Catalytic Degradation of Polyethylene over Mesoporous Molecular Sieve MCM–41 Modified with Heteropoly Compounds

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Abstract

Degradation of polyethylene was performed over MCM-41 molecular sieves modified with heteropoly acid $H_3PW_{12}O_{40}$ (HPW) and its caesium salt $CsHPW_{12}O_{40}$ (CsHPW). High silica zeolite ZSM-5 has also been used as degradation catalyst. The applied catalysts (HPW/MCM-41, CsHPW/MCM-41 and ZSM-5 zeolite) resulted in lowering of temperature of HDPE degradation when compared to the thermal pyrolysis as well as influenced the distribution of the products formed as a result of the cracking process. HPW/MCM-41 use resulted in low amount of gas products and almost 80 wt.% of liquids while cracking over H-ZSM-5 produced gas hydrocarbons with selectivity about 50 wt.%. Liquid product obtained in the presence of HPW/MCM-41 comprised aliphatic hydrocarbons (olefins and paraffins) while cracking carried out over ZSM-5 zeolite resulted mainly in the formation of aromatic compounds.

Introduction

Thermal and catalytic degradation of waste polymers has attracted great attention as a promising technology for waste material utilization and also as an additional source of clean fuels. The disposal of waste polymers by means of landfilling cannot be further accepted because of a decrease in landfill availability and also of the cost increase. Incineration of waste polymers results in environmental danger because of emissions of very different combustion products. Therefore, the chemical degradation of spent polymers towards clean liquid fuel or valuable chemicals has been undertaken in many papers. Thermal degradation usually leads to liquid product containing a mixture of hydrocarbons with a wide range of carbon number (C_6–C_{25}) with maximum about C_3–C_{15} [1–3], while the use of acidic catalyst usually moves the maximum towards shorter hydrocarbons. Silica alumina, zeolites as well as mesoporous materials were tested as catalysts for polymer degradation [4-6]. Mesoporous materials due to the large pore diameter seem to be especially suitable as catalysts for waste polymer degradation. However, all silica mesoporous molecular sieves show very low acidity. The introduction of aluminium ions in MCM-41 framework increases acidity insignificantly, resulting simultaneously in a decrease in the thermal stability of modified material [7]. According to Sakata et al. [8] even non acidic mesoporous silica influenced the polypropylene degradation, which was due to hexagonal pore structure. However, the presence of the acidic centres is crucial for the cracking process. Many attempts have been made to generate acidic sites in the pores of MCM–41 molecular sieve [9, 10]. We have reported earlier that encapsulation of heteropoly acids into MCM–41 pores resulted in the formation of a very acidic system, which was very active for bisphenol–A synthesis in a liquid phase [11].

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Considering the above, in the paper we present polyethylene degradation performed over MCM–41 molecular sieves modified with heteropoly compounds. 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) and its insoluble nonstoichiometric caesium salt ($(CsH)_3PW_{12}O_{40}$) were introduced into mesopores and used for polyethylene degradation. For comparison, ZSM-5 zeolite was also applied as catalyst for the reaction under study.

