

CATALYTIC CRACKING OF HDPE OVER HYBRID ZEOLITIC-MESOPOROUS MATERIALS

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ABSTRACT

The potential application of hybrid ZSM-5/MCM-41 materials for the catalytic degradation of high density polyethylene (HDPE) has been investigated and compared with the behavior of a standard Al-MCM-41 sample. Hybrid zeolitic-mesoporous materials were prepared from zeolite seeds obtained in different stages of ZSM-5 crystallization by variation of the synthesis time. The seeds were assembled around cetyltrimethyl ammonium bromide (CTAB) micelles to obtain hybrid materials having a combination of both zeolitic and mesostructured features. The samples so obtained have exhibited remarkable catalytic activity in the HDPE cracking despite the low temperatures (380 °C) and catalyst loadings used (plastic/catalyst mass ratio =100), leading to polyolefin conversions higher than Al-MCM-41. The product distribution observed with the hybrid materials is closer to that typically obtained in the HDPE cracking over HZSM-5 zeolite, with a high proportion of light hydrocarbons. Moreover, the products present a high content of C₂-C₅ olefins, which is an interesting result regarding its possible use as raw chemicals. Increasing the zeolitic crystallinity of the hybrid materials causes an enhancement in the production of heavier products with boiling points within the gasoline range.

Keywords: HDPE, hybrid zeolitic-mesoporous, plastics catalytic cracking

Introduction

In the last years plastic materials consumption has undergone a significant growth. Society, in general, and the industry, in special, has extensively incorporated plastics for replacing other materials. In a similar way large amounts of plastic wastes are generated annually. At present, landfilling is the main alternative being applied for dealing with these residues, in spite of the large fraction volume (20%) occupied by plastic wastes as a consequence of its low density [1]. Mechanical recycling is aimed to the recovery and reuse of the plastic materials contained in the wastes, although is strongly limited by the low quality of the recycled plastics due to the presence of different polymers, additives and impurities.

Chemical recycling has emerged in the last years as a potentially interesting alternative for the management of plastic wastes by means of its degradation and conversion into a variety of products, useful mainly as raw chemicals or as fuels [2-9]. 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, while the product distribution can be controlled by a right selection of the catalyst type being used. In the case of the HDPE catalytic cracking, a number of acid porous solids, such as amorphous silica-alumina, zeolites and ordered mesoporous materials, have been used as catalysts. The two last catalyst types have been found to be complementary in regards to the product distribution. While ordered mesoporous Al-MCM-41 materials yield hydrocarbons within the gasoline and gasoil fractions, ZSM-5 zeolite directs the catalytic cracking towards light products with a great production of gaseous hydrocarbons. These results have been interpreted in terms of the cracking mechanism [10]. Polyolefin cracking over Al-MCM-41 proceeds by a

random scission mechanism due to its large pore size and mild acidity. In contrast, HZSM-5 zeolite leads to an end-chain cracking pathway, which has been assigned to its strong acidity and small pore size. Moreover, a remarkable cracking activity has been obtained over nanocrystalline ZSM-5 samples, with crystal size in the nanometer range, due to the presence of high external surface area and low diffusional constraints. Thus, nanocrystalline ZSM-5 has shown a significant catalytic activity in the polyethylene cracking even when using high plastic/catalyst ratios and temperatures below 400°C.

In recent years, several authors have reported the synthesis of a new class of porous materials which are supposed to combine the properties of both zeolites and ordered mesoporous aluminosilicates [11-13]. These materials present a mesostructured ordering similar to that of Al-MCM-41, with the difference that the walls are not amorphous but they consist of zeolitic units. As a consequence, drastic improvements in the hydrothermal stability, acid strength and catalytic activity have been reported in the literature for these hybrid zeolitic-mesostructured solids. The present work is aimed to the study of the catalytic properties in the HDPE cracking over hybrid ZSM-5/MCM-41 materials.

