Studies on the conditions of synthesis of picolinic acid by heterogeneous catalytic oxidation of 2-picoline

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Heterogeneous oxidation of 2-picoline over binary P–Ti, Sb–Ti, P–Sb, and V–Ti oxide catalysts was studied over the temperature range of 200–300 °C. The vanadium–titanium catalysts based on titanium dioxide (anatase) were found to be the most selective for picolinic acid. With binary catalysts containing 20–50% of vanadium pentoxide, the selectivity for picolinic acid was 19–22% at the 36–74% conversion of 2-picoline. A distinguishing feature of these catalysts is regular surface stacking of V_2O_5 and TiO_2 crystallites.

Keywords: heterogeneous oxidation, 2-picoline, picolinic acid, vanadium–titanium oxide catalysts

1. Introduction

The products of partial oxidation of 2-picoline – 2-pyridinecarbaldehyde and picolinic acid – are valuable vitamins, feedstocks for synthesis of physiologically active substances, dyes, and other synthetic chemicals. A sufficiently effective method for synthesis of the aldehyde is heterogeneous catalytic oxidation of 2-picoline over vanadium-containing oxide catalysts containing oxides of titanium, phosphorus, or molybdenum as the second component [1–3]. Picolinic acid is produced by liquid-phase oxidation of 2-picoline [4].

Several papers deal with the heterogeneous catalytic oxidation of 2-picoline [5,6]. Vanadium-based systems, viz. vanadium oxide on pumice, vanadium–tin and vanadium–titanium based on the rutile modification of titanium oxide, were used as the catalysts. The experimental temperature ranged between 300 and 400 °C. The reaction products were 2-pyridinecarbaldehyde, pyridine, CO_2, CO, picolinic acid, 2-pyridoin and HCN. Picolinic acid was mainly produced with a selectivity not higher than 4% by consecutive transformation of 2-pyridinecarbaldehyde. The reason for such a low selectivity is a high rate of the acid decarboxylation at over-ambient temperatures. Intentional experiments showed that the high rate of the decarboxylation was attained under not only heterogeneous but also homogeneous conditions [5].

Numerous papers are devoted to the discussion of the data on behavior of isomeric picolines in the reactions of heterogeneous catalytic oxidation and oxidative ammonolysis [7–10]. The authors of these papers emphasize a higher reactivity of 2-picoline and a lower stability of the reaction products.

Conditions of synthesis of nicotinic acid, which also undergoes decarboxylation at above-ambient temperatures, were studied by us earlier. The reaction of formation of 3-pyridinecarbaldehyde followed by its conversion to nicotinic acid was shown to proceed in a rather effective way over vanadium–titanium oxide catalysts based on the anatase modification of titanium dioxide at 250–270 °C [11,12].

Taking into account the above-said, we studied a feasibility of synthesis of picolinic acid by catalytic oxidation of 2-picoline at temperatures below 300 °C. Catalysts based on constituents of the known catalysts for oxidation of 2-picoline to 2-pyridinecarbaldehyde, as well as vanadium–titanium systems effective for oxidation of 3-picoline to nicotinic acid were used for the studies.

2. Experimental

Vanadium–titanium oxide catalysts were prepared according to the procedure given elsewhere [12]. Titanium–antimony oxide catalysts were prepared by co-precipitating titanium tetrachloride and antimony pentachloride from the solutions under the action of ammonia [13]. A phosphorus–antimony sample was prepared by mixing antimony trioxide with phosphoric acid followed by oxidation with hydrogen peroxide, drying, and thermal treatment at 450 °C for 4 h [14]. A phosphorus–titanium sample was produced by mixing a suspension of titanium dioxide hydroxide with phosphoric acid followed by drying and thermal treatment at 450 °C for 4 h.

The catalyst compositions, temperatures of thermal treatments and specific surface areas are summarized in table 1.

Catalytic properties were determined for a 0.25–0.50 mm fraction using a circulating flow installation with a gradientless reactor. The experimental conditions were as follows: reaction temperature was 200–300 °C, contact time 0.4–5.9 s, inlet concentrations of components (vol%): 0.7 of 2-picoline, 20.0 of oxygen, 25.0 of water, 54.3 of nitrogen.

