Journal of Scientific & Industrial Research
Vol. 81, August 2022, pp. 814-820
10.56042/jsir.v81i08.55461

Vapour Phase Synthesis of 2-Methylpyridine and 4-Methylpyridine Over Potassium Salts of 12-Tungstophosphoric Acid

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Received 26 September 2021; revised 22 July 2022; accepted 22 July 2022

Vapor phase dehydrocyclization reaction of acetaldehyde and ammonia was investigated over K salts of 12-tungstophosphoric acid as catalysts in a continuous flow fixed bed reactor at 350–450°C. The yield of 2-methylpyridine and 4-methylpyridine were found to be in the range of 38.0–64.5%. The 2-methylpyridine and 4-methylpyridine are used for the preparation of insecticides, poultry drugs, cattle drugs and anti-tuberculosis drugs, veterinary analgesics etc. respectively. The reaction conditions such as temperature, contact time, and molar ratio for achieving optimal yield with respect to 2-methylpyridine and 4-methylpyridine were discussed. Catalysts were characterized through BET surface area, FT-IR, XRD and TGA. NH_3-TPD studies exhibit the moderate acidity. The morphology of the catalysts was also studied by FESEM.

Keywords: Acetaldehyde, Dehydrocyclization, Heteropoly acid, Insecticides

Introduction

Pyridine bases constitute the nitrogen heterocyclic compounds containing pyridine and alkyl pyridines. Among them pyridine and three picolines are most important. These compounds find wide applications as a building block for various intermediates used in dyes, drugs, agro-chemicals, rubber chemicals and other promising fields. Numerous methods were reported for their synthesis, amongst them dehydrocyclization reaction of aldehyde and NH_3 has been commercially implemented.[1–3] It is a combined reaction of dehydration, dehydrogenation, and coupled with cyclisation. By this process the desired pyridine bases can be prepared depending upon the aldehyde used in presence of specific catalysts. For example, acetaldehyde condenses with ammonia to give mainly 2-methylpyridine and 4-methylpyridine. Similarly, pyridine and 3-methylpyridine are obtained from acetaldehyde, formaldehyde and ammonia.

Considering the importance of these compounds in the industry, many reported catalysts and process parameters were protected by patents.[4,5] We have previous reported synthesis process for pyridine bases using various solid acid catalysts like pore regulated silica alumina,[6] crystalline aluminosilicate[7] and pillared inter layered clays.[8] Liu *et al.* reported the effect of surface acidity on the catalytic activity of co-modified HZSM-5 for the synthesis of pyridine compounds.[9] The synthesis of pyridine compounds through dehydrocyclization of acetaldehyde and NH_3 requires availability of acidic sites in the catalysts.[10,11] Heteropoly acids and their alkali metal salts have recently gained applications as catalysts both in acidic and redox reactions.[12–16] The bulk heteropoly acids due to their low surface area generally have low catalytic functionality. The heteropoly acids supported on solid support is a convenient way to achieve better catalytic activity in gas-solid heterogeneous reaction. Alternatively, alkali metal salts of heteropoly acid shows better surface area and microporous structure and have the potential to show better catalytic activity.[17] The $K_x H_{3-x} PW_{12}O_{40}$ shows considerably high catalyst activity in various acid catalyzed reactions.[18] In these salts the acid phase was significantly distributed on the neutral salt which exhibits improved surface property than the parent acid. Alkali metal salts of tungstophosphoric acid having large surface area have been extensively used as catalysts in reactions like alkylation[19] and acylation.[20]

Commercially pyridine bases can be sourced from coal tar. The process of recovery of pyridine bases from the tar or saturated liquor is lengthy and economically not viable. The present study shows a one-pot synthesis of methyl-pyridines, using tungtophophoric acids. The catalyst shows better

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surface area and stable during the reaction temperature. Methyl pyridines were synthesized using different starting materials under optimum reaction conditions. The present paper reports the vapor phase synthesis of 2-methylpyridine and 4-methylpyridine over K salts of 12-tungstophosphoric acid through dehydrocyclization reaction of acetaldehyde and ammonia. The catalysts were characterized and their catalytic activity and reactivity were correlated. The reactions were conducted at different temperature, ammonia to acetaldehyde mole ratio and contact time. The present work aims to study the reaction conditions for achieving optimal yield with respect to 2-methyl pyridine and 4-methyl pyridine.

