

UDC 547.821.411.4: 547-304.7:542.973

*T. P. MIKHAILOVSKAYA*<sup>1,\*</sup>, *R. KURMAKYZY*<sup>1</sup>,  
*D. K. TOLEMISOVA*<sup>2</sup>, *K. A. KADIRBEKOV*<sup>1</sup>

<sup>1</sup>JSC «A.B. Bekturov Institute of Chemical Sciences», Almaty, Republic of Kazakhstan,

<sup>2</sup>«Gazprom Neft-Kazakhstan» LLP, Almaty, Republic of Kazakhstan.

\*E-mail: tanya2855@mail.ru

### OXIDATIVE AMMONOLYSIS OF 4-METHYLPYRIDINE ON OXIDE VANADIUM-TITANIUM-ZIRCONIUM CATALYST MODIFIED BY TIN AND TUNGSTEN OXIDES

**Abstract.** Catalysts based on vanadium pentoxide modified by Ti, Sn, Zr and W oxides were tested in the oxidative ammonolysis of 4-methylpyridine. The role of the main process parameters such as temperature, the ratio of the initial components in the conversion of the methyl group to the nitrile one, and the optimal conditions for the oxidative ammonolysis of 4-methylpyridine were determined. It is determined that the V-Ti-Zr-O-catalyst and the sample containing 9% of tungsten oxide are superior in catalytic activity to the V-Ti-Zr-Sn-O contact. Conditions that ensure a high selectivity for the formation of 4-cyanopyridine were found. The highest yield of the target product (85-86%) was obtained on V-Ti-Zr-W-O at 270 °C, and the yield of 4-cyanopyridine was 87.5% at 310° C on the V-Ti-Zr-Sn-O catalyst.

The phase composition and structural changes occurring in modified vanadium oxide catalysts have been studied. It is determined that mixed V-Ti-Zr-Sn-O and V-Ti-Zr-W-O catalysts contain  $ZrV_2O_7$ , the monoclinic modification of  $ZrO_2$  (baddeleyite),  $TiO_2$  (anatase),  $SnO_2$ ,  $WO_3$ , and  $V_2O_5$ . In catalysts, it can exist in small amounts as a separate  $VO_2$  phase. The V-Ti-Zr-W-O catalyst showed the best catalytic properties. It has high activity and selectivity towards 4-cyanopyridine.

**Key words:** 4-methylpyridine, oxidative ammonolysis, catalysts,  $TiO_2$ ,  $SnO_2$ ,  $WO_3$ ,  $ZrO_2$ .

**Introduction.** The reaction of oxidative ammonolysis of methylpyridines is the simplest and most convenient method for the synthesis of cyanopyridines [1], which is used as intermediates for the preparation of drugs [2]. 4-cyanopyridine (isonicotinic acid nitrile) obtained by oxidative ammonolysis of 4-methylpyridine is widely used for the production of pharmaceuticals, including anti-tuberculosis drugs, such as thiazide, isoniazid, saluzidum, and others [2], which are necessary for the Republic of Kazakhstan.

Various catalysts based on metal oxides are used in the industry for the synthesis of nitriles. Individual vanadium (V) oxide exhibits high catalytic properties in the oxidative ammonolysis of methyl pyridines processes [3, 4]. Currently,

binary and multicomponent vanadium oxide systems [5], which contain additives of metal oxides [6] having a modifying effect on the properties of oxide catalysts, are used for the oxidative ammonolysis of 4-methylpyridine. Titanium and tin dioxides are used as a component of many catalysts for the oxidation and oxidative ammonolysis of organic compounds. A. Martin, B. Lücke [7] presented a review of the current state in vapor-phase oxidation, ammoxidation of substituted methyl aromatic, and heteroaromatic hydrocarbons using V-containing catalysts. Earlier mixed vanadium-titanium-tin catalysts effective in the oxidative ammonolysis of 4-methylpyridine were developed in the Bekturov Institute of Chemical Sciences [8]. These catalysts showed high catalytic activity in the reaction of oxidative ammonolysis of methylpyridines [9], making it possible to obtain nitriles of pyridine carboxylic acids with a selectivity of 90–95%. However, the process of oxidative ammonolysis of 4-methylpyridine on these catalysts proceeds with the use of significant amounts of ammonia and in the presence of a large amount of water, which complicates the process technology. Also, these contacts operate in the high-temperature range: 360 - 400 °C.

