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SYNTHESIS OF ZIRCONYL NAPHTHENATES ON THE BASIS OF OIL ACIDS AND THEIR APPLYING AS COMPLEX CATALYTIC SYSTEMS IN THE PROCESS OF OLIGOMERİZATİON (POLYMERIZATION) OF ETHYLENE

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A new synthesis method of zirconyl naphthenates on the basis of the petroleum acids separated from Baku oils has been developed. It was determined that conducting the synthesis of zirconyl naphthenates in the medium of water-alcohol mixture promotes to obtaining them in pure form. The structure and composition of synthesized zirconyl naphthenates were studied by NMR, IR spectroscopy, RFA and elemental analysis. It was found that homogeneous metal complex catalysts (zirconyl naphthenates) have high catalytic activity in oligomerization and polymerization processes of ethylene.

Keywords: *zirconyl chloride octahydrate, naphthenic acids, zirconyl naphtenates, ethylene, oligomerization., polymerization.*

Introduction

Naphthenate on the basis of petroleum acids, is widely used in the wide range of areas for many purposes – as catalyst in the process of oxidation of carbohydrates, additives to oils and fuels, absorbing fluids in the textile industry, detergent production and etc. [1, 2].

Carboxylates of transition metals also are of great importance when used as components in complex catalysts in oligomerization and polymerization processes of olefins [3–6]. There are a lot of studies available on the methods of obtaining zirconyl and zirconium carboxylates from aliphatic carbon [7, 8]. However, there is very low sources of literature related to the obtaining of zirconyl naphtenates based on petroleum acids.

The presented article is devoted to developing a synthesis method of zirconyl naphthenates on the basis of petroleum acids and the investigation of structures of the synthesized complexes.

Information about activity and selectivity of the complexes with aluminum organic compounds in the process of oligomerization of ethylene is also given in the presented article.

Experimental section

Petroleum acids separated from Baku oil at 130–160^{0}C, 160–180^{0}C and 180–200^{0}C temperatures (at 2–3 mm Hg) were used for the synthesis of zirconium naphtenates (SN). The physico-chemical parameters of the separated acid are given in the Table 1.

Zirconyl chloride ($ZrOCl_2{\cdot}8H_2O$) was purchased from Ukraine (Dneprodjerjinsk) plant and used as a powder without primary purification. $ZrOCl_2{\cdot}8H_2O$ contains 0.005% of iron, 0.15% Si and 32% zirconium.

Synthesis of zyrconyl naphtenates from separated petroleum acids were provided according to the common scheme below:

$$ZrOCl_2{\cdot}8H_2O + nRCOOK \rightarrow ZrO(RCOO)_nCl_m + nKCl,$$

n=1 or 2, m=0 or 1, R – radical of natural petroleum acids.

Table 1. The physico-chemical parameters of the separated acid

Boiling fractions petroleum acid at 2–3 mm Hg	Acid number N_{ac}	Molecular mas, M_r	Density, ρ_4^{20}, g/cm^3	Refractive index, n_D^{20}
130–160^{0}C	297.34	190	0.9568	1.4624
160–180^{0}C	256.06	210	0.9613	1.4722
180–200^{0}C	223.20	225	0.9625	1.4767

Potassium naphtenates were synthesized by interaction of KOH in 2 N water solution with fraction of petroleum acids. When the ratio of an alcoholic solution of zirconyl chloride and aqueous solution of potassium salts of petroleum acid fraction was 1:1 mole SN4 was synthesized, and when the ratio was 1:2 mole SN1, SN2, SN3 compounds were synthesized. For this purpose, the calculated amount of ethyl alcohol solution of $ZrOCl_2{\cdot}8H_2O$ is added to a three-necked flask equipped with a mixer and dropping funnel and it is cooled in iced water bath up to $10–15^0$C. Then, with intensive mixing, to this solution an aqueous solution of potassium naphtenate droplets was added. Zirconyl naphtenate begins to sediment as white precipitates. After the finishing of adding potassium naphtenate solution, mixing process of the reaction solution continues for 1 hour. Then the precipitate is filtered off through the Buchner funnel at room temperature, separated from water and an alcohol mixture. The precipitate is washed twice with water and alcohol, dried under vacuum at a temperature of $50–60^0$C up to constant weight.

Zirconyl naphthenates which synthesized on the basis of different fractions of petroleum acids were analysed by IR- and ^{1}H NMR-spectroscopy, Differential Scanning Calorimetry (DSC), X-ray fluorescence microscopy and element analysis.