Experimental

Materials

Analytical grade reagents tungstophosphoric acid and other reagents were used. Acetaldehyde used in this reaction was prepared from paraldehyde.[21] Commercial ammonia was used in the gaseous state from cylinder.

Preparation of Catalysts

A stoichiometric amount of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) of 25 g was dissolved in 150 ml of distilled water, and stoichiometric amount of K_2CO_3 in 25 ml water was added to it, effervescence takes place until the reaction ceases. The acidic potassium salt of tungstophosphoric acid ($K_xH_{3-x}PW_{12}O_{40}$) (where, x = 2, 2.5, 3) was precipitated. Then the precipitates of potassium salt of $H_3PW_{12}O_{40}$ namely $K_2HPW_{12}O_{40}$, $K_{2.5}H_{0.5}PW_{12}O_{40}$, and $K_3PW_{12}O_{40}$ (abbreviated as K_2HPW, $K_{2.5}H_{0.5}PW$ and K_3PW respectively) were allowed to settle.[18] The unreacted heteropoly acid were removed by washing with water several times.[18] The salts shows better surface area than the parent acid. It was subjected to drying in an air oven at 110°C for 8 h and then activated at 450°C in a muffle furnace for 4 h. It was then palletized to 6–14 mesh size and used as catalysts for the dehydrocyclization reaction.

Experimental Set Up

A tubular continuous flow fixed bed glass reactor (i.d. 20 mm and length 30 cm) was used to carry out the catalytic reaction. Catalyst of 10 g (6–14 mesh size) was used for each batch of reaction under atmospheric pressure for 2 h. Acetaldehyde was introduced into the reactor by bubbling nitrogen through it at 5–6°C. Ammonia was introduced directly near the catalyst bed with the help of a coaxial tube (around the thermocouple pocket) to avoid condensation of acetaldehyde at lower temperature. The products were collected using ice-cooled trap.

Analytical Techniques

The combined liquid products condensed after each reaction contains mixture of pyridine compounds, unreacted acetaldehyde, ammonia and water. The organic layer was separated by saturating first with K_2CO_3 and then with KOH pellets. A pyridine base in the water free organic layer was determined using perchloric acid titration.[22] Moreover, the individual lower pyridine bases namely pyridine, 2-methylpyridine and 4-methylpyridine were analyzed by a gas chromatograph fitted with FID using chromosorb-p coloumn at 135°C. The unreacted acetaldehyde were determined using standard 2, 4-dinitro phenyl hydrazine solution whereas the ammonia was first absorbed in saturated boric acid, and finally titrated with standard H_2SO_4.

Characterization of Catalysts

Catalysts were characterized for their reproducibility through BET surface area, FT-IR, XRD, NH_3-TPD and FESEM. The BET surface area was analyzed by using Tristar 3000 surface area analyzer (Micromeritics, USA) with N_2 adsorption-desorption at 77 K. The FTIR spectra were recorded using Varian FTIR-800. X-ray diffraction (XRD) pattern recorded in Philips analytical 3710 using Cu Kα radiation. NH_3-TPD studies to identify the acid character of the catalyst were carried out in AutoChem-II, (Micromeritics) Chemisorption's analyzer. The catalyst (1g) was taken in a quartz 'U' tube and degassed at 300°C with ultra-pure nitrogen gas. After cooling, ammonia (20% NH_3 balanced with He gas) was passed again over the sample. The sample was heated at 10°C min^{-1} to final temperature of 800°C and the profile was recorded. To examine the morphology of catalysts, FESEM images of the materials were taken by means of a Zeiss Merlin VP Compact Scanning electron microscope with the resolution of 15 kV. The images were captured at a magnification of 5×10^4.

Results and Discussion

N_2 Adsorption-Desorption

The textural properties of the samples from N_2 adsorption-desorption study are presented in Table 1.

