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Intermolecular cyclization of ethanolamine to 1,4-diazabicyclo (2.2.2) octane over modified pentasil zeolites ☆

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Abstract

The synthesis of 1,4-diazabicyclo (2.2.2) octane (DABCO) over modified ZSM-5 catalysts was carried out selectively in vapor phase with high conversion and yields. Pb, Zr and Cr-modified HZSM-5 zeolites with medium acidity gave high yields of DABCO. The acid sites of medium strength are found to be active for the selective synthesis of DABCO. The life of the catalyst was significantly improved by tuning various reaction parameters. The optimization of reaction parameters like mole ratio of the feed, weight hour space velocity, time on stream, effect of additives in the feed and the mechanism of selective formation of DABCO are described. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ethanolamine; ZSM-5; 1,4-diazabicyclo (2.2.2) octane; Cyclization

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1. Introduction

Nitrogen containing compounds like amines, diamines, saturated and unsaturated heterocyclics are widely used in the bulk chemicals, drug intermediates, fungicides and pesticides due to their high biological activity [1,2]. The synthesis of these cyclic amines although being industrially important attracted lesser attention due to the complexity involved in such cyclization reactions. Few reports by Karpeiskaya et al. [3] and Scriabine [4] for the cyclization of ethanolamine showed the use of cobalt and alumina as suitable catalysts, respectively. Zeolites with their unique shape selective and acidic properties were found to be suitable catalysts for the amination of ethanolamine to ethylenediamine, where 1,4-diazabicyclo (2.2.2) octane (DABCO) was reported to be a minor product [5]. Various cyclization and amination reactions were reported by several groups on the zeolites [6–10]. Although conventional catalysts [3,4] gave higher yields, the selectivity was low and the product separation was difficult. Budnik and Sandner reported the synthesis of DABCO from *N*-aminoethyl piperazine over zeolites [11]. DABCO is very useful as a catalyst in the synthesis of industrially important polyurethane foams [12], in organic synthesis as a versatile reagent and also as a template (structure directing agent) [13] during the synthesis of zeolite catalysts. We report here the optimized reaction parameters for selective synthesis of DABCO from the intermolecular cyclization of ethanolamine over modified ZSM-5 catalysts.

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2. Experimental

HZSM-5 zeolite was supplied by Conteka, Sweden. HZSM-5 ($SiO_2/Al_2O_3 = 30$) was further modified with 5 wt.% of various cations like Pb, Zr, Ni, La by the impregnation method with corresponding nitrate salts as the precursors. The metal contents of the modified zeolites were analyzed (Table 1) on a ICP-MS Ultra Mass (Varian, Australia) instrument. Powder XRD patterns of the calcined products were recorded on a diffractometer with CuK_α radiation at 0.045° at 2θ step size and 0.5 s step time over the range $0° < 2\theta < 60°$. The specific surface area, A_{BET}, was determined from the linear part of the BET plot ($P/P_0 = 0.05–0.30$). 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 $\mathrm{ton\,cm^{-2}}$.

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 $\mathrm{ml\,min^{-1}}$ for another 2 h. The amount of NH_3 desorbed was recorded by TCD signal, at 10 $\mathrm{°C\,min^{-1}}$ 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 tubular downflow pyrex reactor with 20 mm internal diameter. The reaction mixture was fed from the top using a syringe pump (B. Braun, Germany). The products were cooled using an ice-cold trap at the outlet to collect the total amount of products. The products were analyzed by gas chromatography using SE-30 column and FID. The products were confirmed by mass spectra and GC/MS. The liquid product mass balance was about 90–95% and ~5% gases were observed.

3. Results and discussion

The crystallinity of metal cation modified ZSM-5 were studied by XRD using a highly crystallized HZSM-5 as the 100% standard. A good degree of crystallinity was obtained for all the samples, when evaluated by the summation method, for the intensities of typical diffraction peaks between $2\theta = 26°$ and $2\theta = 29°$ [14]. The framework of the modified zeolites was also checked by FT-IR spectroscopy and the crystallinity was found to be retained even after modification. The decrease in surface area of the impregnated samples relative to its protonated one (except Cu and La) was observed, which is due to the presence of metal ion and its oxide species in cavities of the zeolite (Table 1).