Experimental section

1.1. Catalyst preparation

Zeolite seeds obtained in the early stages of ZSM-5 crystallization were assembled around cetyltrimethylammonium bromide (CTAB) micelles to prepare hybrid zeolitic-mesoporous materials. Thereby, a ZSM-5 synthesis gel was prepared according to a procedure earlier reported [14]. The gel was aged for 40 h at room temperature and crystallized at 90 °C under atmospheric pressure in order to promote the generation of the zeolite seeds. Different crystallization times were employed to obtain samples with

different degree of zeolitic crystallinity. Thereafter, the formation of the mesostructure was achieved by the addition of the surfactant (CTAB, Aldrich) and water to the seeds solution, obtaining a mixture with the following molar composition:



After an additional aging period of 4 h at room temperature, the mixture was transferred into an autoclave and heated at 110 °C for 2 days under static conditions. The hybrid zeolitic-mesoporous so obtained was recovered by filtration, being designated as HZM(x), where x represents the crystallization time, expressed in days, of the zeolite seeds. Finally, the HZM samples were subjected to a calcination treatment at 550°C to remove the organics occluded.

Likewise, a sample of standard Al-MCM-41 was synthesized according to a procedure published in literature [15].

1.2. Catalyst characterization

XRD spectra of the catalyst samples were obtained with a Philips X'PERT MPD diffractometer using $\text{CuK}\alpha$ radiation. Both low- and wide-angle X-ray spectra were collected in order to characterize the zeolitic crystallinity and the mesoporous ordering of the samples.

Nitrogen adsorption-desorption isotherms at 77 K of the calcined catalysts were measured with a Micromeritics ASAP 2010 instrument. Previously, the samples were outgassed at 300 °C under vacuum. Surface areas were calculated by applying the Brunauer-Emmet-Teller (BET) equation whereas pore size distributions were determined by the Barret-Joyner-Halenda (BJH) method applied to the adsorption branch of the isotherm. Cylindrical pore geometry was assumed and the Harkins-Jura equation was used to obtain

the thickness of the absorbed layer. The Si/Al atomic ratio of the samples was determined by ICP-AES measurements with a Varian VISTA-AX-CCD equipment.

1.3. TG experiments

Thermogravimetric analysis of pure HDPE, as well as of HDPE mixtures with a 10 wt% of catalyst, were carried out in a TA SDT simultaneous DSC-TGA apparatus under nitrogen atmosphere, using a 5°C/min temperature ramp from ambient temperature up to 700 °C.

1.4. Batch reactor experiments

Catalytic degradation experiments were accomplished at atmospheric pressure in a batch type reactor as illustrated in Figure 1. It consists of a stainless steel batch reactor provided of a helicoidal stirrer, placed in a thermostatic furnace, and operating under a continuous nitrogen flow of 35 NmL min⁻¹, in order to sweep the volatile products. In a typical experiment, 10 g of HDPE and 0.1 g of catalyst (plastic/catalyst mass ratio = 100) were loaded into the reactor. Temperature of the reactor was increased to the reaction temperature (380 °C) at a rate of 6 °C min⁻¹ and maintained for 2 h. The liquid products were condensed and accumulated in an ice trap, whereas the gases produced were collected in a gas bag.

Both gaseous and liquid products were analyzed in a Varian 3800 gas chromatograph. PIONA GC analyses were carried out using a 100 m length × 0.25 mm i.d. Chrompack capillary column. The yield of liquid and gaseous products was determined by dividing the weight of the corresponding fractions by the weight of plastic loaded into the reactor.

RESULTS AND DISCUSSION

1.5. Physicochemical properties of the catalysts

Two different hybrid ZSM-5/MCM-41 materials were prepared by varying the crystallization time of the ZSM-5 synthesis gel, the rest of variables being kept constant. Thus, samples HZM(2) and HZM(6) were obtained for crystallization times of 2 and 6 days, respectively. In both cases, the surfactant was added after the crystallization step to assemble the ZSM-5 seeds around the CTAB micelles, with the aim of obtaining ordered mesoporous materials having zeolitic units within the mesopore walls.

Figure 2 compares the XRD patterns of the standard Al-MCM-41 samples with those of the hybrid materials. In all cases, the low-angle XRD spectra of the calcined samples show a main diffraction peak, placed at $2\theta = 2.1^\circ$ - 2.2° . This peak has been typically observed in Al-MCM-41 samples, being assigned to the presence of a hexagonal mesopore array. On the other hand, the wide-angle spectra of the HZM samples exhibit the XRD pattern typical of the ZSM-5 zeolite, while no diffractions can be observed for the Al-MCM-41 which is consistent with the amorphous nature of its pore walls. For both hybrid samples, a broad bottom reflection in the range $2\theta = 20 - 30^\circ$ is observed, which indicates that the X-ray zeolitic crystallinity is below 100%. As expected, this zeolitic crystallinity is higher for the HZM(6) sample, prepared with a longer crystallization time than the HZM(2) material. These results indicate that the HZM samples possess X-ray features of both zeolites and ordered mesoporous materials.

