbons by heating in inert atmosphere operating under different conditions in temperature range of 400-850 °C [12,13]. Moreover, with the use of catalysts it is possible to reach a higher selectivity in certain products, thus improving their quality and also, to reduce temperature of the process to the 350-550 °C range [14,15]. Normally, the catalysts used in the thermal decomposition of plastic materials are acid solid such as zeolites, amorphous silica-alumina and mesoporous MCM-41 [16-19].

The pyrolysis methods for catalytic recycling of waste is a promising way to convert polymer materials into low molecular weight chemicals which can be used as raw materials for the chemical and petrochemical industry. Catalytic pyrolysis of polyolefins is of great interest because of their potential use as fuels or chemical resource [20].

A new class of ordered mesoporous materials were synthesized via self-assembly of silica and surfactant species [20-23]. The negatively charged silica species interact with surfactant cations under hydrothermal conditions forming the self-assembled mesostructured composite, which after surfactant removal via calcination and/or extraction gives an ordered mesoporous material. The aforementioned class of materials is known as the M41S family and includes structures such as MCM-41 (hexagonal phase) and MCM-48 (cubic phase). The most popular phase, MCM-41, consists of hexagonally ordered channels with amorphous silica walls. The MCM-41 is an attractive material for catalytic application due to the presence of specific Bronsted and Lewis acid sites in its structure. The use of acid catalysis enhances the thermal degradation of synthesis polymers [22-23].

This paper investigates the potential application of thermogravimetry and pyrolysis coupled to GC/MS as a fast method to study the catalytic degradation of plastic polymers and to determine the nature of the products generated when the reaction is carried out in the presence of different acid solids. For the purpose of this work, the mesostructured material AIMCM-41 was synthesized and characterized by chemical analysis, surface property and thermal stability at temperature up to 800 °C. The sample was evaluated for its catalytic activity in the degradation of HDPE using TG analysis. Py-GC/MS was subsequently used to investigate the thermal and catalytic degradation of the HDPE, and to determine qualitatively the effect of catalyst on the nature of the obtained products.

## Materials and methods

The chemicals used to synthesize AIMCM-41 were regular silica (Aldrich Chemical Co.), sodium silicate solution containing 27% SiO<sub>2</sub> and 14% NaOH (Aldrich Chemical Co.), pseudoboehmite, as aluminium source; cetyltrimethylammonium bromide, C<sub>16</sub>H<sub>33</sub>(CH<sub>3</sub>)NBr (Aldrich Chemical Co.), and distilled water. The chemical reactants were mixed in order to obtain gel with the following molar composition: 4 SiO<sub>2</sub> : 0.04 Al<sub>2</sub>O<sub>3</sub> : 1.0 Na<sub>2</sub>O : 1.0 CTMABr : 200 H<sub>2</sub>O (Si/Al = 50).

The pH adjustment was done with 1% acetic acid in ethanol solution [22]. The Reactive hydrogel were placed into the autoclave and submitted to a hydrothermal treatment at 100°C, for a period of 3 days. Each day, the pH was adjusted to 10 with a 30% acetic acid solution. For the structure stabilization, sodium acetate (Carlo Erba) was added to the product (salt/CTMABr = 3), and the material was heated for one additional day. The obtained material was washed with 2% volume HCl/EtOH solution, recovered by filtration and dried at 100°C for 2h, 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 typical MCM-41 structure was characterized by X-ray diffraction, infrared spectroscopy, BET surface area and thermogravimetry. TG analysis was carried out in Mettler equipment, TGA 851 model, using nitrogen as gas carrier flowing at  $30 \text{ mL min}^{-1}$ . The sample was heated from room temperature up to  $800^\circ\text{C}$ , at a heating rate of  $10^\circ\text{C min}^{-1}$ . For the most well-synthesized MCM-41 sample, the parameter relative to the water desorption, surfactant decomposition and silanol decomposition were determined.

Nitrogen adsorption measurements were carried out at  $-196^\circ\text{C}$  using a volumetric adsorption analyzer (ASAP 2010 model) from Micromeritics (Norcross, GA, USA). Each sample (ca 0.1g) was degassed at  $200^\circ\text{C}$  for 2h in the degas port of the instrument. The measurements were carried out over a relative pressure ranging from ca.  $10^{-6}$  to 0.995.

The acid form of the material was obtained by exchanging the AIMCM-41 with  $0,1 \text{ mol L}^{-1}$  of ammonium chloride solution at  $80^\circ\text{C}$  under reflux for 6h, followed by filtration drying and calcination at  $550^\circ\text{C}$  using  $\text{N}_2$  flowing at  $100 \text{ mL min}^{-1}$ , for 2h. The activity of the catalyst for the pyrolysis of HDPE is related with the acid sites present on the surface of material.

