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Zr-BASED HETEROGENIZED CATALYTIC SYSTEMS FOR OLIGOMERIZATION OF ETHYLENE TO OLEFINS AND OIL FRACTIONS

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The process oligomerization of ethylene studied using heterogenized zirconium complexes containing amino- and iminohydrochloride substituents ionic liquid type and alkyl aluminum chlorides as cocatalysts. It was established that the composition of product oligomerization of the ethylene changes depending on the type of zirconium complexes and aluminium organic compound. The polyethylenic oil fractions obtained in the presence of zirconium complexes and ethyl aluminum dichloride $(C_2H_5)_2AlCl_2$ catalyst have highly branched molecules structure, low viscosity indexes contains naphthenic rings. The oligomeric product obtained using of dialkylaluminumchloride $(C_2H_5)_2AlCl$ cocatalyst depending on molar ratio of Zr/Al, reaction temperature and pressure of ethylene is mainly consists of C_4 – C_{10} ofolefin fractions linear structure with the yield of 78.8–91.6%. It was shown that sintesized zirconium complexes may be repeatedly reused in successive ethylene oligomerization for obtaining both α -olefins and polyethylene oil fraction.

Keywords: *zirconium complexes, amino- and iminohydrochloride ligands, ethylene, oligomerization.*

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Introduction

One of the strategic trends in petrochemistry is the development of processes for the production of higher olefins, including linear α -olefins (LAO) obtained by oligomerization of ethylene in the presence of metal complex catalysts. Obtained higher LAOs are used for the production of plasticizers, synthetic oils, corrosion inhibitor, detergents, comonomers for linear low density polyethylene, chemical reagents in oil and mining industry, etc. [1, 2].

In spite of high catalytic activity and selectivity of homogenous transition metal complex catalysts in oligomerization of ethylene, they have essential disadvantages such as difficulties associated with separation of the catalyst from oligomerization products and impossibility of their recycling. Therefore, in recent years homogeneous complex catalytic systems with transition metal have been using in oligomerization of ethylene both as supported on the surface of ionic liquids and in biphasic medium as dissolved in ionic liquids [3–9].

On the basis of conducted researches, suggested by us transition metal precursor containing ionic liquid type ligands in their coordination sphere for ethylene oligomerization and polymerization processes. These precursors, com-

bined with aluminum-organic activators, act as a recyclable heterogeneous oligomerization and polymerization catalysts both in the molecular organic and ionic liquid solvents [10–16].

In this article, extensive results of investigating ethylene oligomerization in hydrocarbon solvents in the presence of complex catalytic systems consisting different ionic liquid type amino- and iminohydrochloride ligands and aluminum alkyl chlorides have been given.

Experimental section

Oligomerization of ethylene. Ethylene oligomerization was carried out in the jacketed autoclave equipped with a magnetic stirrer, thermometer and heated with thermostated water or glycerin. Before charging with reaction mixture and catalyst components, the autoclave was washed with dry toluene and acetone, checked for leak tightness under nitrogen pressure, dried in vacuum under heating by connecting the reactor connected to the vacuum line and heating for 1–1.5 h at 90°C. The catalyst and solvent were placed into reactor under an inert gas atmosphere. The reactor was heated to reaction temperature and then ethylene was pressurized into it with intensively mixing the reaction mixture by magnetic stirrer. The pressure of ethylene in the reactor was controlled by

a manometer. The oligomerization product solution was removed from the reactor by simple decantation. The Zr-component of catalyst, remaining in the reactor, was repeatedly used in the oligomerization process by addition of new portions of solvent and aluminum organic compound. The obtained oligomerization products were washed with aqueous solution of sodium hydroxide for removing aluminum organic compound residues, dried over aluminum oxide and fractionated.

Analytical procedure. Oligomerization products and obtained metal complexes were analyzed by gas and exclusion chromatography, DSC, IR spectroscopy, by methods ^1H NMR-element analysis and scanning electron microscope (SEM).

Molecular-weight distribution (MWD) of the obtained products was studied by size exclusion chromatography method using high performance "Kovo" (Czech Republic) liquid chromatograph with a refractive index detector. Two 3.3 mm×150 mm columns packed with the "Separon-SGX" stationary phase with a particle size of 7 mm and a porosity of 100 Å were used. Dimethylformamide was used as an eluent (flow rate – 0.3 ml/min, temperature – 20–25°C).

