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P. B. VOROBYEV, T. P. MIKHAILOVSKAYA, K. A. KADIRBEKOV, R. KURMAKYZY

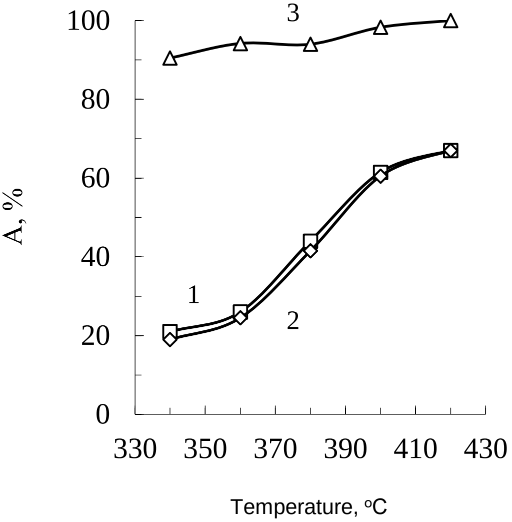
JSC «A.B. Bekturov Institute of Chemical Sciences», Almaty, Republic of Kazakhstan

OXIDATIVE AMMONOLYSIS OF β- AND γ-PICOLINE ON MODIFIED VANADIUM-TITANIUM OXIDE CATALYSTS

Abstract. The modifying effect of chromium (III), tin (IV) and iron (III) oxide additives to the binary V-Ti-oxide system in the reaction of oxidative ammonolysis of β- and γ-picolines was investigated. Relation of the studied oxide systems catalytic activity on the calculated values of proton affinity for the vanadyl oxygen of their surface, which is involved in the deprotonation of methyl substituents converted to a nitrile group, has been established.

Keywords: β-picoline, γ-picoline, oxidative ammonolysis, nicotinonitrile, isonicotinonitrile, catalysts, modification.

As it is known, a binary V-Ti-oxide catalyst [1] differs from individual vanadium pentoxide by higher thermal stability and has high selectivity in oxidative ammonolysis processes of β- and γ-picolines. The disadvantage of this catalyst is its low activity. Figure 1 shows the experiment results on the oxidative ammonolysis of β-picoline on a two-component catalyst with the following composition $V_2O_5 \cdot 16TiO_2$. It was established that this contact is characterized by 90-100% selectivity in a wide temperature range, but the maximum yield of 3-cyanpyridine is only 67% and is reached at 420 °C.

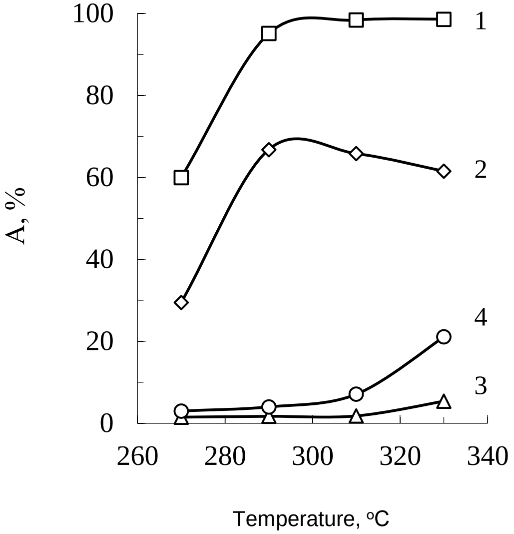


The feed rate of *β*-picoline is 30 g per 1 liter of catalyst in hour.
The molar ratio β-picoline: O_2:NH_3:H_2O = 1:25:9:52.

Figure 1 – Relation of в-picoline conversion (1), yield (2), and selectivity of nicotinic acid nitrile formation (3) on temperature under the conditions of oxidative ammonolysis of в-picoline on $V_2O_5 \cdot 16TiO_2$ catalyst

The aim of this work was to modify the binary V-Ti-oxide catalyst by the additives of the third oxide component to obtain ternary oxide systems and study their catalytic properties in the oxidative ammonolysis process of в- and г-picolines.

