



## **Bimetallic Aluminum Complexes Modified with Chloride Ions of Mn (II), Fe (III), and Ni (II) for Pyrocondensate Oligomerization**

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. All authors contributed in practical work and managed the analysis of the study. All authors read and approved the final manuscript.*

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### **ABSTRACT**

The oligomerization process of pyrocondensate fraction was performed in the presence of catalytic systems which were synthesized by the reaction of aluminium metal (Al) and dichloroethane (DCE) as the basic catalyst and after that were modified with metal chloride of Mn (II), Fe (III), and Ni (II) in the mode of «in situ». The synthesized bimetallic catalytic systems showing higher activity in the oligomerization process of unsaturated hydrocarbons in the pyrocondensate fraction simultaneously, allow reducing the catalyst consumption twice, increasing the molecular weight and softening temperature of the produced petroleum resins. In order to study the composition of the catalytic systems and the effect of the nature of transition metal ions on the catalytic sites of the system, they have been investigated by Dynamic light scattering (DLS), Electron paramagnetic resonance (EPR), X-ray fluorescence microscopy XRF and thermal analyses TG/DTG/DTA techniques. The results revealed that the formed carbon particles during the synthesis process have paramagnetic properties characteristic with delocalized electrons, and the coordination interaction with metal salts form dispersed clusters of  $AlCl_x-MeCl_y/C$  systems with bimetallic centers. The preservation of the activity of these catalytic systems for a

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long time is due to the nanoscale carbon particles generated in the system which play an important role as active centers.

*Keywords: Pyrocondensate; oligomerization; bimetallic catalytic complexes; nano-carbon.*

## 1. INTRODUCTION

Earlier it was known that the liquid products which formed at high-temperature in the pyrolysis process of gaseous hydrocarbons, gasolines and other heavier kinds of raw materials consist basically of aromatic, nonlimiting and limiting hydrocarbons. Liquid products of pyrolysis process (LPP) especially pyrocondensate fraction with boiling temperature of 220°C are raw materials for obtaining aromatic hydrocarbons, such as benzene and also for the synthesis process of petroleum polymer resin (PPR). It is known, that  $\text{AlCl}_3$  and its various complexes including Ziegler-Natta catalysts on the base of alkylaluminum chlorides with compounds of transition metals were used in the catalytic processing's of LPP [1,2]. Nowadays, LPP processing using catalytic complexes is developed to produce petroleum polymer resin (PPR) which are the oligomerization products of nonlimiting hydrocarbons in its structure and also produce highly pure benzen fraction. In this regard cationic catalytic complex (CTC) on the base of metal aluminium and 1,2-dichlorethane was synthesized, and showed higher stable activity in oligomerization processes in comparison with others aluminiferous catalysts [3-5]. To increase the activity of this catalyst and simultaneously improvement the qualitative characteristics of the formed PPR, bimetallic complexes were synthesized in the mode of «in situ» by modification of the initial catalyst CTC with chlorides of transition metals ( $\text{FeCl}_3$ ,  $\text{MnCl}_2$ , and  $\text{NiCl}_2$ ).

The present article discusses the catalytic, thermal and spectroscopic properties of these catalytic systems synthesized on the base of the reaction of aluminum metal with dichloroethane in liquid paraffin and its chloride modifiers of Mn (II), Fe (III), and Ni (II). The effects of temperature, reaction time, and the weight of these catalytic systems on the oligomerization process of pyrocondensate fraction were studied.

