Journal of Catalysis **208,** 332–338 (2002)
doi:10.1006/jcat.2002.3538

Shape-Selective Synthesis of Collidines over Modified Zeolites[1]

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Received September 28, 2001; revised January 11, 2002; accepted January 18, 2002

The shape-selective cyclization of 2-butanone with formaldehyde and ammonia to trimethyl- (collidines) and tetramethyl pyridines was investigated over ZSM-5 catalysts modified by various cations and prepared by conventional impregnation. The shape-selective nature of the catalyst was studied using isobutyl alcohol, 2-butanol, and *t*-butyl alcohol. © 2002 Elsevier Science (USA)

Key Words: **shape selectivity; collidines; ZSM-5; 2-butanone.**

1. INTRODUCTION

Solid acids such as zeolites are widely used as heterogeneous catalysts for the synthesis of specialty and fine chemicals (1–7). The dual properties of acidity and pronounced shape selectivity make zeolites promising catalysts for a variety of organic reactions (8–13). Modified ZSM-5 catalysts have been used for vapor-phase inter- and intramolecular cyclizations in the synthesis of nitrogen-containing heterocyclics (14–23). Among others, pyridine and its alkylated derivatives, which act as precursors for many chemical products of medicinal and agricultural importance, have been synthesized. The synthesis of alkylpyridines by alkylation of pyridine with alcohols, as reported by Kameshwari *et al.* (24), showed that the direct alkylation of pyridine is very difficult, due to the electron-withdrawing nature of the N atom in the pyridine ring. Alternatively, alkylpyridines can be synthesized by both a ring-closing mechanism (25, 26) and isomerization of aromatic amines (27). In general, these mechanisms lead to the formation of many isomers of picolines, lutidines, and collidines.

The selective synthesis of a particular isomer of collidine (2,3,5-trimethylpyridine) is important, since the isomer is the starting material for many drugs, such as Omeprazole (antiulcer). Today, coal tar is the most important commercial source of collidines. Other processes for the synthesis of collidines include ammonolysis of 2-butanone on a two-component metal oxide, cyclotrimerization of propyne with acetonitrile, and refluxing of *N*-2-butylacetamide in hexamethylphosphoramide (HMPA). In the last process, the maximum yield of collidines obtained was 15–30% (28, 29). Remarkably no process starting with relatively cheap chemicals has been applied commercially to the synthesis of collidines.

In this paper, we report for the first time the direct shape-selective synthesis of 2,3,5-collidine starting with 2-butanone (methyl ethyl ketone), formaldehyde, and ammonia over a ZSM-5 catalyst.

2. EXPERIMENTAL

Various H-ZSM-5 samples with SiO_2/Al_2O_3 ratios of 30, 40, and 280 were obtained from Conteka, Sweden. H-ZSM-5 ($SiO_2/Al_2O_3 = 30$) was impregnated with a nitrate solution of Pb, Mn, La, Fe, Cu, or Co to give a 5 wt% metal-ion loading. Powder XRD patterns of the calcined products were recorded on a diffractometer with Cu$K\alpha$ radiation at a 0.045° step size and a 0.5-s step time in the range $0 < 2\theta < 60°$. The specific surface area was determined from the linear part of the BET plot ($P/P_0 = 0.05$–0.30) using a vacuum unit. DTA and TG analyses of both HZSM-5 and transition metal ion incorporated ZSM-5 samples were performed at a heating rate of 20°C min^{-1} under a nitrogen flow of 25 ml min^{-1} using a Metler Toledo (Switzerland) instrument.

NH_3 TPD experiments were performed in a quartz sample cell containing 0.4 g of catalyst. The catalyst was calcined under flowing N_2 for 3 h at 460°C before being cooled to room temperature. Then NH_3 was adsorbed for 2 h, and the physisorbed ammonia was removed by purging the system at 80°C in N_2 at 100 ml min^{-1} for another 2 h. The desorbed NH_3 was continuously recorded by TCD with a 10°C min^{-1} ramping rate from 80 to 600°C and maintained at the final temperature for 20 min.

