

Amino cyclization of terminal (α,ω)-diols over modified ZSM-5 catalysts[☆]

V. Radha Rani, N. Srinivas, S.J. Kulkarni*, K.V. Raghavan

Indian Institute of Chemical Technology, Hyderabad 500007, India

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Abstract

The cyclization of terminal diols with ammonia was carried out over modified ZSM-5 catalyst, to obtain the desired saturated heterocyclic product in high yields and selectivity. In the reaction of 1,4-butanediol and ammonia at 250 °C, >95% yield was obtained of pyrrolidine over FeZSM-5 and CuZSM-5 catalysts. The high yield of piperidine, >62–90% was obtained over NiZSM-5 and CuZSM-5 in the reaction of pentanediol and ammonia. Similarly, \geq 88% yield was obtained of hexamethyleneimine over CeZSM-5 in the reaction of hexanediol and ammonia.

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Keywords: Amination; Diol; Cyclization; ZSM-5; Saturated cyclic amines

1. Introduction

The amination of alcohols and diols to corresponding saturated cyclic amines, heterogeneously—is a complex process and it amplifies when bi- or poly-functional alcohols are used as reactants [1–3]. However, since the saturated cyclic amines are extensively used as detergents, additives and intermediates in the pharmaceutical industry [4,5], various attempts were made to synthesize them [6–11]. Traditionally, they are manufactured from α,ω -alkylene dichlorides which has a well-known disadvantage of being corrosive, due to the formation of hydrogen chloride. The synthesis of cyclic amines by direct cyclization of the corresponding amino-alcohols and -diols have only received little attention in the past [12]. Karpeiskaya et al. [13] reported the cyclization of monoethanolamine

on cobalt catalyst. Venot [14] and Reddy et al. [15] described the cyclization of 5-amino-1-pentanol and the corresponding *N*-alkylated derivatives, using Raney nickel and zeolites, respectively. Scriabine [16] used alumina to catalyze the same cyclization. Ufer and Breuers [17] have reported on cyclization of *o*-amino phenyl-ethanol using several dehydrogenation catalysts. These reactions, when carried out over mixed oxides, showed that the selectivity of the desired products was far below the economically acceptable level. Baiker and co-workers [9,18] reported the synthesis of cyclic amines starting from amino-alcohols over copper-based catalyst. This process was not found to be attractive, as it needed the addition of hydrogen to prevent the formation of dehydrogenation products.

Further, reports for this reaction over zeolites, starting from amino-alcohols [18,19], showed that the selective synthesis of the desired products can be obtained due to the presence of the strong acidic sites in the limited size of the zeolite channels. Here, we report a relatively cheap, non-corrosive and

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* Corresponding author.

E-mail address: sjkulkarni@iict.ap.nic.in (S.J. Kulkarni).

environmentally friendly process for the manufacture of cyclic amines along with properly tuned reaction parameters and catalyst composition.

2. Experimental

HZSM-5 zeolite was supplied by Conteka, Sweden. HZSM-5 (Si/Al = 15) was further modified with 5 wt.% of various cations like Pb, Zr, Co, Cu, La by the impregnation method with the corresponding nitrates as the precursors.

The elemental composition of the resultant solid products was analyzed by ICP-MS. Powder XRD patterns of the calcined products were recorded on a diffractometer with Cu K α radiation at 0.045 step sized and 0.5 s step time over the range $0 < 2\theta < 60^\circ$. The specific surface area, A_{BET} , was determined from the linear part of BET plot ($P/P_0 = 0.05\text{--}0.30$). The DTA and TG analysis of the HZSM-5 and transition metal ion incorporated ZSM-5 were performed with a heating rate of $20^\circ\text{C min}^{-1}$ under a nitrogen flow of 25 ml min^{-1} . FT-IR measurements were performed on a FT-IR spectrophotometer using the KBr self-supported pellet technique. The pellets contained about 1% of finely powdered sample and were pressed at 4 t cm^{-2} .

