Energy Optimisation and Catalytic Degradation of plastic waste
Environment

The demand-driven surge in the production of low biodegradable plastic material is generating a huge build-up of plastic waste and a concomitant environmental problem. An efficient way of solving this problem is the development of catalysts capable of optimising the plastic burning process. This catalytic degradation might also drive molecular cracking processes to generate specific compounds of high added value.

This study sets out to analyse a series of zeolite catalysts (particularly a laboratory synthesised nano-sized catalyst and another of natural origin) that reduce the degradation temperature of polyethylene while also selectively generating compounds with a high commercial demand. The results show that nano-sized catalysts outperform naturally occurring micro zeolites.

The conclusion drawn from this study is that by controlling the properties of the zeolite catalyst it is possible to cut down the energy needed for the thermal degradation of polyethylenes and thus optimise the cracking of the polymer chain in a controlled way, generating gaseous compounds of a high added value

By **FRANCISCO CONTRERAS, FRANCISCO GRACIA** and **HUMBERTO PALZA***. Departamento de Ingeniería Química y Biotecnología, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile. Santiago, Chile. *Head Researcher. Contact address: Beauchef 850, Santiago Chile.

CRISTIAN COVARRUBIAS. Departamento de Ciencias Básicas, Facultad de Odontología, Universidad de Chile.

Plastic's excellent properties and low cost have generated a constantly growing demand in recent decades, unparalleled in other traditional materials[1]. The annual growth in Europe and South America is reckoned to be between 4 and 8%[2]. This soaring demand has been led by polyolefins, such as polyethylene (PE) or polypropylene (PP), on the strength of their growing range of applications, ousting many other kinds of material. This versatility has made polyolefins today's most important polymers in the plastics industry, accounting for 60% of the total plastics marketed[1]. The worldwide PE output is now nearly 90 million tonnes, representing 34% of the market[3]. Europe's average per capita consumption of plastics is estimated to be 100 kilograms adding up to a total yearly consumption of 40 million tons[4,5]. This huge consumption leads to a proportional surge in the amount of plastic waste; due to its low biodegradability, moreover, this waste is becoming a severe environmental problem. For example, Europe consumed 40 million tons of plastic material in 2000, translating into 30 million tons of waste[6].

Plastic waste, much more bulky than traditional organic waste, now occupies a large volume of landfill sites or rubbish tips. About 62% of Europe's waste ends up in these tips[5]. This situation, however, has led to increasing public concern and there is a growing legislative-environmental lobby, like those who advocate a 35% reduction in this type of waste by 2020[7]. Furthermore, the costs of this process, which generates explosive and toxic gases, have increased. One of the first measures taken to try to reduce this glut of plastic waste was energy recycling or direct incineration to generate energy. In Europe 23% of the original waste is now used in this way[5]. Nonetheless this type of recycling also comes in for much

criticism because of the generation of toxic gases, together with the fact that the energy released is often not properly harnessed. It also calls for a high operating temperature and produces a wide range of products that have a very low economic value.

Mechanical recycling, for its part, involving the melting down and remoulding of the thermoplastic waste to form a new product, is generally welcomed by society. Unfortunately, this type of recycled material is of very poor quality due to the degradation reactions during the recycling process, the varying nature and quality of the plastic waste and the presence of additives and impurities in the original plastic. All these factors greatly limit its use possibilities[8]. Moreover, this recycled product is often even more expensive than the virgin material[7]. In the United Kingdom only 17% of plastic waste is mechanically recycled; the rest is dumped in landfill sites or incinerated[7].

Given the complications in the traditional plastic-waste reduction procedures, a technology has recently been developed based on the transformation of plastic waste into high added value hydrocarbons that can serve as chemical products and/or fuel. An initial approach is based on controlled thermal degradation, albeit with the limitation that the required temperature ranges from 500 to 800ºC and the resulting products have high molecular weights and are of an uneven consistency. The thermal degradation of polymers into material of low molecular weight, on the other hand, has the drawback of producing a wide range of waste[2]. Furthermore, the reactions are highly endothermic and hence call for a high energy input[9]. In view of all these snags the use of solid catalysts seems to be a promising approach to solving these problems. In particular the reaction temperature is considerably lower (between 350 and 550ºC), reducing the energy consumption of the process[6,10]. Using this method it is also possible to control the fraction of products and cut down the distribution thereof, making materials of higher added value[11].

