Қазақстанның
Химия Журналы

═══════════

Химический Журнал
Казахстана

═══════════

Chemical journal
of Kazakhstan

P. B. VOROBYEV, T. P. MIKHAILOVSKAYA, O. K. YUGAY, A. P. SEREBRYANSKAYA, R. KURMAKYZY, A. M. IMANGAZY

«A.B. Bekturov Institute of Chemical Sciences» JSC, Almaty, Republic of Kazakhstan

ABOUT PROMOTION THE VANADIUM-TITANIUM OXIDE CATALYST OF OXIDATION β- AND γ-PICOLINES

Abstract. The promoting effect of tin (IV), chromium (III) and zirconium (IV) oxides additives to the binary V-Ti-oxide system in the reaction of partial oxidation of β- and γ-picolines were investigated. A correlation between the catalytic activity of the studied oxide systems and the affinity values of vanadyl oxygen proton of their surface which was involved in the deprotonation of oxidized methyl substituents was established. A hypothesis about the possibility of a synergistic effect with the simultaneous addition to vanadium pentoxide of titanium (IV) oxide and one of the promoter oxides was expressed.

Keywords: oxidation, β-picoline, γ-picoline, nicotinic acid, isonicotinic acid, catalysts, promotion

RESULTS AND DISCUSSION

It was previously established that the modification of vanadium pentoxide with the addition of titanium dioxide leads not only to an increase in the mechanical strength and thermal stability of the catalyst, but also to increase its activity in the partial oxidation of β- and γ-picolines. The goal of this work was to study the promoting effect of tin (IV), chromium (III) and zirconium (IV) oxides additives to the binary V-Ti oxide system with the preparation of three-component catalysts.

The obtained results of the β-picoline oxidation over vanadium – titanium oxide and vanadium – titanium – tin oxide contacts were compared (figure 1). It was established that the modification of the vanadium-titanium catalyst by SnO_2 additives had little effect on the contact activity. The conversion of the initial pyridine base over both catalyst ($V_2O_5 \cdot 16TiO_2$ and $V_2O_5 \cdot 15TiO_2 \cdot SnO_2$) were approximately the same. However, the introduction of tin dioxide into vanadium – titanium catalyst caused a significant increase in the selectivity of nicotinic acid formation. Thus, the selectivity of the nicotinic acid formation over $V_2O_5 \cdot 15TiO_2 \cdot SnO_2$ catalyst at 280°C already was 82%, whereas over vanadium-titanium catalyst under these conditions it did not exceed 64%. At 340°C, the selectivity for acid over the vanadium-titanium catalyst modified by SnO_2 reached 94%, whereas over the vanadium-titanium catalyst - only 62%.

The promoting effect of SnO_2 additives to vanadium-titanium catalyst is probably due to the fact that tin dioxide can change the chemical composition of the catalyst [1]. Introduced SnO_2, due to its oxidizing ability, can act as an oxidizing agent to the lower vanadium oxides and prevent the catalyst from being reduced by an oxidizing organic compound, thereby stabilizing its composition.
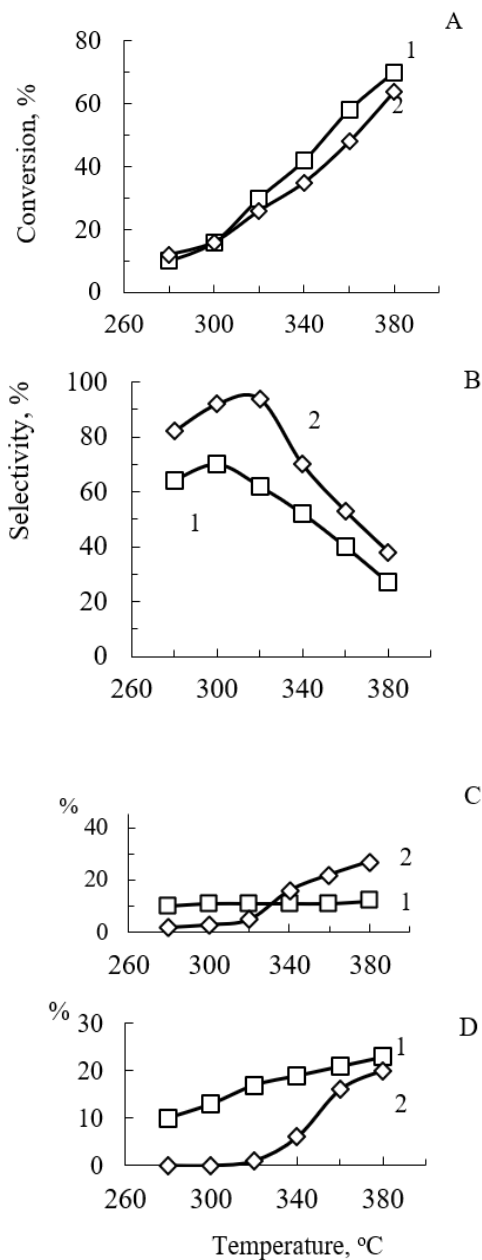
The feed rate of *β*-picoline is 30.8 g per 1 liter of catalyst in hour.
The molar ratio β-picoline:O_2:H_2O = 1:20:175. Designation of curves (%):
A - β-picoline conversion; yield: B - nicotinic acid, C - pyridine, D - CO_2.
Catalysts: *1* - $V_2O_5 \cdot 16TiO_2$, *2* - $V_2O_5 \cdot 15TiO_2 \cdot SnO_2$.

