

# Deaminocyclization of diethylenetriamine to *N*-heterocycles over zeolites

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The deaminocyclization of diethylenetriamine was carried out over HZSM-5 (Si/Al = 30–280), HM, HY, SAPO-40 type catalysts. The reaction was carried out in the temperature range of 300–400°C and 0.5 h<sup>-1</sup> weight hourly space velocity in the presence of water. The total yield of *N*-heterocycles varied from 32 to 77 wt% at 400°C reaction temperature. At a low temperature (300°C), the selectivity to piperazine is more, whereas at 400°C the selectivity to pyrazine and dehydrogenated heterocycles increases due to dehydrogenation over basic centers generated because of the coke.

**Keywords:** zeolites; diethylenetriamine; *N*-heterocycles; deaminocyclization

## INTRODUCTION

Many applications of zeolite molecular sieves in the synthesis of speciality and fine chemicals have been reported.<sup>1–14</sup> We have reported the synthesis of heterocycles from C<sub>1</sub> to C<sub>5</sub> aliphatics using zeolite molecular sieve catalysts.<sup>4,8,14</sup> In the reaction of propylene-oxide and ethylenediamine<sup>4</sup> in presence of steam over HZSM-5 (Si/Al = 30) at 400°C and 1.9 h<sup>-1</sup> weight hourly space velocity, the yields of piperazine and 2-methylpyrazine were 41.6 and 26.0 wt% at 100% conversion, respectively. The reaction of hydroxypropylethylenediamine<sup>4</sup> in the presence of water over a HZSM-5 catalyst at 350°C and 1.9 h<sup>-1</sup> WHSV leads to 76.6 wt% selectivity for piperazine at 65.8% conversion. *N*-methylpiperazine was synthesized from diethanolamine and methylamine over HZSM-5, H-mordenite, and HY, the yield with HZSM-5 being about 90 wt% at 300°C and 80 atmospheric H<sub>2</sub> pressure.<sup>14</sup> The substituted two *N*-containing heterocycles are useful drug intermediates.<sup>4,14</sup>

In this paper, we report the deaminocyclization of diethylenetriamine over various zeolites to obtain preferably two *N*-containing heterocycles.

## EXPERIMENTAL

HZSM-5 (Si/Al = 30, 150, and 280) was supplied by Conteka, Sweden. H-mordenite (Si/Al = 6.0) and HY (Si/Al = 2.5) were supplied by the PQ Corporation. The synthesis of SAPO-(TPA-40 type) has been re-

ported and discussed elsewhere.<sup>11,15</sup> The reaction was carried out using a down-flow, fixed-bed pyrex reactor of 20-mm internal diameter. The reaction was carried out in the temperature range of 300–400°C, 0.5 h<sup>-1</sup> weight hourly space velocity (WHSV), and the amount of catalyst was 4 g (18–30 mesh size). The water was added in the feed in 1:1 by volume ratio. The reaction mixture was fed from the top using a syringe pump (Sage Instruments). The product was cooled using ice-cooled water and collected at the bottom. The products were analyzed by SE-30 (30%) and OV-17 columns. The analysis was confirmed by mass spectra and GC-mass. The mass balance was >90%. The mass balance will be <90% at >350°C in the absence of water in the feed due to high coking.

## RESULTS AND DISCUSSIONS

The reaction of diethylenetriamine was carried out at a 300°C reaction temperature, 0.5 h<sup>-1</sup> WHSV, and 4 g of catalyst (18–30 mesh size). The water was added to diethylenetriamine in a feed 1:1 ratio by volume. The total amount of two *N*-containing six-membered heterocycles formed was 40.4, 40.2, 40.7, 2.3, 10.8, and 42.8 wt% at a conversion of 16–84% over HZSM-5 (30), HZSM-5 (150), HZSM-5 (280), PbZSM-5, HM, and HY catalysts respectively (Table 1). In the case of HZSM-5 (Si/Al = 280), the yield of piperazine obtained was 28.6 wt% at 48.9 wt% conversion at 300°C. The yields of piperazine were 28.6, 22.9, and 13.6 wt% at 300°C and decreased with a Si/Al ratio from 280 to 30 in HZSM-5 catalysts.