HDPE was purchased from Palmann of Brazil Company, in powder form. The polymer was blended in ball mill. Then, the AIMCM-41 catalyst was added to the HDPE at a concentration of 50% in weight. The thermal degradation of HDPE alone and mixed with the catalyst (AIMCM-41/HDPE) was carried out using a thermobalance TA Instruments 2960 model, at temperature range from  $30$  to  $800^\circ\text{C}$ , under nitrogen flow ( $60 \text{ mL min}^{-1}$ ) and heating rates of  $5$ ;  $10$  and  $20^\circ\text{C min}^{-1}$ . The Flynn Wall kinetic method was applied to this process. To each experiment was used approximated  $10 \text{ mg}$ .

The AIMCM-41/HDPE sample was transferred to a tubular quartz microreactor, with 3way valve, heated at  $600^\circ\text{C}$ , under static argon atmosphere. The reactor was connected on line to a Shimadzu GC17-A gas

chromatograph coupled to a QP-5000 mass spectrometer, and the products were analyzed with a capillary column type Petrocol DH-50.

## Results and discussion

A kinetic model is essential for efficient development of economically feasible conversion technologies. The properties and thermal degradation of polymers such as High Density Polyethylene (HDPE) is reasonably well known [23].

The HDPE thermal degradation process is composed by two different reaction types: the polymeric combustion and the thermal cracking. In general, the combustion produces  $\text{CO}_2$  and water, whereas the thermal cracking produces hydrocarbons in the range of  $\text{C}_2$  to  $\text{C}_{30}$ .

The use of atmosphere of argon under the HDPE and MCM-41/HDPE eliminates the oxidant atmosphere and consequently the combustion reactions. The Py-GC/MS analysis showed selectivity to  $\text{C}_3$ - $\text{C}_{13}$  hydrocarbons to the degradation of AIMCM-41/HDPE and  $\text{C}_{11}$  -  $\text{C}_{30}$  to polymer without catalyst. Typical chromatograms are shown in Figure 1.

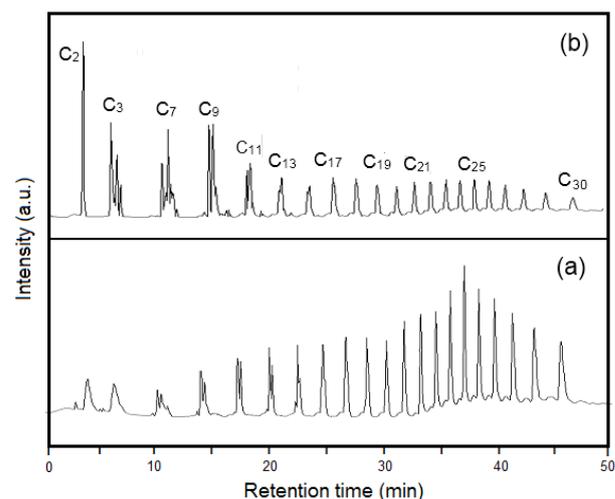


Figure 1 – Chromatograms of the reaction products of the pyrolysis of HDPE: (a) without catalyst; (b) mixed with AIMCM-41.

According to the chromatograms shown in the Figure 1, it is observed that the pyrolysis of High Density Polyethylene (Figure 1a) produces hydrocarbons in a wide range of carbon number, typically for  $C_7 - C_{30}$ . When AIMCM-41 catalyst was added to the polymer (Figure 1b), it is observed a significant formation of hydrocarbon in the range of  $C_2$  and  $C_3$ ; fraction of liquid petroleum gas;  $C_6 - C_9$  (gasoline) and  $C_{11} - C_{17}$  (diesel oil). In general, the obtained compounds by HDPE pyrolysis are paraffins, olefins and aromatics, and they are grouped as  $C_n$ , where “n” represents the number of carbons.

The AIMCM-41 catalyst showed to be active to the pyrolysis of the polyethylene, being a promising catalyst to this process. It is proposed that when occurs the thermal degradation of the polymer, the hydrocarbons fractions access the mesoporous of the AIMCM-41, interact with its acid sites, and promote the high hydrocarbon chain cracking to low hydrocarbons, typically in the range of fuels and middle distillates.

Thermal degradation of polymers take place through chain scission where the breakage of the carbon chain yields free radical segment and non-chain scission reactions involving elimination of small molecule and double bond formation [24]. The mechanism is a radical chain initiated by random scission reaction of the polymer chain.  $\beta$ -Scission reaction of the radical leads to gas and liquid olefins. The termination reaction occurs via combination and the probability of its occurrence is 5-10 times than that of disproportionation [25].

The determination of kinetic parameters such as activation energy ( $E_a$ ) from thermogravimetric data is receiving considerable attention. The determination of  $E_a$  parameter from a single integral thermogravimetric analysis curve (weight loss versus T) needs repeated regression analysis. Differential method based on Flynn and Wall model, are able to present a quick and simple method for determining activation energies

directly from weight loss versus temperature data at multiple heating rates.