Experimental Procedure

MCM-41 was synthesized according to [12] use of the initial gel of the following molar composition: $12xSiO_2$: $0.11 NaOH$: $0.08xTMAOH$: $0.21xMTMABr$: $125xH_2O$.
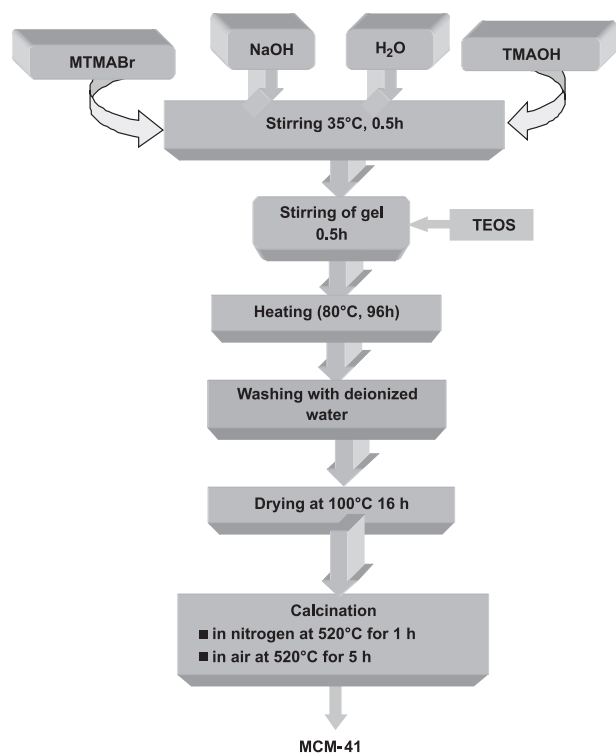
The following materials were used for synthesis:

TEOS (Tetraethoxysilane) – commercial product from Aldrich, used as a source of silicon.

MTMABr (Myristyltrimethylammonium bromide – $CH_3(CH_2)_{13}N(CH_3)_3Br$) – commercial product from Aldrich, used as template;

TMAOH (Tetramethyl ammonium hydroxide – $(CH_3)_4NOH \times 5H_2O$) – commercial product from Aldrich.

The initial gel was crystallized at 80°C for 96 h. The product was washed with deionized water, filtered and dried at 100°C and finally calcined at 520°C for 1 h in nitrogen and then for 5 h in air at the same temperature. The procedure was presented in Scheme 1.

12-tunsto phosphoric heteropoly acid (HPW) from Aldrich was supported on MCM-41 from methanol solution by means of refluxing for 3 h. After filtration the samples were dried at 100°C and calcined at 450°C for 2 h. Concentration of HPW in MCM-41 matrix calculated from the tungsten amount measured by ICP method was about 50 wt.% (it relates to about 2 mol.% of HPW). Caesium salt of HPW on MCM-41 was synthesised by means of reaction of stoichiometric amount of Cs_2CO_3 in methanol with earlier supported HPW (one caesium cation related to one HPW molecule). Stabilization of HPW on MCM-41 by means of interaction with silanol OH groups with subsequent formation of nonstoichiometric caesium salt was presented in Scheme 2.

All the catalysts were characterized by FT-IR spectra and XRD patterns. Surface area and pore diameter were determined by means of nitrogen adsorption at 77 K using ASAP 2000 apparatus (from Micromeritics). XRD patterns were recorded with Brucker diffractometer using CuK_α radiation and they were presented in Fig. 1.

Zeolite ZSM-5 of Si/Al ratio equal to 25 was kindly delivered from Süd Chemie. Protonic form of zeolites ZSM-5 was prepared by means of exchange procedure with ammonium ions from aqueous solution with the fol-
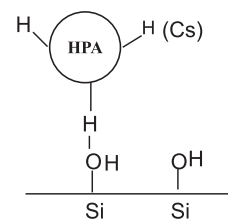
Scheme 2. Interaction of HPW with silanol groups of silica MCM-41 and subsequent formation of nonstoichiometric caesium salt.
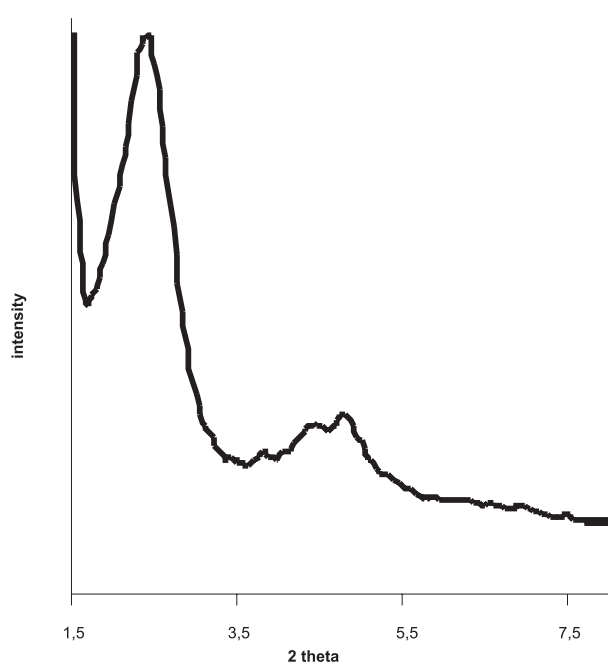

