

Catalytic Conversion of Polyolefins in the Presence of MCM-41 Type Mesoporous Materials

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Abstract—The catalytic activities of mesoporous H–MCM-41 aluminosilicates of different compositions in degradation of polypropylene and a polypropylene–polyethylene mixture into gasoline-range fraction hydrocarbons were compared. A higher yield of the target products (86 wt %) was observed for the sample with a lower aluminum content. Using the results of chromatographic analysis of the catalyzate for the content of the gasoline-range fraction, both saturated and unsaturated hydrocarbons, dominated by products with cyclic structure, were identified in all the samples studied. In the presence of the H–MCM-41 sample with a lower silica modulus, a larger amount of condensation products with a higher calorific value arose from polypropylene degradation. Mesoporous aluminosilicates H–MCM-41 can be regarded as effective catalysts for thermocatalytic conversion of polypropylene to produce the gasoline-range fraction.

Keywords: mesoporous aluminosilicates, catalytic conversion, polyolefins, polypropylene, condensation products

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Steady growth of global plastics production makes plastic waste disposal an extremely urgent problem. Technologies for chemical processing of polymers are being very actively developed now [1–6]. Based on analysis of the available literature on modern methods of plastic waste conversion into motor fuels and petrochemical products, the processes of thermal and catalytic cracking, hydroconversion, and polymers metathesis were identified in [2].

Of particular interest is thermal conversion of polyolefins, affording a fuel-like mixture of hydrocarbons, which allows regarding this class of waste as a nonconventional source of raw materials for production of fuels and oils. The main degradation product of polyolefins at 500°C is a liquid product with a wide fractional composition, and the gas yield does not exceed 5–7% [2], with the hydrocarbon composition being dependent on the polymer structure and the process temperature [5, 7–9]. Polyethylene and polypropylene depolymerization gives mainly unbranched and slightly branched alkanes and a certain amount of C₆–C₂₀ olefins [2, 10–13]. However, the products obtained by thermal conversion of polyolefins have a very broad carbon

number distribution, which limits their use without further processing.

Use of heterogeneous catalysts in thermal conversion of polyolefins allows controlling the composition of the target products, significantly increasing the rate of the reaction of degradation of the initial polyolefins, and lowering the process temperature compared to thermal degradation, which affords significant saving of energy costs [2, 14, 15]. Increases in the yield and selectivity toward the target products can be achieved by varying the acidity and the pore size and structure of the catalyst.

Among a wide range of catalysts used in the degradation processes, the most efficient performance in degradation of polyolefins into hydrocarbons is exhibited by amorphous and structured micro- and mesoporous aluminosilicate catalysts, according to many authors. Each type of catalyst has its own specific features. During the catalytic process, secondary reactions, including cracking, oligomerization, cyclization, aromatization, and isomerization, can proceed on the surface and inside the pores of amorphous aluminosilicates [15]. Microporous zeolite catalysts have highly acidic active

sites; this allows cleavage of the carbon-carbon bonds. However, small pore size of zeolites is responsible for limited accessibility of the acid sites inside the channels for the macromolecules. This steric factor accounts for a higher yield of gaseous products, since the polymer chain contacts the external surface of the zeolite [16–19].

Of great interest is the use of the MCM type mesoporous materials in thermocatalytic conversion processes. By contrast to zeolites, these catalysts have a high surface area and medium-strength active acid sites providing for diffusion of large organic molecules in pores, thereby contributing to a high yield of C_7 – C_{14} liquid products comprising a considerable amount of aliphatic compounds [18, 20, 21]. For example, in [22] the influence of the catalyst acidity and pore size on the yield and composition of the degradation products of polyolefins was studied. The catalytic activities exhibited by ZSM-5, MCM-41, and an amorphous aluminosilicate in thermal conversion at 400°C in a nitrogen flow were compared. MCM-41 showed the highest activity in polypropylene degradation, with thermal degradation of polypropylene on MCM-41 and amorphous SiO_2 – Al_2O_3 proceeding much faster than degradation of high- and low-density polyethylene. Also, differences in the molecular weight distribution of the degradation products were observed. Specifically, the main products in the case of MCM-41 were represented by the liquid fraction in the C_{13} – C_{22} range and gasoline-like hydrocarbons with C_5 and C_8 – C_9 maxima. In the case of ZSM-5 significant amounts of C_3 – C_5 hydrocarbons were obtained [23]. Investigation of the effect exerted by the textural properties of the catalysts on the conversion of polypropylene, polyethylene, and a mixture thereof on the yield and composition of the products of degradation over nanocrystalline zeolite HUN-ZSM-5, microporous ZSM-5, β -zeolite, and mesoporous Al–MCM-41 and Al-SBA-15 with identical Si/Al ratio of 30 revealed that mesoporous catalysts afforded high yields of liquid products comprising a considerable amount of aliphatic compounds. The composition of the liquid and gaseous products from catalytic pyrolysis was found to be similar to that of petroleum-derived fuels [24]. Of interest is the two-stage process of thermocatalytic degradation of high-density polyethylene in the presence of ZSM-5, Y-zeolite, FCC, and MCM-41, which includes thermal degradation of the polymer in the first stage, followed by the conversion of the gaseous products with the use of catalysts in the second stage. A high yield of oil

