ELSEVIER

Applied Catalysis A: General 136 (1996) L1–L6

APPLIED CATALYSIS A: GENERAL

Letter

Synthesis of 3,5-lutidine from propionaldehyde over modified ZSM-5 catalysts [1]

S.J. Kulkarni *, R. Ramachandra Rao, Y.V. Subba Rao, M. Subrahmanyam, A.V. Rama Rao

Indian Institute of Chemical Technology Hyderabad - 500 007, India

Received 1 August 1995; revised 29 November 1995; accepted 30 November 1995

Abstract

The reaction of propionaldehyde, formaldehyde and ammonia was carried out over modified H-ZSM-5 catalysts. Typically over H-ZSM-5 (Si/Al = 150), at 400°C, the yield of 3,5-lutidine was 63.1 wt.-% at 66.2% conversion of propionaldehyde. The cation effect was observed in the increase of collidines in the product. Our studies have established that useful substituted pyridines can be synthesized from C_1–C_4 aldehydes and alcohols in the presence of ammonia via dehydrocyclization and dehydrogenation.

Keywords: H-ZSM-5; 3,5-Lutidine; Propionaldehyde; Cyclization; Zeolites

1. Introduction

Zeolites have been used in the synthesis of speciality and fine chemicals [1–18]. We have reported the synthesis of pyridine and picolines from ethanol [12] and acetaldehyde [19] and 2,6-lutidine from acetone [11]. The synthesis of pyridine and pyridine substitutes has been reviewed in the literature [20,21]. In this paper we report the selective synthesis of 3,5-lutidine from propionaldehyde, formaldehyde and ammonia over modified ZSM-5 catalysts.

* Corresponding author.

[1] IICT Communication No: 3569.

SSDI 0926-860X(95)00325-8

2. Experimental

H-ZSM-5 was supplied by Conteka, Sweden. The Si/Al ratio varied from 30 to 280. H-ZSM-5 (Si/Al = 30) was further modified with 5.0 wt.-% of various cations by the impregnation method.

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 syringe pump (Sage Instruments, USA). The product was cooled using ice-cold 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 using SE-30 (5%) and OV-17 columns. The analysis was confirmed by mass spectra and GC-mass. 3,5-Lutidine was isolated and identified by NMR, mass spectra. The mass balance was $> 90\%$.

3. Results and discussion

The reaction of propionaldehyde, formaldehyde and ammonia was carried out over various modified ZSM-5 catalysts and the results are given in Tables 1 and 2. There is no specific and substantial effect of Si/Al ratio or various cations over the conversion and the formation of 3,5-lutidine. Typically the yields of 3,5-lutidine over H-ZSM-5 (Si/Al = 30), H-ZSM-5(150), Pb-ZSM-5 were 57.9, 63.1 and 56.1 wt.-% at 77.3, 66.2 and 68.2% conversion, respectively. The reaction temperature was 420°C, and a weight hourly space velocity (WHSV) of 0.5 h^{-1} for 4 g of the catalyst. The substitution of transition cations in H-ZSM-5 (30) increased the yield of collidines from 6% to 31 wt.-%. There is no specific trend in the yield of collidines with respect to various cations. The time on

Table 1
Reaction of propionaldehyde, formaldehyde and ammonia to 3,5-lutidine: variation of the catalysts

Catalyst	Temperature (°C)	Time on stream (h)	Conversion of propionaldehyde (%)	Yield (wt.-%) [a]		
				2,6-Lutidine	3,5-Lutidine	Other products [b]
H-ZSM-5 (Si/Al = 30)	420	(3+4)	77.3	8.2	57.9	11.2
H-ZSM-5 (150)	420	4	66.2	0.6	63.1	2.5
H-ZSM-5 (280)	400	2	77.5	19.6	48.5	9.4
W-ZSM-5 (30)	400	1	81.9	8.5	47.9	25.5
Cr-ZSM-5 (30)	400	(3+4)	67.9	7.2	40.5	20.2
Mn-ZSM-5	400	2	84.8	8.7	54.0	22.1
Co-ZSM-5	400	2	74.4	4.7	45.3	24.4
Ni-ZSM-5	400	1	87.1	21.7	46.0	19.4

Weight hourly space velocity (WHSV) = 0.5 h^{-1}, propionaldehyde:formaldehyde = 1:1 molar ratio.
[a] Based on (propionaldehyde + formaldehyde).
[b] Collidines are major products.

