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Letter

A new route for the synthesis of 3,5-lutidine over modified ZSM-5 catalysts

R. Ramachandra Rao, N. Srinivas, S.J. Kulkarni*, M. Subrahmanyam, K.V. Raghavan

Indian Institute of Chemical Technology, Hyderabad, India

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Abstract

The reaction of propanol, formaldehyde and methanol with ammonia was carried out over modified HZSM-5 catalysts, to get 3,5-lutidine selectively. Typically over LaZSM-5 (Si/Al=15), at 400°C the selectivity of 3,5-lutidine is 72.2% at 88.6% conversion of propanol. The effects of temperature, WHSV and mole ratio were studied in the synthesis of 3,5-lutidine over LaZSM-5 catalyst. Our studies have established that pyridine, picolines and lutidines can be synthesized from C_1–C_4 alcohols and aldehydes in the presence of ammonia via dehydrocyclization and dehydrogenation. © 1997 Elsevier Science B.V.

Keywords: ZSM-5; 3,5-Lutidine; *n*-Propanol; Cyclization; 2,6-Lutidine

1. Introduction

Zeolites are widely used in the synthesis of speciality and fine chemicals [1–12]. The synthesis of pyridine and pyridine substitutes has been reviewed in the literature [13–18]. Kijenski et al. reported the synthesis of pyridines from amino alcohols over supported copper catalysts [15], Dinkel [17] reported from acetals and Kameshwari et al. [18] reported the alkylation of pyridines over zeolites. Yasuda and Abe [16] reported the synthesis of 3-picoline and 3,5-lutidine from acrolein, propionaldehyde, formaldehyde and ammonia over CdO–SiO_2–Al_2O_3. But the yield of 3,5-lutidine was low (13%). We have reported the synthesis of pyridine and substituted pyridines from acetaldehyde [10], from ethanol [9], and from acetone [8]. We have reported for the first time the synthesis of 3,5-lutidine from propionaldehyde over modified ZSM-5 catalysts [19]. The yield of 3,5-lutidine was 63.1% with ~95% selectivity. 3,5-lutidine is a very useful intermediate to many drugs like antiulcer drugs (Omeprazole) and anti-inflammatory drugs. In this paper we report the selective synthesis of 3,5-lutidine from propanol, formaldehyde and methanol with ammonia over modified ZSM-5 catalysts.

2. Experimental

H-ZSM-5 zeolite was supplied by Conteka, Sweden. H-ZSM-5 (Si/Al=15) was further modified with 5 wt% of various cations like Pt, Pd, La, Co, Ni and Sm etc. by the impregnation method. The fixed bed vapour phase reactions were carried out using the above catalysts. The reactions were carried out using

*Corresponding author.

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a tubular, down-flow, pyrex reactor with 20 mm i.d. The reaction mixture was fed from the top using a syringe pump (Be Braun, USA). The amount of the catalyst taken for every reaction was 4 g. 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 (30%) column. The analysis was confirmed by mass spectra and GC-mass. The liquid product mass balance was about 80–90% and 5% gases were observed.

Table 1
The reaction with propanol, formaldehyde and ammonia to 3,5-lutidine over various catalysts

S. No.	Catalyst	Time on stream (h)	Conversion of propanol (wt %)	Selectivities of products (%)			
				2,6-Lutidine	3,5-Lutidine	Pyridine and picolines	Others[a]
1	HZSM-5 (Si/Al=140)	4	84.4	6.2	7.9	12.0	73.9
2	LaZSM-5	3	88.6	2.7	72.2	2.7	22.4
		4	88.9	0.8	65.2	1.8	32.2
3	LaHY	4	82.5	0.6	41.1	6.0	52.3
4	LaMCM-41	3	97.3	1.8	52.4	2.6	43.2
		4	92.9	7.0	44.8	4.8	43.4
5	WZSM-5	3	45.6	21.0	64.9	1.0	13.1
		4	23.5	34.9	61.7	–	3.4
6	NiZSM-5	2	86.0	14.4	15.1	16.4	54.1
		4	91.5	18.4	14.4	16.1	51.1
7	SmZSM-5	5	96.6	27.9	23.7	16.1	32.3
8	PtZSM-5	4	89.0	2.6	63.8	5.0	28.6
9	PdZSM-5	4	91.2	10.7	47.8	5.0	36.5
10	GaZSM-5	2	44.9	9.8	75.0	0.6	14.6
		4	39.4	6.4	82.6	5.0	6.0
11	ZrZSM-5	3	90.6	2.6	74.4	1.1	21.9
		4	94.8	2.1	68.6	4.2	25.1
12	CrZSM-5	4	95.8	12.4	16.8	46.5	24.3

Catalyst Wt=4 g; WHSV=0.5 h^{-1}; Reaction temp.=400°C;
Propanol : Ammonia=1 : 6 molar; Propanol : HCHO : Methanol=1 : 0.4 : 0.9 molar; M^{+n}=Metal cation=1 wt%.
[a] Propionaldehyde is the major product.