Figure 1 − The effect of temperature on the *β*-picoline oxidation
in the presence of vanadium-oxide catalysts modified by TiO_2 and SnO_2

Due to SnO_2, the V_2O_5 content in a three-component vanadium-titanium-tin catalyst must be higher than in a two-component vanadium-titanium catalyst. This was confirmed by data on the tin dioxide effects to the composition of the vanadium-titanium catalyst which we obtained earlier using the electron paramagnetic resonance (EPR) method [2].

Under comparable conditions, when 37.8 g of *β*-picoline feeding per 1 liter of catalyst in hour and the molar ratio of *β*-picoline:O_2:H_2O = 1:7:85 with the temperature range from 240 to 320°C, partial oxidation of *β*-picoline was carried out on V-Ti-O- and V-Ti-Cr-O-catalysts. Figure 2 shows the effect of temperature on β-picoline oxidation. It was established that the Cr_2O_3 additives increase the selectivity of the three-component V-Ti-Cr-oxide catalyst for nicotinic acid. The selectivity of nicotinic acid formation increases from 63% to 87% (with the yield increasing from 44 to 66%) at 270°C. The conversion of β-picoline on a modified sample of catalyst at 260-280°C was 5% higher than on the V-Ti-O catalyst sample. When the temperature rises to 300-320°C, the conversion of β-picoline on both catalysts was leveled to 90-93%. On the modified catalyst, oxidative demethylation of the initial substance to form pyridine to a higher extent proceeds, and on the $V_2O_5 \cdot TiO_2$ catalyst – deep oxidation. Thus, it was shown that modifying the V-Ti-O catalyst with chromium (III) oxide leads to a significant increase in the selectivity of the catalyst's action in relation to nicotinic acid.

The tests of zirconium-modified vanadium-titanium oxide catalyst in the reaction of the β-picoline vapor-phase oxidation showed that the introduction of ZrO_2 into the vanadium-titanium oxide catalyst promotes its activity (figure 3). The three-component V-Ti-Zr-oxide contact exceeds the binary V-Ti-oxide catalyst in its catalytic activity in the β-picoline oxidation which is appeared in an increase in the conversion of the initial compound, the yield of nicotinic acid and a decrease in the optimum temperature of its formation.

For a theoretical interpretation of the experimentally obtained information on the promoting effect of oxide modifiers, we carried out quantum chemical calculations using the cluster approximation. The active centers of the surface of the used catalysts were modeled by clusters containing fragments of V_2O_5, TiO_2, SnO_2, Cr_2O_3 and ZrO_2 (table). We proceeded from the idea [3] that various forms of active oxygen are present on the surface of vanadium oxide catalysts, including vanadyl oxygen which participate in the separation of the proton of the oxidizing methyl group at the initial stages of the process.

Optimization of the listed clusters geometry in the tables and the calculation of the total energy values of the initial $E_{initial}$ and protonated E_{fin} structures were carried out using the DFT quantum chemical method (Density Functional Theory) [4] with a two-exponential LanL2DZ basic set with an effective core potential. The calculations were performed by the licensed program "Gaussian 09W", version D.01.