The catalytic reactions were carried out using a tubular, down-flow Pyrex reactor with 20-mm internal diameter. The amount of catalyst used was 4 g of mesh size 18–30. The reaction mixture was fed from the top using a syringe pump (Be Braun, Germany). The products were collected at the bottom and cooled using ice-cold water. One to three ice-cold traps were used at the outlet to collect the total amount of products. The products were analyzed by gas chromatography using a SE-30 column, identified by GC–MS analysis,

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0021-9517/02 $35.00

TABLE 1

Crystallinity, Surface Area, and Acidity (Ammonia Uptake in mmol g^{-1}) of Modified ZSM-5 Catalysts

Zeolite	Percentage crystallinity	Surface area (m^2 g^{-1})	Total acidity (mmol g^{-1})	No. of NH_3 molecules/ unit cell	No. of H_2O molecules/ unit cell
HZSM-5	100	310	1.73	10.1	5.5
PbZSM-5	90	225	1.47	8.6	7.2
MnZSM-5	95	272	0.98	5.4	7.0
LaZSM-5	92	307	3.77	22.0	6.9
FeZSM-5	94	242	1.44	8.5	4.1
CuZSM-5	97	311	1.01	5.9	4.2
CoZSM-5	89	186	1.87	10.9	4.9

and compared with authentic samples. The liquid product mass balance was about 85–90% and traces of gases were observed.

3. RESULTS AND DISCUSSION

The crystallinity of the metal-modified HZSM-5 catalysts was studied by XRD using a highly crystalline HZSM-5 catalyst (Si/Al = 15) as 100% standard. The degree of crystallinity of each sample was evaluated by the summation method, considering intensities of the typical diffraction peaks between $2\theta = 26^\circ$ and $2\theta = 29^\circ$ (Table 1) (30). All samples tested had good crystallinity. According to literature data, the diffraction pattern of ZSM-5 corresponds closely to orthorhombic symmetry. Wu *et al.* (31) observed that with treatments such as ion exchange, the ZSM-5 framework symmetry changes from orthorhombic to monoclinic. No such prominent change in the XRD peaks pertaining to monoclinic symmetry could be observed in the XRD patterns of the modified ZSM-5 catalysts. However, on impregnation, the intensities of the peaks at $2\theta = 7.9^\circ$ and 8.5° decreased in comparison to those for HZSM-5, indicating the presence of inorganic material in the intracrystalline voids. This fact could also be inferred from the decreasing surface areas of the impregnated samples relative to those of the protonated sample (Table 1).

The TGA–DTA curves for the transition metal ion impregnated ZSM-5 catalysts showed a small exotherm between 250 and 300°C, which corresponds to the oxidative degradation of scavenged inorganic species. The weight loss around 150–250°C indicates the interaction of water molecules with the cations and the zeolitic framework. Below 150°C, a water loss peak indicates volume-filling phenomena. The number of water molecules per unit cell as estimated from the TG weight loss of the catalyst between 150 and 250°C (Table 1) showed that the Pb-, Mn-, and La-ZSM-5 samples adsorbed a larger number of water molecules than the HZSM-5 sample, while the Fe-, Co-, and Cu-ZSM-5 samples adsorbed a smaller number.

As observed by Anderson *et al.* (32), Topsøe *et al.* (33), and Babu *et al.* (34), the NH_3 TPD profiles of various metal ion ZSM-5 catalysts showed three peaks at 150–250, 250–350, and 350–450°C corresponding to the desorption of NH_3 from weak, medium, and strong acid sites, respectively. The metal-ion-modified catalysts showed more medium and weak acidic sites than HZSM-5 catalysts. The total acidity of the catalysts followed the order MnZSM-5 < CuZSM-5 < FeZSM-5 < PbZSM-5 < HZSM-5 < CoZSM-5 < LaZSM-5 (Table 1).