Scheme 1. The procedure of mesoporous material (MCM-41) synthesis.

Fig. 1. XDR powder diffraction pattern of MCM-41 after template removal.

lowing calcinations. Acidity of the samples was estimated on the grounds of the activity for cumene cracking. The results are presented in Fig. 2

Polymer (10 g) and catalyst (0.5 g) were placed in heated glass reactor, which was connected to receiver equipped with liquid condesor. The process was performed at 390–400°C (H-ZSM-5, HPW/MCM-41, CsH-PW/MCM-41) and at 440°C (thermal pyrolysis). Gas products were collected in gas-burette. Liquid products were analyzed by GC equipped with FID detector and 10 m non polar HP-1 column.
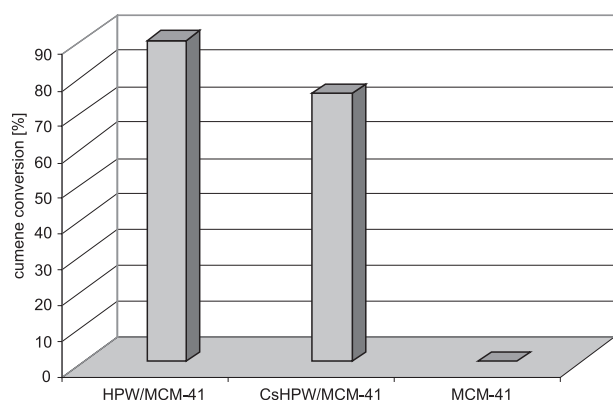
GC MS analysis was performed on AMD 402 apparatus.

Fig. 2. Cumene cracking performed on unmodified and heteropoly compounds modified MCM-41.

Results and Discussion

It is commonly known that hydrocarbon cracking is catalysed by protonic acidic centres. Solid acids like silica alumina and zeolites were applied for this process. Acidic solids, especially zeolites, have also been used for polyolefin recycling by means of cracking process [5, 6, 13], however, the diameter of zeolite micropores brought about a limited contact of polymer with acidic centres located inside the channels and cells. Disclosure of mesoporous molecular sieves delivered exceptional potential catalysts for polymer degradation; however, the acidity of this material appeared to be very low. Modification of mesoporous material structure in order to generate a stronger acidity (by means of introduction of aluminium atoms into structure) resulted in the appearance of acidic centres; however, the thermal stability of modified molecular sieves become lower. Our earlier experiments with modification of M41S molecular sieves with heteropoly acids to generate acidic centres inside the pores appeared successful. HPW/MCM-41 and CsHPW/MCM-41showed high acidity and in consequence a great activity for bisphenol A synthesis and, additionally, the size of modified pores resulted in very high p-selectivity [11]. Therefore, it seemed justified to apply all silica mesoporous molecular sieves Si-MCM-41 modified with HPW and (Cs,H) PW as catalysts for polyolefin's cracking.