^{1}H NMR spectra were recorded on Bruker pulsing Fourier spectrometer(Germany) operating at the frequency of 300.18 MHz with the use of deuterated chloroform as a solvent.

IR spectra were recorded on the ″Bruker″ Fourier spectrometer in the range of 400–4000 cm^{-1} by the "drop" method widespread among KBr prisms.

Diffractograms of the synthesized complexes were drawn out by using an PANalytical EMPYREN X-ray diffractometer produced in the Netherlands.

DSC analysis was carried out on a Thermoelectron Q-20. Differential scanning calorimeter at a heating rate of 10^0C/min in an air or nitrogen atmosphere.

Element distribution of the synthesized zirconyl naphtenates was performed on XGT 7000 X-ray fluorescence microscope of Horiba company (Japan).

Results and Discussion

The yield of the zirconyl napthenates SN1, SN2, SN3 and SN4 syntesized with the above-mentioned method by the interaction of petroleum acid fractions boiling at $130–160^0$C, $160–180^0$C and $180–200^0$C with zirconyl choride at molar ratio of 1:2 and 1:1 are 95.7%, 89.8%, 85.2% and 92.1% respectively. According to the state of aggregation synthesized zirconyl naphthenates are solid products, they dissolve readily in organic solvents (toluene, hexane), however, they do not solve in water and alcohol. The thermal properties of the obtained zirconyl naphthenates (SN1, SN2, SN3) were examined by DSC method. It was determined that, the beginning melting temperature of these complexes is varied among $92–114^0$C. Maximum temperature of these endothermic peaks is $127–145^0$C and the finishing temperature is $140–162^0$C. Enthalpy of the process is ΔH=1.467–3.360 J/g. Thermooxidation temperature of the synthesized zirconyl naphthenates is between $194–205^0$C [9].

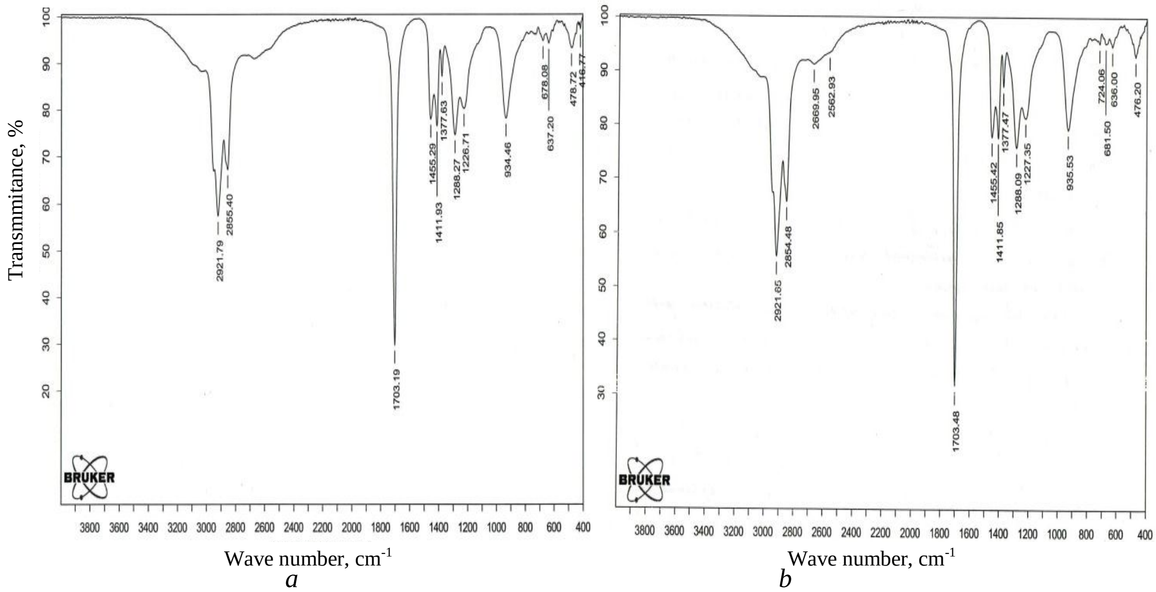
The IR spectra of the natural petroleum acid fractions boiling at 160–180 and $180–200^0$C temperatures (at 3–5 mm Hg) and the zirconyl naphthenates synthesized on the basis of these fractions are given in the Figure 1*a*, 1*b* and Figure 2 respectively. As can be seen from the IR spectra of fraction of petroleum acids absorption band at 1705 cm^{-1} corresponding to the carboxyl group in the acid fraction are observed with high intensity (Figure 1). Absorption bands given below are also observed in IR spectra of these fractions.