hydrocarbons (83.15 wt %) dominated by the gasoline-range fraction was obtained by using MCM-41 and ZSM-5 in a 1 : 1 ratio [25].

Previously, we investigated the regularities of the thermocatalytic conversion of polyethylene in the presence of H–MCM-41 mesoporous materials, as well as of zeolites with different structures (faujasite, ZSM-5, β ($SiO_2/Al_2O_3 = 75$)) [26]. We showed that the yield of liquid hydrocarbons was strongly affected by the structural characteristics of the catalyst. At identical aluminum contents ($SiO_2/Al_2O_3 \sim 80$) the studied samples displayed different activities in polyethylene degradation. The target products were obtained in a maximum amount of 39 wt % in the presence of faujasite. H–MCM-41(70) and H–MCM-41(140) exhibited lower activities (28 and 30 wt %, respectively). The activity of catalysts was found to be dependent on the number and accessibility of the acid sites for the reactants on the catalyst surface and inside the pores. For example, H–MCM-41(70) and H–MCM-41(140), while having different chemical compositions, possess the sets of acid sites of equal strength and are equally active in polyethylene conversion.

The aim of this study was to compare the catalytic activities of mesoporous H–MCM-41 aluminosilicates of different compositions in degradation of polypropylene and a polypropylene-polyethylene mixture into gasoline-range hydrocarbons.

EXPERIMENTAL

In this study, disposable polypropylene cups manufactured in accordance with GOST (State Standard) 50962-96 were studied as polypropylene waste models, as well as 15803-020 grade polyethylene film, GOST 10354-82. Mesoporous materials with the structure of MCM-41 in H-form, prepared in the presence of cetyltrimethylammonium bromide by the conventional hydrothermal synthesis route, were used as catalysts [27]. The characteristics of the catalysts are presented in Table 1.

Experiments on degradation of polypropylene and a polyethylene-polypropylene mixture (1 : 1) were carried out using a flow reactor with a fixed bed of the polymer (polymer mixture) and the catalyst in an argon flow (flow rate 4800 cm^3/h) at a temperature gradually increasing in the range of 300–450°C at a heating rate of 10°C/min, which was followed by keeping under conditions of a controlled temperature of 450°C. To obtain the reaction mixture, a solution of polypropylene (polyethylene-

Table 1. Characteristics of the aluminosilicate catalysts

Sample	SiO ₂ /Al ₂ O ₃ ^a	Specific surface area, m ² /g, <i>S</i> ±5%	Total pore volume, cm ³ /g, <i>V</i> ±5%
H-MCM-41	70	1335	1.59
H-MCM-41	140	1305	1.68

^a Calculated on the basis of the reactant composition for the synthesis.

polypropylene mixture) in *m*-xylene with the polymer : solvent mass ratio of 1 : 4 was prepared. A weighed portion of the catalyst powder was introduced into the hot solution, and the resultant mixture was stirred and then left at room temperature until the solvent evaporated. The reaction mixture was obtained in the form of ~3–4 mm-thick solid films; they which were crushed and loaded into a quartz reactor for further heat treatment of the samples. The mass ratio of the polymer to the catalyst in all the experiments was 10 : 1. A receiving flask for collection of liquid products was arranged at the reactor outlet; it was weighed before and after the experiment. Gaseous degradation products were not collected and not identified. The experiment was continued until the release of liquid products ceased. The yield of the liquid products was calculated as the ratio of the mass of the liquid products to that of the initial polypropylene (wt %).

A sample of polypropylene without the catalyst, which was prepared according to the above-described procedure for the synthesis of solid films, served as a reference.

After completion of the catalytic experiment, the catalyst coated with a layer of carbon deposits remained in the reactor. The reactor was cooled, and a sample was taken for analysis. Thermogravimetric and differential thermal analysis (TGA/DTA) was performed on an SDT Q600 instrument. Heating of reaction mixture samples was carried out at a rate of 10°C/min in an argon atmosphere, and that in the case of the spent catalysts, in air.