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

A catalyst (4 g) was placed into a glass 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 products were cooled using ice-cold traps at the outlet to collect the total amount of products. The products were analyzed by gas chromatography using SE-30 column and high pressure liquid chromatography. The products were confirmed by mass spectra and GC. The liquid product mass balance was about 80–90% and 5% gases were observed.

3. Results and discussions

The crystallinity of metal modified ZSM-5 were studied by XRD using a highly crystallized HZSM-5 as the 100% standard. The degree of crystallinity of each sample was evaluated by the summation method considering the intensities of the typical diffraction peaks between $2\theta = 26$ and 29° [20]. All samples tested had good crystallinity. According to literature data, the diffraction pattern of ZSM-5 corresponds closely to an orthorhombic symmetry. Wu et al. [21] observed that upon certain treatments, such as ion exchange, the ZSM-5 framework symmetry changes from orthorhombic to monoclinic. No such prominent changes in XRD peaks pertaining to monoclinic symmetry could be observed in the XRD patterns of the metal modified ZSM-5 catalysts. However, it could be observed that on impregnation the intensities of $2\theta = 7.9$ and 8.5° showed a decrease in intensities in comparison to HZSM-5 indicating the presence of inorganic material in the intracrystalline voids and may also blocked pore entrances [22,23]. This fact could also be confirmed from the decreasing surface area of the impregnated samples relative to its protonated one (Table 1). Further, one of the characteristic peak of ZSM-5 at $2\theta = 23.9^\circ$ became less distinct on modification with Pb, Co and Zr ions.

NH_3 -TPD profiles of various metal catalysts are given in Fig. 1. The three peaks observed at 150–250, 250–350 and 350–450 $^\circ\text{C}$ corresponds to the desorption of NH_3 from weak, medium and strong acid sites, respectively, as observed by Anderson et al. [24], Topsøe et al. [25] and Babu et al. [26]. The metal cation modified catalyst showed deviation towards the weak acidic nature (i.e. HTD centers deviated into LTD centers). This may be due to the difference in the

Table 1
Physico-chemical properties of various catalysts

Catalyst	NH_3 uptake (mmol g^{-1})	Surface area ($\text{m}^2 \text{g}^{-1}$)	Number of H_2O molecule (cell unit^{-1})
HZSM-5 (30)	1.73	310.0	6.5
CoZSM-5 (30)	1.86	286.4	4.9
CuZSM-5 (30)	1.00	311.4	4.2
PbZSM-5 (30)	1.47	225.5	7.1
LaZSM-5 (30)	3.70	397.8	6.9
ZrZSM-5 (30)	0.99	218.0	10.4