Figure 3 illustrates the N_2 adsorption-desorption isotherms at 77 K and the corresponding BJH pore size distribution curves for the three catalysts considered in this work, whereas Table 1 summarizes their textural properties. The N_2 adsorption isotherm for

the Al-MCM-41 sample presents a sharp inflection in the curve at $P/P_0=0.34$ due to the pore condensation typical for a mesoporous sample with a narrow pore size distribution (type IV isotherm according to the IUPAC classification). The isotherms obtained for the HZM materials with different crystallization times reveal a gradual transition from type IV towards type I isotherms. The latter is typical of microporous solids, as it is the case for ZSM-5 zeolite. A narrow mesopore size distribution is observed in Figure 3.B for the Al-MCM-41 sample, confirming the uniformity of the pores in this material. The HZM samples present a wider distribution of mesopore sizes, which is accompanied by a progressive reduction of the surface area as the zeolitic crystallinity is enhanced. Moreover, the HZM(2) sample exhibits a great N_2 adsorption at high relative pressures, which denotes the presence of a large amount of interparticle porosity. The results of the N_2 adsorption measurements confirm that the HZM samples possess textural properties that combine those of zeolites and ordered mesoporous materials.

1.6. HDPE TG experiments

Figure 4.A shows the TG analysis under nitrogen flow corresponding to pure HDPE and HDPE/catalyst mixtures with 10 wt% catalyst content. The TG analysis of pure HDPE shows a steep weight loss with a maximum in the derivative curve placed at 483 °C, which corresponds with the thermal degradation of this polyolefin. In the case of the HDPE-catalyst mixtures, it is clearly observed that the polymer degradation takes place at quite lower temperatures, due to the polymer catalytic cracking. Thus, for the three catalysts the weight loss starts at temperatures between 350 and 375°C, indicating that a significant reduction occurs in the threshold temperature compared to the thermal degradation. A similar conclusion can be obtained by inspection of the peak temperature in the derivative

curves of Figure 4.B. Moreover, clear differences can be observed in regards to this temperature among the catalysts. Although all of them present similar aluminum content ($\text{Si}/\text{Al} = 30$), the HZM(6) sample exhibit a higher cracking activity with a peak temperature of 403°C , which must be related to its higher zeolitic crystallinity as concluded from the wide-angle X-ray spectra. Very similar results are obtained over the Al-MCM-41 and HZM(2) samples, with temperatures of the peak maximum of 416 and 414°C , respectively. Nevertheless, larger differences are observed between these two samples if the derivative curves are compared at temperatures in the range $420\text{-}450^{\circ}\text{C}$, the peak of the HZM(2) sample being clearly shifted towards lower temperatures compared to that of Al-MCM-41, which indicates the higher HDPE cracking activity of the hybrid material.

1.7. Catalytic cracking of HDPE in the batch reactor

The three catalysts have been tested in the HDPE cracking using a stirred batch reactor. The reaction temperature was fixed at a low value (380°C), whereas a high plastic/catalyst ratio (100) was selected. In previous works, we have observed that under these really mild cracking conditions just catalysts of high activity leads to significant plastic conversions [16]. Figure 5 compares the results so obtained in the HDPE degradation over the different catalysts after 2 h of reaction time. No conversion was detected in a blank thermal reaction, since the temperature used is clearly below the threshold temperature corresponding to the thermal cracking of HDPE ($400\text{-}420^{\circ}\text{C}$), as proved by TG analysis.

Al-MCM-41 showed to be the least active catalyst, leading to a negligible plastic conversion. In the TG experiments, HDPE suffered a partial degradation over this sample at

380°C, although working with a quite higher catalyst loading ($P/C = 10$). The lack of activity of Al-MCM-41 in the batch reactor must be related to the mild reaction conditions used, showing that the acidity of this catalyst is not strong enough to promote the HDPE cracking at temperatures around 380°C. However, Al-MCM-41 has been reported to be active in the catalytic cracking of polyethylene under less restrictive conditions [17].

