Feedstock recycling of polyethylene over AlTUD-1 mesoporous catalyst

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Abstract

The catalytic degradation of high density polyethylene (HDPE) was investigated using AITUD-1 as catalyst, a recently discovered mesoporous aluminosilicate. The catalytic activity of AlTUD-1 was evaluated by TGA measurements, using a polymer/catalyst ratio of 9:1. AlTUD-1 has a Brønsted acidic behaviour, three-dimensional (3D) connectivities and a pore diameters between 2 and 50 nm . Compared to HY zeolite, the large pore size of AITUD-1 enhances a selective catalytic degradation of the polymer and prevents rapid deactivation. Moreover, the apparent activation energy of polymer cracking is much lower than with HY zeolite. For these reasons, AITUD-1 is a potentially interesting catalyst for the catalytic cracking of plastic waste into liquid fuels.

Keywords: Catalytic degradation; AlTUD-1; High density polyethylene; Thermal analysis

Introduction

In recent years, plastic material consumption has undergone a significant growth. Society, in general, and the industry, in particular, have extensively incorporated plastics for replacing other materials; consequently, large amounts of plastic waste are generated annually. Presently, landfilling is the main method used for dealing with residues, in spite of the large fraction volume (20%) occupied by plastic wastes as a consequence of their low density [1].

An alternative method to dispose plastic wastes is represented by thermal degradation. Simple thermal degradation requires high temperatures and usually leads to a wide product distribution with poor economical value. In contrast, catalytic degradation allows the plastic cracking to be performed at

lower temperature and the gaseous and liquid products obtained can be used as fine chemicals or fuels [2].

Among the different catalysts suitable for this process, acid zeolites show very good properties due to their good activity and shape selectivity [3,4]. One of the main problems related to the use of acid zeolites is their progressive deactivation during the process [5-7]. Due to the bulky nature of plastic molecules, the cracking reaction is strongly controlled by the pore size of the catalysts. Several authors have suggested that the initial steps of the polymer degradation over zeolites takes place mainly on the acid sites located on the external surface of the zeolite crystals [8-11]. After the cracking of the first polymer molecules, the smaller units diffuse into the zeolite structure producing coke. The coke formed inside the zeolites blocks the access to acid sites and induces the deactivation of the zeolite [6,7].

Previously, the influence of the acidity of Y zeolites on the catalytic degradation of high density polyethylene was investigated by ion exchange treatments [12] and different $\mathrm{Si/Al}$ ratios [13]. The presence of the dealuminated Y zeolites lead to an increase in the polymer degradation rate owing to the decrease of Al^{+3} cations in the neighboring positions providing strong Brønsted acid sites due to their isolation [13].

The present study explores the catalytic cracking of the same polymer using AITUD-1 as catalyst. This new mesoporous aluminosilicate is characterized by high surface area, high thermal and hydrothermal stability, Brønsted acidic behaviour and 3D connectivities with tunable diameters between 2 and 50 nm [14]. The 3D pores could allow better accessibility of the catalyst compared with one-dimensional pore system as found in other mesoporous materials such as MCM-41 [15-19].

The polymer sample stability, in the presence of AlTUD-1, was studied by Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC). The samples were subjected to dynamic thermogravimetric analysis in order to estimate the activation energy of the process. The residues obtained after isothermal TGA were characterized by DSC to determine the polymer crystallinity.

Experimental section

Materials and reagents

High density polyethylene (HDPE) (Stamylan HD 2H 280, $M_{\mathrm{w}} = 60\ \mathrm{kg/mol}, d = 945\ \mathrm{kg/m^3}, T_{\mathrm{vicat}} = 399\ \mathrm{K}$ (data supplied by manufacturer)) was obtained from DSM.

Chemicals for the synthesis of AlTUD-1 were purchased from Aldrich. The Y zeolite (in the hydrogen form, CBV 400) was obtained from Zeolyst International in powder form. Prior to use, the HY zeolite was previously calcined at 773 K during 8 h under a dry air stream.

Synthesis of the AITUD-1

Two mesoporous catalysts AlTUD-1 (AlTUD-1A and Al-TUD-1B) with different Si/Al atomic ratios, surface areas and porosities were synthesized according to previously published procedures [14,20]. Aluminum isopropoxide (0.03 mol) was added to a mixture of absolute ethanol (0.60 mol), anhydrous 2 -propanol (0.45 mol) and tetraethyl orthosilicate (0.12 mol) under stirring at 318 K . After stirring for a few minutes, the tetraethylene glycol (0.15 mol) was added. The resulting mixture was stirred for 1 h at 318 K . A solution of absolute ethanol (0.60 mol), anhydrous 2-propanol (0.45 mol) and water (0.30 mol) was added drop wise to this mixture. The resulting mixture was stirred for 0.5 h at 318 K . The clear gel obtained after these steps was then aged at room temperature for $12-24$ h, dried at 343 K for $6-12$ h and after drying at 371 K for $12-24$ h, followed by hydrothermal treatment in a Teflon lined autoclave at 453 K for $4-24$ h it was finally calcined in the presence of air at up to 823 K at a temperature ramp of $1\ \mathrm{K\ min}^{-1}$ and subsequent heating at 873 K for 10 h .

