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«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ  
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»  
АКЦИОНЕРЛІК ҚОҒАМЫ

# ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

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## ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

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## **OXIDATIVE TRANSFORMATION 2-, 3- AND 4-METHYLPYRIDINES AT PRESENCE VANADIUM OXIDE CATALYST MODIFIED BY TITANIUM AND ALUMINUM OXIDES**

**Abstract.** Catalytic oxidative transformation of 2-, 3- and 4-methylpyridines (MP) at presence vanadium oxide catalyst modified by additives of titanium and aluminum oxides were studied. According to the degree of conversion in the oxidation reaction, the isomers of methylpyridine are arranged in the following row: 4-MP > 2-MP > 3-MP. The nature of the influence of reaction conditions on the selectivity of the process is established.

**Key words:** oxidation, methylpyridine, isomer, catalysts, selectivity.

**Introduction.** Pyridinecarboxylic acids (picolinic, nicotinic, isonicotinic) and their derivatives are important intermediate products in organic synthesis and are used to produce growth stimulants and chemical plant protection products, drugs. For example, pyridine-2-carboxylic acid and pyridine-2-carbaldehyde are used as starting materials for the synthesis of drugs, herbicides and dyes. Nicotinic acid and its amide are vitamin PP, which relaxes spasmodic coronary vessels and is used for disorders of cerebral circulation, myocardial infarction, angina pectoris. Isonicotinic acid derivatives are also important in medicine. Some substances of this series are valuable chemotherapeutic agents of tuberculosis action.

The partial catalytic oxidation of methylpyridines is the most effective method for the preparation of pyridinealdehydes and pyridinecarboxylic acids. The main component of the catalytic systems for this process is vanadium (V) oxide. To improve its catalytic properties, additives of promoter oxides are used.

Binary oxide systems are widely used for vapor-phase catalytic oxidation of isomeric methylpyridines [1–7]. For example, in patent [2] described the composition of catalysts  $xV_2O_5 \cdot yTiO_2 \cdot zM_aO_b$ , where  $x = 5-40$  wt.%,  $y = 95-60$  wt.%,  $z = 1-10$  wt.% and M is a metalloid additive. Silicon oxide, aluminum oxide, silicon carbide, titanium oxide, diatomaceous earth, zeolite and their mixtures, in particular, with inert aluminum oxide, are used as carriers. The metalloid additive is selected from the group including boron, silicon, germanium, arsenic, antimony, tellurium, polonium, and mixtures thereof.

The authors [3], for the synthesis of pyridinecarboxylic acids, proposed a catalyst from vanadium oxides and titanium on SiC carrier. Binary catalytic system based on vanadium oxides and titanium showed a good efficiency in the oxidation of 3-methylpyridine to nicotinic acid [4, 5].

In JSC «A.B. Bekturov Institute of Chemical Sciences» [6, 7] the catalytic properties of  $V_2O_5$  and two-component V-Ti-oxide catalysts in the vapor-phase oxidation of 3- and 4-methylpyridines were studied.

Isonicotinic acid was synthesized by vapor-phase oxidation of 4-picoline at presence V-Ti-Cr-Al-P catalyst [8]. The effect of the reaction temperature, load, amount of water and oxide promoters on the catalytic characteristics were studied. It was found that the acid promoter can improve the performance of the catalyst, and alkaline oxide by contrast reduce activity.

Analysis of the literature show that oxides of aluminum and titanium are widely used as components of catalytic systems. In this regard, in order to improve the catalytic effect of the vanadium-oxide catalyst in the oxidation of isomeric methylpyridines, it is of interest to modify it by adding titanium and aluminum oxides.

The goal of this work is to study the patterns of partial oxidation of isomeric methylpyridines on a vanadium-oxide catalyst modified with titanium and aluminum oxides, and to establish the relative reactivity of the starting compounds as a function of their structure.

## EXPERIMENT

The initial «pur.» mark methylpyridines, after drying and distillation, had characteristics that correspond to an individual substance (2-methylpyridine – boiling temperature 126-127°/694 millimeter of mercury,  $d_4^{20} = 0.9547$  and  $n_D^{20} = 1.5018$ ; 3 -methylpyridine - boiling temperature 140°/692 millimeter of mercury,  $d_4^{20} = 0.9568$ ,  $n_D^{20} = 1.5050$ ; 4-methylpyridine - boiling temperature 141°/695 millimeter of mercury,  $d_4^{20} = 0.9547$ ,  $n_D^{20} = 1.5058$ ) [9].

Vanadium-titanium-aluminum catalyst consisting of three-components was prepared by mixing the corresponding metal oxides of the grades «puriss.» and «p.a.». The calcination temperature is 650 ° C.