## 2. EXPERIMENTALS

### 2.1 Synthesis of the Catalytic Complexes

Catalytic complex CTC and its modified forms CTC/ $\text{MnCl}_2$ , CTC/ $\text{FeCl}_3$  and CTC/ $\text{NiCl}_2$  were synthesized by Ibragimov et al. [3] in laboratory conditions under atmospheric pressure on the base of the reaction of aluminum metal with dichloroethane in liquid paraffin as solvent in the mode of «in situ», at a certain ratio of initial components in a three-necked flask equipped with mechanical stirrer, reflux condenser and thermometer. The reaction is carried out at temperatures not exceeding 80-85°C as below 60°C it cannot activate the surface of aluminum metal, the formation of the catalytic complex is completed at 20-22 hours and synthesis of bimetallic catalytic complexes was performed at molar ratios of Al to transition metal is equal 1:1 to 16:1, and the best molar ratios of Al to transition metal is more than 8:1 to a complete consumption of Al metal and transition metal salts.

## **2.2 Characterization Techniques**

### **2.2.1 Dynamic light scattering particle size (DLS)**

Particle size and size distribution of the catalytic systems were determined by dynamic light scattering (DLS) with particle size analyzer LB550, Horiba in 1,2-dichloroethane as solvent. The samples were equilibrated in a water bath (from 25 to 70°C) for at least 1 h before the measurements. The solvent 1,2-dichloroethane (DCE) was also tempered at the measurement temperatures. To maximize the accuracy of the measurement, the samples were diluted before the DLS analysis by using the solvent mentioned above. After that the diluted test samples were pipetted in the cuvette and allowed a 3-min temperature equilibration, after which the DLS measurement was promptly started.

### **2.2.2 Electron paramagnetic resonance (EPR) analyses**

Electron paramagnetic resonance (EPR) analyses of the samples were obtained by using of JES-PE-3X «Jeol», and the operating frequency was 9.3 GHz. The values of the magnetic resonance parameters were determined by the position signal of DPPH ( $g = 2.0036$ ) and corrected by comparing the experimental values with the calculated values.

### **2.2.3 Thermal analysis (TG/DTG/DTA)**

Thermal analysis (TG/DTG/DTA) was performed on thermograph Q-1500D MOM in the temperature range 20-850°C in flowing of air. The rate of heating oven was 10°C/min, with using calcined alumina as reference sample.

### **2.2.4 X-ray fluorescence microscopy (XRF)**

X-ray fluorescence microscopy XGT-7000 Horiba (XRF) was used to determine the elemental composition and the distribution of elements in layers of the catalytic systems. Accelerating voltage of 15 kV was used in determining the Al and Cl-elements, and for the elements Mn, Fe, Ni were determined by using X-ray tube voltage of 50 kV with a diameter of the incident X-ray beam 100 microns, the measurement time was 200 sec for each sample. Before measurements, the samples were crushed to powder and pressed at pressure 20 tor/cm<sup>2</sup>.

## **2.3 Test of Catalytic Activity**

The catalytic studies of the oligomerization process were performed on the pyrocondensate fraction (EP-300 Azerbaijan) using the methodology described by Ibragimov et al., in the presence of a catalytic system CTC and its modified forms - CTC/FeCl<sub>3</sub>, CTC/NiCl<sub>2</sub>, CTC/MnCl<sub>2</sub> [3]. The reactions were carried out under atmospheric pressure at temperatures that ranged from 30 to 80°C with time interval varied from 20 to 180 minutes, and the weight of catalysts changed in 0.3-2.0% by weight. Oligomerization process of unsaturated hydrocarbons from pyrocondensate fraction under various conditions was performed in a three-necked flask equipped with mechanical stirrer, reflux system, condenser and thermometer. Analysis of the products before and after reaction was carried out in a gas liquid chromatograph (Agilent 7890A) with Flame Ionization Detector, carrier gas was nitrogen gas with velocity of 2ml/min, Zebron ZB-WAX column was used with length 30 m

and diameter 0.32 mm, and temperature mode of 40-80°C was performed with a linear heating rate of 3°C/min.

### 3. RESULTS AND DISCUSSIONS

The nature of the active sites of the synthesized catalytic systems has been studied using the methods of DLS, EPR, XRF and TG/DTG/DTA.

