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Applied Catalysis A: General 111 (1994) L101–L108

applied catalysis A

Letter

Synthesis of 2-picoline from acetone over modified ZSM-5 catalysts**

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(Received 16 March 1993, revised manuscript received 10 November 1993)

Abstract

In the reaction of acetone, formaldehyde and methanol with ammonia over modified ZSM-5 catalysts, 2-picoline and 2,6-lutidine are synthesized selectively. The catalysts studied were H-ZSM-5 with Si/Al ratios, 30, 150 and 280, Pb-ZSM-5, W-ZSM-5 and modified silica–alumina. The yields of 2-picoline obtained were 30–47 wt.-% at 50–60 wt.-% conversions of acetone. The unconverted acetone and methanol can be recycled to increase the over-all yield. Pb-ZSM-5 was identified as the best catalyst.

Key words: acetone; Pb-ZSM-5; picoline; W-ZSM-5; zeolites; ZSM-5

1. Introduction

Pyridine and substituted pyridines are useful intermediates in pharmaceuticals, herbicides and surface-active agents [1]. The reaction of acetaldehyde, formaldehyde and ammonia over acidic catalysts leads to pyridine and 3-picoline [1,2]. On the other hand, the reaction of acetaldehyde and ammonia gives 2-picoline and 4-picoline. The catalysts used in the preparation of substituted pyridines are Pd–Al_2O_3 promoted by PbO, CuO or SiO_2–Al_2O_3 promoted by ThO_2, ZnO and CdO with 40–60% yield. We have reported [2] the reactions of propylene oxide, propylene glycol; ethylene glycol or acetaldehyde with ammonia over H-ZSM-5 catalyst leading to substituted pyridines and aliphatic amines. Pyridine was also synthesized from ethanol and ammonia over ZSM-5 catalyst in the presence of oxygen with low yields [3]. 2-Picoline was observed as a major side-product in the amination of phenol

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**IICT Communication No. 3151.

SSDI 0926-860X(94)00025-M

over ZSM-5 at higher temperature (510°C) [4]. Picolines were synthesized over various modified SiO_2–Al_2O_3 and pentasil catalysts [5–11].

In this paper, we report the selective synthesis of 2-picoline from acetone, formaldehyde, methanol and ammonia over modified ZSM-5 catalysts, with 2,6-lutidine as a major side product.

2. Experimental

H-ZSM-5 catalysts used in this study were supplied by Conteka, Sweden. The catalyst was modified with a known weight of lead nitrate (20% PbO) and ammonium metatungstate (12 wt.-% W). Silica–alumina used in this study was supplied by Akzo Chemie, Netherlands with 84 : 16 wt.-% of silica–alumina. Modification of the catalysts was carried out by the impregnation technique. The ice-cooled mixture of acetone and 40 wt.-% aqueous formaldehyde was used in the feed. Ammonia gas was introduced separately.

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 end to collect the total amount of products. The products were analyzed by SE-30 (5%) and [chromosorb (5%)] columns. The analysis was confirmed by mass spectra and gas chromatography-mass spectrometry (GC-MS).

3. Results and discussion

The reaction of acetone, formaldehyde and methanol with ammonia was carried out over various ZSM-5 catalysts. The results are tabulated in Table 1. The reaction was carried out

Table 1
The synthesis of 2-picoline from acetone over modified ZSM-5 catalysts

Reaction temperature = 420°C, WHSV = 0.5 h^{-1}, feed: CH_3COCH_3 : HCHO : CH_3OH : NH_3 = (1 : 1.3 : 0.9 : 1.3) molar