Histogram (figure 4) shows an increase in the nucleophilicity (proton affinity, $PA_{V=O}$) of vanadyl oxygen in the series of studied catalysts in partial oxidation of β-picoline: V_2O_5 <V_2O_5-TiO_2 < V_2O_5-TiO_2-SnO_2 < V_2O_5-TiO_2-Cr_2O_3 < V_2O_5-TiO_2-ZrO_2. Experiments have shown that in the same sequence the catalytic
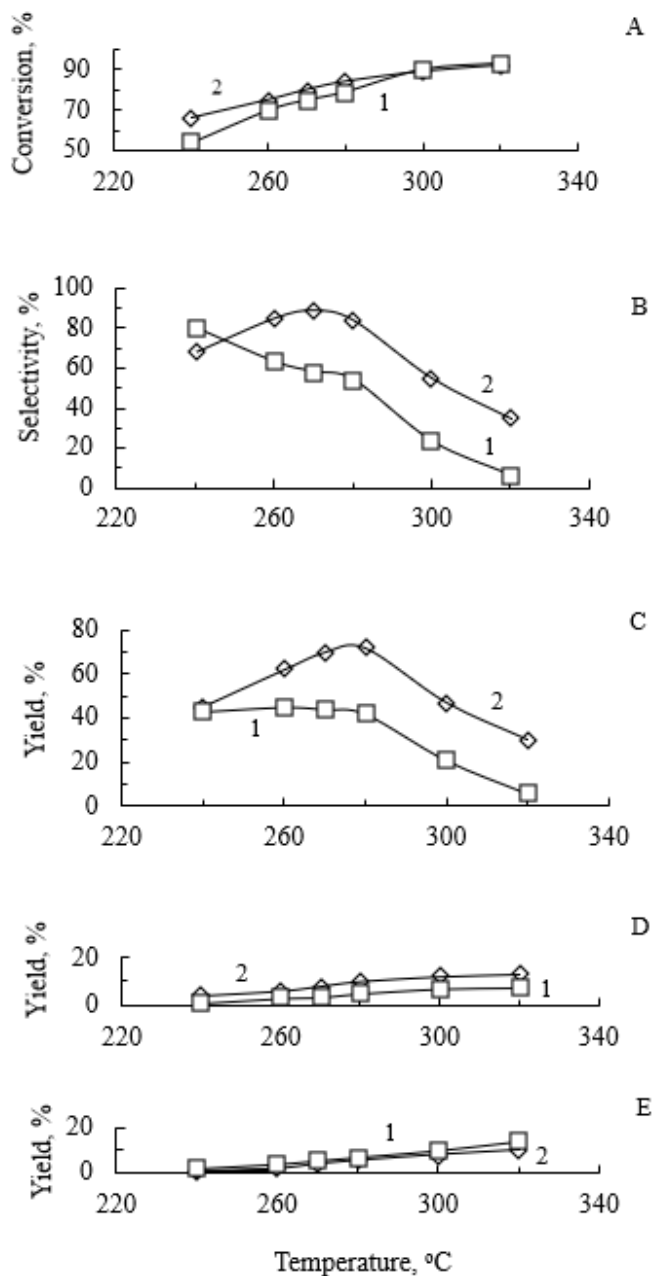
The feed rate of β-picoline is 37.8 g per 1 liter of catalyst per hour.
The molar ratio of β-picoline:O_2:H_2O = 1:7:85. Designation: A - β-picoline conversion;
B, C - selectivity of formation and yield of nicotinic acid; yield: D - pyridine, E - CO_2.

