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# ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

# THE SYNTHESIS OF NEW CATALYTIC COMPLEXES WITH ALUMINIUM COMPOSITION MODIFIED WITH CHROME SALT AND THE STUDY OF THE OLIGOMERIZATION PROCESS OF HEXENE-1 IN THEIR PRESENCE

Speciality: 2314.01 – Petroleum chemistry

Field of science: Chemistry

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**Baku – 2020**

The work was performed in the laboratory ""Catalytic cracking and pyrolysis" of the Y.H.Mammadaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences

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## GENERAL CHARACTERIZATION OF THE WORK

**Actuality of the topic and its application.** A demand on synthetic lubricant oils with low freezing temperature and high viscosity index is growing in the period of strict requirements to motor oils due to the rapid development of the automobile industry. It is known that oligomers obtained by oligomerization and co-oligomerization of α-olefins are valuable raw materials for obtaining synthetic polyalphaolefins oils meeting the modern requirements.

Mainly Ziegler-Natta, cation type catalysts, catalytic complexes on the bases of transition metals and aluminium chlorine organic compounds are widely used for the oligomerization processes. It is known from the reference that the metal-complex catalysts have a number of advantages in terms of selectivity and high conservation of olefins in comparison with cation-type catalysts. But as the catalysts of this type have high hygroscopy, they loose their activity as a result of the interaction even with humid of small amount in the process, as well multistep preparation process and instability of these catalysts make scientists conduct the investigations on synthesis of new catalytic systems. At the same time, low molecule mass of the obtained products influence their quality indicators negatively. In this regard, the synthesis of the catalytic systems providing significant reduction of the catalyst amount, sufficient high activity and stability requires special urgency.

The application of high-quality oils and fuels in machines and engines for operating effectively and in less harmful condition for environment is one of the important factors. In this regard, preparation of new lubricant materials that able to maintain the complex properties stable during the change in the exploitation condition are considered to be required main factors. The exploitation properties of mineral oils, especially thermo-oxidative stability do not meet the modern requirements. These oils are characterized by their low viscosity index and flash point, high freezing temperature. In this view, synthetic oils have a number of advantages in comparison with traditional petroleum oils.

These oils have low freezing point, high viscosity index, thermo-oxidative stability, operating temperature in a wide range, corrosion and hydrolysis resistance, the ability of less evaporation, the ability of easy use with densifying and thightening materials.

Even if traditionally using petroleum-based oils, high-quality additives of different purposes added, they do not often meet the steadily increasing requirements of modern technology. At present the solution for this problem is based on development of efficient synthesis methods of synthetic oils. And meantime polyalphaolefin oils obtained by polimerization of α-olefins are considered synthetic oils of better quality.

Taking these into account, presented dissertation work have been dedicated to the urgent topic as synthesis of bimetallic catalytic complex of high activity by modifying with chrome salt the catalytic complex obtained on the bases of aluminium and 1,2-dichloroethane in purpose of obtaining synthetic polyalphaolefin oils with high quality indicators and oligomerization process with hexene-1 in its presence.

**The purpose and tasks of the research.** The purpose of the presented work consists of the research of the process of bimetallic catalytic complex synthesis with higher activity in comparison with initial CTC, by the modification of aluminium- and DChE –based catalytic complex with chrome salt for obtaining of polialphaolefin oils with high quality indicators and conducting of oligomerization processes.

In accordance with target goal, the following research works have been carried out in presented dissertation:

- Obtaining of a new b,dimetallic catalytic complex by modification of aluminium- and 1,2-dichloroethane-based catalytic complex with chrome salt ($CrCl_3$) in "in situ" mode
- investigation of the nature, the structure of synthesized new bimetallic catalytic complex by different physical and chemical methods

- comparative study of regularities of the oligomerization process in the presence of CTC and CTC/ $CrCl_3$ catalytic complexes of hexene-1, defining of the effect of synthesis condition and the nature of catalytic complex on molecular-mass distribution of polyalphaolefin oils;
- the study of physical and chemical properties of olefin oils during the oligomerization of hexene-1

**Research methods.** Spectral, thermal, gas-chromatographic (EMR, DSC, DTA, SEM, RFM, RFA, DLS, NMR, IR) and other physical and chemical analysis methods have been used to define and analyze accurately the characteristics of initial components used in research work, synthesized catalytic complexes and oligomerization products.

**Main clauses presented to defense:**

- Effect of the different parameters as nature of solvent, molar ratios of initial components, temperature, reaction time on the synthesis of bimetallic catalytic complex modified with chrome salt;
- The study of the nature, composition and structure of initial and modified catalytic complex by different physical and chemical methods;
- Comparative research of the oligomerization process of hexene-1 with the presence of catalytic complexes;
- The study of regularities of the oligomerization process of hexene-1 in the presence of new bimetallic catalytic complex modified with chrome salt and physical and chemical properties of obtained oils.

**Scientific novelty of the research.** For the first time:

- new bimetallic catalytic complex has been synthesized from the modification of catalytic complex (CTC) of aluminium composition with chrome salt ($CrCl_3$) in “in situ” mode , the structure of the complexes and their elemental composition have been studied comparatively by different physical and chemical methods;
- oligomerization process of hexene-1 in the presence of synthesized catalytic complexes have been conducted, with

scientific evidences approved that the activity of CTC/$CrCl_3$ is higher than activity of CTC in optimal conditions;

- The scientific bases of the process of synthesis of synthetic oligoolefin oils in the presence of catalytic complexes have been developed, and defined that long-chain alkyl groups formed as a result of the process provide it with low freezing point (-40÷-50°C) and high viscosity index (120-135);
- Obtaining of synthetic olefin oils with high molecule mass and characterized by narrow molecular-mass distribution during the oligomerization of hexene-1 in the presence of synthesized bimetallic catalytic complex and high physical and chemical indicators of these oils have been proved.

**Theoretical and practical significance of the research.**

The synthesis of catalytic complex with bimetallic center of cluster type provides the stability of catalytic complex during the modification of synthesized aluminium-, 1,2-dichloroethane-based catalytic complex with $CrCl_3$ in "in situ" mode for oligomerization and alkylation processes and in the result it was possible to conduct oligomerization of hexene-1 with high yield.

Althought today in our republic there is a great need of PAO oils, but it was not possible to produce these oils, due to the lack of the efficient industrial catalysts. In the result of the initial laboratory tests, it has been defined that synthesized aluminium-based catalytic complexes in comparison with the cation type catalysts, have a high stable activity and therefore they can be succesfully used synthesis of synthetic oils with high indicators by the oligomerization of low- and high-molecular olefins in the industrial scale.