Preparation of the samples for degradation

Three samples of HDPE and catalysts with different pore structures were prepared by mixing at room temperature the polymer powder with AlTUD-1A, AlTUD-1B (mesoporous structures) and HY (microporous structure), using a polymer/catalyst ratio of $9:1$. The ratio used in this study has been kept constant and equal to 9 , which was shown to be the best ratio for this type of study [21].

Characterization

The elemental chemical analysis was performed by Kingston Analytical Services (UK) using inductively coupled plasma atomic emission spectrometry (ICP-AES). Powder XRD spectra of the catalysts were obtained with a Philips PW1710 diffractometer using $\mathrm{Cu\ K}\alpha$ radiation. Both low- and wide-angle X-ray spectra were collected in order to characterize the crystallinity of the meso- and microporous materials. The textural characterization of the catalysts was based on the N_2 adsorption isotherms, determined at 77 K with a Coulter Omnisorp 100 CX apparatus. The samples were previously outgassed at 423 K under vacuum. The micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) were calculated by the t-method. Surface areas were calculated by applying the BET equation, whereas pore size distributions were determined using the BJH method. Scanning electron microscopy (SEM) was performed using a LEICA Cambridge S360 Scanning Microscope equipped with EDS system. Samples were coated with Au in vacuum to avoid surface charging using a Fisons Instruments SC502 sputter coater. Thermogravimetric analyses (TGA) were carried out using TGA 50 Shimadzu instrument under high purity helium supplied at a constant $50\ \mathrm{mL/min}$ flow rate. Two types of experiments were performed: (i) dynamic experiments where the polymer/catalyst were subjected to different heating rates of 5, 10,15 and $20\ \mathrm{K/min}$, between 300 and 800 K in order to estimate the activation energy of the catalytic degradation process and (ii) isothermal experiments were performed at 473 and 673 K during 8 h . The thermal behaviour of the degraded samples was evaluated using a Perkin-Elmer DSC 7 differential scanning calorimetry (DSC). Samples of ca. 4 mg were heated from 303 to 423 K , at a heating rate of 10 K/min, under a constant 20 mL/min flow rate of nitrogen, in order to estimate the crystallinity of each sample with the same thermal history.

Results and discussion

Physicochemical properties of the catalysts

All catalysts used in this work are aluminosilicate materials with different acidities, porosities and crystallinities. Y zeolite is a crystalline microporous aluminosilicate based on sodalite cages joined by O bridges between the hexagonal faces. Eight such sodalite cages are linked together, forming a large central cavity or supercage with a diameter of 1.3 nm . The supercages share a 12 -membered ring with an open diameter of 0.7 nm .

The pore size is comparable to that of small molecules, allowing them to reach the acid sites located inside the zeolite structure while hindering the access of bulky molecules [22]. AITUD-1 is a new, structured mesoporous aluminosilicate with Brønsted acidic behaviour having three-dimensional connectivities with mesopores between 2 and 50 nm , whose size can be adjusted by changing the synthesis conditions [14].

The textural and surface chemistry properties of the catalysts were studied by different techniques: powder XRD, SEM, isothermal nitrogen adsorption and elemental analysis. This characterization was carried out in more detail on the AITUD-1, since this is a new catalyst.

XRD and SEM studies demonstrate the differences in crystallinity and morphology of all catalysts. The relative crystallinity of HY zeolite was estimated by comparing the intensities with NaY as a standard sample (100% crystalline). The total intensities of the six peaks assigned to [331], [511], [440], [5339], [642] and [555] reflections were used for the comparison according to ASTM D 3906-80 method. The XRD pattern of HY is typical of the faujasite zeolite structure and presents over 80% of crystallinity. On the other hand, the XRD patterns of the AlTUD-1 samples (Fig. 1) show an intense peak at low angle (at $2\theta \sim 1-2^{\circ}$) indicating a mesoporous and amorphous character of the material [20].

SEM analysis of the catalyst confirms the different porosity structures of the aluminosilicate materials used in this work. SEM micrographs of HY and AlTUD-1B (Fig. 2) exhibit two types of particles with different morphologies and dimensions. The SEM micrograph of HY (Fig. 2a) is typical of a microporous crystalline aluminosilicate with regular small particles ($\sim 1\mu$ m), while that of the AITUD-1 samples (Fig. 2b) show large particles ($\sim 200\mu$ m).

The nitrogen adsorption equilibrium isotherms at 77 K for the mesoporous AlTUD-1 catalysts are illustrated in Fig. 3.

The N_2 adsorption isotherms for both AITUD-1 samples are of type IV with a hysteresis loop, according to the IUPAC classification, which is typical for solids with a mesoporous structure [14]. Both adsorption isotherms present a characteristic sharp inflection lower than 0.70 relative pressures due to the pore condensation typical of mesoporous materials.

