

UDC 544.473; 547.313; 549.67

DOI: 10.15372/CSD2019120

Development of an Environmentally Friendly Method for Dec-1-ene Oligomerization in the Presence of Zeolite Catalysts

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(Received August 27, 2018; revised February 19, 2019)

Abstract

The dec-1-ene transformations were studied in the presence of Y, Beta, ZSM-12 and ZSM-5 zeolites in the H-form. It is established that the main products of the reaction in the presence of zeolites H-Y, H-Beta, H-ZSM-12 are dec-1-ene isomers and its oligomers, while in the presence of zeolite H-ZSM-5 dec-1-ene isomerization predominantly occurs. The mentioned catalytic systems can be arranged in the following series by the activity: H-Beta > H-Y > H-ZSM-12 >> H-ZSM-5, and by the selectivity of oligomers: H-ZSM-12 > H-Beta ~ H-Y >> H-ZSM-5 in the temperature range of 150–220 °C. Among oligomers the dimers of decene are predominant, have an alkyl-naphthenic structure, contain unsaturated hydrocarbons with tri- and tetra-substituted double bonds of 2.2–3.2 % was established. Physicochemical properties of the synthesized decene oligomers are similar to the hydrogenated poly- α -olefins obtained on the catalytic AlCl_3 complexes.

Key words: oligomerization, isomerization, cracking, decene-1, oligomers, zeolites

INTRODUCTION

Poly- α -olefin oils (PAOO) are the most essential type of synthetic lubricating oils [1–3] included in the IV group of five, according to the classification of base oils developed at the American Petroleum Institute (API), USA.

In the known industrial technologies of obtaining PAOO, oligomerization of α -olefins is carried out in the presence of aluminium chloride, boron fluoride or their complexes with various compounds [4, 5]. A large number of stages in the process, the formation of a large amount of wastes (chlorides or fluorinated oligomers) high toxicity and corrosion activity of the catalysts used stimulate the search for new ecologically safe catalysts for oligomerization of linear α -olefins.

At the end of the XX century, the leading manufacturers of lubricating oils (Texaco Chem. Corp., USA; Chevron Res. Corp., USA; Enichem

Augusta S.p.A., Italy) developed heterogeneous catalysts based on zeolites for the oligomerization of linear α -olefins [6–12]. The advantages of the use of zeolites include their good ecological safety, thermal stability, the possibility of multiple use, the ability to change activity and selectivity by modifying.

Previously we studied oligomerization of oct-1-en in the presence of zeolites Y (structural type FAU), Beta (BEA), ZSM-12 (MTW) and ZSM-5 (MFI) in the H form [13] and found that the highest activity in oligomerization of oct-1-en is exhibited by zeolites H-Y, H-Beta and H-ZSM-12; under the action of these catalysts, the conversion of the olefin reaches 90–96 %. The major products of oct-1-ene transformation in the presence of zeolites H-Y, H-Beta and H-ZSM-12 are oligomers among which dimers are prevailing. The dimers of oct-1-ene are formed with the highest selectivity (up to 100 %) in the case when zeolite H-ZSM-12

is used as a catalyst. In the present work, we describe the results of the studies of catalytic properties of zeolites H-Y, H-Beta, H-ZSM-12, H-ZSM-5 in dec-1-ene oligomerization.

EXPERIMENTAL

Dec-1-ene (99 %) manufactured by Acros was used in the investigation.

Zeolites H-Y, H-Beta, H-ZSM-12 and H-ZSM-5 were used as catalysts. The methods of their preparation were described in [14–16].

The chemical composition of the resulting zeolite samples was analyzed by means of X-ray fluorescence spectrometry with a Shimadzu EDX-720/900HS instrument (Japan).

The phase composition and crystallinity degree of the samples were determined in comparison with the references using a Bruker D8 Advance diffractometer (Germany) in monochromatized CuK_α -radiation within the angle range 5–40° by 2θ with a step of 0.5 deg/min and accumulation time in each point 20 s.

The sizes of crystallites in zeolites were determined with the help of scanning electron microscopy with a JEOI. JSM-6490 I.V instrument.

To determine the equilibrium adsorption capacities of zeolites with respect to water vapour and *n*-heptane at 23–25 °C and $P/P_s = 0.80$ – 0.85 , the desiccator method was used. It is based on the determination of the complete saturation of zeolite with adsorbate vapour.

The acid properties of the samples of zeolite catalysts were studied by means of temperature-programmed desorption (TPD) of ammonia.