Catalytic Activity

An attempt was made to determine the relationship between the properties of the ZSM-5 catalysts and the yields of the acid-catalyzed cyclization reaction of 2-butanone and formaldehyde with ammonia. At 400°C, the conversion of butanone over HZSM-5 catalysts with varying Si/Al ratios was around 80–90 wt%, whereas the selectivity of collidines decreased with decreasing total acidity (Table 2).

TABLE 2

Cyclization of Butanone and Formaldehyde with Ammonia over HZSM-5: Variation of Si/Al Ratio

Sample no.	Catalyst	TOS (h)	Conversion of 2-butanone (wt%)	Liquid product selectivity (%)				
				Tetramethylpyridine	2,3,5-Collidine	2,3,6-Collidine	Lutidine	Others[a]
1	HZSM-5 (30)[b]	3	95	6	34	25	6	29
		4	91	6	32	24	6	32
2	HZSM-5 (40.9)	3 + 4	92	5	40	24	7	24
3	HZSM-5 (129)	3	95	1	40	23	7	29
		4	88	4	14	9	5	68
4	HZSM-5 (280)	4	81	3	12	9	5	71

Note. Feed: 2-butanone + formaldehyde + ammonia. Molar ratio, 1 : 1 : 5; temperature, 400°C; WHSV = 0.5 h^{-1}.

[a] Mainly aliphatic imine and pyridine derivatives.

[b] The number in parentheses indicates SiO_2/Al_2O_3 molar ratio.

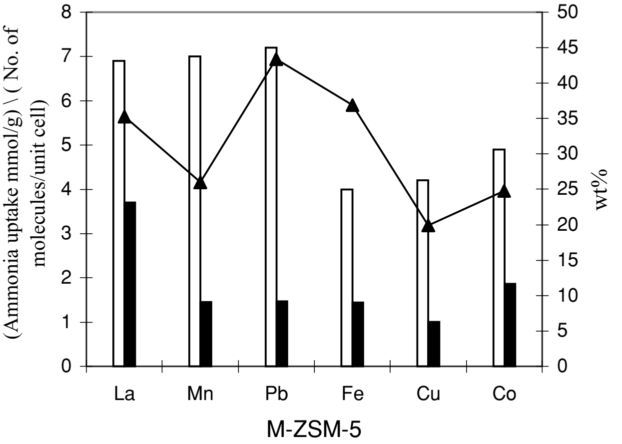

FIG. 1. Cyclization of 2-butanone, formaldehyde, and ammonia: ammonia uptake versus selectivity of 2,3,5-collidine. Feed: 2-butanone + formaldehyde + ammonia. Molar ratio, 1 : 1 : 5; temperature, 400°C; WHSV = 0.5 h^{-1}; metal wt% = 5. (▭) No. of H_2O molecules per unit cell; (▬) ammonia uptake; (▲) selectivity of 2,3,5-collidine.

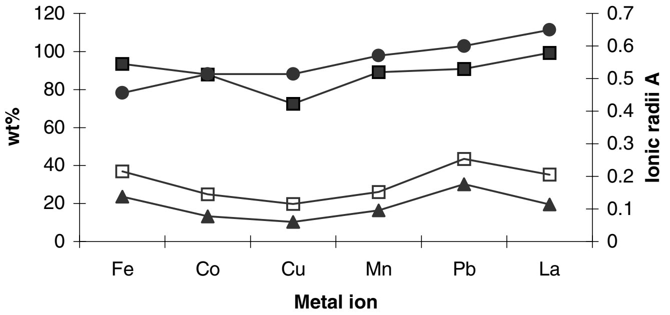

FIG. 2. Cyclization of 2-butanone, formaldehyde, and ammonia: Ionic radii versus activity. (■) Conversion of 2-butanone; (□) selectivity of 2,3,5-collidine; (▲) selectivity of 2,3,6-collidine; (●) ionic radii, corresponding to Fe^{3+}, Co^{3+}, Cu^{2+}, Mn^{3+}, and La^{3+}.

