after emulsifying it with air by passage through centrifuge-like equipment similar to yeast separators. No air compressors are required because the centrifuge sucks the necessary air. All the wort passes through the aerator every 25 minutes. Jonas claims that only 20 horsepower are needed to provide enough air for 13,200 gallons of wort.

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# **CATALYTIC VAPOR-PHASE OXIDATION OF Picolines over** Vanadate Catalysts

## **ROBERT W. LEWIS<sup>1</sup> AND OLIVER W. BROWN**

THE purpose of this investigation was to study the vaporphase oxidation of the picolines over vanadate catalysts in an effort to determine the most favorable conditions for obtaining the pyridine carboxylic acids. The production of these acids by vapor-phase catalytic methods has not been reported previously.  $\beta$ -Picoline has received most attention in this study since its partial oxidation product, nicotinic acid, is of considerable importance.

The vanadates have been useful as catalysts in the oxidation of various organic compounds. In 1928 Maxted and Dunsby (3) oxidized several nitro and halogen derivatives of toluene to the corresponding benzoic acids over tin vanadate. Later Maxted (2) oxidized benzaldehyde, benzyl alcohol, and a number of

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aromatic hydrocarbons over bismuth and tin vanadates. Bismuth vanadate was also used as a catalyst in the oxidation of furfural to maleic anhydride by Milas and Walsh ( $\delta$ ). Kiprianov and Shostak (1) used bismuth, tin, and silver vanadates in the oxidation of benzene to maleic anhydride. Sulfur dioxide was also oxidized to sulfur trioxide over several vanadate catalysts by Neumann (6) and Maxted (4).

In this study the vanadates of five representative metals from different families of the periodic table were used as catalysts. From the results obtained a comparison of the catalytic activities of these various vanadates can be made.

Figure 1 is a diagram of the reaction chamber. Air was the oxidizing agent in all cases and was taken from a compressed air line. The rate of flow of air was measured by a differential level

The vapor-phase oxidation of beta-picoline over five metallic vanadate catalysts was studied. Alpha- and gamma-picolines were oxidized over the most efficient catalyst. Favorable working conditions of each catalyst were determined by studying the effect of temperature, ratio of reactants, and velocity of reactants over the catalyst. The best results were obtained over a tin vanadate catalyst which gave 22.6% nicotinic acid at 275° C., with a 9 to 1 mole ratio of oxygen to beta-picoline.

flowmeter. After passing through a 12-inch column of anhydrous calcium chloride, the air passed through a preheater maintained at a temperature slightly lower than that of the reaction chamber, and then into the reaction chamber. The picoline was forced from a glass reservoir into the reaction chamber by means of compressed air. This air line contained an open-end manometer for measuring the pressure. By this procedure a constant flow of liquid from the reservoir could be maintained. The entering hot air vaporized the liquid and prevented formation of drops and fluctuations in liquid feed. The reaction chamber was heated electrically and the temperature was measured by a thermocouple. The catalyst bed, which was usually 1 inch and never more than 2 inches deep, rested directly on top of the thermocouple. The reaction temperatures of a number of runs were also measured by a thermometer embedded in the catalyst. Results closely comparable to these reported were obtained. The pyridine carboxylic acids were collected in two sublimation chambers connected in series. The exit gases then passed through two water-cooled spiral condensers to the carbon dioxide absorption train. In all experiments the 3/4-inch-diameter reaction chamber was fitted with a Pyrex liner (inside diameter, 16 mm.). In runs carried out without the glass liner, a loose scale of iron oxide formed inside the 3/4-inch iron pipe which served as the reacti n chamber. The purpose of this glass liner was to prevent these oxides of iron from affecting the action of the catalysts. A 6-inch column of pumice which had previously been boiled in concentrated hydrochloric acid was placed in the reaction chamber above the catalyst to serve as a gas preheater and distributor.

Reilly Tar & Chemical Corporation furnished the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -picolines. Each of these picolines was dried over freshly roasted calcium oxide and fractionated. Fractions with 0.5° C. boiling ranges were used in all experiments.

