

ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ  
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ  
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»  
АКЦИОНЕРЛІК ҚОҒАМЫ

# ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

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## ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

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## CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО  
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ  
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК  
им. А. Б. БЕКТУРОВА»

**2 (66)**

АПРЕЛЬ – ИЮНЬ 2019 г.  
ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА  
ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ  
2019

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## CATALYTIC ACTIVITY VANADIUM OXIDE CATALYSTS MODIFIED BY Ti, Sn, Cr OXIDES IN THE PARTIAL OXIDATION OF 3-METHYLPYRIDINE

**Abstract.** The results of catalytic activity of  $V_2O_5 \cdot Me_xO_y$  (Me – Ti, Sn, Cr) binary catalysts and more complex in composition in a wider range of catalytic systems in the partial oxidation of 3-methylpyridine are discussed. It was found that the binary vanadium chromium oxide catalyst showed the greatest activity in this process. Nicotinic acid is obtained with the highest yield (80%) at 330 °C and a molar ratio of reacting substance: 3-methylpyridine: oxygen : water vapor = 1:13:25,5.

**Keywords:** oxidation, 3-methylpyridine, nicotinic acid, catalysts, oxide.

**Introduction.** Catalysis is currently the basis of production of a large number of chemical products [1], one of is nicotinic acid and its derivatives.

Nicotinic acid and its derivatives have a large variety of physiological properties, due to which they are widely used in medicine and agriculture as vitamins, drugs, plant growing regulators.

The vapor-phase oxidation of methylpyridines (MP) by air oxygen in the presence of oxide catalysts is the most cost-effective method for the preparation of pyridinecarboxylic acids. In Bekturov Institute of Chemical Sciences, with the purpose of creating a one-stage technological process for the NA (nicotinic acid) production, the research is being conducted for searching development efficient catalysts of vapor-phase oxidation 3-MP. Well known, vanadium-containing mixed oxide catalytic materials [2, 3] are active in the partial oxidation reactions. Titanium, tin and chromium oxides are widely used as components of catalytic systems [4-6]. For example, the vapor-phase oxidation of 3-picoline to nicotinic acid was studied [4] in the presence of a number mixed oxides  $CrV_{1-x}P_xO_4$  ( $x = 0-1.0$ ). The  $CrV_{0,95}P_{0,05}O_4$  showed the greatest activity from the tested catalysts. Authors [5] have synthesized highly dispersed, multilayer metal oxide catalysts ( $V_2O_5/MO_x/SiO_2$ , M = Ti (IV), Zr (IV) or Al (III)). It was found that surface V cations mainly interact with surface particles of metal oxides (Ti, Zr or Al) on silicon dioxide. It is shown that the catalytic activity of vanadium oxide catalysts can be changed by changing and modifying the oxide support. The influence of additives on the acid-base and redox properties of catalysts in selective oxidation reactions was considered in this article [7]. The development of nicotinic acid technology is described in the work [8].

Due to practical importance of nicotinic acid, the purpose of this work was to search for new active and selective catalysts for the vapor-phase oxidation of 3-methylpyridine.

## EXPERIMENTAL PART

In this work, dried and distilled 3-methylpyridine with boiling point of 140°/692 mm,  $d_4^{20} = 0.9568$ ,  $n_D^{20} = 1.5050$  was used. These characteristics corresponded to the reference data.

As initial components of the catalysts, we used vanadium pentoxide, titanium, tin, chromium dioxides of analytical grade. The initial oxides in a molar ratio of 1:4 were ground in a porcelain mortar to form a homogeneous batch, which then was compressed into tablets of 15 mm in diameter and 3-4 mm in thickness and calcined at 640 °C for 4 hours. After cooling, the tablets were crushed into grains of 3-5 mm in size. Textural characteristics of the synthesized binary catalysts were determined by low-temperature nitrogen desorption method on the NOVA 1000e gas sorption analyzer from Quantachrome (USA).

The oxidation of 3-methylpyridine was carried out in a continuous installation of reaction tube made of stainless steel with a diameter of 20 mm and a length of 150 mm into which 10 ml of a granular catalyst was loaded.

The unreacted 3-methylpyridine and reaction products were trapped in air-lift type scrubbers filled with water and analyzed by gas-liquid chromatography. Nicotinic acid was titrated with 0,035 N alkali using phenolphthalein.

