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Zeolite catalysed intramolecular cyclization of 5-amino-1-pentanol to piperidine bases[a]

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Abstract

5-amino-1-pentanol (5-AP) undergoes facile intramolecular cyclocondensation to piperidine and to methyl or ethyl piperidines in the presence of methanol or ethanol over zeolite catalysts like ZSM-5 (Si/Al = 30, 129, 280), HM and HY. 2-Aminopyran (2-AP) is also observed as a major product in the conversion of 5-AP to piperidine on the ZSM-5 (280) and HY. Piperidine and *N*-methylpiperidine are predominantly formed over HY zeolite with near total conversion (98%) of 5-AP in the 5-AP alkylation with methanol. 2-Methyl piperidine is also formed as a side product in this reaction over all the zeolites studied. Methanol conversion does not show any trend. The HY catalyst is also studied for its ethylation activity of 5-AP with ethanol to synthesize ethyl piperidine bases. The effects of temperature and *W/F* factor on the conversion of 5-AP and ethanol and also on the yields of ethylpiperidines is presented. The possible schemes for the cyclocondensation of 5-AP and alkylation with methanol and ethanol are discussed. No dehydrogenated products (pyridine, picolines and ethylpyridines) are observed in these condensation reactions.

Keywords: Alkylation; 5-Amino-1-pentanol; Condensation; Cyclocondensation; Ethanol; Methanol; Methyl(ethyl) piperidines; Piperidine; *W/F* factor; Zeolites

1. Introduction

Synthesis of saturated cyclic amines is an important reaction because of the various uses of these compounds as detergents, additives and intermediates in the pharmaceutical industry [1,2]. According to earlier reports by Baiker and co-workers [3,4], the synthesis of cyclic amines starting from amino-alcohols over copper based catalysts is not attractive as it needs hydrogen addition to prevent the formation of dehydrogenation products.

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Zeolites are solid acids with high mechanical strength and thermal stability which can be widely used for those types of reactions that proceed by a carbocation mechanism. For example, reactions like isomerizations, dehydrations, dehydrocyclizations and condensations may be routinely carried out over zeolite catalysts with high selectivities at moderate temperatures [5]. In this paper, the cyclocondensation of 5-AP and alkylation with methanol and ethanol over various zeolites is described.

2. Experimental

The various zeolites used in this study were ZSM-5 (Si/Al = 30, 129, 280), HM (Si/Al = 6) and HY (Si/Al = 3) supplied by PQ Corporation, U.S.A. 5-Amino-1-pentanol (Fluka AG) and distilled methanol and ethanol were used as feed. For the synthesis of methyl and ethyl derivatives of piperidine bases, 5-amino-1-pentanol (5-AP), methanol and ethanol were mixed in stoichiometric ratio. The reactions were carried out at different temperatures starting from 200°C to 400°C in a fixed-bed microreactor [6] and the products were analyzed by gas chromatography (GC) using a flame ionization detector (FID). The product analysis was also confirmed by GC-mass spectra.

3. Results and discussion

3.1. Cyclocondensation of 5-AP

The results of cyclocondensation of 5-AP to piperidine at 350°C on various zeolites are given in Table 1. The maximum time-on-stream conversion of 5-AP and yield of piperdine and 2-AP are given. The conversion of 5-AP and the yield of piperidine increase with Si/Al ratio in the ZSM-5 series of catalysts whereas the 2-AP is formed only over the ZSM-5 (Si/Al = 280) catalyst. The conversion and

Table 1
Reaction of 5-amino-1-pentanol (5-AP) over various zeolites

Catalyst	Time-on-stream (h)	5-AP conversion (%)	Yield (%)	
			Piperidine	2-Aminopyran
ZSM-5 (30)	1	18	11	Trace
ZSM-5 (129)	3	15	14	Trace
ZSM-5 (280)	2	90	45	29
HM	1	80	72	8
HY	3	98	69	10

WHSV is 0.47 h^{-1}, weight of the catalyst 4.0 g, reaction temperature is 350°C.