The catalysts most commonly used for optimising the thermal degradation process are porous solid acid catalysts such as amorphous silica alumina, ordered mesoporous material and zeolites[8], the latter being the most studied catalysts. Zeolites are porous crystalline aluminosilicate compositions (natural or synthetic) with a very defined structure formed by tetrahedral units of SiO_4 or AlO_4 connected by oxygen bridges, generating a network of canals, cavities and micropores of a very precise molecular size. Due to these properties and its inherent acidity, zeolite is the main component in the industrial catalysts used in the catalytic cracking of crude oil to produce gasoline.

Catalytic cracking applied to the breakdown of polyolefins has focused mainly on polymer transformation into gaseous and liquid products of interest. In the case of PE, for example it has been reported that the mesoporous material Al-MCM-41 produces hydrocarbons within the gasoline fraction while ZSM-5 directs the cracking towards light compounds with a large production of gaseous and aromatic hydrocarbons[8]. When using Al-MCM-41 as a catalyst the cracking occurs by a mechanism of random scission due to its large pore size and medium acidity. The zeolite HZSM-5, on the other hand, leads to an end-chain cracking pathway due to its small pore size and strong acidity[8]. The catalyst's particle size has been proven to be important; this was confirmed by analysing nanocrystalline zeolite ZSM-5 samples, which show a high cracking activity due to their large external surface and low diffusional constraints[8]. Similar results have been found by studying beta zeolites, where it has been shown that the particles with the smallest crystal size (~ 100 nm) give the best performance due to the bigger surface area and higher production of liquid compounds[12].

Despite the abovementioned evidence, there is still a need for further study of different zeolite catalysts in the degradation of polyolefins. In particular the effect of nano-sized catalysts on the temperature and catalytic degradation of plastics is a variable that has been little studied as yet, despite its promising industrial potential. Furthermore, given the environmental impact of these technologies, there is now a pressing need for studies into the use of natural catalysts to cheapen the implementation of this vital technology. The objective of this article is therefore precisely to study the effect of zeolite catalysts on the degradation of plastic waste. The study will focus in particular on the effect of particle size and acidity on the degradation temperature and breakdown products. A general scheme of the idea behind our research, i.e., the chemical recycling of plastic waste, is shown in figure 1.
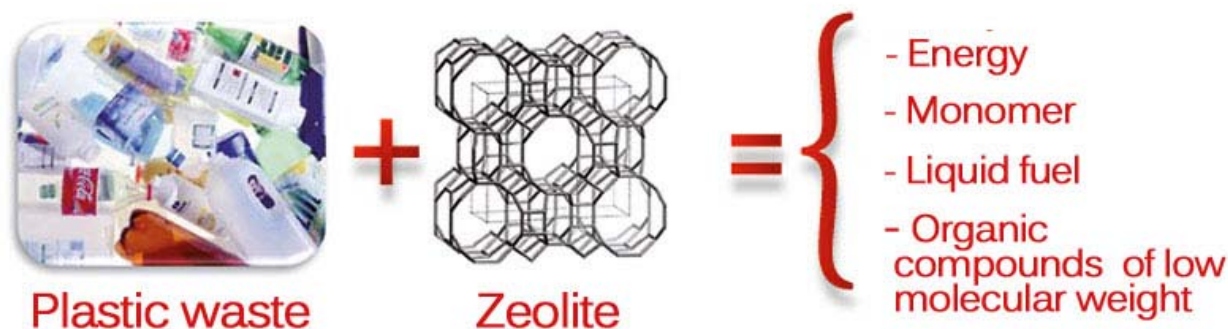
Figure 1. General scheme of the chemical recycling of plastic waste using zeolite catalysts

Materials and Methodology

Preparation of acid zeolites

Natural zeolite (Nat) was subjected to an ionic exchange with a solution of HCl to obtain its protonated form (H-Nat). The exchange with lanthanum was achieved by bringing the H-Nat into contact with a solution of La(NO3)3, obtaining La-H-Nat. The nano-sized zeolite studied is a ZSM-2 (NZeo), obtained using the following molar composition 0.53Li2O:0.5Al2O3:6TMAOH:3.4SiO2:315H2O, in due accordance with previous reports[13]. This zeolite has a pore diameter (pd) of 7.4 Å. Like the natural zeolite it was then protonated (H-NZeo) and modified with lanthanum (La-H-NZeo). Micrographs from electron microscopy show the mean particle size to be 100 nm.