The dehydrogenated products such as 2-methylpyrazine and pyrazine were formed more in the case of HZSM-5 (30) than in HZSM-5 (280). This may be because the coke formed in HZSM-5 (30) is more olefinic than that in HZSM-5 (280).<sup>16–22</sup> With a de-

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**Table 1** Deaminocyclization of diethylenetriamine over zeolites at 300°C

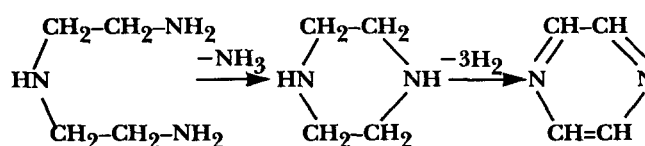
Catalyst	Time on stream (h)	Conversion of diethylenetriamine (%)	Yield (wt%) <sup>a</sup>						Total heterocycles
			Aliphatics <sup>b</sup>	Pyrazine	2-Methylpyrazine	Piperazine	Ethylpyrazine	C <sub>8+</sub> <sup>c</sup>	
HZSM-5 (30) <sup>d</sup>	3	63.9	15.8	7.6	10.2	13.6	9.0	7.7	40.4
HZSM-5 (150)	3	57.9	12.0	2.9	6.9	22.9	7.5	5.7	40.2
HZSM-5 (280)	4	48.9	2.8	8.8	1.1	28.6	2.2	5.4	40.7
PbZSM-5 (30)	3	16.8	8.6				2.3	5.8	2.3
HM	3	26.5	8.7	0.4	1.0	8.7	0.7	7.0	10.8
HY	1	67.9	13.5	8.3	8.6	10.4	15.5	11.6	42.8
SAPO-40 type	4	59.7	16.0	8.3	0.0	4.9	22.9	7.6	36.1
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	3	84.1	26.2	13.8	13.7	3.4	24.6	2.4	55.5

<sup>a</sup> Based on diethylenetriamine.<sup>b</sup> Amines, methylamine, ethylamine.<sup>c</sup> Aromatics (high boilers). Diethylenetriamine: H<sub>2</sub>O = 1:1 by volume. WHSV = 0.5 h<sup>-1</sup>. Catalyst = 4 g. Atmospheric pressure.<sup>d</sup> Si/Al ratio.

creasing Si/Al ratio, generally the coke is olefinic, that is, hydrogen deficient and can abstract the hydrogen and active in the dehydrogenation reactions.<sup>18</sup> The charge from the olefinic coke is transformed to the framework oxygen, which becomes basic in nature<sup>16,18</sup> and is active in dehydrogenation type of base-catalyzed reactions. On the other hand, if the coke formation is more and if it blocks these basic oxygens, then the dehydrogenation may be reduced because of the nonavailability of basic oxygens. This is observed in the case of the HY catalyst. In the case of HZSM-5, the cyclization occurs predominantly at the intersection of the channel. In SAPO, due to the lack of appropriate channel structure and amorphous formation, the activity for cyclization reaction is low.

The deaminocyclization of diethylenetriamine was carried out at 350°C, the results are given in Table 2. With an increasing reaction temperature, the total yield of N-heterocycles increased. The reaction results at 400°C are given in Table 3. The total yields of N-heterocycles were 54.8, 62.6, 56.9, 38.1, and 62.3 wt% over HZSM-5 (30), HZSM-5 (150), HZSM-5 (280), HM and HY catalysts at 58.0–97.5% conversions, respectively. The yields of piperazine obtained were 16.9, 21.9, 3.4, and 29.1 wt% based on diethylenetriamine over HZSM-5 (30), HZSM-5 (150), HZSM-5 (280), and PbZSM-5, respectively. Because

of the high coking and irreversible chemisorption,<sup>18,19</sup> HY zeolite showed low selectivity for piperazine particularly. In various reactions we have observed that HZSM-5 is a good cyclization catalyst.<sup>4,22</sup> One-ring compounds from C<sub>1</sub>–C<sub>5</sub> aliphatics can be obtained over the HZSM-5 catalyst; two-fused-ring heterocycles such as coumarine can be obtained over modified Y zeolite.<sup>8</sup> The stoichiometric equation may be written as follows.