The moderately substituted salts showed higher surface area than the bulk tungstophosphoric acid (15 m^2/g). Thus, the fundamental aspect of the surface area is owing to the generation of micropores on substitution of protons of tungstophosphoric acid by K^+ cation.[23] As a whole, the particular surface area of the K salts of tungstophosphoric acid increases with the increase in the ionic radii of the metal cation.[10]

FTIR

The FTIR spectra of potassium salts of tungstophosphoric acid are shown in Fig. 1. The absorption band at about 3200–3300 cm^{-1} corresponds to ν −OH and 1600–1700 cm^{-1} due to bending of −OH. It is believed that lattice water partially confers Brønsted acidity to the system. The other peaks observed at 1072 cm^{-1}, 975 cm^{-1}, 885 cm^{-1}, 800 cm^{-1} for stretching ν(P-O), ν(W = O), ν(W-O_b-W) and ν(W-O_e-W). A peak at 587 cm^{-1} was assigned to the bending of (O_a-P-O_a).[16] In $K_{2.5}PW$ and K_3PW, the slight broadening of the (W = O) band was detected, one maximum situated at 981 cm^{-1} and other at 999 cm^{-1}. This broadening of the peak (Fig. 2) may be attributed to the direct interaction of K^+ ion with tungstate polyanion.[23] The results acquired from the spectra indicate that the primary Keggin structure remain unchanged.[24]

Table 1 — The textural property of catalysts

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Acidity (mmol/g)
HPW	15.0	—	0.8303
K_3PW	107.4	0.03487	1.8
$K_{2.5}H_{0.5}PW$	100.1	0.02812	3.9
K_2HPW	35.9	0.01083	4.2

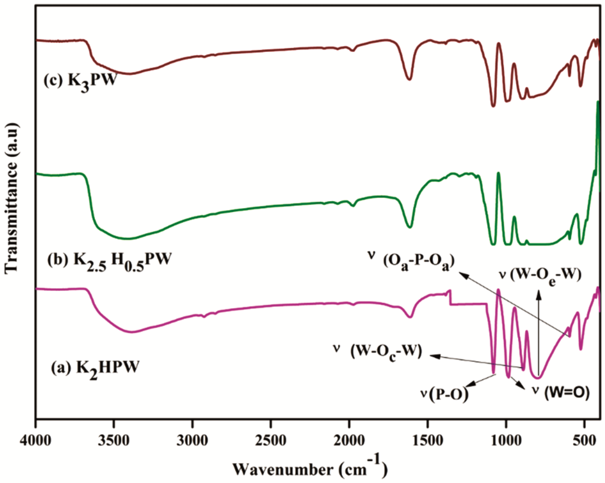


Fig. 1 — FTIR spectra of (a) K_2HPW, (b) $K_{2.5}H_{0.5}PW$ and (c) K_3PW

XRD

The XRD pattern of potassium salts of tungstophosphoric acid (Fig. 3) shows that the salts are in crystalline form. The 2θ value at 10.62°, 15.29°, 18.63°, 21.70°, 24.34° reveals the presence of hydrate phase of $H_3PW_{12}O_{40}.6H_2O$ (JCPDS-761815). It can be inferred that the acid phases are well deposited over the potassium salts.[6] All the XRD spectra of moderately substituted potassium salts indicates body centered cubic structure.[7] In the calcined sample, the dehydrated tungstophosphoric acid forms a surface acid layer on the K_3PW salt as the partially dehydrated tungstophosphoric acid is not stable as separate phase.[8] It can be inferred that the acid phases are well dispersed.[24]

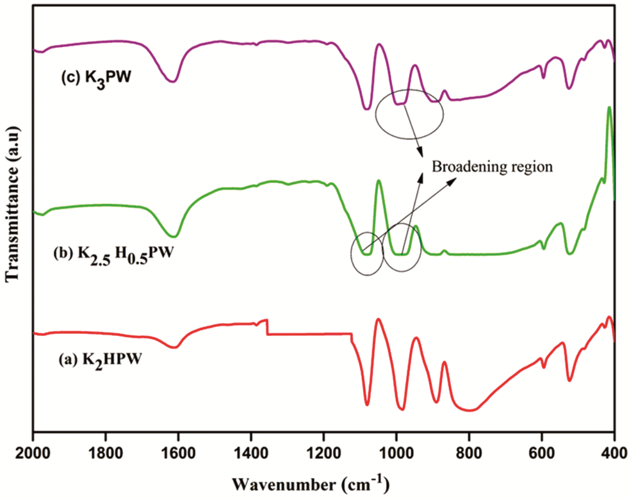


Fig. 2 — FTIR spectra of the spherical portion showing the broadening region.