In this research [10], the W-V-O catalyst obtained by hydrothermal synthesis was tested in the oxidative ammonolysis of another isomer, 3-methylpyridine. Comparison of this contact and the  $\text{VO}_x / \text{WO}_3$  sample obtained by the impregnation method with other catalysts based on V showed that the catalysts with the addition of W showed a higher selectivity to cyanopyridine at the full conversion of the starting methylpyridine.

According to the data [11], zirconium-containing catalysts are used in the reactions of dehydration, isomerization, alkylation, and selective and complete oxidation of hydrocarbons.

Vanadium-zirconium oxide catalysts showed high selectivity in the process of oxidative ammonolysis of 3-picoline [12, 13]. We have previously shown that the oxide vanadium-titanium-zirconium catalyst exhibits high activity and selectivity in the oxidative ammonolysis of 4-methylpyridine, making it possible to obtain 4-cyanopyridine with a yield of 90-95% at a temperature of 260-270 °C and minimum consumption of ammonia [13].

The purpose of this work was to test and compare the catalytic properties of new vanadium oxide catalysts modified by additions of titanium, zirconium, tin, and tungsten oxides under the conditions of oxidative ammonolysis of 4-methylpyridine.

## EXPERIMENTAL PART

Dried and distilled 4-methylpyridine with b.p. of 141°/695 mm Hg,  $d_4^{20} = 0.9547$  and  $n_D^{20} = 1.5058$  were used in this work. The given characteristics were in accordance with the reference data.

V-Ti-Zr-Sn-O and V-Ti-Zr-W-O catalysts were prepared from vanadium (V), titanium (IV), zirconium (IV), tin (IV), and tungsten (VI) oxides. Then, by either pressing or «smearing» the moistened mass into a perforated plate, tablets were molded from the resulting mixture and sintered at a temperature of 650 °C for 2 h.

Oxidation of 4-methylpyridine was carried out in a flow-through unit with a stainless steel reaction tube of 20 mm in diameter and 1000 mm in length, into which 100 ml of a granular catalyst was loaded. Atmospheric air without special purification entered the contact apparatus from the receiver. Synthetic ammonia (liquefied gas GOST-6291-62) was introduced into the reactor from the supplied cylinders.

Unreacted 4-methylpyridine and the reaction products were trapped in water in airlift scrubbers and analyzed by gas-liquid chromatography on a Tsvet-104 chromatograph with a flame ionization detector. A glass column of 1 m long and 4 mm in diameter was filled with a 25% PEG + 2% H<sub>3</sub>PO<sub>4</sub> phase deposited on an INZ-600. The temperature of the thermostat of the column - 130 °C, evaporator - 200 °C. The pressure of the carrier gas of helium was 4.0 kgf/cm<sup>2</sup>, hydrogen was 0.068 kgf/cm<sup>2</sup>, air was 2.5 kgf/cm<sup>2</sup>. The volume of the injected sample was 5 µl. 2,4,6-collidine was used as an internal standard.

The products of deep oxidation were analyzed on an LKhM-8MD chromatograph with a thermal conductivity detector. The stainless steel columns were 3.5 m in length and 3 mm in inner diameter. The adsorbent for the determination of CO was activated carbon of the "AG-5" grade (0.25–0.50 mm), for CO<sub>2</sub> - polysorb-1 (0.16–0.20 mm). The temperature of the thermostat of the columns was 40 °C. In all experiments, the balance for the determined substances was 95–100%.

In parallel, isonicotinic acid was titrated with 0.01 N alkali against phenolphthalein.

## RESULTS AND DISCUSSION

Analysis of the literature indicates that the synthesis of 4-cyanopyridine by oxidative ammonolysis of 4-methylpyridine is carried out with high selectivity. Multicomponent compositions based on vanadium oxides, supported on different carriers, are widely used as catalysts. In the research work carried out at the Institute of Chemical Sciences named after A.B. Bekturov, titanium, tin, and zirconium oxides are widely used to modify vanadium oxide catalysts, which themselves do not possess catalytic activity in the oxidative ammonolysis reaction. Modifying additives can be considered as important components of the catalyst, since when interacting with vanadium oxides, they form solid solutions or chemical compounds. The work of the laboratory, carried out earlier and at present, has shown that the main product of the oxidative ammonolysis of 4-methylpyridine over vanadium oxide catalysts is 4-cyanopyridine. The process of oxidative ammonolysis proceeds, as a rule, at temperatures of 390–450 °C and large amounts of ammonia and water.