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 °C correspond to the desorption of NH_3 from weak, medium and strong acid sites respectively as observed by several other groups [15–18]. The total acidity of the catalysts

Table 1
Characteristic properties of catalysts

S. no.	Catalyst	Metal (wt.%)	Surface area ($m^2\,g^{-1}$)	Acidity (NH_3 uptake $\mathrm{mmol\,g^{-1}}$)			
				150–250	250–350	350–450	Total
1	HZSM-5(30)	–	310.0	1.1773	0.2615	0.3899	1.7286
2	VZSM-5(30)	4.11	290.2	1.3931	0.3486	0.1703	1.9120
3	CrZSM-5(30)	4.56	283.5	0.4213	0.2814	0.1223	0.8250
4	MnZSM-5(30)	4.89	272.5	0.4858	0.1352	0.1019	0.7230
5	CuZSM-5(30)	4.72	311.4	0.5862	0.2478	0.1660	1.0000
6	PbZSM-5(30)	4.37	225.0	0.8947	0.3753	0.1722	1.4720
7	ZrZSM-5(30)	3.92	218.0	0.5173	0.3722	0.1020	0.9900
8	LaZSM-5(30)	4.16	397.8	2.2080	0.4605	1.1065	3.7750

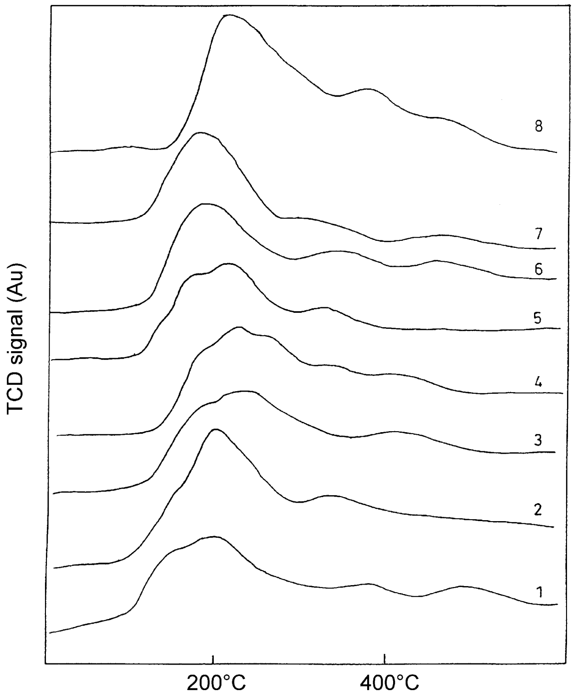

Fig. 1. NH_3 TPD of (1) HZSM-5(30), (2) VZSM-5(30), (3) CrZSM-5(30), (4) MnZSM-5(30), (5) CuZSM-5(30), (6) PbZSM-5(30), (7) ZrZSM-5(30) and (8) LaZSM-5(30).

(Table 1) followed the order: MnZSM-5 < CrZSM-5 < ZrZSM-5(30) < CuZSM-5 < PbZSM-5(30) < HZSM-5(30) VZSM-5 < LaZSM-5(30). The high acidity of LaZSM-5(30) can be attributed to its coordinating ability with ammonia to generate strong Brönsted acidic sites by dissociating H_2O.

4. Catalytic activity

The intermolecular cyclization of ethanolamine in presence of H_2O over HZSM-5 catalysts at 300 °C with 0.5 h^{-1} weight hour space velocity (WHSV) of the total feed was carried out for the selective synthesis of DABCO and the results have been depicted in Table 2. On increasing the SiO_2/Al_2O_3 ratio of HZSM-5 catalyst from 30 to 129 there is an increase in the yield of DABCO and thereafter not much increase in the yield of DABCO was observed. It is generally believed that on increasing SiO_2/Al_2O_3 ratio the strength of the acid sites increases in zeolites [19]. The number of acid sites in HZSM-5 is found to decrease almost linearly with the Si/Al ratio. On the other hand, the number of active acid sites per aluminium atom of the zeolite increases with Si/Al ratio upto the Si/Al ratio 31.1 and levels of there after [20, 21]. Chandawar et al. [22] have studied benzene alkylation with ethanol over pure and modified HZSM-5 zeolites with varying SiO_2/Al_2O_3 ratio. The SiO_2/Al_2O_3 ratio versus alkylation activity shows that the suitable SiO_2/Al_2O_3 ratio for this reaction is 70 and above. Similarly, in the present context for the cyclization of ethanolamine to