Cyclization reactions require a catalyst that contains metal ions and acid sites, since the metal ion and proton have the potential to act as bifunctional catalysts in which all steps occur within one residence time of the molecules inside the zeolite pore. Therefore, the catalyst was modified with various metal cations. PbZSM-5 showed maximum selectivity toward 2,3,5-collidine, with a high conversion (≈91 wt%) of 2-butanone. As shown in Fig. 1 and Table 3, La, Mn, Fe, Co, and CuZSM-5 had lower selectivities, irrespective of their acidities. Metal cations might partially block the channel and thus control the extent of product selectivity (35) (Fig. 2). The medium acid strength and dehydrogenating property of PbZSM-5 seem necessary for the formation of the pyridine ring.

The reaction temperature was varied from 250 to 400°C for the reaction of butanone, formaldehyde, and ammonia over PbZSM-5 (Table 4). The optimum temperature was around 400°C, with tetramethylpyridine and 2,3,5-collidine selectivities of 8 and 43%, respectively. The requirement of a relatively high reaction temperature in conjunction with acid catalysis may be due to the adsorption of product molecules at lower temperatures, thus blocking the active sites for the reaction. As the temperature increases, ammonia, collidine, and other pyridine molecules start to desorb, making sites available for the reaction (14). At the same time, however, sites develop for side reactions, such as the shifting of methyl groups and *trans*-methylation, which are suppressed by the high ammonia flow.

The weight hourly space velocity (WHSV) was varied for this reaction over PbZSM-5 at 400°C (results given in Table 5). When the WHSV was increased to 0.75 h^{-1}, the selectivity decreased, showing that the contact time between the active site and the reactant molecule also plays an important role.

Furthermore, the variation in feed composition showed that in the absence of formaldehyde in the feed no pyridine was formed; instead, imines and aromatics were observed.

TABLE 3

Cyclization of Butanone and Formaldehyde with Ammonia: Variation of Metal-Ion-Modified Catalyst

Sample no.	Catalyst	TOS (h)	Conversion of 2-butanone (wt%)	Liquid product selectivity (%)				
				Tetramethylpyridine	2,3,5-Collidine	2,3,6-Collidine	Lutidine	Others[a]
1	PbZSM-5[b]	4	91	8	43	30	5	14
2	MnZSM-5	2	95	9	29	14	9	39
		4	88	9	25	13	7	46
3	LaZSM-5	4	99	8	35	20	8	29
4	FeZSM-5	4	94	5	37	24	9	25
5	CuZSM-5	2	93	8	33	20	6	33
		3 + 4	73	2	20	10	16	52
6	CoZSM-5	2	89	5	26	16	10	43

Note. Feed: 2-butanone + formaldehyde + ammonia. Molar ratio, 1 : 1 : 5; temperature: 400°C; WHSV = 0.5 h^{-1}; metal = 5 wt%.

[a] Mainly pyridine derivatives.

[b] $SiO_2/Al_2O_3 = 30$.

TABLE 4

Cyclization of Butanone and Formaldehyde with Ammonia: Variation of Temperature

Sample no.	Temperature (°C)	TOS (h)	Conversion of 2-butanone (wt%)	Liquid product selectivity (%)				
				Tetramethylpyridine	2,3,5-Collidine	2,3,6-Collidine	Lutidines	Others[a]
1	250	4	42	9	5	4	11	71
2	300	2	55	13	6	4	2	75
3	350	2	84	5	22	12	11	50
4	380	4	99	6	34	24	7	29
5	400	4	91	8	43	30	5	14

Note. Catalyst: PbZSM-5(30); feed, 2-butanone + formaldehyde + ammonia. Molar ratio, 1 : 1 : 5; WHSV = 0.5 h^{-1}; metal = 5 wt%.

[a] Mainly pyridine derivatives and aliphatic imines.