Already unmodified Si-MCM-41, used as catalysts for polyolefin's degradation, resulted in lowering of degradation temperature when compared to thermal pyrolysis (Fig. 3). Polyethylene degradation perfomed in the pres-
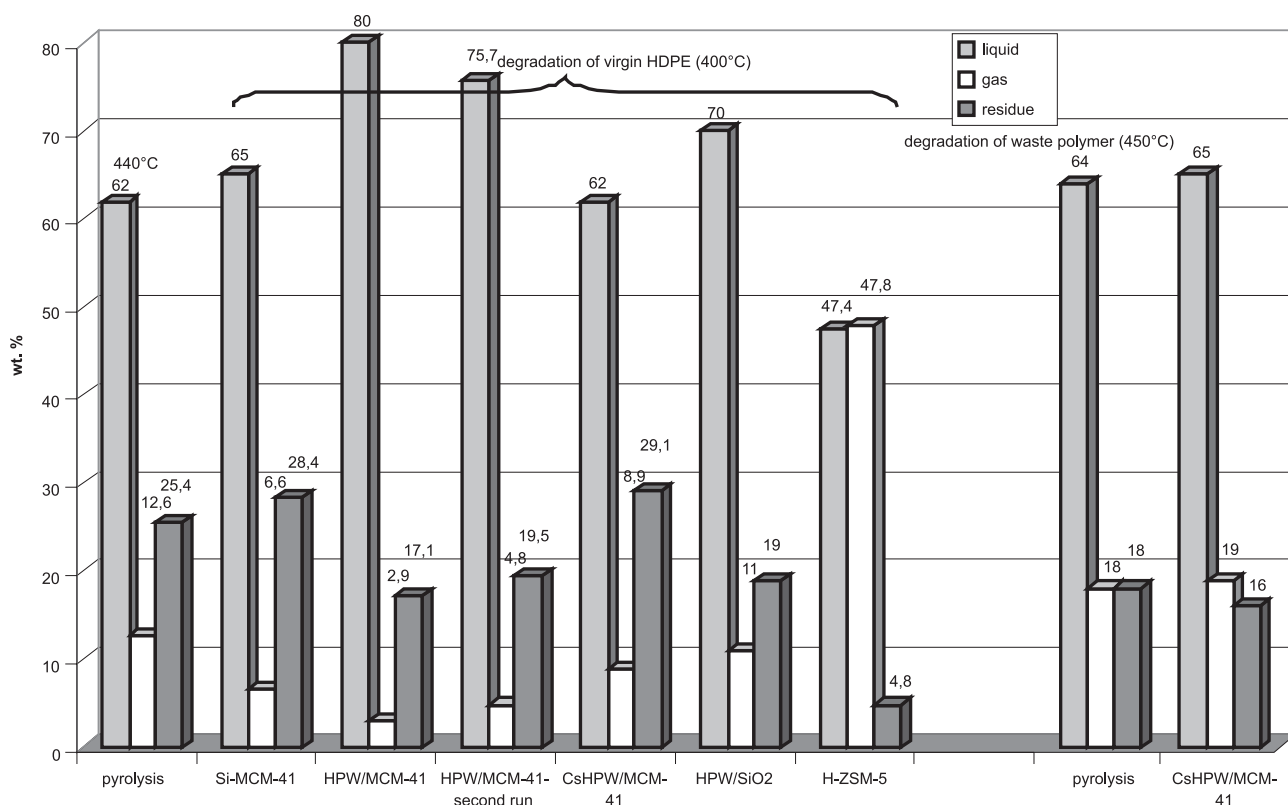

Fig. 3. Product distribution of polymer cracking performed in the presence of different catalysts under atmospheric pressure. Virgin HDPE and waste polyolefin packing were used as a row material.

