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Catalyzed Gas Phase Ammoxidation of 2, 3 and 4-picolines

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Summary

Catalyst gas phase ammoxidation of 2,3, and 4- picolines in a fixed bed reactor is described the catalyst applied composed of Vanadium (V) and tin (Sn) Oxides supported on Al_2O_3 as described in recent papers (1), (2). The effect of NH_3, O_2, contact time and temperature of the picoline mole ratios on the yield and conversion of the products was studied. The conversation and yield are in the rate of 2-picoline> 4-picoline > 3-picoline.

The applied catalyst was active even after 150 hours of reaction. The highest yield obtained of nicotinic acid was 90%, 88%, 87% 2-picoline, 4-picoline and 3-picoline respectively.

Key words: Catalyzed, Ammoxidation, 2,3,4 picolines ,NH3

امكسدة 3,2 و 4- بيكولين في الطور الغازي

راجحة اسماعيل خليل النعيمي
فرع الفسلجة والادوية – كلية الطب البيطري- جامعة بغداد – بغداد- العراق

الخلاصة

تمت دراسة تفاعلات الامكسدة 3,2 و 4- بيكولين في الطور الغازي في مفاعل ذو القاع الثابت. ان العامل المساعد المستخدم يتكون من اوكسيدي الفناديوم والقصدير ومحمول على اوكسيد الالمنيوم قد تم وصفه في بحوث سابقة (1),(2).
ان تاثير النسب المولية للامونيا والاوكسجين وزمن التماس ودرجة الحرارة الى البيكولين على ناتج الامكسدة ونواتج التفاعل الاخرى تمت دراسته وكانت نسبة التحويل 2- بيكولين >4-بيكولين> 3-بيكولين. واعلى نسبة للناتج من حامض النيكوتينك 90%, 88%, 87% ل 2- بيكولين, 4- بيكولين و 3- بيكولين على التوالي وكان العامل المساعد فعالا حتى بعد استخدامه 150 ساعة.

كلمات مفتاحية :- امكسدة , بيكولين, الامونيا.

Introduction

Ammoxidation is a valuable tool for one step synthesis of nitriles (3). The catalytic ammoxidation of hetroalkyl aromatics has been the subject of many patents (4, 5, and 6). Picolines consist of three structural isomers with methyl group at different positions from the nitrogen atom in their pyridine ring (7). The resulting nitriles are important intermediates to produce food industrial, pharmaceutical and petrochemical compounds such as nicotinamides, isonicotinamides and hydrazides (8). Both the conversion and the yield of the reaction depend on various factors such as the mole ratios of O_2, NH_3 and the pyridine derivatives in the reaction mixture, also the type of the catalyst, the reactor used and the temperature at which the reaction is curried out have influence to provide a catalyst with high yield and long life. Ammoxidation of 3- picoline over V2O5 / Ti O_2 showed a relationship between oxidation state of vanadium and ammoxidation activity (9- 12). A new structure of vanadium chromium composite oxide was reported (13). Incorporation of Sn to V_2O_5 / Al_2O_3 system make the catalyst more active and selective towards the formation of products in P-Xyline, O- Xyline and m- Xylines (1, 2).

Ammoxidation of isomeric picolines on Mo/PO catalyst with P/MO=1 was studied by (7, 14). Vanadium- modified zeolite, vanadium containing silico alumino phosphate were used as catalysts (15). The catalytic properties were influenced by chemisorptions of the reactants on the catalyst system (16). In this paper new results of using the catalyst described in earlier papers (1, 2), with development in the preparation technique for the ammoxidation of 2, 4 and 3- picolines to their corresponding nitriles with high yield, selectivity and long life for the catalyst, in an attempt to understand the influence of the methyl group position in the pyridine ring on the conversion of picoline isomers.

Materials and methods

The reactor used for the ammoxidation is the same as described in previous papers (1, 2). (Diag, 1). the same catalyst was applied to resulting reaction mixture was found to include picoline nitriles, amides, carboxylic acids and CO_2, CO, HCN. They were separated through fractional distillation under vacuum and estimated as raw products. Their identification was accomplished by IR spectroscopy, boiling point, melting point and refractive index.

The reactor consists of two Pyrex tubes with a side inlet for thermo couple to measure the temperature at different heights. The upper part is filled with glass severs used for preheating the reacting gasses. The lower tube consists of three different layers of glass, catalyst and glass respectively.