Table 2
Reaction of propionaldehyde, formaldehyde and ammonia to 3,5-lutidine: variation of the catalysts

Catalyst	Temperature (°C)	Time on stream (h)	Conversion of propionaldehyde (%)	Yield (wt.-%) [a]		
				2,6-Lutidine	3,5-Lutidine	Other products [b]
Pb-ZSM-5	400	4	68.2	5.7	56.1	6.4
Pt-ZSM-5	400	4	86.7	10.2	55.0	21.5
Pd-ZSM-5	400	2	85.0	4.6	55.7	24.7
Sm-ZSM-5	400	3	89.7	12.9	58.8	17.9
La-ZSM-5	400	2	86.7	7.4	53.8	25.5
Ti-K-ZSM-5	400	2	90.7	7.9	58.2	24.5
Sb-Bi-ZSM-5	400	1	81.9	30.9	17.5	33.5
Fe-Cr-ZSM-5	400	2	75.9	4.9	42.8	28.2

Propionaldehyde:formaldehyde = 1:1 molar ratio, WHSV = 0.5 h^{-1} at atmospheric pressure.
[a] Based on (propionaldehyde + formaldehyde).
[b] Collidines are major products.

stream is given corresponding to the maximum yield of 3,5-lutidine. With the increase of time on stream the yield decreases.

The reaction temperature was varied from 300° to 420°C in the reaction of propionaldehyde, formaldehyde and ammonia over Pb-ZSM-5(30) catalyst and the results are given in Table 3. At 400°C, the yield of 3,5-lutidine was 56.1% at 68.2% conversion of propionaldehyde. The yield of 3,5-lutidine decreased to 25.5% at 300°C. The effect of weight hourly space velocity (WHSV) in the reaction of propionaldehyde, formaldehyde and ammonia over Pb-ZSM-5, is given in Table 4. The yields of 3,5-lutidine were 45.6, 56.1 and 27.3% at 0.25, 0.5 and 1.0 h^{-1} WHSV, respectively. With the increase of WHSV, the conversion of propionaldehyde decreases from 81.4 to 60.4% at 0.25 to 1 h^{-1} WHSV.

In the reaction of propionaldehyde, formaldehyde and ammonia over Pb-

Table 3
Reaction of propionaldehyde, HCHO with NH_3 over Pb-ZSM-5 catalyst: effect of temperature

S. No.	Temperature (°C)	Time on stream (h)	Conversion of propionaldehyde (wt.-%)	Yield (wt.-%) [a]		
				2,6-lutidine	3,5-lutidine	other [b] products
1	300	2	46.4	4.2	25.5	16.7
2	350	3	56.5	3.6	44.1	8.8
3	380	2	75.5	8.9	40.1	26.5
4	400	4	68.2	5.7	56.1	6.4
5	420	3+4	76.7	3.9	55.1	17.7

Reactants: propionaldehyde:HCHO = 1:1 molar ratio.
WHSV 0.5 h^{-1}; Atmospheric pressure.
[a] Based on aldehydes.
[b] Collidines and pyridine.

Table 4
Reaction of propionaldehyde, formaldehyde and ammonia over Pb-ZSM-5: effect of WHSV

S. No.	WHSV (h^{-1})	Time on stream (h)	Conversion of propionaldehyde	Yield (wt.-%) [a]		
				2,6-Lutidine	3,5-Lutidine	Others [b]
1	0.25	2	81.4	12.1	45.6	23.7
2	0.37	1	84.8	13.2	48.8	22.8
3	0.5	4	68.2	5.7	56.1	6.4
4	0.75	3	69.3	12.2	32.1	25.0
5	1.0	2	60.4	7.6	27.3	25.5

Reaction temperature: 400°C.
Reactants: propionaldehyde:HCHO = 1:1 molar.
[a] Based on ($CH_3CH_2CHO + HCHO$).
[b] Major products are collidines.

Table 5
The reaction of propionaldehyde, formaldehyde and ammonia over Pb-ZSM-5: effect of mole ratio

S. No.	Mole ratio CH_3CH_2CHO:HCHO	Time on stream (h)	Conversion of propionaldehyde (wt.-%)	Yield (wt.-%) [a]		
				2,6-Lutidine	3,5-Lutidine	Others [b]
1	1:0.5	4	74.8	10.0	28.2	36.6
2	1:1	4	68.2	5.7	56.1	6.4
3	1:1.5	2	66.6	6.9	36.0	23.7
4	1:2	2	72.2	8.2	41.5	22.5
5	1:2.5	2	66.5	6.5	38.5	21.5

Reaction temp. 400°C; WHSV = 0.5 h^{-1}, atmospheric pressure.
[a] Based on aldehydes.
[b] Collidines and pyridine are major product.