So, the V-Ti-oxide binary system was modified by the additives of chromium (III) oxide. Oxidative ammonolysis of в-picoline was studied on a sample of the catalyst with $V_2O_5 \cdot 2TiO_2 \cdot 0,5Cr_2O_3$ composition by feeding 37.3 g of the initial substance per 1 liter of catalyst per hour, at 270-350 єC and a molar ratio of в-picoline:O_2:NH_3:H_2O = 1:(15-30):(7.5-15):(100-150). In this process vanadium oxide catalyst modified by titanium and chromium oxides of this composition showed high activity (figure 2). The conversion of в-picoline already at 290 єC is 95.1%. The maximum yield of nicotinonitrile in 65% is achieved at 290-310 єC. At the same time, if temperature increases up to 330 єC, the yield of pyridine increases to 5%, and the yield of carbon dioxide to 21%.



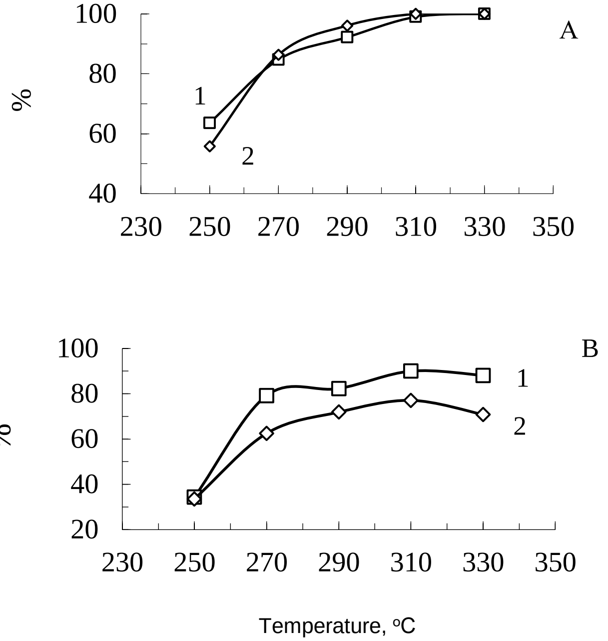
The feed rate of β-picoline is 37.3 g per 1 liter of catalyst in hour.
The molar ratio β-picoline:O_2:NH_3:H_2O = 1:30:7,5:100.

Figure 2 – Relation of в-picoline conversion (1), yield of nicotinic acid nitrile (2), pyridine (3) and CO_2 (4) on temperature of oxidative ammonolysis of в-picoline on $V_2O_5 \cdot 2TiO_2 \cdot 0,5Cr_2O_3$ catalyst

It must be assumed that improving three-component V-Ti-Cr-oxide catalyst activity is associated with a change in the phase composition of the system, due to the ability of chromium (III) oxide to form a chemical compound (chromium orthovanadate) with vanadium pentoxide [2, 3] under heat treatment conditions.

The next modifying additive to V-Ti-oxide binary system was tin dioxide [4, 5]. Since water vapor additives are added to the reaction zone during the oxidative ammonolysis of methylpyridines on vanadium oxide catalysts, we studied the effect of water vapor on the oxidative ammonolysis of β-picoline on $V_2O_5 \cdot 4TiO_2 \cdot 8SnO_2$ catalyst.