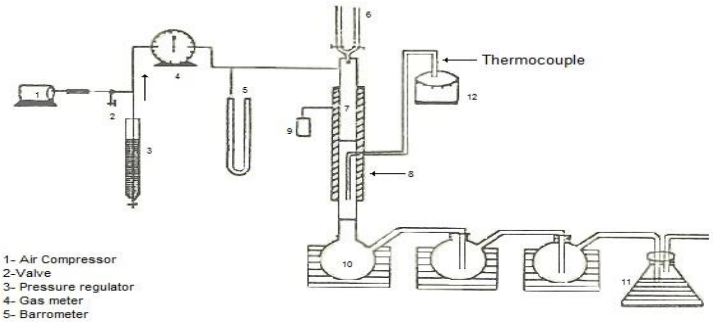


Diagram (1) Schematic Diagram of Ammoxidation Reactions devise used in the present work.

The catalyst is prepared from 40g NH_4VO_3 in 300ml water mixed with 120g of Sn $(NO_3)_2$ in 200 ml water. The PH was adjusted to be 10, the aqueous ammonia was added. The NH_4VO_3 suspension was stirred in a bath at 80-90° c for three hours. Water was removed by distillation using a rotary evaporator and the residue was placed in a drier at 120° c and dried. The product was calcinated at 900°c for 6 hours while passing air (17).

2, 3 and 4- picolines are supplied by Fluka Ac, Buchs, Switzerland. All the reactions are curried out using a self-build Pyrex reactor at the chemistry department, college of science, university of Baghdad.

Results and discussion

The ammoxidation of 2-, 3- and 4-picolines was carried out varying different conditions. These variations included the O_2/picoline, NH_3/picoline mole ratios, contact time and temperature. In each reaction run one parameter only was changed and the other kept constant

in order to determine its effect on the conversion and yield of the reaction. Since the reaction was highly exothermic, the system was cooled down to room temperature under a flow of pure nitrogen. A number of by products were formed such as CO, CO_2, and HCN in an addition to the main products. The obtained yield and conversion are listed in table (1) which shows the effect of reaction variables on the mole % conversion and yield of picolines studied to their sterile nitriles.

Effect of O_2 mole ratio on 2- picoline, 3-picoline and 4-picoline Ammoxidation. The dependence of the yield and conversion of the reaction on the mole ratio of oxygen is shown in (fig. 1) and table (1A). a- An increase in the oxygen to picoline mole ratio causes an increase in the yield of the nitrile formed and reached maximum at 6.0, 8.0, 8.0 mole ratios to 1 mole of picoline with a yield of 90%,88% and 87% for 2-,4- and 3-picolines respectively and a conversion of 70%, 69% and 68%. B- With further increase in O_2/picoline mole ratio, the conversion gradually decreases due to over oxidation of the picoline to oxides of carbon and water.

Effect of Ammonia on 2-, 3-, and 4-picoline Ammoxidation. The ammoxidation yield and conversion were found to increase on using aqueous ammonia solution (30%) instead of gaseous ammonia. The dependence of the reaction yield and conversion of 2-, 3- and 4-picolines on the ammonia quantity is shown in (fig. 2) Table (1B). They increase on increasing the ammonia mole ratio and reaches a maximum yield and conversion using 30, 35, 35 moles of ammonia for each mole of the picoline, and then decreased.

This result may be explained by the competition of the ammonia with the picoline on the same site of the catalyst surface. Another consequence is the decrease in the combustion of CO_2 gas.

The effect of contact time on yield of the main product and conversion is shown in (fig.3) and table (1C). The conversion reaches a maximum at about (1.5) sec. and then declines.

The yield increases gradually and reaches a maximum at (1.5) sec., then with further increase in contact time the yield decreases.

The effect of the reaction temperature on the mole conversion and yield of picoline isomers to their corresponding nitriles is shown in (fig.4) and table (1D).

With an increase in temperature the conversion and yield gradually increase and reach a maximum at 450 °C. Above this temperature such as at 500c° the conversion decreased due to complete oxidation of the picolines and the formation of CO_2 and the yield decreased also.

The effect of temperature on the activity of the catalyst is represented and showed in (fig.4) and table (1D). The catalyst prepared from ammonium vanadate and ammonium stannate showed the highest activity and selectivity with V_2O_5/SnO_2 mole ratio 2:1 on alumina heated to 900c° for six hours. Their mol ratio is 2: 1: 25 respectively.

