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Liquid-Phase Aerobic Oxidation of Petroleum Hydrocarbons in the Catalytic Presence of Nanosized Complexes

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Abstract: Liquid-phase aerobic oxidation of hydrocarbons naphthenic-paraffinic concentrate 217-349^{o}C of Azerbaijan oils blend diesel fraction in the presence of pentanuclear complexes of Cr, Co, Ni and their mixtures with Zn, Cr salts of natural petroleum acids (MeNPA) has been conducted. Dimensions of crystal structure of catalytic complexes was measured by diffractometer NONIUS CAD4 and calculated with aid of NRCVAX^{13} program. The surface of the crystals was analyzed by atomic-force (scanning probe type) microscope SZLM. There have been studied the dependence of yield of petroleum acids on the composition of the catalized. The largest yields of synthetic petroleum acids (SPA) are observed for the catalysts which was taken as mixture. The varying ratio of MeNPA:ComplexMe (Me-metal) significantly affects the performance of the process. Combined use of the catalysts leads to the synergetic effect. The most optimal ratio of catalysts is established as ZnNPA+comp.Co = 2 : 1 (0.1 + 0.05wt.%) and CrNPA+comp.Co= 2 : 1(0.1 + 0.05wt.%), with yields 22.2% and 23.4% of SPA. Along with petroleum acids the SPA contain also fatty acids of isostructure. The results obtained are recommended for realization in an industrial scale for SPA production.

Keywords: Diesel fraction, petroleum hydrocarbons, liquid-phase oxidation, catalysts of oxidation, synthetic petroleum acids

1. Introduction

Oxygen compounds of oil origin are important precursors and products of fine and heavy organic syntheses. Broad areas of natural petroleum acids (NPA) use explain the continued interest in receiving them. However, the maximum amount of NPA in petroleum does not exceed 2-3% wt. The oxidizing transformation of petroleum hydrocarbons to afford respective oxygen containing compounds is estimated as effective approach to the rational processing of oil hydrocarbons raw stock [1-4]. Synthetic petroleum acids (SPA, including oxyacids, OSPA) obtained by this type of hydrocarbons oxidation are welcomed to be full-fledged substitutes for naturally occurring petroleum acids. The chemical structure of SPA allows to produce a variety of commercially valuable derivatives so that a claim to the SPA manufacturing is an urgent issue of the present day. It is known that oxidation of naphthenic-paraffinic hydrocarbons of petroleum fractions is the most promising way of synthesis synthetic petroleum acids [5-13]. The works on creation of new selective catalysts possessing high activity for oxidation of oil fractions are continued. Thus, the synthesis of the SPA with a high-yield is of a great practical importance, and accordingly we involve a naphthenic-paraffinic

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hydrocarbons concentrate of Baku oil blend as a major research object to conduct the research work to obtain the targeted products.

This work has been devoted to the aerobic oxidation of naphthenic-paraffinic concentrate 217-349°C in the presence of five-cored complexes Cr, Co and Ni, and their mixture with Zn and Cr salts of natural petroleum acids (NPA). The aim of work-to achieve higher parameters of preparation of SPA and OSPA by special preparation of the catalysts. It should be noted that the idea to use this type of complexes as catalyst for the oxidation process belongs to the Institute of Petrochemical Processes.

2. Materials and Methods

The diesel fraction was used in the feedstock oxidation, which was previously dearomatized. It is known from the literature references that o- and p-substituted phenoles with a strong anti-oxidant properties is formed from aromatic hydrocarbons in co-oxydation process and it prevents the running of the oxydation process of naphthene-parafin hydrocarbons. In this regard it is necessary to dearomatize the diesel fraction before to oxidize. By taking into consideration that the diesel fraction (DF) mentioned below boiled in 217-349°C is purified from aromatic hydrocarbons and sulfur compounds content by extraction method and obtained positive results. As an extractant has been used the n-methyl pyrrolidon (NMP). Extraction process with NMP is realized in 4 stages. Defined that the amount of aromatic hydrocarbon in the content of fraction decreases from 16% nearly to 1 % by taking NMP:df = 3:1.

The results are presented in Table 1.

Table 1. The results of stage extraction by NMP of the diesel fraction

The number of stages	DF:NMP	Yield of raffinate, % wt	Yield of extract, % wt	Aromatic hydrocarbons,%	Amount of sulfur,%
I stage	2:1	98.3	1.7	11	0.07
II stage	2:1	89.7	10.3	6-7	0.05
III stage	2:1	83.6	16.4	3	0.04
IV stage	2:1	79.8	20.2	<1	0.03

Some physical-chemical indices of the diesel fraction before and after the extraction have been determined and presented in Table 2.