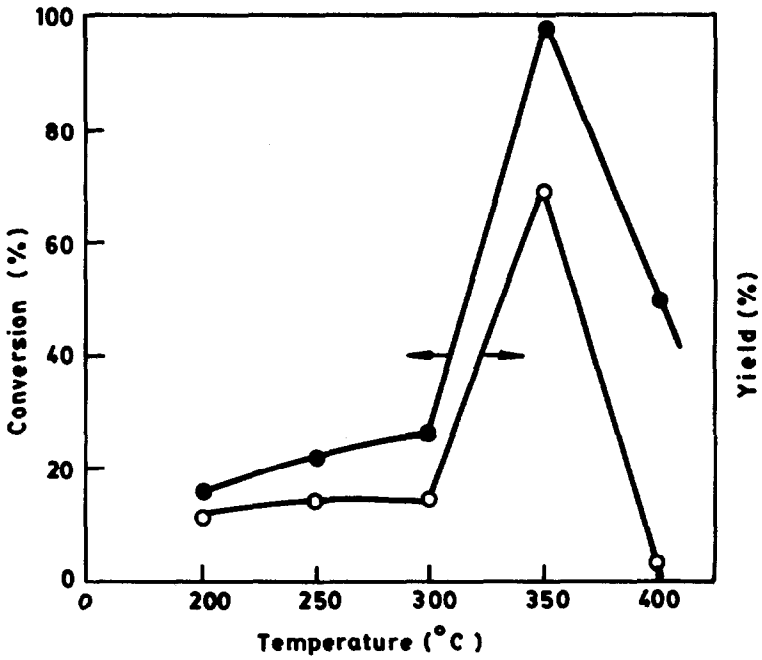


Fig. 1. Effect of temperature on conversion of 5-AP and yield of piperidine on HY catalyst.

yield of piperidine is plotted in Fig. 1 against the temperature on HY catalyst. The conversion increases slowly but continuously with temperature upto 300°C and at 350°C suddenly increases to 98% and then decreases to 50% 5-AP at 400°C. Also the yield of piperidine increases from 200°C to 300°C, at 350°C it reaches 69% and then starts decreasing to 4% at 400°C. Fig. 2 compares the variation in conversion of 5-AP and yield of piperidine with time-on-stream on the HY catalyst, showing

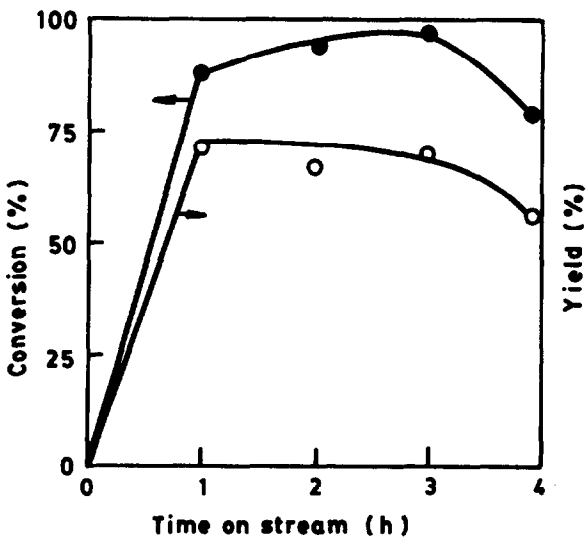
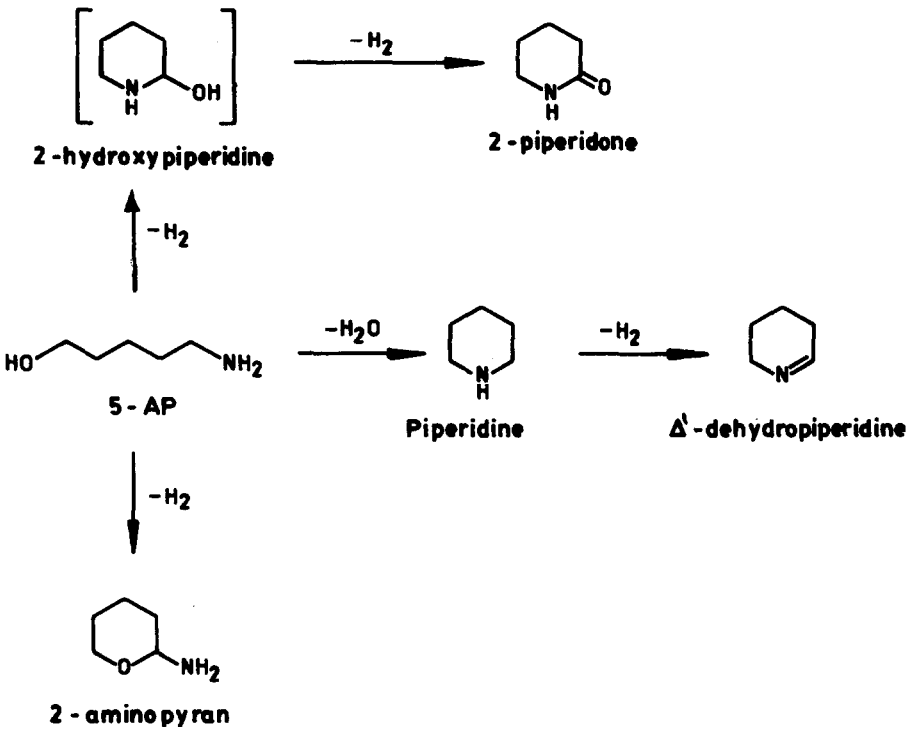