The distributions of olefins in obtained oligomer product by oligomerization of ethylene were performed by gas chromatography (GC) analysis. The last was carried out using an Agilent 7820A GC with a column of 30 m in length and 0.53 mm in diameter. The analyses were performed as follows: temperature increasing from 35 to 130°C at a rate of 75°C min⁻¹ and from 130 to 220°C at a rate of 2°C min⁻¹. The rate of flow of

carrier gas (helium) was 30 ml/min⁻¹. The temperature of the evaporator was 320–350°C.

^1H NMR spectra of obtained oligomers and synthesized complexes were recorded on a Bruker pulsing Fourier spectrometer (Germany) operating at the frequency of 300 MHz. DMSO and chloroform were used as a solvent.

IR spectra were recorded on the "BRUKER" Fourier spectrometer in the range of 50–4000 cm⁻¹.

The differential thermal analysis (DTA) of these complexes were recorded via "STA Platinum" (Germany) thermal derivatograph, the microphotos surface of these were scanned via "Hitachi – S3400 N" SEM microscope (Japan).

The synthesis of "grafted" ionic liquid type zirconium complexes. Heterogenized "grafted" ionic liquid type zirconium complexes containing amino- and iminohydrochloride ligands were synthesized in THF via the reaction of ZrCl_4 with different sterically hindered substituted phenolderivatives 2-piperidinylmethyl-4-methylphenol (L1), 2-morpholylmethyl-4-methylphenol (L2), 2-diethylaminomethyl-4-methylphenol (L3) and 2-[(2,6-di(isopropyl)phenyl)imino]phenol (L4) at a molar ratio of the reactants of 1:2 or 1:3. The synthesis of these complexes carried out in a three-necked flask under inert atmosphere. Obtained complexes are not soluble in hydrogen solvents, but dissolve in DMSO and ionic liquids. They are unstable in air. General synthesis scheme of complexes is illustrated below:

MC1 – n=2, L=L1
 MC2 – n=3, L=L1
 MC3 – n=2, L=L2

MC4 – n=2, L=L3
 MC5 – n=2, L=L4

Results and discussion

The HCl released by the interaction of catalyst components connecting with nitrogen atom of the ligand form quaternary ammonium salts. Obtaining of quaternary ammonium salts via the combination of releasing HCl with nitrogen atom of ligand have been proved by IR- and metod ^1H NMR spectroscopies. IR spectroscopy and ^1H NMR of MC1 from the series of synthesized complexes were given figure 1a and 1b respectively. Deformation vibrations 2536 cm^{-1} , 2573 cm^{-1} , 2636 cm^{-1} , valence vibration 1614 cm^{-1} and signal of chemical shift at 10.05 ppm (N–H bond of $\text{N}^+\text{R}_3\text{H}$ group) related to the ammonium group of MC1 zirconium complex are observed in the IR- and ^1H NMR spectrums respectively.

Fig. 1. The IR (1a) and ^1H NMR (1b) spectra of MC1.

It was determined that in the composition of the synthesized zirconium compounds containing two substituents imino- and aminophenol ligands contain 1 molecule THF as coordinated to the Zr metal according to the calculated number of protons on the basis of integral curves in

tensity in NMR spectrum of complexes (1.74 and 3.46 ppm). In the IR spectrum of the complexes absorption bands are observed at 1053 cm^{-1} , 1121 and 1153 cm^{-1} corresponding to the valence vibration of C–O–C bond of THF which used as solvent in the synthesis of these complexes. Bands in the absorption area of $530\text{--}600\text{ cm}^{-1}$, characteristic for stretching vibrations of Zr–O bond and 280 cm^{-1} absorption band characteristic for stretching vibrations of Zr–Cl bond were also observed.

The amorphous or crystalline structure of the synthesized zirconium complexes were studied by X-ray analysis. It has been established that the amorphous structure takes place of crystalline structure when increased the size of organic ligand in the structure of the complex. For example, MC1 zirconium complex obtained on the basis of 2-methylpiperidinyl-4-methylphenol has amorphous structure whereas 3-substituent MC2 synthesized based on the same ligand has crystalline structure [17].