Oligomerization of dec-1-ene in the presence of zeolite catalysts was carried out for 1–5 h in a continuously rotating thermostated autoclave at 150–250 °C without any solvent. The amount of the catalyst was 10–30 mass %. Before catalytic tests, zeolite samples were subjected to thermal treatment in the air at 540 °C for 4 h.

The reaction mixture was separated from the catalyst by filtering and analyzed by means of gas-liquid chromatography (GLC) with a Carlo Erba HRGS 5300 Mega Series chromatograph with a flame ionization detector. Analysis conditions: a glass capillary column 25 m long, SE-30 phase, analysis temperature 50–280 °C with programmed heating 8 °C/min, detector temperature 250 °C, evaporator temperature 300 °C, carrier gas – helium (30 mL/min).

To determine the composition of the oligomer fraction, analysis by means of high performance

liquid chromatography (HPLC) was carried out with a Shimadzu LC-20 Prominence instrument (Japan). Analysis conditions: polystyrene column Plgel 500 Å, toluene flow rate 0.8 mL/min, refractometric detector RID-20A.

Reaction products were characterized with the help of the following methods: gas chromatography – mass spectrometry, IR, NMR ^1H and ^{13}C spectroscopy, ^{13}C -DEPT.

IR spectra were recorded with an IR Fourier transform spectrometer VERTEX 70v in tablets with KBr.

NMR ^1H and ^{13}C spectra were recorded with a Bruker AVANCE-400 spectrometer with the working frequency for ^1H nuclei 400.13 MHz, for ^{13}C nuclei 100.62 MHz in standard cells 5 mm in diameter for the solutions of substances in CDCl_3 , Benzene- d_6 , toluene- d_8 were used as internal standards.

High-resolution mass spectra were recorded with an instrument manufactured by Fisons company; the chromatograph is equipped with a DB 560 capillary quartz column 50 m long.

Physicochemical properties of decene oligomers (solidification temperature, flash point, viscosity) were determined using standard procedures [17].

Iodine number (IN) – the amount of iodine consumed for 100 mL of hydrocarbon (in grams) was determined according to the procedure described in [18].

RESULTS AND DISCUSSION

Physicochemical characteristics of the studied zeolite samples are presented in Table 1. All of them contain no admixture phases, the degree of their crystallinity is close to 100 %, crystallite size is 1–10 μm .

The acidity spectra of zeolite catalysts, recorded by means of TPD NH_3 , contain two peaks characterizing “weak” acid centres with the temperature maximum T_{max} within the region 100–350 °C (T_1) and “strong” acid centres with T_{max} in the region above 350 °C (T_2). Chemical transformations of zeolites take place mainly with the participation of the “strong” acid centres the concentration of which decreases in the sequence: H-Y > H-Beta > H-ZSM-12 > H-ZSM-5. The strength of these sites, which was estimated from the shift of the temperature maximum T_2 in thermodesorbograms to the higher temperature region, increased passing from zeolite H-Y to zeolites H-Beta, H-ZSM-12 and H-ZSM-5.

TABLE 1
Physicochemical characteristics of zeolite samples

Parameter	H-Y	H-Beta	H-ZSM-12	H-ZSM-5
SiO ₂ /Al ₂ O ₃ (M)	5.0	18.0	24.0	30.0
Phase composition, %	100	100	100	100
Crystallinity degree, %	~100	~100	~100	~100
Decationation degree, α	0.96	0.97	0.97	0.97
Crystal size, μ	1–10	1–10	1–10	1–10
Equilibrium adsorption capacity for vapour, cm ³ /g:				
H ₂ O	0.30	0.18	0.14	0.14
C ₇ H ₁₆	0.30	0.31	0.17	0.17
Concentration of acid centres, mmol NH ₃ /g _{cat}				
C _I	622	530	409	380
C _{II}	560	340	280	240
C _{total}	1202	870	689	620
Temperature of peak maximum, °C:				
T ₁	250	280	300	290
T ₂	430	450	450	450

Note. C_I, C_{II}, C_{total} are the concentrations of weak (I), strong (II) acid centres and the total concentration, respectively.