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

On the basis of the results of thermogravimetric analysis of samples, apparent activation energies for the overall degradation of polymer can be determined by considering curves of mass loss against temperature, at different heating rates. Since the mass loss is indicative of the scission of the chemical bonds leading to volatilization, it is clear that even at the lowest heating rate, this process becomes noticeable only above de  $350^\circ\text{C}$ . The activation energies ( $E_a$ ) expressed in  $\text{kJ mol}^{-1}$  for the thermal degradation of the HDPE and AIMCM-41/HDPE were determined from the slope of the logarithm of heating rates curves as a function of the reciprocal absolute temperature, as visualized in the Figures 2 and 3. 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, mainly the activation energy relating to the process.

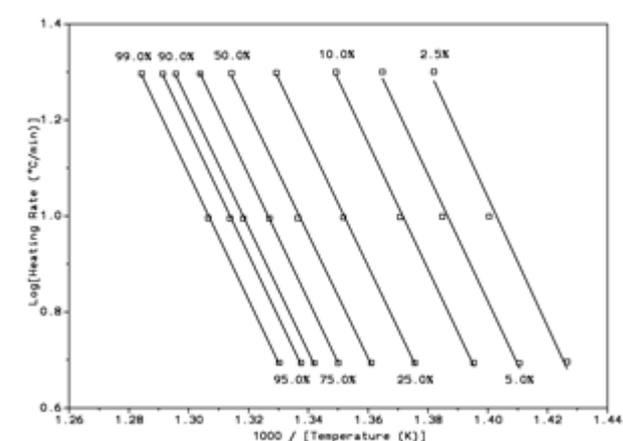


Figure 2. Curve for determination of  $E_a$  for HDPE.

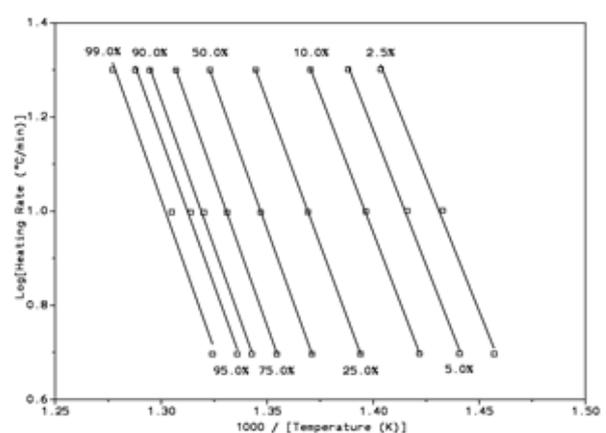


Figure 3. Curve for determination of  $E_a$  for HDPE containing 50% mass of AIMCM-41.

Reliable methods for determination the activation energy by using dynamic integral TG curves at several heating rates have been proposed by Osawa [27] and Flynn and Wall [26]. 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 [28] where it was demonstrated that the heating rate and the absolute temperature can be related as follows:

$$\frac{\partial \log \beta}{\partial 1/T} \cong - \left[ \frac{0,457}{R} \right] \cdot E$$

The insertion of the  $R$  ( $18.2 \text{ Cal mol}^{-1}\text{K}^{-1}$ ) gives the expression below, for obtained for  $E$ , as:

$$E_a \cong -4,35 \frac{\partial \log \beta}{\partial 1/T}$$

Thus, it was possible to calculate the activation energy relating to the thermal degradation of the HDPE polymer by using the slope of the logarithmic heating rate curve as a function of reciprocal temperature. The  $E_a$  values observed for the polymer degradation

without catalyst was  $270 \text{ kJ mol}^{-1}$  against  $163 \text{ kJ mol}^{-1}$  in the present of AIMCM-41. These results indicate that this material may have acted as a cracking catalyst for HDPE, enhancing the generation of light products of potential industrial use, such as liquid petroleum gas, gasoline and diesel. The lower value of activation energy evidenced that the AIMCM-41 is an efficient catalyst for the HDPE degradation process.

## Conclusions

The products resulted from HDPE pyrolysis by AIMCM-41 are distributed in a narrow range of carbon,  $\text{C}_2\text{-C}_4$ ,  $\text{C}_5\text{-C}_{10}$ ,  $\text{C}_{11}\text{-C}_{17}$ , typically LPG, gasoline and diesel oil, respectively, evidencing that the pyrolysis mechanism is a function of the pore system combined with acid properties of the mesoporous catalyst. The activation energy for the process, as determined from multiple heating rate TG curves and Flynn-Wall kinetic model, decreased from  $270 \text{ kJ mol}^{-1}$  (HDPE without catalyst) to  $163 \text{ kJ mol}^{-1}$  (HDPE/AIMCM-41), evidencing that that the mesoporous MCM-41 containing acid sites, generated by the aluminum, acted as a good catalyst for pyrolysis of polyethylene.

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