**Approbation and application.** 23 scientific works, including 9 articles and 14 lectures have been published on the dissertation topic. The main results of the dissertation work have been reported in the following conferences: Republican Scientific-practical conference dedicated to the 100$^{th}$ anniversary of academician S.J.Mehdiyev (Baku, 2014), Sumgait III Republican Scientific Conference on "Modern problems of chemistry of monomers and polymers" (Sumgait, 2015), Republican Scientific Conference dedicated to the 50$^{th}$ anniversary of establishing the Institute of

Chemistry of Additives (Baku, 2015), Republican Scientific Conference dedicated to the 50$^{th}$ anniversary of establishing of Sumgait Polymer Materials Institute (Sumgait, 2016), IX Baku International Mammadaliyev Conference on Petrochemistry (Baku, 2016), Republican Scientific Conference dedicated to the 80$^{th}$ anniversary of the Institute of Catalysis and Inorganic Chemistry (Baku, 2016), Republican Scientific and Technical Conference dedicated to the 90$^{th}$ anniversary of professor S.A.Sultanov (Baku, 2017), International Scientific conferences dedicated to the 91$^{st}$, 94$^{th}$, 95$^{th}$ and 96$^{th}$ anniversary of nationwide leader Heydar Aliyev (Ganja, 2014, 2017, 2018, 2019), Scientific Conference on "Naghiyev's readings" dedicated to the 100$^{th}$ anniversary of academician M.Naghiyev (Baku-2018), The International Scientific Conference "Actual Problems of Modern Chemistry" dedicated to the 90$^{th}$ anniversary of the Academician Y.H.Mammadaliyev Institute of Petrochemical Processes (Baku - 2019), 6th International Conference on Thermophysical and Mechanical Properties of Advanced Materials and 8th Rostocker Symposium on Thermophysical Properties for Technical Thermodynamics (Turkey, Izmir, September 2019). 9 scientific articles related to the dissertation work have been published in journals "Processes of petrochemistry and oil refining", "Azerbaijan Chemical Journal", "Chemical Problems", "Journal of Advances in Chemistry", "Azerbaijan Oil Industry".

**The name of the organization in which the dissertation is implemented.** The disseration work has been conducted in the laboratory of "Catalytic cracking and pyrolysis" on scientific-research plan (Government registration №0113Az 2035) of the Institute of Petrolchemical Processes of ANAS.

**The volume and the structure of the work.** The dissertation consists of introduction, four chapters, results, 160 references, and there are 152 pages, including 29 tables and 39 figures,7 graphics.

In the introduction of the dissertation has been presented and supported the information about the urgency of the topic, the purpose of the research, scientific novelty, theoretical and practical significance.

In the first chapter, theoretical bases of oligomerization process of olefins, general information on synthesis of polyalphaolefin oils, literature materials about characteristics of olefin oils and their application areas have been commented, the oligomerization processes of olefins in the presence of different catalysts have been investigated in the literature review.

In the second cahpter, physical and chemical properties of used initial raw material, reagents have been shown, the information about conducting technique of synthesis and oligomerization process of the catalytic system, physical and chemical research methods used for analysis of the obtained products have been given.

In the third chapter – The synthesis of new bimetallic catalytic complex, the determination of its nature, physical and chemical properties from the modification of aluminium-containing catalytic complex with chrome salt ($CrCl_3$) for oligomerization of olefins have been investigated.

In the fourth chapter – The oligomerization process of hexene-1 in the presence of new bimetallic catalytic system modified with chrome salt have been investigated, the issues of the study of physical and chemical properties of obtained oil fractions and mechanism of the oligomerization process of hexene-1 have been explored.

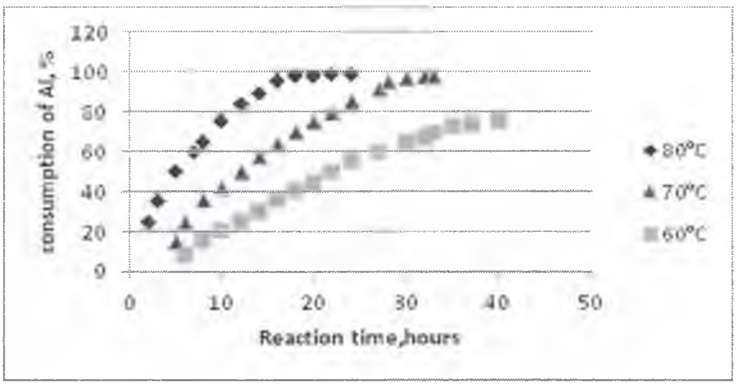
## MAIN CONTENT OF THE WORK

The research work has been conducted on synthesis of bimetallic complex with new high stable activity by modification of obtained catalytic complex on the bases of aluminium metal and $C_2H_4Cl_2$ with chrome salt in “in situ” mode, comparatively study of physical and chemical parameters of initial and modified catalytic complexes and the investigation of oligomerization process of hexene-1 with their presence.

The synthesis of catalytic complex modified with chrome salt have been implemented by adding $CrCl_3$ to the system in the period of formation of initial radicals during the interaction effect of Al and 1,2-dichloroethane in the heptane medium taken as a solvent. The effect of the different factors (reaction period, temperature, molar ratio of initial raw materials, molar ratio of Al:Cr) on synthesis of the catalytic complex have been studied [2].

The process of synthesis of the catalyst mostly depends on molar ratio of the initial components. According to the stoichiometric equation, while taking a molar ratio of aluminium and dichloroethane as Al:DChE=1:1,5, the experiments show that as metallic aluminium does not fully enter the reaction, the catalyst with maximum yield can not be obtained. The reason of this is the volatility of DChE during the process of synthesis and conducting the reaction with more complex mechanism. During the investigations it has been defined that if take molar ratio of aluminium and dichloroethane as 1:2 in the process of catalytic complex synthesis, then the catalyst with maximum yield can be obtained.

Katalizatorun sintezi prosesi ilkin komponentlərin mol During the synthesis of the catalytic complex, purification of aluminium surface from oxid layer occurs firstly, therefore aluminium does not enter the reaction. As seen from the Graphic (graphic 1), the activation period of Al surface increases while temperature decreases and its exploitation begins after 1 h. at 80°C, at 60°C it begins after 6 h. and it takes more time for fully utilization of aluminium. During the experiments have been defined that increasing the reaction period up to 20-22 h. leads to the fully utilization of Al.