Dec-1-ene, similarly to oct-1-ene studied by us previously, is transformed in the presence of zeolite catalysts into isomers and oligomers. Reaction products contain the isomers of dec-1-ene differing from each other by the position of the double bond (*cis*- and *trans*-isomers of dec-2-, -3-, -4-, -5- and -6-enes), and structural isomers (methyl nonenes, dimethyl octenes, trimethyl heptenes *etc.*). Dimers and trimers of decene are

observed in the oligomers. In addition, oligomers of olefins with the molecular masses smaller than those of the dimers of decene are present (they are designated as the oligomers of cracking products, OCP). These compounds are formed as a result of destruction of decenes with the formation of olefins with a smaller molecular mass, which are then oligomerized into hydrocarbons C_{*m*}H_{2*m*}, where *m* = 11–19.

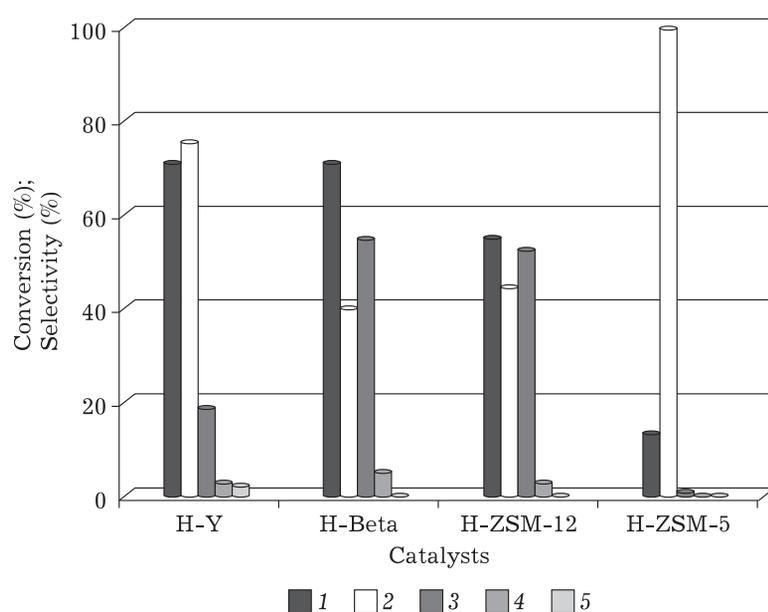


Fig. 1. Effect of the structural type of zeolite on conversion and on the composition of the products of dec-1-ene transformation (reaction conditions: catalyst 10 mass %, 180 °C, 5 h): 1 – conversion; 2 – isomers; 3 – dimers; 4 – trimers; 5 – OCP.

The results of dec-1-ene oligomerization in the presence of zeolite catalysts are shown in Fig. 1. The total activity of the catalysts, which was estimated from the conversion of dec-1-ene, is maximal for zeolites H-Y and H-Beta (71 %), and decreases when passing to pentasil H-ZSM-12 (55 %) and H-ZSM-5 (13 %). However, zeolite catalysts may be arranged according to their activity in oligomerization in the following sequence: H-Beta \approx H-ZSM-12 > H-Y \gg H-ZSM-5. Under the mentioned conditions (10 mass % catalyst, 180 °C, 5 h), the major products of the reaction on zeolites H-Beta and H-ZSM-12 are decene oligomers, on zeolite H-Y – mainly isomers of decene, on zeolite H-ZSM-5 – practically only decene isomers (99.4 %). Prevailing in the formed oligomers of decene are dimers. Their amount is maximal in the oligomer fraction formed on zeolite H-ZSM-12 (91 %). In the oligomers obtained on zeolite H-Beta, the fraction of dimers reaches 89 %, on zeolite H-Y – 76 %. It should be noted that the larger is the diameter of zeolite pores, the higher is the fraction of trimers in the oligomers: H-ZSM-12 (5.5 %) < H-Beta (8.4 %) < H-Y (14 %).

Comparison of the activity of the studied catalysts in dec-1-ene oligomerization with their acid properties and the characteristics of the porous structure shows that the most active catalysts (according to the total olefin conversion) in the reaction are zeolites H-Beta and H-Y, which possess high concentrations of acid centres (see Table 1) and the broadest channels (the size of channels in zeolite Beta is 0.66×0.77 nm) and cavities (the size of cavities in zeolite H-Y is 0.75 nm). Zeolite H-ZSM-12, in spite of the activity close to that of zeolite H-Beta in oligomerization) lags behind the

latter in total activity. This may be due either to the smaller concentration of reaction centres or to the structural features. H-ZSM-12, unlike all other catalysts, possesses not a three-dimensional system of channels but a two-dimensional one, which may hinder the diffusion of the molecules of reagents and reaction products inside the lattice. Zeolite with the most narrow pores H-ZSM-5 (channel size 0.56 nm and 0.51×0.55 nm) exhibits a minimal activity in the reaction and catalyzes only isomerization of dec-1-ene.