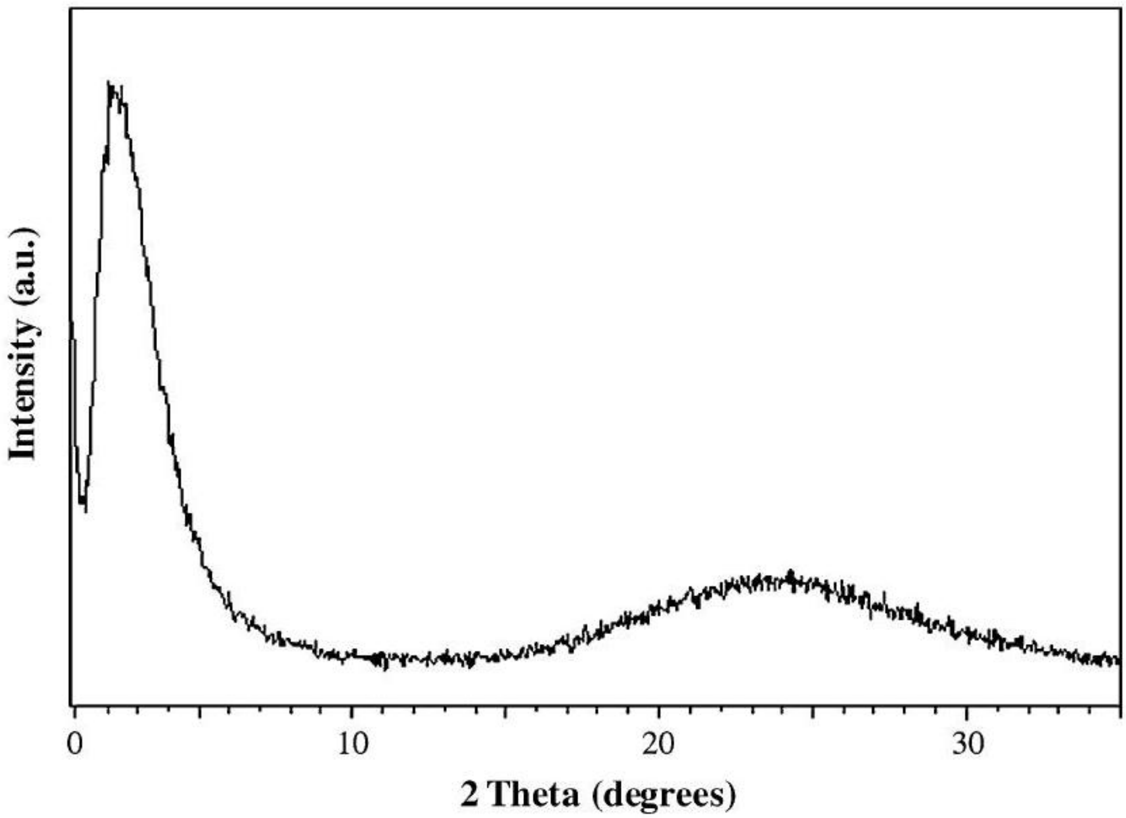

Fig. 1. XRD powder pattern of AlTUD-1.

The pore volume distribution of both mesoporous samples, calculated by the analysis of the desorption isotherm using the BJH method is presented in Fig. 4.

Table 1 summarizes the textural properties of the different catalysts used in this work. The surface areas of the AITUD-1 samples are lower than that of HY. Both AITUD-1 samples exhibit a very wide distribution of pore sizes. In addition to micropores, AlTUD-1A presents mesopores in the whole range between 1 and 40 nm , with two maxima at 2 – 4 and 10 – 20 nm , while AlTUD-1B reveals no micropores and mesopores with a maximum at 2 – 4 nm.

The surface area and total pore volume of AITUD-1B are lower than AITUD-1A. These differences are due to the variation of the hydrothermal treatment time and of the calcination conditions during the synthesis of the catalysts [14].

The catalytic properties of the catalysts can be related to their Si/Al ratio measured by ICP-AES elemental analysis. A lower Si/Al ratio generally implies a higher catalytic activity due to the presence of a higher number of Brønsted acid sites. The HY zeolite presents the highest number of acid sites due to the lowest Si/Al ratio and to the fact that a part of the Al site is not accessible in mesoporous materials since they are incorporated inside the walls surrounding the mesopores. Moreover, the strength of acid sites in mesoporous materials is generally lower compared to that in zeolites [16].

The two AlTUD-1 samples have different Si/Al atomic ratios which imply different degree of acidity. The Si/Al ratio for AITUD-1B is 1.4 higher than for AITUD-1A. It is known that for zeolites, the acid strength of a given site will increase when there is a decrease in the number of aluminum species in next nearest neighboring positions (NNN) of the aluminum which supports the acid sites. A completely isolated aluminum tetrahedron will have zero NNN (ONNN) and will support the strongest type of framework Brønsted acid site [5]. Since this new mesoporous material has a Brønsted acidic behaviour the same effect could be expected.

Thermal stability studies on the polymer/catalysts samples

Dynamic thermogravimetric analyses were performed to evaluate the cracking activity of the catalysts. As an example, Fig. 5a shows the weight loss of the samples as a function of the temperature, measured at 5 K/min. Fig. 5 b shows the corresponding derivative curves (DTG curves). As it can be seen in Fig. 5a, the degradation processes occur in a two step weight loss (the second one is the most relevant) and the residue obtained is ca. of 10% when the catalyst is present. These two steps can be clearly observed in Fig. 5b, one at lower temperature, which appears as a shoulder and the other at higher temperatures, which appears as a sharp peak.