Figs. 1, 2 show the dependence of DLS spectra of samples on the temperature. The particle size results showed that clusters are formed in the synthesis process of the CTC by interaction of catalyst components, whose dimensions are distributed in the range of 8.7 to 66.6 nm (with an average particle size of 27.4 nm).

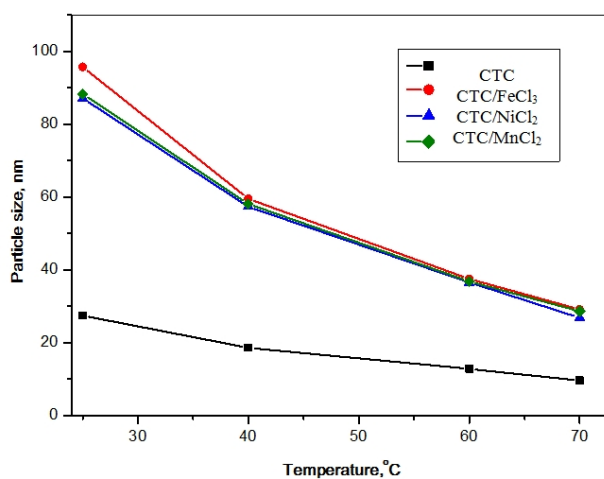


Fig. 1. Change of particle size of samples at different temperatures

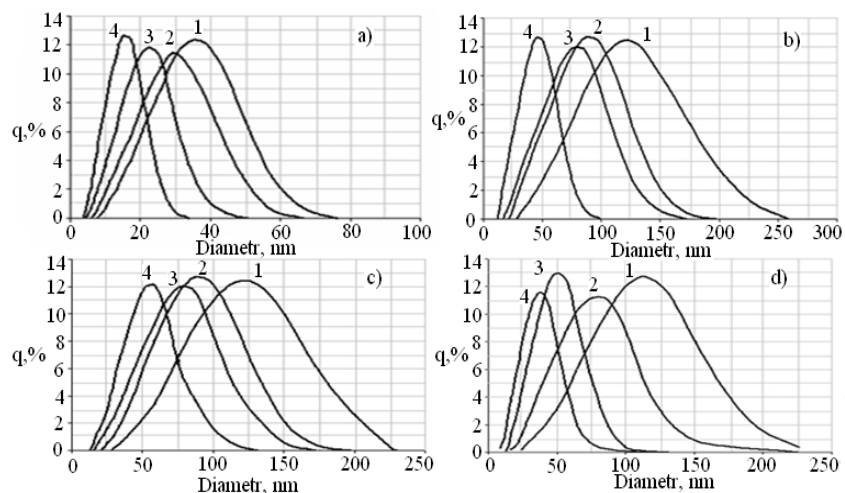
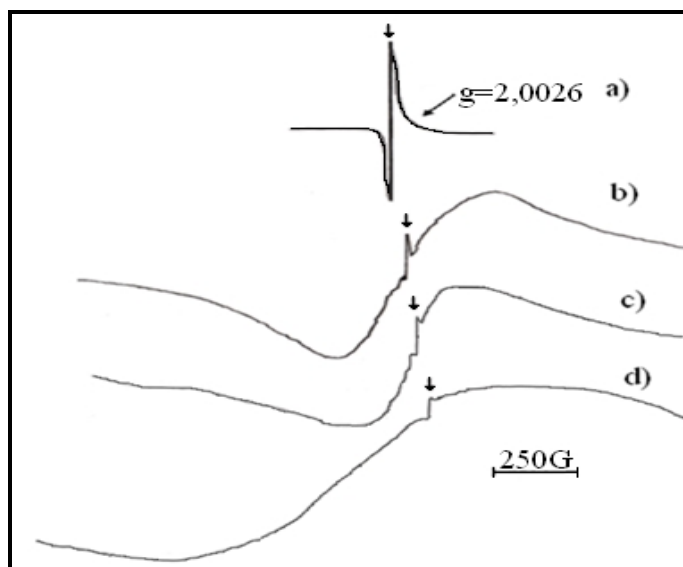


Fig. 2. DLS spectra of the catalytic samples a) CTC b) CTC/FeCl<sub>3</sub>, c) CTC/NiCl<sub>2</sub>, d) CTC/MnCl<sub>2</sub>.at different temperatures: (1) 25°C (2) 40°C (3) 60°C (4) 70°C.