The study of vapor-phase oxidation of methylpyridines was carried out in the flow-reactor. In the reaction tube of stainless steel 1X18H10T with an internal diameter of 20 mm and a length of 1000 mm were loaded 100 ml of catalyst in the form of granules with a size of 3-5 mm. The reaction products were caught in scrubber-type airlift, irrigated with water. Chromatographic analysis of oxidation products was carried out by chromatograph «Color-106» with a flame ionization detector. Argon was used as the carrier gas. A glass column with a length of 1000 mm and a diameter of 4 mm is filled with adsorbent INZ-600 containing liquid phase of 25% PEGA + 2% H<sub>3</sub>PO<sub>4</sub>. The column thermostat temperature is 125 °C, the evaporator temperature is 200 °C. The pressure of the carrier gas of argon is 4.0 kgf/cm<sup>2</sup>, air - 2.4 kgf/cm<sup>2</sup>.

Pyridinecarboxylic acids were determined by titration with an alkali solution with a known titer. The products of deep oxidation were analyzed on an LHM-8MD chromatograph with a thermal conductivity detector. Stainless steel columns had a length of 3.5 m and an internal diameter of 3 mm. The adsorbent for determining CO was activated carbon of the AG-5 brand (0.25-0.50 mm), for CO<sub>2</sub> – polysorb-1 (0.16-0.20 mm). The temperature of the column thermostat is 40 °C.

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## RESULTS AND DISCUSSION

The selection of catalytic systems characterized by high selectivity towards pyridinecarboxylic acids is an important task.

Earlier we studied the catalytic activity of binary V-Ti-O and V-Al-O catalysts in the partial oxidation of 2-methylpyridine [10]. It has been established that the oxide vanadium-aluminum catalyst is less active in this process than the vanadium-titanium contact. With the highest yield (35-45%), picolinic acid is formed on a binary vanadium-aluminum catalyst at a temperature of 390-400 °C and a molar ratio of 2-picoline: O<sub>2</sub>: H<sub>2</sub>O = 1: 33.5: 46.

The behavior of binary V<sub>2</sub>O<sub>5</sub>·Me<sub>x</sub>O<sub>y</sub> (Me – Ti, Fe, Sn, Al, Zr, Cr) catalysts in the partial oxidation of 3-methylpyridine was studied [11].

In order to search for new active and selective catalysts for the vapor-phase oxidation of 2-, 3-, and 4-methylpyridines, we prepared and tested a three-component vanadium-oxide catalyst modified by titanium and aluminum oxides.

The study of the effect of temperature on the vapor-phase oxidation of 2-methylpyridine on the V-Ti-Al-O catalyst showed that the catalyst is not sufficiently active, since at 270 °C the conversion of the starting material is 27.7%. It was established that with an increase in the amount of water supplied from 36.2 to 197 moles, the amount of pyridine-2-carbaldehyde and pyridine increases per 1 mole of 2-methylpyridine. Thus, adding 36.2 mol of water to 1 mol of 2-methylpyridine at 310 °C increase the yield of pyridine-2-carbaldehyde from 16.9 to 44.5%. A further increase amount of water insignificantly influence on the conversion of 2-methylpyridine. When apply 2-methylpyridine, air and water in a molar ratio of 1: 14.5: 113.1 respectively at temperature 310 °C, the highest yield of pyridine-2-carbaldehyde was reached about 53.9%. The selectivity of its formation was up 67.7%. The conversion of 2-methylpyridine under these conditions was about 79.6%.

The vapor-phase oxidation of 3-methylpyridine was studied on the same catalyst. The study process was carried out with a wide variation of parameters. Thus, the amount of water supplied to the reaction zone was changed from 36.2 to 197 mol per mole of the starting 3-methylpyridine, and the oxygen supply was from 14.5 to 29.1 mol per mole of the starting material. The reaction temperature was 250-350 °C. On this catalyst, when studying the effect of oxygen amount, it was established that with an increase in oxygen supply, the conversion of the starting methylpyridine hardly changes. With an increase in the amount of air in the reaction mixture, a decrease in the yield of pyridine-3-carbaldehyde is observed. The maximum yield of nicotinic acid (48.8% with a selectivity of formation of 58.3%) was achieved when 29.1 mol of atmospheric oxygen per mole of starting 3-methylpyridine was supplied. The amount of pyridine varies little with changes in air supply and increases slightly with increasing temperature.