The deep oxidation products were analyzed by LXM-8MD chromatograph with a thermal conductivity detector. The stainless steel columns had a length of 3,5 m and an inner diameter of 3 mm. The adsorbent for CO detection was an AG-5 activated carbon (0,25-0,50 mm), for CO<sub>2</sub> – polysorbent-1 (0,16-0,20 mm). The temperature of the thermostat was 40 °C.

## RESULTS AND DISCUSSION

Catalysts of the composition V-Ti-O, V-Sn-O and V-Cr-O were prepared and tested for the purpose to development new active and selective catalysts for the vapor-phase oxidation of 3-methylpyridine.

We investigated the general laws of the reaction, in particular, the effect of temperature, the amount of oxygen (air) and water vapor on the yield of the main products of the reaction.

Figure 1 shows the results showing the change in the conversion of 3-methylpyridine and the yield of nicotinic acid on binary vanadium oxide catalysts depending on temperature under comparable conditions. It is shown that binary vanadium titanium and vanadium tin catalysts exhibited insufficiently high activity in 3-methylpyridine oxidation and were inferior to vanadium-chromium contact.

The vanadium chromium catalyst showed the greatest activity among the tested catalysts, on which conversion of 3-methylpyridine at temperature of 350-370 °C reached 91-93%. The degree of conversion of the initial substance to V-Sn-O in the studied temperature range was 65-82%, and on V-Ti-O - only 54-66%. In terms of catalytic activity, the tested binary systems can be arranged in the following row: V-Cr-O > V-Sn-O > V-Ti-O.

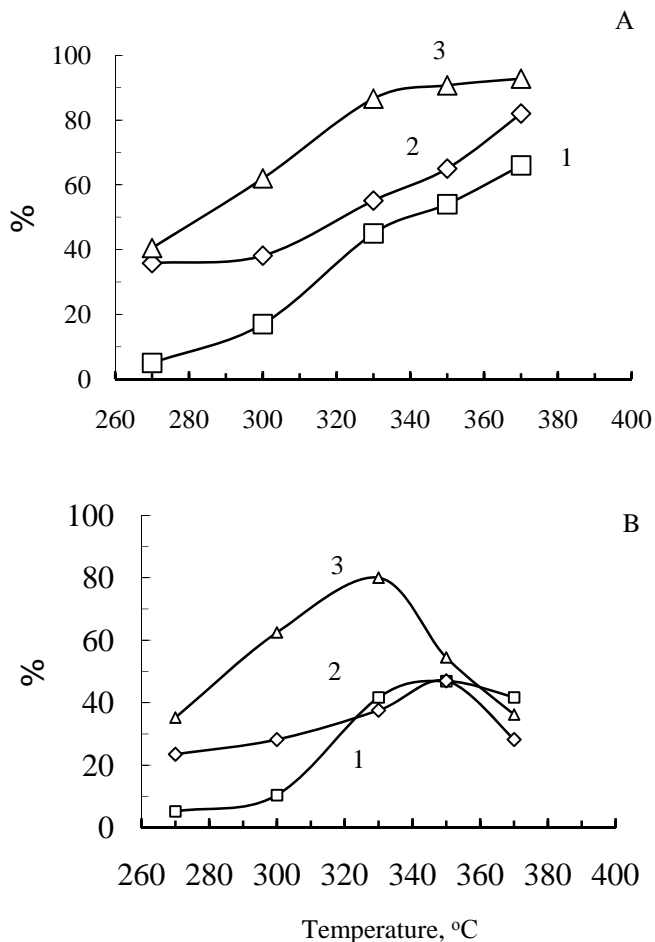


Figure 1 – Influence of temperature on the conversion of 3-methylpyridine (A) and yield of nicotinic acid (B) under oxidation conditions over the  $V_2O_5 \cdot 4TiO_2$  (1),  $V_2O_5 \cdot 4SnO_2$  (2),  $V_2O_5 \cdot 4Cr_2O_3$  (3) catalysts.

The feed rate of 3-methylpyridine – 36 g, air 550 L, water 177,7 g per 1 L of the catalyst in hour.  
Mole ratio of 3-methylpyridine:O<sub>2</sub>:H<sub>2</sub>O = 1:13:25.5

It is known from the literature that most of the operational (catalytic, sorption, pigment) properties of metal oxides are associated with the dispersity and characteristics of the porous materials structure. The influence of such parameters as the specific surface area (SSA), the total pore volume (VS) is decisive in the course of heterogeneous processes.