From the thermogravimetric results it can be observed that for the catalyzed process the degradation takes place at quite lower temperatures when compared with pure HDPE [21], due to the polymer catalytic cracking. Thus, for the three catalysts the weight loss starts at temperatures between 500 and 700 K , indicating that a significant reduction occurs at the

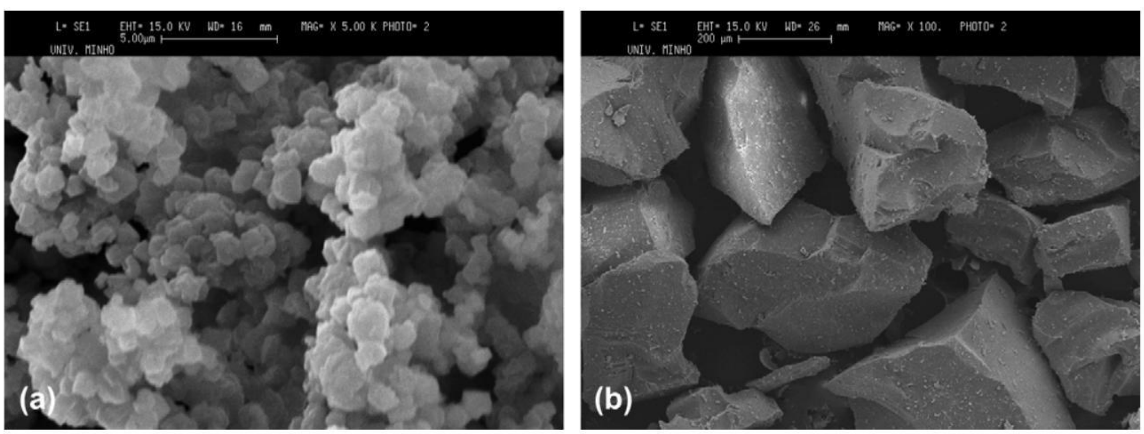

Fig. 2. SEM micrographs with different resolutions: (a) 5000 × for HY and (b) 100 × for AlTUD-1B.

onset temperature. As expected, HY zeolite, which has the strongest acidity, gives the lowest value of onset temperature [12]. AlTUD-1B presents an intermediate behaviour: the onset temperature is slightly higher than HY but lower than AITUD1A. The differences obtained for the two AlTUD-1 samples can be explained by different Si/Al ratios and their porous structure (values in Table 1): (i) higher Si/Al for AlTUD-1B means a reduction of the number of Al^{+3} cations in the neighboring positions, which provides strong Brønsted acid sites due to their isolation [5,13] and (ii) absence of micropores in AITUD-1B probably allows the polymer to diffuse more efficiently inside the catalyst, providing a better accessibility to the active Brønsted acid sites.

The onset and the maximum decomposition temperatures obtained in the thermogravimetric analysis (under the same experimental conditions) are shown in Table 2 [23].

In all cases, the presence of the catalysts affects the decomposition process, reducing considerably the maximum decomposition temperature (Fig. 5b/Table 2). However, the AlTUD-1 samples have a stronger effect.

To evaluate the effect of the catalysts on the activation energies (E_a) on the polymer/catalysts polymer degradation, the activation energies were calculated from the experimental data using the method of multiple heating rates [24]. This method is considered more appropriate to obtain kinetic parameters than others that are based on single heating rates [25]. From