Oligomers of decene are formed with the highest selectivity on zeolite catalysts H-Beta and H-ZSM-12. This may be due to the presence of the strongest acid centres on their surface. These centres promote oligomerization as shown previously [19]. A lower selectivity of oligomer formation on zeolite H-Y in comparison with zeolites H-Beta and H-ZSM-12 may be explained by the presence of weaker acid centres in zeolite H-Y [20].

For all the studied catalyst samples, the effect of reaction conditions on the conversion of dec-1-ene and the composition of reaction products were studied. The conversion of the initial olefin increases with an increase in process temperature from 150 to 200 °C and the amount of the catalyst from 10 to 30 mass %, which is the evidence of the availability of acid centres (Fig. 2). Almost complete conversion of dec-1-ene (more than 95 %) is achieved on zeolites H-Beta and H-ZSM-12 at 200 °C in the presence of the catalyst at a level of 20–30 mass %, while on zeolite H-Y it is achieved under more rigid conditions: 250 °C and 30 mass %, respectively. As we have already mentioned, zeolite H-ZSM-5 exhibits low activity within the studied range of reaction pa-

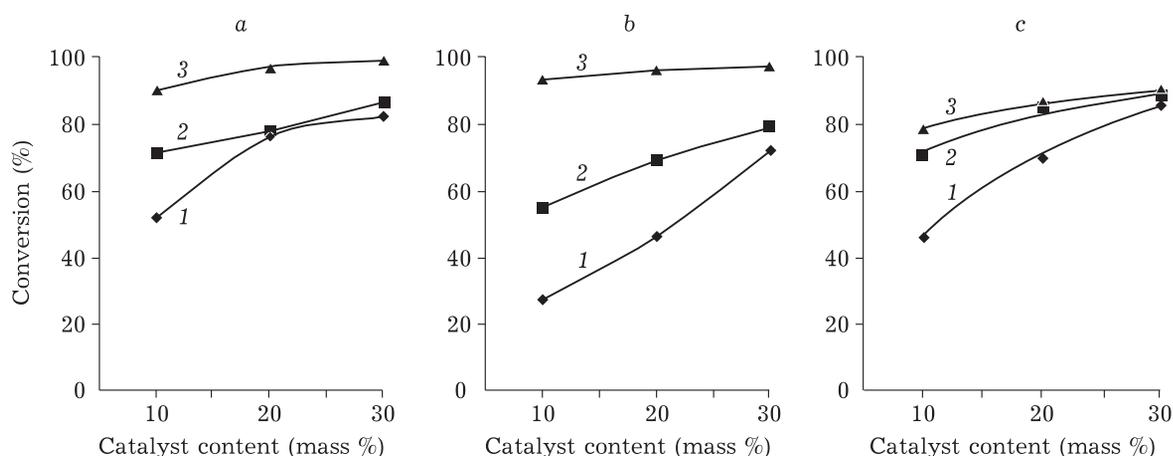


Fig. 2. Dependence of the degree of dec-1-ene transformation on reaction temperature and catalyst content: a – zeolite H-Beta, b – zeolite H-ZSM-12, c – zeolite H-Y. Here and in Fig. 3: temperature, °C: 150 (1), 180 (2) and 200 (3).