Specific surface area and textural characteristics of the synthesized binary and more complex catalysts are represented in table 1.

Table 1 – Textural characteristics of the synthesized catalysts

Catalyst's composition	SSA, m <sup>2</sup> /g	V <sub>Σ</sub> , sm <sup>3</sup> /g·10 <sup>-3</sup>	D of pore, nm
V-Cr-O	1,29	0,7029	2,2
V-Sn-O	0,64	0,3523	2,1
V-Ti-O	0,31	0,1675	2,2
V-Ti-Sn-O	0,99	0,5295	2,1
V-Ti-Sn-Cr-O	1,10	0,5626	2,1

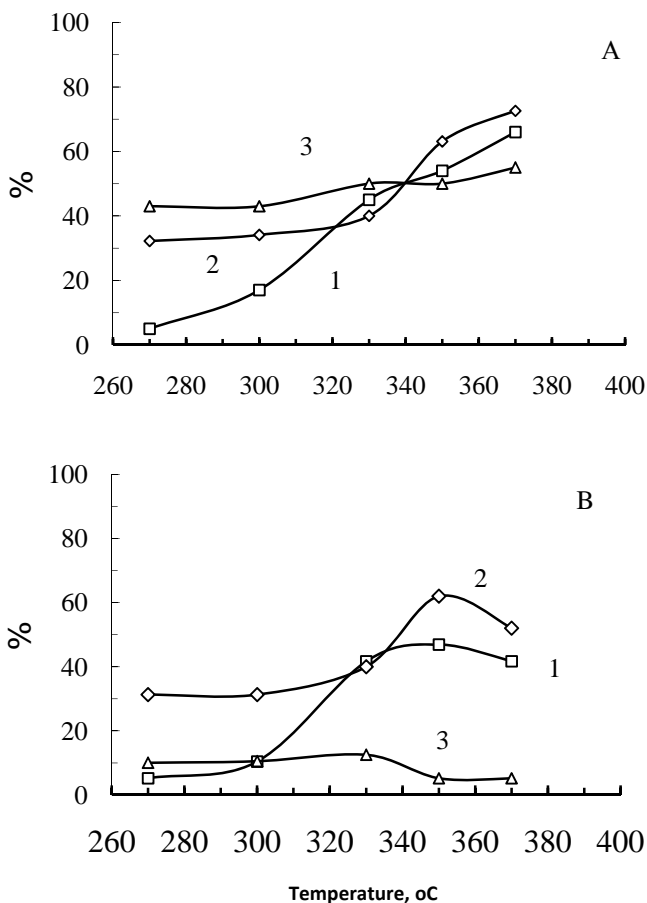


Figure 2 – Influence of temperature on the conversion of 3-methylpyridine (A) and yield of nicotinic acid (B) under oxidation conditions over the V<sub>2</sub>O<sub>5</sub>·4TiO<sub>2</sub> (1), V<sub>2</sub>O<sub>5</sub>·4TiO<sub>2</sub>·4SnO<sub>2</sub> (2), V<sub>2</sub>O<sub>5</sub>·4TiO<sub>2</sub>·4SnO<sub>2</sub>·4Cr<sub>2</sub>O<sub>3</sub> (3) catalysts.

The feed rate of 3-methylpyridine – 36 g, air 550 L, water 177,7 g per 1 L of the catalyst in hour.  
Mole ratio of 3-methylpyridine:O<sub>2</sub>:H<sub>2</sub>O = 1:13:25.5

The results showed that the vanadium chromium (V-Cr-O) catalyst has a higher specific surface ( $1.29 \text{ m}^2/\text{g}$ ) than the vanadium-tin ( $0.64 \text{ m}^2/\text{g}$ ) and vanadium titanium catalysts ( $0.31 \text{ m}^2/\text{g}$ ), which led to an increase in its catalytic activity.

The main product of 3-methylpyridine oxidation is nicotinic acid. Figure 1B shows that its yield on binary vanadium oxide catalysts decreases in the following row: V-Cr-O > V-Sn-O > V-Ti-O. From the presented data it is clearly seen that the oxide vanadium chromium catalyst showed the greatest selectivity in the formation of the target product. The conversion of 3-methylpyridine at temperature of  $370 \text{ }^\circ\text{C}$  on this catalyst, when feeding initial reagents with a molar ratio of 3-methylpyridine: $\text{O}_2$ : $\text{H}_2\text{O}$ =1:13:25,5, was 92.8%, and nicotinic acid was obtained with the highest yield 78-80% at a temperature of  $330 \text{ }^\circ\text{C}$ . The selectivity of the nicotinic acid formation reached 92.4%.