## PROCEDURE AND ANALYTIC METHOD

When a run was to be made, the temperature was adjusted and air was started through the furnace at the desired rate. A measured volume of picoline was delivered into the reservoir from a calibrated pipet, and sufficient pressure was placed on the reservoir to force the liquid through the capillary at the desired rate. Since the heat of reaction was considerable, it was necessary to effect some cooling. Experience showed that the temperature could be controlled fairly closely  $(\pm 3^{\circ} \text{ C}.)$  by directing a small electric fan toward the furnace during the course of the reaction. The exit gases from the reactor were passed through the carbon dioxide absorption train during the run and for 5 minutes thereafter. This time was sufficient to flush all carbon dioxide from the reactor. The furnace was flushed with air at least an hour before the sublimation chambers were removed. During this time all the solid products were removed from the furnace and the water from the reaction was evaporated from the condensers. The evaporation of this water was necessary since the small

amounts of dissolved carbon dioxide which it contained caused errors in the subsequent titration of the pyridine carboxylic acids.

After the flushing period was finished, the solid products were washed from the condensers and sublimation chambers with nearly boiling distilled water. The pyridine carboxylic acids formed were, in most cases, white. A melting point of 233° to 234° C. for the nicotinic acid and the fact that it did not lower the melting point of c.p. nicotinic acid indicated that the product was reasonably pure. In cases where the reaction was carried out below the most favorable temperature, the product was slightly discolored by the unchanged picoline. When the temperature was too high, the product was white but less abundant.



Figure 1. Reaction Chamber

The yields of pyridine carboxylic acids were estimated by titration with 0.05-0.10 N sodium hydroxide which had previously been standardized against C.P. nicotinic acid. To determine the extent of complete oxidation, the quantity of carbon dioxide in the exit gas was determined. In the carbon dioxide absorption train magnesium perchlorate was the dehydrating agent and ascarite was used to remove carbon dioxide. Precautions necessary in the combustion analysis of nitrogen containing organic compounds were taken. Since in most experiments pyridine carboxylic acid equivalent to 15-30 ml. of 0.05 N sodium hydroxide and 1.3-1.8 grams of carbon dioxide were formed, the yields could be determined fairly accurately. Oxidations carried out under identical conditions gave closely comparable results. The results reported are the average of at least two runs.

## PREPARATION OF CATALYSTS

The vanadate catalysts were prepared in as nearly the same manner as possible. When the physical form of the catalyst permitted, no support was used. A celite support was used in cases where the vanadate was extremely fine and would not adhere on molding. The catalysts were not subjected to preliminary heat treatment. The reagents used in the preparations were c.p. grade.

TIN VANADATE. A solution of 12 grams of anhydrous stannic chloride in 200 cc. of distilled water was added to a solution of 20 grams of ammonium metavanadate in 500 cc. of hot distilled water until precipitation was complete. The red precipitate was washed by decantation with about 20 liters of distilled water, filtered, and dried at 100° C. Catalyst of 10-20 mesh size was used.

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0.80 8	, p-pre	onne pass	sed per run	volume	or catalyst	, 5.08 cc. 0	r 0.0~0.2 g
Run No.	Temp., ° C.	Air, % of Theory for Nicotinic Acid <sup>a</sup>	Mole Ratio. O2/ <i>β</i> -Picoline	<i>b</i> -Picoline, Grams/Hr.	Nicotinic Acid, % of Theory	CO2, % of Theory (by Com- plete Oxidation)	Nicotinic Acid, % Based on <i>β</i> - Picoline Oxidized
$1 \\ 2 \\ 3 \\ 4$	$247 \\ 265 \\ 275 \\ 290$	600 600 600 600	9 9 9	$1.86 \\ $	$7.8 \\ 11.4 \\ 14.0 \\ 9.8$	$\begin{array}{c} 49.0 \\ 52.5 \\ 55.3 \\ 76.0 \end{array}$	$13.7 \\ 17.8 \\ 20.2 \\ 11.4$
5 6 7 8 9	$275 \\ 275 $	500 550 600 650 700	$7.5 \\ 8.25 \\ 9 \\ 9.75 \\ 10.5$	$1.86 \\ 1.86 \\ 1.86 \\ 1.86 \\ 1.86 \\ 1.86 \\ 1.86 $	$11.2 \\ 12.0 \\ 14.0 \\ 12.2 \\ 11.7$	$54 \\ 55.3 \\ 51.5 \\ 40.0$	$18.2 \\ 20.2 \\ 19.1 \\ 22.6$
$10 \\ 11 \\ 12 \\ 13$	$275 \\ 275 $	600 600 600 600	8 8 8 8	$3.72 \\ 1.86 \\ 1.24 \\ 0.93$	$1.0 \\ 14.3 \\ 18.2 \\ 12.0$	55.0 6 <b>3</b> .2	20.7 22.2
a Dr	y <b>a</b> ir c	onsidered	21% oxyge	n (by volu	ume).		