The reaction mechanism of ammoxidation of picoline about the same as that of toluene. First picoline is oxidized on the surface of V_2O_5 to be stabilized on the surface as the reaction intermediate ion wich reacts with $NH_3$to form the nitrile. The reduced sites then reoxidized by oxygen to repeat the reaction.

The highest catalytic activity might be associated with the formation of $VSnO_4$ species. This is also supported by the influence of chemisorptions of the reactance on the catalytic properties of the catalyst system.

The reaction mechanism was investigated by kinetic and infrared studies. Alumina takes a role of converting the absorbed carboxilate ion into nitrile. The V_2O_5 supported on AL_2O_3 catalyst has a bifunctional activity. Increasing the V_2O_5 fraction causes an increase in the reaction yield. The selectivity of the catalyst depends on its chemical composition.

% conversion = (no. of reacted mole/ no. of starting material moles) x 100

% of yield = (no. of moles of produced nitriles / no. of moles of reacted material) x 100

Both % conversion and % yield for the studied picoline structural isomers 2-, 3-, and 4-picoline in the rate of 2-picoline > 4-picoline > 3-picoline. In other words the Ortho, Para isomers > the Meta isomer, which can be rationalized neither by steric effects nor by the thermo dynamic site of view. The highest yield obtained were 90%, 88% and 87% for 2-picoline, 4-picoline and 3-picoline respectively and so the highest conversion were 70%, 69%, 68%.

The catalyst was active even after 150 hours reaction. However the V_2O_5 and SnO_2 catalyst prepared here was found to be very effective to the ammoxidation reaction of picolines.

Table 1 effect of reaction variables on the conversion

Table 1A Effect of O_2/picoline mole ratio on the % conversion Of 2-,3- and 4- picolines to Nicotinic Acid.

	O2/picoline	Conversion%
2-picoline	1	30
	2.5	40
	4.0	50
	6.0	61
	8.0	70
3-picoline	10.0	45
	1	31
	2.5	44
	4.0	51
	6.0	57
	8.0	68
	10	49
4-picoline	1	29
	2.5	42
	4.0	53
	6.0	59
	8.0	69
	10.0	40

Table 1 B effect of NH_3 / picoline mole ratio on the % of 2-,3- and 4- picolines to Nicottinic Acid

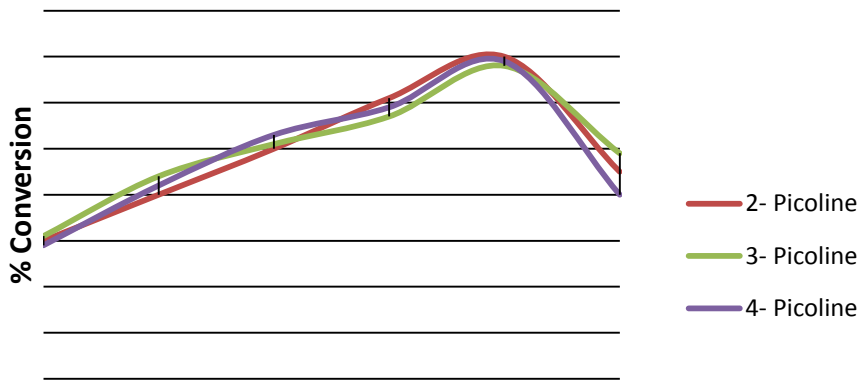
	NH_3/picoline	Conversion%
2-picoline	10	40
	15	50
	25	60
	30	70
	35	50
	40	44
3-picoline	10	30
	15	45
	25	55
	30	60
	35	68
	40	42
4-picoline	10	30
	15	40
	25	50
	30	60
	35	69
	40	40

Table1C Effect of the contact time (sec.) on on the %conversion and %yield of 2-,3- and 4-picolines to Nicotinic Acid

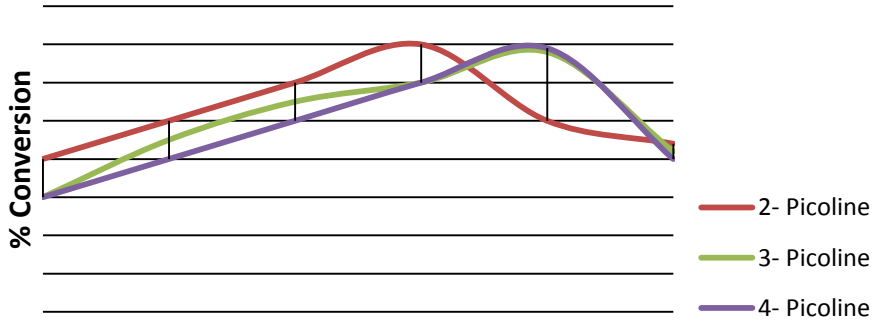
	Contact time / sec.	Conversion %	Yield %
2- picoline	0.4	30	40
	0.5	40	57
	0.6	50	62
	1.0	61	75
	1.5	70	90
	2.0	45	80
3- picoline	0.4	31	39
	0.5	44	50
	0.6	51	58
	1.0	57	70
	1.5	68	87
	2.0	49	74
4- picoline	0.4	29	38
	0.5	42	55
	0.6	53	62
	1.0	59	73
	1.5	69	88
	2.0	52	70