Fig. 2. Time-on-stream conversion and yield of piperidine on HY catalyst at 350°C.



Scheme 1. Reactions of 5-AP.

a noteworthy result. The conversion increases with time-on-stream to a maximum value of 98% at 3 h whereas the yield of piperidine decreases. The coke deposition on the internal surface of the catalyst may be responsible for the decrease in the yield of piperidine. 5-Aminopentanol has undergone both acid and base-catalysed intramolecular cyclization giving rise to piperidine and 2-aminopyran. The products of these two processes are quite distinct; acid catalysis produces piperidine, whereas base catalysis leads to 2-aminopyran. The mechanistic features of this transformation are depicted in Scheme 1 under the experimental conditions of the reaction [4]. It has been reported that during organic transformations partial coking of H-ZSM-5 takes place [7]. This coke which blocks the acidic sites, is of olefinic character (basic in nature) and is catalytically active [7]. Only few works have been published dealing with the composition and nature of the coke formed on ZSM-5 [8,9]. In addition, the cyclodehydration yields reported from our laboratory [10,11] and by others increase from H-ZSM-5 (30) to H-ZSM-5 (280). This is because a sufficient number of acidic centers is available in H-ZSM-5 (280). Furthermore, the extent of cyclization in the case of H-ZSM-5 (30) is small [10,11]. Thus, in agreement with literature evidence, the formation of 2-AP over H-ZSM-5 (30) and H-ZSM-5 (129) is found to be smaller than over H-ZSM-5 (280) catalysts.

The products are identified by means of GC and GC-mass spectral analysis of the product mixture. 2-Hydroxypiperidine is quite unstable, whereas piperidone is

ruled out based on the analysis of the products. The Δ'-dehydropiperidine formation is also ruled out since this requires dehydrogenation of piperidine for which a metal loaded zeolite is needed. Therefore, the discussion is mainly focused on the two different products i.e., piperidine and 2-aminopyran.

3.2. Synthesis of methylpiperidines

The conversion of 5-AP, methanol and the yield of various products in the synthesis of methylpiperidines at 350°C on different zeolites is given in Table 2. The reaction results shown are the maximum obtainable for the given time-on-stream. The conversion of 5-AP is maximum on ZSM-5 (Si/Al = 30), ZSM-5 (Si/Al-280) and HY, whereas methanol conversion is maximum on the HM catalyst. The yields of *N*-methyl and 2-methylpiperidines and 2-aminopyran are higher on the ZSM-5 (280), HM and HY catalysts when compared to ZSM-5 (30) and ZSM-5 (129). Time-on-stream variation in the yield of *N*-methyl and 2-methylpiperidines is presented in Fig. 3 for these catalysts. On ZSM-5 (280) the yield of *N*-methylpiperidine increases from 40 to 53 with a time-on-stream of 4 h, whereas on HM catalyst the yield of this product decreases from 60 to 30 and on HY catalyst the yield stays constant irrespective of increases in the time-on-stream. The time dependence of the yield of 2-methylpiperidine determined for ZSM-5 (280), HM and HY catalyst samples is almost the same, with 5% variation. The overall yield on any of the catalysts does not increase more than 10%. The effect of temperature on the conversion of 5-AP, methanol and on the yields of *N*-methyl and 2-methylpiperidines on the HY catalyst are presented in Table 3. As can be seen from the data, a discrepancy is found in the conversion of 5-AP measured as a function of temperature. Comparison of the conversion of 5-AP with increasing reaction temperature showed that the features are worth noting. The observation of a progressive loss of activity is probably a result of excessive coking of the zeolite catalysts. However, the methanol conversion remains almost the same except for a decrease