TABLE I. OXIDATION OF  $\beta$ -PICOLINE OVER TIN VANADATE (0.93 g.  $\beta$ -picoline passed per run; volume of catalyst, 5.08 cc. or 6.0-6.2 g.)

BARIUM VANADATE. Twenty grams of 10–20 mesh celite chips were placed in 100 cc. of saturated barium chloride solution. The solution was forced into the celite by repeatedly evacuating the system and allowing it to come to atmospheric pressure. Finally the solution was evaporated to dryness. The chips containing barium chloride were poured into a solution of 9.5 grams of ammonium metavanadate in 200 cc. of hot distilled water. The liquid and loose precipitate were poured off and the chips were dried at 100° C. The resulting catalyst consisted of 11% barium vanadate.

POTASSIUM VANADATE. Twenty grams of ammonium metavanadate were dissolved in 500 cc. of hot distilled water. The quantity of potassium hydroxide theoretically necessary to liberate the ammonia was added and the solution was boiled until ammonia could not be detected with litmus. Twenty grams of 10-20 mesh celite chips were added and the solution was evaporated to dryness. The resulting catalyst consisted of 44% potassium vanadate.

FERRIC VANADATE. A solution of 20 grams of ferric chloride in 100 cc. of distilled water was added to a solution of 28 grams of ammonium metavanadate in 600 cc. of hot distilled water. The resulting precipitate was washed by decantation with approximately 15 liters of distilled water, filtered, and dried at 100° C. Catalyst of 10-20 mesh size was placed in the furnace.

SILVER VANADATE. A solution of 12 grams of ammonium metavanadate in 300 cc. of hot distilled water was added to a solution of 14 grams of silver nitrate in 200 cc. of distilled water. The resulting precipitate was washed with approximately 20 liters of distilled water, filtered, and dried at 100° C. Catalyst of 10-20 mesh size was placed in the furnace.

#### **OXIDATION OF PICOLINES OVER TIN VANADATE**

The variables which are most important in a vapor-phase catalytic oxidation are temperature, ratio of reactants, and flow rate of reactants over the catalyst or contact time. A summary of these variables in the oxidation of  $\beta$ -picoline over tin vanadate is shown in Table I.

The yield of nicotinic acid based on picoline oxidized was calculated on the assumption that all  $\beta$ -picoline not oxidized to nicotinic acid or carbon dioxide remained unchanged. This assumption was necessary since unreacted picoline was not recovered. The yield of nicotinic acid obtained in a single pass (nicotinic acid, per cent of theory) was measured directly.

The results in Table I indicate that a temperature of  $275^{\circ}$  C. is most favorable for the production of nicotinic acid over tin vanadate. It is interesting to note that this temperature checks

closely with the temperature used by Maxted in the oxidation of a large group of organic compounds over tin vanadate.

The results of runs 5-9 of Table I indicate that 600% of the air theoretically necessary for the production of nicotinic acid gives the most favorable ratio of reactants and contact time under the conditions described. When the air is in excess of 600% of theory or in excess of a 9:1 mole ratio of oxygen to  $\beta$ -picoline, the yields of both nicotinic acid and carbon dioxide decrease. This behavior is contrary to what might be expected at first glance. However, increasing the ratio of air to  $\beta$ -picoline increased the space velocity or decreased the contact time, which probably accounts to a great extent for the smaller yields of oxidation products. The results of runs 10–13 (Table I) show the effect of contact time at constant air ratio to be significant. A further explanation for this decrease in oxidation products is a possible lowering of the effective (reaction zone) temperature because of the additional heat capacity of the flowing mixture relative to the heat generated by the reaction.

The results of runs 10–13 also show that 1.25 grams of picoline per hour with a 9:1 mole ratio of oxygen to  $\beta$ -picoline is the most favorable flow rate of picoline over this catalyst. The most favorable conditions found here for the production of nicotinic acid are listed for run 12.