- Stretching vibrations at 2922 cm^{-1}, 2951 cm^{-1} and deformation vibrations at 1412 cm^{-1}, 1455 cm^{-1} of C–H bond of CH_2 groups.
- Deformation vibrations at 1377 cm^{-1} and stretching vibrations at 2856 cm^{-1} of C–H bond of CH_3 groups.
- Stretching vibrations at 960 cm^{-1} of C–H bond of CH_2 group of naphthenic ring.
- Stretching vibrations at 1226, 1288, 1703 and 2678 cm^{-1} corresponding to carboxylic group.

The intensity of absorption bands of carboxyl groups of zirconyl naphthenates SN2, SN3 and SN4 synthesized on the basis of those fraction is very low (1705 cm^{-1}). This fact proves that obtained zirconyl naphthenates contain traces of free petroleum acids.

As can be seen from Figure 2 synthesized zirconyl napthenates contain absorption bands characteristic for stretching vibrations of Zr=O and Zr–O bonds at 463 cm^{-1}, 648 cm^{-1} and 1045 cm^{-1}. Furthermore, obtained SN2, SN3 and SN4 zirconyl compounds contain the deformation and stretching vibrations according to absorption bands noted below.

- Deformation vibration at 1440 cm^{-1} and stretching vibrations at 2919 and 2949 cm^{-1} of C–H bond of CH_2 groups.



a *b*

Fig. 1. IR spectra of petroleum acid fractions boiling at 160–180^{0}C (*a*) and 180–200^{0}C (*b*).

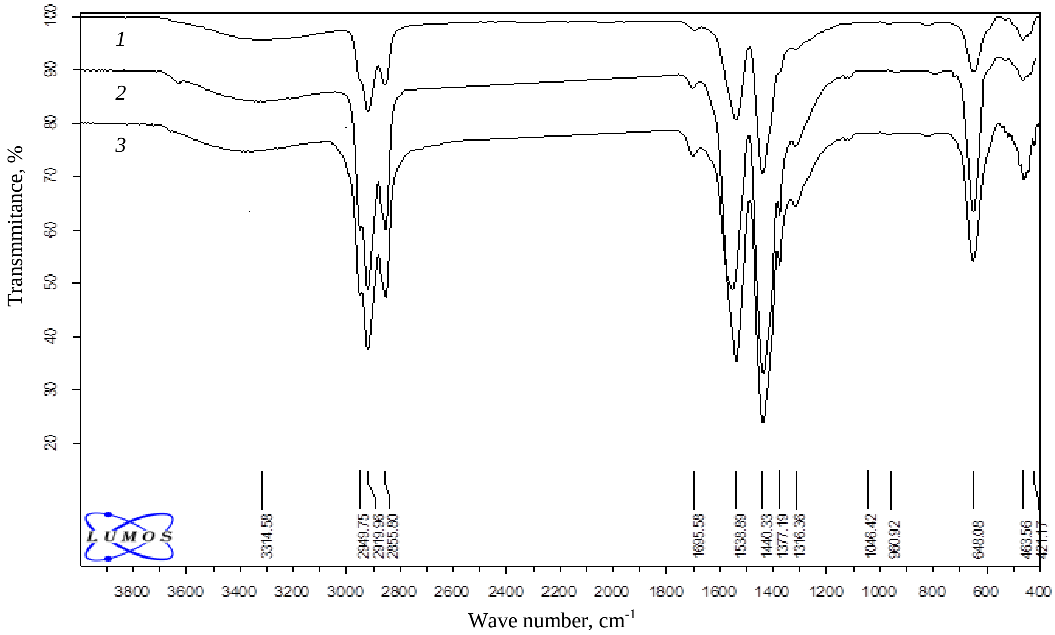


Fig. 2. IR spectra of SN2 (*1*), SN3 (*2*) zirconyl naphthenates obtained on the basis of petroleum acid fractions boiling at 160–180^{0}C, 180–200^{0}C and SN4 (*3*) zirconyl naphthenat chloride synthesized on the basis of petroleum acid boiling at 160–180^{0}C.