Table 2
Reaction of 5-AP with methanol over various zeolites

Catalyst	Time-on-stream (h)	Conversion (%)		Yield (%)		
		5-AP	Methanol	*N*-methyl piperidine	2-Methyl piperidine	2-Amino pyran (2-AP)
ZSM-5 (30)	3	100	83	60	1	4
ZSM-5 (129)	1	33	90	20	4	Trace
ZSM-5 (280)	3	100	84	53	7	21
HM	1	84	94	60	9	3
HY	3	100	80	69	8	6

WHSV is 0.44 h^{-1}, reaction temperature is 350°C, mole ratio of 5-AP and methanol is 1 : 1, weight of the catalyst 4.0 g.

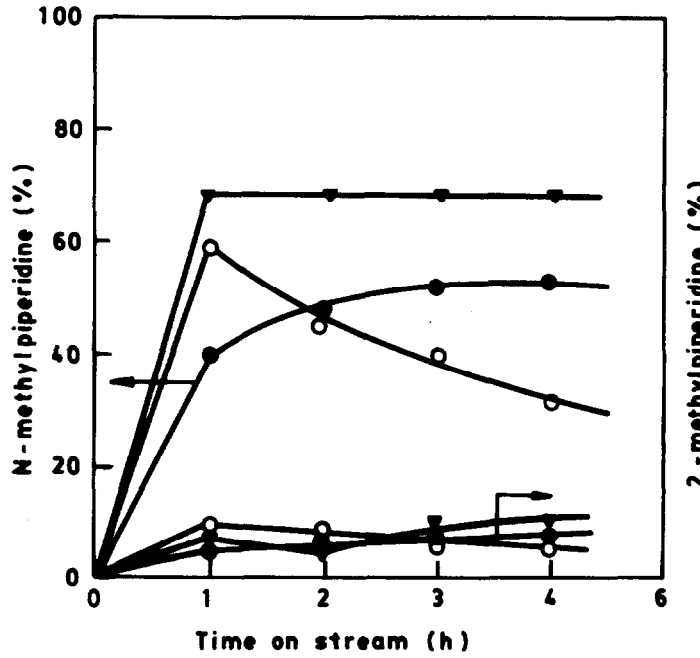


Fig. 3. Time-on-stream yield of *N*-methyl and 2-methyl piperidines at 350°C. (▼) HY, (●) ZSM-5 (280), (○) HM.