Introduction of the chloride metal of Mn (II), Fe (III), and Ni (II) in the synthesis process of the CTC leads to a noticeable change in the particle size distribution in the range of 25.7 to 225.8 nm with an average particle size of 87.1 nm for CTC/NiCl<sub>2</sub>, 88.2 for CTC/MnCl<sub>2</sub> nm and 95.7 nm for CTC/FeCl<sub>3</sub>. This increase in the particle size of the modified catalytic systems can be interpreted on the fact of the formation of bimetallic centers. Measurements carried out at different temperatures showed that the increase in temperature to 70°C promotes triple reduction in the average particle size of these modified catalytic system.

Formation of carbon particles in the initial and bimetallic catalytic systems, as well as generation of the interconnection of Me-C were confirmed by analysis of the EPR. Fig. 3 shows the spectra of the samples EPR of the initial CTC and its modifications.



**Fig. 3. EPR spectra at 293 K: (a) CTC (b) CTC/MnCl<sub>2</sub> (II), (c) CTC/FeCl<sub>3</sub> (d) CTC/NiCl<sub>2</sub>**

In the EPR spectra (Fig. 3a) CTC sample showed a narrow signal with a line width  $\Delta B=1.2\text{mT}$  and  $g=2.0026$  belonging to the paramagnetic nature of the formed carbon [6-10]. The manifestation of magnetism in carbon materials due to the occurrence of carbon vacancies at the exit of the structural atomic lattice as a result of C - C bond breakage and formation of defects belonging to the backs of structures produced by the interaction of carbon particles with ferromagnetic metals. In addition, the value of g-factor of the signal belonging to carbon ratio in the EPR spectra of the sample is close to the value g-factor of the free carbon (2.0023).

The intensity and shape of the signals of carbon structures depend on the content of the metal in the catalytic samples and the experimental conditions. The width and g-factor of this signal is almost independent of temperature measurements in the range 77-563K. Bimetallic catalytic systems detected in the spectrum showed two types of EPR signals - wide and narrow signals. Narrow signal is indicated for paramagnetic properties of the formed carbon, wide signal is indicated for the magnetic clusters of transition metals (Fig. 3b, 3c, 3d)). There is also a noticeable change in the signal width of carbon in the bimetallic catalytic systems.

The effect of temperature on the intensity of the flow meter signal is described by the Curie law  $\chi \sim C/T$  which is almost typical for such systems [11-13].

Values of g - factor and the width ( $\Delta V$ ) for broad signals are listed below:

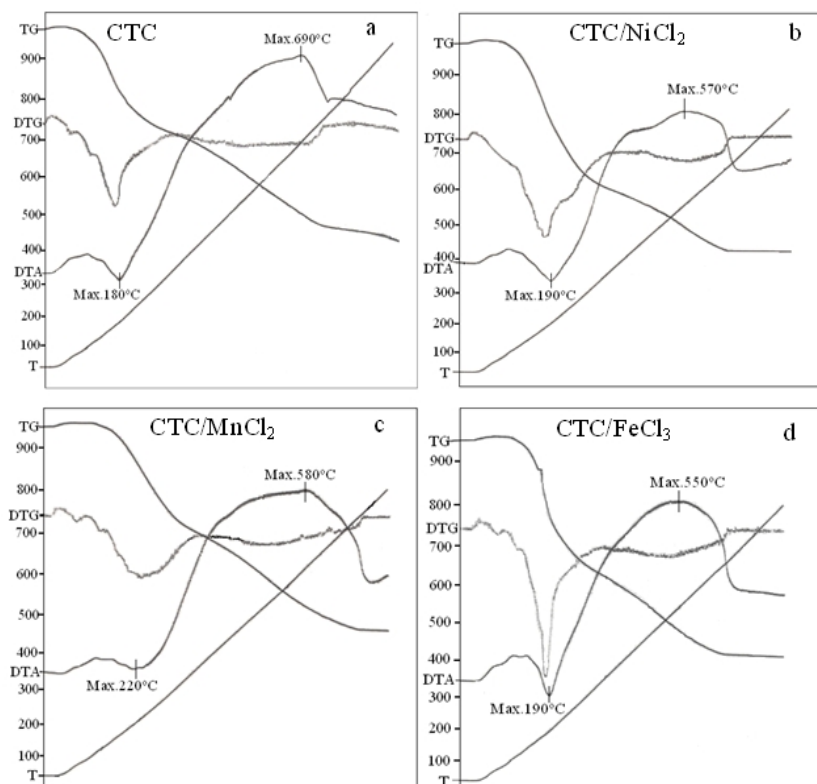
Bimetallic catalytic systems	g – factor	$\Delta V$ , mT
CTC/MnCl <sub>2</sub>	2.005	83.3
CTC/NiCl <sub>2</sub>	2.239	196.6
CTC/FeCl <sub>3</sub>	2.005	59.7

The methods of TG/DTG/DTA studied the thermal properties of the synthesized catalytic systems and the effect of Fe<sup>3+</sup>, Mn<sup>2+</sup>, and Ni<sup>2+</sup> as transition metals on the formation of carbon-based materials in these catalytic systems. Table 1 shows the thermal parameters of CTC and its modified forms. According to TG/DTG/DTA data it was observed that, the samples were evaluated in three stages in the temperature range of 20-850°C in flowing of air.

**Table 1. Thermo-physical parameters of the samples CTC and its modified forms**

Catalysts	$\Delta T_{\text{endo}}$ , °C	$T_{\text{max.}}$ , °C	$\Delta m_1$ , %	$\Delta T_{\text{exo.}}$ , °C	$T_{\text{max.}}$ , °C	$\Delta m_2$ , %	$\Sigma m$ , %	Residual mass% at 850°C
CTC	90-370	180	31.6	370-800	650	32.42	64.8	35.2
CTC/NiCl <sub>2</sub>	100-350	190	41.09	350-650	570	14.90	56.00	44.0
CTC/MnCl <sub>2</sub>	130-360	220	28.40	360-760	580	21.10	49.90	50.1
CTC/FeCl <sub>3</sub>	90-340	190	36.90	340-750	540	21.36	57.5	42.5

The first stage (up to 180-220°C) is observed for the thermal decomposition of the crystallized water molecules, The second stage (up to 340-370°C) is due to the thermal decomposition of dry solid residue CTC and its modified forms may be due to the collapse of aluminum compounds and these 3d metal complexes of organic and inorganic nature with simultaneous processes of sublimation of some compounds and the evaporation of solvent residue, accompanied by an endothermic effect (Fig. 4). The third stage of weight loss at temperatures from 350-800°C is characterized by the oxidative destruction of relatively stable catalyst components - metal chlorides and carbon particles. This stage is accompanied by oxidation of carbon nanoparticles with an exothermic effect [14-16]. At 800°C the modified chloride samples CTC and carbon particles are completely oxidized.



**Fig. 4. TG/DTG/DTA curves of the samples (a) CTC (b) CTC/NiCl<sub>2</sub> (c) CTC/MnCl<sub>2</sub> (d) CTC/FeCl<sub>3</sub>**

As discussed above, the catalyst CTC is the solid product of the reaction between aluminum metal and dichloroethane. The solid products which dried at 100°C represent a composite of inorganic salts and carbon particles. These solid residues of samples were characterized by XRF analysis as shown in Table 2.