The surface structures of the MC1 and the complex catalyst system obtained by its interaction with $(\text{C}_2\text{H}_5)_3\text{AlCl}_2$ were investigated by the SEM. It was determined that MC1 zirconium complex (Figure 2a) and the prepared complex catalytic system (Figure 2b) have a lots of pores and channels where the reacting components can be placed, which favors its reuse as heterogeneous catalyst in the oligomerization process of ethylene. It is evident from the SEM Figure that on the surface of the complex does not change after oligomerization of ethylene.

Thermo-physical properties of heterogenized zirconium phenolic complexes were investigated by DTA. The thermograms of synthesized MC1 zirconium compound and complex catalytic system obtained by interaction of its with $(\text{C}_2\text{H}_5)_3\text{AlCl}_2$ at molar ratio of 25:1 is given in Figure 3a and 3b respectively.

As can be seen from the pictures, the thermal decomposition of the MC1 zirconium compound and the catalytic system prepared based on its pass several stages through, and their thermograms are sharply differ from each others. The initial temperature of the thermal decomposition of MC1 zirconium compound and the complex catalytic system prepared on the basis its is 251 and 149°C respectively.

Fig. 2. Scanning electron microscope images of MC1 (a) and complex catalyst system (b) (x 500F).

Fig. 3. The thermograms of MC1 zirconium compound and the complex catalytic system obtained by interaction of its with $(C_2H_5)_2AlCl_2$ at molar ratio of 25:1.

The end temperatures of thermo decomposition of these complexes are 500 and 457^oC respectively. When carrying out process oligomerization of ethylene at 150^oC the activity of the catalytic system begins to decline after a certain period of time because of decreasing the initial temperature of thermal decomposition of catalytic system formed by interaction of MC1 zirconium complex with aluminium organic compounds.

Oligomerization of ethylene to LAO in the presence of heterogenized zirconium complexes with "grafted" ionic liquid ligand

The process oligomerization of ethylene was investigated at various temperatures in the presence of catalytic systems consisting of synthesized zirconium complexes and $(C_2H_5)_2AlCl$

as cocatalyst and obtained results were given in Table 1. As it seen from the table 1, the activity of the catalytic systems and the MWD of obtained oligomer product depend on the composition of zirconium complexes and reaction temperature. The composition of the oligomer product obtained in the presence of catalytic systems based on MC1, MC2, MC3 and MC4 zirconium complexes containing aminohydrochloride ligands comprise mainly C₄–C₁₂ olefins. The amount of C₆–C₁₀ olefin fraction in the presence of these catalytic systems is 61.3–69.4%.

The use of the 2-[(2,6-di(isopropyl)phenyl)-iminomethyl]phenol as ligand containing electron donor isopropyl substituent in the synthesis of MC5 zirconium complex cause an increase in electron density in the Zr atom.

Table 1. Oligomerization of ethylene in the presence of various zirconium complexes and temperatures (reaction time – 30 min, solvent – 50 ml toluene, Zr:Al=1:25, P= 2,5 MPa, temperature – 90°C)

Zr complexes	Activity, g oligomer/g Zr·h ⁻¹	T, °C	Composition of oligomeric product, weight %						
			C ₄	C ₆	C ₈	C ₁₀	C ₆ –C ₁₀	C ₁₂ –C ₁₈	C ₂₀
MC1	828	70	23.7	28.5	21.6	15.8	65.9	10.4	–
	1438	90	15.2	27.1	25.1	17.2	69.4	15.4	–
	2422	120	6.6	24.2	30.2	21	75.4	17.1	0.9
	2145	150	2.4	15.8	32.4	26.2	74.6	21.2	2.0
MC2	850	90	26.3	28.6	18.2	14.5	61.3	12.4	–
MC3	1720	90	19.8	28.2	24.3	16.3	68.8	11.4	–
MC4	2521	90	17.8	28.2	20.6	19.1	67.9	14.3	–
MC5	2014	70	10.2	33.4	27.2	20.8	81.4	8.4	–
	2177	90	7.8	29.2	26.1	25.2	80.5	11.7	–
	3240	100	5.4	22.6	27.4	29.6	79.6	13.8	1.2
	3843	120	3.5	20.7	31.8	23.9	76.4	15.6	4.5

Increasing electron density at Zr atom reduce the β -H elimination. This makes it easy to insert of ethylene molecule into Zr–C bond and occurs the growth of the oligomer chain. Therefore, the amount of high molecular by mass olefins increases in the obtained oligomer product, and the yield of C₆–C₁₀ olefin fraction is 83.2%.