The purpose of this work was to search for new active catalysts for the oxidative ammonolysis of 4-methylpyridine with a sufficiently high selectivity for the target product. In this regard, vanadium-titanium-zirconium catalysts were of interest, which showed high activity and selectivity in the oxidative ammonolysis of 4-methylpyridine [14].

The aim of this work was to study the catalytic activity of new modified oxide V-Ti-Zr-O-catalysts, additionally containing tin dioxide and tungsten oxide, in the oxidative ammonolysis of 4-methylpyridine. The prototypes of the catalysts were tested in a laboratory unit in the reaction of the oxidative ammonolysis of 4-methylpyridine with a wide variation of the process parameters. The effect of the main process parameters - temperature, the ratio of the starting components on the oxidative ammonolysis of 4-methylpyridine under conditions of low  $\text{NH}_3$  concentration and without water supply was studied to assess the catalytic characteristics of these contacts.

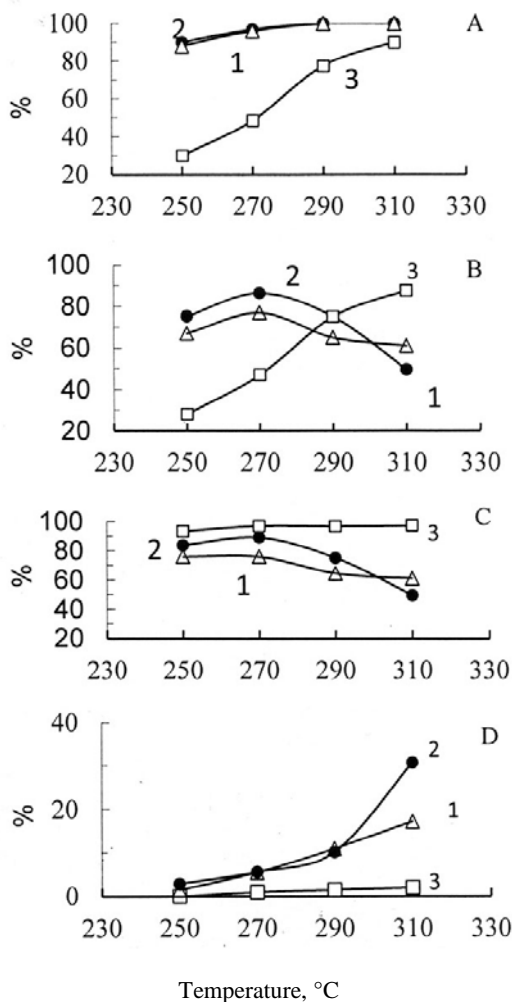
Figure under comparable conditions shows the test results of V-Ti-Zr oxide catalysts containing 9% of tungsten oxide and 9% of tin oxide, at a feed rate of the starting material - 43 g, air - 1500 l, ammonia - 22.8 l per 1 liter of catalyst per hour, which corresponds to the molar ratio of 4-methylpyridine:  $\text{O}_2$ :  $\text{NH}_3$  = 1: 30: 2.9. It can be noted that under these conditions the least active catalyst turned out to be a catalyst containing tin dioxide: the conversion of 4-methylpyridine is only 30% at a temperature of 250 °C. With an increase of the temperature in the reaction up to 310 °C, the conversion of the starting material increases to 90%.

The V-Ti-Zr-O-catalyst and the sample containing 9% of tungsten oxide are much more active than the V-Ti-Zr-Sn-O-contact, the conversion of 4-methylpyridine on these catalysts reaches 85-90 % at a temperature of 250°C, and it becomes complete at a temperature of 290 °C.

The main reaction product is 4-cyanopyridine. The yield of the target product on the V-Ti-Zr-O-catalyst under these process conditions was 65-77% at a temperature of 250-270°C, on the V-Ti-Zr-WO contact - 76-85% and on the V-Ti-Zr - Sn-O-catalyst - 15-38%. The selectivity of 4-cyanopyridine formation on a catalyst containing tin (IV) oxide is 90-95%. On the other two catalysts, the selectivity of the formation of the target product is lower: for example, on V-Ti-Zr-WO it is 82-85% in the low-temperature region (250-270 °C) and the lowest selectivity is on the V-Ti-Zr-O-catalyst - 60-72%.