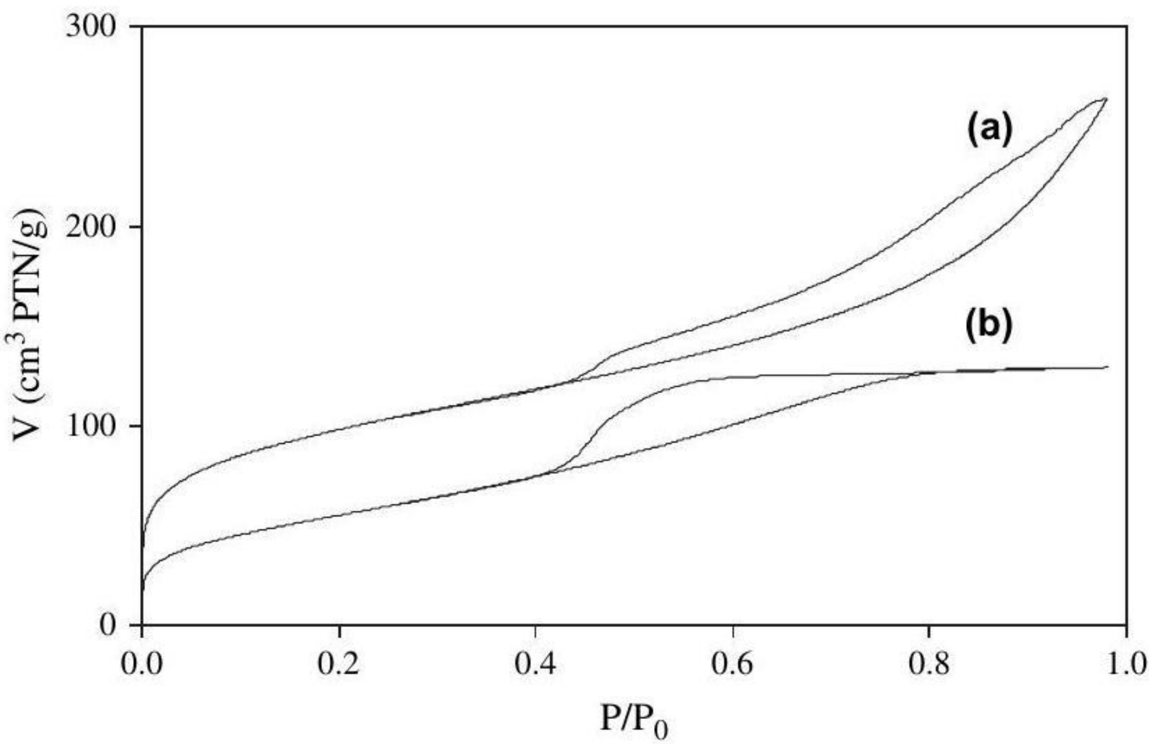

Fig. 3. Nitrogen adsorption-desorption equilibrium isotherms at 77 K of the mesoporous samples: (a) AlTUD-1A and (b) AlTUD-1B.

the TGA curves at each heating rate the temperature is estimated for a specific conversion level. Using the plot of the logarithms of the heating rates against the reciprocals of the corresponding values of the absolute temperature, a straight line is obtained whose slope is proportional to the activation energy. The gradients of the various lines are very similar resulting in analogous values of the activation energy at different residual weights for all degradation processes and can be accepted as an indication of the accuracy of the method. The values obtained for the activation energies along conversion are shown in Fig. 6.

The addition of catalysts decreases the activation energy obtained for HDPE. The results indicate that the energy required to degrade HDPE is lower with AlTUD-1B followed by AITUD-1A and HY. The activation energy calculated for AlTUD- 1 B is about 33 kJ/mol lower than that for HY and is comparable to the value reported in literature for another structured mesoporous material, Al-containing MCM-41 [10]. The lower activation energy observed with the AlTUD-1 samples is attributed to their mesoporous structure which is more accessible to large molecules like polymers than the microporous framework of zeolites [8,10]. The difference in activation energy between the two AlTUD-1 catalysts can be attributed to the absence of microporosity and highest Si/Al ratio in AlTUD-1B.

To gain further information about the catalytic degradation of HDPE, two isothermal TGA runs were performed at 473

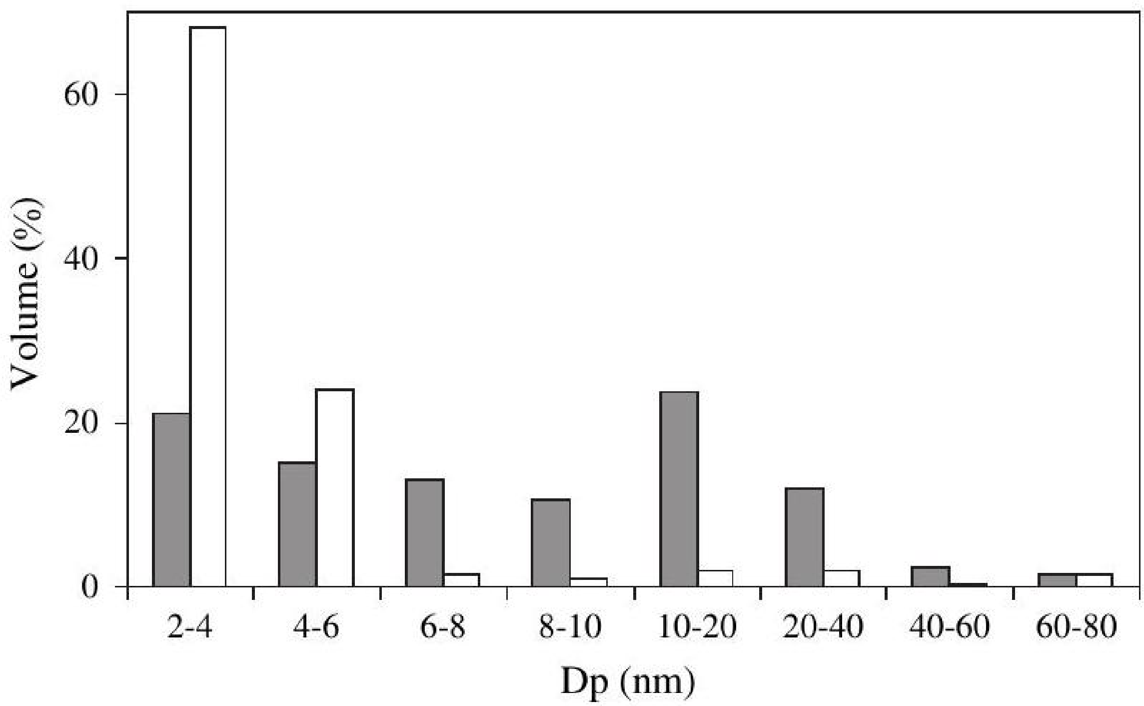

Fig. 4. Pore volume distribution of the mesoporous samples determined from equilibrium isotherms at 77 K: (□) AlTUD-1A and (□) AlTUD-1B.