Table 2
The reaction of propanol to 3,5-lutidine over LaZSM-5 catalyst: Effect of temperature

S. No.	Temperature (°C)	Time on stream (h)	Conversion of propanol(wt %)	Selectivities of products (%)			
				2,6-Lutidine	3,5-Lutidine	Pyridine and picolines	Others[a]
1	300	1	72.9	4.7	2.7	22.3	70.3
		4	67.4	—	—	16.3	83.7
2	350	3	56.4	0.7	41.3	3.3	54.7
		4	88.9	0.8	65.2	1.8	32.2
3	380	4	61.5	1.0	33.5	4.3	61.2
4	400	3	88.6	2.7	72.2	2.7	22.4
		4	88.9	0.8	65.2	1.8	32.2
5	420	4	87.2	2.5	59.6	17.0	20.9

Catalyst Wt=4 g; WHSV=0.5 h^{-1};
Propanol : Ammonia=1 : 6 molar;
Propanol : HCHO : Methanol=1 : 0.4 : 0.9 molar.
[a] Propionaldehyde is the major product.

3. Results and discussion

The reaction of propanol, formaldehyde and methanol with ammonia was carried out over various modified ZSM-5 catalysts; the results are given in Table 1. Typically, the selectivities of 3,5-lutidine over LaZSM-5, LaHY and LaMCM-41 were 72.2, 41.1 and 52.4% at 88.6, 82.5 and 97.3 wt% conversion of propanol, respectively. No special trend of shape selectivity with respect to pore size was observed. The reaction temperature was 400°C with 0.5 h^{-1} weight hourly space velocity (WHSV) for 4 g of the catalyst. The conversion of propanol and the selectivities of all products, including pyridine, picolines and 2,6-luti-

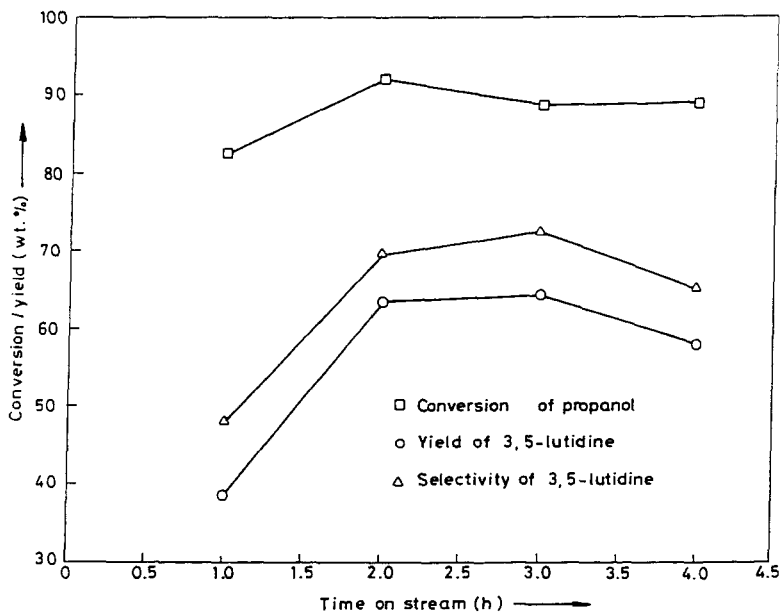

Fig. 1. Synthesis of 3,5-lutidine over LaZSM-5; Catalyst=LaZSM-5(30 mole ratio=propanol+HCHO+NH_3=1 : 0.9 : 0.9; WHSV=0.5 h^{-1}, Reaction temp.=400°C.

Table 3
The reaction of propanol to 3,5-lutidine over LaZSM-5 catalyst: Effect of WHSV

S. No.	WHSV	Time on stream (h)	Conversion of propanol (wt %)	Selectivities of products (%)			
				2,6-Lutidine	3,5-Lutidine	Pyridine and picolines	Others[a]
1	0.25	4	97.6	3.3	90.5	0.3	5.9
2	0.37	5	100.0	1.2	76.8	—	22.0
		4	85.0	1.3	70.8	—	27.9
3	0.50	3	88.6	2.7	72.2	2.7	25.4
		4	88.9	0.8	65.2	1.8	32.2
4	0.75	4	55.0	3.2	45.8	1.0	50.0
5	1.00	5	70.4	2.5	53.8	3.8	39.9
		4	60.5	1.6	50.7	3.2	44.5

Catalyst Wt=4 g; Reaction temp.=400°C.
Propanol : Ammonia=1 : 6 molar.
Propanol : HCHO : Methanol=1 : 0.9 : 0.9 molar.
[a] Propionaldehyde is the major product.