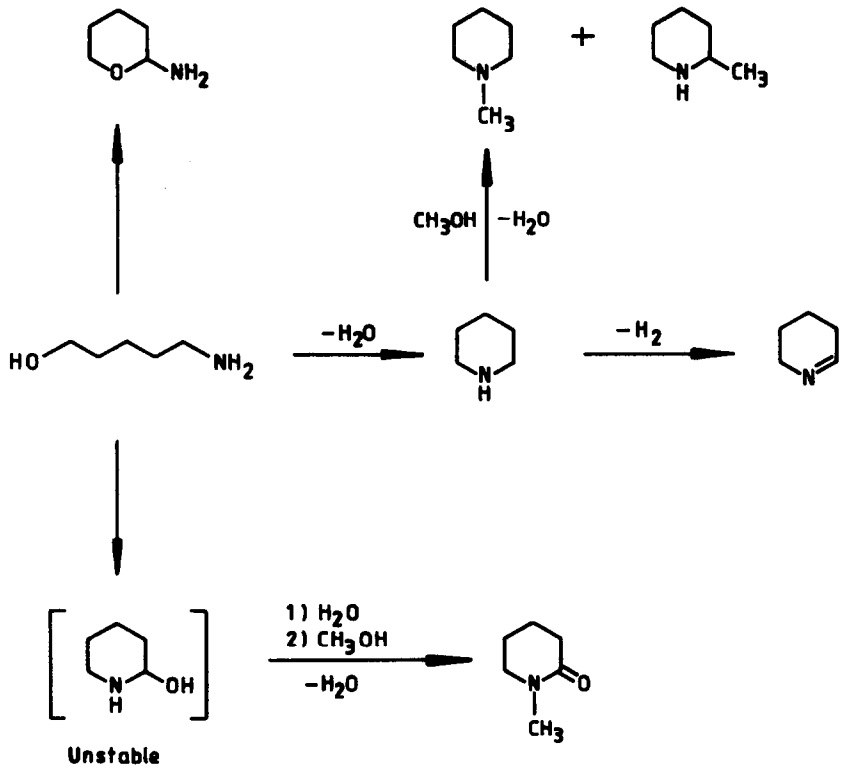
at 300°C and then rises again with temperature. There is no general trend observed in the percent yield of *N*-methylpiperidine and 2-methyl piperidine with respect to the increase in temperature as shown in Table 3. Recently Sato et al. [12] reported that smooth reaction and smooth desorption favours high selectivity to products. Our reaction's product distribution indicates that 350°C is the optimum temperature required for a good desorption of the products. At 400°C *N*-methylpiperidine falls to 56% which may be due to coking. Reactions of 5-AP in the presence of methanol are presented in Scheme 2.

Formation of methylpiperidine isomers comes about through alkylation of the piperidine intermediate with methanol and simultaneous dehydration. Zeolites are

Table 3
Effect of temperature on the conversion of 5-AP, methanol and on the yield of *N*-methyl and 2-methylpiperidines on HY catalyst

Temp. (°C)	Conversion (%)		Yield (%)	
	5-AP	Methanol	*N*-methylpiperidine	2-Methylpiperidine
200	100	90	63	5
250	89	97	65	7
300	75	84	63	11
350	100	85	69	8
400	78	80	56	11

WHSV is 0.44 h^{-1}, mole ratio of 5-AP and methanol is 1 : 1, time-on-stream is 3 h, weight of the catalyst 4.0 g.



Scheme 2. Reactions of 5-AP in the presence of CH_3OH.

well known alkylation catalysts [5,13] and this mechanism appears to be very plausible in the proposed form. Experimental evidence clearly indicated that zeolite-catalysed cyclodehydration and cyclodehydrogenation seem to offer a unique possibility of not forming dimethylpiperidines by virtue of their shape-selective effects. Whereas our results on the synthesis of picoline-pyridines over H-ZSM-5, HM, and HY with and without modifiers as well as those from the literature [10,11] reported di and tri-methyl substituted heterocycle formation. The present work supports the structural correlation of product distribution for 5-AP alkylative cyclization over the zeolites studied. 2-Hydroxypiperidine, which is unstable, undergoes *N*-methylation to give *N*-methyl-2-piperidone, also confirmed by the molecular ion peak in the mass spectrum at 113. As mentioned in the discussion of Scheme 1, here also we obtained 2-aminopyran (2-AP) as one of the products.

3.3. Synthesis of ethylpiperidines

The HY catalyst was choosen to synthesize ethylpiperidine bases from 5-AP and ethanol in a 1 : 1 molar ratio as the feed. On this catalyst the effect of temperature on conversion of 5-AP and ethanol and on the yields of various products is given in Table 4. The conversion of 5-AP and ethanol increases with temperature. Simi-

Table 4
Effect of temperature on the yields of piperidine bases in 5-AP and ethanol reaction on HY catalyst

Temp. (°C)	Conversion (%)		Yield (%)		
	5-AP	Ethanol	Piperidine	*N*-ethyl-piperidine	2-Ethyl-piperidine
200	38	64	0.3	0.7	0.4
250	56	88	0.7	32.3	0.7
300	96	74	Trace	59.4	3.9
350	99	75	14	37.0	17.8
400	100	80	4.4	35.4	24.5