ence of Si-MCM-41 occurred at a lower temperature (400°C), while thermal pyrolysis required 440°C. On the other hand, product distribution was similar in both processes. (Fig. 3). The similarity in product distribution was not surprising considering that Si-MCM-41 molecular sieves showed only silanol OH groups. However, Sakata et al. [8] have indicated that the hexagonal structure of mesoporous sieves, used for polyolefin degradation, changed distribution of hydrocarbons present in a liquid product. Seddegi et al. [13] have found that the cracking process over Si-MCM-41 molecular sieves results in the products, which indicates the carbenium ion mechanism of the reaction. In consequence, the authors claimed that silanol groups present in all silica mesoporous material showed an acidic character. However, it cannot be excluded that some impurities of aluminium, originating from an inorganic reagent, may be introduced into MCM-41 structure leading to an appearance of acidic centres. On the other hand, many authors [14, 15, 16] have claimed that insertion of aluminium into silica mesoporous material generated rather weak acidic centres, which were insufficient for the reactions requiring a strong acidity, like cracking. Unmodified MCM-41 used as catalyst for model reaction of cumene cracking did not show any catalytic activity (Fig. 2). Katovic et al. [17] reported, that Al-MCM-41 in contact with ammonia show very weak IR spectra described to ammonium ion, formed as a result of proton transfer from OH group to ammonia. It indicated that the number of acidic groups, able to interact with such a strong base, as ammonia, was very low. Additionally, thermal treatment, applied for template removal, may easily extract aluminium from MCM-41 structure to extraframework positions [18]. Considering the above, even if some aluminium impurities were introduced into MCM-41 structure during synthesis, they should influence the polymer cracking very slightly. Nevertheless, the comparison of the distribution of liquid hydrocarbons obtained over all silica mesoporous molecular sieve used for polyethylene degradation, with the product composition
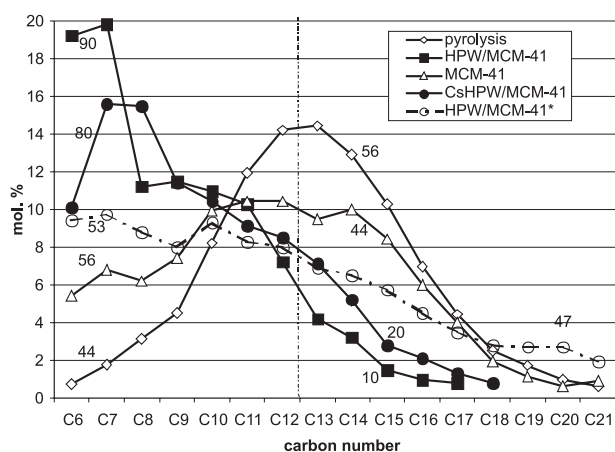
resulting from thermal pyrolysis has pointed at some differences (Fig. 4). Thermal degradation resulted in about 40 mol.% of petrol-like hydrocarbon fractions ($C_6 - C_{12}$) and in about 60 mol.% of higher hydrocarbons, while in the presence of Si-MCM-41 catalyst, the contribution of petrol like fraction increased almost to 56 mol.%.

The generation of acidic centres in M41S channels by means of encapsulation of heteropoly acids resulted in distinctively higher yield of liquid product and in a very little amount of gas product (Fig. 3). Accommodation of caesium salt (CsHPW) in MCM-41 channels led to a little lower polymer conversion. An unreacted residue came to about 30 wt.%. Lower activity of CsHPW/MCM-41 may be due to partial blockage of MCM-41 channels with bulky, non soluble CsHPW. The partial blockade of mesoporous by CsHPW was reported in the earlier work [11]. Narrower entrance to the channels results in limited contact of polymer with acidic centres located inside the channels. Additionally, part of acidic protons was substituted by caesium cations, which resulted in lowering the number of acidic centres in modified system. It was confirmed by lower activity of CsHPW/MCM-41 for cumene cracking, when compared to HPW/MCM-41 (Fig. 2). HPW supported on amorphous silica showed relatively high polymer decomposition (Fig. 3) as the acidic centres were easily available for reagents. The use of HPW-modified Si-MCM-41 as catalyst for polyolefin degradation led to decrease temperature of polymer degradation when compared to thermal pyrolysis of about 40°C and also influenced the product composition. The amount of liquids increased from 62 wt.%, obtained in thermal pyrolysis process, to 80 wt.%, in the presence of HPW/MCM-41 (Fig. 3). Contribution of gas products decreased significantly (Fig. 3), and instead of C_1 and C_2 hydrocarbons being major ingredients in gas phase from thermal pyrolysis of HPDE, mainly C_3 and C_4 appeared after catalytic cracking, performed in the presence of HPW/MCM-41 and CsHPW/MCM-41 (Fig. 5).