Degradation Test

The PE catalytic degradation was carried out in a Pyrex semibatch reactor, which was heated by a thermal cracking reactor with programmable controller. A defined amount of the PE was then mixed with the catalyst inside the reactor. The system was heated up to 400, 450 or 500° C in steps of about 6°C/min under a nitrogen flow; it was then left to react for 40 minutes once the study temperature had been reached. The gaseous products were captured in gas collection bags and the liquids were retrieved in a cold trap and NaCl (-20º C), and then weighed. The collected gases were analysed by gas chromatography.

The gaseous fraction was analysed by gas chromatography (Perkin Elmer Clarus 500) fitted with a Flame Ionisation Detector (FID) and a Capillary Column HP-Plot/Al2O3 (Agilent), to determine the presence and concentration of different hydrocarbons (C1-C6). A packed column (Supelco 60/80 Carboxen 1000) was also used in line with a thermal conductivity detector (TCD) for analysing the amount of CO_2.

The PE used in the study is linear with a mean molecular weight of 120,000 g/mol; it was synthesised in our laboratory using a metallocene catalyst Et(Ind)2ZrCl2 in presence of the co-catalyst methylaluminoxane in concentrations of 3.5 x 106 mol of catalyst, Al/Zr ratio of 3000, 2 bar and 60º C. The thermogravimetric analyses (TGA) were conducted in a Netzsch TG 209 F1 Iris under a nitrogen environment with a flow of 25 ml/min from room temperature up to 600º C at a heating rate of 20º C/min. For each experiment 4.7 mg of polymer (<120 mesh) was mixed with the desired amount of catalyst (typically 2 mg, 30% of the total mass).

Results

Optimisation of thermal degradation

Table 1 gives a summary of the catalysts studied and their respective chemical modifications. Note that the nano-sized zeolite (~100 nm) without any type of modification shows a high acidity in comparison, for example, with natural zeolite. On the other hand the modifications made with protons and lanthanum are effective in terms of increasing catalyst acidity, especially that of the natural catalyst, boosting it by more than one order of magnitude. Note also that, although the pure nano-sized catalyst shows a high acidity in comparison with the natural catalyst, the latter obtains the highest acidity once modified.

Table 1. Main characteristics of the various zeolites studied

Catalyst	E° (mV)	Total number of acid sites [µeq m^{-2}]
NZeo	200	1.7
H-NZeo	318	1.9
La-H-NZeo	310	1.8

Catalyst	E° (mV)	Total number of acid sites [μeq m^{-2}]
Nat	40	1.7
H-Nat	400	1.5
La-H-Nat	500	1.4