Table 1
Physicochemical properties of the catalysts

	HY	AlTUD-1A	AlTUD-1B
Si/Al	2.80	3.50	4.85
S_{BET} (m^2/g)	730	357	204
V_p (cm^3/g)[a]	0.300	0.409	0.201
V_{micro} (cm^3/g)[b]	0.300	0.078	0
S_{meso} (m^2/g)	0	189	204

[a] Total pore volume, measured at $p/p_0 = 0.98$.
[b] Total micropore volume.

and 673 K . The temperatures used were selected to include both the polymer melting point and the onset temperature. It has been shown previously, that isothermal experiments are very useful to investigate the catalytic activity of the catalyst in HDPE degradation [12].

Fig. 7 shows the behaviour of the HDPE over catalysts at the lower and higher temperatures for 8 h .

Fig. 7a shows the results obtained at lower temperature and it was observed that the more pronounced weight loss of the samples occurs for HY zeolite. For both AITUD-1, the weight loss is significantly lower, and particularly for AlTUD-1B, for which the weight loss remains almost constant along the time scale.

For higher temperature, the catalysts present similar behaviour. After 30 min from the beginning of the catalytic degradation, the weight loss of the HDPE in all catalysts is pronounced. However, for HY the weight loss occurs slightly faster than AlTUD-1 catalysts (Fig. 7b).

The differences observed in the cracking activities of all catalysts are due to the acidic character and the pore structure.

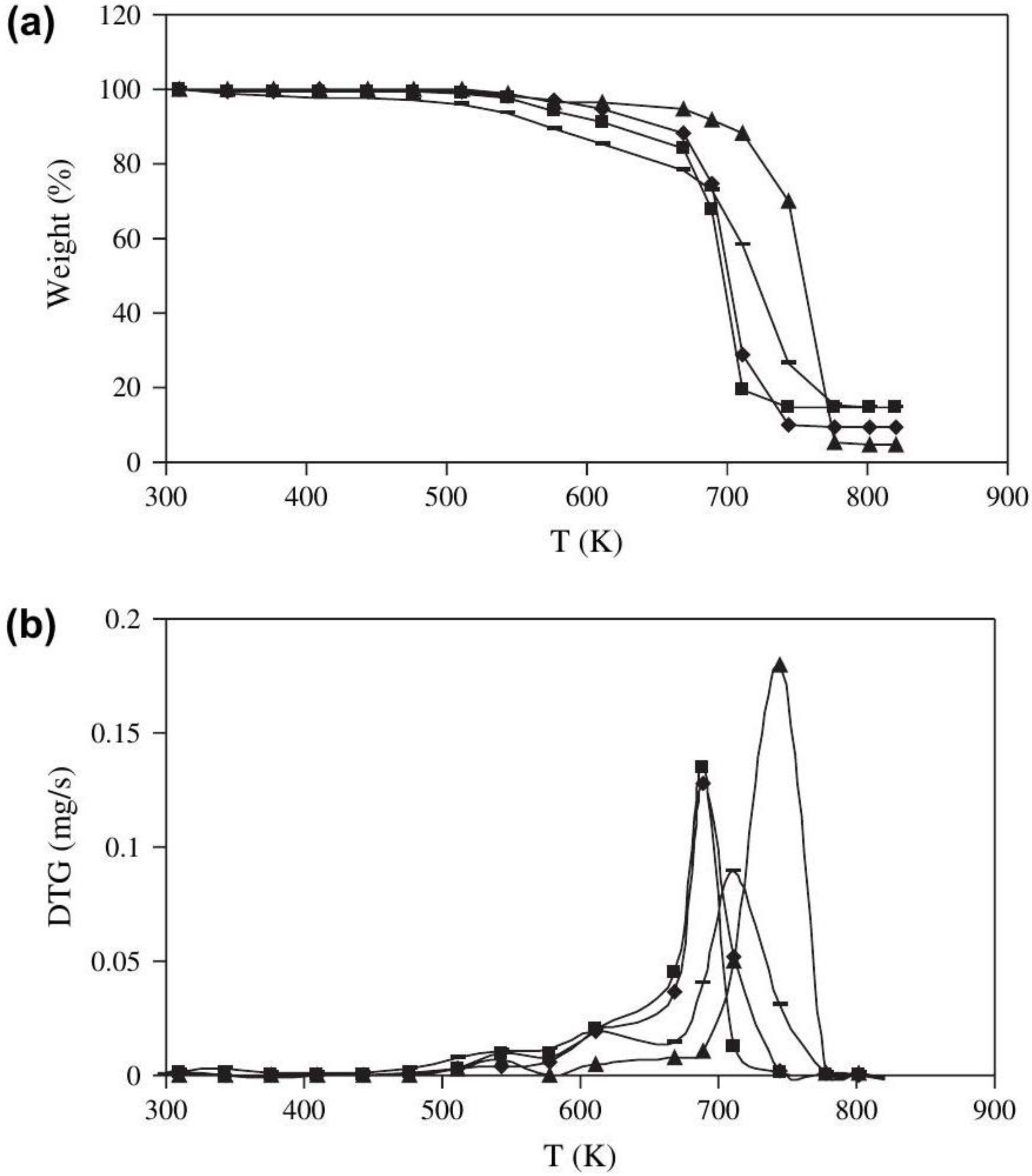

Fig. 5. (a) TG and (b) DTG curves obtained for the samples: (Δ) HDPE, (-) HDPE + HY, ( ) HDPE + AITUD-1A and (■) HDPE + AITUD-1B.