Graphic 1. The graphic of the dependence of aluminium conversion on reaction period at different temperatures

The effect of molar ratio of Al:Cr on the synthesis process of bimetallic complex have been investigated and defined that a certain part of metal chloride precipitates in low molar ratios as Al:Cr=1:1÷16:1 and prevents the formation of bimetallic catalytic complex. The investigations have showed that when Al:Cr=8:1, it is possible to synthesize the catalytic complex with high yield.
If the amount of the metal chloride is less than optimal ratio (12:1, 16:1), the excess amount of aluminium-organic compounds causes the formation of bimetallic centers of low activity in the system by the reduction of the transition metal ions.

**The determination of aluminium, 1,2-dichloroethane-containing catalytix complex and physical and chemical parameters of its modification with chrome salt**

The catalytic complexes have been investigated by modern analysis methods for studying their composition and structure. The samples have been dried at 70-150°C for research of RFM, RFA, SEM, DTA, EMR analysis methods of catalytic complexes. The description (magnified 100 times) by scanning electrone microscope (SEM) and its RFA spectra of dried catalyst samples have been given in the following figure.

As seen from the Figure (figure 1), while the particles in CTC catalytic complex are in the form of large aggregates, the particles in the bimetallic complex obtained by adding to the system the chrome salt are more disperced [18].

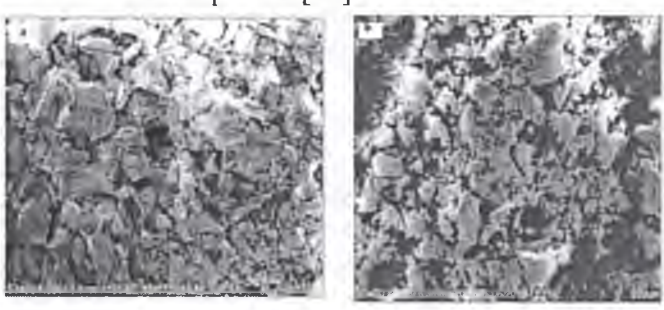


Figure 1. SEM description of the initial (a) and modified (b) catalytic complexes

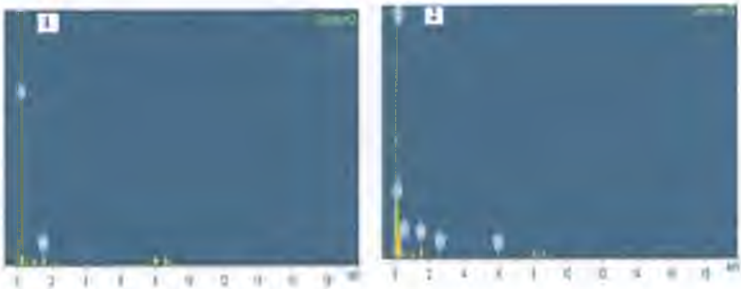


Figure 2. RFA spectra of the elemental composition of samples: 1-CTC, 2- $CTC/CrCl_3$

As seen from Figure 2, the main mass of the initial catalyst sample constitutes the elements of Al, Cl. Besides these elements, it is possible to see Cr element in the catalyst sample modified by chrome salt.

The structure of the carbon sample separated by hydrolysis and deposition from the catalytic complex have been studied by X-ray phase analysis method and the phase composition have been shown in Figure 3.

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As seen from the Figure 3 the structure of the residue separated from catalytic complex by hydrolysis and decomposition have been studied by X-ray phase analysis methods[1] and its phase composition has been shown in Figure 3. As seen from the Figure 3, in phase diagram of residue separated from CTC in angles of $2\theta$= 22.316, 24.616, 27.350, 28.778, 33.110, 35.229, 39.637, 42.911, 43.683, 44.539, 48.846, 52.790, compatible peaks to $C_{40}$-$C_{50}$ mixed carbon phases have been found, and line diagram of nanocarbon phase ($C_{40}$-$C_{50}$) with monoclinic crystal cage have been shown in the figure 4 [18].

[1]Chernorukov, N.G., Theory and Practice of X-ray Fluorescent Analysis, Electronic teaching and learning tutorial / N.G Chernorukov, O.V.. Niprukh . –Nijny Novgorod: -2012. -57 p.

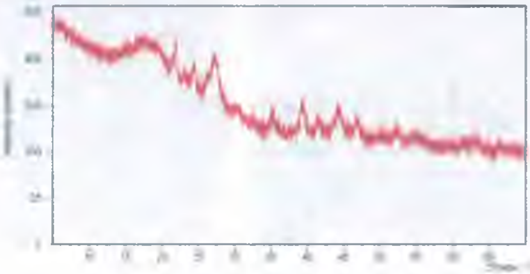


Figure 3. Phase composition of the residue obtained from the hydrolysis of the catalytic complex

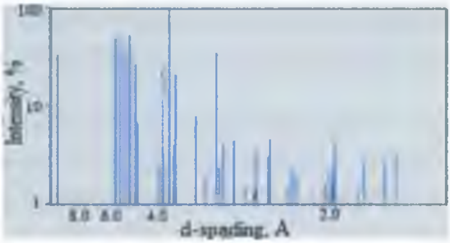



Figure 4. Line diagram of nanocarbon ($C_{40}$-$C_{50}$)

The form and structure of particles in obtained carbon sample have been studied by SEM and have been described in Figure 5.