Table 4
The reaction of propanol to 3,5-lutidine over LaZSM-5 catalyst: Effect of mole ratio

S. No.	Molar ratio[b]	Time on stream (h)	Conversion of propanol (wt%)	Selectivities of products (%)			
				2,6-Lutidine	3,5-Lutidine	Pyridine and picolines	Others[a]
1	1 : 0.9 : 0.9	3	88.6	2.7	72.2	2.7	22.4
		4	88.9	0.8	65.2	1.8	32.2
2	1 : 0.9 : 0	4	83.5	3.0	30.0	12.8	54.2
3	1 : 0 : 1.8	2	57.7	1.4	44.7	1.4	52.5
		4	44.4	2.2	13.5	8.8	75.5
4	1 : 0.4 : 0.9	5	75.0	2.2	32.3	17.6	47.9
		4	73.6	2.3	29.0	2.0	66.7
5	1 : 0.2 : 0.5	3	76.5	5.5	37.3	18.4	38.8
		4	62.0	1.1	34.6	8.5	55.8
6	1 : 0.9 : 3.7	4	67.3	0.4	72.2	0.8	26.6

Catalyst Wt=4 g; WHSV=0.5 h^{-1}; Reaction temp: 400°C.
Propanol : Ammonia=1 : 6 molar;
[a] Propionaldehyde is the major product.
[b] Propanol : HCHO : Methanol molar ratio.

Table 5
The reaction of isopropanol to 3,5-lutidine over various catalysts

S. No.	Catalyst	Time on stream (h)	Conversion of isopropanol (wt%)	Selectivities of products (%)			
				2,6-Lutidine	3,5-Lutidine	Pyridine and picolines	Others[a]
1	HZSM-5	3	74.5	38.5	12.2	16.2	33.1
	(Si/Al=140)	4	53.4	41.4	10.2	13.2	35.2
2	HZSM-5	2	78.0	26.8	11.6	13.0	48.6
	(15)	4	87.4	21.9	17.6	4.6	55.9
3	LaZSM-5	4	76.0	35.8	16.7	0.5	47.0
4	PtZSM-5	2	41.8	33.4	13.8	—	52.8
		4	67.8	18.4	12.8	2.8	66.0
5	PdZSM-5	4	70.7	15.1	4.2	26.0	54.7
6	GaZSM-5	4	16.4	67.0	20.0	6.0	7.0

Catalyst Wt=4 g; WHSV=0.5 h^{-1}; Reaction temp.=400°C.
2-Propanol : Ammonia=1 : 6 molar.
2-Propanol : HCHO : Methanol=1 : 0.9 : 0.9 molar.

dine, are given. The conversion of HCHO was 100%. In other products, propionaldehyde is the major product. The time on stream is given, corresponding to the maximum selectivity of 3,5-lutidine. The time on stream at 4 h is also given for all the catalysts for comparison. A typical plot of conversion (%), selectivity (wt%) vs time on stream is given in Fig. 1. The coking is mainly responsible for the decrease in the conversion.

The reaction temperature was varied from 300 to 420°C in the reaction of propanol, formaldehyde, methanol and ammonia over LaZSM-5 [15] catalyst; the results are given in Table 2. The maximum selectivity of 3,5-lutidine 72.2% was observed at 400°C and started decreasing with the increase of temperature. The selectivity of other products, mainly propionaldehyde, decreases with the increase of temperature. In this reaction, due to coking the shape selectivity for 3,5-lutidine is improved, because collidines could not diffuse out. The coking reduces the intersection and/or pore diameter. At the same time the optimum number of active centres are sufficient for the main reaction. The effect of weight hourly space velocity (WHSV) is also varied over LaZSM-5 [15] for this reaction at

400°C; the data is given in Table 3. The selectivities of 3,5-lutidine were 90.5, 76.8 and 72.2% at 0.25, 0.37 and 0.5 h^{-1} WHSV, respectively. The selectivity of 3,5-lutidine is decreased at high flow rates, due to the increase of propionaldehyde in the product. The conversion decreased with WHSV, as given in Table 3.

The effect of mole ratio of propanol, formaldehyde and methanol was studied for this reaction over LaZSM-5 [15] at 400°C and 0.5 h^{-1} WHSV; the results are given in Table 4. The maximum selectivity of 3,5-lutidine was observed at 1 : 0.9 : 0.9 molar ratio of propanol, formaldehyde and methanol. Methanol was used mainly as the additive for formaldehyde, because polymerization of formaldehyde takes place at higher amounts of formaldehyde. As we decrease the formaldehyde mole ratio, the selectivity of 3,5-lutidine starts decreasing. The selectivity of 2,6-lutidine was in the range of 1 to 5%.