In contrast, both hybrid zeolitic-mesoporous materials presented activity for the HDPE cracking in the batch reactor. The conversion obtained over the HZM(2) sample was c.a. 17 %, in spite of the low differences observed in the TG experiments between the peak temperature of this sample and that of the Al-MCM-41 material. Likewise, the HZM(6) sample leads to a conversion close to 68 %, remarkably higher than that obtained with HZM(2) sample, as it could be expected from the above mentioned TG results. The HDPE cracking activity of the hybrid materials seems to be directly related with their zeolitic crystallinity.

The product distribution obtained with both HZM samples is compared in Figure 6 in terms of carbon atom number. In both cases, C_4 hydrocarbons are the main products formed from the HDPE degradation. For the HZM(2) sample, the selectivity towards C_4 compounds is over 40 %, while the overall selectivity corresponding to the C_2 - C_5 fraction accounts is around 90 %. Very small amounts of compounds higher than C_5 were detected with this catalyst. Regarding the HZM(6) material, a wider product distribution was obtained. Although C_4 hydrocarbons are also the main products, significant amounts of hydrocarbons with boiling points in the gasoline range are detected.

The product distribution and the activity observed over HZM materials can be explained on the basis of its bimodal microporous-mesoporous structure and its acid strength. Polyolefin cracking over Al-MCM-41 is known to occur mainly by a random

scission mechanism, yielding a broad product distribution with significant amounts of hydrocarbons up to C₂₅. On the other hand, the prevalent polyolefin cracking mechanism over ZSM-5 is the end-chain scission, which leads to distributions with a maximum centered at C₄ and a second maximum between C₇-C₉. The latter is originated by oligomerization and aromatization reactions of the gaseous olefins. Both HZM samples yield a product distribution similar to that of ZSM-5 zeolite, which suggests that the main cracking mechanism taking place is end-chain scission. This type of cracking is promoted by acid sites stronger than those present in Al-MCM-41. Comparing the distribution obtained over both HZM samples, an enhancement in the selectivity towards the C₇-C₉ fraction at expense of the C₃-C₄ fraction is observed for the HZM(6) catalyst. This behaviour can be assigned to a greater extent of oligomerization and cyclization reactions over the hybrid sample with the highest zeolitic crystallinity.

The product distributions in terms of selectivity by hydrocarbon groups obtained over the HZM samples are shown in Figure 7. C₂-C₅ olefins are the main component of the gaseous fraction obtained in HDPE cracking reactions. Thus, the HZM(2) sample exhibited a very high selectivity towards C₂-C₅ olefins (~75%). In contrast, the selectivity towards C₂-C₅ olefins drops for the HZM(6) catalyst while the formation of hydrocarbons in the gasoline fraction increases significantly. In both cases, the selectivity towards the gasoil fraction is very low, with values underneath 2%. These results clearly suggest that the reaction proceeds mainly by an end-chain scission mechanism. A very intense cracking process has taken place, indicating the presence of strong acid sites in the hybrid zeolitic-mesoporous materials which are accessible for the polyolefin molecules.

These results show that, although the textural properties of the hybrid materials are intermediate between those of ZSM-5 zeolite and Al-MCM-41, or even very similar to

those of the ordered mesoporous materials, as in the case of the HZM(2) sample, their catalytic activity and selectivity in the HDPE cracking resembles mainly the behaviour of the HZSM-5 zeolite. Therefore, the zeolitic nature of the pore walls in these materials is the essential factor determining their catalytic properties in the HDPE degradation.

Conclusions

The results reported and discussed in the present work demonstrate that hybrid zeolitic-mesoporous show promising properties to be used as catalysts in the cracking of HDPE. HZM materials exhibit higher degradation activity than a sample of Al-MCM-41 with the same aluminum content. Significant HDPE conversions were achieved in a batch reactor over the HZM samples in spite of working at low temperature and high plastic/catalyst ratio. Under these conditions, no activity was detected over the Al-MCM-41 material.

Light hydrocarbons with a narrow product distribution and rich in olefins are the main components obtained over the HZM catalysts, while the production of heavy fractions is negligible. These results suggest that an end-chain scission mechanism is governing the overall catalytic process. The formation of gasoline range hydrocarbons was observed over the HZM sample prepared with the longer crystallization time, and having the highest zeolitic crystallinity.