S. No.	Catalyst	Time-on-stream (h)	Conversion (wt.-%) with respect to		Yield (wt.-%)[a]			2-Picoline / 4-Picoline
			Acetone	Formaldehyde	2-Picoline	4-Picoline	Lutidine[b]	
1.	H-ZSM-5 (30)	2	40.8	100	27.0	3.0	10.8	9.0
2.	H-ZSM-5 (150)	4	58.7	100	33.5	4.0	21.2	8.4
3.	H-ZSM-5 (280)	3	41.1	100	28.0	–	13.1	–
4.	Pb-ZSM-5	2	69.0	100	35.0	8.0	26.0	4.4
5.	W-ZSM-5	(2+3)	51.2	100	29.0	–	22.2	–
6.	PbSA (1)	2	59.5	100	16.0	2.0	41.5	8.0
7.	PbSA (2)	2	22.6	100	6.8	2.0	13.8	3.4

[a]Based on acetone.
[b]2,6-Lutidine is >90% among lutidines.

at 420°C with a 0.5 h^{-1} weight hourly space velocity for 4 hour on stream. Three H-ZSM-5 catalysts with (Si/Al) = 30, 150 and 280 were tested. H-ZSM-5 (30), H-ZSM-5 (150) and H-ZSM-5 (280) showed 40.8, 58.7 and 41.1% conversion of acetone, respectively. The yields of 2-picoline for H-ZSM-5 (30), H-ZSM-5 (150) and H-ZSM-5 (280) were 27.0, 33.5 and 28.0 wt.-% based on acetone and (2-/4-picoline) ratios were 9.0, 8.4% and 'very high', respectively. H-ZSM-5 (150) showed the highest activity for the formation of 2-picoline. 4-Picoline was not observed in the case of H-ZSM-5 (280). To get a high activity in the dehydrocyclization reaction, an optimum number of active centres are required. With the increase of the (Si/Al) ratio there was an increase in the (2-/4-picoline) ratio. The yield of total lutidines obtained was 10–40 wt.-% and 2,6-lutidine was >90% among the lutidines. Bipyridine (<10%) compound was also obtained at lower (350°C) temperature confirmed by GC-MS.

In the case of Pb-ZSM-5 and W-ZSM-5, the conversions of acetone were 69.0 and 51.2 wt.-% while the yields of 2-picoline were 35.0 and 29.0 wt.-%, respectively. The yield of 4-picoline observed was low (2 wt.-%). Thus lead and tungsten have a promoting effect in increasing the yield of 2-picoline. The lead promoted silica–alumina PbSA (1) and PbSA(2) showed 16.0 and 6.8 wt.-% 2-picoline formation. In the case of Pb-ZSM-5 and W-ZSM-5, the yield of lutidines was 18–25 wt.-%.

To understand the stoichiometry, the following different reactions were carried out over Pb-ZSM-5 (150) at 420°C and 0.5 h^{-1} WHSV, (1) acetone, formaldehyde, methanol and ammonia, (2) acetone, formaldehyde (1:1.05 molar) and ammonia, (3) acetone, formaldehyde (4:1) and ammonia, (4) acetone, methanol and ammonia and (5) acetone and ammonia. The experimental data are given in Table 2. The selectivity among the picolines and yield of 2-picoline were enhanced predominantly after addition of formaldehyde to the feed. The molar ratios of acetone to formaldehyde were varied widely, including a ratio of 1:3, but formaldehyde polymerized, forming a solid and coke in the pre-heater zone; so the addition of methanol is essential to enhance the yield. The stoichiometry may be suggested as follows for the formation of picoline.

$$\text{acetone} + 3\ \text{formaldehyde} + \text{ammonia} \rightarrow \text{picoline} + 4\ \text{water} \quad (1)$$

As lutidines are also observed in the products, the mechanism and stoichiometry may also be represented as given in Scheme 1.