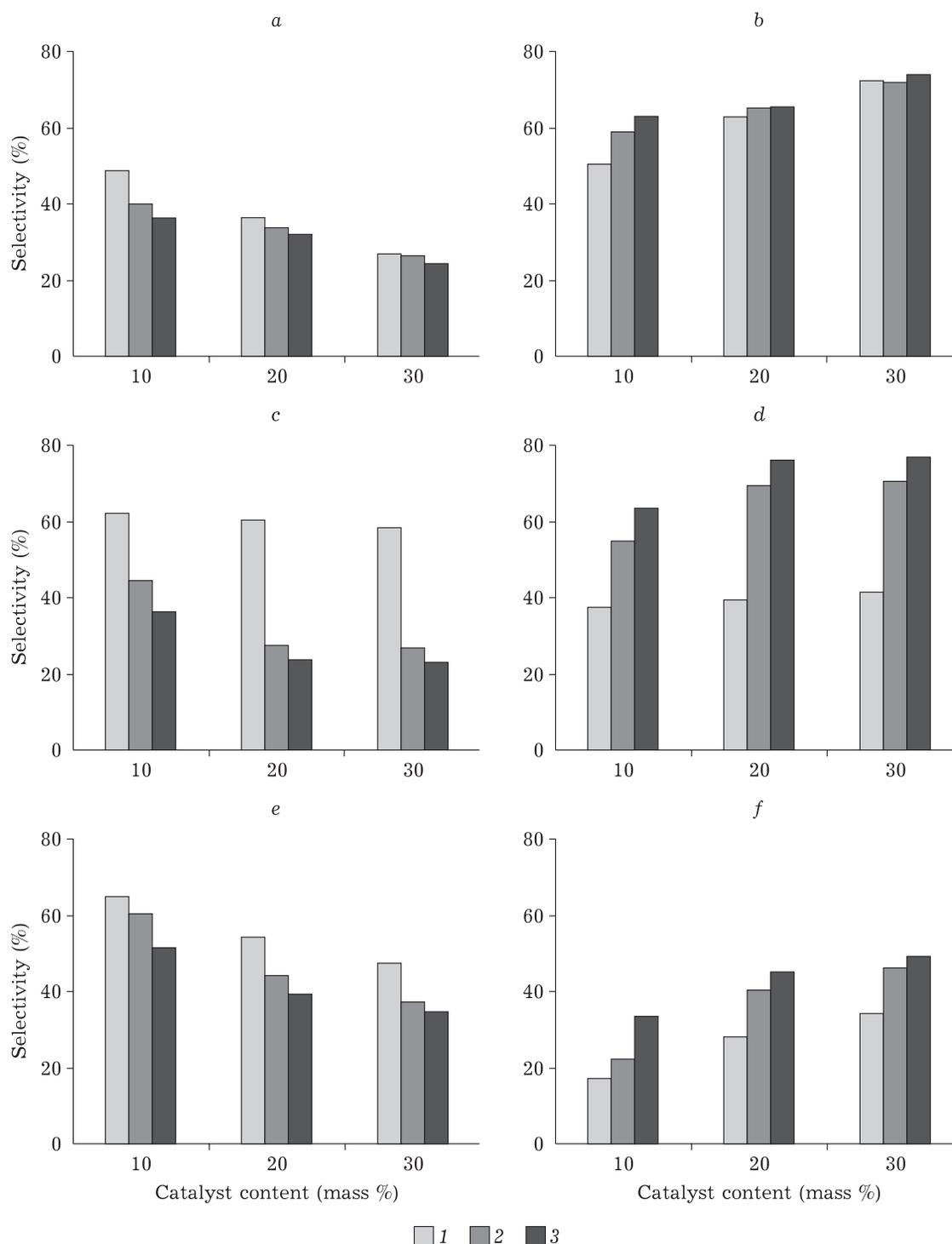


Fig. 3. Dependence of the selectivity of the formation of isomers (a, c, e) and oligomers (b, d, f) of decene-1 on reaction temperature and catalyst content: a, b – zeolite H-Beta, c, d – zeolite H-ZSM-12, e, f – zeolite H-Y. For designations, see Fig. 2.

rameters, and the conversion of dec-1-ene on this catalyst at 250 °C and catalyst content 30 mass % was 45 %.

In the case of zeolites H-Y, H-Beta and H-ZSM-12, the content of decene isomers decreases and the fraction of oligomers increases with an increase

in temperature and the amount of the catalyst (Fig. 3). With an increase in reaction temperature, an increase in the amount of trimers is observed in the composition of the oligomers of decene. In the presence of zeolite H-ZSM-5 within the temperature range 150–200 °C and with the catalyst con-

TABLE 2

Physicochemical properties of a mixture of decene oligomers (di- and trimers)

Parameter	Decene oligomers obtained on zeolite H-Beta (dimers – 89.4 and trimers – 10.6 mass %, respectively)	Hydrogenated decene oligomers obtained on AlCl ₃ [3]	
		dimers	trimers
Temperature, °C:			
of solidification	–59	70	66
of flash	141	120	168
Viscosity, s/St, at temperature, °C:			
20	18.4	–	–
40	9.6	–	–
100	1.2	1.19	2.64
Iodine number	2.8	–	0.2

Note. Dash means the absence of data.

tent 10–30 mass %, mainly the polymers of decene were obtained (98.5–99.6 %).