Chromatographic and NMR techniques were used for analysis of the starting 2-picoline (Pic) and the reac-

Table 1
Characterization of catalysts.

Chemical composition (wt%)	Calcination temperature (°C)	Specific surface area (m^2/g)	Phase composition
3 P_2O_5–97 Sb_2O_5	450	35	Amorphous
4 P_2O_5–96 TiO_2	450	30	Anatase, rutile, P_2O_5 traces
7 Sb_2O_5–93 TiO_2	750	30	Solid solution Sb_2O_5 into rutile
50 Sb_2O_5–50 TiO_2	750	25	$TiSb_2O_6$
100 TiO_2	450	300	Anatase
10 V_2O_5–90 TiO_2 [V–Ti(10/90)]	450	230	Anatase
20 V_2O_5–80 TiO_2 [V–Ti(20/80)]	450	27	V_2O_5 + anatase
50 V_2O_5–50 TiO_2 [V–Ti(50/50)]	450	27	V_2O_5 + anatase

Table 2
Oxidation of 2-picoline over various oxide catalysts.

Catalyst composition (wt%)	T (°C)	τ (s)	X (%)	S (%)				$W \times 10^{10}$ (mol/m^2 s)
				PA	Ald	Pyr	CO_2	
3 P_2O_5–97 Sb_2O_5	300	2.4	6.1	–	83.5	7.3	9.2	6.3
4 P_2O_5–96 TiO_2	250	0.7	2.0	–	47.0	–	53.0	7.2
7 Sb_2O_5–93 TiO_2	230	4.0	13.4	–	19.0	60.0	21.0	5.2
50 Sb_2O_5–50 TiO_2	230	3.0	8.8	–	45.0	47.3	7.7	5.1
20 V_2O_5–80 TiO_2	230	0.4	5.3	–	81.0	10.0	9.0	19.2

tion products: 2-pyridinecarbaldehyde (Ald), picolinic acid (PA), pyridine (Pyr), 2-pyridinol (P-ol), 2-pyridoin (PK), CO_2.

Chromatographic analysis was carried out using a chromatograph Tsvet-500 equipped with heat conduction and flame ionization detectors. A column filled with Porapak Q was used for analysis of 2-picoline, 2-pyridinecarbaldehyde, pyridine, and CO_2. A column filled by Carbowax 6000 was used for analysis of picolinic acid and pyridinol.

NMR spectroscopy was used for determination of 2-pyridoin. ^{13}C NMR spectra were recorded using a MSL-400 spectrometer (Bruker) at 100.6 MHz. The solution (acetone, 298 K) to be analyzed contained the tautomeric en-1,2-diol form of 2-pyridoin, which gives the lines (δ, ppm) at 157.11 (α-C), 147.05 (α-CH), 139.23 (γ-CH), 136.47 (OC=CO), 122.93 (β-CH), 120.20 (β-CH) in the $^{13}C\{^1H\}$ NMR spectra. The concentration of 2-pyridoin was found by comparing integral intensities of these lines to those of 2-picoline at 158.92 (α-C), 149.31 (α-CH), 138.29 (γ-CH), 124.71 (β-CH), 122.23 (β-CH), 24.04 (CH_3).

3. Results and discussion

Table 2 shows the data on oxidation of 2-picoline at a conversion of up to 15% over catalysts of various chemical compositions. The reaction products in this experiment were 2-pyridinecarbaldehyde, pyridine and CO_2. No formation of picolinic acid was observed with all of the examined catalysts. The only product which held the carbon atoms in its side chain was 2-pyridinecarbaldehyde. The phosphorus–antimony and vanadium–titanium catalysts revealed the highest selectivity to the aldehyde. Since the phosphorus–antimony catalyst was active at as high temperature as 300 °C but picolinic acid is unstable at this temperature, the vanadium–titanium system was chosen as the most promising one for studying conditions of the synthesis of picolinic acid.

