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Synthesis of pyridine and picolines from ethanol over modified ZSM-5 catalysts[1]

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Abstract

In the reaction of ethanol, formaldehyde and ammonia over modified ZSM-5 catalysts, pyridine and picolines are synthesized. The catalysts studied were H-ZSM-5 with Si/Al ratios, 30, 150 and 280, Pb-ZSM-5 and W-ZSM-5. The yields of pyridine and picolines were 20–40 and 10–25 wt.-%, respectively. The pyridine/picoline ratio in the products increased with the Si/Al ratio of the ZSM-5. For the first time, the non-oxidative transformation of ethanol and ammonia to pyridine has been achieved in high yields.

Key words: Picolines; Pyridine; Zeolites; ZSM-5

1. Introduction

Pyridine and picolines are useful intermediates in the synthesis of herbicides pharmaceuticals and surface-active agents [1]. On commercial scale, pyridine and picolines are synthesized using SiO_2–Al_2O_3 catalysts promoted by ThO_2, ZnO or CdO with 40–60% yield [1]. We have studied [2] the reactions or propylene oxide, propylene glycol, ethylene glycol, acetaldehyde [3] or acetone [4] with ammonia over modified ZSM-5 and SiO_2–Al_2O_3 promoted by Pb, Cu, Cr, etc. Van der Gaag et al. [5] carried out the reaction of ethanol and ammonia to pyridine in presence of oxygen over ZSM-5. In this reaction, due to oxygen in the feed, carbon dioxide was formed as a major product. 2-Picoline was observed as a major side-product in the amination of phenol over ZSM-5 at 510°C [6]. Pyridines were synthesized from acetaldehyde over various modified SiO_2–Al_2O_3 and

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pentasil catalysts [7–13]. The reaction of acetaldehyde and ammonia over H-ZSM-5 leads to 2- and 4-picolines. On the other hand the reaction of acetaldehyde, formaldehyde and ammonia over H-ZSM-5 leads to pyridine and 3-picoline [13].

In this paper, we report the synthesis of pyridine and picolines from ethanol, formaldehyde and ammonia over various ZSM-5 catalysts, in absence of oxygen in feed.

2. Experimental

H-ZSM-5 catalysts used in this study were supplied by Conteka, Sweden. The H-ZSM-5 (Si/Al = 150) was modified by a known weight of lead nitrate (20% PbO) or ammonium meta-tungstate (12 wt.-% W). The modification of the catalyst was carried out by the impregnation technique. Distilled ethanol and 40% aqueous formaldehyde and ammonia gas were used in the feed.

The reactions were carried out using a tubular, down-flow pyrex reactor with 20 mm internal diameter. The reaction mixture was fed from the top using a Sage syringe pump. The product was cooled using ice-cooled water and collected at the bottom. A sufficient number of ice-cooled traps were used at the outlet to collect the total amount of products. The products were analyzed by gas chromatography (GC) using Chromosorb-101 (5%) and SE-30 (5%) columns. The analysis was confirmed by mass spectra and GC-mass.

3. Results and discussion

The reaction of ethanol, formaldehyde (40% aqueous solution) and ammonia was carried out over various ZSM-5 catalysts. The results are depicted in Table 1. The reaction was carried out at 420°C with 0.5 h^{-1} weight hourly space velocity (WHSV) for 4 h on stream. H-ZSM-5 catalysts with (Si/Al) = 30, 150 and 280 were tested. H-ZSM (30), H-ZSM (150) and H-ZSM-5 (280) showed 36.7, 72.5 and 42.7 conversion (%) of ethanol respectively. The yields of pyridine for H-ZSM-5 (30), H-ZSM-5 (150) and H-ZSM-5 (280)

Table 1
Reaction of ethanol, formaldehyde and ammonia over ZSM-5 catalysts

Reaction temperature = 420°C; WHSV = 0.5 h^{-1}; conversion of formaldehyde = 100%; feed = $CH_3CH_2OH:HCHO:NH_3$ = 1:0.8:1.5

S.No.	Catalyst	Time on stream (h)	Conversion of ethanol (%)	Yield (wt.-%)[a]				Pyridine
				Pyridine	2-Picoline	3-Picoline	Lutidine	Picolines
1.	ZSM-5 (30)	4	36.7	19.4	8.3	4.8	4.2	1.48
2.	ZSM-5 (150)	4	72.5	38.5	5	18.5	10.5	1.63
3.	ZSM-5 (280)	3+4	42.7	24.5	6	5.9	6.3	2.05
4.	Pb-ZSM-5	2+3	36.0	22	3.3	8.2	2.5	1.91
5.	W-ZSM-5	4	39.8	24	3	10.3	2.5	1.80