By varying the process conditions for the tested catalyst samples, it was possible to select conditions that ensure a high selectivity for the formation of 4-cyanopyridine. From the data shown in the figure, it can be noted that the optimal process temperature was significantly different: for a vanadium-titanium-zirconium catalyst and a sample containing 9% of tungsten oxide, the process temperature at which the highest yield of the target product (85-86%) was obtained at a temperature of 270 °C, and for the V-Ti-Zr-Sn-O catalyst - 87.5% at a temperature of 310 °C.

The phase composition and structural changes occurring in modified vanadium oxide catalysts have been studied. It is shown that when zirconium dioxide is introduced into catalysts containing 6-12%  $\text{V}_2\text{O}_5$ ,  $\text{TiO}_2$ -anatase does not transform into rutile, and a solid solution of  $\text{VO}_2$ - $\text{TiO}_2$  is not formed in this system of oxides. According to the data of X-ray phase analysis, it was found that  $\text{SnO}_2$  and  $\text{WO}_3$  exist as a separate phase, the formation of chemical compounds of these oxides with vanadium pentoxide was not found. Zirconium dioxide at a temperature of



The feed rate of 4-methylpyridine 43 g per 1 liter of catalyst per hour.  
 4-Methylpyridine : O<sub>2</sub> : NH<sub>3</sub> = 1 : 30 : 3.

Catalysts: 1 – V-Ti-Zr-O, 2 – V-Ti-Zr-O + 9,0 % WO<sub>3</sub>, 3 – V-Ti-Zr-O + 9,0 % SnO<sub>2</sub>.

The effect of temperature on the conversion of 4-methylpyridine(A),  
 the yield of isonicotinitrile(B), selectivity of isonicotinitrile formation(C), CO<sub>2</sub>(D)

600-620 °C forms a chemical compound with V<sub>2</sub>O<sub>5</sub> - zirconium divanadate. It was found that mixed V-Ti-Zr-Sn-O and V-Ti-Zr-W-O catalysts contain ZrV<sub>2</sub>O<sub>7</sub>, the monoclinic modification of ZrO<sub>2</sub> (baddeelite), TiO<sub>2</sub> (anatase), SnO<sub>2</sub>, WO<sub>3</sub>, and V<sub>2</sub>O<sub>5</sub>. In catalysts, it can exist in small amounts as a separate VO<sub>2</sub> phase.

The chemical and phase composition of mixed vanadium oxide catalysts formed during operation ensures their catalytic action in the oxidative ammonolysis of 4-methylpyridine to 4-cyanpyridine.

Comparison of the catalytic activity of oxide V-Ti-Zr, V-Ti-Zr-Sn and V-Ti-Zr-W catalysts in the reaction of oxidative ammonolysis of 4-methylpyridine has been carried out. It was found that the V-Ti-Zr-W-O catalyst showed the best catalytic properties under these conditions. It has high activity and selectivity of action in relation to isonicotinitrile. The conditions for carrying out the reaction of oxidative ammonolysis of 4-methylpyridine on this catalyst have been found, which provide the possibility of obtaining 4-cyanopyridine with a yield up to 85-90 mol. %.