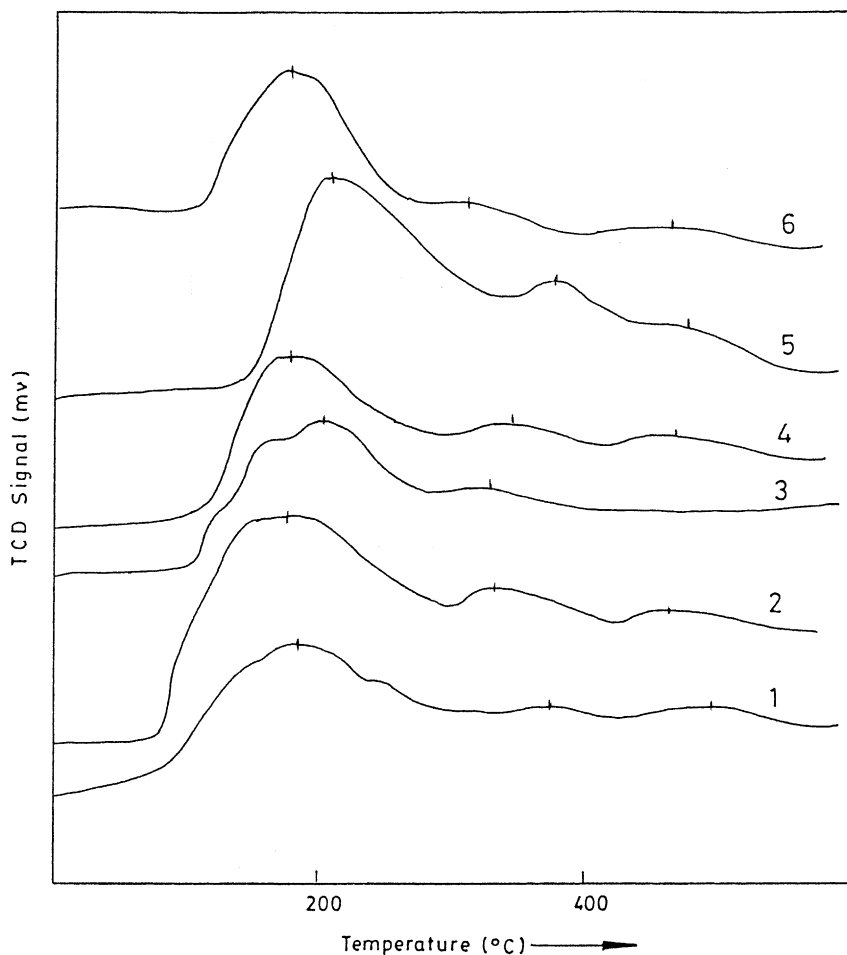


Fig. 1. NH_3 -TPD profiles of: (1) HZSM-5 (30); (2) CoZSM-5 (30); (3) CuZSM-5 (30); (4) PbZSM-5 (30); (5) LaZSM-5 (30); (6) ZrZSM-5 (30).

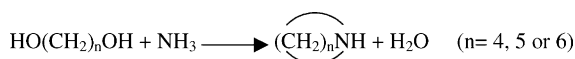
electronegativity of oxygen and metal ion [27]. The total acidity of the catalysts (Table 1) followed the order: ZrZSM-5 (30) < CuZSM-5 (30) < PbZSM-5 (30) < HZSM-5 (30) < CoZSM-5 (30) < LaZSM-5 (30). The high acidity of LaZSM-5 (30) can be attributed to its co-ordinating ability with ammonia to generate strong Brönsted acidic sites by dissociating H_2O . This is, in addition to its capability to act as a strong Lewis acid. Similarly, from the acid association constants of lead in aqueous solution, it could be concluded that these ions easily form basic species $\text{Pb}(\text{OH})^{(2-n)+}$ [28].

FT-IR for the transition metal impregnated ZSM-5 catalysts shows the deviation from the character-

istic peak of five-membered ring building units at 550 cm^{-1} . The variation in this frequency indicates the influence of the cation over the framework. Lanthanum has affected the zeolite framework more predominantly [29,30].

4. Catalytic activity

The general stoichiometric reaction for the vapor-phase amino intramolecular cyclization of α,ω -diols with ammonia to *N*- and *O*-containing cyclic compounds over modified ZSM-5 catalyst can be written as shown in Scheme 1.



Scheme 1.