TABLE 5

Cyclization of Butanone and Formaldehyde with Ammonia: Variation of WHSV

Sample no.	WHSV (h^{-1})	TOS (h)	Conversion of 2-butanone (wt%)	Liquid product selectivity (%)				
				Tetramethylpyridine	2,3,5-Collidine	2,3,6-Collidine	Lutidines	Others[a]
1	0.250	3 + 4	98	2	22	18	17	41
2	0.375	4	99	5	32	23	12	28
3	0.500	4	91	8	43	30	5	14
4	0.750	2	100	23	15	17	1	44
		4	76	22	17	12	2	47

Note. Catalyst: PbZSM-5 (30); feed: 2-butanone + formaldehyde + ammonia. Molar ratio, 1 :1 : 5; temperature: 400°C; metal = 5 wt%.

[a] Mainly pyridine derivatives.

TABLE 6

Cyclization of 2-Butanol and Formaldehyde with Ammonia: Variation of Catalyst

Sample no.	Catalyst	TOS (h)	Conversion of 2-butanol (wt%)	Liquid product selectivity (%)				
				Tetramethylpyridine	2,3,5-Collidine	2,3,6-Collidine	Lutidines	Others[a]
1	HZSM-5 (30)[b]	2	100	18	25	9	19	29
		4	75	15	34	24	8	19
2	PbZSM-5 (30)	2	77	7	24	24	8	37
3	LaZSM-5 (30)	3	98	11	25	9	10	45
4	ZrZSM-5 (30)	3	99	16	24	8	9	43
5	WZSM-5 (30)	3	67	5	20	28	7	40

Note. Feed: 2-butanol + formaldehyde + ammonia. Molar ratio, 1 : 1 : 5; temperature: 400°C; WHSV = 0.5 h^{-1}; metal = 5 wt%.

[a] Mainly pyridine derivatives and aliphatic amines.

[b] The number in parentheses indicates SiO_2/Al_2O_3 molar ratio.

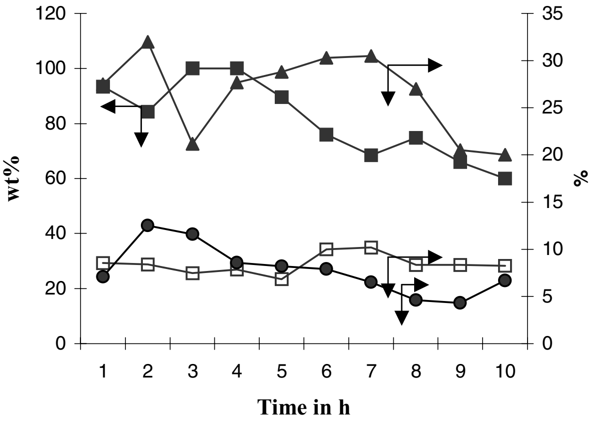

FIG. 3. Cyclization of 2-butanone, formaldehyde, and ammonia versus time on stream. (■) Conversion of 2-butanone; (□) selectivity of 2,3,5-collidine; (▲) selectivity of 2,3,6-collidine; (●) selectivity of tetramethylpyridine.

When the reaction was carried out without ammonia, only aromatics were obtained; when the reaction was carried out with only 2-butanone, aromatics and cracking products were obtained. The required high NH_3 pressure is explained by the need to replace product pyridine molecules with NH_3, and the higher ratio of formaldehyde than required by stochiometry is due to the polymerizing nature of formaldehyde at a higher temperature.

The reaction was carried out for 10 h to test the life of the catalyst over the PbZSM-5 catalyst at 400°C. The conversion, along with the selectivity to collidines, dropped to 60 wt% after 10 h (Fig. 3). This is due to the high coking accompanying the shape-selective collidine formation from tetramethylpyridine. The reaction was also carried out with 2-butanol instead of with 2-butanone to study the mechanism. The yields are comparatively low under the same conditions (Table 6). The collidine fraction was treated with a calculated amount of HCl, the water was removed by azeotropic distillation with C_6H_6, and the residue was cooled. The crystalline HCl salts were treated with NaOH, and the bases were extracted with C_6H_6 and rectified to give not only pure 2,3,6-collidine but also other collidines (36). Pyridine derivatives were separated from the collidine fraction by forming complexes with $CuCl_2$ or Cu_2Cl_2 in methanol and by fractional distillation (37).