[a]Based on ethanol.

were 19.4, 38.5 and 24.5 wt.-% and pyridine/picolines ratios were 1.48, 1.63 and 2.03, respectively. H-ZSM-5 (150) showed the highest activity. Pyridine/picolines ratio increases with the Si/Al ratio, from 1.48 to 2.05. In the case of Pb-ZSM-5 and W-ZSM-5, the conversions with respect to ethanol were 36 and 39.8, while the yields of pyridine based on ethanol were 22.0 and 24.0 wt.-%, respectively. The pyridine/picoline ratios were 1.91 and 1.80.

The variation of the molar ratio of ethanol to formaldehyde was studied and is given in Table 2. The reaction of ethanol, formaldehyde and ammonia was carried out at 420°C over Pb-ZSM-5 (4 g) with 0.5 h^{-1} WHSV. The conversion of ethanol varied from 29.6 to 53.2% and the yield of pyridine was from 18.6 to 25.9 wt.-% based on ethanol. The pyridine/picolines ratio varied from 1.34 to 2.13. There was no specific trend with respect to molar ratio. Formaldehyde in the feed affects the synthesis of pyridine(s) predominantly as shown in Scheme 1 (a). The reaction of ethanol and ammonia without formaldehyde over Pb-ZSM-5 at 420°C and 0.5 h^{-1} WHSV leads to 6.1, and 55.3 wt.-% pyridine and picolines, respectively, at 85.6% conversion of ethanol as shown in Table 2. The reactions of ethanol and a mixture of ethanol and formaldehyde were carried out over Pb-ZSM-5, W-ZSM-5 and H-ZSM-5 (30) [14] and reported in Table 3. In case of H-ZSM-5 and W-ZSM-5, ethanol leads to various aliphatics and aromatics. On the other hand, in the case of Pb-ZSM-5 ethanol leads to 38.4 wt.-% acetaldehyde and no aromatics were observed. The addition of formaldehyde in feed over Pb-ZSM-5 increased acetaldehyde to 47%.

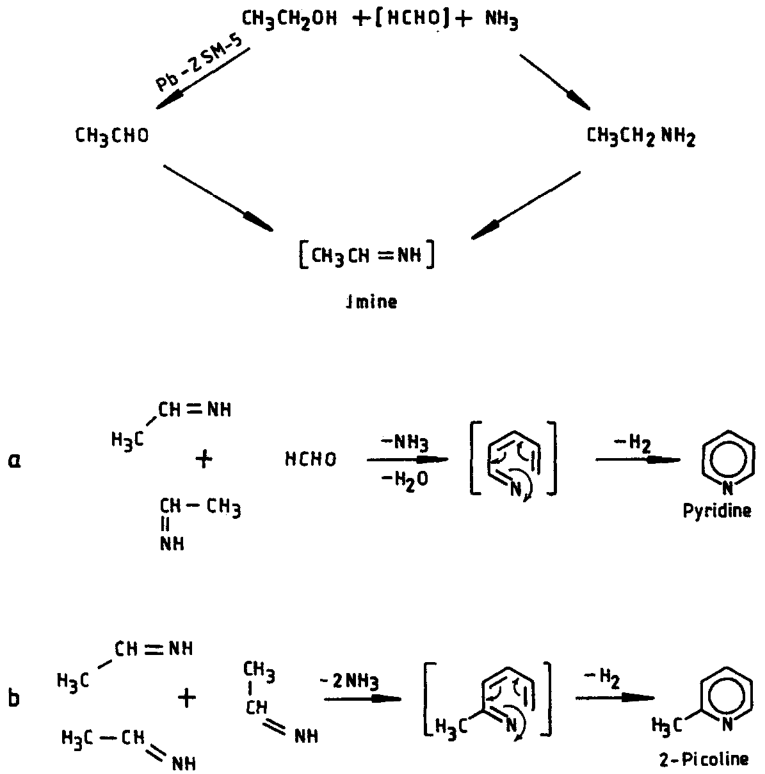
From the product distribution and the literature evidence [1], the reaction scheme is proposed and depicted in Scheme 1. The imine formation was reported by Golunski and Jackson [1]. Ethanol with ammonia over H-ZSM-5 and W-ZSM-5 [3,13] at 420°C leads predominantly to the formation of ethylamine. Thus we believe that the imine formation results from the reaction of acetaldehyde with ammonia over Pb-ZSM-5 and via dehydrogenation of ethylamine over various zeolites as shown in Scheme 1. Due to the presence of ammonia, the formation of hydrocarbons is reduced drastically. Nayak and Choudhary [14]