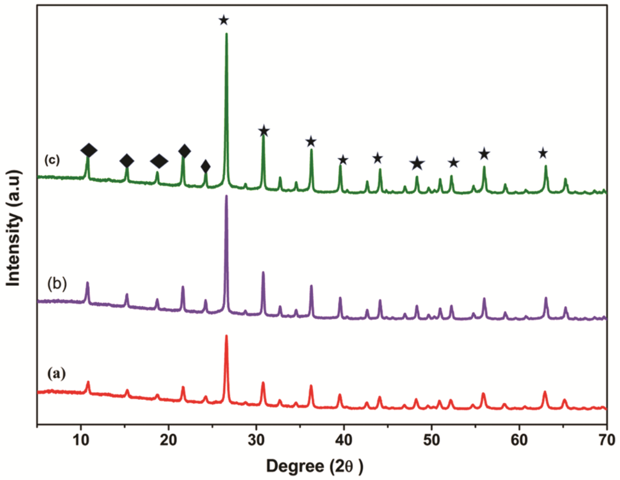


Fig. 3 — XRD pattern of (a) K_2HPW, (b) $K_{2.5}H_{0.5}PW$ and (c) K_3PW (♦ Hydrated phase of $H_3PW_{12}O_{40}.21H_2O$) (* $K_xPW_{12}O_{40}$ Phase)

NH_3-TPD

TheNH_3-TPD profiles of potassium salts of tungstophosphoric acid are shown in Fig. 4. The acidity of K_2HPW, $K_{2.5}H_{0.5}PW$ and K_3PW are also presented in Table 1. In K_2HPW the peak at 132°C is attributed to weak acid sites and the peak at 616°C may be due to strong acid sites. In $K_{2.5}H_{0.5}PW$ the peak at 590°C is attributed to strong acid sites with moderate acidity. In K_3PW the peak at 120°C may be due to physiosorbed ammonia. Thus, the acidity can be substantially decreased with increase in the K^+ ion concentration in the material.[25] This catalytic activity may be responsible for the vapor phase transformation of aldehyde and ammonia to 2- and 4-methyl pyridine.

FESEM

The surface morphology of K_2HPW, $K_{2.5}H_{0.5}PW$ and K_3PW were studied by FESEM is illustrated in Fig. 5. It can be observed from figure that the salts are spherical in size with 100–150 nm diameter in average. From the micrograph, it can be inferred that the particles are having irregular shape with well-defined crystalline particles. The surface of $K_{2.5}H_{0.5}PW$ appears rough as compared to K_2HPW. This might be the reason for higher surface area of $K_{2.5}H_{0.5}PW$ which is confirmed by BET-SA analysis. It can be seen from the image (B) that; some pores have been created during the modification process which might enhance the catalytic efficiency.[8]