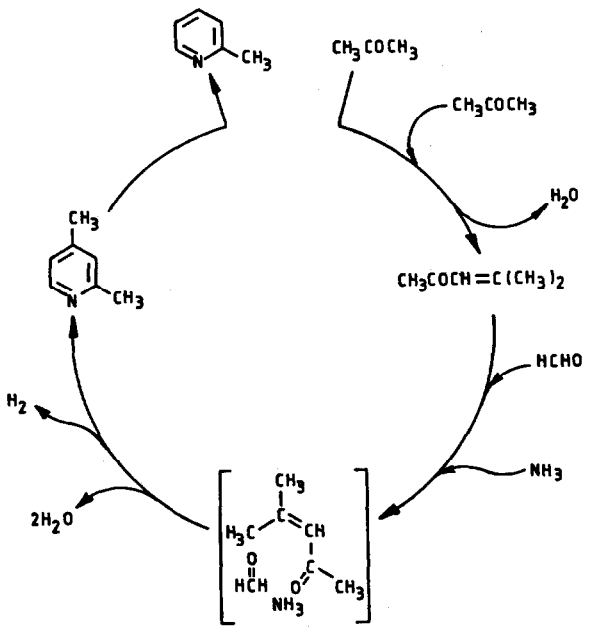
The influence of the WHSV is depicted in Table 3. The WHSV was varied from 0.25 to 1 h^{-1}. The reaction of acetone, formaldehyde, methanol with ammonia was carried out over Pb-ZSM-5 at 420°C. The conversions of acetone for 1, 0.75, 0.50, 0.37 and 0.25 h^{-1} WHSV were 59.3, 72.6, 69.0, 68.2 and 69.4 wt.-% and yields for 2-picoline were 15.6, 31.5, 35, 47.5 and 45 wt.-%, respectively. With the increase of WHSV, the yield increased upto 0.37 h^{-1}. The ratio of 2-picoline/4-picoline increased with the decrease of WHSV. The experimental data in Table 4 indicate that 2-picoline in the product increases, as the amount of lutidines decreases. The reaction of lutidine and water (1:2.5 mol) over Pb-ZSM-5 at 420°C and 0.5 h^{-1} WHSV leads to >5.6 wt.-% 2-picoline and 3.6% pyridine at >90% conversion of lutidine. The reaction of 2,6-lutidine, water and ammonia also leads to the formation of >10% 2-picoline and pyridine. The reaction of methanol over Pb-ZSM-5 and W-ZSM-5 at 420°C and 0.5 h^{-1} WHSV leads to the formation of 79.1, 36.4% formaldehyde

Table 2
The synthesis of 2-picoline from acetone: the variation of feed

Catalyst = Pb-ZSM-5 (150), reaction temperature = 420°C, WHSV = 0.5 h^{-1}

S. No.	Feed	Molar ratio	Time-on-stream (h)	Conversion (wt.-%)		Yield (wt.-%)[a]			2-Picoline / 4-Picoline
				Acetone	Formaldehyde	2-Picoline	4-Picoline	Lutidines[b]	
1.	(CH_3COCH_3 + HCHO + CH_3OH + NH_3)	1:0.5:0.9:1.3	2	69.0	100	35.0	8.0	26.0	4.4
2.	(CH_3COCH_3 + HCHO + NH_3)	1:1.05:1.3	2	64.4	100	40.0	7.0	17.4	5.7
3.	(CH_3COCH_3 + HCHO + NH_3)	4:1:1.3	3	28.5	100	20.0	–	8.5	–
4.	(CH_3COCH_3 + CH_3OH + NH_3)	1:2:1.3	3	25.6	–	20.6	–	5.0	–
5.	(CH_3COCH_3 + NH_3)	1:1.3	3	15.0	–	5.0	–	10.0	–

[a]Based on acetone.
[b]2,6-Lutidine is > 90%.



Scheme 1.

at 80.4, 37.6% conversion of methanol respectively. Under our experimental conditions, 2-picoline and 2,6-lutidine were the major products.