- Deformation vibrations at 1377 cm^{-1} and stretching vibrations at 2856 cm^{-1} of C–H bond of CH_3 groups.
- Stretching vibrations at 960 cm^{-1} of C–H bond of CH_2 group of naphthenic ring.
- Absorption bands at 1317, 1440 and 1556 cm^{-1} corresponding to COO$^-$ group.

The IR spectra of zirconyl naphthanates synthesized in water medium from petroleum acids with boiling temperature of 160–180^{0}C is given in Figure 3. It is clear that in the IR spectra of synthesized zirconyl napthtenates, the intensity of absorption bands 1705 cm^{-1} of carboxyl groups of zirconyl napthtenates which synthesized in water medium is by far higher. This proves the fact that obtained zirconyl napthtenate compounds contain free petroleum acids in its composition. Zirconyl napthtenates are solid, not soluble in alcohol and in order to purify it from acids remaining in its composition they should be washed repeatedly with alcohol. According to results of the analyses, synthesis of zirconyl napthtenates in alcohol–water medium is more advantageous than when carried in water medium [7].

^{1}H NMR spectra of synthesized zirconyl napthtenates were recorded at room temperature with the use of deutarated chloroform as solvent. ^{1}H NMR spectra of SN3 zirconyl naphthenate obtained on the basis of petroleum acid with the boiling temperature of 160–180^{0}C is given in Figure 4. As can be seen from the ^{1}H NMR spectra a chemical shift is not observed corresponding to the proton of the carboxyl group. In the ^{1}H NMR spectra of SN3 chemical shift signals are observed for 0.89 and 1.27 ppm, the methyl and methylene group protons respectively. The resonance signals in the region of 1.4–1.8 ppm refer to naphthenic protons. The resonance signals in the region of 2.05 ppm are related to the first –CH_2-group which is directly attached to carboxyl group. At the same time, chemical shift of protons of the aromatic nucleus of very low intensity were observed in the ^{1}H NMR spectra of SN2. Analogical chemical shifts of zirconium napthtenates SN1, SN3 and SN4 synthesized based on petroleum acids with boiling temperature 130–160^{0}C, 160–180^{0}C and 180–200^{0}C were observed of different intensity in the similar manner to SN2.

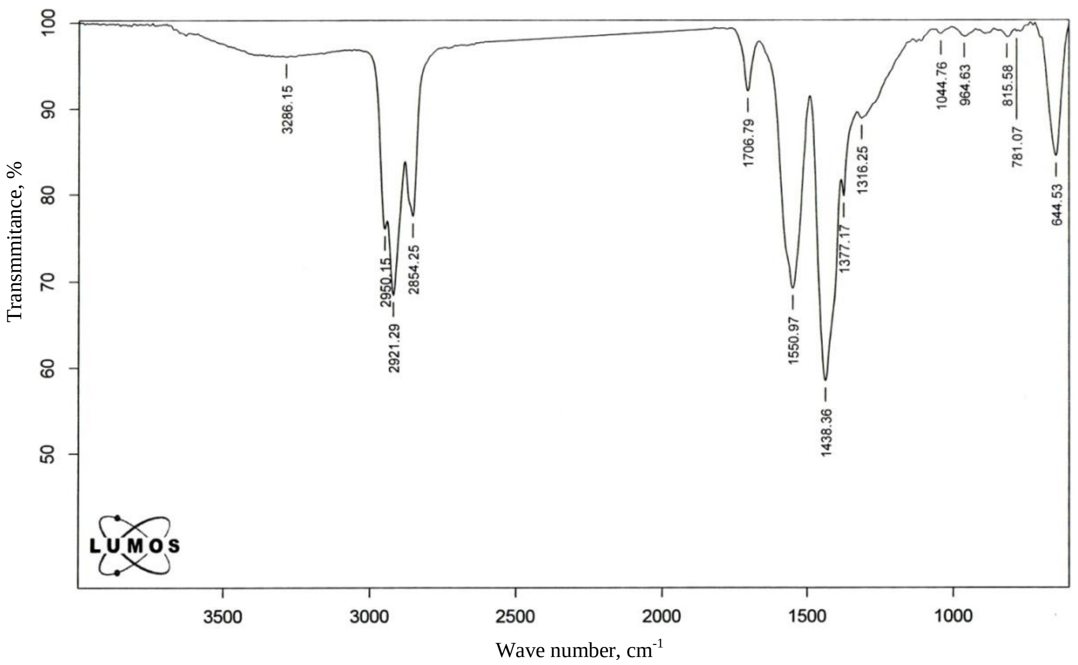


Fig. 3. IR spectra of zirconyl naphthenate synthesized on the basis of petroleum acid fraction with the boiling temperature of 160–180^{0}C in the water medium.