Table 2
Synthesis of DABCO: variation of Si/Al ratio of HZSM-5 catalyst

S. no.	Catalyst	TOS (h)	% Conversion of ethanolamine	Yield of liquid products (%)		
				DABCO	Piperazine	Others[a]
1	HZSM-5(30)	3	93.9	60	3.2	30.7
		4	68.1	52.2	3.3	12.6
2	HZSM-5(129)	3	88.3	60.1	9.0	19.2
		4	89.5	62.5	8.3	18.7
3	HZSM-5(150)	2	87.0	62.5	6.2	18.3
		4	84.0	60.2	6.6	17.2
4	HZSM-5(280)	2	94.6	73.2	5.1	16.3
		4	89.5	62.9	6.4	20.2

Ethanolamine: H_2O (feed) = 1:3 (by volume); reaction temperature: 300 °C; WHSV: 0.5 h^{-1}; catalyst wt.: 4 g.

[a] Lower aliphatic amines and piperazine derivatives are the major components.

Table 3
Synthesis of DABCO: variation of catalysts

S. no.	Catalyst	TOS (h)	% Conversion of ethanolamine	Yield of liquid products (%)		
				DABCO	Piperazine	Others[a]
1	VZSM-5(30)	4	97.3	60.4	3.2	33.7
2	CrZSM-5(30)	4	98.4	71.6	0.1	26.7
3	MnZSM-5(30)	2	97.2	29.2	11.6	56.4
		4	59.8	22.7	9.7	27.4
4	NiZSM-5(30)	1	95.4	58.9	3.8	32.7
		4	82.1	50.2	7.1	24.8
5	CuZSM-5(30)	4	95.2	51.2	4.8	39.2
6	PbZSM-5(30)	1	99.2	77.9	2.6	18.7
		4	93.3	69.5	5.7	18.1
7	LaZSM-5(30)	4	51.8	27.4	9.8	14.6
8	ZrZSM-5(30)	2	96.2	78.5	4.6	13.1
		4	96.7	75.7	5.9	15.1
9	GaZSM-5(30)	4	68.4	50.7	9.1	8.6
10	PtZSM-5(30)	2 + 3	86.6	53.8	4.8	28.0
		4	89	50.7	5	33.3
11	RhZSM-5(30)	4	98.8	57.6	4.7	36.5
12	PdZSM-5(30)	2	88.3	51.9	6.3	31.1
		4	83.8	50.9	7	23.9
13	WZSM-5(30)	2	88.8	78.8	3.8	6.2
		4	98.3	72.8	4.7	20.8

Ethanolamine: H_2O (feed) = 1:3 (by volume); temperature: 300 °C; WHSV: 0.5 h^{-1}; all metals: 5 wt.%; catalyst wt.: 4 g.

[a] Lower aliphatic amines and piperazine derivatives are the major components.

DABCO the SiO_2/Al_2O_3 of 129 and above are found to be more suitable.

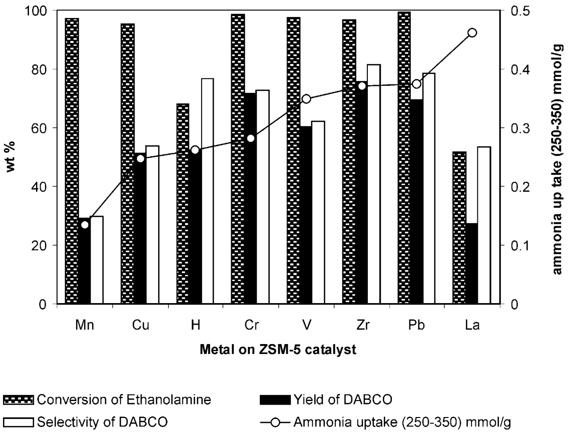

Fig. 2. Effect of acidity of metal modified HZSM-5 catalysts on the synthesis of DABCO.

