

Catalytic Degradation of Polyethylene in the Presence of Synthetic Aluminosilicates

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Abstract—Degradation of polyethylene in the presence of synthetic amorphous aluminosilicates as catalysts to form petroleum-like hydrocarbons was studied.

The amount of difficultly degradable industrial and domestic wastes steadily increases. Large-tonnage wastes from polyethylene packing materials are incinerated or disposed of. However, they can be a valuable secondary raw material for chemical industry.

It is known that thermolysis of polyethylene yields lower olefins [1]. A wide range of products which are frequently characterized as petroleum-like hydrocarbons can be obtained by catalytic degradation of polyethylene. This process can be catalyzed by aluminosilicates of different compositions. Among them, zeolites are used most frequently [2–4].

Natural aluminosilicates, clays, were proposed to produce liquid hydrocarbons from polyethylene [5].

The aim of this study was to determine the features of this process in the presence of model catalysts, synthetic aluminosilicates.

It is believed that the reactive components of a clay catalyst of polyethylene thermolysis are aluminosilicates. Their catalytic activity depends on the acidity of the samples. The aluminosilicate acidity is caused by the presence of aluminum. Therefore, the catalytic activity of aluminosilicates of similar structure in polyethylene degradation should correlate with the aluminum content of the catalysts.

EXPERIMENTAL

Eight aluminosilicates with different aluminum contents and hydrated silica sample were prepared.

Since the acidity of aluminosilicates increases with increasing aluminum content to 13–17 wt %, we studied the catalysts with the aluminum content in the range including this interval.

Catalysts were prepared by coprecipitation from solution. An ethanol solution of tetraethoxysilane (tetraethoxysilane : ethanol weight ratio 1 : 1) was mixed with a 6% aqueous solution of aluminum nitrate. An ammonium hydroxide solution was added to pH 9. The mixture was stirred for 1 h with a magnetic stirrer and allowed to stand for 24 h to complete precipitation. The precipitate was filtered off and calcined in a muffle furnace at 600°C. The composition and some properties of the catalysts are presented in Table 1.

The powder X-ray diffraction patterns of the catalyst samples were recorded on DRON-3 diffractometer using $\text{CuK}\alpha$ radiation.

Table 1. Properties of catalysts

Sample no.	Aluminum content, wt %	Specific surface area, $\text{m}^2 \text{g}^{-1}$	Total pore volume, $\text{cm}^3 \text{g}^{-1}$
1	0	149	0.6
2	1.6	167	1.0
3	2.4	110	0.5
4	5.8	208	0.9
5	8.1	129	0.6
6	12.0	324	0.8
7	12.9	184	0.9
8	16.3	183	0.9
9	22.9	216	0.8

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The specific surface area, pore volume, and pore size distribution were determined by low-temperature adsorption and thermal desorption of nitrogen on an ASAP-2010 unit.

The sample morphology was studied by scanning electron microscopy on a Quanta 200 3D microscope. To estimate the sample uniformity, the aluminum content of the samples was determined by energy-dispersive X-ray spectroscopy (EDX) on a spectrometer attached to the microscope. It is known that EDX allows nondestructive determination of the local composition of a sample. Three measurements in different points of the surface were performed for each sample. The results are presented in Table 2.

The surface acidity of aluminosilicate samples were estimated by the Hammett procedure.

Catalytic degradation of polyethylene was studied on a flow unit in an argon flow. The reaction mixture was prepared as follows. A weighed portion of powdered catalyst was added to heated *m*-xylene. The mixture was vigorously stirred and allowed to stand to complete evaporation of the solvent. The polyethylene : catalyst weight ratio was 3 : 1 or 5 : 1. Polyethylene films crushed to 2–3-mm particles were loaded in a quartz reactor and heated in an argon flow to 400°C. The liquid products were collected in a receiving flask.

The degree of polyethylene degradation was estimated by the gravimetric yield of liquid and solid hydrocarbons. Gaseous thermolysis products were not collected and identified.

The liquid products were analyzed by chromatography–mass spectrometry on Saturn 200 chromatograph–mass spectrometer (Varian) with an ion trap. The mixtures were separated on a 30-m quartz capillary column 0.25 mm in diameter coated with CP-Sil 8 CB stationary phase.