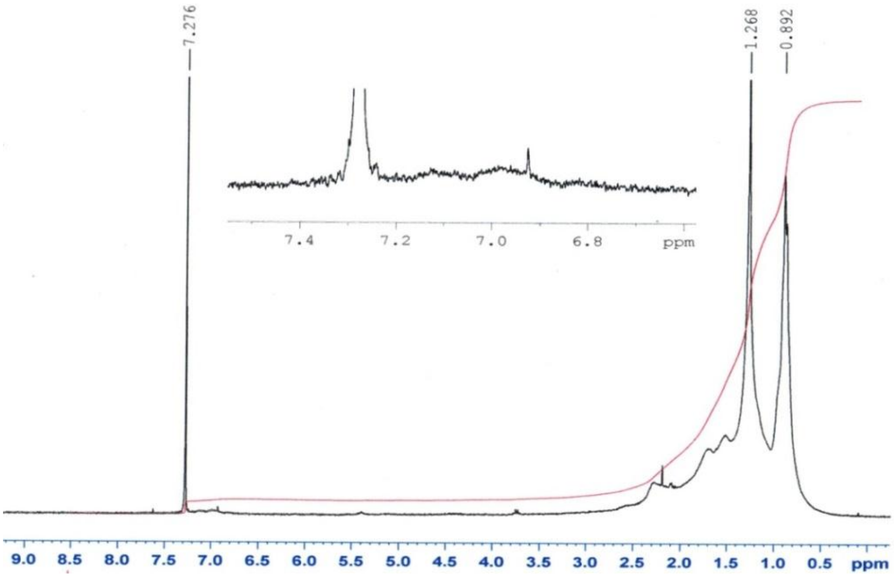


Fig. 4. ^{1}H NMR spectra of zirconyl naphthenate (SN2) obtained from petroleum acid boiling at 160–180^{0}C (at 5 mm Hg).

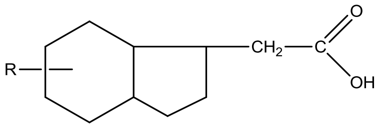
Table 2. Average structural parameters of the synthesized zirconyl naphthenates

Zirconyl naphthenate	Distribution of hydrogen atoms by structural groups, %					Aromatization degree	Isoparaffin index
	H_{Ar}	H_α	H_n	H_p	H_γ	f_a	J
SN3	0.4	8.3	24.6	35.8	30.8	0.02	0.57
SN4	1.2	11.2	20.5	37.3	29.8	0.05	0.53

H_{Ar} – amount of protons in aromatic nucleus, H_α – amount of protons on methylene groups attached to carboxyl group at α-position, H_p and H_n – contents of hydrogen atoms in the alkyl chain and naphthenic CH and CH_2 fragments respectively, Hγ – content of hydrogen atoms in the terminal methyl groups.

The average structural parameters, isoparaffin index and degree of aromatization of SN3 and SN4 zirconyl napthtenates were calculated according to the method [10] on the basis of average molecular mass values, ^{1}H NMR data and were given in Table 2. As it is clear from the table, zirconyl naphthenates gained on the basis of relatively high-boiling fractions (180–200^{0}C) contain 1.2% aromatics. The percentage of protons of napthtenic hydrocarbons decreases from 24.6% to 20.5%.

From the source in the literature [1, 11], is known that oil acids extracted from Baku oil contain, condensed bicyclic hydrocarbons consisting in cycles of 5 or 6 members are relatively more (more than 42%). Relatively light fractions contain cyclohexane carboxylic acid and its derivatives. On the basis of information obtained from IR and NMR spectroscopy analysis results about fractional composition and structural parameters of the petroleum acid (Table 2) it has been identified that besides other components, there are condensed naphthenic acids which contain 5 and 6 membered cycles with common structure below [12].



R = CH_3, C_2H_5 and etc.

