

Short Communication

Catalytic synthesis of *N*-methylpiperazine from diethanolamine and methylamine by cyclodehydration reaction†

K Nagaiah, A Sudhakar Rao^a, M Subrahmanyam,
S J Kulkarni* & A V Rama Rao

Indian Institute of Chemical Technology,
Hyderabad 500 007, India

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The intermolecular cyclization of diethanolamine and methylamine has been carried out over copper-chromite, zinc-chromite, Cu-Al₂O₃ and Ni-SiO₂ catalysts in the temperature range from 250 to 350°C and 80 atm. hydrogen pressure leading to *N*-methylpiperazine. The selectivity of *N*-methylpiperazine is higher (>95%) at a conversion of >75% for copper-chromite and Cu-Al₂O₃ in comparison to that of Ni-SiO₂ catalyst.

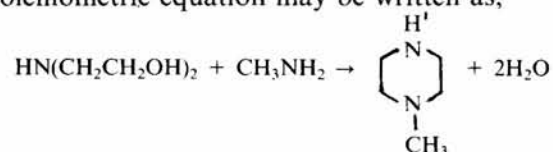
The synthesis of *N*-methylpiperazine was carried out in a number of ways in an autoclave under pressure¹. It is used as an intermediate in the manufacture of pharmaceuticals and insecticides and also as a surface-active agent and selective solvent for the extraction of aromatics from hydrocarbon mixtures². The inter- and intramolecular cyclization reactions of C₁₋₃ aliphatics with ammonia or aliphatic amines and β-hydroxy-propyl-ethylenediamine to 1- or 2-*N*-containing heterocycles over chromite and various zeolite catalysts have already been reported³⁻⁵. *N*-Methylpiperazine has been synthesized⁶ from diethanolamine and methylamine over various zeolites at 300°C and 80 atm hydrogen pressure with >90% yield based on diethanolamine and >90% selectivity. In this communication, the cyclization of diethanolamine and methylamine to *N*-methylpiperazine has been reported under the same conditions except that copper-chromite, Cu-γ-Al₂O₃, zinc-chromite and Ni-SiO₂ have been used as catalysts for the first time.

Experimental procedure—The Cu-1800P (CuO:Cr₂O₃ = 51:46, SA = 30 m²/g), Cu-0203T (CuO:Cr₂O₃ = 80:20, SA = 6 m²/g), Zn-0312T (ZnO:Cr₂O₃ = 73:21, SA = 130 m²/g) were supplied by

M/s Harshaw, Cleveland, USA. The Girdler (Louisville, USA) G-33 contains 27.3 wt% Ni over SiO₂ support with surface area of 96 m²/g. 30 Wt% Cu-γ-Al₂O₃ was prepared by the impregnation with required amount of copper nitrate over M/s Harshaw Al₂O₃-111-61E support of SA = 150 m²/g. The catalyst was dried in the oven at 120°C overnight. All the catalyst samples of 18-30 mesh size were used after reducing with hydrogen at 350°C for 4 h.

The reactions were carried out in an experimental set-up described elsewhere⁶. The reaction mixture was fed through a calibrated burette using the feeder (Lewa, Germany). The product was cooled using ice-cooled water and collected at the bottom. The ice-cooled traps were used at the outlet to collect the total amount. The product was collected every hour. The products were analyzed by GC using SE-30 (5%) column of 3 m length and 2 mm diameter. The analysis was confirmed by MS and GC-MS. The 50 g-catalyst (HZSM-5) scale experiment was carried out for the best catalyst under the optimized conditions and the isolated yields are given elsewhere⁶.

Results and discussion—The reaction of diethanolamine and methylamine was carried out in the temperature range from 250 to 350°C, 0.5 h⁻¹ weight hourly space velocity (WHSV), 80 atm pressure of hydrogen and 1:2 molar ratio of diethanolamine to methylamine. The results are given in Table 1. The stoichiometric equation may be written as,



The detailed reaction parameters optimization was done for this reaction over zeolites and reported elsewhere⁶. At atmospheric pressure, the yield of *N*-methylpiperazine was <10%. In the absence of hydrogen flow the selectivity and yield of *N*-methylpiperazine was much lower due to the formation of 2-methylpyrazine and pyrazine particularly. In presence of hydrogen flow, however, piperazine was side product.

The yields of *N*-methylpiperazine at 250°C, under the present experimental conditions as mentioned above, were 77.0, 66.5, 90.2, 7.7 and 27.7 wt% based on diethanolamine over Cu-1800P, CuO-Al₂O₃, Cu-0203T, Zn-0312T and G-33 catalysts, respectively. The yields of *N*-methylpiperazine at 300°C were 76.5, 58.5, 77.1, 52.6 and 27.2 wt% based on

*Author to whom correspondence should be addressed

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^aDeceased

Dedicated to Dr A V Rama Rao on his 60th birthday

Table 1—Synthesis of *N*-methylpiperazine from diethanolamine and methylamine

S No	Catalyst	Yield of <i>N</i> -methylpiperazine ^a , wt%					
		TOS ^b , h	Yield at 250°C	TOS, h	Yield at 300°C	TOS, h	Yield at 350°C
1	Cu-1800P	3	77.0(95) ^c	3	76.5(95)	1	42.4(95)
2	30% CuO- γ -Al ₂ O ₃	2	66.5(95)	1	58.5(95)	1	14.6(95)
3	Cu-0203T	3	90.2(95)	1	77.1(95)	1	49.6(95)
4	Zn-0312T	2	7.7(95)	3	52.6(95)	3	29.2(95)
5	G-33	2	27.7(56)	2	27.2(60)	3	12.3(49)

^aYield based on diethanolamine, ^bTOS = Time on stream; ^cNumber in parentheses indicates the % selectivity.

diethanolamine over Cu-1800P, CuO-Al₂O₃, Cu-0203T, Zn-0312T and G-33 catalysts respectively. Except for G-33 catalyst, the selectivities for *N*-methylpiperazine were >90% under H₂ flow. With the increase of reaction temperature and time on stream, the yield decreases due to the coking; and the time on stream corresponding to maximum yield is reported in Table 1.

Thus copper containing Cu-1800P, Cu-0203T are found to be better cyclization catalysts than Ni-SiO₂ (G-33) catalyst.

References

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