Fig. 4. Carbon number distribution of liquid products from thermal and catalytic degradation of HDPE performed at 400°C (HPW/MCM-41*− the second run).
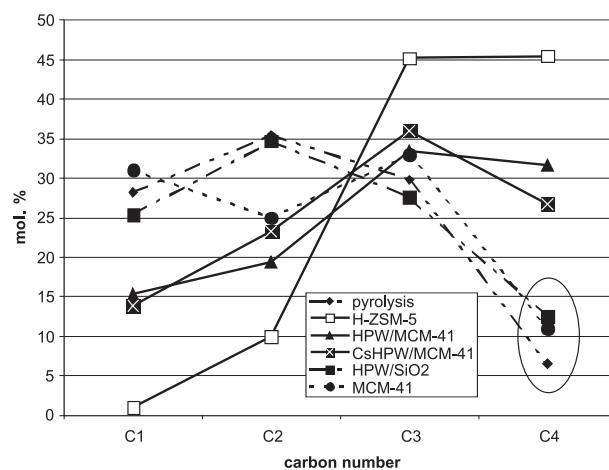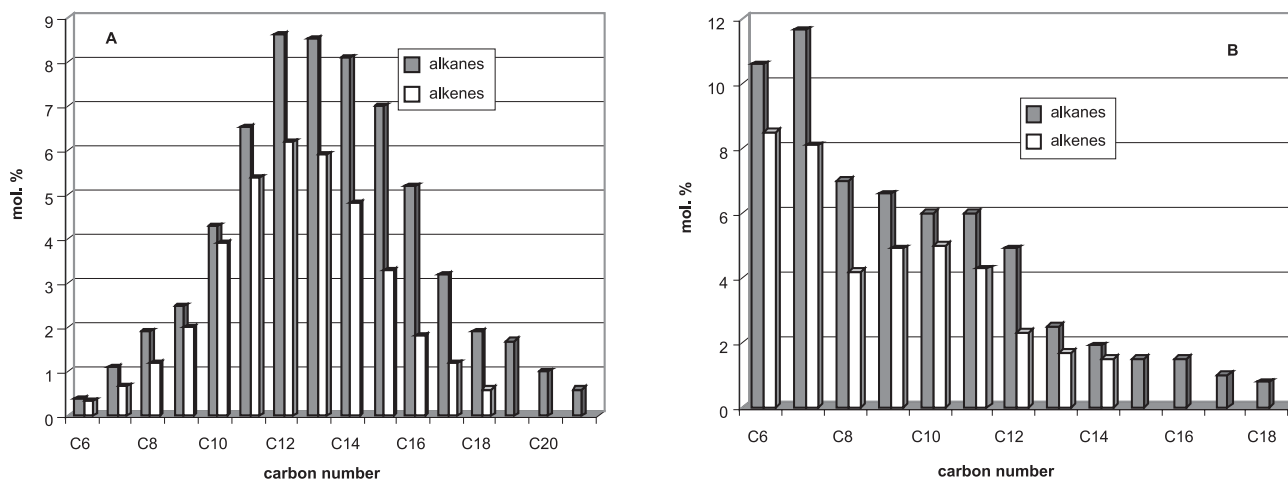

Fig. 5. Carbon number distribution of gas product from thermal and catalytic degradation of HDPE performed at 400°C.