Table 2. Physical-chemical indices of the diesel fraction before and after the extraction

Indices	Diesel fraction	
	Before extraction	After extraction
Molecular weight, M_w	225	200
Density, ρ_4^{20}, kq/m^3	842	835.9
Refraction coefficient, n_D^{20}	1.4677	1.4638
Kinematic viscosity, at 20°C, mm^2/s	5.71	5.52
Freezing temperature, °C	minus 41.4	minus 51
Boiling temperature, °C	217-349	220-340
Acid number (A.n.), mqKOH/q	1.73	-
Iodine number, at100 q fuel, qJ_2	2.25	-
Amount of sulfur, % wt.	0.0936	0.03
Amount of the aromatic hydr., % wt	~17-18	1

Five-cored complexes [Cr_5(tripyridyldiamine)$_4Cl_2$], [Co_5(tripyridyldiamine)$_4Cl_2$] and [Ni_5(tripyridyldiamine)$_4Cl_2$] as well as its mixture with Zn, Cr salts of natural petroleum acids (ZnNPA, CrNPA) were employed as catalyst. The Zn and Cr salts of NPA have been synthesized from sodium salt of NPA by exchange reaction [14]. The complexes have been synthesized at Taiwan Academy of Sciences and their structures have been determined by newest physical-chemical methods [15,16]. Dimensions of crystal structure of catalytic complexes was measured by diffractometer NONIUS CAD4 and calculated with aid of NRCVAX[13] program. The chemical structure of the Ni-complex is presented in the figure 1.

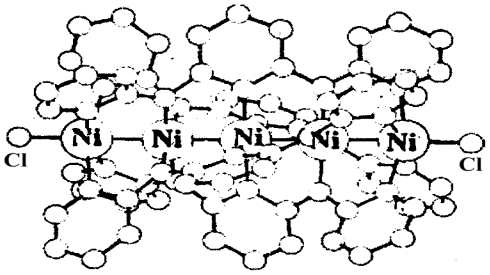
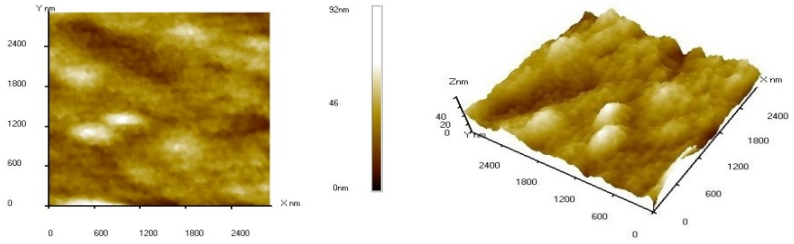


Fig 1. The chemical structure of the Ni- complex

The surface of the crystals was analyzed by atomic-force (scanning probe type) microscope SZLM. The two-dimensional (a) and three-dimensional (b) images and histogram of the crystal surfase of the Ni-complex, which was analized by atomic-force microscope, are presented in the fig. 2 and 3.



a) **b)**

Fig.2. Two- (a) and three- (b) dimensional images of the crystal surfase

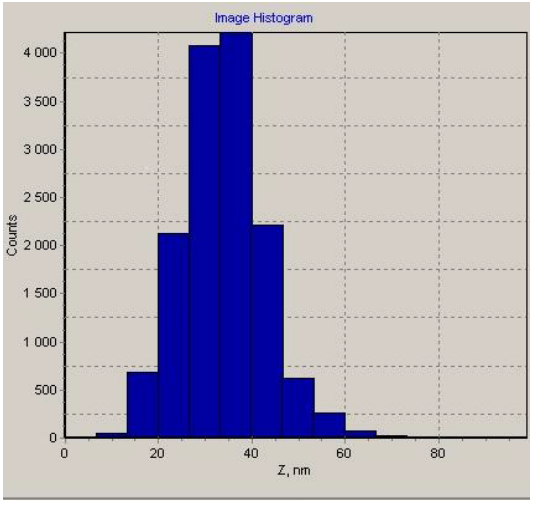


Fig. 3. Histogram of the crystal surfase of the Ni complex

As can be seen from the histogram, the uneven surface is roughly 25-45 nm. Maximum uneven, with the seat on the surface, determined by the score points labeled probe. The maximum score points over 4250. Space between the marked points on the X axis about 6.87 nm, and the Y axis - 8.98 nm during the probe movement.

The catalytic oxidation process is realized for 6 hours at temperature 135°C in a barbotage reactor. The construction of a reactor and principle of its work are presented in works [17,18]. The acid number (A.n.) of the oxidation products were determined according to the standard, conventional methods [19].

The spectra of the nuclear magnetic resonance of SPA were taken on universal NMR-spectrometer «Bruker MSL-300» with magnetic field intensity 7 Tesla (working frequency on nuclei ^{1}H-300 MHz).

3. Results and Discussion

Relevance obtaining the synthetic acids with high yield is a problem in the world, specially in Azerbaijan [20,21]. Thus, we decided to start research in this branch in our laboratory.