An increase in the process temperature above 200 °C causes enhancement of the destruction of decene isomers and oligomerization of the formed low-molecular compounds; the amount of the latter in the reaction mixture starts to increase. For instance, the selectivity of OCP formation in the reaction mass obtained on zeolites H-Y and H-ZSM-5 (250 °C, catalyst 30 mass %), is 26–27 %. The smallest amount of OCP is formed on zeolite H-Beta (from trace amounts up to 1–2 %). No OCP formation is observed on zeolite ZSM-12 within the whole studied range of reaction conditions (150–250 °C, catalyst 10–30 mass %). The results provide evidence for the absence of the cracking activity of this catalyst.

The structure of the obtained dec-1-ene dimers was studied by means of IR and NMR spectroscopy. The results of the investigation show that aliphatic cyclic compounds prevail in them. The high spectral density within the spectral range ¹³C 12–50 ppm points to the naphthene nature of the compounds.

Unsaturated compounds are present in insignificant amount. They are represented mainly by olefins with tri- and tetrasubstituted double bonds. Their presence is confirmed by the weak signals observed within the range 120–140 ppm in the ¹³C spectrum. These signals characterize carbon atoms at tri- (120, 140 ppm) and tetrasubstituted double bonds (120, 130 ppm), and weak signals in the NMR ¹H spectrum in the region 4.7–5.4 ppm, which are due to the protons of –C=H<, =CH–, =CH₂ groups. It follows from the ratios of the integral intensities of the bands characterising methyl and methylene groups that hydrocarbon chains are branched but not linear.

Intense absorption bands in the IR spectra are observed at 1380 and 1460 cm^{–1}, characteristic of –CH₃ and –CH₂– groups, and at 720 cm^{–1}, corresponding to the higher deformation vibrations of C–H in non-branched –(CH₂)_n– chains. The presence of compounds containing *trans*-disubstituted double bonds is confirmed by the absorption band observed at 970 cm^{–1}.

The physicochemical characteristics (solidification temperature, flash point) of dec-1-ene oligomers obtained in the presence of zeolite H-Beta are presented in Table 2. Comparing these data with the properties of hydrogenated oligomers of decene obtained under the action of AlCl₃ [4], one can see that the oligomers synthesized in the presence of zeolites are characterized by the same low solidification temperatures and close viscosity. The low IN of decene oligomers is the evidence of the insignificant amount (2.8–3.2 %) of unsaturated compounds and determines the possibility of their use without the hydrogenation stage.

CONCLUSION

For the purpose of developing an ecologically friendly heterogeneous catalytic method of obtaining the oligomers of dec-1-ene, a systematic investigation of the oligomerization of dec-1-ene in the presence of zeolites H-Y, H-Beta, H-ZSM-12 and H-ZSM-5 was carried out. It was established that the activity and selectivity of zeolite catalysts in olefin oligomerization are due both to the concentration and strength of Brønsted acid centres and to the structural features of the lattice.

The highest selectivity (64–77 %) in dec-1-ene oligomerization with nearly complete conversion of the olefin (200 °C, catalyst 10–30 mass %) is exhibited by zeolites H-Beta and H-ZSM-12. Zeo-

lite H-Y is less selective in the oligomerization of dec-1-ene: for the same conversion, selectivity with respect to oligomers is 33–49 %. Zeolite H-ZSM-5 at 150–200 °C exhibits low activity and promotes mainly isomerization of dec-1-ene. With an increase in temperature to 250 °C, destruction processes are enhanced, and the content of oligomers $C_m H_{2m}$ (where $m = 11 - 19$) in reaction products increases.

Among decene oligomers formed on zeolites H-Y, H-Beta and H-ZSM-12, dominate dimers comprising 76–100 % of the fraction of oligomers. Decene dimers are formed most selectively on zeolite H-ZSM-12 (91–100 %).

Investigation of the chemical structure of decene oligomers showed the predominance of hydrocarbons with alkyl naphthene structure. The amount of unsaturated compounds in the oligomer fraction is at a level of 2.2–3.2 %. The physicochemical properties of the obtained decene oligomers (solidification temperature, flash point, viscosity) are close to the characteristics of hydrogenated poly- α -olefins synthesized in the presence of $AlCl_3$. The formed products may be related to the bases of low-viscosity oil to be used for obtaining hydraulic liquids in aviation and other machines operating at low temperatures, drill oils and liquids for the seabed mining of natural gas, high-speed spindle oil and cosmetics [4].

Acknowledgements

The studies have been performed with the financial support from the Council for the Grants of the President of RF for young scientists and post-graduates (Project SP-2137.2018.1).

Structural studies were carried out at the Shared Equipment Centre “Agidel” at the Institute of Petrochemistry and Catalysis RAS.

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