Table 2. Yield of the liquid degradation products of polypropylene and the polypropylene-polyethylene mixture (1 : 1) in the presence of H-MCM-41

Sample	Liquid products, wt % (±2%)
H-MCM-41(70) + PP	56
H-MCM-41(140) + PP	86
H-MCM-41(140) + PE+PP (1 : 1)	57

The liquid degradation products were analyzed on an Agilent 7890A gas chromatograph with a flame ionization detector. The products were separated on an HP-5ms quartz capillary column (30 m × 0.25 mm × 0.25 μm); temperature program from 30 to 260°C (heating rate 5°C/min); vaporizer temperature 300°C.

RESULTS AND DISCUSSION

In the preliminary experiments the thermal conversion of polypropylene in the absence of a catalyst under the specified conditions gave no liquid products. Data on the yield of the target degradation products of polypropylene and the polypropylene-polyethylene mixture (1 : 1) in the presence of mesoporous materials are presented in Table 2.

As follows from Table 2, a higher yield of the target products is observed for the sample with a lower content of aluminum. However, our previous experiments aimed at qualitative assessment of the acidity by the indicator method demonstrated that H-MCM-41 (70) and H-MCM-41(140) have the same set of medium-strength acid sites in the *pK_a* range of 2.1–5.0 [26]. A comparative analysis of the previously obtained results on the polyethylene conversion into a set of liquid hydrocarbons in the presence of H-MCM-41(70) and H-MCM-41(140) [26] and the results presented in Table 2 shows that the catalysts studied are more efficient in the polypropylene degradation. As expected, introduction of polyethylene into the reaction mixture causes reduction in the yield of the liquid fraction, which is due to the peculiar structural feature of the macromolecules of the polymers studied. Since every second carbon atom in the polypropylene macrochain is tertiary, the carbon-carbon bonds in polypropylene are weaker compared to polyethylene. The side-chain methylene groups increase the effective chain cross-sectional area of the polypropylene molecules compared to polyethylene, which promotes better interaction with the active sites inside the pores [22].

Thermal analysis of the studied samples showed that the thermocatalytic conversion of polypropylene proceeds in the temperature range of 350–450°C, and

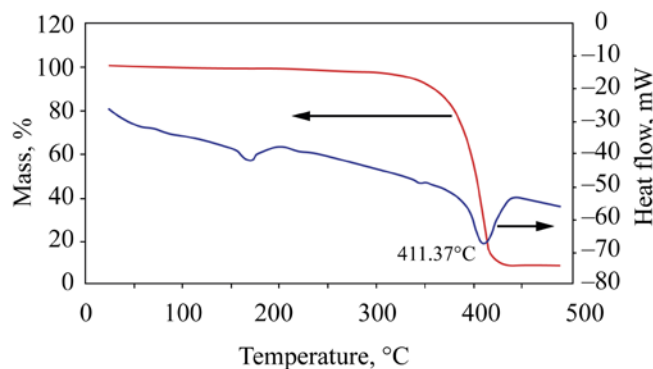


Fig. 1. TGA/DSC curves for the H-MCM-41(140) + PP sample.

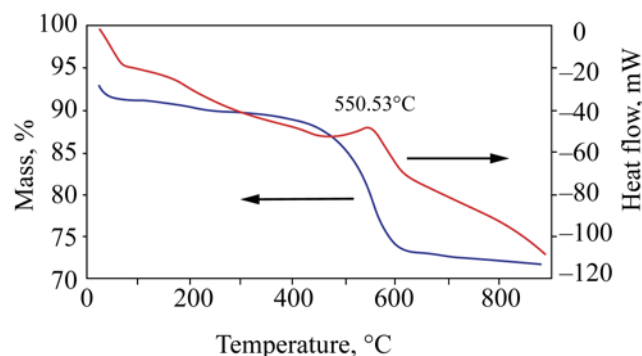


Fig. 2. TGA/DSC curves for the spent catalyst H-MCM-41(70) + PP.

that of the polyethylene-polypropylene mixture, at 390–480°C, which is attributable to a higher temperature of polyethylene degradation. The presence of the catalyst caused reduction of the temperature of the catalytic process compared to thermal conversion. For all the samples studied the TGA/DSC curves of the same type were obtained; Fig. 1 shows the results for H-MCM-41(140)+PP taken as an example.

Table 3 presents the TGA/DSC data for the polymer-catalyst samples, as well as those for the polypropylene sample for comparison.