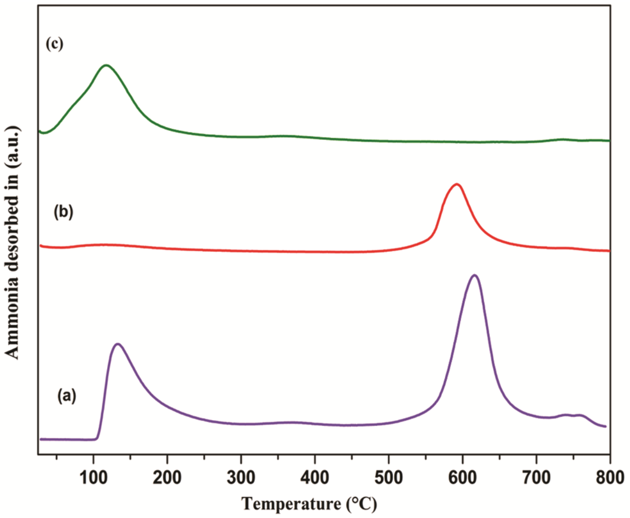


Fig. 4 — NH_3-TPD of (a) K_2HPW, (b) $K_{2.5}H_{0.5}PW$ and (c) K_3PW

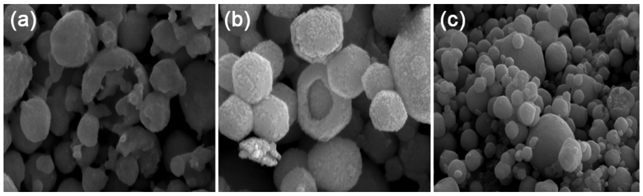


Fig. 5 — FESEM of (a) K_2HPW, (b) $K_{2.5}H_{0.5}PW$ and (c) K_3PW

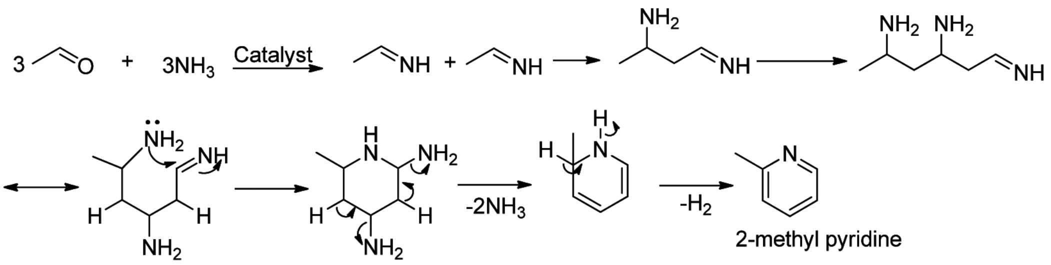
Synthesis of 2-Methyl Pyridine and 4-Methyl Pyridine

The synthesis of 2 and 4 picoline from acetaldehyde and ammonia is supposed to be a multistep reaction which includes condensation (Aldol or Michael type), cyclisation and dehydrogenation (Scheme 1 and 2 respectively). Plausible mechanism for the formation 2-methyl pyridine and 4-methyl pyridine are given in scheme 1 and 2 respectively. The aldol route favours the formation of 2-methyl pyridine while Michael route accounts for the formation of 4-methyl pyridine.

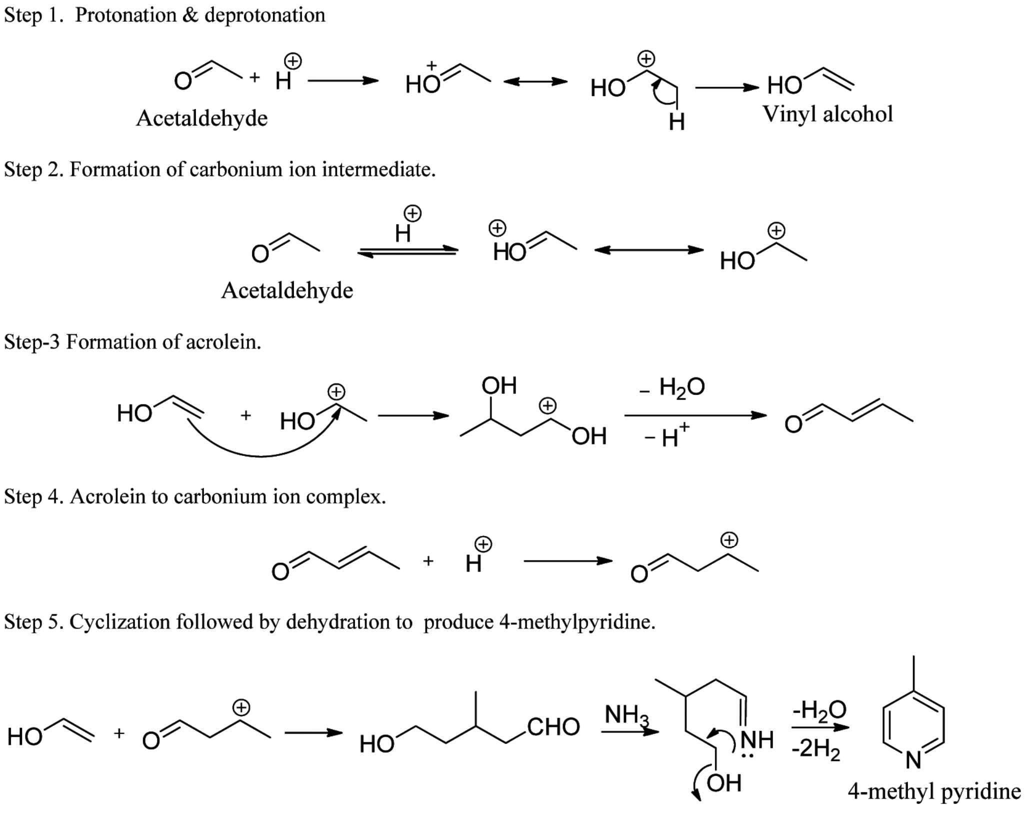
Acid sites present on the catalyst are predominantly responsible for the above reactions. Acidity of potassium salts of tungstophosphoric acid is due to presence of H^+ ion present in the salt.[26] Both the acidic and neutral forms of this heteropoly acids show reactivity even though the reaction is acid catalyzed one.[27]As pointed out by Niiyama *et al.*[27] that acidity occurs due to the Lewis acidity of metal cation while Brønsted ones are because of hydrolysis in presence of water. Tatematsu *et al.*[28] and Okuhara *et al.*[29] have described that non-stoichiometry of cation/polyanion may also results in acidic properties. Ultimately, the acidity of the catalyst will influence the catalytic activity. Keeping this in view, potassium salts of different H^+ ion content were prepared by stoichiometrically replacing H^+ with K^+. Thus, potassium salts of tungstophosphoric acid of composition $K_2HPW_{12}O_{40}$, $K_{2.5}H_{0.5}PW_{12}O_{40}$, and $K_3PW_{12}O_{40}$ were prepared and their catalytic activities were evaluated (Table 2).