The interesting aspect of the study is that the deamination occurs over acidic catalysts resulting in heterocycles, which are enhanced at high temperature. The products such as ethyl- and methylpyrazine were obtained because of the cracking of diethylenetriamine. The alkylation of piperazine occurs because of the availability of CH<sub>3</sub><sup>+</sup> and C<sub>2</sub>H<sub>5</sub><sup>+</sup> species formed during the cracking.

In conclusion, deaminocyclization of diethylenetriamine to two N-containing heterocycles was observed over zeolites. Typically in the deaminocyclization of

**Table 2** Deaminocyclization of diethylenetriamine over zeolites at 350°C

Catalyst	Time on stream (h)	Conversion of diethylenetriamine (%)	Yield (wt%) <sup>a</sup>						Total heterocycles
			Aliphatics <sup>b</sup>	Pyrazine	2-Methylpyrazine	Piperazine	Ethylpyrazine	C <sub>8+</sub> <sup>c</sup>	
HZSM-5 (30) <sup>d</sup>	2	91.4	29.2	24.2	11.1	13.9	10.3	2.7	59.5
HZSM-5 (150)	3	85.1	15.2	13.0	15.4	7.1	14.7	19.7	50.2
HZSM-5 (280)	4	35.3	4.0	2.4	3.0	18.0	4.1	3.8	27.5
PbZSM-5 (30)	4	26.3	14.2			7.2		4.9	7.2
HM	3	77.6	21.2	14.0	3.1	17.8	3.9	17.6	38.8
HY	4	86.1	22.2	18.0	14.6	4.7	18.7	7.9	56.0
SAPO-40 type	3	74.7	17.0	13.6	0.0	9.2	24.9	10.0	47.7
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	3	82.7	7.0	26.4	0.0	20.5	4.4	24.4	51.3

<sup>a</sup> Based on diethylenetriamine.<sup>b</sup> Amines, methylamine, ethylamine.<sup>c</sup> Aromatics (high boilers). Diethylenetriamine: H<sub>2</sub>O = 1:1 by volume. WHSV = 0.5 h<sup>-1</sup>. Catalyst = 4 g. Atmospheric pressure.<sup>d</sup> Si/Al ratio.

**Table 3** Deaminocyclization of diethylenetriamine over zeolites at 400°C

Catalyst	Time on stream (h)	Conversion of diethylenetriamine (%)	Yield (wt%) <sup>a</sup>						Total heterocycles
			Aliphatics <sup>b</sup>	Pyrazine	2-Methylpyrazine	Piperazine	Ethylpyrazine	C <sub>8+</sub> <sup>c</sup>	
HZSM-5 (30) <sup>d</sup>	3	93.8	31.6	24.5	7.9	16.9	5.5	7.4	54.8
HZSM-5 (150)	3	96.2	25.3	26.6	8.8	21.9	5.3	8.6	82.6
HZSM-5 (280)	4	78.4	14.3	16.2	16.2	3.4	21.1	7.2	56.9
Pb-ZSM-5 (30)	4	58.9	24.2		0.4	29.1	3.0	2.2	32.5
HM	3	79.7	20.1	5.9	7.1	13.2	11.9	21.5	38.1
HY	4	90.2	11.7	20.5	13.8	2.6	25.4	16.2	62.3
SAPO-40 type	3	96.9	50.9	8.6	10.4	3.3	10.3	13.4	32.6
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	3	97.5	18.1	46.7	0.0	20.5	5.3	6.9	72.5

<sup>a</sup> Based on diethylenetriamine.<sup>b</sup> Amines, methylamine, ethylamine.<sup>c</sup> Aromatics (high boilers). Diethylenetriamine: H<sub>2</sub>O = 1:1 by volume. WHSV = 0.5 h<sup>-1</sup>. Catalyst = 4 g. Atmospheric pressure.<sup>d</sup> Si/Al ratio.

diethylenetriamine over HZSM-5 (280), ~30% piperazine was obtained at 300°C. Because of dehydrogenation, products such as pyrazine were obtained at high (~400°C) temperatures over (more) acidic zeolites.

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