The weight percent conversion of acetone, yield of 2,6-lutidine based on acetone and selectivity with respect to the variation of the weight hourly space velocity in the reaction of acetone, formaldehyde, methanol and ammonia over Pb-ZSM-5 at 420°C is shown in Fig. 1. Thus Scheme 1 is plausible to account for the formation of 2,6-lutidine and other products. We have varied the acetone to formaldehyde ratio from 1 : 3 to 4 : 1 with or without

Table 3
The synthesis of 2-picoline from acetone: the effect of WHSV

Reaction temperature = 420°C, catalyst = Pb-ZSM-5 (150), Feed: CH_3COCH_3 : HCHO : CH_3OH : NH_3 = (1 : 1.3 : 0.9 : 1.3) molar

S. No.	Weight hourly space velocity (h^{-1})	Time-on-stream (h)	Conversion (wt.-%) with respect to		Yield (wt.-%)[a]			2-Picoline / 4-Picoline
			Acetone	Formaldehyde	2-Picoline	4-Picoline	Lutidines[b]	
1.	1.00	4	59.3	100	15.6	4.5	39.2	3.5
2.	0.75	1	72.6	100	31.5	6.0	35.1	5.3
3.	0.50	2	69.0	100	35.0	8.0	26.0	4.4
4.	0.37	(3+4)	68.2	100	47.5	8.0	12.7	6.0
5.	0.25	2	69.4	100	45.0	6.0	18.4	7.5

[a]Based on acetone.
[b]2,6-Lutidine is >90%.

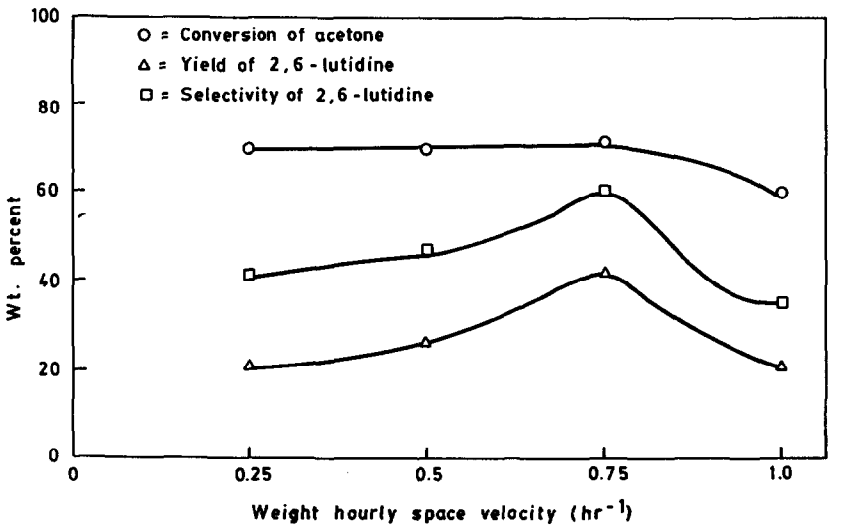


Fig. 1. Acetone conversion, yield and selectivity of 2,6-lutidine as a function of weight hourly space velocity.

methanol. The experiments in which polymerized formaldehyde was not observed in the pre-heater zone are reported. The experimental data in Table 2 indicate that the increase of formaldehyde in the feed increases the amount of 2-picoline in the product. This may be explained by the stoichiometric Eq. (1). The reaction of acetone over H-ZSM-5 and the various parallel reactions involved in such intermolecular cyclization to heterocycles are also reported and discussed in refs. [11] and [12].

The experimental data regarding the effect of the reaction temperature on the synthesis of 2-picoline are given in Table 4. The reaction of acetone, formaldehyde, methanol 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 of acetone were 26.0, 50.5, 53.8, 44.0 and 69.0 wt.-%, and yields of 2-picoline were

Table 4
The synthesis of 2-picoline from acetone: the effect of temperature

Catalyst = Pb-ZSM-5 (4 g), WHSV = 0.5 h^{-1}, feed: CH_3COCH_3:HCHO:CH_3OH:NH_3 = (1:1.3:0.9:1.3) molar

S.No.	Reaction temperature (°C)	Time-on-stream (h)	Conversion (wt.-%)		Yield (wt.-%)			2-Picoline / 4-Picoline
			Acetone	Formaldehyde	2-Picoline	4-Picoline	Lutidines[b]	
1.	420	2	69.0	100	35.0	8.0	26.0	4.4
2.	400	(2+3)	44.0	100	32.0	7.0	5.0	3.6
3.	380	2	53.8	100	43.0	10.0	0.8	4.3
4.	350	3	50.5	100	32.0	7.0	11.5	4.6
5.	300	3	26.0	100	14.5	4.0	7.5	3.6

[a]Based on acetone.
[b]2,6-Lutidine is >90%.