It is evident from Table 2 that a total yield of 57.3% of pyridine bases comprising 19.3% of 2-methylpyridine, 20.9% of 4-methylpyridine, 1.3% of pyridine and 15.8% of higher pyridine bases were obtained over K_3PW at 430°C. Under the similar reaction condition, the catalyst $K_{2.5}H_{0.5}PW$ gave the maximum yield of 64.5% of pyridine bases comprising of 2-methylpyridine (31.2%), 4-methylpyridine (23.0%) apart from pyridine (3.7%) and higher pyridine bases (5.4%). Thus, there is an improvement in the yield of pyridine bases when 0.5 K^+ of K_3PW were replaced by H^+. However further replacement of potassium did not increase the yield.

K_2HPW gave a total yield of 60.2% of pyridine bases comprising 21.3% of 2-methylpyridine, 20.8%



Scheme 1 — Formation of 2-methyl pyridine



Scheme 2 — Formation of 4-methyl pyridine

Table 2 — Effect of potassium salts of tungstophosphoric acid on the yield of pyridine bases

Sl No	Catalyst	Product analysis (mol%)				
		2-methyl pyridine	4-methyl pyridine	Pyridine	Higher PB	Total PB
1	K_3PW	19.3	20.9	1.2	15.8	57.2
2	$K_{2.5}H_{0.5}PW$	31.2	23.0	3.7	6.6	64.5
3	K_2HPW	21.3	20.8	2.8	15.2	60.1

(Temperature: 425°C, NH_3/CH_3CHO mole ratio: 0.90, Contact time: 2.80 s, PB: Pyridine Bases)

of 4-methylpyridine, 2.9% of pyridine and 15.2% of higher pyridine bases. Table 1 shows that as the acidity increases from K_3PW to $K_{2.5}H_{0.5}PW$, the yield of pyridine bases also increases. Further, despite having higher acidity of K_2HPW, it is catalytically less active due to lower surface area and pore volume compared to $K_{2.5}H_{0.5}PW$ (Table 1). There is only marginal increase in the yield of pyridine bases when $K_{2.5}H_{0.5}PW$ was used as catalyst. Hence optimization of process parameters was carried out by changing the temperature, contact time and NH_3/CH_3CHO mole ratio using $K_{2.5}H_{0.5}PW$ as catalyst and the results are summarized in Table 3.