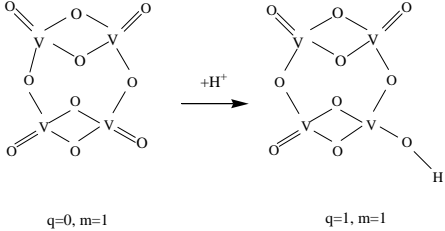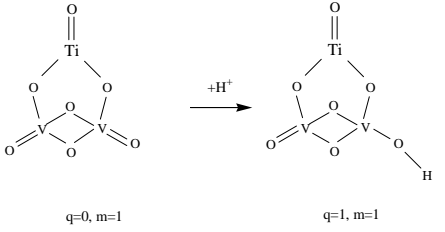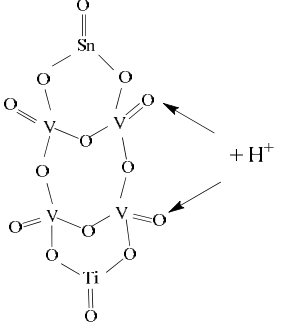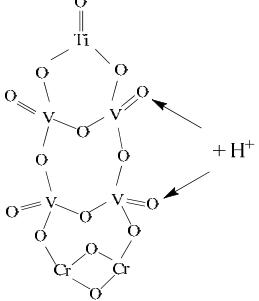Figure 2 − The effect of temperature on the yield
of β-picoline oxidation products over (1) $V_2O_5 \cdot TiO_2$; (2) $V_2O_5 \cdot TiO_2 \cdot Cr_2O_3$ catalysts
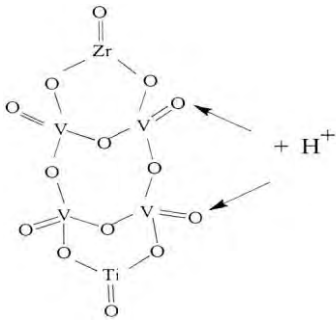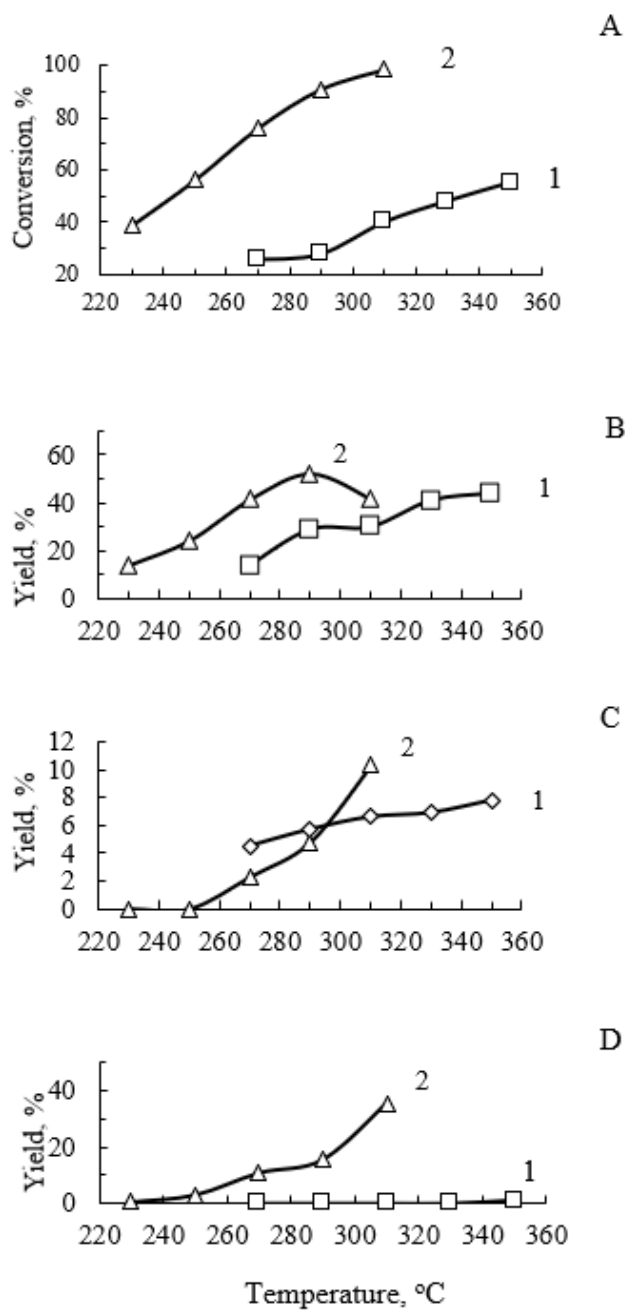
The feed rate of β-picoline 36 g per 1 liter of catalyst per hour.
The molar ratio β-picoline:O_2:H_2O = 1:25:115.

Figure 3 − The effect of temperature on (A) the conversion of β-picoline,
(B) the yield of nicotinic acid, (C) pyridine and (D) CO_2
under oxidation conditions over (1) V-Ti-O and (2) V-Ti-Zr-O catalysts

The total energies of vanadium-containing clusters and their protonated forms (E_{total}),
the affinity for the proton of oxygen bound to the vanadium ion ($PA_{V=O}$),
calculated by the DFT method (B3LYP / LanL2DZ)

Reaction	$-E_{total}$, a.u.		$PA_{V=O}$[1], kJ·mol^{-1}
	initial state	final state	
[structure: dimeric vanadium-oxygen cluster, q=0, m=1 → +H⁺ → protonated form q=1, m=1 with OH]	1038,1701913	1038,458359	756,6
[structure: Ti-containing vanadium-oxygen cluster, q=0, m=1 → +H⁺ → q=1, m=1 with OH]	727,7636779	728,0689935	801,6
[structure: Sn and Ti containing vanadium-oxygen cluster + H⁺]	1400,87024	1401,18833	**835,1**
		1401,16991	786,8
[structure: Ti and Cr containing vanadium-oxygen cluster + H⁺]	1645,2941769	1645,6212657	858,8
		1645,6283228	**877,3**