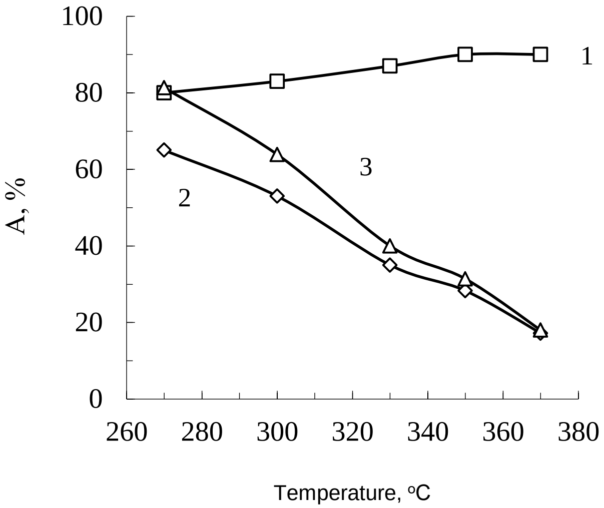
As it is seen from figure 3, the introduction of 8.7 moles of water into the reaction zone at a molar ratio of β-picoline:O_2:NH_3=1:40:5 is accompanied by decrease in the yield of 3-cyanpyridine from 90% to 75%. Comparison of the results in figures 1 and 3 shows that the modification of V-Ti-oxide binary catalyst with tin dioxide causes a significant increase in catalytic activity, which is appeared in an increase in β-picoline conversion, 3-cyanopyridine yield and a decrease in the optimal temperature process by 100 °C.



The feed rate of *β*-picoline is 27.3 g per 1 liter of catalyst in hour.
The molar ratio β-picoline:O_2:H_2O = 1:40:5. Water mol/mol: 1 – 0; 2 – 8,7.

Figure 3 – The effect of water on the conversion of β-picoline (A) and yield nitrile nicotinic acid (B) under oxidative ammonolysis conditions β-picoline over $V_2O_5 \cdot 4TiO_2 \cdot 8SnO_2$ catalyst

A three-component oxide $V_2O_5 \cdot 4TiO_2 \cdot 0{,}5Fe_2O_3$ system, which was tested in the reaction of oxidative ammonolysis of в-picoline, was synthesized by modifying the V-Ti-oxide binary catalyst with the addition of iron (III) oxide (figure 4). It was found that the three-component catalyst turned out to be more active than the two-component one (figure 1), and even at 270 °C the conversion of the initial substance was 80%, and the yield of 3-cyanpyridine – 65% (selectivity 81%). Further temperature increase led to a decrease in the yield of nicotinonitrile and the selectivity of its formation, apparently as a result of an increase in the proportion of destructive oxidation processes.



The feed rate of β-picoline is 35 g per 1 liter of catalyst in hour.
The molar ratio β-picoline:O_2:NH_3:H_2O = 1:14:6:26. A, %:
1 - β-picoline conversion; 2 - yield of 3 cyanpyridine, 3 - selectivity of 3 cyanpyridine formation

Figure 4 − The effect of temperature on oxidative ammonolysis of β-picoline on $V_2O_5 \cdot 4TiO_2 \cdot 0{,}5Fe_2O_3$ catalyst

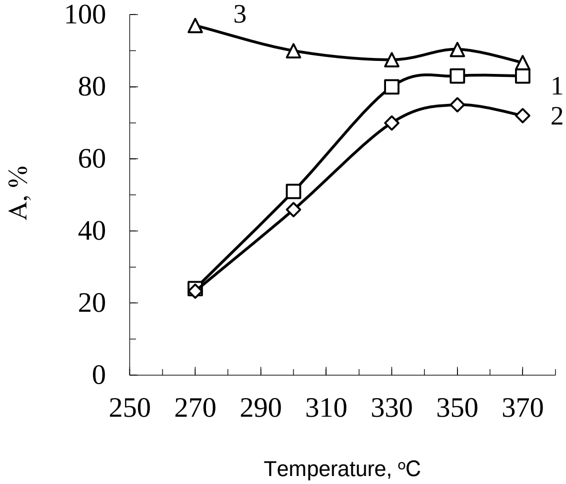
Thus, as a result of the study, it was found that the additives of chromium (III), tin (IV) and iron (III) oxides to the V-Ti-oxide binary catalyst has a promoting effect that leads to catalytic activity increase under conditions of oxidative ammonolysis of β- picoline.