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Table 1. - Physicochemical properties of the catalysts.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore Diameter (\AA)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Si/Al	d_{100} (nm)
Al-MCM-41	937	25.9	0.99	30	4.2
HZM(2)	847	27.2	1.69	30	4.2
HZM(6)	646	24.7	0.70	31	4.1

FIGURE CAPTIONS

Figure 1. – Schematic diagram of the experimental pyrolysis system.

Figure 2. – Low-angle (A) and wide-angle (B) XRD spectra of the calcined samples.

Figure 3. – Nitrogen adsorption-desorption isotherms at 77 K and pore size distribution for the calcined samples.

Figure 4. – TG analyses: A) Weight loss. B) Differential curves.

Figure 5. – HDPE conversion in the batch reactor (380 °C, 120 min, P/C = 100).

Figure 6. – Product distribution per carbon atom number for the HDPE catalytic cracking over HZM(2) and HZM(6) hybrid materials.

Figure 7. – Selectivity by groups obtained for the HDPE catalytic cracking over HZM(2) and HZM(6) hybrid materials.

Figure 1.

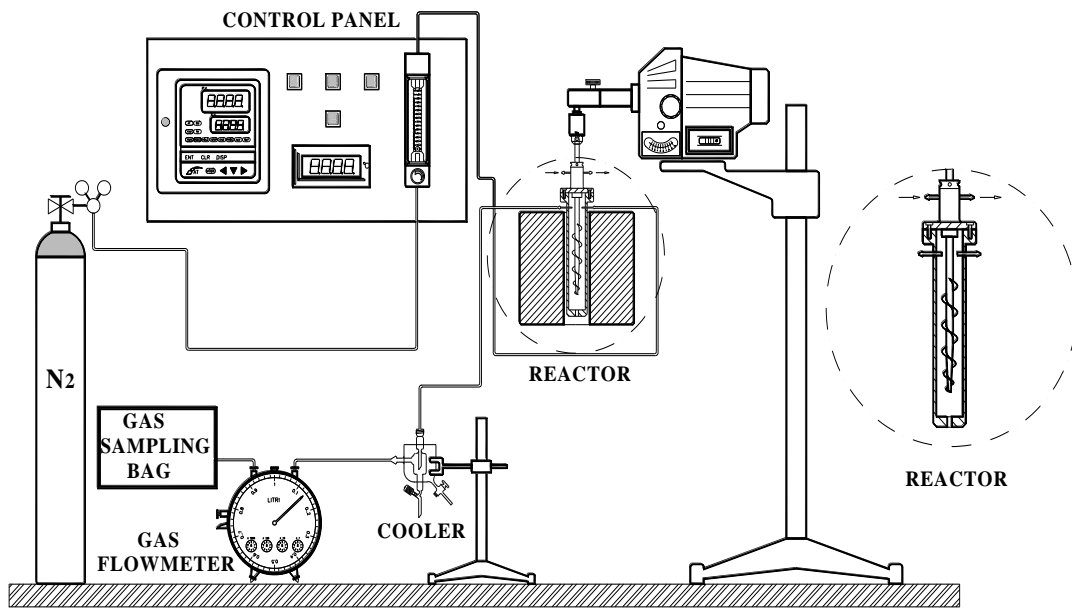


Figure 2.