The study of the effect of water additives on the oxidation of 3-methylpyridine on this catalyst showed that in an anhydrous mode, the yield of nicotinic acid does not exceed 21.7% (selectivity of formation 31.9%) at 350 °C. It was

established that the introduction of 36.2 mol of water per mole of 3-methylpyridine into the reaction zone promotes at a temperature of 350 °C an increase in the conversion of the starting 3-methylpyridine from 68.1% to 92.8%, which is accompanied by an increase in the yield of nicotinic acid from 28.8% up to 37.5%. An increase in the concentration of water in the contact zone to 197 mol per mole of 3-methylpyridine causes a further increase in the yield of nicotinic acid to 48.8% at a molar ratio of 3-methylpyridine: O<sub>2</sub>: H<sub>2</sub>O = 1: 29.1: 197.

Thus, the test of V-Ti-Al-O catalyst in the oxidation of 3-methylpyridine showed that this catalytic system is characterized by high total selectivity for pyridine-3-carbaldehyde and nicotinic acid (95%), but the conversion of the starting 3-methylpyridine does not exceed 92 %.

Next, on this sample, the oxidation of 4-methylpyridine was studied. The maximum yield of pyridine-4-aldehyde (58.8%) was obtained at a temperature of 290 °C in experiments without the addition of water. It is established that the increase in the reaction temperature contributes to the conversion of intermediate pyridine-4-carbaldehyde to isonicotinic acid. The maximum yield of isonicotinic acid (54.3%) was obtained at a temperature of 330 °C and 36.2 moles of H<sub>2</sub>O per mole of 4-methylpyridine were fed to the reaction zone. A further increase in the amount of water supplied has almost no effect on the conversion of the starting methylpyridine. The increase in the molar ratio of water: 4-methylpyridine from 36.2 to 197 moles per 1 mole of the starting material has little effect on the yield of pyridine-4-carbaldehyde and isonicotinic acid.

Experimental data obtained testing vanadium-oxide catalyst modified by titanium and aluminum oxides showed that this catalyst had a less catalytic activity in the oxidation of 3-methylpyridine. The conversion of 2- and 4-methylpyridines is higher than the conversion of the 3-isomer. The degree of conversion of the studied isomers in the oxidation reaction increases in the following row: 3-MP < 2-MP < 4-MP (figure).

It has been established that under the conditions of studying, the V-Ti-Al-O catalyst during the oxidation of 2-methylpyridine showed high selectivity in the formation of pyridine-2-carbaldehyde, which with the highest yield (53.9%) is formed at a temperature of 310 °C. It is noted that this catalyst is characterized by a high total selectivity of the formation of the corresponding pyridinaldehydes and pyridinecarboxylic acids (nicotinic and isonicotinic) in the oxidation of 3- and 4-isomers. This indicator at a temperature of 290-310 °C for 3-methylpyridine was 86-95%, and for 4-methylpyridine – 76.5- 80%.

When interpreting experimental data on the relative reactivity of isomeric methylpyridines, it was assumed that these compounds are among weak CH-acids, and under the action of a strong base are able to split a proton from the methyl group to form a carbanion, for example, in liquid-phase deuterioexchange [12-15]. In a heterogeneous catalytic oxidation of methylpyridines, nucleophilic forms of surface oxygen can play the role of proton acceptors [16]. Obviously, the rate of the oxidation reaction of methylpyridines should be influenced by the

