Modified ZSM-5 Catalysts for the Synthesis of Five- and Six-Membered Heterocyclics†

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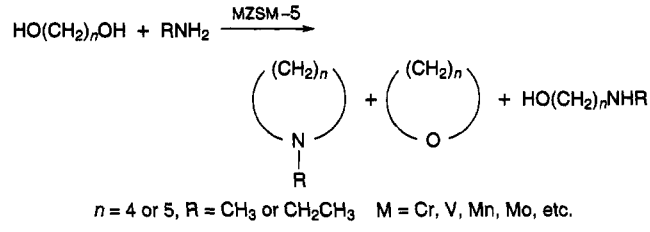
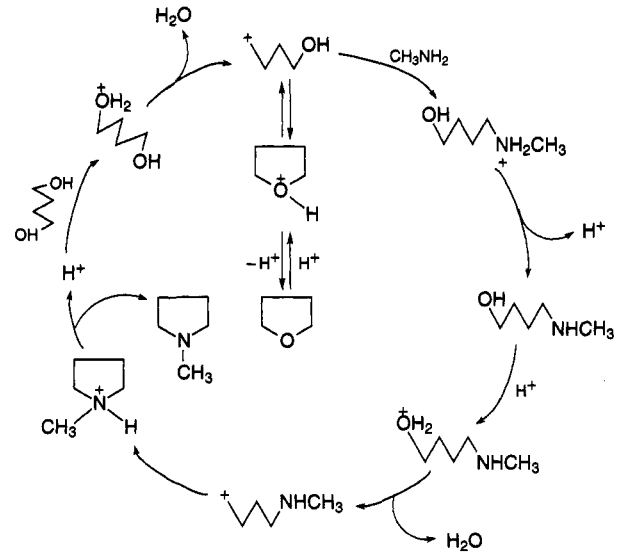
Heterocyclic compounds are widely distributed in nature and are essential to human life; they play a vital role in metabolism. Because of their extensive practical use, the literature of the subject is correspondingly vast.[1] Among heterocyclic compounds, alkylpyrrolidine and -piperidine, dialkylpiperizine, DHP, etc. often attract the most attention. Zeolites, being acidic, have proved to be better catalysts in the synthesis of fine chemicals, based on their activity, selectivity, reusability, and nonpolluting nature.[2–4] Moreover, there are very few reports of the syntheses of heterocyclics over zeolites even though it is of topical interest.[5–7] Herewith, we are reporting the vapor-phase intermolecular cyclization of diol and alkylamine to N- and O-containing cyclic compounds over modified ZSM-5 catalysts (Scheme 1) for the first time.

Scheme 1



Scheme 2. Plausible Reaction Mechanism To Form THF and *N*-Methylpyrrolidine



The reaction results of 1,4-butanediol and methylamine over different modified ZSM-5 catalysts are depicted in Table 1. All the catalysts were activated for 4 h at 420 °C in air before doing the reaction. The yield of *N*-methylpyrrolidine (NMP) has been enhanced by using an excess of methylamine. The optimum temperature to obtain more NMP is 300 °C. At lower temperatures (<300 °C), >90% tetrahydrofuran (THF) was obtained. On the other hand, at >300 °C, side products including aromatics increased.[8] In the case of CrZSM-5, the NMP product selectivities were 64.2, 28.5, and <15 at 300, 350, and 400 °C, respectively. However, the VZSM-5, MoZSM-5, and MnZSM-5 are not showing much difference in the formation of NMP with temperature, but the side products were increased to 7%. Interestingly, VZSM-5 was yielding NMP but the SAPO, VAPO, and VSAPO were not, even though the main constituent is vanadium. This may be due to the channel/structure of the ZSM-5, or the impregnated vanadium residing in the channels/pores may be responsible. Altogether, the promoting effect of cations to form NMP is in the following order: Cr > V > Mn > Mo > Pb ≃ Cu > W.

The plausible mechanism for the formation of NMP and THF is shown in Scheme 2. CrZSM-5 is a bifunctional catalyst with $[Cr(OH)]^{2+}$ and H^+ as active centers. The bifunctionality and polarizability of the cation are responsible for the formation of NMP. Brönsted acidic centers are formed in the dissociation of water.[9] The

$$Cr^{3+} + H_2O \rightarrow [Cr(OH)]^{2+} + H^+ \qquad (1)$$

polarizability of Cr^{3+} (or cation) is responsible for the dissociation of water resulting in the bifunctional nature of the catalyst. Because of the absence of amine in feed, the product is only THF. The 1,4-butanediol interaction with Brönsted acidic center H^+, followed by dehydration, results in the primary carbocation as shown in Scheme 2. The primary carbocation is stabilized by $[Cr(OH)]^{2+}$ species in the ZSM-5 channel, as depicted in Figure 1. The channel size (5.6 Å) of ZSM-5 may also restrict the formation of stable secondary cation is due to geometric constraints. Secondly, the reaction of methylamine with THF is also taking place. On the basis of the product distributions in the reactions in Table 2, the reaction route may be proposed as BD to THF to MAB to NMP (Scheme 2).

The activity of CrZSM-5 (unless stated) was checked in the experiments with various substrates (Table 2). CrZSM-5 proved to be active in most of the cases and N- and O-containing cyclic compounds were obtained in good yields. The striking feature of this system is the 98.2% conversion of γ-butyrolactone (entry 8) to 1-methyl-2-pyrrolidone under mild conditions. The reaction of aniline (entry 4) was found sluggish. This can be easily explained as due to the difficulty in diffusion of product out of the channels of zeolite. In regard to molar ratio, in the reaction

† IICT communication no. 3309. Dedicated to Dr. A. V. Rama Rao on his 60th birthday.