When the polymer is thermally degraded with no type of catalyst, its temperature of maximum degradation (Tmax) is 492.5° C. When the degradation occurs in presence of the nano-sized catalyst, however, the Tmax drops right down to 418.7° C. Not only Tmax falls but also the initial degradation temperature. Examples of the curves obtained by thermogravimetry are shown in figure 2. In particular it shows the results for the pure polymer and for the polymer in presence of the various nanocatalysts.
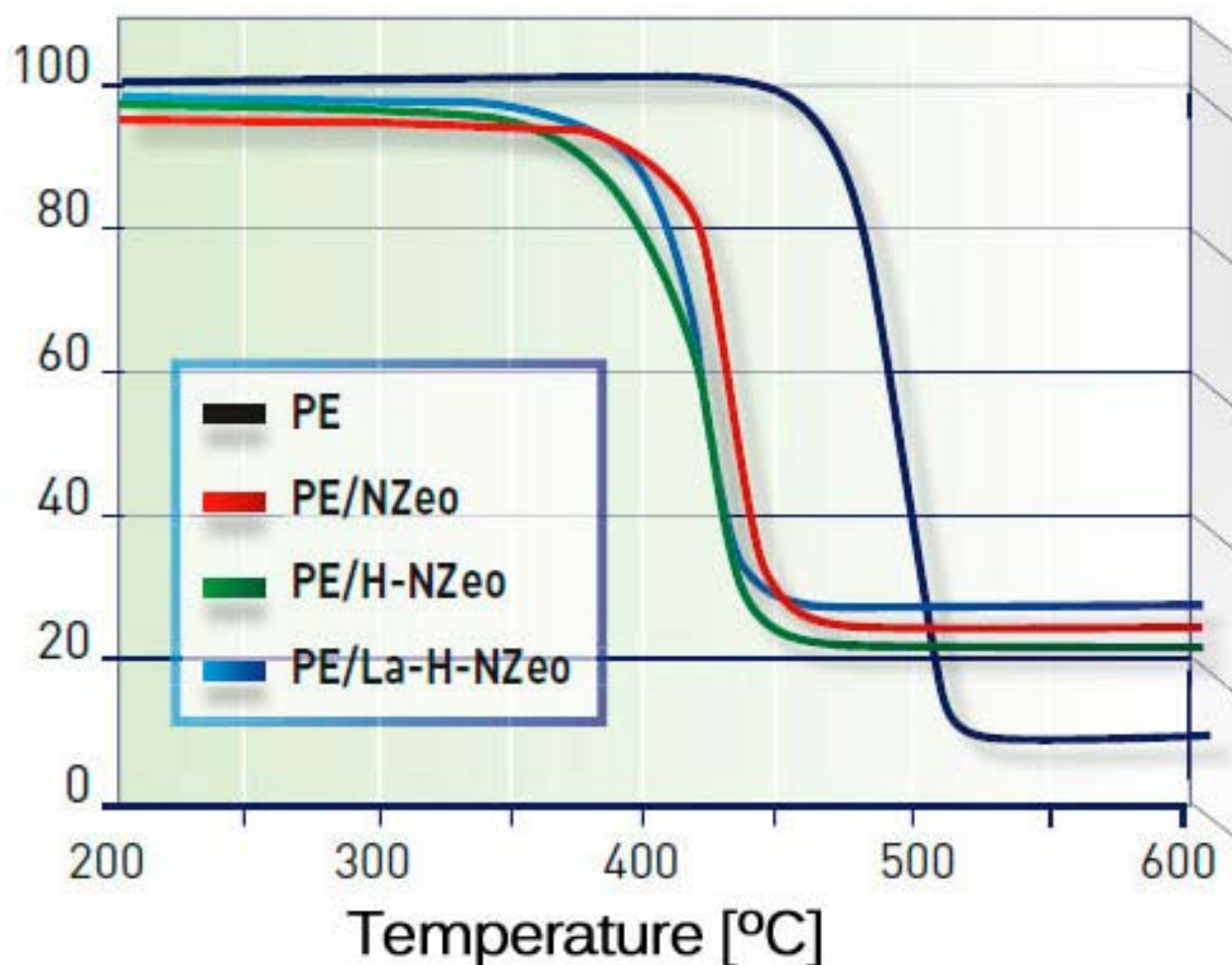

Figure 2. Thermogravimetric analysis of the pure polymer in presence of different nanocatalysts.

Table 2 sums up the effect of the type of particle and its acidity on Tmax. It also shows the Tmax without a catalyst. This table shows the marked effect of catalyst acidity and crystal size. Natural zeolite without modification has no significant degradation effect due to its low acidity. As the modification-induced acidity increases, however, Tmax is brought down by over 50° C. These results show the strong impact of catalyst acidity on the degradation process. Nonetheless our results also show that catalyst size is another important variable. This is brought out by a comparison of the Nzeo catalyst with NatZeo. The modified natural particle show a considerably higher acidity than the nano-sized particle but the latter brings about the bigger Tmax fall. This confirms that the smaller catalysts, ipso facto with a larger surface area, act more efficiently on the polymer degradation process.

Table 2. Effect of the type of catalyst on the polyethylene degradation temperature. Tmax: temperature of maximum weight loss in a TGA test

Catalyst	T$_{max}$ [°C]
N/A	492.5

Catalyst	T_{max} [°C]
NZeo	428.2
H-NZeo	422.3
La-H-NZeo	418.7
Nat	490.2
H-Nat	446.2
La-H-Nat	444.0

A direct consequence of the marked fall in degradation temperatures (table 2) is that the necessary thermal degradation temperature in a reactor might be up to 70° C lower than that necessary in direct pyrolysis. As pointed out in the introduction to this study, therefore, the use of catalysts of this type made cut down the necessary energy input for thermally breaking down polymers.