Table 2
Synthesis of pyridine from ethanol: the variation of molar ratio in feed

Reaction temperature = 420°C; catalyst = Pb-ZSM-5 (4 g); conversion of formaldehyde = 100%; WHSV = 0.5 h^{-1}

S.No	Feed molar	Time on stream (h)	Conversion of ethanol (%)	Yield (wt.%)[a]				Pyridine / Picoline
				Pyridine	2-Picoline	3-Picoline	Lutidine	
1.	Ethanol + HCHO + NH_3							
	1:3.38 molar	1	46.3	25.6	5.2	10.6	4.9	1.62
2.	1:1.26	3	29.6	18.6	2.8	5.9	2.3	2.13
3.	1:0.83	2+3	36.0	22	3.3	8.2	2.5	1.91
4.	1:0.56	4	36.2	21.1	5.3	6.9	2.9	1.72
5.	1:0.21	3+4	53.2	25.9	10.2	9	8.1	1.34
6.	Ethanol + NH_3	4	85.6	6.1	29.9	25.4[b]	(6.3 + 17.9)[c]	0.11

[a]Based on ethanol.
[b]Also contains 4-picoline.
[c]Ethylamine (14%) + other products.



Scheme 1. Synthesis of pyridine and picolines from ethanol.

Table 3
Variation of feed composition of ethanol over zeolites

Reaction temperature = 420°C; WHSV = 0.5 h^{-1}

Catalyst (4g)	Pb-ZSM-5	W-ZSM-5	H-ZSM-5	Pb-ZSM-5
Feed	Ethanol + H_2O	Ethanol	Ethanol	Ethanol + formaldehhyde (1:1) molar
Time-on-stream (h)	(3+4)	(3+4)	(1+2)	(1+2)
Conversion of ethanol (%)	67.8	75.6	92.5	59.4
Product distribution (%)				
Ethanol	32.2	24.4	7.5	40.6
Acetaldehyde	38.4	-	-	47.0
Aliphatics	29.4	28.2	73.8	12.4
Aromatics				
C_6	-	6.1	0.2	-
C_7	-	14.2	2.5	-
C_8	-	15.9	6.1	-
C_{9+}	-	11.2	9.9	-

reported the effect of ammonia, pyridine and quinoline on the conversions of alcohols and alkenes over ZSM-5 catalysts. The desorption of products is accelerated by the presence of water in the feed. The stoichiometric equations for the reactions may be written as follows,

$$2C_2H_5OH + HCHO + NH_3 \longrightarrow C_5H_5N(\text{pyridine}) + 3H_2O + 3H_2$$

$$3C_2H_5OH + NH_3 \longrightarrow C_5H_4NCH_3(\text{picoline}) + 3H_2O + 4H_2$$

The experimental data regarding the effect of the reaction temperature on the synthesis of pyridines are given in Table 4. The reaction of ethanol, formaldehyde with ammonia was carried out over 4 g Pb-ZSM-5 catalyst at 0.5 h^{-1} WHSV in the temperature range of 300 to 420°C. At reaction temperatures 300, 350, 380, 400 and 420°C, the conversions with respect to ethanol were 25.7, 22.3, 47.5, 44.9 and 36 and yields of pyridine were 15.5, 14.2, 24.0, 24.0 and 22.0 wt.-%, respectively. The pyridine/picolines ratio was in between 1.33 and 1.91. There is not much effect of the reaction temperature on the selectivity.

The effect of WHSV is depicted in Table 5. The WHSV was varied from 0.25 to 1 h^{-1}. The reaction of ethanol, formaldehyde with ammonia was carried out over Pb-ZSM-5 at 420°C. The molar ratio in the feed was 1:0.8:1.5. The conversions with respect to ethanol for 0.25, 0.37, 0.50, 0.75 and 1.0 h^{-1} WHSV were 39.2, 32.7, 36, 31.2, and 21.2% and yields for pyridine were 22.1, 18.6, 22.0, 18.0 and 14.0 wt.-%, respectively. With the increase of WHSV conversions and yield decreased. The ratio of pyridine/picolines increased with the increase of WHSV.