The results obtained in the oxidation of  $\alpha$ - and  $\gamma$ -picolines over tin vanadate are summarized in Table II. Runs 1–6 show that

TA	BLE .	11. OXIDATIO	N OF $\alpha$ - AND $\gamma$ -Pi VANADATE	COLINE	S OVER	Tin
	(0.93 (	g, picoline passed	per run; volume of	catalys	t, 5.08 cc	»,)
Run No.	Temp., ° C.	Air, % of Theory for Picolinic Acid	Mole Ratio, O <sub>2</sub> /β-Picoline	Picoline, Grams/Hr.	α-Pyridine Car- boxylic Acid, % of Theory	y-Pyridine Car- boxylic Acid, % of Theory
1 2 3 4 5 6	$210 \\ 220 \\ 230 \\ 255 \\ 265 \\ 290$	600 600 600 600 600 600 600	9 9 9 9 9 9 9	$1.86 \\ $	$\dot{6.8}$ 16.9 18.8 14.7 13.0	4.9 8.5 8.5 10.5 8.9 7.5
7 8 9 10 11 12	$255 \\ 255 $	400 500 600 700 800 900	$\begin{array}{c} 6 \\ 7.5 \\ 9 \\ 10.5 \\ 12 \\ 13.5 \end{array}$	$1.86 \\ $	3.6 15.0 18.8 17.0 10.0	1.2 10.0 10.6 11.1 11.0
$13 \\ 14 \\ 15 \\ 16$	$255 \\ 255 $	$\begin{cases} 600 \text{ with } \alpha_{-}, \\ 900 \text{ with } \gamma_{-} \end{cases}$	$\left.\begin{array}{c} 9 \text{ with } \alpha^{-}, \\ 13.5 \text{ with } \gamma^{-} \end{array}\right\}$	$2.79 \\ 1.86 \\ 1.24 \\ 0.93$		
8 9 10 11 12 13 14 15 16 TABLE	255 255 255 255 255 255 255 255 255 255	$\begin{cases} 500 \\ 600 \\ 700 \\ 800 \\ 900 \\ \hline \\ 600 \text{ with } \alpha_{-1} \\ 900 \text{ with } \gamma_{-1} \\ \hline \\ Oxidation of the test of test $	$\begin{array}{c} 7.5 \\ 9 \\ 10.5 \\ 12 \\ 13.5 \\ 7 \\ 13.5 \text{ with } \alpha_{-7} \\ 13.5 \text{ with } \gamma_{-} \end{array}$	1.86 1.86 1.86 1.86 1.86 1.86 1.86 1.86	15.0 18.8 17.0 10.0 8.6 18.8 13.7 11.8	1 1 1 1

No.	Temp., ° C.	Air, % of Theory for Nicotinic Acid	Mole Ratio, O1/\$-Picoline	β-Picoline, Grams∕Hr.	Nicotinic Acid, % of Theory	CO2, % of Theory (by Complete Oxidation)	Nicotinic Acid, % Based on A- Picoline Oxidized
1 2 3 4 5 6 7	275 290 320 330 340 350 365	600 600 600 600 600 600 600	9 9 9 9 9 9	$1.86 \\ 1.86 \\ 1.86 \\ 1.86 \\ 1.86 \\ 1.85 \\ 1.85 \\ 1.86$	2.22.37.512.612.812.36.6	$\begin{array}{r} {\bf 33.0} \\ {\bf 43.2} \\ {\bf 57.0} \\ {\bf 60.1} \\ {\bf 62.0} \\ {\bf 64.2} \\ {\bf 65.0} \end{array}$	$\begin{array}{r} 6.2 \\ 5.1 \\ 11.6 \\ 17.3 \\ 17.1 \\ 16.1 \\ 9.2 \end{array}$
	340 340 340 340 340 340	300 500 600 700 800	$4.5 \\ 7.5 \\ 9 \\ 10.5 \\ 12$	1.86 1.86 1.86 1.86 1.86	$1.0 \\ 8.3 \\ 12.8 \\ 12.2 \\ 9.5$	$\begin{array}{r} {\bf 40.0} \\ {\bf 64.0} \\ {\bf 62.0} \\ {\bf 57.5} \\ {\bf 57.0} \end{array}$	$2.4 \\ 11.5 \\ 17.1 \\ 18.0 \\ 14.3 $
$13 \\ 14 \\ 15 \\ 16$	$340 \\ 340 $	600 600 600 600	9 9 9	$3.72 \\ 2.23 \\ 1.86 \\ 1.24$	$5.0 \\ 14.2 \\ 12.8 \\ 11.5 $	$47.0 \\ 55.0 \\ 62.0 \\ 70.0$	$9.6 \\ 20.5 \\ 17.1 \\ 14.1$