Possible Mechanism

A mechanism that might explain the product distribution is given in Fig. 4. The mechanism explains the variation in the product yields. Over modified ZSM-5 catalysts, alcohols react to form a ketone by dehydrogenation, and the ketone reacts with ammonia to form an imine. Two such imines react with formaldehyde, resulting in deaminocyclization. Finally, tetramethylpyridine is formed by dehydrogenation. The amount of tetramethylpyridine is low, but this can be explained on the basis of the *product shape selectivity* of the zeolites. Namba *et al.* (38) reported that only isomers smaller than 1,2,4-trimethylbenzene and 1,2,4,6-tetramethylbenzene will pass through the channels of ZSM-5 zeolites and that the formation of other isomers can occur only on the outer surface in the methylation of 1,2,4-trimethylbenzene with methanol. In our case, the molecular size of 2,3,5,6-tetramethylpyridine is slightly larger than that of the ZSM-5 channels. This molecule will therefore

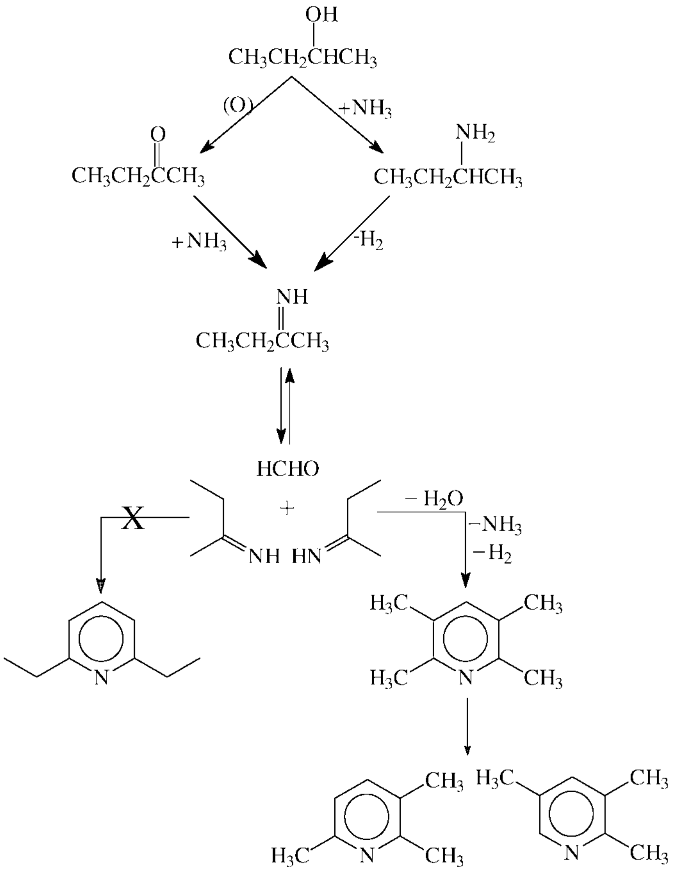

FIG. 4. Possible mechanism for formation of collidines.