4.1. 1,4-Butanediol

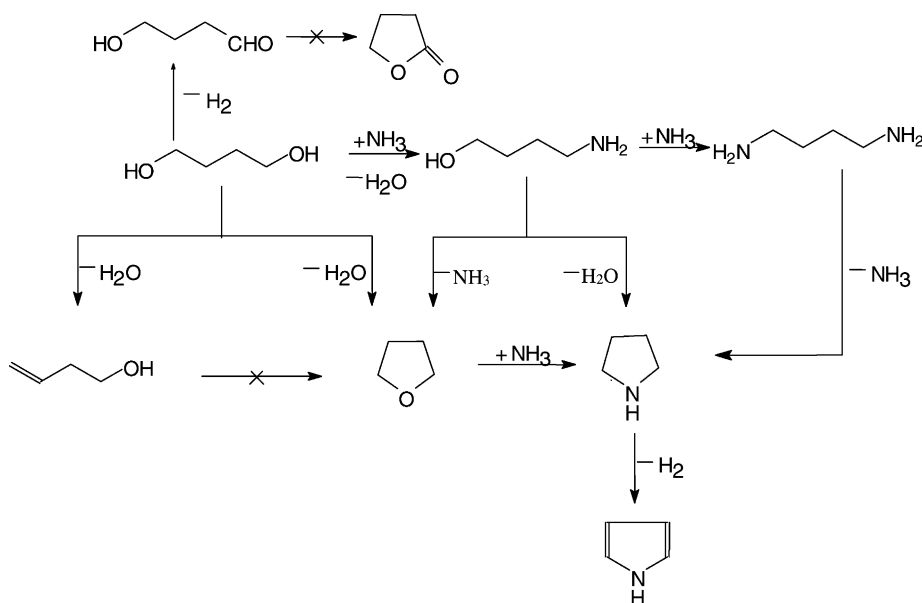
The various products which result in the reaction of 1,4-butanediol with ammonia over various ZSM-5 (30) catalysts at 250 °C with 0.5 h⁻¹ weight hourly space velocity (WHSV) are as depicted in Scheme 2. The product distributions obtained over various metal cation modified ZSM-5 catalyst are listed in Table 2. The reaction on HZSM-5 (30) catalyst shows that although there is high conversion of the reactant, the yields of the desired product, pyrrolidine is low. In order to reduce the coke formation, water was used in the reaction mixture and it also acts as the solvent for the product desorption. However, the yields of pyrrolidine and THF enhanced as the reaction time was increased over metal modified ZSM-5 catalyst. Of all the catalysts studied, CuZSM-5 catalyst excelled with high activity and selectivity towards the desired product [9]. Further, even the presence of optimum strength of acidic sites is crucial for the high activity and selectivity [31,32]. LaZSM-5 leads to the formation of

the dehydrogenated product, pyrrole with high selectivity. Ammonia and amines are assumed to adsorb on Brönsted acid sites and form ammonium species as seen from the IR studies [33]. The results also suggest that strong acidic sites in the limited size of the zeolite channels are favorable for the selective synthesis of cyclic amines by suppression of bulky polyamines formation, which shows the specific property of shape selectivity nature of the uniform porous catalysis.

4.2. 1,5-Pentanediol

Important reaction products observed for the reaction of 1,5-pentanediol with ammonia over various ZSM-5 (30) catalysts were piperidine (I), pyridine (II), 5-amino-1-pentanol (III) and pyran (IV) at 280 °C with 0.5 h⁻¹ WHSV. Scheme 3 shows the relevant reactions leading to these products.

The reaction when carried out over HZSM-5 catalyst with varying Si:Al ratio resulted in cyclized products, mainly piperidine and pyran. It can be seen from Table 3, that the optimum yield of the desired product piperidine is over HZSM-5 (41). Further, in order to study the possibility of formation of dehydrogenated piperidine product (i.e. pyridine), the ZSM-5 catalyst was loaded with various metal ions having different



Scheme 2. Amino cyclization of 1,4-butanediol.