).93 g.	of <b>β</b> -1	picoline p	assed per n	un; volun	ne of cataly	/st, 10.2 cc	. or 6.6 g.)
Run No.	Temp., ° C.	Air, % of Theory for Nicotinic Acid	Mole Ratio, O₂/β-Picoline	<b>β-</b> Picoline, Grams/Hr.	Nicotinic Acid, % of Theory	CO2, % of Theory (by Complete Oxidation)	Nicotinic Acid, $\%$ Based on $\beta$ - Picoline Oxidized
$1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7$	290 317 335 340 353 365 380	600 600 600 600 600 600 600	9 9 9 9	1.861.861.861.861.861.861.861.86	Trace 1.1 2.4 2.5 4.5 9.8 9.5	$\begin{array}{r} 6.6\\ 15.2\\ 22.3\\ 24.1\\ 36.0\\ 57.0\\ 74.0 \end{array}$	6.7 9.7 9.4 11.1 14.6 10.2
	365 365 365 365 365	700 600 500 400 300	10.5 9 7.5 6 4.5	1.86 1.86 1.86 1.86 1.86 1.86	6.7 9.7 12.3 13.4 Trace	$\begin{array}{r} {48.0} \\ {57.4} \\ {58.0} \\ {70.0} \\ {68.0} \end{array}$	$12.3 \\ 14.5 \\ 17.5 \\ 16.1 \\ \dots$

TABLE IV. OXIDATION OF  $\beta$ -Picoline over Potassium VANADATE

TABLE V. OXIDATION OF B-PICOLINE OVER FERRIC VANADATE 0.93 g. of 8-picoline passed per run: volume of catalyst, 5.08 cc. or 1.4 g

	Brath Bra	Contract Learning	· · · · · · · · · · · · · · · · · · ·			,, 0.00	
Run No.	Temp., ° C.	Air, % of Theory for Nicotinic Acid	Mole Ratio, O <sub>2</sub> / <b>β-</b> Picoline	B-Picoline, Grams/Hr.	Nicotinic Acid, % of Theory	CO2, % of Theory (by Complete Oxidation)	Nicotinic Acid, % Based on <i>β</i> - Picoline Oxidized
$1 \\ 2 \\ 3 \\ 4$	260 280 300 320	600 600 600 600	9 9 9 9	$1.86 \\ 1.86 \\ 1.86 \\ 1.86 \\ 1.86 \\ 1.86 $	$1.2 \\ 4.3 \\ 6.8 \\ 7.8$	$8.0 \\ 17.1 \\ 27.4 \\ 51.4$	$13.0 \\ 20.1 \\ 19.9 \\ 13.2$
5 6 7 8 9	300 300 300 300 300 300	300 400 500 600 700	$4.5 \\ 6 \\ 7.5 \\ 9 \\ 10.5$	$1.86 \\ $	$3.0 \\ 4.2 \\ 7.0 \\ 6.8 \\ 4.7$	$\begin{array}{r} 44.0\\ 44.1\\ 39.7\\ 27.4\\ 16.8 \end{array}$	$\begin{array}{r} 6.4 \\ 8.7 \\ 14.9 \\ 19.9 \\ 21.9 \end{array}$

with  $\alpha$ - and  $\gamma$ -picolines the catalyst is active in the same temperature range as in the oxidation of the beta isomer. However, the optimum yields of picolinic acids were obtained at a slightly lower temperature. The need for a fairly large excess of air in this reaction is demonstrated. When the amount of air dropped to 400% in the case of  $\alpha$ -picoline and 500% in the case of  $\gamma$ -picoline (with contact times increased proportionately), the decreases in acid yields were extremely sharp.