The composition of obtained oligomer products were investigated by IR spectroscopy and ¹H NMR method. The IR spectra of obtained oligomer product have characteristic bands at 908 and 992 cm⁻¹ corresponding to deformation vibrations of C–H bonds of vinyl groups (–CH=CH₂), at 1640 cm⁻¹ corresponding to valence vibration of C=C bonds of vinyl groups in the LAOs and at 887 cm⁻¹ corresponding to deformation vibrations of C–H bonds of vinylidene groups. It was determined that the formation of vinylidene type oligomers during the process of oligomerization depends on the presence of the oligomers in the reaction medium. Increasing the content of oligomers increase the likelihood of entering ethylene into co-oligomerization reaction with the oligomers in the reaction medium. In the result, in the content of oligomer product increases the amount of vinylidene type oligomers.

As it seen from Table 1, increasing the reaction temperature cause an decrease of low molecular by mass olefins and increase the amount of the C₈–C₁₈ fraction in obtained oligomer product. In the presence of MC1, at 70°C, the oligomerization product mainly consists of C₄–C₈ LAO and the yield of this fraction is 73.8%. Increasing the reaction temperature from 70 to 150°C in the presence of MC1 and MC5 zirconium complexes lead to decrease the

amount of butenes from 23.7% to 2.4% and from 10.2% to 3.5% respectively. In this case, the amount of C₈–C₁₈ fraction in the obtained oligomer product increases from 47.8% to 79.8% and from 56.4% to 71.3% respectively.

The molar ratio of Zr:Al influence both catalytic activity and MWD. In the case of MC1 with Zr/Al = 1:30, the catalyst activity is 1438 g oligomer (g Zr)⁻¹ h⁻¹ whilst this ratio is increased to Zr/Al = 1:80 the catalyst activity increases to 3800 g oligomer (g Zr)⁻¹ h⁻¹ and the amount of butenes in obtained oligomer product decreases from 15.2% to 2.4% respectively. But, the amount of C₆–C₁₀ fraction is increased from 69.4% to 82.7%. On the contrary, increasing the molar ratio of Zr/Al in the presence of MC5 zirconium complex with the iminohydrochloride ligand led to decrease the amount of C₆–C₁₀ fraction from 85.2% to 57.8%.

Heterogenized zirconium complexes with "grafted" ionic liquid ligands were repeatedly used several times in oligomerization process of ethylene for production of both α -olefins and polyethylene oil fractions [18]. It was determined that the MWD of oligomer product and the catalytic activity of MC1 and MC5 zirconium complexes used in recycling oligomerization of ethylene have been slightly changed (Table 2). Thus, the amount of C₄ increased from 15.8% to 18.4% in 3 cycle oligomerization of ethylene in the presence of MC1 zirconium complex, but any change in the distribution of C₆–C₁₀ oligomers were not observed.

The optical density of the absorption bands belong to olefins obtained in the presence of MC1 zirconium complex which used in recycling ethylene oligomerization were given in Table 3.

Table 2. The results of the recycling ethylene oligomerization process in the presence of complex catalytic systems consisting of MC1 and MC5 zirconium complexes and $(C_2H_5)_2AlCl$ (reaction condition: 0.42 mmol MC1 and MC5, reaction time – 30 min, Zr:Al=1:35, ethylene pressure – 2.5 Mpa, solvent – 50 ml toluene)

Zirconium complexes	Activity of catalyst g oligomer / g Zr h ⁻¹	Distribution of the oligomer product, %					
		C ₄	C ₆	C ₈	C ₁₀	C ₁₂ -C ₁₈	C ₂₀₊
MC1	1438	15.8	27.5	25.8	16.2	15.3	–
MC1	1386	17.1	26.8	24.8	17.1	14.2	–
MC1	1312	18.4	28.2	24.6	16.5	12.3	–
MC5	2177	6.8	29.2	26.1	25.2	12.7	–
MC5	2100	8.9	28.6	25.8	24.7	12	–
MC5	2065	11	28.2	25.2	23.9	11.7	–