Fig. 6 Alkanes and alkenes distribution of liquid products from thermal (**A**) and catalytic (**B**- HPW/MCM-41) degradation of HDPE.
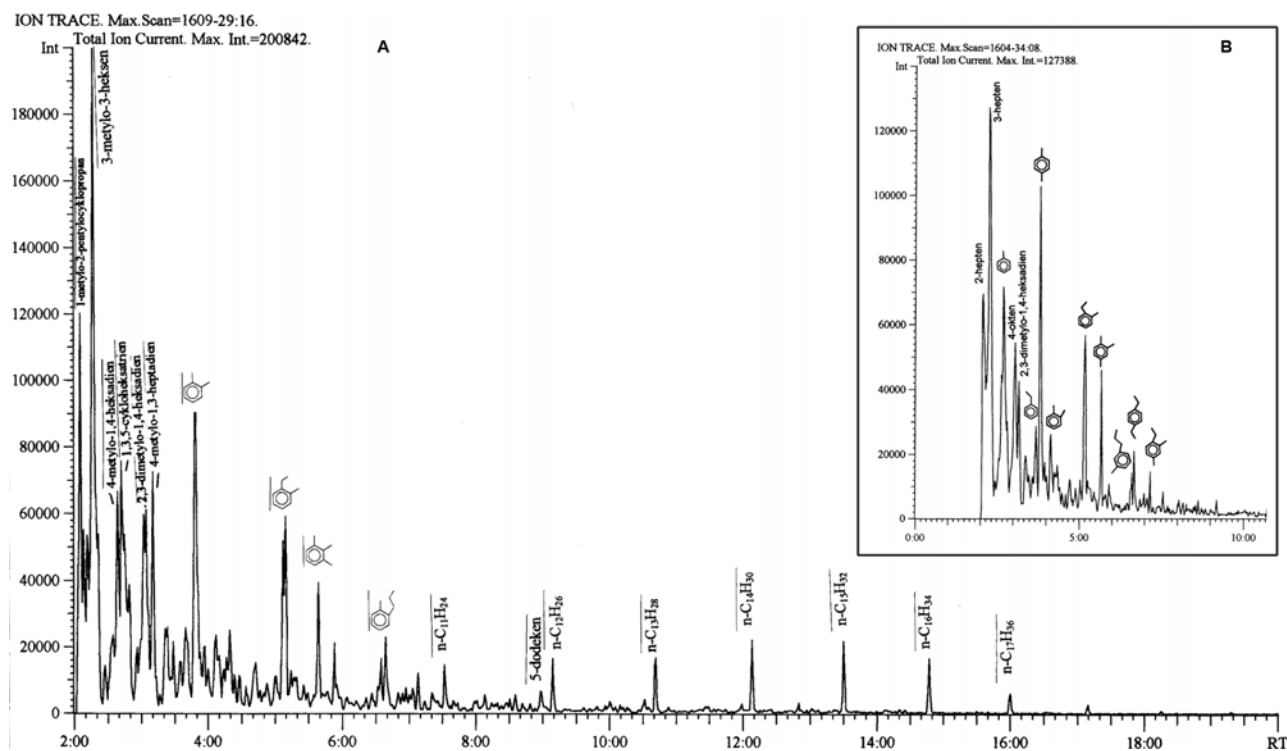

Fig. 7. (**7A**) – GC MS analysis of the first drops of liquids obtained from catalytic degradation of HDPE performed at 400°C in the presence of H-ZSM-5; inset, (**7B**) GC MS analysis of liquids obtained after 2 h of catalytic degradation of HDPE performed at 400°C in the presence of H-ZSM-5.

A liquid produced by HDPE degradation over HPW/MCM-41 contains a significant amount of petrol-like hydrocarbons (contribution of $C_6 - C_{12}$ fraction shows about 90 mol.% – Fig. 4). Caesium salt of HPW encapsulated in MCM-41 resulted in the formation of about 80 mol.% of petrol-like fraction.