Table 2
Amino cyclization of 1,4-butanediol in the variation of catalysts

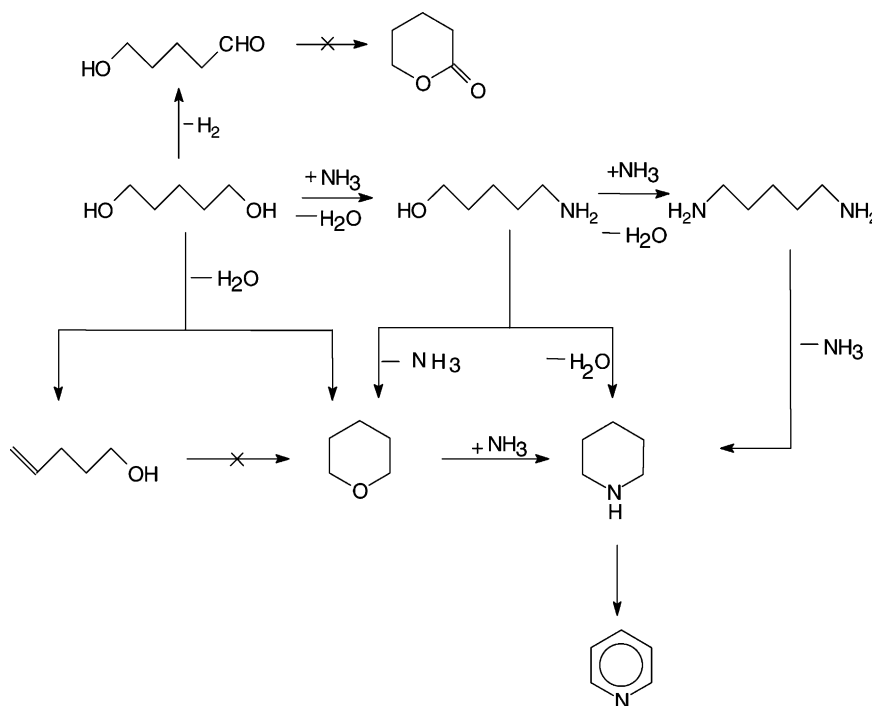
S. no.	Catalyst	TOS (h)	Conversion of 1,4-butanediol (%)	Yield of products (wt.%)				
				THF	Furan	Pyrrole	Pyrrolidine	Others
1	HZSM-5 (30)	3	99.9	44.3		3.4	41.0	11.2
		4	93.3	23.3			16.0	54.0
2	CrZSM-5 (30)	3	86.1	52.7	20.3			13.1
3	FeZSM-5 (30)	4	99.9				95.9	4.0
4	MnZSM-5 (30)	2	95.8	17.5		36.2	27.5	14.6
5	CuZSM-5 (30)	4	99.9				99.0	0.9
6	LaZSM-5 (30)	3	99.9			93.8	3.0	3.1

Feed: 1,4-butanediol + H₂O + NH₃; 1,4-butanediol:H₂O = 1 : 3 (volume ratio); NH₃, 30 cm³ min⁻¹; temperature, 250 °C; WHSV, 0.5 h⁻¹; catalyst weight, 4 g; metal weight, 5 wt.%.

dehydrogenation activity. The product distributions obtained over various metal ions modified ZSM-5 catalysts are listed in Table 4. The complete or partial dehydrogenated piperidine product, i.e. pyridine or dehydro piperidine was found in traces. However, of all the metal ion impregnated catalysts studied, nickel

ion showed high activity and selectivity towards the formation of saturated cyclic amines [34].

When the reaction temperature was varied from the optimum temperature of 280 °C, the conversion of the reactant showed a drastic decrease with very low selectivity as shown in Table 5. The yield of dehydro-



Scheme 3. Amino cyclization of 1,5-pentenediol.

Table 3

Amino cyclization of 1,5-pentanediol in the Si/Al variation

S. no.	Catalyst	TOS (h)	Conversion of 1,5-pentanediol (%)	Yield of products (wt.%)				
				Pyran	Pyridine	Piperidine	5-Amino pentanol	Others
1	HZSM-5 (30)	2	42.0	10.7	6.6	23.7	0.5	0.5
		4	17.4	8.5	2.5	5.5	0.9	
2	HZSM-5 (40.9)	2	96.1	4.1		81.3	1.87	8.83
		4	99.9	10.4		79.5		10.0
3	HZSM-5 (129)	2	96.7	38.7	7.63	24.3	2.7	23.4
		3	98.0	28.2	8.7	26.0	3.6	31.5
4	HZSM-5 (280)	1	82.3	18.8		31.5	10.2	21.8
		4	92.4	11.0		41.5	11.0	28.9

Feed: 1,5-pentanediol + H₂O + NH₃; 1,5-pentanediol:H₂O = 1 : 3 (volume ratio); NH₃, 30 cm³ min⁻¹; temperature, 280 °C; WHSV, 0.5 h⁻¹; catalyst weight, 4 g.

generated product, i.e. pyridine increased on deviation on either sides of the optimum temperature.