The binary catalyst with the $V_2O_5 \cdot 8TiO_2$ composition and ternary oxide systems obtained by its modification were studied in the process of oxidative ammonolysis of γ-picoline. On a two-component catalyst (figure 5), the degree of conversion of the initial substance (83%), yield (75%), and selectivity of the target 4-cyanopyridine formation (90.4%) are acceptable from a practical point of view only at 350 ºC.

In the process of oxidative ammonolysis of г-picoline, a modified catalyst with the $V_2O_5 \cdot 2TiO_2 \cdot 0{,}5Cr_2O_3$ composition was tested (figure 6). This contact was characterized by higher activity in comparison with a two-component catalyst.

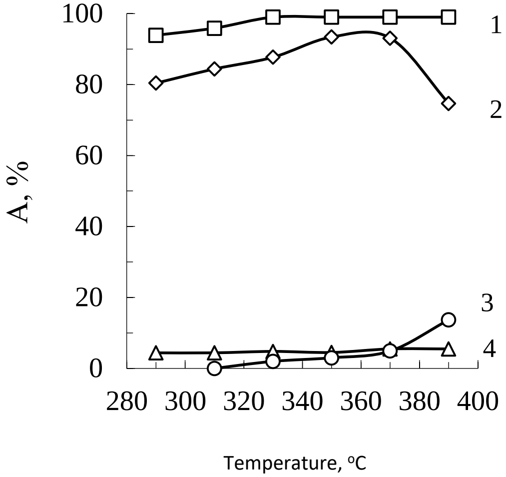
Already at 290 °C the conversion of the initial substance exceeded 90%. The highest yield of isonicotinic acid nitrile was 93.4% and was reached at 350-370 °C and a molar ratio of γ-picoline:O_2:NH_3 = 1:30:7,5.

Modification of the V-Ti-oxide binary system by adding tin dioxide leads to a sharp increase in the activity of the catalyst in the reaction of oxidative ammonolysis of γ-picoline.



The feed rate of γ-picoline is 35 g per 1 liter of catalyst in hour.
The molar ratio initial substance: O_2:NH_3:H_2O = 1:14:6:26,4.

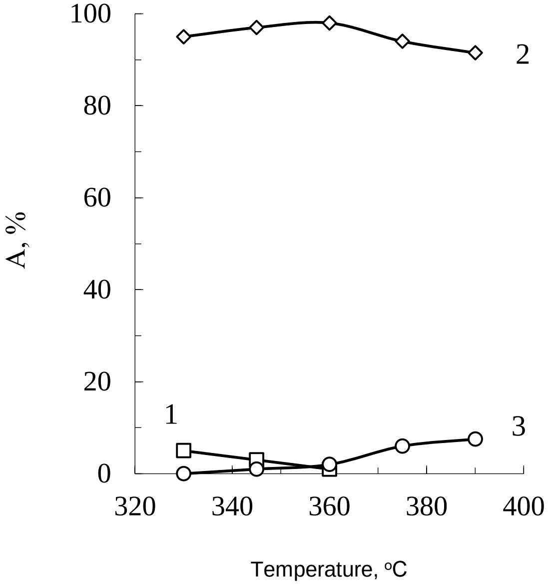
Figure 5 – Relation of γ -picoline conversion (1), yield (2), and selectivity of 4-cyanpyridine formation (3) on temperature of oxidative ammonolysis of γ -picoline on $V_2O_5 \cdot 8TiO_2$ catalyst



The feed rate of γ-picoline is 37.3 g per 1 liter of catalyst in hour.
The molar ratio of γ-picoline:O_2:NH_3 =1:30:7,5.

Figure 6 – Relation of γ-picoline conversion (1), yield of isonicotinic acid nitrile (2), pyridine (3) and CO_2 (4) on temperature of oxidative ammonolysis of γ-picoline on $V_2O_5 \cdot 2TiO_2 \cdot 0{,}5Cr_2O_3$ catalyst

The three-component catalyst with the $V_2O_5 \cdot 8TiO_2 \cdot 8SnO_2$ composition is characterized by high conversion of the initial substance (95% at 330 °C) when loading 117.2 g of γ-picoline per 1 liter of catalyst in hour (figure 7).