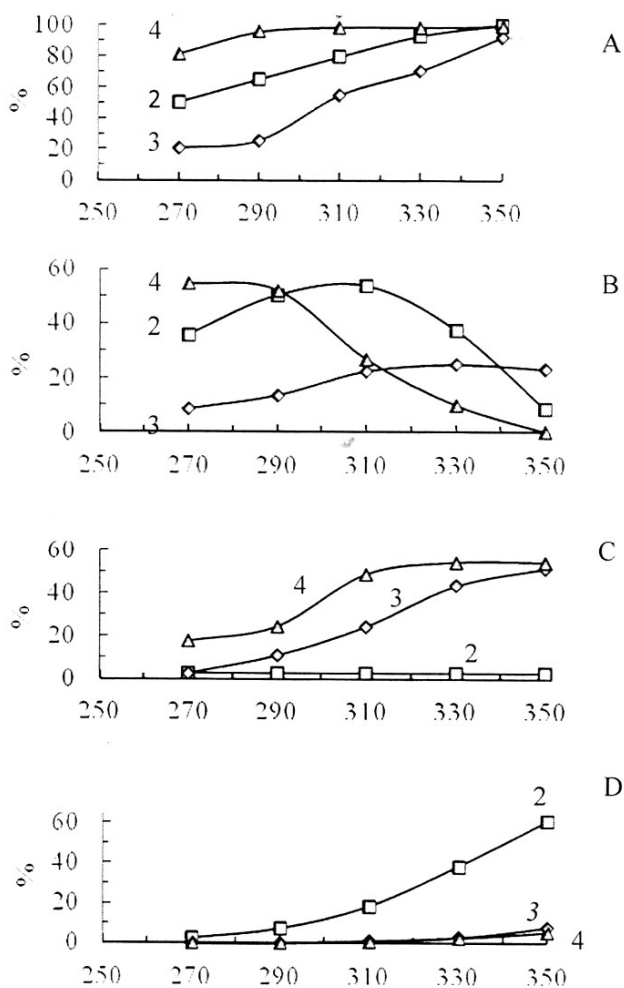


Figure 1 – The effect of temperature on the conversion of methylpyridines (A), the yield of pyridinealdehydes (B), pyridinecarboxylic acids (C) and pyridine (D) under oxidation conditions on a V-Ti-Al-O catalyst.

Experience conditions. The feed rate of methylpyridine 36 g, air 600 l, water 788 gr. 1 liter of catalyst per hour. The molar ratio of the original substance:  $O_2$ :  $H_2O$  = 1: 14.5: 113.1.

The designation of the curves: 2 - 2-picoline and products of its transformations, 3 - 3-picoline and products of its transformations, 4 - 4-picoline and products of its transformations.

proton mobility of the methyl substituent, which can be estimated by the value of the enthalpy of deprotonation.

Reliable experimental data of the CH-acidity in the gas phase do not known for all methylpyridines. Therefore, using the ab initio quantum chemical method (ab initio, basis HF/6-31G\*) [17], we calculated the enthalpy of deprotonation of

methyl groups (DPE) characterizing this property of substrates, based on the total energies of carbanions and initial molecules (table 1, 2):



$$\text{DPE} = E_{\text{tot.}}(\text{A}^-) + E_{\text{tot.}}(\text{BH}^+) - E_{\text{tot.}}(\text{AH}) - E_{\text{tot.}}(\text{B}), \quad (2)$$

In catalytic oxidation reactions of methylpyridines, various forms of active oxygen on the surface of vanadium oxide can play the role of a proton acceptor (B). For the same proton acceptor, the difference  $E_{\text{tot.}}(\text{BH}^+) - E_{\text{tot.}}(\text{B})$  in equation (2), equal to the proton binding energy, can be considered constant, and to calculate the deprotonation enthalpy characterizing the relative strength of CH-acids, use the equation:

$$\text{DPE} = E_{\text{tot.}}(\text{A}^-) - E_{\text{tot.}}(\text{AH}). \quad (3)$$

The lone pair of carbanion electrons is located on the highest filled molecular orbital (HFMO). The stability of the carbanion is determined by the degree of delocalization of the negative charge [18]. The more the lone electron pair is delocalized, the lower the energy level of the highest filled molecular orbitals and, therefore, the more stable the carbanion. In turn, the more stable the carbanion is, the more the equilibrium of reaction (1) is shifted to the right and the higher the rate of further transformation of the carbanion to pyridinecarbaldehyde and pyridinecarboxylic acid. In table 1 shows the calculated values of the energy of higher filled molecular orbitals of intermediate carbanions ( $E_{\text{HFMO}}$ ) for the studied CH-acids. It can be seen that there is a correlation between the values of  $E_{\text{HFMO}}$  carbanions resulting from the deprotonation of methyl substituents and the rate of their oxidation under the conditions of the catalytic reaction (figure).

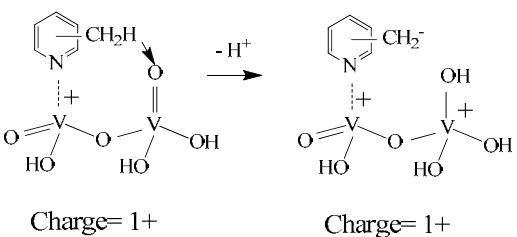
Table 1 – Total energies of molecules of acids and their anions ( $E_{\text{full.}}$ ), Enthalpies of deprotonation of compounds in the gas phase (DPE), energy of higher filled molecular orbitals of anions ( $E_{\text{HOMO}}$ ), calculated by ab initio method (basis HF / 6-31G \*)

#	Initial Molecule	$-E_{\text{tot.}}$ , a.u.		DPE <sup>1</sup> , kJ·mol <sup>-1</sup>	$-E_{\text{HOMO}}$ , kJ·mol <sup>-1</sup>
		molecules (AH)	anions (A <sup>-</sup> )		
1	4-Methylpyridine	285,734727	285,098174	1671	100,9
2	2-Methylpyridine	285,736485	285,087542	1703,8	65,9
3	3-Methylpyridine	285,732945	285,077944	1720	37,5
<i>Note.</i> 1 – $\text{DPE} = E_{\text{tot.}}(\text{A}^-) - E_{\text{tot.}}(\text{AH}) \cdot 2625,46$ .					