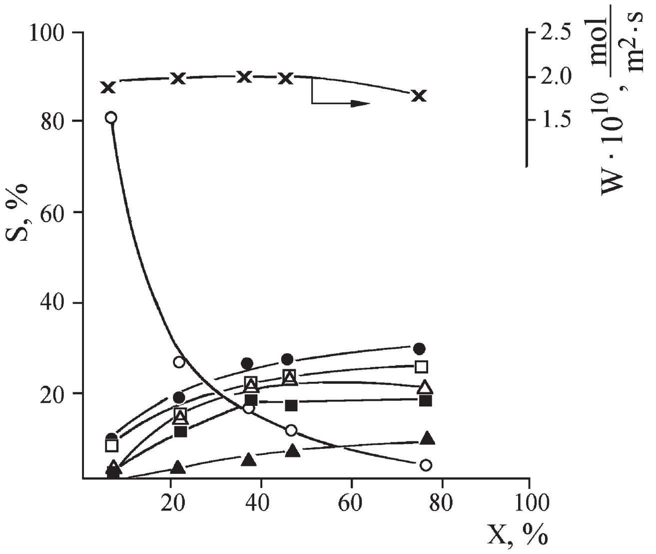


Figure 1. Rate of oxidation of 2-picoline (×) and selectivities for picolinic acid (△), 2-pyridinecarbaldehyde (○), pyridine (●), 2-pyridinol (▲), 2-pyridoin (■) and CO_2 (□) versus conversion of 2-picoline. V–Ti(20/80). $T = 230$ °C.

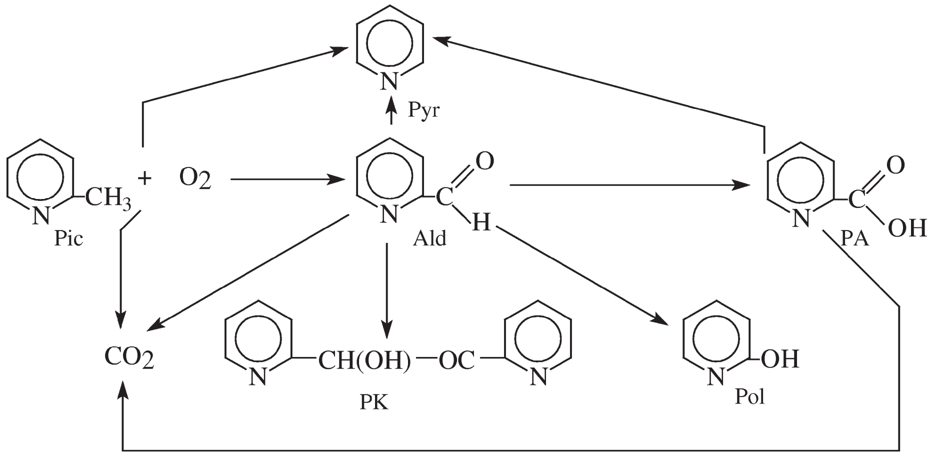
The rate of conversion of 2-picoline and selectivities to the reaction products vs. conversion are plotted in figure 1 for the V–Ti(20/80) catalyst. The aldehyde predominates among the products formed by parallel routes; the selectivity to the aldehyde decreases sharply (from 80 to 3%) as the conversion increases from 5 to 74%. Consecutive transformations of the aldehyde yield picolinic acid, 2-pyridinol, destruction products (pyridine and CO_2), and the condensation product (2-pyridoin). An increase in the conversion results in a corresponding increase in selectivities to these products. The selectivity to picolinic acid is 22–19% at the conversion ranging between 36 and 74%. The rate of conversion of 2-picoline varies only slightly over a wide range of conversion.

Table 3 presents results of examination of vanadium–titanium samples in the oxidation of 2-picoline. The catalytic properties are seen to be strongly influenced by the chemical composition of the catalysts.

The formation of a large quantity of destruction products and 2-pyridoin is observed in the presence of individual titanium dioxide, while the selectivity to the aldehyde is about 5%. Introduction of vanadium pentoxide in an amount of 10% results in an increase by an order of magnitude in the rate of oxidation of 2-picoline at a low selec-

Table 3
Oxidation of 2-picoline over vanadium–titanium oxide catalysts.