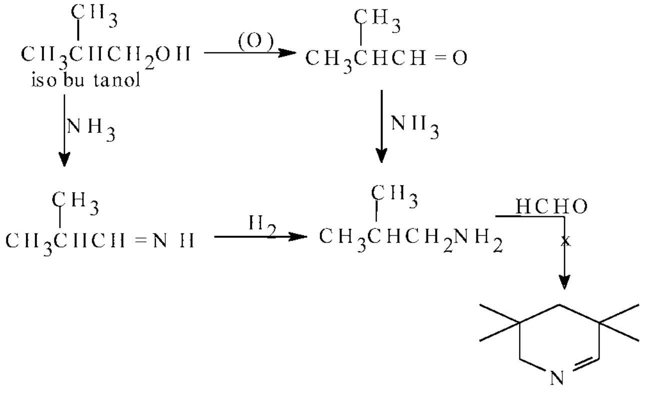

FIG. 5. Possible mechanism for isobutanol.

TABLE 7

Variation of Feed Composition

Sample no.	Feed	TOS (h)	Percentage conversion of C_4	Liquid product selectivity (%)					Aliphaticamines + others
				3,5-Diethyl pyridine	Tetramethyl pyridine	2,3,5-Collidine	2,3,6-Collidine	Lutidines	
1	Butyraldehyde + HCHO + NH_3	3	96	66				6	28
		4	94	68				4	28
2	2-Butanol + HCHO + NH_3	2	77	—	7	24	24	8	37
3	2-Butanone + HCHO + NH_3	4	91	—	8	43	30	5	14
4	Isobutanol + HCHO + NH_3	3	45	—	—	—	—	—	79^b+ 21
5	*t*-Butanol + HCHO + NH_3	2	36	—	—	—	—	—	59^c+ 41
6	*t*-Butanol[a] + HCHO + NH_3	3	97	—	—	—	—	—	95^c+ 5
		4	94						40^c + 60

Note. Catalyst = PbZSM-5 (30) (5 wt%); catalyst weight = 4 g; reaction temperature = 400°C; WHSV = 0.5 h^{-1}.

[a] Catalyst = Hβ.

[b] Isobutylamine.

[c] *t*-Butylamine.

have difficulty in passing through the channels of the catalyst, resulting in both demethylation and the formation of various trimethylpyridines (2,3,5- and 2,3,6-collidines), dimethylpyridines (lutidines), and monomethylpyridines (picolines). This explains the product selectivity of the ZSM-5 catalyst.

The mechanism for the reaction of isobutanol with formaldehyde and ammonia (Table 7, Fig. 5) indicates the restriction imposed on the transition-state formation at the intersections of the ZSM-5 channels. When the reaction with *t*-butyl alcohol was carried under the same conditions, no heterocyclic compound was formed, indicating the requirement of α-hydrogens for imine formation, which is a key intermediate for the formation of heterocyclic compounds. *tert*-Butylamine was formed instead. At the same time, the rate of diffusion of *t*-butyl alcohol into the zeolite channels will be less due to its larger molecular size (39). This shows the *reactant shape selectivity* of this catalyst. With butyraldehyde as the reactant, the selective formation of 3,5-diethylpyridine was observed (Table 7).

4. CONCLUSIONS

In the reaction of 2-butanone and 2-butanol with formaldehyde and ammonia over ZSM-5 catalysts, trimethyl (collidines) and tetramethyl pyridines were obtained. With 2-butanone, formaldehyde, and ammonia over 5% PbZSM-5 (Si/Al = 15), 43% 2,3,5-collidine and 30% selectivity of 2,3,6-collidine were obtained at 91% conversion of 2-butanone at 400°C. Higher yields of Collidines were obtained with 2-butanone than with 2-butanol. With *n*-butanol, 2-butanol, isobutanol, or *t*-butanol as C_4-reactant, the main product obtained was 3,5-diethylpyridine, collidines, aliphatic amines, or *tert*-butylamine, respectively. The formation of collidines, aliphatic amines, and *tert*-butylamine was governed by product shape selectivity, intermediate shape selectivity, and reactant shape selectivity, respectively.

ACKNOWLEDGMENTS

We are thankful to DST, India, for financial support. One of the authors, N.S., is thankful to UGC, India, for a Senior Research Fellowship. We are thankful to Professor R. Prins for many valuable suggestions and to M. Radha Kishan for his help.

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