Thermogravimetric analysis revealed a more significant decrease in temperature of the polypropylene degradation over H-MCM-41(70) compared to H-MCM-41(140). However, this observation cannot be regarded as a common pattern, because our earlier experiments on polypropylene degradation in the presence of amorphous aluminosilicates with different aluminum contents revealed the lack of dependence of the decrease in the maximum temperature of polypropylene degradation on the increase in the aluminum content of the catalyst sample [28].

Obviously, the liquid products comprise not only the gasoline-range fraction hydrocarbons. The liquid catalyzate was separately analyzed for the content of the gasoline-range fraction (C_5 – C_{12}), and the presence of both

saturated and unsaturated hydrocarbons in all the studied samples was observed. Dominant products for each case were identified. For polypropylene degradation over H-MCM-41(70) the prevalence of C_5 – C_8 hydrocarbons with a high yield of methylcyclohexane (13.1 mg/cm³) was revealed, and in the case of H-MCM-41(140) C_5 – C_6 hydrocarbons dominated by iso-pentane (6.9 mg/cm³) were obtained. Degradation of the mixture of the polymers gave an insignificant amount of the gasoline-range fraction, and only C_5 hydrocarbons were identified.

Thermocatalytic degradation of polyolefins resulted in the formation of a solid carbon residue, condensation products (CP), on the surface of the aluminosilicates. This leads to deactivation of the catalyst, which, in turn, significantly affects the composition of the target products and the conversion of polyolefins. Understanding the formation mechanism, as well as studying the composition and structure of CP, provide the possibility to control this process by selecting effective catalysts and designing appropriate process flowsheets [29–32].

Thermal analysis of both samples of the spent catalysts yielded TGA/DSC curves of the same type (Fig. 2). The curves show two temperature ranges of mass loss. The temperature range of 110–350°C, most probably, corresponds to dehydration and dehydroxylation of

Table 3. TGA/DSC data for the samples of polypropylene and the polypropylene-polyethylene mixture (1 : 1) in the presence of H-MCM-41

Sample	PP	H-MCM-41(70) + PP	H-MCM-41(140) + PP	H-MCM-41(140) + PE + PP (1 : 1)
T_{max} , °C	448	396	411	444

Table 4. TGA/DSC analysis data for the catalyst samples coated with a CP layer

Sample	T_{\max} , °C	Sample mass loss, wt %	Heat released, kJ/g CP
H-MCM-41(70) + PP	551	16.8	6
H-MCM-41(140) + PP	548	10.1	1
H-MCM-41(140) + PE + PP (1 : 1)	552	11.8	3

the catalyst. The mass loss in the temperature range of 400–650°C is associated with CP oxidation on the surface of the samples.

Table 4 shows that the maximum temperatures of the CP oxidation for all the studied samples are nearly identical (548–552°C). Notably, polypropylene conversion over the two studied samples gave condensation products of different nature. Specifically, formation of CP with a noticeably higher calorific value and in a larger amount in the case of the H-MCM-41(70) sample compared to the H-MCM-41(140) sample was revealed. This suggests an important role played by the number of acid sites, in spite of their identical strengths. The content of acid sites in the sample with a lower silica modulus is higher than that in the H-MCM-41(140) sample, and with acid sites contributing to the polymerization of unsaturated hydrocarbons this leads to a relatively higher content of the condensation products. Interestingly, introduction of polyethylene into the sample with this catalyst results caused an increase in the content of carbonaceous deposits. This is consistent with our previous data [26] on the CP formed during polyethylene conversion; specifically, the calorific value of such CP is 2–4 times higher than that of the deposits resulted from polypropylene degradation.

CONCLUSIONS

Mesoporous aluminosilicates H-MCM-41 show high activity in thermocatalytic conversion of polyolefins into liquid hydrocarbons. With a decrease in the aluminum content in the catalysts their ability to convert polypropylene into gasoline-like hydrocarbons tends to increase, apparently due to a lower consumption of polypropylene for the formation of the condensation products. Degradation of the polyethylene-polypropylene mixture over the same catalyst gives target gasoline-like products in a lower yield. In the presence of the H-MCM-41 sample with a lower silica modulus, a larger amount of the condensation products arises from polypropylene degradation, and their calorific value is higher. Mesoporous aluminosilicates H-MCM-41 can be regarded as effective catalysts for thermocatalytic

conversion of polypropylene to produce the gasoline-range fraction.

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CONFLICT OF INTEREST

The authors declare no conflict of interest requiring disclosure in this article.

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