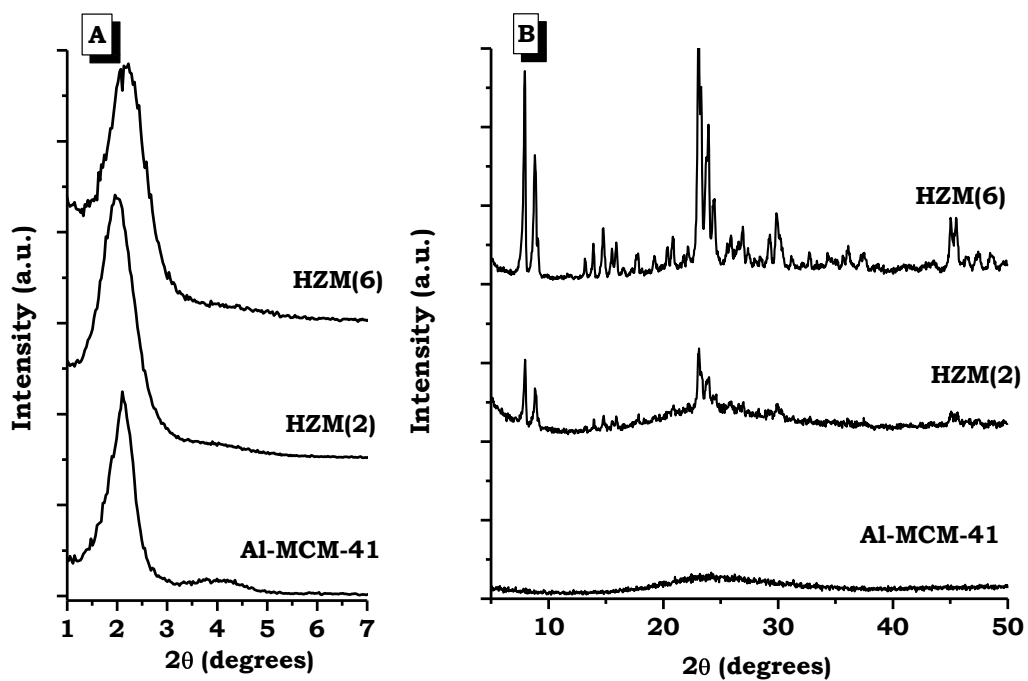


Figure 3.