Table 3. The optical density of the absorption bands related to olefins obtained in the presence of MC1 zirconium complex in recycling ethylene oligomerization (reaction condition: 0.42 mmol zirconium complex, time-30 min, molar ratio of Zr:Al=1:35, ethylene pressure 2.5 MPa, solvent-50 ml toluene)

D ₈₈₆	D ₉₀₈	D ₉₆₇	D ₉₉₃	D ₁₃₈₇	D ₁₄₅₇	D ₁₆₄₁
0.032	0.048	0.006	0.020	0.027	0.054	0.022
0.024	0.055	0.002	0.030	0.050	0.055	0.032
0.018	0.061	–	0.038			0.039

As it seen from the Table 3, the composition of the obtaining oligomer product depends on ethylene recycling oligomerization process [19]. The optical density of absorption band related to vinylidenes obtained in the third cycling oligomerization reduced prior to 0.018 ($D_{886}=0.018$) while the optical density of absorption band of deformation vibration of C–H bond corresponding to vinylidenes groups in the oligomer product obtained in the first oligomerization cycle of ethylene is 0.032 ($D_{886}=0.032$). The optical density of absorption bands related to internal olefins (967 cm^{-1}) obtained in the presence of MC1 zirconium complex is $D_{967}=0.006$, but the signal corresponding to the appropriate absorption band in the third cycle oligomerization of ethylene are not observed. However, optical density of absorption bands belong to deformation vibration

of 908 and 993 cm^{-1} vinyl groups of α -olefins obtaining in the presence of MC1 zirconium complex in recycling oligomerization of ethylene increased from $D_{908}=0.048$ to $D_{908}=0.061$ and from $D_{993}=0.020$ to $D_{993}=0.038$ respectively. As shown in Table 2 there was an increase in optical density of absorption band related to 1641 cm^{-1} valence vibration of C–C bond of vinyl groups of α -olefins from $D_{1641}=0.022$ to $D_{1641}=0.039$.

Oligomerization of ethylene to poly-ethylene oil fraction

The process oligomerization of ethylene in the presence of complex catalytic systems consisting of synthesized zirconium complexes and $C_2H_5AlCl_2$ as cocatalyst, in different hydrocarbon solvents and adding π -electronodonor modifiers was studied and obtained results were given in Table 4.

Table 4. The oligomerization of ethylene in the presence of heterogenized zirconium complexes, $C_2H_5AlCl_2$, and various modifiers (temperature – 90°C , solvent – 50 ml, time – 5 h, pressure of ethylene – 2.5MPa).

MC	Al:Zr:M molar ratio	Activity, g oligomer/g Zr h ⁻¹	Composition of product, mass %		Kinematic viscosity, mm/s ⁻¹		IV	Freeze point °C	Flash point °C
			<350°C	>350°C	40°C	100°C			
MC1	25:1:0	378	37.8	62.2	83.36	8.70	68	-20	205
MC1	25:1:0	450	49.2	50.8	–	–	–	–	–
MC1 ^a	25:1:5	305	24.4	75.6	754.2	38.5	86	-10	–
MC1 ^b	25:1:1	428	27.6	72.4	88.38	9.92	90	-20	210
MC1 ^b	25:1:2	400	22.8	77.2	198.8	25.2	94	-25	215
MC2	30:1:0	354	47.4	52.6	78.62	8.25	62	-24	198
MC2	30:1:0	502	51.2	48.8	–	–	–	–	–
MC2 ^a	25:1:5	309	29.6	70.4	682.4	30.6	82	-20	210
MC3	25:1:0	385	43.0	57.0	240.3	16.5	64	-18	195
MC3 ^a	25:1:5	256	30.5	69.5	306.2	26.2	84	-25	203
MC4	25:1	1250	86.0	14.0	–	–	–	–	–
MC5	28:1	1100	94.0	6.0	–	–	–	–	–

a – durene, b – 4,4-dipyridyl

As evident from the Table 4, the amount of oil fraction obtained in the presence of MC1, MC2 and MC3 zirconium complexes containing amino hydrochloride ligands is higher than 50% compared to complexes containing imino hydrochloride ligands and oxygen atom. The amount of oil fraction with boiling temperature above 350°C in the obtaining oligomer product in the presence of complexes containing iminohydrochloride ligands and oxygen atom changes within 6–14%. The influence of the modifier to the yield and the properties of oil fractions obtained in the presence of different zirconium complexes were studied (Table 3). As can be seen from the table the yield of the oil fraction boiling at higher than 350°C obtained in the presence of MC1 zirconium complex in the absence of modifier is 62.2, the kinematic viscosity 83.36 cSt at 40°C, 8.70 cSt at 100°C and index viscosity is 68. Addition of 4,4'-dipyridyl as modifier to the catalytic system at molar ratio of Zr:Al:M=1:25:1 under the same condition cause an increase the yield of the oil fraction up to 77.2%. Kinematic viscosity at 40°C and 100°C and index viscosity is 754.2 sCt, 38.5 sCt and 86 respectively.