Breakdown Products
Table 3 sums up the effect of the catalyst on the breakdown products. In particular it shows the percentage in weight of the (gaseous) volatile compounds with respect to liquids of a higher molecular weight. This table confirms that the type of particle and its acidity not only modify the degradation temperature but also the breakdown products. In particular, the nano-sized zeolite produces the largest amount of gaseous compounds, and the higher the acidity the higher is the catalytic activity for producing volatile compounds. Additionally, chromatographic column analysis, revealing the composition of the gaseous products, showed that these catalysts are highly selective towards propylene (~ 70%) and propane (~ 15%). This shows that the use of zeolite catalysts promotes selectivity towards specific products of high added value.

Table 3. Effect of the type of catalyst on the breakdown products. Reaction temperature: 450° C

Catalyst	% volatile compounds	% liquids	% solids and wax
N/A	47	51.1	2
NZeo	83	14.8	2
H-NZeo	87	10.7	2
La-H-NZeo	91	7.5	2
Nat	38.1	13.2	48.7
H-Nat	49.1	23.2	27.7
La-H-Nat	63.4	11.8	24.8

Discussion

The results of this work shed light on the two most important variables in the catalytic degradation of plastic waste: particle size and acidity. In particular, the effect of nanocatalysts on the catalytic degradation of plastic waste has been little studied hitherto, even though it has a very promising potential. The use of nano-sized zeolites with a bigger pore size (pd=7.4 Å for ZSM-2) than the nano-sized ZSM-5 zeolite (pd~ 5.5 Å) considerably improves the efficiency of the process, as shown in this study. This effect is reflected in the degradation temperatures, which are brought down most by nano-sized catalysts. Nonetheless, our results show that the acidity is not the only parameter controlling this process since the catalyst with the highest acidity does not achieve the highest activity. Although the two catalysts studied herein both brought down the degradation temperature and hence reduced the necessary energy input, the larger specific area of NZeo makes it more active.

The effect of the nano-sized structure is borne out by analysing the breakdown compounds. In the scientific literature on this subject it is difficult to find volatile compound productivities higher than 80% w/w[14,15,16,17] , even in other nano-sized catalysts. In our case, however, the Nzeo-based catalysts achieve a 90% gas proportion. This result shows that the crystal size and catalyst pore diameter, together with acidity and crystal structure, could control the production of gaseous compounds, as in the case of the particle NZeo[18]. This is confirmed by analysing the natural zeolite; although it has a higher acidity than NZeo, it produces a lower amount of gaseous compounds. Even the catalyst La-H-Nat, with higher acidity, cannot match the gaseous compound content of NZeo.

Our results show the complexity of these systems, since different reactions simultaneously vie with each other, and each has its own kinetic behaviour depending on the properties of each catalyst. In particular, competition between thermal pyrolysis and the catalytic cracking sought in the system may mean that certain deposition or chain growth reactions are favoured to build up heavy or light compounds according to the catalyst's specific area or acidity[15,19]. The high production of gaseous compounds in the zeolites studied herein, especially NZeo, is due to the overcracking that occurs in very acidic environments[17]. The initial cracking fragments may hence spread through the catalyst's pores and continue reacting in these cavities, producing more gaseous compounds [15,21]. Thus, a catalyst with a larger specific area, such as the nano-sized particles, may perform this process better. This model is confirmed by analysing the lower amount of gases produced by natural micro-sized zeolite in comparison with the nano-sized catalyst, even though both have similar pore sizes (pd ~ 7.4 Å for NatZeo). The reduction of secondary reactions in the zeolite particles, due to the steric limitations associated with their small pore size, explains the formation of larger hydrocarbons. Further alkene reaction is thus inhibited; this explains the selectivity of these systems in favour of the formation of propylene and other alkene molecules[16]. Note also that other variables such as pore size may cause other nano-sized zeolite particles (e.g. beta) to generate mainly liquid compounds, as recently reported[12].

Conclusions

Our results show that the use of zeolites is a viable method for optimising the polyethylene degradation process. By modifying the characteristics of the zeolite, in particular the particle size and acidity, it is possible to control the degradation reactions. The nano-sized zeolites achieve a bigger degradation-temperature fall and a larger production of gaseous compounds than natural zeolites. This higher catalytic activity is explained by the larger specific external surface area of the nano-sized compounds, favouring the surface cracking process. Moreover, by means of acidic modifications, the natural zeolites can perform as well as polyethylene degradation facilitators; together with their low price this makes their use commercially feasible in industrial applications. The use of these catalysts could therefore be applied at industrial level to cut down the energy input of the plastic waste degradation process, while at the same time generating volatile compounds of high commercial value, such as propylene.