**Table 2. Percentage of elements in the samples and their distribution over the depth at 100°C**

Samples name	Elements, wt. %						Element distribution over depth, μm		
	Al	Cl	C	Mn	Fe	Ni	Mn	Fe	Ni
CTC	8.88	35.04	56.08	-	-	-	-	-	-
CTC/MnCl <sub>2</sub>	9.37	40.51	47.36	2.76	-	-	0.123	-	-
CTC/FeCl <sub>3</sub>	6.43	47.29	43.11	-	3.17	-	-	0.124	-
CTC/NiCl <sub>2</sub>	11.81	49.90	35.53	-	-	2.76	-	-	0.885

\*C content was determined by the balance of the calcinations of the samples at 100°C.

Data Listed in Table 2 showed that, the elemental distributions of these metals in the carbon matrix are significantly different for each sample [17].

Table 3 presents the XRF data of elemental and chemical composition of the residual samples CTC, CTC/MnCl<sub>2</sub>, CTC/FeCl<sub>3</sub>, and CTC/NiCl<sub>2</sub> after TG/DTG/DTA analysis (from room temperature to 850°C). This behavior was studied by Ibrahimov et al. [17]. The distribution of the Ni element over depth at 850°C temperatures is higher than that of Mn, Fe elements and that provides the higher catalytic activity of the catalytic system of Ni (CTC/NiCl<sub>2</sub>) towards the oligomerization of pyrocondensate fraction.

As seen from Table 3, samples after thermal treatment at 850°C metal salts converted into oxides. The sample CTC is made up 99.02% of aluminum oxide and 0.98% of carbon. Introduction of 3d-metals in the catalytic CTC shifts the maximum temperature ( $T_{max}$ ) of the carbon nanoparticles oxidation at low temperature region. This indicates the fact, that Fe, Mn, and Ni metals which present in these catalytic systems are directly involved in the created nanostructured carbon particles. Reducing the maximum temperature ( $T_{max}$ ) corresponding to the oxidation of carbon particles in bimetallic systems is explained by the dispersion of carbon particles resulting from the interaction of transition metals with carbon and lead to increase in their structural defects. The higher rate of the dispersion process of carbon nanoparticles enhances the surface area of the carbon support and consequently enhances the activity of the metal centers.

Oligomerization process of pyrocondensate fraction was achieved on the catalytic complex CTC, and the modified metal salts of Fe, Mn, and Ni at different molar ratios of aluminum to metal of Fe, Mn, and Ni (Al:Me). Table 4 shows the data of the catalytic activity of the synthesized catalytic systems towards the oligomerization reaction of pyrocondensate fraction. As seen from Table 4 the conversion of unsaturated hydrocarbons from pyrocondensate oligomerization process depends on the ratio of the catalyst components and molar ratio of Al:Me = 8:1. The bimetallic catalytic complexes showed a higher activity towards oligomerization reactions compared with the original CTC. Bimetallic catalytic complex CTC/NiCl<sub>2</sub> showed higher activity in comparison with the initial CTC and other modified forms. It is assumed that, the variation of the molar ratios of aluminum and transition metal components formed bimetallic catalytic complexes with different structures, characterized by their activity, where the ratio of bimetallic complexes Al:Me = 8:1 exhibited higher activity towards the oligomerization process of pyrocondensate fractions. The higher metal halides ratio more than (8:1) ratio did not participate in the formation of the active catalytic sites and accumulated in the system as a physical mixture, and consequently have an adverse effect on the conversion of unsaturated hydrocarbons. At low concentrations of metal chlorides, an excess of alumino organic compound is formed which reduces the transition metal ions and leads to decrease the bi-metal centers. Tables 5, 6, 7 presents the results of oligomerization process of pyrocondensate in the presence of CTC and its modified forms at various reaction conditions with catalyst components ratio Al: Me = 8:1).