In order to increase the selectivity of DABCO, HZSM-5(30) catalyst was modified with various metal ions as is shown in Table 3, Fig. 2. Among the metal modified catalysts Cr, Pb, Zr, W gave better selectivity. The higher and lower acidic strength of La and MnZSM-5 respectively, showed deviation from the optimum condition of medium acidity for the synthesis of DABCO. Thus, resulting in lower conversion and yield of the products. A decreased selectivity over CuZSM-5(30) may be due to the reductive nature of Cu ions which leads to the formation of dehydrogenated products like pyrazine and its derivatives. It is observed that the catalysts with medium acidity gave better results. The acid sites of medium strength are found to be active for the selective synthesis of DABCO. The catalytic activity of the metal modified zeolites with respect to the concentration of the acid sites of medium strength (250–350 °C in the TPD of ammonia) is presented

Table 4
Synthesis of DABCO: variation of temperature

S. no.	Temperature (°C)	TOS (h)	% Conversion of ethanolamine	Yield of liquid products (%)		
				DABCO	Piperazine	Others[a]
1	250	4	60.0	35.0	2.0	23.0
2	300	1	99.2	77.9	2.6	18.0
		4	93.3	69.5	5.7	18.0
3	350	4	93.3	66.4	3.0	23.9
4	400	4	96.5	53.7	2.1	40.7

Catalyst: 5 wt.% PbZSM-5(30); ethanolamine: H_2O (feed) = 1:3 (by volume); WHSV: 0.5 h^{-1}; catalyst wt.: 4 g.

[a] Lower aliphatic amines and piperazine derivatives are the major components.

in Fig. 2. The presence of noble metals like Pt, Pd and Rh resulted an increase in the life of the catalyst, although they showed lower activity.

As the synthesis of DABCO was found to be highly sensitive towards the reaction conditions, attempt was made to optimize the parameters like temperature, WHSV, molar ratio etc.

The variation in catalytic activity and selectivity towards the synthesis of desired products on varying the reaction temperature from 250 to 400 °C over PbZSM-5(30) catalyst at 0.5 h^{-1} are given in Table 4. The optimum temperature was found to be 300 °C. Deviation from either side of the required temperature showed a decrease in the yield and selectivity of DABCO. Lower temperatures (<400 °C) do not favor the formation of pyrazine and its derivatives hence the selectivity of piperazine and DABCO increases [23]. At higher temperatures, an increase in the Lewis acidic sites [24] may due to the dehydration of Brönsted acidic sites which leads to the formation of pyrazine derivatives. Moreover, at higher temperatures the degradation of ethanolamine to the aliphatic amines is also possible which leads to decrease the selectivity of DABCO.

The WHSV was varied over PbZSM-5(30) catalyst at 300 °C with 1:3 volume ratio of ethanolamine and water, and the results are given in Table 5. The optimum WHSV was found to be 0.5 h^{-1} with high conversion of 93.3 wt.% and yield of 69.5%. Increasing the WHSV from 0.5 to 1.0 h^{-1} increased the selectivity of DABCO, but the conversion of ethanolamine decreased, which may be due to the low contact time between catalytic bed and the reactant, thus suppressing the side reactions which in turn influence selectivity. The low

Table 5
Synthesis of DABCO: variation of WHSV

S. no.	WHSV (h^{-1})	TOS (h)	% Conversion of ethanolamine	Yield of liquid products (%)		
				DABCO	Piperazine	Others[a]
1	0.25	2	86.3	57.4	4.5	24.4
		4	84.7	59.8	3.8	21.1
2	0.50	1	99.2	77.9	2.6	18.7
		4	93.3	69.5	5.7	18.1
3	0.75	1	62.7	49.3	6.4	7.0
		4	54.8	45.9	3.2	5.7
4	1.00	2	56.6	46.4	3.8	3.8
		4	49.8	43.6	2.7	3.5

Catalyst: 5 wt.% PbZSM-5(30); ethanolamine: H_2O (feed) = 1:3 (by volume); temperature: 300 °C; catalyst wt.: 4 g.

[a] Lower aliphatic amines and piperazine derivatives are the major components.