Table 2
TG and DTG results obtained for the polymer/catalysts samples

Samples	T_{onset} (K)	$T_{maximum}$ (K)[a]
HDPE [21]	715	744
HDPE + HY	665	710

HDPE + AITUD-1A	675	689
HDPE + AITUD-1B	669	689

[a] Maximum decomposition temperature observed in DTG curves.

Acid-catalyzed degradation of hydrocarbons is known to proceed via carbonation mechanisms, initiated either by proton donation (Brønsted acid sites, strong acid sites) or by hydride abstraction (Lewis acid sites, mild acid sites) [5,9]. In the case of HY zeolite, the initial polymer cracking probably occurs at the acid sites located on the external surface of the zeolite crystals or at the pore openings. This cracking produces smaller molecules, which are able to diffuse inside the zeolite and transformed into coke due to the presence of strong Brønsted acid sites, leading to obstruction of the microporous structure [26]. It is known that the products of the catalytic degradation are volatile hydrocarbons in the range $C_3 - C_5$ [27,28].

In analogy with what found for mesoporous AlMCM-41, AITUD-1 is expected to cause less coke formation and, therefore, suffer less deactivation than zeolite HY [10]. The determination of the distribution of the molecules produced by cracking of the HDPE over AlTUD-1 will be carried out in future work.

The residues obtained from the 473 K isothermal TGA experiment, were analyzed by DSC to evaluate the effect of the catalysts on the polymer crystallinity. Values in Table 3 indicate that the reduction of crystallinity was higher in the presence of HY and very similar in the other cases [12]. This behaviour can be attributed to the diversity of the products obtained after HDPE catalytic degradation due to the presence of different pore structures. In the presence of HY the amount of smaller molecules obtained by the polymer cracking is more relevant than AITUD-1 catalysts. This fragmentation and the little size of products imposed by the microstructure of HY are more efficient in the reduction of the polymer crystallinity, as at 473 K this catalyst is more active than AlTUD-1.

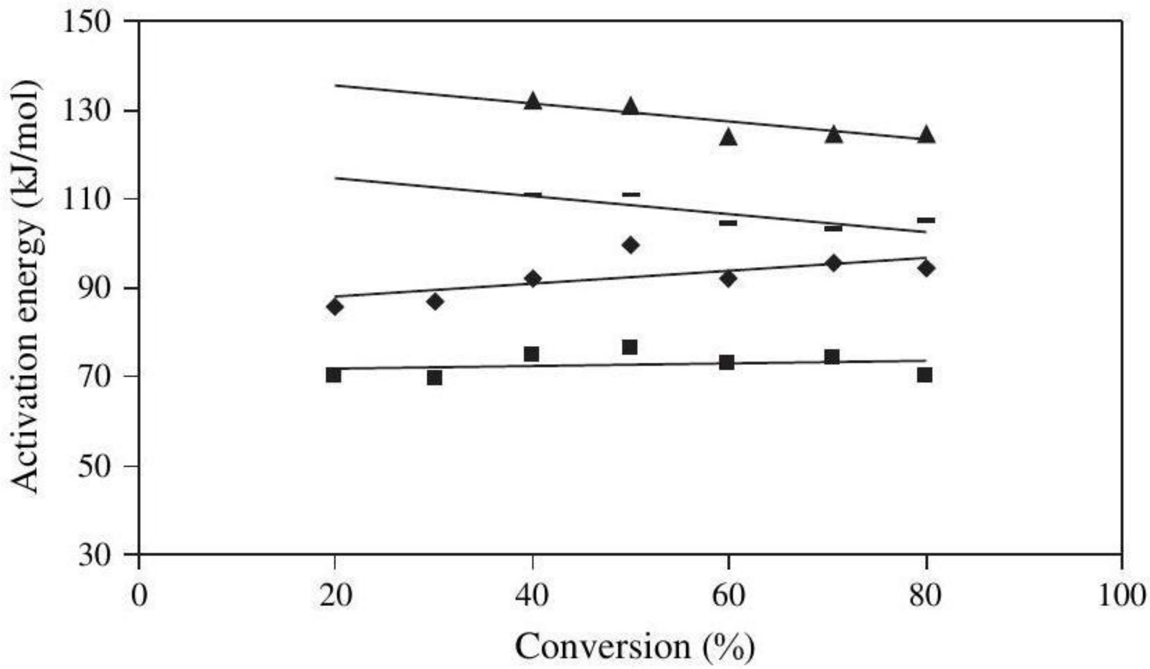

Fig. 6. Activation energy vs. conversion for the samples: (Δ) HDPE, (-) HDPE + HY, ( ) HDPE + AlTUD-1A and (■) HDPE + AlTUD-1B.