	1444,2396955	1444,5640152 851,5 1444,5829975 **901,3**

Note. $1 - PA = (E_{initial} - E_{final}) \cdot 2625,46.$
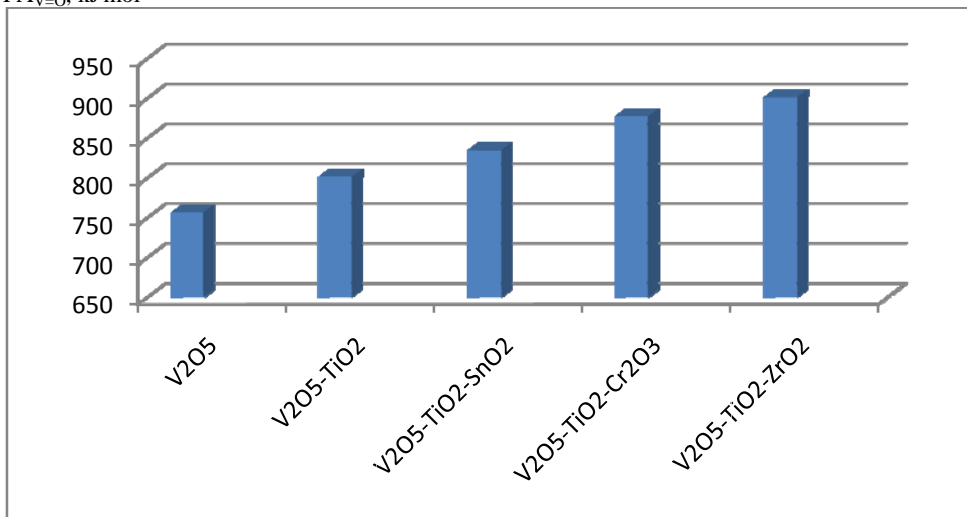
$PA_{V=O}$, kJ·mol^{-1}

Figure 4 − Proton affinity to vanadyl oxygen ($PA_{V=O}$) of a catalyst
from individual vanadium pentoxide, binary and ternary catalysts

activity increases, assessed by the conversion of the initial material and the yield of nicotinic acid.

It is noteworthy that a significant increase in $PA_{V=O}$ and, accordingly, an improvement in the catalytic properties (figure 1-3) in the transition from indivi-dual vanadium pentoxide and binary V-Ti oxide contact to ternary oxide systems. The observed pattern may be due to a synergistic effect [5].

Figure 5 shows the test results for V-, V-Ti- and V-Ti-Sn-oxide catalysts under comparable conditions in the vapor-phase oxidation of γ-picoline. It can be noted that in the performed experiments, the V-Ti-O and V-Ti-Sn-O contacts in their catalytic activity in the vapor-phase oxidation of γ-picoline are better than
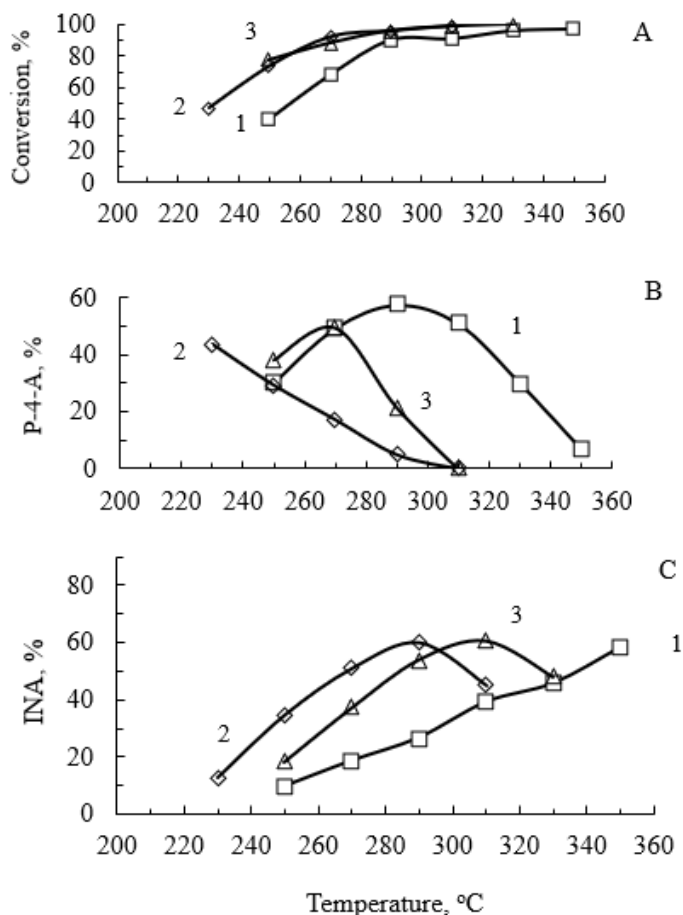
The feed rate of γ-picoline 36 g per 1 liter of catalyst per hour.
The molar ratio of γ-picoline:O_2:H_2O = 1:14:110. The designation of the curves (catalysts):
1 - V_2O_5, 2 - V_2O_5·8TiO_2, 3 - V_2O_5·8TiO_2·8SnO_2.