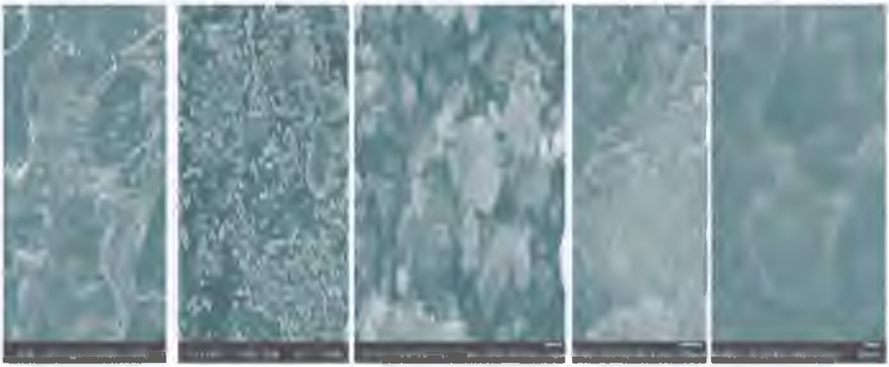


Figure 5. Microfotography of the obtained nanocarbon

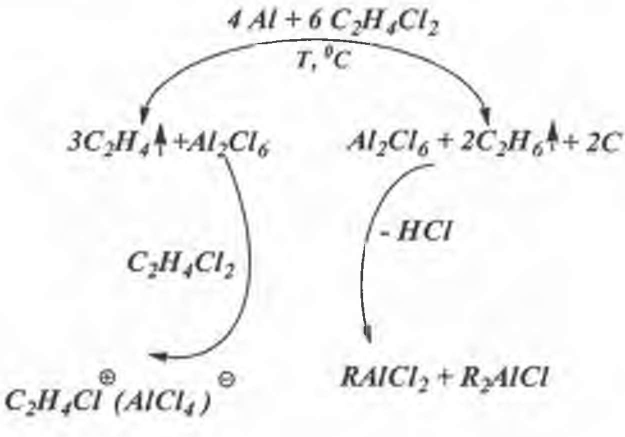
In Figure 5 the SEM description of carbon sample in consecutively 100,1000,10000,100000, 500000 times magnified size have been presented. As seen from the description, obtained carbon particles consist of porous structured tubes and the formation of defect structures in the porous structure and nanotubes formed as a result of aggregation are observed.

The existence of the carbon particles in CTC and its modificate and the formation of Al-metal-C interactions have been studied by Electro Magnetic Resonance (EMR) spectroscopy. It has been determined, that 2 types of signals are observed on the EMR spectra of the studied samples: wide and narrow. The width of spectral line is observed in each of narrow signal samples with $\Delta B=1.1\text{-}1.2$ mT and g= 2.003. But change in magnetic coverage of the delocalized electrones characteristic for carbon is observed in bimetallic catalytic complex. An enhanced peak with the parameter of $\Delta B=59.5$ mT, g=2.006 is observed by bandwidth in spectra as a result of the interaction of the carbon with delocalized electron with chromium salt unpaired electrones. The magnetism in carbon compounds is connected to releasing of atoms from the cage by breaking of C-C bonds, formation of carbon vacancies and spin defects in the structure in the result of interaction of carbon particles with ferromagnetic metals.

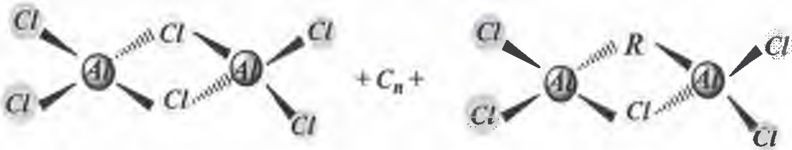
The method of Dynamic Light Scattering (DLS) allows determining the sizes of catalytic particles in the bimetallic complex obtained by the initial catalytic complex in liquid phase and its modification with chromium salt. It has been determined that CTC and its modificate with chromium salt consist of nano-dispersed clusters with the sizes in the range of 11.9-44.2 nm and 37.4-142.0 nm, correspondingly. The largeness of the particles in bimetallic complex in comparison to CTC particles proves its more activity and Thermal properties of the initial and modified bimetallic catalytic complex, effect of $Cr^{3+}$ transition metal ions on the bimetallic complex have been studied by thermogravimetric (TGA) and differencial thermogravimetric (DTA) analyses. It has been determined three-stage mass loss is occured in each of CTC and

$CTC/CrCl_3$ samples. But the processes run rapidly and relatively at low temperatures at all stages due to the effect of $Cr^{3+}$ ions on the complex structure in $CTC/CrCl_3$ sample. Reduction in carbon oxidation temperature in bimetallic catalytic complex sample reveals, that interaction of ion-coordination type bimetallic centres, obtained by addition of $Cr^{3+}$ ions to the catalytic system with carbon particles causes further increase in its defect structure.

According to the conducted researches have been defined that as a the result of interaction effect of metallic aluminium with 1,2 dichloroethane in its activating presence in heptane medium at temperature of 80-85°C the complex system is formed [10]. The occured reactions during the synthesis of catalytic complex in simplified form can be showed by the following equations. It can not be excluded that $AlCl_3$ obtained during the synthesis interacts with 1,2-dichloroethane remaining in the system and formed the complex as follows. Also by taking into consideration the separation of HCl in the synthesis of the catalytic complex and formation of alkyl radicals by decomposition of heptane molecules taken as solvent, we can say that the complex with different catalytic activity than $AlCl_3$ is formed in the system.




R - $C_2H_5$-$C_4H_9$




R - alkyl radicals.

In the synthesis process of CTC by entering chrome salt to the system in “in situ” mode in time of formation of the radicals, bimetallic complex with the complex structure is formed. As chrome is transition element, it interacts with aluminium and carbon compounds due to the half-level of d-electrone and a stable system is formed. And this is observed in formation of difference in physical and chemical properties of modified bimetallic catalytic complex in comparison with initial catalysts. Ions of the included metal salt cause the increase of catalyst intensity. It is supposed that active bimetallic catalytic centers with catalytic effect in oligomerization process have the following structure.

Oligomerization reactions of hexene-1 in the presence of synthesized catalytic complexes follow the sequence of the traditional polimerization reactions. It is supposed that the oligomerization with CTC follows the cation polimerization mechanism, with CTC/$CrCl_3$ follows the anion-coordination polimerization mechanism.

### The study of the oligomerization process of hexene-1 in the presence of initial catalytical complex and its modification with chrome salt

The oligomerization of hexene-1 in the presence of CTC and CTC/ $CrCl_3$ have comparatively been investigated and studied the effect of catalyst concentration, reaction period and temperature [17, 22]. According to the experiment it has been determined that oligomerization rate of hexene-1 directly depends on catalyst concentration. The increasing the catalyst concentration to certain extent accelerates the oligomerization of hexene-1. During the oligomerization with CTC, in reaction in 1% mas. concentration of catalyst when hexene-1 fully undergo the conversion, this concentration in the presence of CTC/$CrCl_3$ constitutes 0,5% mas. In higher concentrations of catalyst hexene-1 enter the reaction with spurt and it is impossible to regulate the process.

The effect of reaction period on oligomerization process of hexene-1 in the presence of new catalysts is studied at interval of 10-70 min. During the experiments it is turned out that during the first 10 min. T≤300°C fraction by taking advantage was 58% in oligomerization product of hexene-1 in the presence of CTC/$CrCl_3$, but when the reaction period increased up to 60 min. in oligomerization product the maximum yield of oil fraction of 300-500°C are observed. During 60 min. process stabilizes and further increase of reaction period does not affect the yield of oligomerization product. If CTC was taken as catalyst, the yield of target fraction (Fr.300-500) is relatively low in an interval of proper reaction period in all cases in comparison with the bimetallic complex.