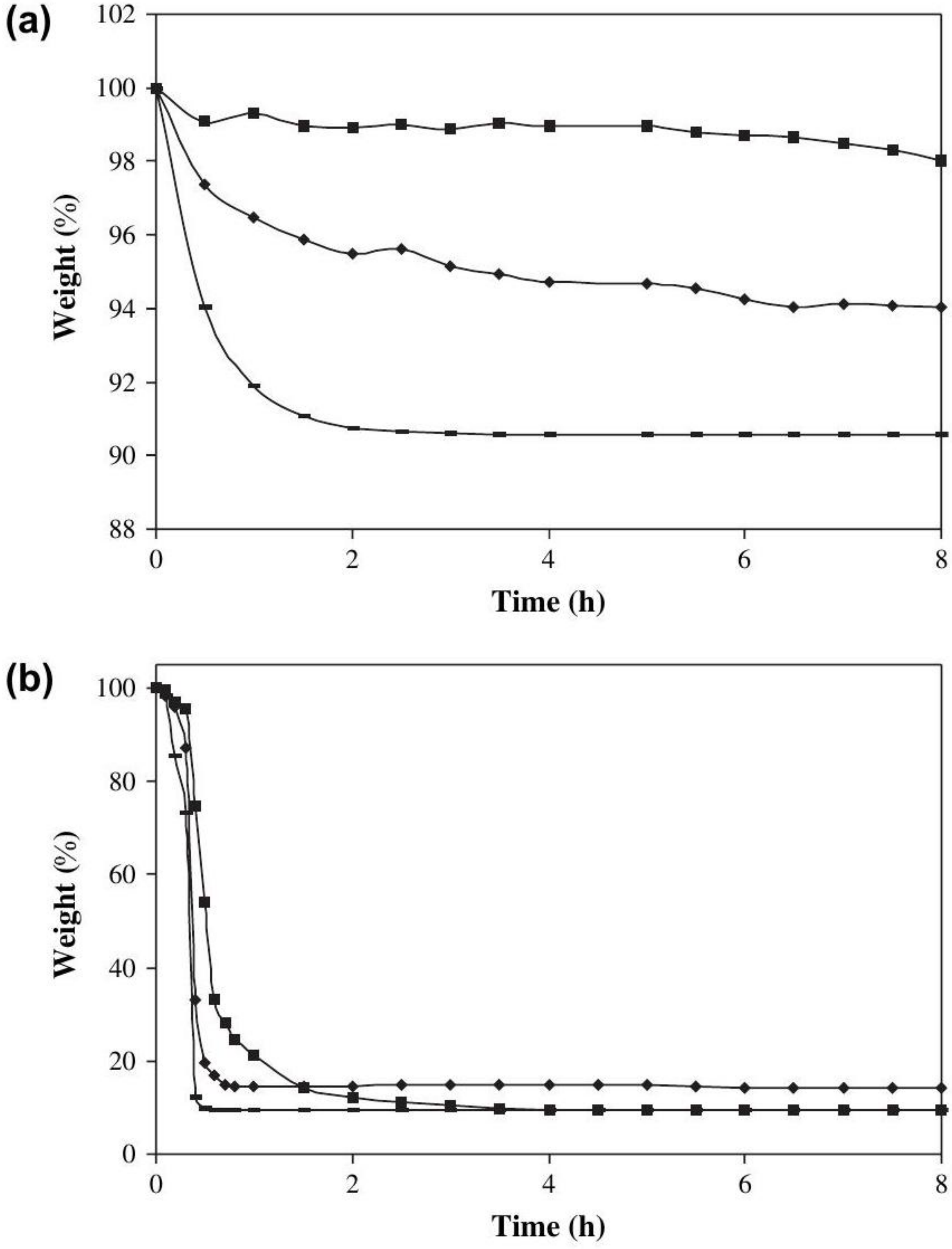

Fig. 7. Isothermic thermogravimetric curves obtained for the samples at (a) 473 K and (b) 673 K: (—)HDPE + HY, (—)HDPE + AITUD − 1 A and (HDPE + AlTUD-1B.

When taken together, the results from dynamic combined with isothermic experiments clearly prove that AITUD-1 catalysts have potential to be used in polymer catalytic degradation.

Conclusions

The catalytic degradation of HDPE using catalysts with different porosity structures - two mesoporous (AlTUD-1A and B) and one microporous (HY zeolite) - was studied by thermogravimetric analysis. Apparent activation energies for the catalytic degradation of HDPE, calculated on the basis of Ozawa mathematical model were in the following order:

HY > AlTUD-1A > AlTUD-1B
The results clearly show that the catalytic degradation of polymers depends on the chemical and physical characteristics

Table 3
DSC results obtained for the polymer/catalysts samples

Samples	ΔH_f(J/g)	χ(%)^a
HDPE	161.6	51.3
HDPE + HY	91.8	33.1
HDPE + AITUD-1A	122.6	44.3
HDPE + AITUD-1B	129.7	46.8

of the catalysts. The acidity and the pore structure play an important role in the performance of the catalysts studied. More open structure allows the better accessibility of HDPE molecules to the active sites inside the catalytic structure. It was demonstrated that the new 3D mesoporous materials, Al-TUD-1, show promising catalytic properties for the cracking of polymeric wastes into liquid feedstock.

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[a] The degree of crystallinity was calculated considering that, for polyethylene, the theoretical heat of fusion (ΔH_f) is 277.1 J/g [29].