4.3. 1,6-Hexanediol

The reaction of 1,6-hexanediol with ammonia when carried out over various ZSM-5 (30) catalysts

at 300 °C temperature with 0.5 h⁻¹ WHSV, yielded hexamethyleneimine selectively with 50–80% conversion of 1,6-hexanediol as given in Table 6. The formation of hexamethyleneimine via both dehydrocyclization of aminol and amination of the oxepane was promising over CeZSM-5 with 88 wt.% yield. The formation of the desired product according to

Table 4

Amino cyclization of 1,5-pentanediol in the variation of catalysts

S. no.	Catalyst	TOS (h)	Conversion of 1,5-pentanediol (%)	Yield of products (wt.%)				
				Pyran	Pyridine	Piperidine	5-Amino pentanol	Others
1	MnZSM-5 (30)	2	99.9	36.2		46.7	11.0	6.0
		4	99.9	18.5		67.3	5.9	8.2
2	CoZSM-5 (30)	3	87.1	30.3		9.5	42.8	4.5
		4	99.9	17.5		56.0	9.2	17.2
3	NiZSM-5 (30)	2	99.9	4.0		84.6	2.8	8.5
		4	99.9	4.6		90.2	1.0	4.1
4	CuZSM-5 (30)	1 + 2	99.9	9.8	2.8	76.4	2.9	8.0
		3 + 4	99.9	19.0		62.2		18.7
5	ZnZSM-5 (30)	3	99.9	16.5		54.9	11.0	17.5
		4	99.9	14.7		46.7	14.0	24.5
6	PbZSM-5 (30)	2	99.9	28.6		55.2	2.8	13.3
		3	99.9	12.7		81.8		5.4
7	ZrZSM-5 (30)	2	99.9	33.4		43.9	11.6	11.0
8	MoZSM-5 (30)	2	97.6	29.0		29.0	18.5	21.1
		4	91.6	30.6		19.4	35.0	6.6

Feed: 1,5-pentanediol + H₂O + NH₃; 1,5-pentanediol:H₂O = 1 : 3 (volume ratio); NH₃, 30 cm³ min⁻¹; temperature, 280 °C; WHSV, 0.5 h⁻¹; catalyst weight, 4 g; metal weight, 5 wt.%.

Table 5
Amino cyclization of 1,5-pentanediol in the variation of temperature

S. no.	Temperature (°C)	TOS (h)	Conversion of 1,5-pentanediol (%)	Yield of products (wt.%)				
				Pyran	Pyridine	Piperidine	5-Amino pentanol	Others
1	250	4	31.7	6.4	3.6	6.4	5.9	9.4
2	280	1 + 2	99.9	9.8	2.8	76.4	2.9	8.0
		3 + 4	99.9	19.0		62.2		18.7
3	300	3	32.4	6.6	6.0	8.7	0.5	10.6
4	350	3	51.4	6.8	2.5	26.2	8.8	7.1

Catalyst, CuZSM-5 (30); feed: 1,5-pentanediol + H₂O + NH₃; 1,5-pentanediol:H₂O = 1 : 3 (volume ratio); NH₃, 30 cm³ min⁻¹; WHSV, 0.5 h⁻¹; catalyst weight, 4 g; metal weight, 5 wt.%.

the Scheme 4 was further confirmed by carrying out the cyclocondensation reaction of 6-amino-1-hexanol with water over CuZSM-5 catalyst at 300 °C temperature.