The reaction of ethanol, formaldehyde and ammonia was carried out at 420°C over Pb-ZSM-5 with 0.5 h^{-1} WHSV for 11 h on stream. The data are depicted in Table 6. There was no predominant deactivation upto 11 h on stream. The conversion of ethanol varied from 37 to 68% and yield of pyridine was in the range of 21.6 to 40.4 wt.-%. The pyridine/picolines ratio was between 1.4 to 1.85. Typically for the 10th hour on stream, the yield of pyridine was 40.4 wt.-%, the conversion of ethanol was 68% and the ratio of pyridine to picolines was 1.71.

Van der Gaag et al. [5] reported the synthesis of pyridines from ethanol and ammonia in presence of oxygen with the formation carbon dioxide as a major products. The exoth-

Table 4
Synthesis of pyridine from ethanol over ZSM-5 catalysts: the effect of temperature

Catalyst = Pb-ZSM-5 (4 g); WHSV = 0.5 h^{-1}; conversion of formaldehyde = 100%; feed = CH_3CH_2OH:HCHO:NH_3 = 1:0.8:1.5

S. No.	Reaction temperature (°C)	Time-on-stream (h)	Conversion of ethanol (%)	Yield (wt.-%)[a] Pyridine	2-Picoline	3-Picoline	Lutidine	Pyridine / Picolines
1.	300	3	25.7	15.5	2.3	7.2	0.7	1.64
2.	350	1	22.3	14.2	2.7	5	0.4	1.84
3.	380	1	47.5	24	8.5	9.5	5.5	1.33
4.	400	2	44.9	24	6	8.5	6.4	1.65
5.	420	2+3	36.0	22	3.3	8.2	2.5	1.91

[a]Based on ethanol.

Table 5
Synthesis of pyridine from ethanol: the effect of weight hourly space velocity

Reaction temperature = 420°C; catalyst = Pb-ZSM-5 (4 g); conversion of formaldehyde = 100%; feed: $CH_3CH_2OH:HCHO:NH_3$ = 1:0.8:1.5

S.No.	Weight hourly space velocity (h^{-1})	Time-on-stream (h)	Conversion of ethanol (wt.-%)	Yield (wt.-%)[a]				Pyridine
				Pyridine	2-Picoline	3-Picoline	Lutidine	Picolines
1.	0.25	1	39.2	22.1	6.3	7.3	3.6	1.62
2.	0.37	4	32.7	18.6	3.7	8.5	1.9	1.52
3.	0.50	2+3	36.0	22	3.3	8.2	2.5	1.91
4.	0.75	2	31.2	18	2	8.4	2.8	1.73
5.	1.0	4	21.2	14.0	0.8	4.2	2.1	2.8

[a]Based on ethanol.

Table 6
Synthesis of pyridine from ethanol: the time-on-stream effect

Catalyst = Pb-ZSM-5; WHSV = 0.5 h^{-1}; conversion of formaldehyde = 100%; $C_2H_5OH:HCHO:NH_3$ = 1:0.8:1.5

Time-on-stream (h)	Conversion of ethanol	Yield (wt.-%)[a]				Pyridine
		Pyridine	2-Picoline	3-Picoline	Lutidine	Picoline
1	38.3	21.6	3.8	10.4	2.5	1.5
2	37.2	21.3	2.7	10.7	2.5	1.6
3	46.8	27.2	3.7	13.0	2.9	1.6
4	46.2	28.1	3.5	12.7	1.9	1.7
5	43.1	24.1	6.0	11.4	1.6	1.38
6	61.1	33.1	7.2	14.5	6.3	1.52
7	42.5	26.0	2.8	11.5	2.2	1.81
8	58.9	34.4	4.1	15.9	4.5	1.72
9	65.0	37.7	4.7	17.8	4.8	1.67
10	68.0	40.4	4.7	18.8	4.1	1.71
11	55.1	34.4	3.6	14.9	2.2	1.85

[a]Based on ethanol.

ermicity and the formation of carbon dioxide associated with oxidation of ethanol is avoided in this new process. The selectivity and high yield for pyridine or picolines can be obtained with appropriate choice of catalyst and feed composition.

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