Table 6
Synthesis of DABCO: effect of H_2O content in the feed composition

S. no.	Ethanolamine: H_2O (volume ratio)	TOS (h)	% Conversion of ethanolamine	Yield of liquid products (%)		
				DABCO	Piperazine	Others[a]
1	1:1	2	90.1	62.9	7.8	19.4
		4	75.6	60.0	8.0	7.6
2	1:2	2	91.1	65.0	7.1	19.0
		4	88.0	60.7	7.7	19.6
3	1:3	1	99.2	77.9	2.6	18.7
		4	93.3	69.5	5.7	18.1
4	1:4	3 + 4	92.4	67.8	1.9	22.7

Catalyst: 5 wt.% PbZSM-5(30); temperature: 300 °C; WHSV: 0.5 h^{-1}; catalyst wt.: 4 g.

[a] Lower aliphatic amines and piperazine derivatives are the major components.

yield at 0.25 h^{-1} WHSV is may be due to the increase in the formation of side products due to very high contact time.

In order to study the effect of water on catalytic activity and selectivity, the volume ratio of ethanolamine to water was varied from 1:1 to 1:4 and the results are given in Table 6. Lower volume ratios of 1:1 and 1:2 resulted in decreasing the conversion of ethanolamine although the yields and selectivities are good. At 1:3 and 1:4 volume ratio the conversion of ethanolamine was high with increased yields and selectivity. This may be due to the fact that the amount of reactant passed over the catalyst per hour is lower compared to the ratio 1:1 and 1:2. But in the absence of water conversion and yields were much lower, which shows that steam has the expected tendency to reduce coke formation.

As the synthesis of DABCO is potentially of importance to industry, a study of catalyst life is crucial. For this, the reaction of ethanolamine was carried out in the presence of water on PbZSM-5(30) for 20 h. Fig. 3 shows that the conversion was stable for 10 h at around 95.1%, but a gradual decrease in the yields of DABCO was observed with the increase in time. After 10 h, both conversion and yields decreased due to the deactivation of the catalyst.

The reaction of ethanolamine, ethylenediamine and H_2O in 1:1:2 volume ratio was carried out over metal modified ZSM-5(30) catalysts at 300 °C with 0.5 h^{-1} and the results are depicted in Table 7. The results show that the impregnation of metal ions decreased the yields and selectivity of DABCO and major products formed were alkylated amines.

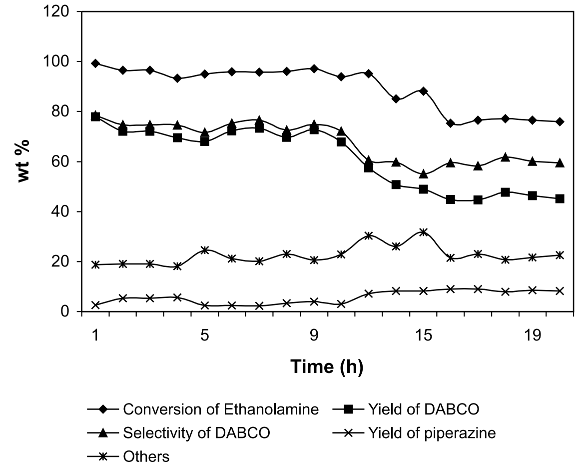

Fig. 3. Effect of time on stream on synthesis of DABCO.

Table 8 shows the effect of additive on the reaction mixture. By the addition of ethylenediamine to the feed, selectivity of DABCO decreased but that of piperazine increased. Similarly, when the reaction was carried out in the presence of ammonia, the selectivity to DABCO decreased, but it increased the aminated product i.e. ethylene diamine and polyalkylated acyclic amines.

Table 7
Synthesis of DABCO from ethanolamine and ethylenediamine: variation of catalyst

S. no.	Catalyst	TOS	% Conversion of ethanolamine	Yield of liquid products (%)		
				DABCO	Piperazine	Others[a]
1	HZSM-5(30)	2 + 3	99.3	65.3	14.4	19.3
		4	99.4	63.9	13.6	21.9
2	PbZSM-5(30)	1	98.2	61.8	27.7	8.7
		4	75.7	49.3	22.3	4.1
4	KZSM-5	2	50.3	32.2	17.0	1.1
		4	43.8	29.9	13.5	0.4
5	ZrZSM-5(30)	1	85.6	58.0	16.5	11.1
		3 + 4	80.5	53.9	23.3	3.3
6	LaZSM-5(30)	2	43.3	15.0	28.3	0.0
		3 + 4	47.7	14.3	23.2	10.2

Feed: ethanolamine + ethelenediamine + H_2O; ethanolamine:ethylenediamine:H_2O = 1:1:2 (by volume); temperature: 300 °C; WHSV: 0.5 h^{-1}; metal wt.: 5 wt.%; catalyst wt.: 4g.