**Table 3. Elemental and chemical composition of samples at 850°C for 2 h in air and its thickness over layers**

Samples	Chemical composition in oxides, wt.%				Elements , wt.%					Volatile components, wt.%	Ash contents, wt.%	Thickness over layers, $\mu\text{m}$
	Al <sub>2</sub> O <sub>3</sub>	MnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	NiO	Al	Mn	Fe	Ni	C			
CTC	99.02	-	-	-	52.92	-	-	-	0.98	83.25	16.75	-
CTC/MnCl <sub>2</sub>	80.19	19.81	-	-	42.44	12.52	-	-	-	77.95	22.05	0.322
CTC/FeCl <sub>3</sub>	81.34	-	18.66	-	43.05	-	13.05	-	-	75.70	24.30	0.310
CTC/NiCl <sub>2</sub>	86.41	-	-	13.59	43.05	-	-	10.67	-	74.17	25.83	1.1991

\*C content was determined by the balance of the calcinations of the samples at 850°C.

**Table 4. The effect of catalyst components ratio (Al:Me) on the oligomerization process of pyrocondensate fraction. (catalyst concentration-0.5% wt.; temperature – 70°C, the reaction time–1 hour, the content of unsaturated hydrocarbons-32% wt.)**

CTC					
Values after treatment	The content of unsaturated hydrocarbons,% wt.	1.19			
	The dried residue ,% wt.	30.81			
	The molar ratio of the components, Al: Me	4:1	8:1	12:1	16:1

From data in Table 5 it was observed that, by increasing reaction temperature from 30 to 80°C the content of the unsaturated hydrocarbons decreases in the presence of the catalytic complex CTC, and its modifications. Furthermore the yield of the oligomerized products increased with increasing in temperature reaction, but the products have lower softening temperatures, sparingly soluble in aromatic solvents.

**Table 5. Effect of temperature on the oligomerization process of pyrocondensate fraction (weight of catalyst 0.5% wt., Reaction time - 60 min)**

Temperature, °C	The content of unsaturated hydrocarbons after treatment wt.%			
	CTC	CTC/FeCl <sub>3</sub>	CTC/MnCl <sub>2</sub>	CTC/NiCl <sub>2</sub>
30	13.30	7.45	5.96	5.0
40	10.90	5.94	4.98	3.80
50	7.67	3.94	2.78	2.20
60	3.20	1.75	0.86	0.61
70	1.19	0.54	0.43	0.30
80	0.96	0.34	0.28	0.13

**Table 6. Effect of catalyst weight on the oligomerization process of pyrocondensate fraction (reaction temperature was 70°C, reaction time - 60 min.)**

The catalyst weight, %wt.	The content of unsaturated hydrocarbons after treatment wt.%			
	CTC	CTC/FeCl <sub>3</sub>	CTC/MnCl <sub>2</sub>	CTC/NiCl <sub>2</sub>
0.3	4.80	3.57	2.51	1.43
0.5	1.19	0.54	0.43	0.30
0.7	1.0	0.29	0.13	0.04
1.0	0.5	0.16	0.08	0.02
1.5	0.2	0.15	0.08	0.01
2.0	0.18	0.14	0.06	0.00

From Table 6 it was found that, by increasing the weight of catalytic complexes in the reaction zone below a certain level has a positive effect on the output of the oligomerization process. Thus, the bimetallic catalytic system, particularly the catalytic system of CTC/NiCl<sub>2</sub> exhibits higher activity in comparison with the initial CTC. Relative increase of its concentration to 1.0% by weight promotes substantially complete conversion of unsaturated hydrocarbons in the pyrocondensate fraction.