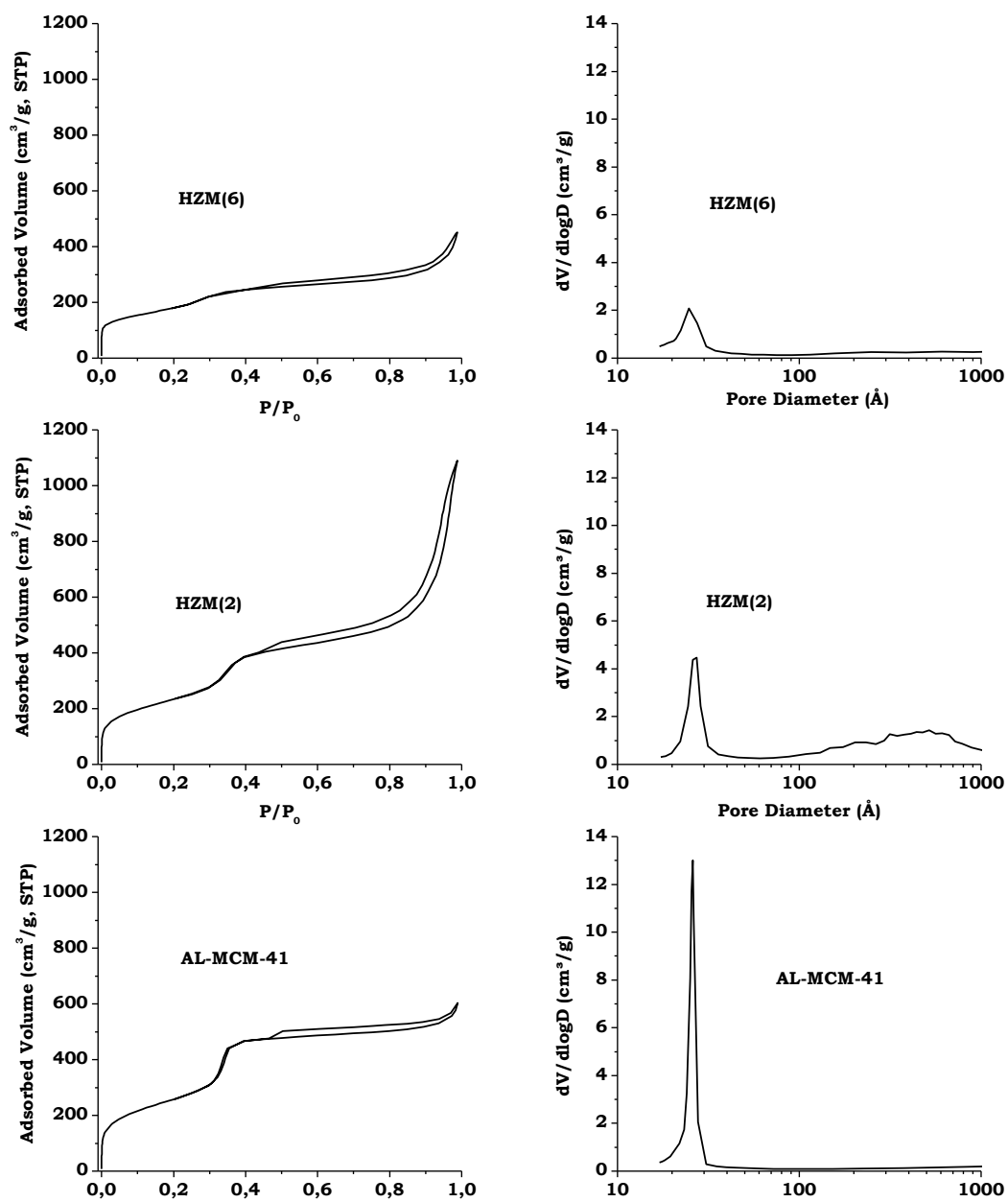


Figure 4.

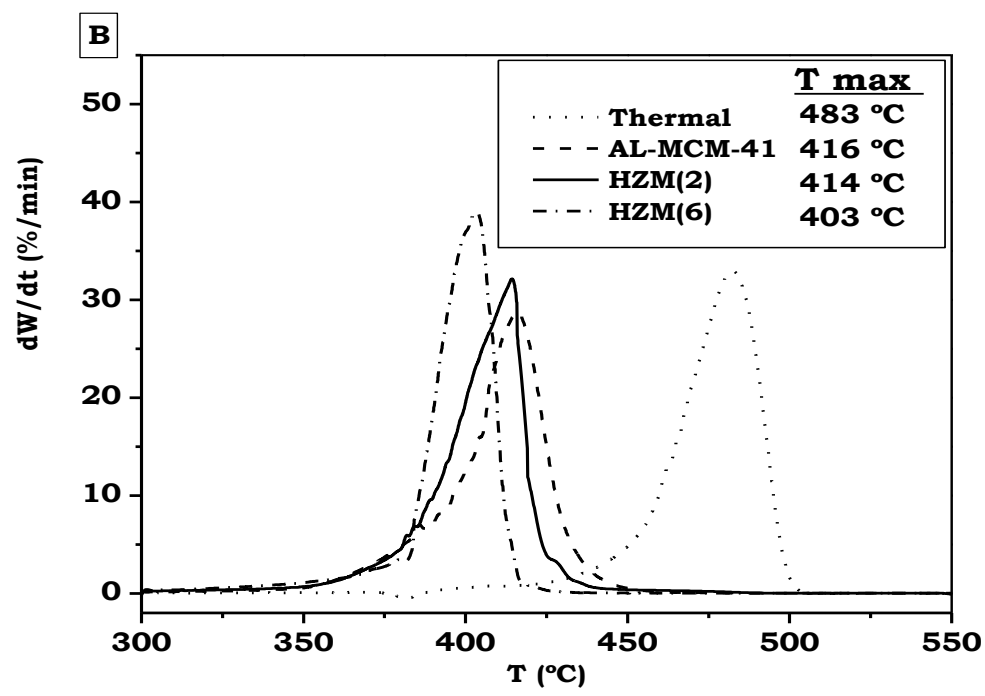
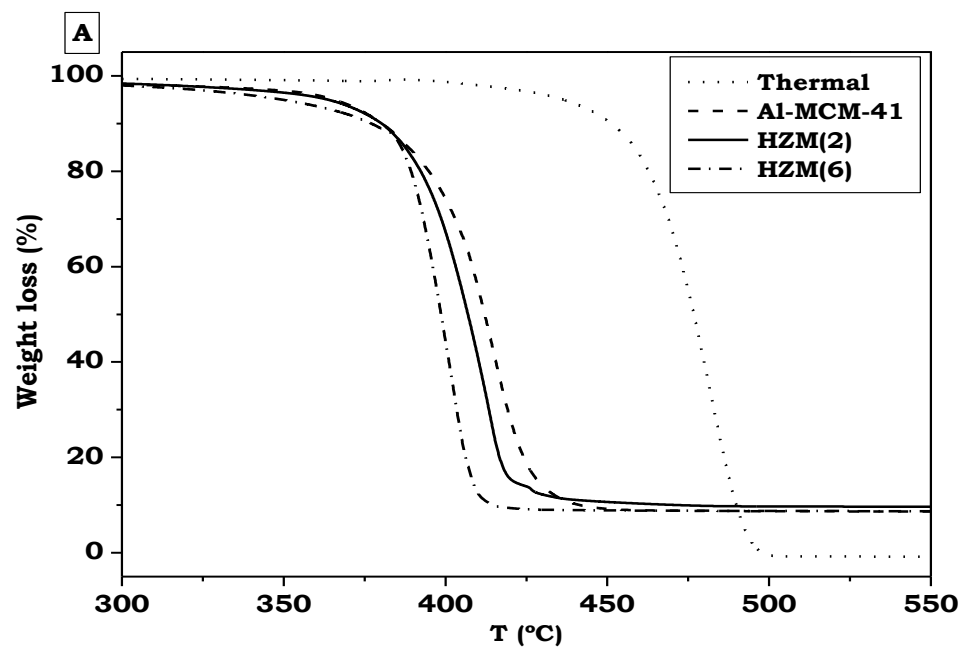