The fraction of oligomer product boiling at 43–100°C obtained in the presence of catalytic system consisting of MC1 zirconium complex and (C₂H₅)AlCl₂ was investigated and the mass chromatogram of the separated fraction was given at Figure 4. It is seen that the obtained

oligomeric product in the presence of stronger Lewis acid as cocatalyst comprise a lot of isoolefins [20].

MWD of obtained oil fractions in the presence of complex catalytic systems consisting of MC1, MC2 and MC3 heterogenized zirconium complexes with "grafted" ionic liquid ligands were analyzed by Size Exclusion Chromatography. It was determined that oil fraction have the molecular masses within limits $M_w=423-484$, $M_n=307-390$. The obtained oil fractions have a narrow MWD and the degree of polydispersity (M_w/M_n) depend on the composition from the catalytic systems changes within 1.17–1.36.

¹H NMR spectrum of the oil fractions obtained at using MC1, MC2 and MC3 zirconium complexes are given in the Figure 5(a-c). The peaks are observed in the field with chemical shift 1.5 – 1.8 ppm refer to naphthenic protons and a weak signal 4.8–5.8 ppm indicating a small amount of vinyl and vinilydene type double bonds in the ¹H NMR-spectrum of the obtained oil fractions. The average structural parameters of obtained oil fractions were calculated according to the method [21, 22] on the basis of average molecular weights values, ¹H NMR and element analysis data. It was determined that, depending on the composition of the catalytic system, the number of carbon atoms in paraffin and naphthenic fragments changes within 16.9 to 23.6 and 4.1 to 5.9, respectively.

Fig. 4. Mass chromatogram of oligomer product boiling at 43–100°C obtained in the presence of catalytic system consisting of MC1 zirconium complex and (C₂H₅)AlCl₂.

It can be noted according to the number of the carbon atoms in the naphthenic rings there are 4 and 6 members of naphthenic rings on the composition of the obtained oil molecules. The content of terminal methyl groups changes within 7–8.5 depending on the composition of the catalyst systems. According to the researches, it can be concluded that, in the presence of catalytic systems consisting of heterogenized zirconium complexes with amino hydrochloride type "grafted" ion liquid substituents and $(C_2H_5)AlCl_2$ containing Zr in the metal-organic catalytic center hydrocarbon molecules having isostructure, containing naphthenic rings are obtained as a result of consecutive and parallel oligomerization, isomerization and cyclization reactions. Obtained oil fractions have a relatively low index viscosity because of hydrocarbon molecules containing naphthenic rings and having isostructure. A weak resonance signal in the, 1H NMR spectrum indicates oligoethylene molecules in these fractions are contained small amounts of double bonds.

To find the necessary application area for obtained polyethylene oil fractions were prepared oil compositions on the basis of these oil fractions by adding 5, 10 and 30% of dioctyl ether of alkenyl succinic acid and the viscosity properties of these compositions were studied. When adding 5 % of dioctyl ether of alkenyl succinic acid to the polyethylene oil fractions, the kinematic viscosity 11.64 sCt at 40°C, 105.47 cSt at 100°C and index viscosity is 98. The addition of 10 and 30% of dioctyl ether of alkenyl succinic acid to this fraction, index viscosity of the prepared oil fraction increased 106 and 118 unit respectively. Also, addition of dioctyl ether of alkenyl succinic acid has had a positive effect on the freeze and flash point temperatures of oil compositions [23]. Adding dioctyl ether of alkenyl succinic acid 5%, 10% and 30% over to the polyethylene oil fraction reduces freezing temperature of obtained oil fractions prior to -14, -25 and -35°C respectively (Table 5).

Fig. 5. 1H NMR spectrum of the oil fractions obtained in the presence of MC1(a) MC2(b), MC3(c).