Figure 5 − The effect of temperature on (A) the conversion of γ-picoline,
(B) the yield of pyridine-4-carbaldehyde and (C) isonicotinic acid
under oxidation conditions over vanadium oxide catalysts of different composition

V_2O_5. It can be seen that pyridine-4-aldehyde is formed least of all on the binary V-Ti-O catalyst, and the addition of tin dioxide to the catalyst increases its amount in the reaction products. The highest yield of isonicotinic acid on all three catalysts was 60%: at 350°C over vanadium pentoxide, at 290°C over V-Ti-O, and at 310°C over V-Ti-Sn-O catalysts.

From the earlier obtained data analysis of the γ-picoline vapor-phase oxidation over binary V_2O_5·4TiO_2 and 2V_2O_5·Cr_2O_3 catalysts, it follows that in this reaction, the binary vanadium – titanium oxide contact showed a higher catalytic activity than the vanadium-chromium oxide. These data are consistent with the

results of quantum-chemical calculations in the cluster approximation, which showed that the vanadium-titanium cluster is characterized by a higher affinity for the proton (nucleophilicity) of vanadyl oxygen responsible for the deprotonation of the oxidizing methyl group of the substrate. It can be considered by the higher degree of γ-picoline conversion and the shift of the maxima of the pyridine-4-carbaldehyde and isonicotinic acid yield to lower temperatures, compared with the binary vanadium-chromium oxide contact.

Comparison of the results of the γ-picoline partial oxidation over the $V_2O_5 \cdot 4TiO_2$ binary catalyst and the $2V_2O_5 \cdot 4TiO_2 \cdot Cr_2O_3$ ternary catalyst showed that with simultaneous modifying of vanadium pentoxide with titanium (IV) and chromium (III) oxides, a synergistic effect was observed [5], in a significant increase in the yield of isonicotinic acid and a decrease in the optimum temperature of its formation in the case of a three-component catalyst (figure 6).

Modification of the $V_2O_5 \cdot 4TiO_2$ binary system by adding zirconium dioxide (figure 7) leads to an increase in γ-picoline conversion, a decrease in the yield of intermediate pyridine-4-carbaldehyde, obviously, as a result of an increase in its
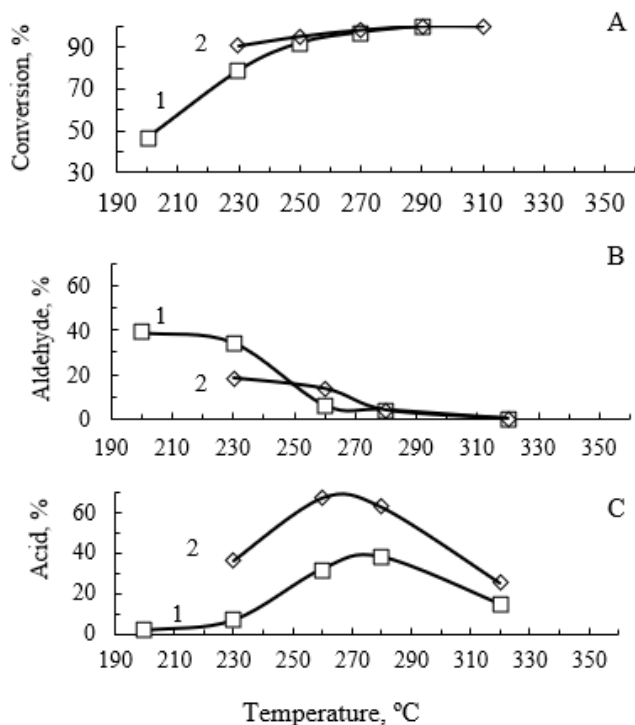
The feed rate of γ-picoline is 28.6 g per 1 liter of catalyst per hour.
The molar ratio of γ-picoline:O_2:H_2O=1:18,3:123. Designation of curves, %:
A - γ-picoline conversion, yield: B - pyridine-4-carbaldehyde, C - isonicotinic acid.