X-ray analysis of synthesized zirconyl naphthenates (SN2 and SN3) is carried out and the diffractograms are given on Figure 5. According to the diffractograms of SN2 and SN3, the obtained complexes also contain amorphous segments, as well as peaks characterized by a high intensity of crystalline substance (30–35 θ). This is due to the presence of KCl in the composition of the complex as an additional product. It was found that the synthesized zirconium naphthenates are completely amorphous, as can be seen from the diffractograms recorded after the KCl is washed with water (Figure 5).

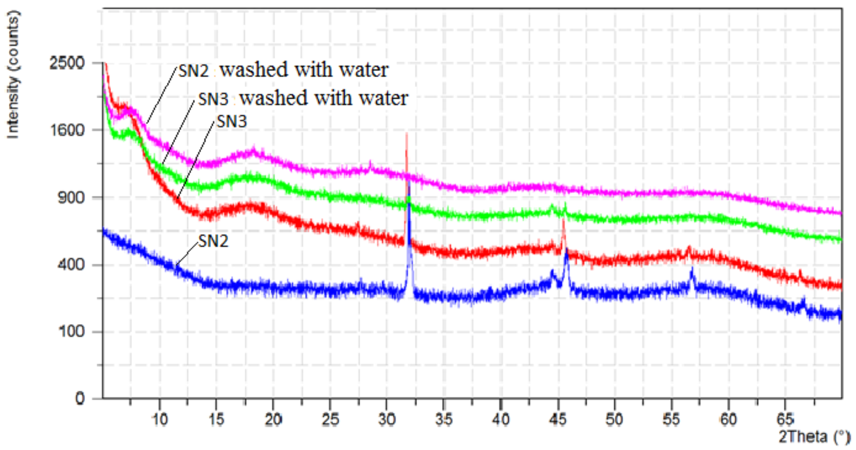
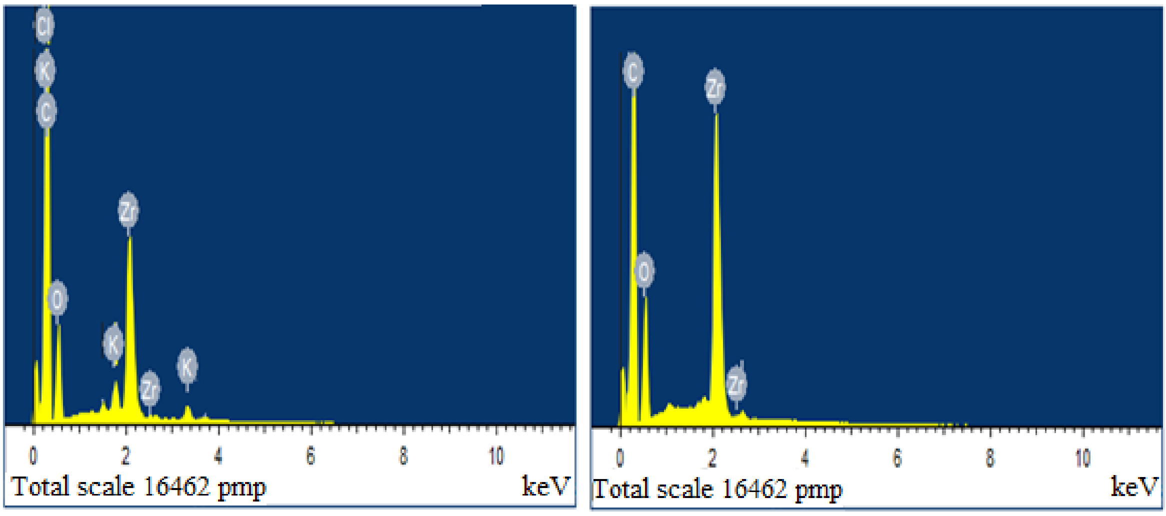


Fig. 5. Diffractograms of SN2 and SN3 zirconyl naphthenates and after washing with water of them.



a *b*

Fig. 6. X-ray fluorescence microscopic images of SN2 zirconyl naphthenate before (6*a*) and after washing its with water (6*b*).

The spectra of zirconyl naphthenates SN2 synthesized from petroleum acids with boiling temperature of 160–180^{0}C recorded on X-ray fluorosence microscope before and after washing with water and dried under vacuum are shown on Figure 6*a* and 6*b* respectively. As it can be seen from the figures after washing with water the SN2 zirconyl naphthenate, KCl containing in the composition of the complex is washed away. As seen from the X-ray fluorescence microscopy spectra of SN2 zirconyl naphthenate washed with water does not contain KCl. This is consistent with the results of X-ray analysis.