Table 5. Viscosity-temperature properties of oil composition on the basis of dioctyl ether of alkenyl succinic acid (SD) and polyethylene oil (PO) fraction

PO:SD, %	Kinematic viscosity, mm ² /s			IV	Temperature, °C	
	100	40	-20		freezing point	fashing point
100 : 0	13.06	125.92	—	62	-12	190
0 : 100	3.28	9.22	1739.04	277	-56	218
95 : 5	11.64	105.47	19720.96	98	-14	192
90 : 10	11.03	91.32	12110.7	106	-28	196
70 : 30	7.85	52.08	4547.84	118	-35	202

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SİRKONIUM ƏSASLI HETEROGENLƏŞDİRİLMİŞ KATALİTİK SİSTEMLƏR İŞTİRAKINDA ETİLENİN OLEFİNLƏRƏ VƏ YAĞ FRAKSİYALARINA OLİQOMERLƏŞMƏSİ

M.C.Xamiyev

Etilenin oliqomerləşməsi prosesi tərkibində amino- və iminohidroxlid əvəzedicilər saxlayan ion maye tipli heterogenləşdirilmiş sirkonium kompleksləri və sokatalizator kimi alkilalüminium xloridlərdən istifadə etməklə öyrənilmişdir. Müəyyən edilmişdir ki, etilenin oliqomerləşmə məhsulu istifadə olunan sirkonium kompleksindən və alüminium üzvi birləşməsinin növündən asılı olaraq dəyişir. Sirkonium kompleksləri və sokatalizator kimi $(C_2H_5)_2AlCl_2$ iştirakında alınmış polietilen yağ fraksiyası yüksək şaxəli quruluşda olub, naften həlqələri saxlayır və aşağı özlülük indeksinə malikdir. Etilenin oliqomerləşməsi prosesində sokatalizator kimi $(C_2H_5)_2AlCl$ -dən istifadə edildikdə alınmış oliqomer məhsul Zr/Al molyar nisbətindən, reaksiya temperaturundan etilenin təzyiqindən asılı olaraq əsasən 78.8–91.6% çıxımla C_4 – C_{10} xətti quruluşlu α – olefin fraksiyasından ibarət olur. Göstərilmişdir ki, sintez olunmuş sirkonium kompleksləri həm polietilen yağ fraksiyasının, həm də xətti quruluşlu α -olefinlərin alınması üçün etilenin oliqomerləşməsi prosesində təkrar istifadə oluna bilirlər.

Açar sözlər: zirconium kompleksləri, amino- və iminohidroxlid liqandlar, etilen, oliqomerləşmə.

ОЛИГОМЕРИЗАЦИЯ ЭТИЛЕНА В ОЛЕФИНЫ И МАСЛЯНЫЕ ФРАКЦИИ В ПРИСУТСТВИИ ГЕТЕРОГЕНИЗИРОВАННЫХ КАТАЛИТИЧЕСКИХ СИСТЕМ НА ОСНОВЕ Zr

М.Д.Хамиев

Изучен процесс олигомеризации этилена с использованием гетерогенизированных фенолятных циркониевых комплексов содержащих amino- и иминогидрохлоридные заместителями ионно-жидкостного типа, с алюминийхлоридами в качестве сокатализатора. Установлено, что состав продукта олигомеризации этилена меняется в зависимости от ионно-жидкостного заместителя в циркониевых лигандах и алюминий органических соединений. Полиэтиленовая масляная фракция, полученная в присутствии циркониевых комплексов и $(C_2H_5)_2AlCl_2$ сокатализатора, имеет высокоразветвленную структуру, низкий индекс вязкости и содержит наftenовые кольца. Продукт олигомеризации, полученный с использованием $(C_2H_5)_2AlCl$ в качестве сокатализатора, состоит, в основном, из C_4 – C_{10} α -олефиновой линейной структуры с выходом 78.8–91.6 %. В зависимости от молярного соотношения Zr/Al, от температуры реакции и давления этилена меняется состав продукта реакции. Показано, что синтезированные циркониевые комплексы могут быть повторно использованы в процессе олигомеризации этилена как, для получения масляной фракции полиэтилена, так и для получения олефинов линейного строения.

Ключевые слова: циркониевые комплексы, amino- и иминогидрохлоридные лиганды, этилен, олигомеризация.