The effect of the temperature on oligomerization process of hexene-1 in the presence of CTC and CTC/$CrCl_3$ have been investigated. According to the experimental results have been defined that increasing the temperature to certain extent provides fully oligomerization of hexene-1 by affecting positively to the process in the presence of both catalysts. It has been defined that the maximum yield of oil fraction T>300°C is observed at temperature of 50°C. Thought the yield of the purposeful oil fraction (Fr.300-500°C) obtained from oligomerization of hexene-1 in the presence of CTC is 87 %, the yield of the oil fraction obtained in the presence of CTC /$CrCl_3$ constitutes 89 % mas. At temperatures above 50°C, the yield of dimerization and trimerization products (Fr.≤300°C) of hexene-1 increases.

The influence of molar ratio of Al:Cr in bimetallic catalytic complex on the oligomerization process of hexene-1 have been studied. In the reactions conducted in different molar ratios of Al:Cr=(4-16):1 by taking the catalyst concentration of 0.5 % mas., temperature of 50°C, the reaction period of 60 min., have been defined that the bimetallic catalytic complex in molar ratio of Al:Cr=8:1 shows high activity in the oligomerization process of hexene-1 (Table 1).

Table 1.

The influence of molar ratio of Al:Cr on the oligomerization process of hexene-1 (The catalyst concentration: CTC – 1% mas., CTC/$CrCl_3$ – 0.5 % mas., temperature – 50°C, the reaction period – 60 min.)

| Catalyst | Molar ratio of Al:Cr | Yield of oil fractions, % mas. | | | |
|---|---|---|---|---|---|
| | | 300-350°C | 350-400°C | 400-450°C | 450-500°C |
| CTC | - | 22 | 30 | 25 | 10 |
| CTC/$CrCl_3$ | 4:1 | 12 | 19.6 | 31.8 | 12 |
| | 8:1 | 10 | 17 | 44 | 18 |
| | 12:1 | 12 | 16 | 41 | 16.9 |
| | 16:1 | 20 | 30.6 | 25.8 | 11.2 |

As seen from the Table, oligomerization degree of hexene-1 decreases by increasing Al:Cr from (8:1) up to 16:1 in the bimetallic catalytic complex, it almost differs little from CTC in molar ratio of 16:1. And a decrease of conversion degree in the oligomerization process of hexene-1 in lower molar ratios (4:1) of the components have been observed. According to the obtained results, it can be considered that the amount of metal salt taken in the bimetallic complex synthesized in molar ratio of Al:Cr=16:1 is not sufficient for complete formation of bimetallic centers. But decreasing the oligomerization degree of hexene-1 in the presence of the bimetallic complex in molar ratio of Al:Cr=4:1 can be explained by negative influence of an excess amount of $CrCl_3$ remaining in the form of mechanical mixture in the composition of the complex on the process.

According to the conducted experiments, an optimal condition for oligomerization process of hexene-1 in the presence of the bimetallic catalytic complex has been defined as: the reaction period – 60 min., the catalyst concentration – 0.5 % mas., molar ratio of Al:Cr=8:1of the components, temperature – 50°C. But the condition of oligomerization process of hexene-1 in the presence of CTC is as the reaction period – 60 min., the catalyst concentration – 1 % mas., temperature – 50°C.

It has been defined that it is possible to obtain oligomers with high physical indicators from oligomerization of hexene-1 in optimal condition in the presence of CTC and CTC/$CrCl_3$ [16]. The yield and some physical properties of the oil fraction (Fr. 300-500°C) obtained from oligomerization of hexene-1 in the presence of CTC and CTC/$CrCl_3$ are given in the table.

Table 2.

The yield and indicators of the oil fraction obtained from oligomerization of hexene-1 in the presence of CTC and CTC /$CrCl_3$ (Concentration of the catalyst: CTC – 1 % mas., CTC /$CrCl_3$ - 0,5 % mas., reaction time – 60 min., temperatur of 50°C)

| Fr. 300-500°C indicators of oil fractions | Catalysts | |
|---|---|---|
| | CTC | CTC/$CrCl_3$ |
| Yield, % (for total amount of oligomerization product) | 87 | 89 |
| Viscosity, $mm^2$/sec,40°C | 21,585 | 23,611 |
| Viscosity, $mm^2$/sec, 100°C | 4,1172 | 5,488 |
| Viscosity index | 111 | 122 |
| Density,kg/$m^3$ | 833,4 | 836,6 |
| Refractive index | 1,4625 | 1,4632 |
| Iodine number, grJ/100 gr | 1,6 | 1,1 |
| Flash point, °C | 220 | 234 |
| Freezing point, °C | -43 | -48 |

As seen from the Table 2, it was possible to increase the yield of the fraction (Fr.300-500°C) obtained by oligomerization of hexene-1 by adding $CrCl_3$ to the catalytic complex on the bases of aluminium and 1,2-dichloroethane up to 89 % and improve other properties.

The composition, physical and chemical properties of oil fractions have been investigated by using modern analysis methods.

Thermal and thermo-oxidative stability of the fraction (Fr.300-500°C) obtained from oligomerization of hexene-1 in the presence of CTC and CTC/$CrCl_3$ have been studied by DSC analysis. During the analysis of DSC curves of oligohexene fractions obtained in the presence of CTC and its modificate has been known that while a change in thermal properties of obtaind oil by using CTC occurs at 174,49°C, but when oligomerization of hexene-1 is conducted in the presence of catalytic system modified with chrome, obtained oil are stable up to 193,93°C from the thermal point of view [23].

The oils obtained by CTC and CTC/$CrCl_3$ have been investigated by DTA method, and it has been known from oil fraction thermograms that if DTG curve is recorded maximum at 285°C when CTC is taken as a catalyst for oligomerization of hexene-1in the presence of CTC/$CrCl_3$, maximum of oil decomposition velocity has replaced up to 330°C in the presence of CTC/$CrCl_3$, in the result this difference have constituted 45°C. And it can be concluded that PAO oils obtained from CTC/$CrCl_3$ are more stable to the temperature effect in comparison with initial catalytic complex.

In order to study the thermo-oxidative stability of oil fraction of 300-500°C synthesized at temperatures of 40°C, 50°C, 60°C in the presence of CTC-Cr, the experiments have been conducted on GOST 11063-77 and the results are given in Table 3.