Table 1D effect of temperature °C the % conversion of 2-,3- and4-picolines to Nicotinic Acid

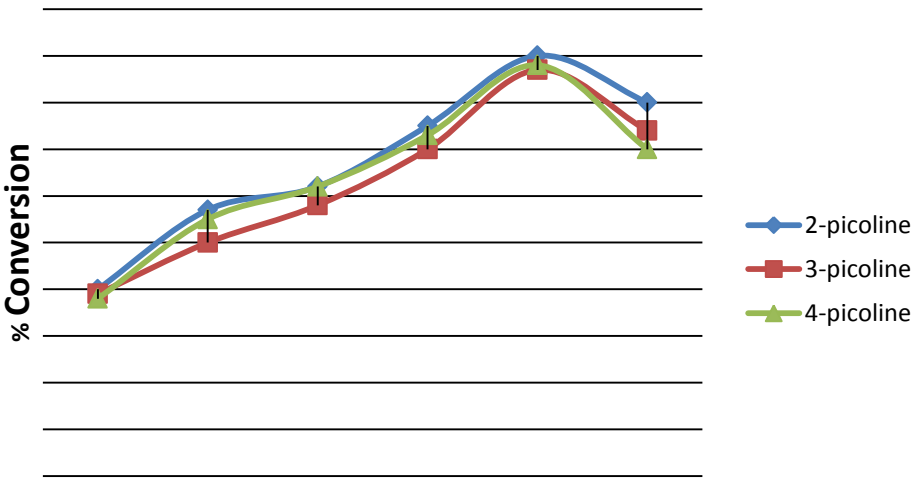
	Temperature	Conversion%
2-picoline	250	30
	300	40
	350	50
	400	61
	450	70
	500	45
3-picoline	250	31
	300	44
	350	51
	400	57
	450	68
	500	49
4-picoline	250	29
	300	42
	350	53
	400	59
	450	69
	500	52



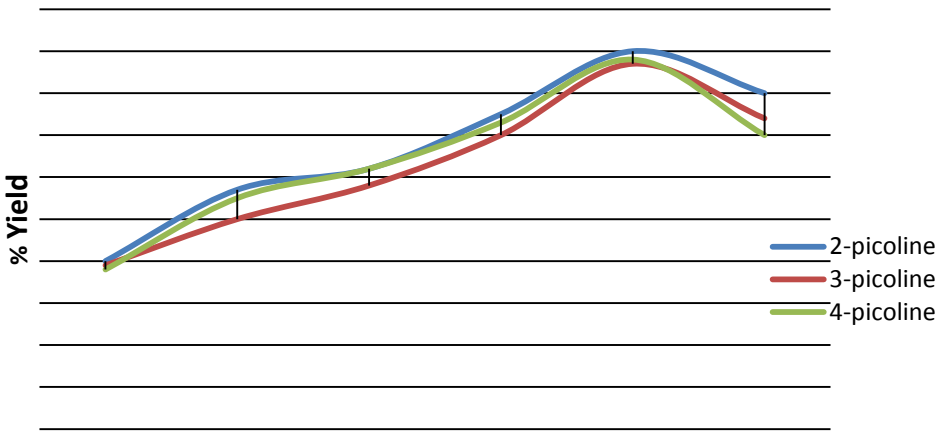
(Fig. 1) plot of %conversion of 2-,3- and 4-picolines vs. O2/picoline mole ratio



(Fig.2) plot of %conversion of 2-, 3- and 4- picolines vs. NH3/picoline mole ratio



(Fig. 3) plot of %conversion of 2-, 3- and 4-picolines vs. contact time (sec.)



(Fig. 4) plot of %yield of nicotinic acid from 2-, 3- and 4-picolines vs. contact time (sec.)

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