Further, as hexamethyleneimine acts as the intermediate for the synthesis of ϵ -caprolactam, which in turn is used on a large scale in Nylon production, the direct synthesis of ϵ -caprolactam was attempted via the cyclization of 6-amino caproic acid and water (1:5 volume ratio) at 350 °C over various ZSM-5 catalyst as given in Table 7. The high yield of 77% caprolactam was obtained over HZSM-5 (129).

A comparison of the reaction temperatures required for obtaining the desired product reveals a pronounced influence of the hydrocarbon backbone length in the reactant diols OH-(CH₂)_n-OH. The optimum reaction

temperature was found to increase with increasing chain length.

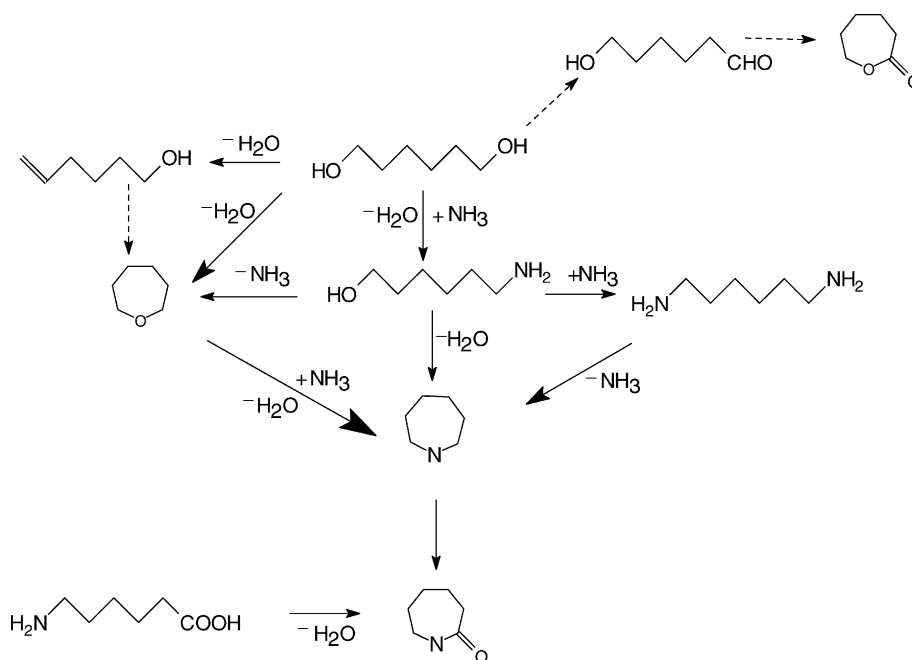
It can be also seen that structure of the alcohol, i.e. the distance of the functional groups, determines the direction of the amination reaction. The short-chain tends to dimerize to form stable cyclic compounds or produce oligomers, depending on the catalyst and reaction conditions [35]. Ethanolamine dimerizes to (intermolecular cyclization) to the five- or six-membered rings. Dehydrogenation of the cyclic products becomes dominant at high temperatures, leading to thermodynamically more stable aromatic compounds.

The plausible mechanism for the formation of cyclic amines is as shown in Fig. 2. M-ZSM-5 (metal ion modified ZSM-5 catalyst) is a bifunctional catalyst

Table 6
Amino cyclization of 1,6-hexanediol in the variation of catalysts

S. no.	Catalyst	TOS (h)	Conversion of 1,6-hexanediol (%)	Yield of products (wt.%)			
				Hexamethyleneimine	Oxepane	6-Amino 1-hexanol	Others
1	HZSM-5 (30)	3	73.6	49.2	15.9	1.4	7.1
2	HZSM-5 (280)	3	62.8	34.3	12.8	10.7	5.0
3	CrZSM-5 (30)	3	99.9	20.3	58.3	5.9	15.4
4	CuZSM-5 (30)	1	99.9	68.4	12.7	3.4	15.4
		3	99.9	30.9	41.4	4.1	23.5
5	NiZSM-5 (30)	3 + 4	98.6	18.6	28.4	19.6	32.0
6	CeZSM-5 (30)	3	99.9	88.3		4.5	7.1

Feed: 1,6-hexanediol + H₂O + NH₃; 1,6-hexanediol: H₂O = 1 : 3 (volume ratio); NH₃, 30 cm³ min⁻¹; temperature, 300 °C; WHSV, 0.5 h⁻¹; catalyst weight, 4 g; metal weight, 5 wt.%.