The reaction of 2-propanol with formaldehyde, methanol and ammonia was carried out instead of *n*-propanol over various catalysts; the results are given in Table 5. The reaction temperature was 400°C with 0.5 h^{-1} WHSV. In this case, 2,6-lutidine was observed as a major product due to the position of –OH at the second carbon atom in 2-propanol. Typically, the selectivities of 2,6-lutidine were 38.5, 26.8, 35.8, 33.4 and 67.0% over HZSM-5 (Si/Al=140), HZSM-5 (Si/Al=15), LaZSM-5, PtZSM-5 and GaZSM-5 at 74.5, 78.0, 76.0, 41.8 and 16.4 wt% conversions of 2-propanol.

The possible mechanism can be explained with respect to the product distribution, as given in Fig. 2. The mechanism explains the variation in selectivity. The first step may be the formation of propionaldehyde, which was observed in the products. Propionaldehyde may form imine by reacting with ammonia. Two such imines may react with formaldehyde (or methanol) and by cyclization and dehydrogenation lead this compound may to 3,5-lutidine. The active sites for the cyclization and dehydration are Brønsted acidic centres and cations [20–22]. The cations also generate H^+ [20]. The aldehyde formation, dehydrogenation of amine and imine were observed over cations like Pb, Zr, W, [7,9]. The cations seriously affect the selectivity of the products. LaZSM-5 is the better catalyst with respect to the selectivity of 3,5-lutidine. The coking tendency varies for almost every catalyst. Due to the coking, H^+-

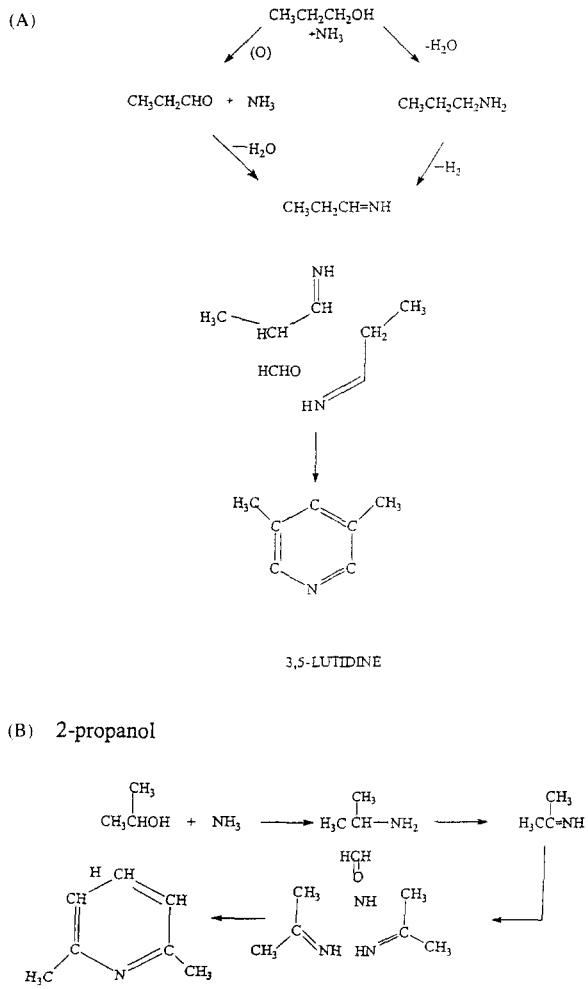

Fig. 2. Reaction mechanism in the reaction of propanol/2-propanol formaldehyde and ammonia over ZSM-5 catalyst.

zeolite deactivates faster than La-zeolite and the conversion and yield of 3,5-lutidine decreased, more than for H^+-zeolite. Among ZSM-5, Y and MCM-41, due to the intersection and channel structure favouring cyclization under study, LaZSM-5 is a better catalyst. The mechanism is also discussed elsewhere [8,9]. With time on stream, the coking increases, so as a result, the conversion or the yield of 3,5-lutidine decreases. The variation in selectivity is a resultant effect due to various factors like number and nature of active sites, coking or poisoning availability of ammonia and may not be correlated to a single factor. This work will be further extended and studied in case of

butanol, formaldehyde and ammonia to heterocycles, which is in progress. Thus a number of useful substituted pyridines can be formed from C_1–C_4 alcohols and aldehydes in the presence of ammonia via dehydrocyclisation and dehydrogenation.

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