Effect of Temperature

The effect of reaction temperature on the yield to picolines was also studied. Various experiments at different temperature from 350–450°C were carried

Table 3 — Experimental conditions and details of the product analysis

Run No	Reaction conditions			Product analysis (mol%)				
	Tempe-rature (°C)	Contact time (s)	NH_3/CH_3-CHO mole ratio	2-methyl pyridine	4-methyl pyridine	Pyridine	Higher pyridine bases	Total pyridine bases
1	350	2.82	0.89	16.2	13.4	2.5	11.1	43.2
2	375	2.82	0.88	12.8	13.6	3.5	21.3	51.2
3	400	2.81	0.88	25.2	20.2	3.1	12.1	60.6
4	425	2.80	0.90	31.2	23.0	3.7	6.6	64.5
5	450	2.83	0.89	24.0	21.8	3.4	12.3	61.5
6	425	1.61	0.91	24.7	12.6	2.9	20.6	60.8
7	425	2.80	0.90	31.2	23.0	3.7	6.6	64.5
8	425	3.81	0.89	23.1	18.6	1.5	16.2	59.4
9	425	5.15	0.92	12.2	10.9	0.9	26.2	50.2
10	425	2.80	0.26	18.8	15.0	1.4	18.0	53.2
11	425	2.80	0.64	25.5	20.1	2.2	14.2	62.0
12	425	2.80	0.90	31.2	23.0	3.7	6.6	64.5
13	425	2.81	1.04	23.2	18.1	3.8	12.7	57.8
14	425	2.81	1.20	9.3	7.5	1.8	19.4	38.0

out using $K_{2.5}H_{0.5}PW$ catalyst. The Table 3 shows that the total yield of pyridicne bases were initially low and it gradually increases upto 425°C. At higher temperature the yield decreases this may be due to plausible cracking of acetaldehyde. Further, the reactions were carried out at optimum temperature of 425°C.

Effect of Contact Time

The contact time was also a very important parameter for reaction optimization. To understand the effect of contact time, the reactions were carried by changing the volume of catalyst under specified reaction condition (Table 3). Reaction variables like temperature (425°C) and NH_3/CH_3CHO mole ratio (0.90) were kept constant. Table 3 shows that contact time plays an important role in the reaction. With increase in contact time the yield increase and shows maxima at 2.80 s. Lower contact time did not permit enough time for the desired reaction to proceed for completion, in contrast at higher contact time the undesirable reaction predominated leading to lower yield of pyridine bases.

Effect of NH_3 to CH_3CHO Mole Ratio

To study the effect of NH_3 to CH_3CHO mole ratio, experiments were conducted using $K_{2.5}H_{0.5}PW$ catalyst at different mole ratio of reactants. Other reaction variables like temperature (425°C) and contact time (2.80 s) was kept constant. It is evident (Table 3) that on increasing the NH_3/CH_3CHO mole ratio the yield of pyridine bases gradually increases till 0.9 and then decreases. It may be presumed that at higher NH_3/CH_3CHO mole ratio, some of the active acidic sites might have been deactivated resulting in the loss of activity of the catalyst.

Conclusions

Both 2-methylpyridine and 4-methylpyridine were synthesized using potassium salts of 12-tungstophosphoric acid from vapor phase reaction of acetaldehyde and ammonia. Among the potassium salts tested, $K_{2.5}H_{0.5}PW$ gave maximum yield of 2-methylpyridine and 4-methylpyridine. The 2-methylpyridine is used to prepare 2-vinyl pyridine (copolymer with acrylonitrile, butadiene, and styrene), Polyvinyl pyridine, ion exchange, film material, dyeing of acrylonitrile fiber. The 4-methyl pyridine has potential for industrial separation of p-xylene from mixed xylenes (Clathration process). The maximum yield of pyridine bases obtained was 64.5% comprising of 31.2% of 2-methyl pyridine, 23.0% of 4-methyl pyridine, 3.7% of pyridine and 6.6% of higher pyridine bases with optimal reaction parameter of reaction temperature at 425°C, contact time of 2.80 S^{-1}, and molar ratio NH_3/CH_3CHO of 0.9. The morphology of the catalyst suggests that the pores were found in $K_{2.5}H_{0.5}PW$ during modification and confirmed by FESEM. TPD studies exhibit the moderate acidity of the catalysts. It is observed that catalyst having high surface area is favorable for the reaction rather than the acidity of the catalyst. The process produces mixture of pyridines, and with further focus on suitable modification of catalyst site for better selectivity.

Acknowledgements

The authors thank CSIR-New Delhi for financial support.

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