Table 5
The synthesis of 2-picoline from acetone: the time-on-stream effect

Catalyst = Pb-ZSM-5 (150), reaction temperature = 420°C, feed = (CH_3COCH_3 : HCHO : CH_3OH : NH_3) = (1:1.3:0.9:1.3) molar

S. No.	Time-on-stream (h)	Conversion (wt.-%)		Yield (wt.-%)[a]			2-Picoline / 4-Picoline
		Acetone	Formaldehyde	2-Picoline	4-Picoline	Lutidines[b]	
1.	1	50.5	100	31.0	6.5	13.0	4.8
2.	2	69.0	100	35.0	8.0	26.0	4.4
3.	(3+4)	50.9	100	31.0	5.0	14.9	6.2
4.	(5+6)	51.5	100	31.0	4.0	16.5	5.2
5.	7	50.3	100	35.0	6.5	8.8	5.4

[a]Based on acetone.
[b]2,6-Lutidine is >90%.

14.5, 32, 43, 32.0 and 35 wt.-% respectively. The (2-picoline/4-picoline) ratio was between 3.6 and 4.6. There is not much effect of the reaction temperature on the selectivity ratio. On the other hand, promoters like lead or tungsten affect the selectivity considerably.

The reaction of acetone, formaldehyde, methanol and ammonia was carried out at 420°C over Pb-ZSM-5 (150) for 7 h and time-on-stream effect is given in Table 5. There was no notable deactivation. For 1, 2, (3+4), (5+6) and 7 hour on stream, the conversions of acetone were 50.5, 69.0, 50.9, 51.5 and 50.3 wt.-% while yields for 2-picoline were 31.0, 35.0, 31.0 and 35.0 wt.-%, respectively. The (2-picoline/4-picoline) ratio varied from 3.7 to 6. Pb-ZSM-5 showed the best activity for the synthesis of 2-picoline and 2,6-lutidine from acetone.

Acknowledgement

We are thankful to the referee for suggesting the stoichiometry of the reaction and emphasizing the discussion regarding it.

References

[1] S.E. Golunski and D. Jackson, Appl. Catal., 23 (1986) 1.
[2] S.J. Kulkarni and M. Subrahmanyam, Ind. J. Chem., 30A (1991) 1041.
[3] F.J. Van der Gaag, F. Louter, J.C. Oudejans and H. Van Bekkum, Appl. Catal., 26 (1986) 191.
[4] H. Van Bekkum and H.W. Kouwenhoven, in M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, C. Montassier and G. Pérot (Editors), Heterogeneous Catalysis and Fine Chemicals (Studies in Surface Science and Catalysis, Vol. 41), Elsevier Amsterdam, 1988, p. 45.
[5] T. Miyake, K. Noguchi and K. Imamura, British Patent 1 579 473 (1980).
[6] Y. Minato and S. Yasuda, US Patent 3 932 421 (1976).
[7] D. Feitler, W. Schimming and H. Wetstein, US Patent 4 675 410 (1987).
[8] Y. Kusunoki, H. Okazaki, Y. Sato and E. Sano, US Patent 3 781 292 (1973).
[9] T. Matsumoto and A. Tamano, US Patent 3 417 092 (1968).

[10] C.W. Hargis, US Patent 3 829 428 (1974).
[11] R. Ramachandra Rao, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, presented at 11th National Symposium on Catalysis, Hyderabad, April 1993.
[12] S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, Ind. J. Chem., 32A (1993) 28.