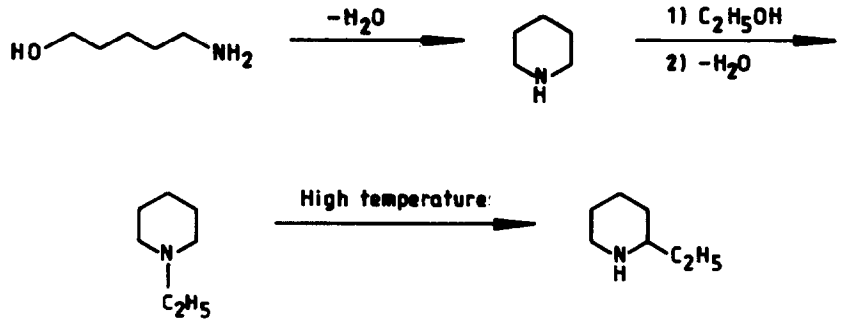
WHSV = 0.43 h^{-1}, mole ratio of 5-AP and ethanol is 1 : 1, time-on-stream is 1 h, weight of the catalyst 4.0 g.

larly, the yields of piperidine and 2-ethylpiperidine also increase, whereas the yield of *N*-ethylpiperidine first increases to 59.4% and then decreases with temperature. It seems that at higher temperatures there is a facile migration of the ethyl moiety from the 1 (i.e. nitrogen) to the 2 (i.e. carbon) position. Hence, lower temperatures, probably around 300°C, are required for the maximum yield of *N*-ethylpiperidine. The effect of the W/F (g_{cat} h $mmol^{-1}$) factor on the variation in the conversions of 5-AP, ethanol and yields of the three products was also studied in this reaction and is presented in Table 5. The conversion of 5-AP is unaffected whereas the ethanol conversion increases up to certain level and then comes down. The W/F factor also effects the yields of the three products, piperidine, *N*-ethylpiperidine and 2-ethylpiperidine in the 5-AP alkylation with ethanol, as shown by the data. The percent yield of piperidine, *N*-ethylpiperidine and 2-ethylpiperidine was measured as a function of W/F. The results indicate a shift in the product distribution. Therefore, experimental evidence shows that the reaction should be operated at a W/F value of 0.126 in order to get the maximum yield of *N*-ethylpiperidine. Whereas the maximum for 2-ethylpiperidine is seen at W/F 0.210. Piperidine reaches 14% at $W/F = 0.252$. Scheme 3 shows the ethylation of 5-AP to ethylpiperidine bases. Here also the 5-AP first undergoes intramolecular cyclocondensation, followed by ethylation with ethanol to give *N*-ethylpiperidine base with isomerisation to 2-ethylpiperidine.

Table 5
W/F effect on the reaction of 5-AP and ethanol on HY catalyst at 350°C

W/F (g_{cat} h m mol^{-1})	Conversion (%)		Yield (%)		
	5-AP	C_2H_5OH	Piperidine	*N*-ethyl-piperidine	2-Ethyl-piperidine
0.126	100	80	2	45	24
0.168	100	81	1	36	24
0.210	97	85	2	21	28
0.252	99	75	14	37	18

Mole ratio of 5-AP and ethanol is 1 : 1, time-on-stream is 1 h.



Scheme 3. Ethylation of 5-AP.

4. Conclusions

The cyclocondensation of 5-amino-1-pentanol has been shown to be an effective process for the preparation of saturated pyridine bases over zeolite catalysts. The selectivity to piperidine and 2-aminopyran depends on the type of zeolite used. 350°C is the best temperature for the maximum conversion of 5-AP and high yield of piperidine and *N*-methylpiperidine on the various zeolites employed in the reaction. *N*-methylpiperidine is the major product observed in the alkylation of 5-AP with methanol. The yield of this product is also influenced by the nature of the zeolite catalyst. The time-on-stream yield of this product exhibits opposite trends on the ZSM-5 (280) and HM catalyst. The HY catalyst is the best choice for the maximum production of piperidine, *N*-methylpiperidine and *N*-ethylpiperidine bases in the three condensation reactions. A temperature of 300°C with short contact time is the most suitable condition for maximum yield of *N*-ethylpiperidine on this catalyst. The time-on-stream yield of piperidine is decreased in the cyclocondensation of the 5-AP and the *N*-methylpiperidine remains constant in the alkylation of 5-AP with methanol on this catalyst.

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