The results of investigations show that carrying out the synthesis of zirconyl naphthenates on the based petroleum acid fractions in the water-alcoholic medium permits to obtain more pure desired product. Therefore, unreacted petroleum acids are removed from the reaction medium as a solution in alcohol, and the obtained zirconyl naphthenate is pure and no additional washing steps are necessary.

The complex catalytic systems consisting of zirconyl naphthenates synthesized on the basis of petroleum acids and alkyl aluminum chlorides ($(C_2H_5)_nAlCl_{3\text{-}n}$) were tested in the oligomerization process of ethylene under the mild condition. Product of oligomerization obtained from SN2 and SN3 zirconyl naphthenate with the use of $(C_2H_5)_3Al_2Cl_3$ as a cocatalyst in the toluene medium, in the temperature range of

70–140^{0}C, under the pressure of ethylene 10–50 atm consists mainly of linear α-olefines with a number of carbons varied among C_4–C_{20+}. Increasing the temperature of the reaction from 70 to 140^{0}C in the presence of SN2 leads to the decrease of butene quantity in the oligomerization product from 63.04 to 10.7%. Therefore the percentage of C_{10}–C_{18} fractions accounts for 43.5% when this number for C_4–C_8 fractions of the product obtained in the temperature of 70^{0}C is 96.2% [13, 14]. It was determined that, it is possible to obtain both oligomers and polymers, depending on the type of aluminum organic compound used as cocatalyst in the presence of the synthesized zirconyl naphthenate.

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NEFT TURŞULARI ƏSASINDA SİRKONİL NAFTENATLARIN SİNTEZİ VƏ ONLARIN ETİLENİN OLİQOMERLƏŞMƏSİ (POLİMERLƏŞMƏSİ) PROSESİNDƏ KOMPLEKS KATALİTİK SİSTEM KİMİ TƏTBİQİ

Ə.Ə.Xanmətov, K.Ş.Hacıyeva, M.C.Xamiyev, R.V.Əliyeva, H.R.Əzizbəyli, S.F.Əhmədbəyova

Bakı neftlərindən ayrılmış neft turşuları fraksiyaları əsasında sirkonil naftenatların yeni sintez üsulu işlənib hazırlanmışdır. Müəyyən edilmişdir ki, sirkonil naftenatların sintezinin spirt-su mühitində aparılması onları qarışıqlardan təmizlənmiş halda almağa imkan verir. Sintez olunmuş sirkonil naftenatların quruluş və tərkibləri İQ- və NMR-spektroskopiya, RFA, element analizi üsulları vasitəsilə öyrənilmişdir. Sintez olunmuş sirkonil naftenatlar əsasında homogen metal kompleks katalizatorun etilenin oliqomerləşmə və polimerləşmə prosesində yüksək katalitik aktivliyə malik olduğu müəyyən edilmişdir.

Açar sözlər: *sirkonil xlorid, neft turşuları fraksiyaları, sirkonil naftenatlar, etilen, oliqomerləşmə.*

СИНТЕЗ ЦИРКОНИЛНАФТЕНАТОВ НА ОСНОВЕ НЕФТЯНЫХ КИСЛОТ И ПРИМЕНЕНИЕ ИХ В КАЧЕСТВЕ КОМПЛЕКСНЫХ КАТАЛИТИЧЕСКИХ СИСТЕМ В ПРОЦЕССЕ ОЛИГОМЕРИЗАЦИИ (ПОЛИМЕРИЗАЦИИ) ЭТИЛЕНА

А.А.Ханметов, К.Ш.Гаджиева, М.Д.Хамиев, Р.В.Алиева, Г.Р.Азизбейли, С.Ф.Ахмедбекова

Разработан новый способ синтеза нафтенатов цирконила на основе нефтяных кислот, выделенных из Бакинских нефтей. Установлено что, проведение синтеза нафтенатов цирконила в водно-спиртовой среде способствует получению их очищенными от примесей. С помощью метода ЯМР и ИК-спектроскопии, РФА и элементного анализа изучены структура и состав синтезированных нафтенатов цирконила. Установлено, что гомогенные металлкомплексные катализаторы (нафтенаты цирконила) проявляют высокую каталитическую активность в процесс АХ олигомеризации и полимеризации этилена.

Ключевые слова: *хлорид цирконила, фракции нефтяных кислот, нафтенаты цирконила, этилен, олигомеризация, полимеризация.*