## REFERENCES

- [1] Suvorov B.V. Oxidative ammonolysis of organic compounds. Alma-Ata: "Science" of the Kazakh SSR, 1971. 210 p.
- [2] Yakhontov L.N., Karpman Ya.S. Coke-chemical  $\beta$ -picolinic fraction as a complex raw material in the production of heterocyclic drugs // *Chem. Heterocycl. Compd.* 1981. No. 4. P. 435-447.
- [3] Vorobyev P.B., Gabdrakipov V.Z., Mikhailovskaya T.P., Sembaev D.Kh. Reactivity of isomeric picolines under conditions of oxidative ammonolysis on a vanadium oxide catalyst // *Russian Journal of General Chemistry.* 2001. Vol. 71, No. 4. P. 605-607. Doi 10.1023/A:1012395504813
- [4] Suvorov B.V., Mikhailovskaya T.P. Synthesis of 4-cyanopyridine by oxidative ammonolysis of 4-picoline on vanadium-titanium-tin catalyst // *Russian Journal of Applied Chemistry.* 1995. Vol. 68, No. 2. P. 275-277.
- [5] Kulkarni S.J., Ramachandra R.R., Subrahmayam M., Farsinavis S., Kanta R.P., Rama R.A.V. Oxidation and ammoxidation of 4-picoline over vanadium-silico-aluminophosphate catalysts // *Indian J. of Chem. Sect. A.* 1996. Vol. 35, No. 9. P. 740-745.
- [6] Jacques C. Vedrine. *Metal Oxides in Heterogeneous Catalysis.* 2018. 618 p. <https://doi.org/10.1016/C2016-0-01790-4>
- [7] Martin A., Lücke B. Ammoxidation and Oxidation of Substituted Methyl Aromatics on Vanadium-containing Catalysts // *Catalysis Today.* 2000. Vol. 57, No. (1-2). P. 61-70. DOI: 10.1016/S0920-5861(99)00309-0
- [8] Mikhailovskaya T.P., Yugay O.K., Chukhno N.I., Sembaev D.Kh. Oxidative Ammonolysis of 3- and 4-Pyridines on Vanadium Oxide Catalysts Modified with Titanium and Tin Oxides // *Russian Journal of Applied Chemistry.* 2012. Vol. 85, No. 2. P. 191-195.
- [9] Glubokovskikh L.K., Mikhailovskaya T.P., Suvorov B.V. Nitriles of picolinic and isonicotinic acids, their synthesis and some aspects of practical use // *Russian Journal of Applied Chemistry.* 1999. Vol. 72. No. 7. P. 1139-1142.
- [10] Yoshinori Goto, Ken-ichi Shimizu, Toru Murayama, Wataru Ueda. Hydrothermal synthesis of microporous W-V-O as an efficient catalyst for ammoxidation of 3-picoline // *Appl. Catal. A General.* 2015. 509. DOI: 10.1016/j.apcata.2015.10.011
- [11] Burch R. *Zirconium in Catalysis – Its Uses and Potential* // England: University of Liverpool, 1987. 26 p.
- [12] Chary K.V.R., Kishan G., Narayana K.V., Bhaskar T. Ammoxidation of 3-Picoline to Nicotinonitrile over Highly Dispersed  $V_2O_5/ZrO_2$  Catalysts // *J. Chem. Research (S).* 1998. P. 314-315.
- [13] Sembaev D.Kh., Ivanovskaya F.A., Pochtennaya V.M. Catalysts for Alkylbenzene and Alkylpyridine Ammoxidation // *Eurasian Chem. Tech. Journal.* 2000. No. 2. P. 113-116.
- [14] Sembaev D.Kh., Mikhailovskaya T.P., Serebryanskaya A.P. Oxidative ammonolysis of 4-methylpyridine on oxide vanadium-titanium-zirconium catalyst // *Izvestiya MES RK, NAS RK. Ser. chem.* 2003. No. 6. P. 89-94.

Резюме

*Т. П. Михайловская, Р. Курмакызы, Д. К. Толемисова, К. А. Қадирбеков*

ҚАЛАЙЛЫ ЖӘНЕ ВОЛЬФРАМ ОКСИДТЕРІМЕН ТҮРЛЕНДІРІЛГЕН  
ОКСИДТІ ВАНАДИЙ-ТИТАНИЙ-ЦИРКОНИЙ КАТАЛИЗАТОРЫНДА  
4-МЕТИЛПИРИДИНДІ ТОТЫҚТЫРА АММОНОЛИЗДЕУ

4-метилпиридинді тотықтыра аммонолиздеуде Ti, Sn, Zr және W оксидтерімен түрлендірілген, негізгі құраушысы ванадий пентоксиді болып табылатын катализаторлар сыналды. Үдерістің негізгі параметрлерінің - температураның, метил тобының нитрил тобына айналуындағы бастапқы компоненттер қатынасының рөлі айқындалды; 4-метилпиридинді тотықтыра аммонолиздеудің оңтайлы шарттары анықталды. V-Ti-Zr-O-катализаторының және құрамында 9% вольфрам оксиді бар үлгінің каталитикалық белсенділігі жағынан V-Ti-Zr-Sn-O катализаторынан жоғары екендігі анықталды. 4-цианпиридин түзілуінің жоғары талғамдылығын қамтамасыз ететін шарттар табылды. Мақсатты өнімнің ең жоғары шығымы (85-86%) V-Ti-Zr-W-O-да 270°C-та алынды, ал V-Ti-Zr-Sn-O катализаторында 4-цианпиридиннің шығымы 310 °C температурада 87,5 %-дықұрады.