As seen from Table 3 precipitation amount in oil fractions changes a little depending on time. The amount of precipitation formed in synthesized oil fractions of 300-500°C during 40 h. at temperatures of 40°C, 50°C, 60°C constitutes 0,067 %, 0,055 %, 0,061 % accordingly. It has been defined by conducting investigations for comparing that the amount of precipitation in T-46 mineral base oil properly was 0,8 % during 10 h., 1,5 % in 20 h., 2 % in 30 h., 2,25 % in 40 h. As seen from the results, oil fractions obtained from oligomerization of hexene-1 in the presence of CTC/$CrCl_3$ show high thermostability property [23].

Table 3.

Dependance on time of precipitation formation at 200°C in oil fractions of 300-500°C obtained at various temperatures (1 - 40°C; 2 - 50°C; 3 - 60°C)

| Time,hours | Amount of sediment,%wt. | | | |
|---|---|---|---|---|
| | T-46 mineral base oil | Oil fractions obtained at different temperatures | | |
| | | 1 | 2 | 3 |
| 10 | 0,8 | 0,033 | 0,03 | 0,022 |
| 20 | 1,5 | 0,04 | 0,037 | 0,034 |
| 30 | 2,0 | 0,053 | 0,049 | 0,045 |
| 40 | 2,25 | 0,067 | 0,055 | 0,061 |

IR spectra have been drawn for the analysis of the composition of samples. During the comparative analysis of IR spectra of hexene-1 and oligomer products, it has been defined that intensity of peaks characteristic for unsaturation observed in IR spectrum of monomer has significantly decreased in oil fractions, and this indicates a small amount of double bond in oligomer products.

The oil fractions have been investigated by the method of nuclear magnetic resonance (NMR). In the Figure (figure 6) NMR $^1H$ spectra of oligohexene fraction ($t_q$= 300-500°C) obtained in the presence of CTC (a) and CTC/$CrCl_3$ (b) have been given.

The relative share of protons in structural fragments have been defined by integration of absorption strips. The results of the conducted calculations have been given in the Table 4.

As seen from the Table 4, a comparative analysis of hexene-1 and oligomer products taken as monomer have been conducted and the share of $CH_2$ (paraffin) groups in obtained oil fractions in the presence of different catalysts relatively increases 2 times, and hydrogen atoms share in olefin structures decreases from 25 % to ~ 2,6 %. Thus, proved the availability in slight amount of double bond in the composition of the obtained oil fractions according to designated structural parameters of the products obtained from oligomerization of hexene-1 in the presence of new aluminium-containing catalytic complexes by NMR method [16].

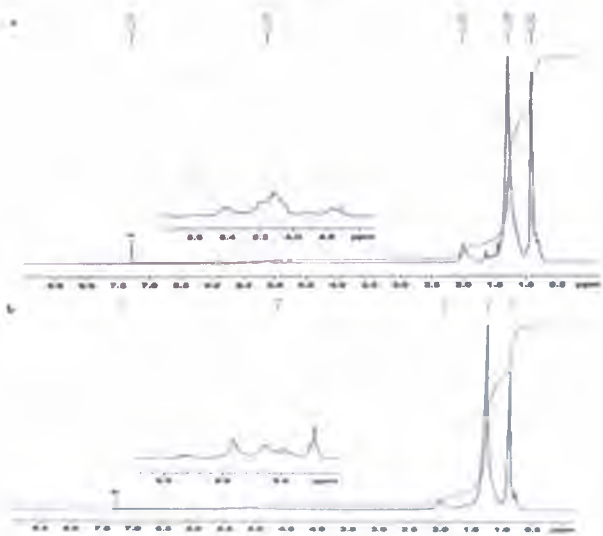


Figure 6. NMR $^{1}H$ spectra of oligohexene fraction ($t_q$= 300-500°C) obtained in the presence of CTC (a) and CTC/$CrCl_3$ (b)

Table 4.

Structural Parameters of oil fractions obtained by oligomerization of hexene

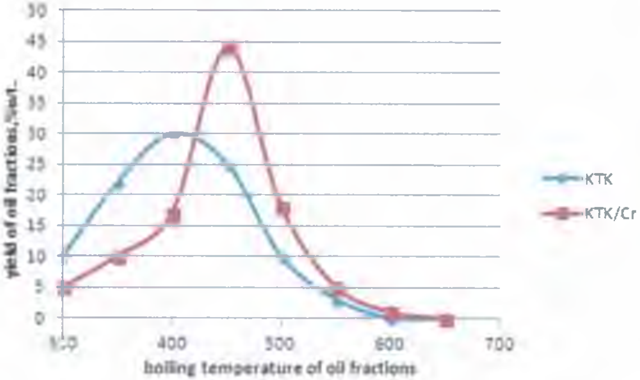
| Number of samples | Distribution of hydrogen atoms on structural groups,% | | | | | Iso-paraffin index |
|---|---|---|---|---|---|---|
| | Olefin groups | Placed near the double bond | Naphthene groups | Paraffin groups | | |
| | -CH=CH- >C=$CH_2$ >C=CH- | $CH_2$ | CH, $CH_2$ | $CH_2$ | $CH_3$ | I |
| I | 25 | 16,7 | - | 33,4 | 25,0 | - |
| II | 2,6 | 6,4 | 4,5 | 57,0 | 29,5 | 0,35 |
| III | 1,4 | 4,5 | 4,9 | 62,0 | 27,2 | 0,29 |

I – Hexene-1, II – Oil fraction 300-500°C (CTC- 1%), III– Oil fraction 300-500°C (CTC/$CrCl_3$ - 0,5 % mas.)

[2]Dormidontov, Y.P. UV, IR, NMR spectroscopy methods and their application in organic chemistry,teaching aid PSU Faculty of Chemistry / Y.P. Dormidontov – Perm: - 2001. - 79 p.

As seen from the table, a comparative analysis of hexene-1 and oligomer products taken as monomer have been conducted and the share of $CH_2$ (paraffin) groups in obtained oil fractions in the presence of different catalysts relatively increases 2 times, and hydrogen atoms share in olefin structures decreases from 25 % to ~ 2,6 %. Thus, proved the availability in slight amount of double bond in the composition of the obtained oil fractions according to designated structural parameters of the products obtained from oligomerization of hexene-1 in the presence of new aluminium-containing catalytic complexes by NMR method [16].