Scheme 4. Amino cyclization of 1,6-hexanediol.

with $[M(OH)]^{n+}$ and H^+ ions as active centers. The bifunctionality and polarizability of the cation are responsible for formation of the desired product. Brønsted acidic centers are formed in the dissociation of water [36]. The polarizability of the cation is responsible for the dissociation of water resulting in the bifunctional nature of the catalyst. HZSM-5 catalysts are active in dehydrocyclization of diol and ammonia or amino alcohol, in this case bifunctionality is not re-

quired. Because of the absence of ammonia, oxygen containing heterocyclics and acyclic dehydrated products are formed. The terminal diols interaction with Brønsted acidic center H^+ , followed by dehydration results in the primary carbocation as shown in Fig. 2. The primary carbocation is stabilized by $[M(OH)]^{n+}$ species in the ZSM-5 channels. The channel size of ZSM-5 may also restrict the formation of stable secondary cation due to geometric constraints.

Table 7

Amino cyclization of 6-amino caproic acid in the variation of catalysts

S. no.	Catalyst	TOS (h)	Conversion of 6-amino caproic acid (%)	Yield of products (wt.%)	
				ϵ -Caprolactam	Others
1	HZSM-5 (30)	4	58.1	24.4	33.7
2	HZSM-5 (129)	4	92.8	70.4	22.4
3	PbZSM-5 (30)	4	95.0	75.1	19.9
4	ZnZSM-5 (280)	2	95.4	60.0	35.4

Feed: 6-amino caproic acid + H_2O ; 6-amino caproic acid: H_2O = 1 : 3 (volume ratio); temperature, $350^\circ C$; WHSV, $0.5 h^{-1}$; catalyst weight, 4 g; metal weight, 5 wt.%; in others pentylamine was major.

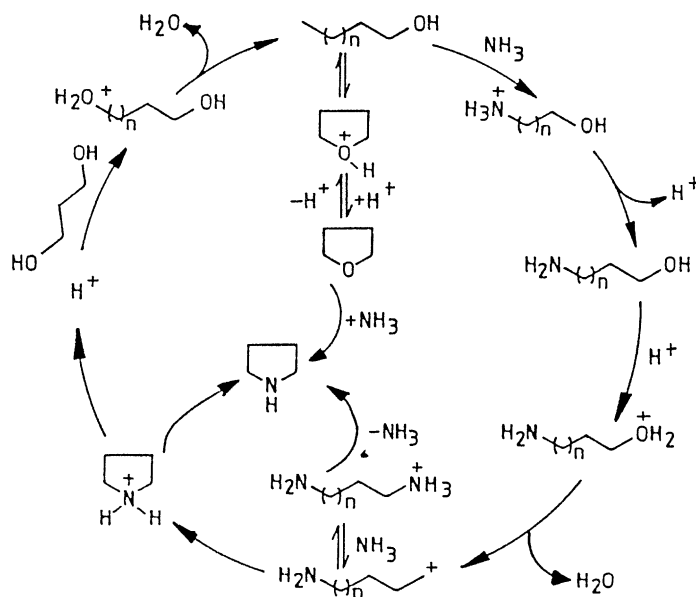


Fig. 2. The plausible mechanism for diol cyclization and stabilization of primary carbocation over MZSM-5.

5. Conclusions

Amination of diols over zeolites was carried out with high selectivity towards saturated cyclic amines over transition metal ion modified ZSM-5 catalyst. The high conversions were obtained at a relatively milder reaction conditions in absence of hydrogen.

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