Catalyst composition	T	τ	X	S (%)						$W \times 10^{10}$
(wt%)	(°C)	(s)	(%)	PA	Ald	Pyr	CO_2	P-ol	PK	(mol/m^2 s)
100 TiO_2	230	3.4	17.0	–	4.1	24.6	16.3	tr.	55.0	0.7
	245	3.4	26.8	–	5.7	30.1	20.1	tr.	44.1	1.0
10 V_2O_5–90 TiO_2	200	2.1	73.2	7.5	1.1	5.0	11.5	tr.	76.9	6.2
	230	0.5	31.0	4.5	8.0	30.3	19.8	tr.	37.4	10.5
	230	1.1	60.5	4.7	1.3	35.0	21.1	tr.	38.9	10.0
20 V_2O_5–80 TiO_2	230	0.4	5.3	–	81.0	10.0	9.0	tr.	–	19.2
	230	2.9	36.5	22.0	15.8	25.4	18.9	3.0	14.9	20.0
	230	3.2	45.9	22.0	12.0	26.0	20.0	7.0	13.0	20.0
	230	5.9	73.6	19.0	2.1	27.8	24.0	10.0	17.0	17.5
	245	2.9	52.1	22.9	8.8	28.5	25.3	6.0	8.5	27.0
50 V_2O_5–50 TiO_2	230	2.0	31.9	19.5	16.6	19.6	11.7	3.0	29.6	19.3
	245	2.0	46.2	18.5	16.8	13.2	18.4	4.0	29.0	27.3
	260	2.0	51.9	21.4	13.0	14.4	23.1	8.0	20.0	32.0



Scheme 1.

tivity to the products of partial oxidation. An augmentation of the concentration of vanadium pentoxide to 20% favors the increase in activities and selectivities to the aldehyde and picolinic acid, a crucial decrease in the quantity of the condensation product and additional formation of pyridinol being observed. The further introduction of vanadium pentoxide to 50% does not change the activity and selectivity to the products of partial oxidation but results in a decrease of the ratio of the amounts of destruction products to the condensation product. With all the examined catalysts, an elevation of the reaction temperature by 15–30 °C does not influence the selectivities to the products of partial oxidation but changes the reaction route towards the formation of the destruction products thus decreasing the yield of the condensation product.

In accordance with the experimental data, oxidation of 2-picoline over the vanadium–titanium oxide catalysts may be shown schematically as in scheme 1. 2-pyridinecarbaldehyde is produced by the parallel route, and picolinic acid by the consecutive route. Some overoxidation of picolinic acid is observed.

The destruction products, pyridine and CO_2, are formed by both parallel and consecutive routes. 2-pyridoin is a product of the aldehyde condensation and is also formed by the consecutive route. The contribution of this route depends on the catalyst composition. A small quantity of 2-pyridoin is produced over the V–Ti(20/80) catalyst, but it becomes much higher over the catalyst V–Ti(50/50). With individual titanium dioxide and the catalyst V–Ti(10/90) 2-pyridoin is the main reaction product.

Individual titanium dioxide (anatase) reveals a low selectivity and activity to the oxidation of 2-picoline. However, it must be noticed that its activity to this reaction is higher than that observed for oxidation of 3-picoline [12]. Such a behavior seems to be a natural result, since 2-picoline is a stronger base than 3-picoline, and superacidic Lewis acid sites occur at the anatase surface [15]. The acid–base interaction results in formation of the products of destruction and condensation.

From the literature data, individual vanadium pentoxide reveals a low selectivity to partial oxidation of 2-picoline; it is suggested as a catalyst for dealkylation of 2-picoline to pyridine [16,17].

Physicochemical properties of the binary vanadium–titanium system based on the anatase modification of titanium dioxide are described in [12]. From XRD data, the

V_2O_5 phase was only observed in the samples containing 20 wt% or more of vanadium pentoxide which were subjected to thermal treatment at 450 °C. EM studies [12,18] of the binary samples with less than 20% of V_2O_5 showed highly dispersed TiO_2 crystallites and associates of vanadium pentoxide arranged randomly with respect to one another. As to binary samples characterized as two-phase (V_2O_5 + anatase) systems, there was observed an interaction between anatase and V_2O_5, i.e., a regular arrangement and stacking of their crystallographic lattices within a thin boundary layer.