Liquid products received as a result of degradation process contained paraffins and olefins; however, the paraffins prevailed both in the presence and the absence of a catalyst. Fig. 6 presents the contribution of paraffins and olefins in liquids produced from thermal pyrolysis (A)

and from catalytic process performed in the presence of HPW/MCM-41 catalyst (B). Spent HPW/MCM-41 catalyst applied for polymer degradation, showed only a little lower activity for polymer conversion (Fig. 3); however, the distribution of the hydrocarbons in the liquid product resembled this noted for pyrolysis process (Fig. 4). It indicates that the availability of acidic centres was limited, probably because of heavy product adsorption (catalyst was used in the second run without regeneration).

Polymer degradation over H-ZSM-5 zeolite occurred at a temperature lower than that required for thermal py-

rolysis. The rate of degradation was also faster and the process was completed after 2 h on stream, while thermal pyrolysis of the same amount of polymer occurred for 5 h. The conversion to gas hydrocarbons (C_1–C_4) achieved about 50 wt.% (Fig. 3) and the main ingredients of gas product were hydrocarbons C_4 and C_3 (90 mol.%) instead of C_1 and C_2 resulting from thermal pyrolysis. (Fig. 5). On the grounds of GC-MS analysis it was shown that the liquid product resulted from HDPE degradation over ZSM-5 zeolite contained mainly aromatic hydrocarbons, which substituted for benzene (Fig. 7 B). GC-MS analysis of the initial drops of liquid products from HDPE degradation performed over H-ZSM-5 showed the presence both aliphatic hydrocarbons and some amounts of the aromatic ones (Fig. 7 A), while the liquids collected after 2 h of the reaction comprised mainly benzene-substituted compounds (Fig. 7 B). It suggested that the long contact time of liquids with catalyst of MFI structure resulted in aromatization. Zeolites ZSM-5 are known as catalysts active for aromatization reaction. The subsequent runs performed over regenerated zeolite ZSM-5 resulted in practically the same yield of liquid and gas products as it was noted over the fresh catalyst.

Degradation of polyethylene spent packing both by non catalytic and catalytic procedure required a higher temperature (450°C) when compared to the virgin HDPE (about 400°C). The distribution of products (residue, liquids and gas hydrocarbons) for non-catalytic and catalytic (performed over CsHPW/MCM-41) processes was very similar Considering the high thermal stability of CsHPW (the Keggin structure is prevented up to 600°C [19, 20]). It seems probable that additives modifying plastics, partly neutralize the acidic centres, leading to lowering of catalytic activity.

Gas product resulting both from pyrolysis and from catalytic degradation of spent PE packing contained mainly C_1, C_2 and C_3 hydrocarbons with only traces of C_4. Distribution of liquid hydrocarbons resulting from polyethylene packing catalytic degradation did not show clear maximum; however, the petrol fraction (C_6–C_{12}) made up 62%. Contrary to virgin HDPE, the ratio of parafins and olefins was about 1, while virgin HDPE degradation resulted in higher part of saturated hydrocarbons.

The use of H-ZSM-5 zeolite for spent PE decomposition resulted, similarly as for virgin HDPE, in high yield of gas products containing mainly C_3 and C_4 hydrocarbons, while the liquids were composed mainly of aromatic hydrocarbons.

Conclusions

1. MCM-41 molecular sieves modified with heteropoly compounds catalyse degradation of polyethylene material with the formation of liquids containing predominantly petrol-like hydrocarbons (C_6–C_{12}).
2. Only aliphatic hydrocarbons (paraffins and olefins with the molar ratio of an/en about 1.6) were formed as a result of catalytic cracking of HDPE in the presence of HPW/MCM-41 and CsHPW/MCM-41.
3. Polyethylene degradation over ZSM-5 zeolites produced liquids contained mainly aromatic hydrocarbons, while gas product formed with high yield was predominantly composed of C_3 and C_4 hydrocarbons.

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