The feed rate of γ-picoline is 117.2 g per 1 liter of catalyst in hour.
The molar ratio of γ-picoline: O_2:NH_3:H_2O = 1:15:5:5.

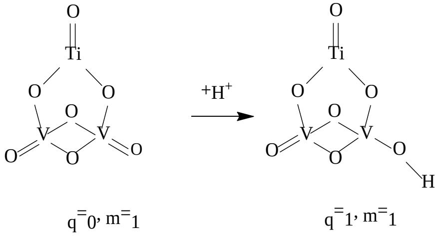
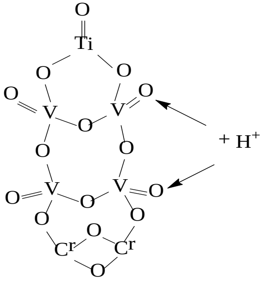
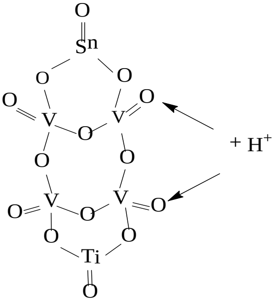
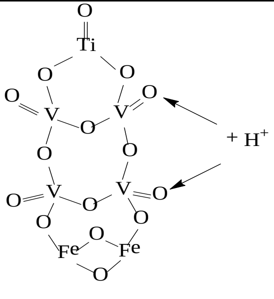
Figure 7 − Relation of the yield of unreacted γ-picoline (1), yield of nicotinic acid nitrile (2), and CO_2 (4) on temperature under conditions of oxidative ammonolysis on $V_2O_5 \cdot 8TiO_2 \cdot 8SnO_2$ catalyst

One of the reasons for the observed synergistic effect [6] as a result of the simultaneous promoting effect of titanium (IV) oxide and one of the chromium (III), tin (IV) or iron (III) oxides on the catalytic activity of the modified vanadium oxide contact may be an increase under their influence of nucleophilicity vanadyl oxygen involved in the separation of the proton from the oxidizable methyl substituent. It is generally accepted that activity and selectivity of vanadium oxide catalysts for hydrocarbon oxidation is associated with the presence of various forms of oxygen bound to vanadium on the surface of the catalyst, with doubly bound vanadium oxygen lattice (V = O) plays an important role [7].

To verify this assumption, we made quantum chemical calculations in cluster approximation. The active catalysts sites were modeled by clusters containing fragments of vanadium pentoxide, titanium oxide (IV), and modifying oxides (table).

According to the calculation results given in the table, when passing from V-Ti-oxide binary system to V–Ti–Cr-, V–Ti–Sn- and V–Ti–Fe-oxide triple systems, the affinity for the proton of vanadyl oxygen of the catalyst surface sharply

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],
	Initial cluster	Protonated cluster	kJ·mol^{-1}
	727,7636779	728,0689935	801,6
	1645,2941769	1645,6212657	858,8
		1645,6283228	877,3
	1400,87024	1401,18833	835,1
		1401,16991	786,8
	1719,4881230	1719,812782	852,4
		1719,8158258	860,4
Note. [1] $PA_{V=O} = (E_{initial} - E_{protonated}) \cdot 2625{,}46$.			

increases ($PA_{V=O}$), under the influence of which the proton of the oxidizing methyl substituent of the chemisorbed substrate molecules is detached at the initial stages of oxidative ammonolysis, which supports the hypothesis of a synergistic effect. It should be noted that the results of theoretical calculations are consistent with the experimental data presented in the article on the relative activity of the studied catalysts in the processes of oxidative ammonolysis of β- and γ-picolines.

EXPERIMENTAL PART

The initial methylpyridines after drying and distillation had characteristics that correspond to an individual substance (β-picoline – b.p. 140°/692 mmHg, d_4^{20}=0,9568, n_D^{20}=1,5050; γ- picoline – b.p. 141 °/695 mmHg, d_4^{20}=0,9547, n_D^{20}=1,5058) [8].