[a] Lower aliphatic amines and piperazine derivatives are the major components.

Table 8
Synthesis of DABCO: variation in feed composition (effect of additives)

S. no.	Feed	Volume ratio	TOS (h)	% Conversion of ethanolamine	Yield of liquid products (%)		
					DABCO	Piperazine	Others[a]
1	Ethanolamine + H_2O	1:3	1	99.2	77.9	2.6	18.7
			4	93.3	69.5	5.7	18.1
2	Ethanolamine + ethylenediamine + H_2O	1:1:2	1	98.2	61.8	27.7	8.7
			4	75.7	49.3	22.3	4.1
3	Ethanolamine + NH_3 + H_2O	1:5:3	3	99.9	57.7	8.1	34.1
			4	99.9	59.9	7.3	32.6

Catalyst: 5 wt.% PbZSM-5(30); temperature: 300 °C; WHSV: 0.5 h^{-1}; catalyst wt.: 4 g.

[a] Lower aliphatic amines and piperazine derivatives are the major components.

The possible sequence leading to the synthesis of DABCO and piperazine derivatives can be explained on the basis of product distribution as shown in Fig. 4. Intermolecular dehydrocyclization of two molecules of ethanolamine leads to the formation of piperazine. Piperazine further reacts with one more ethanolamine molecule to form *N*-aminoethyl piperazine by *N*-alkylation. Then by dehydro and deamino cyclization DABCO results. Alkyl piperazine is formed by the alkylation of piperazine with aliphatic amines. Pyrazine derivatives can form via dehydrogenation of piperazine and alkylated piperazine at higher temperature in presence of strong acidic sites.

5. Conclusions

The selective synthesis of DABCO was carried out over modified and unmodified HZSM-5 catalysts. The increase in the Si/Al ratio increased the yield of DABCO. The modification of the HZSM-5(30) zeolite with metal like Pb, Cr, W and Zr increased the yield of DABCO to considerable

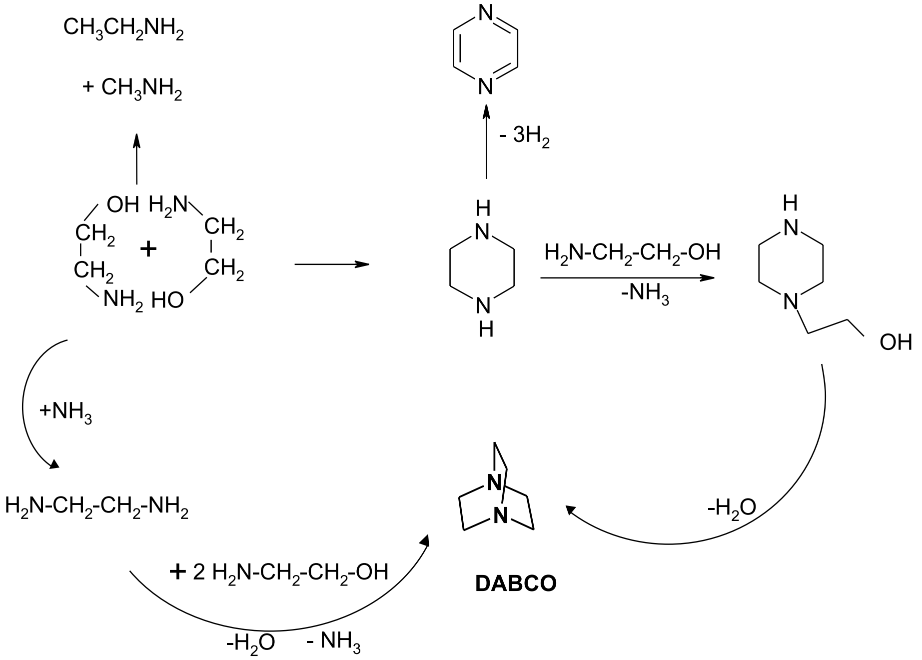

Fig. 4. A scheme for the formation of DABCO from ethanolamine.

extent. Zeolites with acid sites of medium strength are found to be active for the selective synthesis of DABCO.

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