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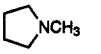
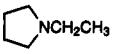
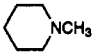
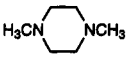
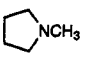
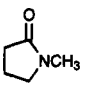
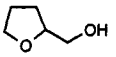
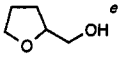
Table 1. Reaction of 1,4-Butanediol and Methylamine with Different Catalysts[a]

entry	catalyst	temp, °C	time on stream, h	yield (%) NMP	THF	MAB	others
1	HZSM-5(30)	300	4	5	90	–	5
2	HZSM-5(280)	400	2	19.4	69.2	7	4.4
3	CrZSM-5	300	3	64.2	32.0	2.5	1.0
4	VZSM-5	300	5	46.9	52.1	0.4	0.5
5	MoZSM-5	300	4	37.2	54.6	6.8	1.4
6	MnZSM-5	300	6 + 7	43.5	55.9	0.35	0.15
7	CuZSM-5	400	3	25.7	62.0	8.2	4.0
8	WZSM-5	400	2	16.7	54.7	16	12.6
9	PbZSM-5	300	6	26	54	12.5	7.5
10	VAPO	300	1	–	100	–	–
11	SAPO	300	1	–	100	–	–
12	VSAPO	300	1	–	100	–	–

[a] Weight of the catalyst = 4.0 g. W.H.S.V. = 0.5 h^{-1}. Molar ratio of methylamine to 1,4-butanediol = 4. Conversion of 1,4-butanediol is 100% in all cases. NMP = *N*-methylpyrrolidine; THF = tetrahydrofuran; MAB = 4-(*N*-methylamino)-1-butanol; others = toluene, xylenes, etc.

Table 2. Cyclization of Different Substrates over CrZSM-5[a]

entry	substrate I	substrate II	time on stream, h	N-containing cyclic product	yield (%)
1	HO(CH2)4OH	NH_3	4		48.0
2	HO(CH2)4OH	CH_3NH_2	3		64.2
3	HO(CH2)4OH	$CH_3CH_2NH_2$	3		59.6
4	HO(CH2)4OH[b]	$C_6H_5NH_2$	4		94.0
5	HO(CH2)4OH	CH_3NH_2	1		31.2
6	$HN(CH_2CH_2OH)_2$[c]	CH_3NH_2	2		41.0
7	 [d]	CH_3NH_2	4		48.0
8		CH_3NH_2	4		98.2
9		CH_3NH_2	3	no reaction	–
10	 [e]	–	3		38.0

[a] CrZSM-5 = 4.0 g. The molar ratio of substrate I to substrate II is 0.25. W.H.S.V. = 0.5 h^{-1}. Temperature = 300 °C. The conversion of substrate I is 100% (unless stated). Major side products are O-containing cyclic compounds and traces of amino alcohols. [b] Substrates are in 1:1. [c] The other major product is 1-methylpiperazine. [d] Conversion of THF is 64%. [e] Conversion is 43%.

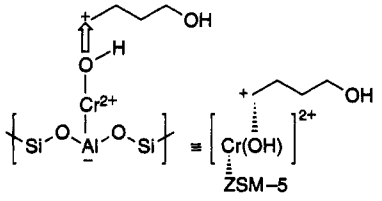


Figure 1. Stabilization of primary carbocation over CrZSM-5.

of diethanolamine (DEA) with methylamine at a 1:4 molar ratio (entry 6), the main product was 1,4-dimethylpiperazine and the conversion of DEA was 100%. Under identical conditions at a 1:1 molar ratio, the conversion of DEA decreased to 46% and the products were *N*-methylpiperazine and morpholine. For the preparation of *N*-methylpiperazine, selectively, over HZSM-5, hydrogen pressure was required.[10] The present catalytic system was exploited for the rearrangement of tetrahydrofurfuryl alcohol to DHP (entry 10), but in the presence of methylamine (entry 9) no reaction was observed.

Thus, the modified ZSM-5 catalysts are very active in the syntheses of N- and O-containing cyclic compounds and due to their characteristic applications it can be adoptable in any laboratory.

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Experimental Section

All the chemicals were reagent grade and used without further purification. ZSM-5 (Si/Al = 30) was obtained from Conteka, Sweden. GC analysis was conducted on a Chemito 3865 India instrument equipped with a SE30 (30%) column. All the products showed satisfactory spectral data.

Preparation of CrZSM-5. 18–30-Mesh HZSM-5 (Si/Al = 30) (4.0 g) was added to a solution of chromium trioxide (0.4 g, 4.0 mmol) in 50 mL of methanol. It was stirred occasionally for 10 h. Then the methanol was evaporated totally. The resultant CrZSM-5 (4.2 g) was activated at 420 °C for 4 h. A similar procedure was adopted for other catalysts.

Typical Reaction Procedure. The reaction was carried out in a tubular, down-flow reactor with 20 mm i.d., 4.0 g of CrZSM-5 was loaded in the reactor, and the temperature was tuned to 300 °C. The mixture of 1,4-butanediol (7.0 mL, 0.079 mol) and 40 wt % methylamine (25.0 mL, 0.316 mol) was fed from the top using a Sage syringe pump with a flow rate of 2.0 mL/h. The products were condensed at the bottom by circulating ice-cooled water. The product NMP was identified by NMR and GC/mass spectroscopy and quantified by GC (64.2% yield). The yield and selectivity were determined in following way:

$$\text{yield (wt \%)} = \frac{\text{g of NMP formed} \times 100}{\text{g of butanediol taken in feed}}$$

$$\text{selectivity (\%)} = \frac{\text{g of NMP formed} \times 100}{\text{g of butanediol converted}}$$

The mass balance was >95%.