The life of tin vanadate as a catalyst in this oxidation is not long; it is much longer-lived as a catalyst in the oxidation of toluene. In the oxidation of picoline a physical change takes place in the vanadate; it is much more finely divided and is covered with a black deposit when removed from the reaction chamber. Attempts to reactivate it by heating in a stream of air at 475° C. for 16–18 hours were unsuccessful. It is probable that the life of this catalyst might be lengthened by placing it on the proper support. The tin vanadate was much more active when first placed in the furnace. For example, 80-90% of the first 4-5 grams of  $\beta$ -picoline passed over the catalyst was oxidized to carbon dioxide and no nicotinic acid was detected. During the passage of the first 5-6 grams of picoline, the catalyst was gradually deactivated. The activity then remained rather constant while the next 25-30 grams of picoline were passed. The results in all the tables were taken while the activity of the catalyst was constant; i.e., a run made at the beginning of the study gave yields which correlated closely with the results of a run carried out under the same conditions at the close of the study.

#### OXIDATION OF $\beta$ -PICOLINE OVER BARIUM VANADATE

The results obtained in the oxidation of  $\beta$ -picoline over barium vanadate are given in Table III. Optimum yields of acid can be obtained over a fairly wide temperature range (runs 1-7). Although this is an advantage over tin vanadate, the yields of acid

per pass were considerably lower over barium vanadate. Increasing the ratio of air to picoline (runs 8-12) caused the yields of nicotinic acid to pass through a maximum. A low mole ratio of air to  $\beta$ -picoline with the proportionately longer contact time was favorable to carbon dioxide production and unfavorable to nicotinic acid production. As the ratio of air to  $\beta$ -picoline increased beyond 9 to 1 (with contact time decreased), the yields of both carbon dioxide and nicotinic acid decreased slightly, the decrease in acid becoming more apparent at a 12 to 1 ratio. Barium vanadate had at least 50% longer life than tin vanadate. After more than 40 grams of  $\beta$ -picoline had passed over the barium vanadate, the yields of nicotinic acid had decreased only slightly.

## OXIDATION OF $\beta$ -PICOLINE OVER POTASSIUM VANADATE

The results obtained in the oxidation of  $\beta$ -picoline over potassium vanadate are summarized in Table IV. A fairly high temperature is reached before potassium vanadate becomes active. The outstanding feature of this catalyst is its extremely short life. After about 18 grams of  $\beta$ -picoline have passed over it, the yields of acid and carbon dioxide had decreased to about 70% of the yields obtained after 5-10 grams of picoline had passed. For this reason the study was discontinued before the effect of flow rate of picoline was determined.

## **OXIDATION OF 8-PICOLINE OVER FERRIC VANADATE**

The results of the oxidation of  $\beta$ -picoline over ferric vanadate are shown in Table V. Ferric vanadate was the least efficient catalyst studied. Above 300° C. the nicotinic acid was very dark colored. For this reason the later runs were made at 300° C. Because of the unsuitable product and the low acid yields the study was discontinued before the effect of flow rate of reactants was determined.

## OXIDATION OF &-PICOLINE OVER SILVER VANADATE

The oxidation of  $\beta$ -picoline over silver vanadate was studied between 255° and 370° C, with an oxygen to  $\beta$ -picoline ratio of 1.5-10.5 to 1. Not more than 1-2% of nicotinic acid was produced in any experiment. At 350° C. and with a 9 to 1 oxygen to  $\beta$ -picoline ratio almost 70% of the picoline was completely oxidized. Less drastic conditions produced less carbon dioxide, but the acid yields did not increase appreciably. The silver vanadate was very light and porous but shrank considerably during use. A suitable support which would eliminate such shrinkage would probably make silver vanadate a more efficient catalyst.

### SUMMARY

This investigation showed that the vanadate catalysts described were too active to produce good yields of pyridine carboxylic acids. With tin vanadate, the best catalyst studied, 81.4% of the  $\beta$ -picoline passed was used up while only 18.2% was converted to nicotinic acid. Barium vanadate was slightly less active under the most favorable conditions found here, and the yield of nicotinic acid based on picoline oxidized compared favorably with the results obtained over tin vanadate. Each catalyst required a large mole ratio of air to picoline and short contact time for most favorable results. Each catalyst underwent a preliminary deactivation period while the first few grams of picoline were passed. The activities of the catalysts then remained constant for some time.

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