TO FIND OUT MORE

1. Galli P.,Vecellio G. Polyolefins: The most promising large-volume materials for the 21st century J. Polym. Sci. Part A: Polymer Chemistry. 2004;42:396-415.

2. Neves I.C., Botelho G., Machado A.V., Rebelo P. The effect of acidity behaviour of Y zeolites on the catalytic degradation of polyethylene. Eur. Polym. J. 2006;42:1541-1547.

3. Chum P.S., Swogger K.W. Olefin polymer technologies-History and recent progress at The Dow Chemical Company. Progress in Polymer Science 2008;33:797-819.

4. Association of Plastic Manufacturers in Europe (APME), Summary Report: An analysis of plastics consumption and recovery in Europe 2002&2003, Brussels, Belgium, 2004.

5. Aguado J., Serrano D.P., San Miguel G., Escola J.M., Rodríguez J.M. Feedstock recycling of polyethylene in a two-step thermocatalytic reaction system. J. Anal. Appl. Pyrol. 2007;78:153-161.

6. Hwang E.Y., Kim J.R., Choi J.K., Woo H.C., Park D.W. Performance of acid treated natural zeolites in catalytic degradation of polypropylene. J Anal. Appl. Pyrol. 2002;62:351-357.

7. Garforth A.A., Ali S., Hernández-Martínez J., Akah A. Feedstock recycling of polymer wastes. Current Op. Sol. Stat. Mat. Sci. 2004;8:419-425.

8. García R.A., Serrano D.P., Otero D. Catalytic cracking of HDPE over hybrid zeolitic-mesoporous materials J. Anl. Appl. Pyrol. 2005;74:379-386.

9. Durmus A., Koc S.N., Pozan G.S., Kasgoz A. Thermal-catalytic degradation kinetics of polypropylene over BEA, ZSM-5 and MOR zeolites. Appl. Cat. B: Env. 2005;61:316-322.

10. Fernandes G.J.T., Fernández V.J., Araujo A.S. Catalytic degradation of polyethylene over SAPO-37 molecular sieve. Cat. Today. 2002;75:233-236.

11. Filho J.G.A.P., Graciliano E.C., Silva A.O.S., Souza M.J.B., Araujo A.S. Thermo gravimetric kinetics of polypropylene degradation on ZSM-12 and ZSM-5 catalysts. Catal. Today 2005;107:507-512.

12. Lee, Y.J., Kim J.H., Kim S.H., Hong S.B., Seo G. Nanocrystalline beta zeolite: An efficient solid acid catalyst for the liquid-phase degradation of high-density polyethylene. Appl. Cat. B: Env. 2008; 83:160–167.

13. Covarrubias C., Quijada R., Rojas R. Synthesis of nano-sized ZSM-2 zeolite with potential acid catalytic properties. Microp. Mesop. Mat. 117 2009; 117:118-125.

14. Manos G., Garforth A., Dwyer J. Catalytic degradation of high-density polyethylene over different zeolitic structures. Ind. Eng. Chem. Res. 2000;39:1198-1202.

15. Mastral J.F., Berrueco C., Gea M., Ceamanos J. Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 zeolite. Polym. Deg. Stab. 2006;91:3330-3338.

16. Manos G., Garforth A., Dwyer J. Catalytic degradation of high-density polyethylene on an ultrastable-Y zeolite. Nature of initial polymer reactions, pattern of formation of gas and liquid products, and temperature effects. Ind. Eng. Chem. Res. 2000;39:1203-1208.

17. Manos G., Yusof I.Y., Papayannakos N, Gangas NH. Catalytic cracking of polyethylene over clay catalysts. Comparison with an ultrastable Y zeolite. Ind. Eng. Chem. Res. 2001;40:2220-2225.

18. Covarrubias C., Gracia F., Palza H. Catalytic degradation of polyethylene using nano-sized ZSM-2 zeolite. Appl. Cat. A: General 2010;384:186-191. [19] Singh B., Sharma N. Mechanistic implications of plastic degradation. Polym. Degrad. Stab. 2008;93: 561-584.

19. Seo Y.H., Lee K.H., Shin D.H. Investigation of catalytic degradation of high-density polyethylene by hydrocarbon group type analysis. J. Anal. Appl. Pyrol. 2003;70:383-398.