Due to the presence of a nitrogen heteroatom in the ring, the starting materials are able to interact with the Lewis acid center of the vanadium oxide catalyst surface at the initial stages of the process. To assess the relative reactivity of the methyl groups of the studied compounds under conditions simulating their chemisorption on the surface of the vanadium oxide catalyst and activation of the

oxidizing methyl substituent, we constructed complexes of substrates and intermediate carboanions with the active center, which was simulated by a dual-core cluster containing the vanadium cation (Lewis acid center) and vanadyl oxygen (methyl proton acceptor) (table 2).

Table 2 – The total energies of methylpyridines and their carbanions associated with a dual-core cluster ( $E_{full}$ ), the deprotonation energies of chemisorbed substrates (DPE), calculated by the DFT method (B3LYP / LanL2DZ). Proton acceptor - vanadyl oxygen

Reaction	$-E_{tot.}$ , a.u.		DPE <sup>1</sup> , kJ mol <sup>-1</sup>
	chemisorbed molecule	chemisorbe d carbanion	
 <p>Charge= 1+</p>	883,4948748 (3)	883,404028 (3)	238,5 (3)
	883,4968877 (2)	883,429740 4 (2)	176,3 (2)
	883,497472 (4)	883,438186 (4)	155,7 (4)
<p>Note. 1 – DPE = (<math>E_{end.} - E_{beginning}</math>) · 2625.5.</p>			

To optimize the geometry and calculate the total energy of the complexes, the B3LYP density exchange-correlation functional and the two-exponent basis set LanL2DZ with an effective core potential were used [19]. The calculations were carried out in the Born-Oppenheimer approximation using the GAUSSIAN 09W program, version D.01.

According to the calculation results given in table 2, the enthalpy of deprotonation of the methyl groups of substrates associated with the cluster decreases in the order 3-methylpyridine > 2-methylpyridine > 4-methylpyridine. In the same sequence, according to experimental data, the reactivity of the starting compounds increases, assessed by their conversion and the yield of partial oxidation products (figure, A, B, C).

**Conclusion.** Thus, the study performed is another confirmation of the hypothesis about the mechanism of the catalytic partial oxidation of methylpyridines with a heterolytic cleavage of the C–H bond in the oxidizing substituent.

It should be noted that due to the peculiarity of the structure of 2-methylpyridine, an increase in the reaction temperature contributes to an increase in the proportion of oxidative elimination processes of the substituent in position 2, leading to the formation of pyridine (figure, D).



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**Резюме**

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**ТИТАН ЖӘНЕ АЛЮМИНИЙ ОКСИДТЕРІМЕН ТҮРЛЕНДІРІЛГЕН  
ВАНАДИЙ ОКСИДТІ КАТАЛИЗАТОРЫНДА 2-, 3-, ЖӘНЕ  
4- МЕТИЛПИРИДИНДЕРДІҢ ТОТЫҒУЫ**

Метилпиридиндердің изомерлерін газ күйінде тотықтыруда ванадий оксидті катализатордың қасиетіне титан және алюминий оксидтерінің әсері талқыланады. Катализатор қатысында тотығу мына қатарда төмендейді: 4-метилпиридин > 2-метилпиридин > 3-метилпиридин.

**Түйін сөздер:** тотығу, метилпиридиндер, изомер, катализаторлар, селективтілі.

**Резюме**

*П. Б. Воробьев, Т. П. Михайловская, Д. К. Толемисова*

**ОКИСЛИТЕЛЬНЫЕ ПРЕВРАЩЕНИЯ 2-, 3- И 4-МЕТИЛПИРИДИНОВ  
НА ВАНАДИЙОКСИДНОМ КАТАЛИЗАТОРЕ,  
МОДИФИЦИРОВАННОМ ОКСИДАМИ ТИТАНА И АЛЮМИНИЯ**

Обсуждается влияние оксидов титана и алюминия на каталитические свойства ванадийоксидного катализатора в парофазном окислении изомерных метилпиридинов. По способности окисления изомеры располагаются в нижеследующий ряд: 4-метилпиридин > 2-метилпиридин > 3-метилпиридин.

**Ключевые слова:** окисление, метилпиридины, изомеры, катализаторы, селективность.