The results obtained in the present work reveal that two-phase samples, where the interaction of the crystallites occurs, are more active and selective, compared to the other samples of the vanadium–titanium system, to formation of 2-pyridinecarbaldehyde and to consecutive transformation of the aldehyde to picolinic acid. The higher activity and selectivity to the products of partial oxidation may result from a variation in the oxygen state induced by the interaction of anatase crystallites with V_2O_5. A lower energy of the oxygen bond and a higher mobility of oxygen were shown [19] for the sample V–Ti(20/80) against the individual oxides. Since, according to the literature data [20], the formation of the products of partial oxidation of 2-picoline in the presence of vanadium-containing catalysts involves the oxygen of the catalyst lattice, such a change in the oxygen state in binary vanadium–titanium catalysts may be a reason for the increase in the yield of partial oxidation products.

Therefore, binary vanadium–titanium catalysts containing 20–50% of vanadium pentoxide and titanium dioxide (anatase) are more effective against the other known catalysts and allow for picolinic acid to be produced with the selectivity of 19–22% at a conversion ranging between 36 and 74% under the conditions of heterogeneous oxidation of 2-picoline at 230–260 °C.

References

[1] Patent 936871 (BDR) (1957).

[2] L.Y. Leitis and M.V. Shimanskaya, Chem. Heterocycl. Comp. 3 (1967) 507.

[3] M.V. Shimanskaya, Y.F. Ozis and L.Ya. Leitis, *Uspekhi Geterogennogo Kataliza v Kcimii Geteroziklicheskikh Soedinenii* (Zinatne Press, Riga, 1984).

[4] Yu.I. Chumakov, *Pyridine Bases* (Tekhnika Press, Kiev, 1965).

[5] S. Jaras and S.T. Lundin, J. Appl. Chem. Biotechnol. 27 (1977) 499.

[6] S.K. Bhattacharyya, V. Shankar and A.K. Kar, Ind. Eng. Chem. Prod. Res. Dev. 5 (1966) 65.

[7] S.L.T. Andersson and S. Jaras, J. Catal. 64 (1980) 51.

[8] L.Ya. Leitis, M.V. Shimanskaya and V.A. Slavinskaya, Izv. Akad. Nauk Latv. SSR, Ser. Khim. 6 (1968) 1061.

[9] I.I. Kan, A.D. Kagarlickii and B.V. Suvorov, Izv. Akad. Nauk Kaz. SSR, Ser. Khim. 3 (1974) 57.

[10] B.V. Suvorov, L.K. Glubokovskikh, I.I. Kan, T.P. Tolmacheva and V.V. Demin, Zh. Priklad. Khim. 51 (1988) 180.

[11] WO 95/20577 (03.08.95).

[12] E.M. Al'kaeva, T.V. Andrushkevich, G.A. Zenkovets, G.N. Kryukova, S.V. Tsybulya and E.B. Burgina, in: *3rd World Congress on Oxidation Catalysis*, Stud. Surf. Sci. Catal., Vol. 110 (Elsevier, Amsterdam, 1997) p. 939.

[13] I.P. Olenkova, G.A. Zenkovets and D.V. Tarasova, Izv. Akad. Nauk SSSR, Neorg. Mater. 13 (1977) 383.

[14] G.A. Zenkovets and D.V. Tarasova, Izv. Sib. Otdel. Akad. Nauk SSSR, Ser. Khim. 5 (1984) 56.

[15] G.A. Zenkovets, A.M. Volodin, A.F. Bedilo, E.B. Burgina and E.M. Al'kaeva, Kinet. Katal. 38 (1997) 73.

[16] B.V. Suvorov, L.K. Glubokovskikh and I.I. Kan, Zurn. Prikl. Chim. 53 (1980) 2519.

[17] USSR Inventor's Certificate 578310, published B.I. 40 (1977).

[18] G.N. Kryukova, D.O. Klenov and G.A. Zenkovets, React. Kinet. Catal. Lett. 60 (1997) 179.

[19] V.M. Bondareva, T.V. Andrushkevich and Y.D. Pankratiev, React. Kinet. Catal. Lett. 61 (1997) 337.

[20] M. Shimanskaya, L. Leitis, R. Skolmeistere, I. Iovel and L. Golender, *Vanadia Catalysts for the Oxidation of Heterocyclic Compounds* (Zinatne Press, Riga, 1990).