Түрлендірілген ванадий оксиді катализаторларда болатын құрылымдық өзгерістер және фазалық құрам зерттелді. Аралас V-Ti-Zr-Sn-O және V-Ti-Zr-W-O катализаторларында  $ZrV_2O_7$ , моноклиндік түрленімдердің  $ZrO_2$  (баддеелит),  $TiO_2$  (анатаз),  $SnO_2$ ,  $WO_3$  және  $V_2O_5$  бар екендігі анықталды. Катализаторларда жеке фаза ретінде аз мөлшерде  $VO_2$  болуы мүмкін. V-Ti-Zr-W-O катализаторы ең жақсы каталитикалық қасиеттерді көрсеткені анықталды. Ол 4-цианпиридинге қатысты жоғары белсенділік пен талғамдылыққа ие.

**Түйін сөздер:** 4-метилпиридин, тотықтыра аммонолиздеу, катализаторлар,  $TiO_2$ ,  $SnO_2$ ,  $WO_3$ ,  $ZrO_2$ .

Резюме

*Т. П. Михайловская, Р. Курмакызы, Д. К. Толемисова, К. А. Қадирбеков*

ОКИСЛИТЕЛЬНЫЙ АММОНОЛИЗ 4-МЕТИЛПИРИДИНА  
НА ОКСИДНОМ ВАНАДИЙ-ТИТАН-ЦИРКОНИЕВОМ КАТАЛИЗАТОРЕ,  
МОДИФИЦИРОВАННОМ ОКСИДАМИ ОЛОВА И ВОЛЬФРАМА

В окислительном аммонолизе 4-метилпиридина испытаны катализаторы на основе пентоксида ванадия, модифицированные оксидами Ti, Sn, Zr и W. Выявлена роль основных параметров процесса - температуры, соотношения исходных компонентов в превращении метильной группы в нитрильную; определены оптимальные условия окислительного аммонолиза 4-метилпиридина. Установлено, что V-Ti-Zr-O-катализатор и образец, содержащий 9 % оксида вольфрама, по каталитической активности превосходят V-Ti-Zr-Sn-O-контакт. Найдены условия, обеспечивающие высокую селективность образования 4-цианпиридина. Наибольший выход целевого продукта (85-86 %) получен на V-Ti-Zr-W-O при температуре 270 °C, а на катализаторе V-Ti-Zr-Sn-O выход 4-цианпиридина составил 87,5 % при температуре 310 °C.

Изучен фазовый состав и структурные изменения, происходящие в модифицированных оксидованадиевых катализаторах. Установлено, что смешанные V–Ti–Zr–Sn–O и V–Ti–Zr–W–O катализаторы содержат  $ZrV_2O_7$ , моноклинную модификацию  $ZrO_2$  (баддеелит),  $TiO_2$  (анатаз),  $SnO_2$ ,  $WO_3$  и  $V_2O_5$ . В катализаторах в небольших количествах может существовать в виде отдельной фазы  $VO_2$ . Установлено, что V–Ti–Zr–W–O катализатор проявил наилучшие каталитические свойства. Он обладает высокой активностью и селективностью действия по отношению к 4-цианпиридину.

**Ключевые слова:** 4-метилпиридин, окислительный аммонолиз, катализаторы,  $TiO_2$ ,  $SnO_2$ ,  $WO_3$ ,  $ZrO_2$ .

#### Information about authors:

<i>Mikhailovskaya Tatyana Petrovna</i>	Candidate of Chemical Sciences, Assoc. Professor, senior researcher, JSC «Institute of chemical sciences named after A.B. Bekturov», Almaty, the Republic of Kazakhstan; tanya2855@mail.ru; <a href="https://orcid.org/0000-0002-0987-0809">https://orcid.org/0000-0002-0987-0809</a>
<i>Kurmazyzy Raya</i>	Research Scientist, JSC «Institute of chemical sciences named after A.B. Bekturov», Almaty, the Republic of Kazakhstan; kurmazyzy@mail.ru; <a href="https://orcid.org/0000-0002-8286-689X">https://orcid.org/0000-0002-8286-689X</a>
<i>Tolemisova Dinara</i>	Cand. chem. sci., Head of Boraldai Testing Laboratory, Gazprom Neft-Kazakhstan LLP, Almaty, the Republic of Kazakhstan; tolemisova@mail.ru; <a href="https://orcid.org/0000-0002-0567-7067">https://orcid.org/0000-0002-0567-7067</a>
<i>Kadirbekov Kairat</i>	Dok. chem. sci., Assoc. Professor, Head of the Laboratory of oil chemistry and petrochemical synthesis JSC «Institute of chemical sciences named after A.B. Bekturov», Almaty, the Republic of Kazakhstan; kkairati@mail.ru; <a href="https://orcid.org/0000-0003-3141-7661">https://orcid.org/0000-0003-3141-7661</a>