It has been found that the maximum results are obtained in the presence of the mixture of the catalysts. Features of the SPA and OSPA isolated from the oxidate (part of hydrocarbons converted to the oxygen containing compounds) are presented in Table 3:

Table 3. Data on aerobic oxidation of naphthenic-paraffinic hydrocarbons of the diesel fraction

Catalytic system (Ct.)	[Ct], % wt	A.N. of oxidate, mgKOH/g	SPA		OSPA	
			A.N., mgKOH/g	Yield,%	A.N., mgKOH/g	Yield,%
$Co_5(tpda)_4Cl_2$	0.1	58.8	140.5	21.5	125.5	6.4
$Ni_5(tpda)_4Cl_2$	0.1	56	125	18	120	7
$Cr_5(tpda)_4Cl_2$	0.1	41	130	15	122.5	7
ZnNPA+comp.Co	0.15(0.1+0.05)	6.,3	145.1	22.2	126.5	5.8
ZnNPA+comp.Cr	0.15(0.1+0.05)	57	132.6	19	122.3	8.8
CrNPA+comp.Co	0.15(0.1+0.05)	61	142.4	23.4	125	6.9
CrNPA+comp.Ni	0.15(0.1+0.05)	57.6	130.2	21.8	124.2	6.8

Note: It has been presented the acid number of the non-distiiled synthetic acids in the table. The acid number of the distilled synthetic acids is roughly 220-245 mgKOH/g.

According to the results of data (table 3) can conclude that, raw materials losses in the oxidation process are insignificant – a yield of oxidate is ~96-97%. The transition metals (Co^{2+}, Ni^{2+}, Cr^{3+}) in catalyst play main role in oxidation process. In the conditions of experiment of Co-complex is more active than Ni- and Cr-complexes. For example, in the presence of Co complex yield of SPA is 21.5%, where as for Ni and Cr complexes yield of SPA 18% and 15% perspectively. It happens for a reason, each Co atom in molecule produce intermediate complexes with hydroperoxides and the result catalytic activity is multiple.

As we can see in the table 3, the varying ratio of MeNPA:ComplexMe (Me-metal) significantly affects the performance of the process. With the decrease of the content of the complexes by 2 times in the catalyst systems, the yield of SPA reaches maximum. Thus the evidence of synergetic effect is available.

The NMR spectra of the obtaining SPA is presented in the figure 4.

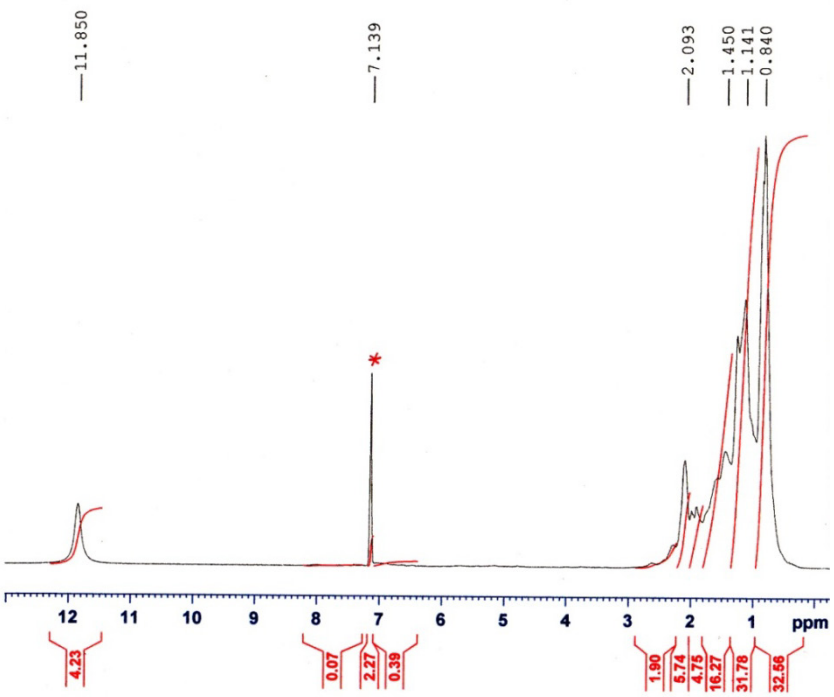


Fig.4. The NMR spectra of the obtaining SPA

In the spectra the signals corresponding to naphthene rings (1.5-1.9 ppm), and also the following: 0.9 ppm (CH_3-), 1.25 ppm (CH_2-), 11.7-11.9 ppm (-COOH) and 2.1-2.3 ppm CH_2- groups located in α- position to COOH- group are observed.

Oxidates produced in the oxidation as well as products derived from the SPA and OSPA are excellent precursors for synthesis of the actual commercially demanded reagents.

4. Conclusion

For the fist time it have been used pentanuclear complexes Co, Cr and Ni as catalyst in the oxidation process. It has been determined that it possible receive the mixture SPA and OSPA with high yield from the aerobic oxidation of naphthenic-paraffinic hydrocarbons with using these complexes. It was proved that the highest catalytic activity achieved with Co complex in oxidation process (yield of SPA 21.5% and OSPA 6.4%). The varying ratio of MeNPA:ComplexMe (Me-metal) significantly affects the performance of the process. The joint use of the catalysts at ratio of Cr NPA+comp.Co (2:1) and total content of the catalysts 0.15% mass leads to the synergetic effect and highest yield of SPA and OSPA - 30.3% in this series.

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