Molecule-mass distribution of oil fractions obtained from oligomerization of hexene-1 with CTC and CTC/$CrCl_3$ are also investigated for the yield of the fraction and the results are shown in Graphic 2. As seen in the Graph, oil fractions distribution in the narrow interval (400÷500$^0$C) in the presence of the CTC and CTC/$CrCl_3$ have been observed [11]. A change in MMD characteristics of oils synthesized in the presence of CTC and CTC/$CrCl_3$ are explained with formation of new bimetallic centers allowing the creation of relatively high-molecular oligomers having narrow MMD in the oligomerization process of CTC during the modification with chrome salt.




Graphic 2. Molecule mass distribution of oil fractions obtained from the oligomerization of hexene-1 in the presence of CTC and CTC/$CrCl_3$ catalysts

It is clear from the investigations conducted by physical and chemical analysis methods that there are signals specific to unsaturated hydrocarbons in the composition of synthetic polyalphaolefin oils obtained from the oligomerization of hexene-1 in the presence of new catalytic complexes, but as there is no aromatic hydrocarbons, these oils differs from base oils with their thermo-oxidative stability. After hydrogenation, these oils can be recommended for exploitation as motor oils.

## RESULTS

1. The synthesis of bimetallic catalytic complex of high stable activity from the modification of CTC with chrome salt has been conducted in order to intensify the oligomerization process of olefins. It has been defined that the bimetallic complex in comparison with the initial CTC in oligomerization processes of olefins (hexene-1) shows significant activity with lower concentration (0,5 % mas.) and raises the oligomerization of hexene-1 up to 99,8% mas. [2].

2. The effect of different parameters as solvent nature, molar ratios of initial components, temperature, reaction period, molar ratios of Al:Cr on the synthesis of CTC/$CrCl_3$ catalytic complex have been studied and the optimal condition for the process are defined as: reaction period – 20-22 h., temperature of 80-85, Al:Cr=8:1 molar ratios of components [13].

3.The nature, composition and structure of the initial and modified catalytic complex have been comparatively investigated by different physial and chemical methods. It has been defined that disperced nanosized clusters with Al-Me//C active bimetallic centers in the system are formed during the modification of the initial catalyst. Thus, the average sizes of the particles and their distribution for size in the system change by entering the chrome salt to the system. Due to the formation of such structure in the catalytic complex, the bimetallic complex shows high, stable catalytic activity during the oligomerization processes [8,10,12,14].

4.The oligomerization process of hexene-1 in the presence of CTC and CTC/$CrCl_3$ has been comparatively investigated, the effect of different parameters on process has been studied. The optimal condition for the oligomerization process of hexene-1 in the presence of bimetallic catalytic complex: reaction time – 60 min., concentration of the catalyst - 0,5% mas., molar ratio of the components Al:Cr=8:1, temperature of 50°C have been defined [3,9,16].

5. It has been defined that it is possible to obtain synthetic oils characterized by the yield of 89%, high viscosity index (122), with low feezing point (-48), narrow molecule-mass distribution (Mw/Mn = 1,16) during the oligomerization of hexene-1 with CTC/$CrCl_3$ and after hydrogenation these oils can be recommended for exploitation as high-quality motor oils [11,13,23].

**The results of the dissertation are reflected in the following scientific works:**


1. Ibrahimov, H.J. , Ibrahimova, Z.M., Gasımova, K.M., Kolchikova, İ.V., Gasımova, G.F., Alizadeh, Sh.A., Hasanova A.B., Alaskerova S. Synthesis of new bimetallic catalytic complexes on the bases of aluminium and transition metals // Scientific conference "Actual problems of modern biology and chemistry", dedicated to the 91st anniversary of national leader Heydar Aliyev, - Ganja: - May 12-13, - 2014, - pp.227-230.
2. Ibrahimov, H.J., Gasımova, K.M., Ibrahimova, Z.M., Kolchikova, I.V., Alizadeh, Sh.A., Alasgarova, S.M. Synthesis of catalytic complex with new aluminium composition for oligomerization process of hexene-1 // Materials of Republican Scientific-practical conference on petrochemical synthesis dedicated to the 100th anniversary of academician S.J.Mehdiyev (Baku, 2014), - Bakı: - 2-3 dekabr, - 2014, - s.173-178.
3. Ibrahimov, H.J., Alizadeh, Sh.A., Ibrahimova, Z.M., Gasımova, K.M., Hasanova, A.B. The oligomerization of hexene-1 in the presence of aluminium-containing new catalytic complex modified with chrome salt // Republican

Scientific Conference on topic of "Lubricant materials, fuels, special liquids, additive and reagents" dedicated to the 50th anniversary of establishing the Institute of Chemistry of Additives named after academician A.Guliyev, Theses of reports, - Baku: - October 13-14, - 2015, - p.91.

4. Alizadeh, Sh.A., Hasanova, A.B., Ibrahimov, H.J. The oligomerization of hexene-1 in the presence of new bimetallic catalytic complex // Ministry of Education of Azerbaijan Republic, Sumgait State University, Polymer Materials Institute of ANAS. Materials of III Republican Scientific Conference on Modern problems of chemistry of monomers and polymers, - Sumgait: - November 05-06, - 2015, - pp.45-46.
5. Ibrahimov, H.J. Perspectives for the synthesis of polyalphaolefin oils / H.J.Ibrahimov, Sh.A.Alizadeh, Z.M.Ibrahimova [et al.] // Azerbaijan National Academy of Sciences, Academician Y.H.Mammadaliyev Institute of Petrochemical Processes, Processes of Petrochemistry and Oil refining, – Baku: - 2015. №16.3(63), - pp.265-280.
6. Ibrahimov, H.J. Utilization of waste water in the treatment processes of liquid products of the pyrolysis / H.J.Ibrahimov, M.I.Rustamov, Z.M.Ibrahimova, İ.V.Kolchikova, Sh.A.Alizadeh [et al.] // Azerbaijan National Academy of Sciences, Academician Y.H.Mammadaliyev Institute of Petrochemical Processes, Processes of Petrochemistry and Oil refining, – Baku: - 2015 - №16.4(64), - pp.360-365.
7. Ibrahimov, H.J., Alizadeh, Sh.A., Gasimova, K.M., Ibrahimova, Z.M. About bimetallic catalytic complexes of aluminium composition // IX Baku International Mammadaliyev Conference on Petrochemistry, - Baku: - October 4-5, - 2016, - p.36.
8. Ibrahimov, H.J., Gasımova K.M., Ibrahimova, Z.M., Alizadeh, Sh.A., Kolchikova, I.V., Alasgarova, S.M. Investigation of bimetallic catalytic complexes of nano-sized carbon-based aluminium composition for oligomerization and polimerization processes // Materials of Republican

Scientific Conference dedicated to the 80th anniversary of the ANAS Institute of Catalysis and Inorganic Chemistry named after M.Naghiyev, - Baku: - November 15-16, - 2016, - pp.184-185.