ZSM-5, the effect of mole ratio of CH_3CH_2CHO to HCHO was studied and the results are given in Table 5. The maximum yield of 3,5-lutidine was 56.1 wt.-% obtained at a 1:1 mole ratio of CH_3CH_2CHO to HCHO. With the increase and

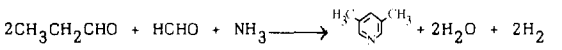
Table 6
The reaction of propionaldehyde over Pb-ZSM-5: variation of feed

S. No.	Catalyst	Feed	Time on stream (h)	Conversion of propionaldehyde (wt.-%)	Yield (products wt.-%) [a]		
					2,6-Lutidine	3,5-Lutidine	Others [b]
1	Pb-ZSM-5	Propionaldehyde + methanol + NH_3	1	76.5	10.9	22.0	43.6
2	Pb-ZSM-5	Propionaldehyde + NH_3	1	69.5	6.9	10.5	52.1
3	W-ZSM-5	Propionaldehyde + CH_3CHO + HCHO + NH_3	4	82.6	35.9	21.0	25.7

Reaction temperature: 400°C; WHSV = 0.5 h^{-1}.
[a] Based on hydrocarbons.
[b] In others; pyridine and collidines.

decrease of the mole ratio, other products like collidines and pyridine increased. The yield of 2,6-lutidine was in the range of 5–10 wt.-%.

In the reaction of propionaldehyde and ammonia, in presence and absence of methanol, the yield of collidines increased to 40–52 wt.-%. By the addition of acetaldehyde and formaldehyde, 2,6-lutidine in the products increased to 35.9 wt.-%. The results are depicted in Table 6. In the reaction of CH_3CH_2CHO and HCHO over Pb-ZSM-5, the condensation of propionaldehyde was observed. The stoichiometric equation may be written as follows:



The first step may not the formation of imine. The first mechanistic step is the condensation of propionaldehyde followed by cyclization with inclusion of ammonia and formaldehyde. Thus a number of useful substituted pyridines can be formed from C_1 to C_4 aldehydes and alcohols in the presence of ammonia via dehydrocyclization and dehydrogenation.

Acknowledgements

We are thankful to Dr. U.T. Bhalerao, Director-in-charge and Dr. P. Kanta Rao for encouragement. One of us, RRR is thankful to CSIR for a senior research fellowship.

References

[1] W. Hölderich, M. Hesse and F. Naumann, Angew. Chem. Int. Ed. Engl., 27 (1988) 226.
[2] C.B. Dartt and M.E. Davis, Catal. Today, 19 (1994) 151.
[3] S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, Indian J. Chem. A, 32 (1993) 28.
[4] S.J. Kulkarni and M. Subrahmanyam, Indian J. Chem. A, 30 (1991) 1041.
[5] M. Subrahmanyam, S.J. Kulkarni and A.V. Rama Rao, J. Chem. Soc., Chem. Commun., (1992) 607.
[6] M. Subrahmanyam, S.J. Kulkarni, B. Srinivas and A.R. Prasad, J. Indian Chem. Soc., 69 (1992) 681.
[7] Y.V. Subba Rao, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, J. Chem. Soc., Chem. Commun., (1993) 1456.
[8] Y.V. Subba Rao, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, Tetrahedron Lett., 34 (1993) 7799.
[9] M. Subrahmanyam, S.J. Kulkarni and B. Srinivas React. Kinet. Catal. Lett., 49 (1993) 455.
[10] S.J. Kulkarni, R. Ramachandra Rao, M. Subrahmanyam and A.V. Rama Rao, J. Chem. Soc., Chem. Commun., (1994) 273.
[11] A.V. Rama Rao, S.J. Kulkarni, R. Ramachandra Rao, amd M. Subrahmanyan Appl. Catal. A, 111 (2) (1994) L101.
[12] S.J. Kulkarni, R. Ramachandra Rao, M. Subrahmanyam and A.V. Rama Rao, Appl. Catal. A, 113 (1994) 1.
[13] K. Nagaiah, S. Sudhakar Rao, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, J. Catal., 147 (1994) 349.

[14] Y.V. Subba Rao, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, J. Org. Chem., 59 (1994) 3998.
[15] K. Nagaiah, A. Sudhakar Rao, M. Subrahmanyam, S.J. Kulkarni and A.V. Rama Rao, Indian J. Chem. Technol., 1 (1994) 356.
[16] K. Nagaiah, A. Sudhakar Rao, M. Subrahmanyam, S.J. Kulkarni and A.V. Rama Rao, Indian J. Chem. Technol., 1 (1994) 359.
[17] Y.V. Subba Rao, P. Vijayanand, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, Synth. Commun., 25 (6) (1995) 849.
[18] M. Subrahmanyam, A.R. Prasad, S.J. Kulkarni and A.V. Rama Rao, Indian J. Chem. B, 34 (1995) 573.
[19] R. Ramachandra Rao, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, React. Kinet. Catal. Lett., (1995) in press.
[20] B. Elvers (Editor), Ullmann's Encyclopedia of Industrial Chemistry, VCH, Vol. A 22, 1993, pp. 399–430.
[21] S.E. Golunski and D. Jackson, Appl. Catal., 23 (1986) 1.