Figure 5.

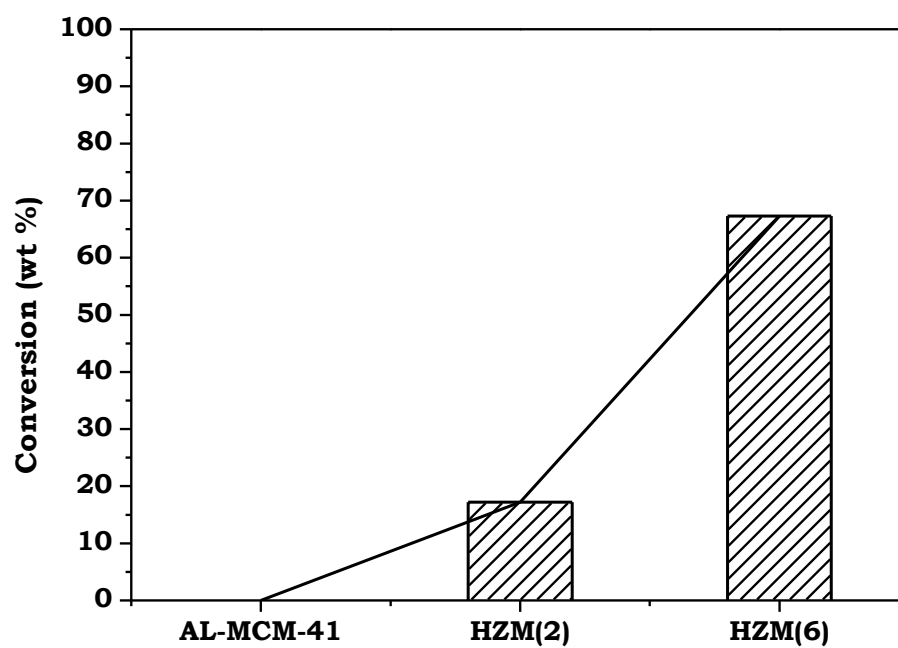


Figure 6.

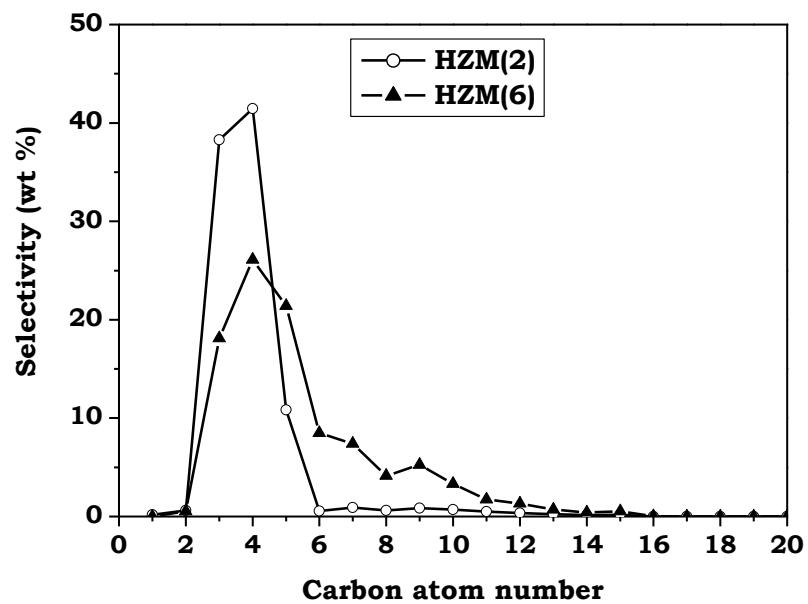


Figure 7.