9. Ibrahimov, H.J., Alizadeh, Sh.A.,Gasımova, K.M. The oligomerization of α-olefins in the presence of new catalytic complexes // Polymer Materials Institute of ANAS. Materials of Republican Scientific Conference on topic of "The chemistry of macromolecules, organic synthesis and composite materials" dedicated to the 50th anniversary of establishing of Polymer Materials Institute, - Sumgait: - October 20-21, - 2016, - p.85.
10. Ibrahimov, H.J., The application of nanosized carbon aluminium bimetallic catalytic complexes in the oligomerization processes / H.J. Ibrahimov, K.M.Gasımova, Z.M.Ibrahimova, Sh.A. Alizadeh [et al.] // Azerbaijan Chemical Journal, – Baku: - 2016, - № 4, - pp. 64-68.
11. Ibrahimov, H.J., Gasımova, G.F., Ibrahimova, Z.M., Alizadeh, Sh.A., Aleskerova, S.M., Bagirzade, N.R., Hashimzade, Z.F.The study of effect of the catalytic systems obtained by modification of CTC and its transition metals on the oligomerization process of hexene-1 // Ministry of Education of Azerbaijan Republic, Ganja State University. Urgent problems of modern natural and economical sciences / International Scientific conference dedicated to the 94th anniversary of nationwide leader Heydar Aliyev, Part I, - Ganja: - May 4-5, - 2017, pp.110-113
12. Ibrahimov, H.J., Gasımova, K.M., Alizadeh, Sh.A., Qasimova, G.F., Aleskerova, S.M. The synthesis and study of new bimetallic catalytic systems for oligomerization processes on the bases of transition metals, aluminium and dichloroethane // Academician Y.Mammadaliyev Institute of Petrochemical Processes of ANAS. Republican Scientific and Technical Conference dedicated to the 90th anniversary of professor S.A.Sultanov, - Baku: - October 3, - 2017, - p.19.

13. Ibragimov, H.J. Investigation the oligomerization process of hexene-1 // Journal of Advances in Chemistry/ H.J.Ibragimov, Sh.A Alizadeh., F.A. Amirov [et.al] Vol.14, - Baku: - December 2017, - No. 1 - pp.6169-6173
14. Ibrahimov, H.J., Alizadeh, Sh.A. About the synthesis and nature of aluminium-containing new catalytic complexes // Ministry of Education of Azerbaijan Republic, Ganja State University. International Scientific conference dedicated to the 95th anniversary of nationwide leader Heydar Aliyev, Urgent problems of modern natural and economical sciences, Part I, - Ganja: - May 04-05, - 2018, - pp.259-261.
15. Ibrahimov, H.J., Alizadeh, Sh.A., Guliyev, A.D., Gasimova, G.F. About the physical and chemical properties of aluminium-containing new bimetallic catalytic complex modified with chrome salt / // Institute of Catalysis and Inorganic chemistry of ANAS. Materials of the Scientific Conference "Naghiyev's readings" dedicated to the 100th anniversary of academician M.Naghiyev, - Baku: - 2018, - p.155.
16. Ibrahimov, H.J., The effect of different parameters on the oligomerization process of hexene-1 in the presence of the bimetallic catalytic complex / H.J.Ibrahimov, Sh.A.Alizadeh., F.A. Amirov [et al.] // Journal of Chemical Problems, - Baku: - 2018, - №1, - pp.86-92.
17. Ibrahimov, H.J., The study of physical and chemical properties of products obatined by oligomerization of hexene-1 / H.J. Ibrahimov, Sh.A.Alizadeh // Azerbaijan Oil Industry, - Baku: - 2018, № 9, pp.67-70.
18. İbrahimov, H.C. Investigation of aluminum-containing catalytic complex and its bimetallic catalytic complex modified by chromium salt / H.C.İbrahimov, Sh.A.Alizadeh., A.D.Guliyev [& et.al.] // Azerbaijan National Academy of Sciences, Y.H.Mammadaliyev İnstitute of Petrochemical Processes. Processes of Petrochemistry and Oil refining (PPOR) , - Baku: - 2018, Vol.19, - No4, - pp.405-410

19. Ibrahimov, H.C., Alizadeh, Sh.A. The study of oil fractions obtained from the oligomerization process of hexene-1. Ministry of Education of Azerbaijan Republic, Ganja State University / International Scientific conference dedicated to the 96$^{th}$ anniversary of nationwide leader Heydar Aliyev, Urgent problems of modern natural and economical sciences, Part I, - Ganja: - 2019, - May 03-04, Ganja-2019, pp. 213-214
20. Ibrahimov, H.J., Alizadeh, Sh.A., Akhundova, K.M., Mammadov, F.F. The study of oligomerization process of hexene-1 in the presence of aluminium-chrome-based new bimetallic catalytic complex // The İnternational Scientific Conference "Actual Problems of Modern Chemistry" Dedicated to the 90$^{th}$ anniversary of the Academician Y.N.Mammadaliyev İnstitute of Petrochemical Processes, - Baku: - 2019, - p.335.
21. Ibrahimov, H.C., Alizadeh, Sh.A., Zamanova, L.S. The study of aluminium and chrome based new bimetallic catalytic complex // 6th International Conference on Thermophysical and Mechanical Properties of Advanced Materials and 8th Rostocker Symposium on Thermophysical Properties for Technical Thermodynamics, - Izmir: - September 22-24, - 2019, - p. 66.
22. Alizadeh., Sh.A. Investigation of the oligomerization process of hexene-1 in the presence of the catalytic complex modified with chrome salt // - Baku: Chemical Problems, - 2019. №3(17), - pp.444-449.
23. Alizadeh, Sh.A. The obtaining of high thermostable synthetic oils from oligomerization of hexene-1 // - Baku: Processes of Petrochemistry and Oil refining (PPOR) , - 2019. Vol.20, No3, - pp.206-211.

The defense will be held on « 17 » march 2020 at $10^{00}$ at the meeting of the Dissertation council ED 1.16 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Y.H.Mammadaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences

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Abstract was sent to the required address on 14 february 2020

Signed for print: 12.02.2020

Paper format: A5

Volume: 36764

Number of hard copies: 20