As initial components of catalysts, we used «pure for analysis» vanadium pentoxide and oxides of titanium (IV), tin (IV), chromium (III), and iron (III). 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.

Oxidative ammonolysis of β- and γ-picolines was carried out on a continuous action 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 products of partial oxidative ammonolysis were captured with water in an air-lift scrubber and analyzed by gas-liquid chromatography.

The products of deep oxidation were captured 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.

To optimize the geometry and calculate the total energy of the clusters modeling the active centers of the catalysts, we used the exchange-correlation B3LYP density functional method and two-exponential Lanl2DZ basis set with an effective core potential [9]. The calculations were carried out in the Born-Oppenheimer approximation using the Gaussian 09W”, version D.01.

REFERENCES

[1] Suvorov B.V., Sembaev D.Kh., Kagarlitsky A.D., Kolodina I.S., Loyko A.I., Bukeikhanov N.R. et al. Oxide catalyst for the oxidation and oxidative ammonolysis of organic compounds // Bulletin of the Academy of Sciences of the Kazakh SSR. 1974. N 10. P. 16-23.

[2] Pletnev R.N., Gubanov V.A., Fotiev A.A. NMR in vanadium oxide compounds. M.: Nauka, 1979. 128 p.

[3] Cheshnitsky S.M., Fotiev A.A., Surat L.L. Phase relations in the V_2O_5 – Cr_2O_3 system // Zh. non-organ. chemistry. 1984. Vol. 29, N 10. P. 2699-2701.

[4] Sembaev D.Kh., Saurambaeva L.I., Pochtennaya 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. № 5. P. 49-55.

[5] 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.

[6] Golodov V.A. Synergistic phenomena in catalysis // Russian Chemical Journal. 2000. Vol. XLIV, N 3. P. 45-57.

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

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

[9] Koch W., Holthausen M. C. A Chemist’s Guide to Density Functional Theory. Ed. 2. Weinheim: Wiley-VCH, 2001. P. 293.

Резюме

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

β - ЖӘНЕ γ -ПИКОЛИНДЕРДІҢ ТОТЫҒУ АММОНОЛИЗІНІҢ ВАНАДИЙ-ТИТАН ОКСИДТІК КАТАЛИЗАТОРЫН МОДИФИКАЦИЯЛАУ ТУРАЛЫ

β- және γ-пиколиндердің тотығу аммонолиз реакциясындағы бинарлық V-Ti-оксиді жүйесіне хром (III), қалайы (IV) және темір (III) оксидтерін қосудың модификациялық әсері зерттелді. Зерттелетін оксиді жүйелерінің каталитикалық белсенділігінің нитрилді топқа айналатын метил алмастырғыштарының депрототандануына қатысатын олардың бетіндегі ванадилді оттегі протонына есептелген жақындығына тәуелділігі анықталды.

Түйін сөздер: β-пиколин, γ-пиколин, тотықтырғыш аммонолиз, никотинонитрил, изоникотинонитрил, катализаторлар, модификациялау.

Резюме

П.Б. Воробьев, Т.П. Михайловская, К.А. Кадирбеков, Р. Курмакызы

О МОДИФИЦИРОВАНИИ ВАНАДИЙ-ТИТАНОКСИДНОГО КАТАЛИЗАТОРА ОКИСЛИТЕЛЬНОГО АММОНОЛИЗА β- И γ-ПИКОЛИНОВ

Исследовано модифицирующее действие добавок оксидов хрома (III), олова (IV) и железа (III) к бинарной V-Ti-оксидной системе в реакции окислительного аммонолиза β- и γ-пиколинов. Установлена зависимость каталитической активности изученных оксидных систем от расчетных величин сродства к протону ванадильного кислорода их поверхности, участвующего в депротонировании метильных заместителей, превращающихся в нитрильную группу.

Ключевые слова: β-пиколин, γ-пиколин, окислительный аммонолиз, никотинонитрил, изоникотинонитрил, катализаторы, модифицирование.