**Table 7. Effect of reaction time on the oligomerization process of pyrocondensate fraction (the catalyst weight of 0.5 wt%, the reaction temperature was 70°C)**

Reaction time, min.	The content of unsaturated hydrocarbons after treatment wt.%			
	CTC	CTC/FeCl <sub>3</sub>	CTC/MnCl <sub>2</sub>	CTC/NiCl <sub>2</sub>
20	10.6	8.7	6.8	5.9
30	7.4	5.4	4.9	3.1
40	4.5	3.2	2.7	1.8
60	1.19	0.54	0.43	0.3
90	1.0	0.46	0.32	0.26
120	0.9	0.34	0.28	0.24
140	0.7	0.30	0.24	0.22
160	0.52	0.25	0.22	0.2
180	0.49	0.2	0.19	0.15

Analysis of products under the influence of reaction time on the oligomerization process of pyrocondensate (Table 7) shows that, the most intensive process occurs in the first 60 minutes of contacting the feedstock with the catalyst. A further increase in reaction time does not significantly affect the content of unsaturated hydrocarbons in the pyrocondensate fraction.

Bimetallic catalytic systems are not only affects the conversion of unsaturated hydrocarbons, but also the properties of the petroleum resin. Table 8 shows some parameters of PPR synthesized in the presence of CTC and bimetallic catalytic systems.

As shown in Table 8 the catalytic systems of CTC modified with transition metals enable decrease of catalyst weight from 1% to 0.5% by weight to produce higher PPR yields reach to 99.3 in case of the catalytic complex modified with NiCl<sub>2</sub>. In the processing of

pyrocondensate fraction simultaneously, it was observed an increase in the molecular weights, softening point, and reducing the polydispersity of the formed petroleum resins.

**Table 8. The effect of catalyst type on the parameters of the petroleum resins (Al: Me = 8:1 mol, temperature - 70 °C, reaction time – 1 h)**

Values after treatment	Catalytic systems				
	CTC	CTC	CTC/NiCl <sub>2</sub>	CTC/MnCl <sub>2</sub>	CTC/FeCl <sub>3</sub>
The catalyst weight, wt%.	1	0.5	0.5	0.5	0.5
PPR yield, wt%.	98.3	94.2	99.3	98.1	97.9
Molecular weight of PPR	540	700	1200	1100	1000
Softening temperature of PPR, °C	74	85	110	99	96
M <sub>w</sub> /M <sub>n</sub>	1.32	1.2	1.06	1.08	1.08
Color of PPR, mq I <sub>2</sub> /100ml	59	50	25	30	30

*M<sub>w</sub>: Weight – average molecular weight*

*M<sub>n</sub>: Number - average molecular weight*

#### 4. CONCLUSIONS

It is shown that the bimetallic catalytic systems CTC/MnCl<sub>2</sub>, CTC/FeCl<sub>3</sub>, and CTC/NiCl<sub>2</sub> in comparison with the original catalyst CTC have higher catalytic activity towards the pyrocondensate oligomerization. The catalytic activity of the studied catalytic complexes can be arranged as follow: CTC/NiCl<sub>2</sub>>CTC/MnCl<sub>2</sub>>CTC/FeCl<sub>3</sub>>CTC. DLS, EPR, XRF and TG/DTG/DTA methods established that the modification of the original catalyst of iron chloride (III), manganese (II) and nickel (II) are formed dispersed clusters AlCl<sub>x</sub>-MeCl<sub>y</sub>/C with bimetallic centers that catalyze the oligomerization process of pyrocondensate fraction. The analysis of these results of experiments allowed establishing the optimal conditions for the oligomerization process of pyrocondensate fraction in the presence of CTC and its modified forms of Mn (II), Fe (III), and Ni (II) chlorides, namely: temperature - 70°C, catalyst concentration - 0.5% wt., and reaction time - 60 minutes. Also studies showed that in the presence of new bimetallic catalytic complexes synthesized by modifying the catalytic complex CTC with transition metal chlorides, can improve the efficiency of the oligomerization process of unsaturated hydrocarbons from pyrocondensate fraction using low catalyst concentrations.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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