Our results showed that the composition and yield of polyethylene thermolysis product significantly depend on the catalyst composition. Aluminosilicates with a low aluminum content (>3 wt %) catalyzed polyethylene degradation only to solid waxy products. In this case, no liquid products are formed at both polyethylene : catalyst ratios. Liquid products are formed in the presence of aluminosilicates containing more than 5.8 wt % aluminum. It should be noted that only liquid products were observed at a polyethylene : catalyst ratio of 3 : 1. At a polyethylene : catalyst ratio of 5 : 1, polyethylene degrades to form a mixture of liquid and solid

Table 2. Comparative results of chemical and energy-dispersive X-ray (EDX) analysis of the samples

Aluminum content, wt %			
chemical analysis	EDX data		
5.8	5.8	6.8	6.2
12.0	12.3	14.3	15.0
12.9	15.3	13.2	12.9
16.3	15.9	15.8	15.7
22.9	23.5	23.4	22.8

Table 3. Yield of polyethylene thermolysis products depending on the aluminum content of the catalyst

Al content, wt %	Yield of liquid products, wt %, at indicated polyethylene : catalyst ratio	
	3 : 1	5 : 1
0	0	0
1.6	0	0
2.4	0	0
5.8	69	51
8.0	48	43
12.0	50	44
12.9	57	56
16.3	69	52
22.9	49	56

hydrocarbons. The yield of the liquid products in the presence of almost all the examined catalysts at a polyethylene : catalyst ratio of 3 : 1 is higher than that at a ratio of 5 : 1 (Table 3).

The liquid products contain linear and branched isomers of C₅–C₂₆ alkanes and alkenes and aromatic hydrocarbons. For example, the fraction of low-boiling C₄–C₁₀ hydrocarbons (bp < 200°C) in the products obtained in the presence of aluminosilicate with 5.8 wt % aluminum content reaches 77 wt %. The olefin content in this fraction is higher by a factor of approximately 2 than that of paraffin hydrocarbons. The content of cyclic and aromatic hydrocarbon is 9 and 19 wt %, respectively. It should be noted that this fraction contains significant amounts of linear and branched heptenes (11 wt %) and xylenes (17 wt %). Among C₁₁–C₂₆ hydrocarbons, paraffins prevail and virtually no olefins are detected. High content of low-boiling hydrocarbons in the liquid products makes these fractions promising as raw materials for production of gasolines and solvents.

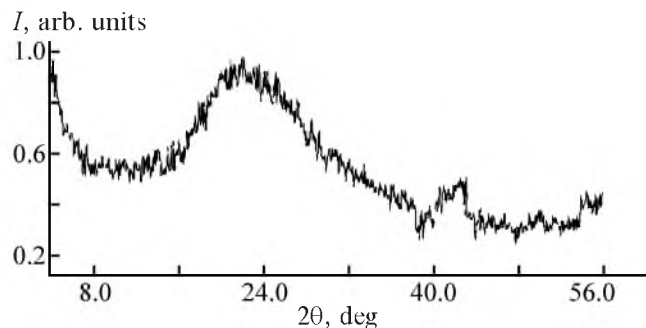


Fig. 1. X-ray diffraction pattern of aluminosilicate with 5.8 wt % aluminum content. (*I*) Intensity and (2θ) Bragg angle.

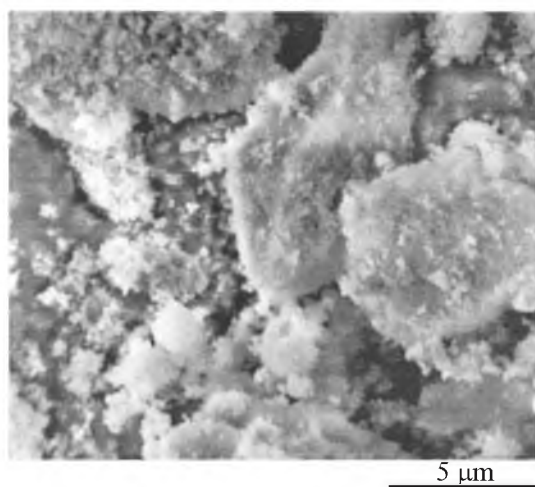


Fig. 2. Electron micrograph of aluminosilicate with 5.8 wt % aluminum content.