Figure 6 − The effect of temperature on the oxidation of γ-picoline
on catalysts $V_2O_5 \cdot 4TiO_2$ (1) and $2V_2O_5 \cdot 4TiO_2 \cdot Cr_2O_3$ (2)
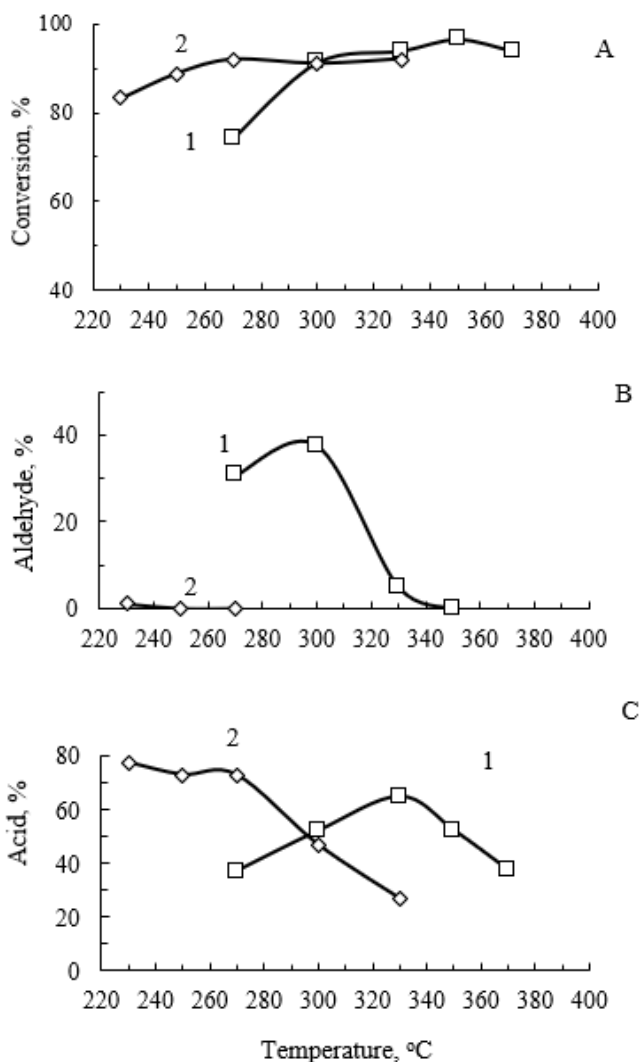
The feed rate of γ-picoline 36 g per 1 liter of catalyst per hour.
The molar ratio of γ-picoline:O_2:H_2O=1:13:25,5.

Figure 7 − The effect of temperature on (A) the conversion of γ-picoline,
(B) the yield of pyridine-4-carbaldehyde and (C) isonicotinic acid
under oxidation conditions over (1) $V_2O_5 \cdot 4TiO_2$ and (2) $V_2O_5 \cdot 4TiO_2 \cdot 4ZrO_2$ catalysts

conversion rate to isonicotinic acid. As a result of promotion, the yield of acid over the ternary V-Ti-Zr-oxide catalyst increases significantly, and its maximum shifts to lower temperatures. All this indicates the presence of a synergistic effect [5] as a result of the simultaneous addition of titanium dioxide and zirconium dioxide to vanadium pentoxide.

EXPERIMENTAL

The initial methylpyridines after drying and distillation had characteristics that correspond to an individual substance (β-picoline – b.p. $140^\circ/692$ mmHg, $d_4^{20} = 0.9568$, $n_D^{20} = 1.5050$; γ- picoline – b.p. $141^\circ/695$ mmHg, $d_4^{20} = 0.9547$, $n_D^{20} = 1.5058$ [6].

As initial components of catalysts, we used «*pure for analysis*» vanadium pentoxide and oxides of titanium, tin, chromium, and zirconium. The initial oxides with the desired molar ratio were ground in a porcelain mortar to form a homogeneous mixture, which was then pressed into tablets with a diameter of 15 mm and a thickness of 3-4 mm and calcined at 640°C for 4 hours. After cooling, the tablets were crushed into grains of a size of 3-5 mm.