Based on the obtained results, we prepared mixed catalytic systems: triple - V-Ti-Sn-O, containing vanadium, titanium and tin oxides, and more complex - V-Ti-Sn-Cr-O, with addition of chromium oxide to the composition, the additives of which to vanadium pentoxide had the best effect on the catalytic activity in 3-methylpyridine oxidation.

Figure 2 shows the test results of these catalysts. It is seen from the figure that in the low-temperature region of the process ( $270$ - $340 \text{ }^\circ\text{C}$ ) the V-Ti-Sn-Cr-O catalyst shows higher activity than the vanadium titanium tin and binary vanadium titanium contacts. In the same order, the specific surface area of the samples is also changed:  $S_{\text{sp.}}(\text{V-Ti-Sn-Cr-O}) = 1.1 \text{ m}^2/\text{g}$ ,  $S_{\text{sp.}}(\text{V-Ti-Sn-O}) = 0.99 \text{ m}^2/\text{g}$  and  $S_{\text{sp.}}(\text{V-Ti-O}) = 0.31 \text{ m}^2/\text{g}$ . Attention is drawn to the fact that more complex catalytic compositions are characterized by low activity in 3-methylpyridine oxidation: even at temperature of  $370 \text{ }^\circ\text{C}$ , the conversion of the initial material does not exceed 73%.

**Conclusion.** As it is seen from the obtained data, complex mixed catalysts of the studied composition turned out to be ineffective for the process of 3-methylpyridine oxidation to nicotinic acid.  $\text{V}_2\text{O}_5$ - $\text{Me}_x\text{O}_y$  binary catalysts are more effective in the process of partial 3-methylpyridine oxidation, and the vanadium-chromium oxide catalyst showed the best catalytic properties. There is a definite correlation between the specific surface area of the samples and their catalytic activity in the process.

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### Резюме

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#### 3-МЕТИЛПИРИДИННІҢ ПАРЦИАЛДЫҚ ТОТЫҒУЫНДА Ti, Sn, Cr ТОТЫҚТАРЫМЕН МОДИФИЦИРЛЕНГЕН ВАНАДИЙ ТОТЫҚТЫ КАТАЛИЗАТОРЛАРДЫҢ БЕЛСЕНДІЛІГІ

Бинарлық  $V_2O_5 \cdot Me_xO_y$  (Me - Ti, Sn, Cr) және оданда күрделі катализдік жүйелердің 3-метилпирдиннің парциалды тотығуындағы катализдік белсенділігін зерттеу нәтижелері талқыланады. Бұл процесте бинарлық ванадийхром тотықты катализатордың жоғары белсенділік көрсетететіні анықталды. Ең жоғары өнімділігі (80%) никотин қышқылы 330 °C температурада және 3-метилпирдин :  $O_2$  :  $H_2O$  = 1: 13: 25,5 қатынаста алынды.

**Түйін сөздер:** парциалды тотығу, 3-метилпирдин, никотин қышқылы, катализаторлар.

### Резюме

*Т. П. Михайловская, П. Б. Воробьев, Р. Курмақызы, Қ. А. Кадирбеков*

#### КАТАЛИТИЧЕСКАЯ АКТИВНОСТЬ ОКСИДНОВАНАДИЕВЫХ КАТАЛИЗАТОРОВ, МОДИФИЦИРОВАННЫХ ОКСИДАМИ Ti, Sn, Cr, В ПАРЦИАЛЬНОМ ОКИСЛЕНИИ 3-МЕТИЛПИРИДИНА

Обсуждаются результаты исследования каталитической активности бинарных  $V_2O_5 \cdot Me_xO_y$  (Me – Ti, Sn, Cr) и более сложных по составу каталитических систем в парциальном окислении 3-метилпиридина. Установлено, что бинарный оксидный ванадийхромовый катализатор проявил наибольшую активность в данном процессе. Никотиновая кислота с наибольшим выходом (80 %) получена при температуре 330 °C и мольном соотношении 3-метилпирдин :  $O_2$  :  $H_2O$  = 1:13:25,5.

**Ключевые слова:** окисление, 3-метилпирдин, никотиновая кислота, катализаторы.