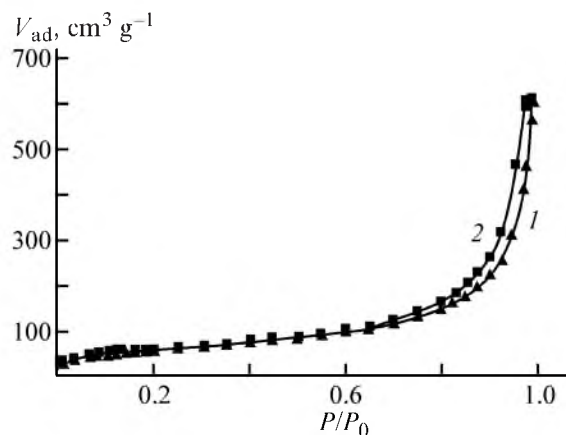


Fig. 3. Nitrogen (1) adsorption and (2) desorption isotherms on aluminosilicate with 5.8 wt % aluminum content. (V_{ad}) Adsorbed volume and (P/P_0) relative nitrogen pressure.

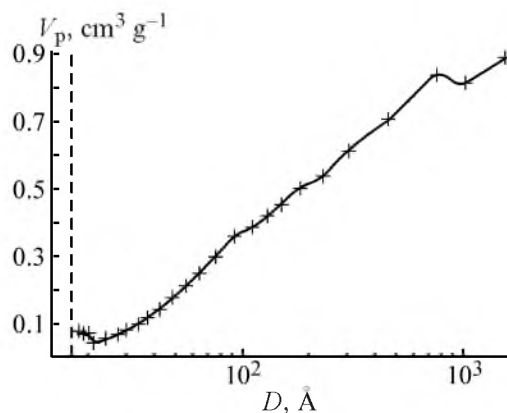


Fig. 4. Pore size distribution of aluminosilicate with 5.8 wt % aluminum content. (V_p) pore volume and (*D*) pore diameter.

X-ray diffraction analysis showed that all samples were X-ray amorphous. The X-ray diffraction patterns of all the samples are similar (Fig. 1). As seen from electron micrographs (magnification $\times 15000$), the samples are characterized by a broad particle size distribution (Fig. 2).

The low-temperature nitrogen adsorption and thermal desorption isotherms for all samples are also similar (Fig. 3) and are of type IV [6]. These isotherms suggest mesoporous structure of the samples. The system in question is characterized by capillary condensation. The hysteresis loops are of type A and are typical of uniformly packed agglomerates and globules of similar size.

The pore size distribution of the aluminosilicates is rather broad. The pore size distribution of one of the examined samples is shown in Fig. 4. All samples contain significant amount of macropores.

The sample acidity was determined using appropriate indicators. All samples have acid sites affecting the color of indicators with $3.46 < pK_a < 5.0$. At the same time, only aluminosilicates that catalyze polyethylene degradation to liquid products also contain acid sites changing the color of indicators with $pK_a > 6.40$. These sites are absent in aluminosilicates with a low aluminum content, which are inactive in polyethylene conversion to liquid products. Apparently, the behavior of aluminosilicates in polyethylene degradation depends on not only the number but also the strength of the acid sites.

CONCLUSIONS

(1) Amorphous aluminosilicates with the aluminum content exceeding 5.8 wt % are effective cata-

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lysts of degradation of polyethylene waste into liquid hydrocarbons.

(2) The catalytic activity depends on not only the aluminum content but also the uniformity of aluminum distribution and the strength of acid sites of the catalyst surface.

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REFERENCE

1. Bryk, M.G., *Destruktsiya napolnennykh polimerov* (Degradation of Filled Polymers), Moscow: Khimiya, 1989.
2. Seo, Y.H., Lee K.H., and Shin, D.H., *J. Anal. Appl. Pyrol.*, 2003, vol. 70, no. 2, pp. 383–398.
3. Ali, S., Garforth, A.A., Harris, D.H., et al., *Catal. Today*, 2002, vol. 75, nos. 1–4, pp. 247–255.
4. Cardona, S.C. and Corma, A., *Appl. Catal. B: Environ.*, 2000, vol. 25, nos. 2–3, pp. 151–162.
5. RF Patent 2262520.
6. Gregg, S.J. and Sing, K.S.W., *Adsorption, Surface Area and Porosity*, London: Academic, 1982.