Oxidation of β- and γ-picolines was carried out on a continuous installation with a 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. Unreacted β- and γ-picolines and reaction products were captured with water in an air-lift scrubber and analyzed by gas-liquid chromatography. Pyridinecarboxylic acids were detected by «pH-150MI» pH-meter and titration with 0.035 M KOH.

The products of deep oxidation were analyzed by the 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_2 - polysorb-1 (0.16-0.20 mm). The temperature of the column thermostat was 40°C.

REFERENCES

[1] Sembaev D.Kh., Saurambaeva L.I., Venerable V.M. Effect of SnO_2 on the formation of the phase composition and catalytic properties of a vanadium-titanium catalyst // News of the Academy of Sciences of Kazakhstan. Chemical Ser. 1992. N 5. P. 49-55.

[2] Saurambaeva L.I., Sembayev D.Kh., Kasymbekova Z.K., Agashkin O.V. About the role of SnO_2 in the formation of the catalytic properties of the V_2O_5-TiO_2 system in the oxidative ammonolysis of β-picoline // News of the Academy of Sciences of Kazakhstan. Chemical Ser. 1993. N 5. P. 56-61.

[3] Margolis L.Ya. Oxidation of hydrocarbons on heterogeneous catalysts. M.: Chemistry, 1977. 328 p.

[4] Koch W., Holthausen M.C. Chemist's Guide to Density Functional Theory / Ed. 2. Weinheim: Wiley-VCH, 2001. 293 p.

[5] Tretyakov V.F., Ilolov A.M., Talyshinsky R.M. Synergies in crystallization, catalysis, chemical and biological induction // Dokl. Academy of Sciences of the Republic of Tajikistan. 2009. Vol. 52, N 10. P. 789-792.

[6] Reference of a chemist. Vol. II. L.−M.: Chemistry, 1964. 1168 p.

Резюме

П. Б. Воробьев, Т. П. Михайловская, О. К. Югай,
А. П. Серебрянская, Р. Құрмақызы, А. И. Иманғазы

β- ЖӘНЕ γ- ПИКОЛИНДЕРДІҢ ТОТЫҒУЫНДА ВАНАДИЙ ТИТАН
ОКСИДТІК КАТАЛИЗАТОРЛАРДЫҢ ПРОМОТОРЛАУ ТУРАЛЫ

Қалайы (IV), хром (III) және цирконий (IV) оксидтерін бинарлы V-Ti - оксидтік жүйесіне қосу барысында β- және γ-пиколиндердің парциалды тотығу реакциясы кезіндегі промоторлық әсері зерттелді. Зерттелген оксидті жүйелердің каталитика-лық белсенділігі мен тотығатын метилді орынбасарларды депротонизациялауға қатысатын олардың бетіндегі ванадилді оттегінің протонына туыстық шамалары арасында корреляция орнатылды. Ванадий пентоксидіне (IV) титан оксидін және промоторлы оксидтердің біреуін бір мезгілде қосу кезіндегі синергетикалық әсердің болу мүмкіндігі туралы гипотеза айтылды.

Түйін сөздер: тотығу, β-пиколин, γ-пиколин, никотин қышқылы, изоникотин қышқылы, катализаторлар, промоторлеу.

Резюме

П. Б. Воробьев, Т. П. Михайловская, О. К. Югай,
А. П. Серебрянская, Р. Курмакызы, А. И. Имангазы

О ПРОМОТИРОВАНИИ ВАНАДИЙТИТАНОКСИДНОГО КАТАЛИЗАТОРА
ОКИСЛЕНИЯ β- И γ-ПИКОЛИНОВ

Исследовано промотирующее действие добавок оксидов олова (IV), хрома (III) и циркония (IV) к бинарной V-Ti-оксидной системе в реакции парциального окисле-ния β- и γ-пиколинов. Установлена корреляция между каталитической активностью изученных оксидных систем и величинами сродства к протону ванадильного кис-лорода их поверхности, участвующего в депротонировании окисляющихся метиль-ных заместителей. Высказана гипотеза о возможности синергического эффекта при одновременном добавлении к пентоксиду ванадия оксида титана (IV) и одного из оксидов-промоторов.

Ключевые слова: окисление, β-пиколин, γ-пиколин, никотиновая кислота, изоникотиновая кислота, катализаторы, промотирование.